

Temporal variability of uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios in the Mississippi river and its tributaries

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Abstract

$^{234}\text{U}/^{238}\text{U}$ activity ratios and total dissolved uranium concentrations in the Lower Mississippi River at New Orleans, LA have been analyzed on a bi-weekly basis over 2003–2004. During this time period, the range in $^{234}\text{U}/^{238}\text{U}$ activity ratios is approximately 17% (from 1.241 to 1.473), while uranium concentrations span an even greater range of 130% (0.28 to 1.33 ppb). There is no correlation between uranium activity ratio and discharge, and only a very weak correlation between uranium concentration and discharge. In order to examine the cause of the substantial variability in the lower river concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios, we sampled the four major tributaries of the Mississippi River (Ohio, Missouri, Upper Mississippi, and Arkansas Rivers). Each river was sampled four times, each time representing a unique discharge season. In general, lithological and climatological parameters in the tributary sub-basins exert the greatest control on Lower Mississippi River uranium concentration and isotope signatures. These parameters may also be influenced by groundwater infiltration below the confluences of the major tributaries.

Our temporal analysis suggests that if one were to estimate Mississippi River uranium fluxes to the ocean based on single-point sampling during 2003–2004, significant over- or under-estimations of these values would ensue. Our two-year average Mississippi River uranium-flux values suggest that previous best estimates of the contribution of Mississippi River uranium to the global average riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio are too high by 36%. If other major world rivers are as poorly constrained with respect to uranium systematics as the Mississippi River, then the global average riverine U flux and $^{234}\text{U}/^{238}\text{U}$ activity ratio need to be revised.

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1. Introduction

Uranium has a long residence time in the ocean (~400 ka; Chen et al., 1986), and behaves conservatively under oxic conditions. As a consequence, the uranium concentration of seawater is relatively constant (~3.2 ppb;

Chen et al., 1986). Riverine input is the major source of dissolved uranium to the global ocean (average riverine uranium ~0.31 ppb; e.g., Palmer and Edmond, 1993; Henderson, 2002; Dunk et al., 2002). This uranium is not in isotopic secular equilibrium. Indeed, the global riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio is estimated to be greater than 1 (~1.17; Chabaux et al., 2003), because ^{234}U is preferentially leached from α -recoil damage sites in rocks and sediments during weathering. Since rivers

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supply the major part of the uranium signal to the oceans, the $^{234}\text{U}/^{238}\text{U}$ activity ratio of seawater is also in secular disequilibrium, and is equal to 1.146 (e.g., Henderson and Anderson, 2003). Over the past 360 ka, as a result of steady-state behavior, this ratio has remained relatively constant (<15‰ variance; Henderson, 2002). Understanding the causes of the temporal variations in riverine uranium activity ratios should allow a better understanding of the variability of the same ratios in the ocean.

While several studies have focused on the removal of uranium in river–ocean boundaries and estuarine systems (e.g., Swarzenski and McKee, 1998; Andersson et al., 1995, 1998, 2001), few evaluate the variability of uranium in the river proper (e.g., Scott, 1982), before the freshwater–saline water interface. Average values for global riverine uranium input, which constrain the oceanic elemental and isotopic uranium budget, are based on a few large rivers which have been sampled a minimal number of times (e.g., Palmer and Edmond, 1993, Chabaux et al., 2003). Although global uranium riverine fluxes are being refined as more rivers are sampled and evaluated, problems remain with respect to insufficient sampling methodologies and broad generalizations about specific river systems. Limited sampling of rivers may not capture the large temporal variations in uranium concentrations, and may therefore over- or under-estimate true riverine uranium fluxes. Although limited point sampling of riverine uranium may suffice in some watersheds that experience little variation in flow parameters annually (Palmer and Edmond, 1993), one should not make these generalizations a priori. When possible a time-series analysis of dissolved riverine uranium is a much more effective way of constraining uranium fluxes to the ocean. Previous studies have considered dissolved uranium variations along with other trace metals within a watershed on a semi-annual basis (Shiller and Boyle, 1987) and monthly timescales (Snow and Spalding, 1994; Shiller, 1997). However, higher-frequency time-series analyses are uncommon. Even less common are studies which concentrate on the temporal variability of uranium disequilibrium isotope ratios in rivers (e.g., Riotte and Chabaux, 1999; Andersson et al., 2001; Riotte et al., 2003).

Here, we undertake a detailed study of the spatial and temporal variability of elemental and isotopic dissolved uranium in the Mississippi River and its tributaries. The Mississippi River is the world's third largest river with respect to drainage basin area, the sixth largest in terms of water discharge, and the sixth largest with respect to sediment load (Meade, 1996). We focus on the operationally-dissolved fraction of uranium (that fraction which passes through a <0.2 μm filter). This fraction

contains uranium in colloidal form, which has been shown to influence the fate of dissolved uranium in rivers elsewhere (e.g., Kalix River system, Andersson et al., 1998, 2001; Amazon River system, Swarzenski et al., 2004). Unlike the Kalix and Amazon River systems in which up to 90% of the dissolved uranium flux is carried by the colloidal fraction, only ~30% of the dissolved uranium flux is carried in this form in the Mississippi River (Swarzenski and McKee, 1998). In addition, it is likely that sorbed uranium is easily desorbed in the Mississippi River because of its high alkalinity (Langmuir, 1978). Furthermore, any exchange between dissolved uranium and colloids or particulates is unlikely to affect the $^{234}\text{U}/^{238}\text{U}$ isotope ratios of the dissolved uranium, as research has shown that isotope exchange between the various carriers of uranium is very rapid (Porcelli et al., 1997; Andersson et al., 2001).

Our 2-year, bi-weekly sampling of the Lower Mississippi River enables an accurate determination of this major world river's uranium flux. Additionally, we sampled the four major tributaries of the Mississippi River (Ohio, Missouri, Upper Mississippi, and Arkansas Rivers). Each river was sampled four times, each time representing a unique discharge season. Uranium isotope activity ratios of tributary waters are used to estimate the contribution of the various tributary sources of uranium to the lower river and, in turn, the role that changing the conditions of such sources through time might have had on the uranium isotopic composition of the oceans.

2. Methodology

2.1. Lower river time-series and river cross-section sampling methods

During a two-year period thirty-eight samples of the Lower Mississippi River were collected bi-weekly within the city of New Orleans, LA behind the Audubon Park boat launch (see Fig. 1 for location). For each sampling, water was collected nearly simultaneously at two locations within the river; from near the river bank and within the center thalweg. One-liter samples were collected using acid-washed HDPE bottles at three separate time intervals over a continuous flow of one-hour sampling via Masterflex peristaltic pumps at roughly 2 L/min. All samples were collected using acid-washed, Teflon-lined peristaltic tubing attached to silicone pump tubing. All tubing and bottles were flushed with ambient river water immediately prior to collection (a minimum of 5 min of flush time for tubing and 3 rinses for each bottle). Center-channel samples were collected aboard the R/V Eugenie. A consistent sampling depth (5 m) was

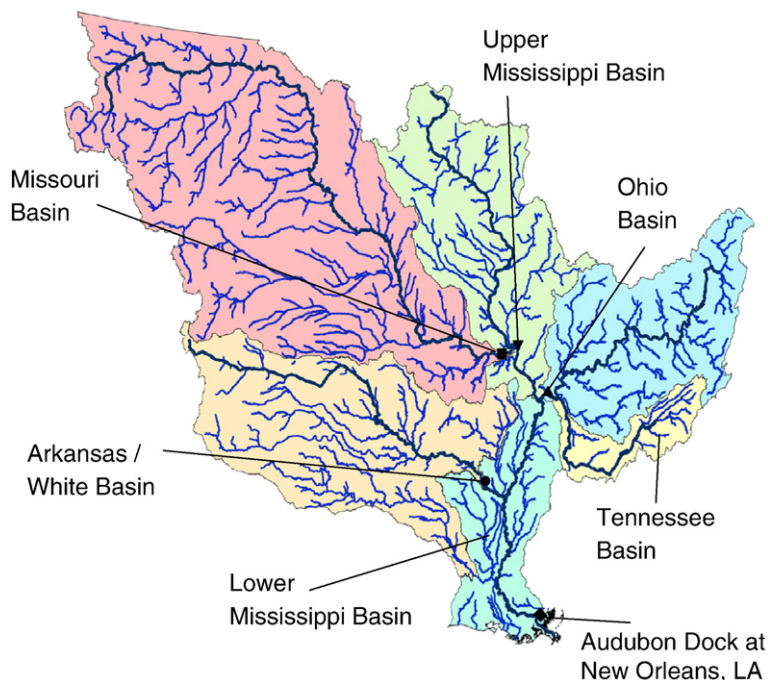


Fig. 1. A map of the Mississippi River watershed. Samples were collected for the Lower Mississippi River basin at New Orleans, LA (Audubon Dock, N 29°55.222'–W 90° 08.287'). The Ohio (N 37° 00.059'–W 89°09.825'), Missouri (N 38°33.657'–W 91° 00.552'), and the Upper Mississippi Rivers (N 38°52.962'–W 90°11.291') were all sampled near the main stem confluence, while the Arkansas River (N 33°59.269'–W 91°21.747') was sampled further upstream.

maintained using a 100-lb sounding weight which kept the sampling tube directed upstream into the flow; thereby collecting a discharge-weighted sample for the entire cross-sectional area of the river (Moody and Meade, 1994). Near-bank samples during the 2003–2004 sampling season were collected via a drop weight at the dock. However, during 2004–2005 at this location, collection was performed with an apparatus custom-designed to relocate the sampling tube approximately 7 m away from the dock into the channel in order to reduce any eddy effects caused by the flow around the dock.

2.2. Tributary sampling methods

During 2004, samples were collected four times from four of the major tributaries of the Mississippi River (Missouri, Ohio, Upper Mississippi, and Arkansas; see Fig. 1 for sampling location). At each of these tributaries the sampling procedures followed were the same as those performed during the bank sampling of the lower river. In each tributary, samples were collected at: 1) the point nearest to confluence with the main stem of the Mississippi River in order to incorporate smaller tributaries entering above the confluence and, 2) the outer edge of a bend in the river to most nearly mimic

the locations for the lower river study. Samples were filtered (<0.2 μm polycarbonate filters) and acidified with ultra-pure nitric acid (to inhibit biologic growth) in the field prior to returning to the lab. The Missouri River was sampled at Washington, Missouri, the Upper Mississippi River at West Alton, Missouri, the Ohio River at Cairo, Illinois, which is down river from the confluence of the Tennessee River, and the Arkansas River at Gillette, Arkansas (see Fig. 1 for locations). These samples were collected during four different seasonal flow regimes throughout the year in order to try to obtain the broadest spectrum of variability (see Fig. 2 for sampling times and relative tributary discharges).

2.3. Analytical procedures

The bi-weekly lower river samples were filtered in the lab by vacuum through pre-weighed 0.2-μm Millipore polycarbonate filters in order to obtain an operationally defined dissolved fraction. All filtrates were acidified to 2% HNO₃ using ultra-pure acid and analyzed directly for ²³⁴U/²³⁸U isotope ratios using the Finnigan Element 2 ICP-MS at Tulane University using procedure outlined in Pourmand et al. (2004). Briefly, to correct for abundance

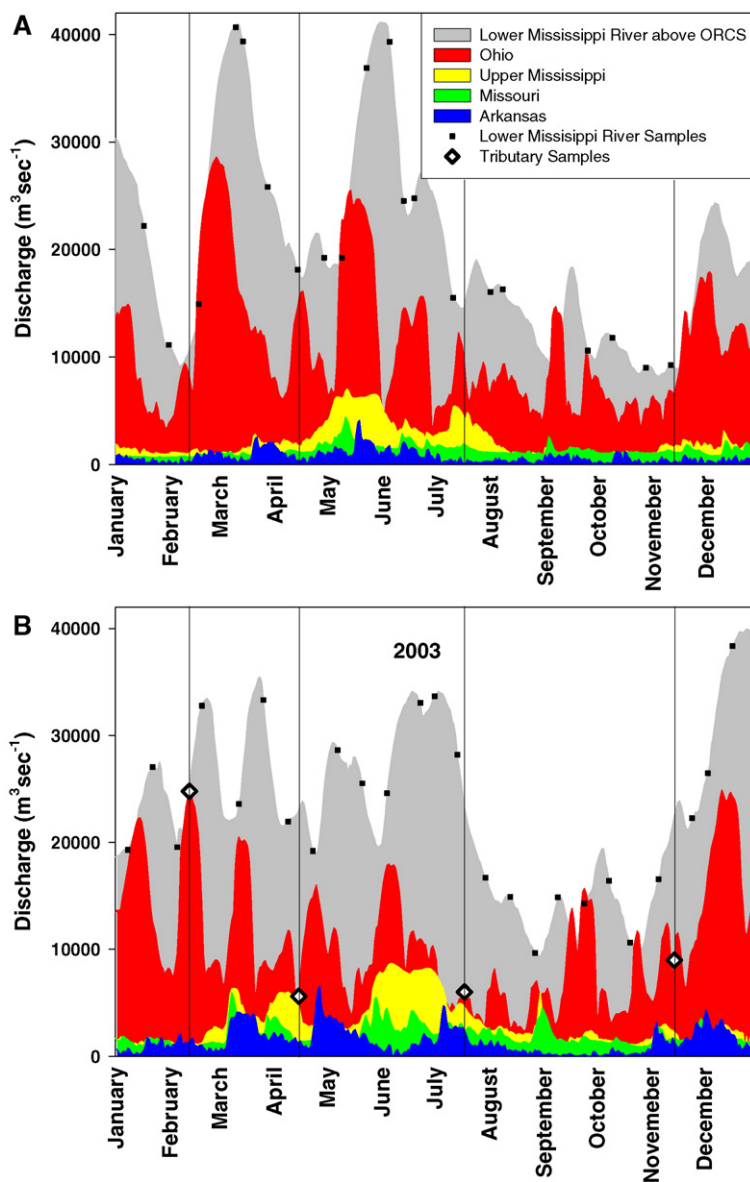


Fig. 2. Hydrographs representing the temporal discharge curves (2003—A; 2004—B) of each Mississippi River tributary and the Lower Mississippi River above the Old River Control Station (ORCS). See text for the identification of each USGS discharge gauging site. The black squares on the Lower Mississippi River discharge curve represent the sampling dates for all lower river samples collected in both years. The black diamonds on the 2004 hydrograph represent the dates of tributary sampling. The timing of the 2004 tributary sampling attempted to capture various climatic and discharge seasons.

sensitivity, the counting intensities of the half masses $^{236.5}\text{U}$, $^{235.5}\text{U}$ and $^{234.5}\text{U}$ were measured. Assuming an exponential decrease in the abundance sensitivity on the down-mass side of ^{238}U , the abundance sensitivity at mass ^{234}U , measured during each sample analysis, was less than 1 ppm/amu. Instrumental mass fractionation was estimated in two ways: by measuring $^{235}\text{U}/^{238}\text{U}$ ratios ($=0.00725$) in each sample and by measuring, within each batch of samples, the SRM U500 enriched ^{235}U standard

($^{235}\text{U}/^{238}\text{U}=0.9997$). Mass biases measured during the course of this study were consistently lower than 1%/amu. In-run precisions for the $^{234}\text{U}/^{238}\text{U}$ ratio (Table 2) are consistently lower than 1% at the 1σ level. Repeated measurements of the $^{234}\text{U}/^{238}\text{U}$ ratios of the SRM U500 standards during the course of this study yielded an external reproducibility of 0.15%, while those of the SRM 3164 natural U standard yielded an external reproducibility of 1.6%. This level of external reproducibility is

adequate for the present study given the large range in the observed uranium isotope ratios (total range of 26%; see section 3.3). Uranium concentration data were obtained by separate isotope dilution analyses in which small aliquots (~ 2 mL) of each acidified sample were spiked with a known amount ^{236}U . Blank corrections were smaller than the analytical uncertainty, and were, therefore, not necessary.

3. Results

3.1. Lower river discharge

The most accurate discharge numbers for the river at New Orleans are data from the United States Geologic

Survey site at Tarbert Landing, Mississippi (Fig. 3). This site gives a meaningful representation of the discharge at New Orleans because it is located below the Old River Control Structure (ORCS) that diverts $\sim 30\%$ of the Mississippi River discharge down the Atchafalaya River. The annual variation in total discharge varies erratically over 2003. The year begins with a low discharge of $6272 \text{ m}^3 \text{ s}^{-1}$ in early February, and is followed rapidly by two spikes of $28,112 \text{ m}^3 \text{ s}^{-1}$ and $28,240 \text{ m}^3 \text{ s}^{-1}$ in early March and late May, respectively. After relatively low discharges for summer and early fall, the total discharge reaches its lowest value in early November ($5740 \text{ m}^3 \text{ s}^{-1}$) before rising again in early 2004. In 2004, there were less dramatic peak high and low discharges, ranging only from a spring high of $24,892 \text{ m}^3 \text{ s}^{-1}$ in mid-March to a

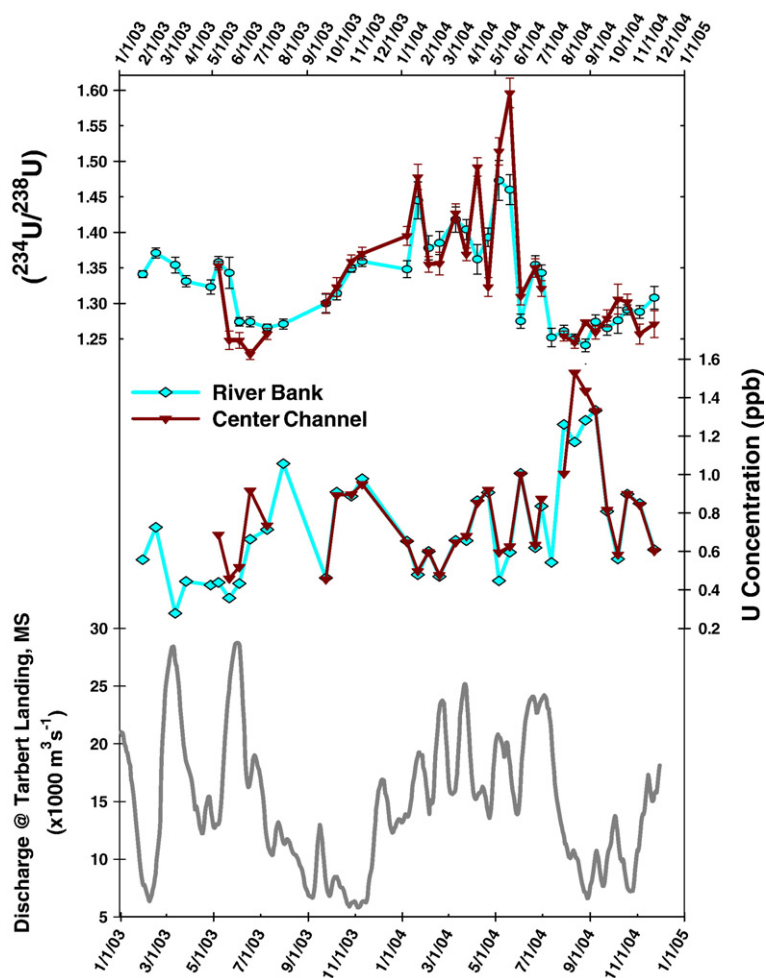


Fig. 3. Bi-weekly temporal measurements of uranium concentration and isotope activity ratios for the Lower Mississippi River from January 2003 to December 2004. Both river bank and center-channel results are displayed. Discharge, as measured daily at Tarbert Landing, MS, is represented by the bold grey line in the bottom graph. The center and uppermost graphs represent the total riverine uranium concentration and activity ratios at each of the sampling times for the 2-year study. Diamonds represent the samples from the near-bank site, while triangles represent the center-channel samples. Breaks in the center-channel data set occur on dates when conditions did not permit center-channel river sampling.

fall low of $6524 \text{ m}^3 \text{ s}^{-1}$ in late August. In 2004, there was more variability on shorter timescales, but with less extreme differences between the highs and lows, yielding a more traditional year with a more distinct and consistent rising discharge associated with upper basin snow melt, as well as increased spring precipitation.

3.2. Thalweg versus river bank uranium analyses in the lower river

It is important to compare the data obtained from the center river channel and those obtained from the near-bank site on the dock. This comparison is necessary in order to test the possibility of collecting samples from the bank in large rivers where center-channel sampling is difficult. It should be noted that the first 5 samples collected in early 2003 as well as 2 other samples obtained later in the 2-year study were collected from the bank and do not have center-channel counterparts. These center-channel river samples were not collected at these times because the research vessel was unavailable on the planned sampling dates. In all but 8 samples dissolved uranium concentrations in the water from both sites exhibit a difference of 5% or less. The largest observed difference in concentration between the two locations ($\sim 44\%$) occurred on May 9, 2003. The first four samples in May through June 2003 showed the greatest river bank–thalweg differences. These differences may have been caused by the eddy artifact mentioned above. In addition, samples collected closest to the river bank may record uranium systematics that are different from those in the river center because of the effects of sediment resuspension. For the most part, the $^{234}\text{U}/^{238}\text{U}$ activity ratios at both sites are within measurement error of each other. In all but 4 cases the center-channel and near-bank uranium activity ratios exhibited differences of 5% or less. The largest difference in activity ratios (9%) occurred in May 2004. The general agreement between bank and thalweg samples may be due to the fact that our sampling location was along a straight stretch of the river, which was well below any upriver confluence.

3.3. Lower river uranium concentrations and activity ratios

Uranium concentrations in the Lower Mississippi River (Fig. 3, Table 1) vary temporally by approximately 130%, from a low of 0.28 ppb in March 2003 to 1.33 ppb in early September 2004. There is significant variability ($\sim 80\%$) over short timescales as well, with the most notable example occurring between July 13,

2004 (0.54 ppb) and July 29, 2004 (1.26 ppb). This dramatic change occurred during a rapid drop in discharge, suggesting that rising or falling discharge can affect uranium concentrations. Many abrupt variations in discharge and uranium concentrations (Fig. 3) can be seen on sub-monthly scales, supporting the argument that frequent sampling is needed in order to identify short-timescale variability. Dissolved U concentrations exhibit a weak negative correlation with total discharge ($r^2=0.3$). The highest concentrations during the 2-year period occur during the lowest discharge in September 2004. The lowest uranium concentration occurs during the highest discharge in April 2003.

$^{234}\text{U}/^{238}\text{U}$ activity ratios in the Lower Mississippi River also show a considerable amount of variation during the 2-year study (Fig. 3, Table 1). The total variability in uranium isotope ratios measured in the lower river is 17%, ranging from a high of 1.473 in early May 2004, to a low of 1.241 in late August 2004. In 2003 the $^{234}\text{U}/^{238}\text{U}$ activity ratios do not exhibit the same rapid extreme variations observed in 2004. $^{234}\text{U}/^{238}\text{U}$ activity ratios in the lower river do not show any significant variability with discharge ($r^2=0.1$).

3.4. Tributary discharge, uranium concentrations, and activity ratios

During 2004, four major tributaries (Upper Mississippi, Missouri, Ohio, and Arkansas Rivers) of the Mississippi River were each sampled four times. The discharge values for the Upper Mississippi, Missouri, Ohio, and Arkansas Rivers were retrieved from USGS gauge sites 05587450 (~ 25 – 30 river km from Upper Mississippi sampling site), 06934500 (~ 40 – 50 river km from Missouri sampling site), 03611500 (~ 55 – 65 river km from Ohio sampling site), and 07263450 (~ 120 – 160 river km from Arkansas sampling site), respectively.

The Ohio River's contribution to the total lower river discharge was the greatest and ranged from 24% in July to 53% in February (Fig. 2, Table 2). The Upper Mississippi River contributed the second largest amount to the total discharge followed by the Missouri and then the Arkansas Rivers (Fig. 2, Table 2).

The uranium concentration in the Ohio River ranged from 0.38 ppb in February to 0.58 ppb in July. The Upper Mississippi River showed a greater variability, with a low of 0.94 ppb in April to a high of 2.46 ppb in July. The Missouri River exhibited the greatest variation in uranium concentration ranging from 1.43 ppb in November to 4.05 ppb in April. The Arkansas River experienced the least variation ranging only from 0.42 ppb in February to 0.68 ppb in April.

Table 1

Dissolved elemental and isotopic uranium data measured for the Lower Mississippi River site at New Orleans, LA (N 29°55.222'–W 90° 08.287')

Date	Discharge Tarbert Landing, MS (m ³ s ⁻¹)	Center-channel		Bank	
		²³⁴ U/ ²³⁸ U activity ratios	U concentration (ppb)	²³⁴ U/ ²³⁸ U activity ratios	U concentration (ppb)
01-31-03	7,787			1.341±0.005	0.56
02-17-03	1,067			1.371±0.007	0.73
03-14-03	26,759			1.354±0.011	0.29
03-28-03	18,123			1.331±0.008	0.44
04-29-03	13,677			1.323±0.01	0.43
05-09-03	13,422	1.353±0.006	0.69	1.358±0.008	0.44
05-23-03	25,995	1.248±0.013	0.46	1.343±0.022	0.36
06-05-03	27,496	1.248±0.011	0.52	1.274±0.006	0.43
06-19-03	17,387	1.228±0.007	0.92	1.274±0.007	0.66
07-11-03	11,015	1.257±0.008	0.74	1.266±0.005	0.71
08-01-03	11,298			1.271±0.007	1.06
09-25-03	7,504	1.300±0.014	0.46	1.300±0.013	0.46
10-09-03	8,240	1.323±0.013	0.89	1.314±0.009	0.91
10-28-03	6,258	1.359±0.009	0.90	1.349±0.005	0.89
11-11-03	6,343	1.370±0.009	0.95	1.359±0.007	0.98
01-08-04	13,677	1.395±0.013	0.65	1.348±0.012	0.65
01-22-04	19,227	1.478±0.018	0.50	1.445±0.026	0.48
02-05-04	13,904	1.355±0.011	0.60	1.378±0.017	0.60
02-19-04	23,390	1.356±0.016	0.48	1.385±0.016	0.47
03-11-04	16,820	1.427±0.013	0.65	1.418±0.018	0.66
03-25-04	23,503	1.369±0.009	0.68	1.404±0.014	0.66
04-08-04	15,546	1.492±0.013	0.85	1.362±0.021	0.86
04-22-04	13,734	1.323±0.013	0.92	1.393±0.013	0.91
05-06-04	20,558	1.514±0.019	0.60	1.473±0.028	0.45
05-20-04	18,094	1.596±0.021	0.63	1.460±0.021	0.60
06-03-04	17,387	1.310±0.012	1.00	1.275±0.01	1.01
06-22-04	23,390	1.350±0.013	0.64	1.354±0.013	0.62
06-30-04	23,899	1.321±0.011	0.87	1.343±0.011	0.84
07-13-04	20,020			1.252±0.013	0.54
07-29-04	11,865	1.254±0.007	1.01	1.261±0.008	1.26
08-12-04	10,477	1.245±0.008	1.53	1.250±0.007	1.17
08-26-04	7,079	1.274±0.003	1.44	1.241±0.009	1.28
09-08-04	10,534	1.259±0.009	1.33	1.274±0.010	1.33
09-23-04	10,222	1.279±0.012	0.82	1.265±0.010	0.81
10-07-04	11,723	1.306±0.021	0.58	1.276±0.018	0.56
10-19-04	7,532	1.302±0.011	0.90	1.291±0.007	0.90
11-04-04	11,667	1.257±0.014	0.84	1.288±0.009	0.85
11-23-04	15,716	1.271±0.019	0.60	1.308±0.016	0.61
Average 2003	13,491	1.298±0.010	0.72	1.322±0.009	0.62
Average 2004	15,651	1.352±0.013	0.82	1.337±0.014	0.79
2-year average	14,798	1.336±0.012	0.79	1.331±0.012	0.72

Missing values for center-channel samples are due to the unavailability of a research vessel.

Average single- and two-year values are presented.

²³⁴U/²³⁸U activity ratios for the Ohio River ranged from 1.21 in July to 1.36 in February, while the Upper Mississippi River had ²³⁴U/²³⁸U activity ratios ranging from 1.16 in July to 1.34 in February. The Missouri River presented significantly higher ²³⁴U/²³⁸U activity ratios, ranging from 1.34 in July to 1.51 in February. These values for the Missouri River show less variance than, but falls within the range of, values for the Platte

River system (1.18 to 1.69), a tributary of the Missouri River entering upstream of our sampling site (Snow and Spalding, 1994). The Arkansas River also exhibited high ²³⁴U/²³⁸U activity ratios, ranging from 1.26 in July to 1.39 in February. All four tributaries followed the same general trend as the Lower Mississippi River with respect to the annual fluctuations in ²³⁴U/²³⁸U activity ratios. That is, ²³⁴U/²³⁸U activity ratios are higher in

Table 2

Dissolved elemental and isotopic uranium data measured for the Mississippi River tributaries are used to construct a tributary discharge-weighted mass balance model for uranium concentrations and activity ratios in the Lower Mississippi River

River site	Discharge (m ³ /s)	% Contribution to Lower River	²³⁴ U/ ²³⁸ U	U concentration (ppb)
<i>February</i>				
Missouri	1,097	4.0%	1.510±0.005	2.02
Ohio	14,518	53.4%	1.362±0.005	0.38
Upper Mississippi	1,569	5.8%	1.383±0.005	0.95
Arkansas	1,022	3.8%	1.385±0.005	0.42
Total tributary discharge	18,206	66.9%		
Calculated missing source		33.1%	1.336	0.35
Lower Mississippi	27,206	100%	1.385±0.016	0.47
<i>April</i>				
Missouri	1,999	8.3%	1.370±0.007	4.05
Ohio	10,982	45.6%	1.295±0.01	0.51
Upper Mississippi	4,313	17.9%	1.273±0.016	0.94
Arkansas	2,284	9.5%	1.374±0.013	0.68
Total tributary discharge	19,578	81.3%		
Calculated missing source		18.7%	1.874	0.57
Lower Mississippi	24,088	100%	1.393±0.013	0.91
<i>July</i>				
Missouri	2,486	12.5%	1.336±0.006	2.76
Ohio	4,865	24.4%	1.210±0.005	0.58
Upper Mississippi	4,433	22.3%	1.164±0.012	2.26
Arkansas	2,065	10.4%	1.261±0.019	0.65
Total tributary discharge	13,848	69.6%		
Calculated missing source		30.4%	1.408	0.67
Lower Mississippi	19,900	100%	1.261±0.008	1.26
<i>November</i>				
Missouri	1,999	8.1%	1.366±0.006	1.43
Ohio	9,735	39.2%	1.237±0.003	0.47
Upper Mississippi	3,254	13.1%	1.193±0.019	1.79
Arkansas	1,884	7.6%	1.370±0.006	0.55
Total tributary discharge	16,872	68.0%		
Calculated missing source		32.0%	2.216	0.11
Lower Mississippi	24,820	100%	1.308±0.016	0.61

For each month, discharge is averaged over the whole month for each tributary and the lower river.

February and drop off in the summer months before starting to rise again during the late fall and early winter months.

4. Discussion

4.1. Controls on tributary uranium concentrations and activity ratios

Differences in uranium isotope ratios and concentrations between each of the studied tributaries may be partly due to the different lithologies in each drainage basin, as has been proposed previously (Sarin et al., 1990; Plater et al., 1992; Pande et al., 1994; Riotte and Chabaux, 1999; Durand et al., 2005). In rocks older than a few million years old, ²³⁴U/²³⁸U activity ratios should

be in secular equilibrium since ²³⁴U is the relatively short-lived great-granddaughter of the long-lived ²³⁸U. However, the highly energetic alpha decay of ²³⁸U damages a mineral's crystalline lattice and allows its great-granddaughter to be more mobile during weathering of rock by meteoric waters (Thurber, 1962). Increased physical weathering and the resulting decrease in grain size increase the mineral surface area (per unit volume). This increases the number of alpha recoil fractures that are exposed to the surface of the grains which, in turn, allows for an increased rate of ²³⁴U removal (e.g., Robinson et al., 2004). The rate of removal is expected to decline with time as the more labile uranium is removed first, leaving the less mobile uranium in the mineral crystalline lattices (Latham and Schwarcz, 1987). Rock type determines rock

weathering rates. Carbonates weather the most rapidly followed by shales and sandstones, while plutonic and metamorphic shield rocks weather the most slowly (Bluth and Kump, 1994; Amiotte Suchet et al., 2003). Within the Mississippi River Basin as a whole, the most rapidly physically weathered rocks are located in the Missouri River sub-basin with its headwaters in the North American Rocky Mountains. It is possible that the rate of removal of uranium and, specifically, the ^{234}U in these Cenozoic–Quaternary rocks is relatively rapid because of constant exposure of fresh sandstone and carbonate surfaces during uplift. This may explain the consistently higher uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios in the Missouri River samples. It has also been suggested that the higher concentrations associated with the Missouri River reflect the fact that its headwaters in the Platte River water shed drain uraniumiferous rocks (Snow and Spalding, 1994). In contrast to the Missouri River, the Arkansas and Ohio Rivers both have lithologies dominated by Paleozoic and Mesozoic rocks that are undergoing less physical weathering. These rocks may have already experienced a decrease in uranium removal rates, demonstrated by their consistently lower uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios. The relatively high concentrations of uranium in the Upper Mississippi River sub-basin may be the result of higher concentrations within the parent rocks, or the relative ease with which shale (the predominant rock type) is physically and chemically weathered.

The varying climates in the different sub-basins may also exert control on the uranium concentrations and activity ratios. In order to investigate climate as a controlling parameter one can group the Upper Mississippi and Ohio basins together, and the Arkansas and Missouri basins together, as these pairs share relatively similar climates. The Arkansas and Missouri River basins have arid to semi-arid climates, while the Ohio and Upper Mississippi River basins have climates that are temperate-humid. Climate differences, as distinct as these, have been hypothesized to affect the $^{234}\text{U}/^{238}\text{U}$ activity ratio in surface waters of southern African and in other rivers throughout the world (Kronfeld and Vogel, 1991; Kronfeld et al., 2004). These authors suggest that rivers that drain regions with arid climates are more likely to have $^{234}\text{U}/^{238}\text{U}$ activity ratios that are greater than those that drain regions with humid climates. Their reasoning is based on the idea that regions with arid climates have higher rates of physical weathering which, in turn, create more surfaces from which to leach recoil ^{234}U . Hence, the more arid environments of the Arkansas and Missouri River drainage basins may

lead to the higher $^{234}\text{U}/^{238}\text{U}$ activity ratios observed in their surface waters. Conversely, Kronfeld and Vogel (1991) hypothesize that rivers in humid regions yield $^{234}\text{U}/^{238}\text{U}$ activity ratios that are closer to those of the parent rocks that their surface waters drain. Within this context, the lower $^{234}\text{U}/^{238}\text{U}$ activity ratios of the Ohio and Upper Mississippi Rivers may be explained.

4.2. Controls on lower river uranium concentrations and activity ratios

Often when considering the larger rivers of the world and their contributions to the uranium budget of the ocean, it is common to analyze uranium in samples close to a river's mouth in order to obtain the best estimate of riverine export. Such sampling may be sufficient in some large rivers such as the Amazon whose entire drainage basin is located within the tropics. Uranium isotope ratios in the Amazon River are relatively low and uniform and probably reflect the dominance of chemical weathering in the tropical watershed (Swarzenski and McKee 1998). Contrary to the Amazon, other major world rivers such as the Ganges–Brahmaputra, Yellow, and Huang Ho basins all more closely resemble the Mississippi watershed in that the lithologies and climate conditions vary within each basin. In the case of the Mississippi, the drainage basin is clearly not nearly as uniform. Indeed, the Mississippi River watershed spans a variety of lithologic and climatic regimes as discussed above. Hence, if one is to understand the controls of the Lower Mississippi River signatures with respect to uranium concentrations and isotope ratios, there is an obvious need to understand the influence of the individual basins that contribute to the lower river. This is the first temporal study of uranium concentrations and isotope ratios of the Lower Mississippi River, and more importantly, the first in which there is a temporal analysis of the same parameters in the major Mississippi tributaries.

In order to evaluate the contribution of dissolved uranium from the tributaries to the lower river; we used the approximation that the average travel time of water from the tributary sampling sites to the lower river is ~ 10 days. In Fig. 4, we compare the $^{234}\text{U}/^{238}\text{U}$ activity ratios of the tributaries with those of the Lower Mississippi River ~ 10 days after the retrieval of the tributary samples. One would expect that because uranium behaves conservatively and is homogeneously distributed within the surface waters of the Mississippi River that lower river $^{234}\text{U}/^{238}\text{U}$ activity ratios, to preserve mass balance, would be within the range of those ratios of the major tributary rivers. This is the case for all of the data

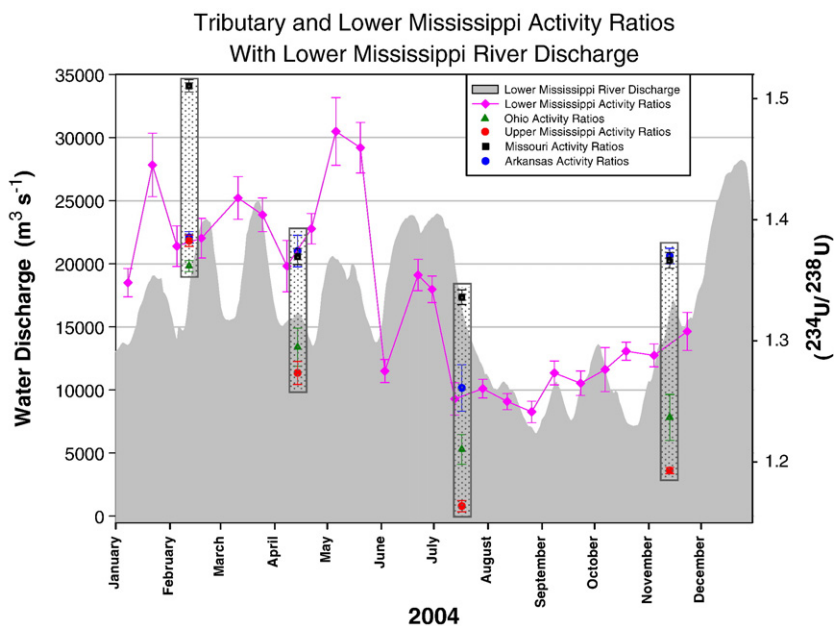


Fig. 4. $^{234}\text{U}/^{238}\text{U}$ activity ratios in each of the tributaries and the Lower Mississippi River plotted versus time. The grey shaded area represents the Lower Mississippi River discharge measured at Tarbert Landing, MS. Vertical bars group tributary samples together. At each tributary sampling event, lower river uranium isotope activity ratios lie within the range of tributary uranium isotope activity ratios. See text for a discussion of the mass balance implications.

except for the sampling which took place in April (Fig. 4, bar which contains all of the tributary data falls below the lower river $^{234}\text{U}/^{238}\text{U}$).

To more completely understand how lower river uranium signatures are controlled by the upper tributaries a discharge-weighted mass balance model of the uranium is needed. In order to create this model, one must establish the extent to which the individual tributary discharges contribute to the lower river discharge. As $\sim 30\%$ of the Mississippi River is diverted down the Atchafalaya River at the Army Corps of Engineers' ORCS, we need to determine the river discharge above the ORCS. This discharge value was estimated by adding the Lower Mississippi and Atchafalaya River discharges measured below the ORCS. The discharge values for these two rivers were obtained from the Army Corps of Engineers stations nearest to the ORCS on the down river side at Tarbert Landing, MS and Simmesport, LA respectively. In order to compensate for water entering the Atchafalaya River above the ORCS via input from the Red River, a blanket contribution of 5% was subtracted from the Atchafalaya discharge value before adding it to the Lower Mississippi River discharge value. To be consistent with our earlier estimates of travel time from source to the lower river, we offset the total discharge of the lower river above the ORCS by 10 days relative to the discharges of the

tributaries. The discharge for the lower river and each of the tributaries was averaged for each month that the samples were collected. Using the calculated value for discharge above the ORCS, we were able to determine the percent contribution of each tributary to the total discharge of the lower river. This also allowed an estimate of the fraction of lower river discharge that was not accounted for by the four tributaries sampled in this study. The fraction of this "missing source" ranged from 19% in April to 33% in February (Table 2). By simple mass balance we are able to calculate the dissolved uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios of the missing source of water (Table 2). If this missing source were to be dominated by overland flow within the stretches of the river between our tributary sites and the lower river, it is likely that the missing source would yield concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios within the ranges of the tributaries found throughout the basin. Conversely, if the missing source were dominated by groundwater supplied to the river's base flow, it is likely that the missing source will show high $^{234}\text{U}/^{238}\text{U}$ activity ratios (longer exposure times of water with rock create build-up of displaced ^{234}U through time) and relatively lower concentration levels.

In February, during the highest discharge associated with the early freshet of 2004, the low concentrations and near-riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio of the missing

source of water suggests that its input is likely dominated by increased overland flow, possibly associated with the melting of relatively uranium-deficient snow. In April and July, the moderate concentrations and relatively high $^{234}\text{U}/^{238}\text{U}$ activity ratios calculated for the missing source of water may suggest more of a mixture between groundwater inputs and overland flow. Lastly, in November, the extremely low concentration and high $^{234}\text{U}/^{238}\text{U}$ activity ratio required of the missing sources suggests a predominance of groundwater input. In contrast to the case in February, it is possible that more precipitation is being locked in snow on land causing groundwater to play a more significant role in contributing to the uranium signature of the lower river.

4.3. Implications for global budgets of uranium

Dunk et al. (2002) reevaluated the global oceanic budget of uranium for the Holocene. Among the various source and sink parameters controlling this budget, they believed that the riverine supply term is the best constrained. The results presented here question the validity of this assumption. During the 2-year period of our study, the average discharge ($14,798 \text{ m}^3 \text{ s}^{-1}$) of the Mississippi River closely resembles the 35-year average ($14,011 \text{ m}^3 \text{ s}^{-1}$). We obtain an average uranium concentration of 0.72 ppb (based on 38 sample dates), which is significantly higher than those concentrations reported in the literature (0.309 ppb, Palmer and Edmond, 1993; 0.495 ppb, Dunk et al., 2002). Given our broad sampling efforts over varying seasons and discharges, we have confidence that our results are accurate and robust. Using the estimated average annual discharge of $14,011 \text{ m}^3 \text{ s}^{-1}$, a water flux of $442 \times 10^{12} \text{ kg yr}^{-1}$ is obtained. The latter number is used to estimate the flux of uranium from the Mississippi River to the ocean. Over our 2-year sampling period these fluxes show a significant variability of 27% (2003 U flux is $1.16 \times 10^6 \text{ mol U yr}^{-1}$; 2004 U flux is $1.46 \times 10^6 \text{ mol U yr}^{-1}$). The 2-year average uranium flux is $1.34 \times 10^6 \text{ mol U yr}^{-1}$.

The temporal variability of Mississippi River uranium signatures observed here suggests that single spot-sampling of rivers to estimate fluxes of uranium can lead to meaningless results. For example, a uranium flux of $0.51 \times 10^6 \text{ mol U yr}^{-1}$ is estimated if one were to use the data collected on March 14, 2004, when the uranium concentration of the lower river was very low (0.28 ppb). This value is more than a factor of 2 lower than the 2-year average. At the other extreme, using data collected on September 8, 2004 when the river had a uranium concentration of 1.33 ppb yields a flux of

$2.48 \times 10^3 \text{ mol yr}^{-1}$, almost a factor of 2 greater than the 2-year average. Furthermore, our 2-year average uranium flux ($1.34 \times 10^6 \text{ mol yr}^{-1}$) is significantly greater than the value estimated by Palmer and Edmond (1993) ($0.76 \times 10^6 \text{ mol yr}^{-1}$). Dunk et al. (2002) used the discharge estimate from Palmer and Edmond (1993) but quoted a higher uranium concentration yielding a U flux value ($1.20 \times 10^6 \text{ mol yr}^{-1}$) closer to that calculated here. A more rigorous understanding of the temporal variability of uranium in major world rivers is required before any attempt is made to constrain the true flux of uranium to the oceans.

Chabaux et al. (2003) state that the average global riverine $^{234}\text{U}/^{238}\text{U}$ activity ratios of 1.17 based on 50% of the global exported U flux is too low if the ocean is to be in steady-state with respect to $^{234}\text{U}/^{238}\text{U}$ activity ratios. Indeed, Chabaux et al. (2003) suggest that in order to maintain the seawater steady-state $^{234}\text{U}/^{238}\text{U}$ activity ratio (1.144; e.g., Henderson et al., 1993; Henderson, 2002); the global average riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio is required to be between 1.25 and 1.35. Since there seems to be little variability in the global oceanic $^{234}\text{U}/^{238}\text{U}$ activity ratio through time (Henderson, 2002), many have called upon sources other than riverine to supply the steady-state ocean with greater quantities of ^{234}U . It has been suggested, for example, that direct groundwater input and marine sediment pore waters may influence or buffer the seawater $^{234}\text{U}/^{238}\text{U}$ activity ratios (Ku et al., 1977; Borole et al., 1982; Dunk et al., 2002). However, the extent to which other sources are required is not well known. Indeed, our study suggests that the riverine supply of ^{234}U is ill-constrained and that the average global riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio may be significantly higher or, even lower than that reported. In the case of the Mississippi River, our best estimate of the uranium-flux-weighted contribution to the global average riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio is lower by 36% than that calculated using a single data point from Moore (1967) in the review by Chabaux et al. (2003). Because Mississippi River discharge is only a small fraction of the total global riverine discharge, the global average river $^{234}\text{U}/^{238}\text{U}$ activity ratio is lowered only by about 3%. However, if other major rivers have similar variability in their uranium-flux-weighted contributions to the global average river $^{234}\text{U}/^{238}\text{U}$ activity ratio (i.e., as high as 36% in the case of the Mississippi) then changes to this global average activity ratio could be significant. Indeed the variability could account for the inequality between the “observed” average of 1.17 and the estimated value (1.25–1.35) needed to satisfy the steady-state requirement for uranium in the oceans. For example, if each

major river's uranium-flux-weighted contribution were under-estimated by 10%, then the global average river $^{234}\text{U}/^{238}\text{U}$ activity would equal 1.29 (within the range for uranium steady-state). On the other hand, if each major river's uranium-flux-weighted contribution were overestimated by 10% then the global average river $^{234}\text{U}/^{238}\text{U}$ activity would be much lower (1.05). This value requires a significantly increased supply of ^{234}U to the ocean from sources other than rivers.

Large river basins may contribute widely varying uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios to the ocean depending on conditions in the upper river basin tributaries. It is clear that estimates of annual input based on only a few samples may result in over- or under-estimated fluxes of uranium to the ocean. Based on the southern African Rivers, Kronfeld and Vogel (1991) suggested that the global average riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio is being under-estimated. They suggest that more sampling in other regions is needed to better constrain the estimated global average riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio. We agree with this assessment and suggest further that, in addition to greater spatial coverage, more rigorous temporal sampling is necessary for rivers that have been studied previously so that more accurate representations may be made of uranium fluxes to the ocean. In the case of the Lower Mississippi River, different uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios depend on the relative contributions of the source water uranium systematics which, in turn, are dependent on climatic and lithologic parameters in the individual sub-basins. These findings imply that in other large basins within encompass various climatic regimes, such as the Ganges–Brahmaputra, Yellow, or Huang Ho River systems, similar processes may lead to inaccurate estimates of their uranium contributions to the oceans.

5. Conclusions

We present empirical evidence that more rigorous temporal sampling of rivers is needed in order to better constrain the global uranium budget of the ocean. We show that in a major world river such as the Mississippi, which is considered to be well constrained, the uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios are significantly variable on timescales of 2 weeks or less. Our cross-river transect suggests that near-bank sampling on the outer bend of a river yields a representative sample of the homogenized waters of the center-channel surface waters. This conclusion is of importance in that a greater sampling efficiency is possible for regions in which it is not feasible for center-channel sampling via research vessel. A discharge-balance of the major contributing tributaries in

the Mississippi River Basin can reasonably predict lower river uranium concentrations and isotope ratios. Changes in the relative contribution of the various source waters, which exhibit varying uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios, seem to be the main cause of the observed variations for the same parameters in the lower river. In some cases, up to about 30% of the discharge in the Lower Mississippi River is not accounted for by its main tributaries. While additional surface runoff could be a possible source of the missing discharge component between the upper river sampling sites and the lower river location, the uranium isotope systematics suggest an important role for groundwater infiltration.

Riverine uranium flux is likely not as well constrained as previously thought, and should not be assumed to be a “known” quantity. The idea that the global riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio is too low to account for the steady-state invariance of the oceanic $^{234}\text{U}/^{238}\text{U}$ activity ratio needs to be revisited. Clearly, further work is needed to more clearly define and constrain major world river uranium inputs to the global ocean.

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References

- Amiotte Suchet, P., Probst, J., Ludwig, W., 2003. Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochemical Cycles* 17, 1–13.
- Andersson, P.S., Ingri, J., Porcelli, D., Wasserburg, G.J., 1998. Particle transport of ^{234}U – ^{238}U in the Kalix River and in the Baltic Sea. *Geochimica et Cosmochimica Acta* 62, 385–392.
- Andersson, P.S., Ingri, J., Wasserburg, G.J., Porcelli, D., Gustafsson, O., 2001. The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary. *Geochimica et Cosmochimica Acta* 65, 13–25.
- Andersson, P.S., Wasserburg, G.J., Chen, J.H., Papanastassiou, D.A., Ingri, J., 1995. U-238, U-234 and Th-232–Th-230 in the Baltic Sea and in River Water. *Earth and Planetary Science Letters* 130, 217–234.
- Bluth, G., Kump, L., 1994. Lithologic and climatologic controls of river chemistry. *Geochimica et Cosmochimica Acta* 58, 2341–2359.
- Borole, D.V., Krishnaswami, S., Somayulu, B.L.K., 1982. Uranium isotopes in rivers, estuaries and adjacent coastal sediments of

- western India: their weathering, transport and oceanic budget. *Geochimica et Cosmochimica Acta* 46, 125–137.
- Chabaux, F., Riotte, J., Dequincey, O., 2003. U–Th–Ra fractionation during weathering and river transport. In: Bourbon, B., Henderson, G.M., Lundstrom, C.C., Turner, S.P. (Eds.), *Uranium-Series Geochemistry*. The Mineralogical Society of America, pp. 533–576.
- Chen, J.H., Edwards, R.L., Wasserburg, G.J., 1986. 238-U, 234-U and 232-Th in seawater. *Earth and Planetary Science Letters* 80, 241–251.
- Dunk, R.M., Mills, R.A., Jenkins, W.J., 2002. A reevaluation of the oceanic uranium budget for the Holocene. *Chemical Geology* 190, 45–67.
- Durand, S., Chabaux, F., Rihs, S., Düringer, P., Elsass, P., 2005. U isotope ratios as tracers of groundwater inputs into surface waters: example of the Upper Rhine hydrosystem. *Chemical Geology* 220, 1–19.
- Henderson, G.M., 2002. Seawater ($^{234}\text{U}/^{238}\text{U}$) during the last 800 thousand years. *Earth and Planetary Science Letters* 199, 97–110.
- Henderson, G.M., Anderson, R., 2003. The U-series toolbox for paleoceanography. In: Bourbon, B., Henderson, G.M., Lundstrom, C.C., Turner, S.P. (Eds.), *Uranium-Series Geochemistry*. The Mineralogical Society of America, pp. 493–531.
- Henderson, G.M., Cohen, A.S., O’Nions, R.K., 1993. $^{234}\text{U}/^{238}\text{U}$ ratios and ^{230}Th ages for Hateruma Atol corals: implications for coral diagenesis and seawater $^{234}\text{U}/^{238}\text{U}$ ratios. *Earth and Planetary Science Letters* 115, 65–73.
- Kronfeld, J., Vogel, J.C., 1991. Uranium isotopes in surface waters from southern Africa. *Earth and Planetary Science Letters* 105, 191–195.
- Kronfeld, J., Godfrey-Smith, D.I., Johannessen, D., Zentilli, M., 2004. Uranium series isotopes in the Avon Valley, Nova Scotia. *Journal of Environmental Radioactivity* 73, 335–352.
- Ku, T.H., Krauss, K.G., Mathieu, G.G., 1977. Uranium in open ocean: concentration and isotopic composition. *Deep Sea Research* 24, 1005–1017.
- Langmuir, D., 1978. Uranium solution-mineral equilibria at the temperatures with application to sedimentary ore deposits. *Geochimica et Cosmochimica Acta* 42, 547–569.
- Latham, A.G., Schwarcz, H.P., 1987. On the possibility of determining rates of removal of uranium from crystalline igneous rocks using U-series disequilibria-1: a U-leach model, and its applicability to whole-rock data. *Applied Geochemistry* 2, 55–65.
- Meade, R.H., 1996. Contaminants in the Mississippi River, 1987–1992. U.S. Geol. Surv. Circular 1133. USGS, Reston, Va., 140 pp.
- Moody, J.A., Meade, R.H., 1994. Evaluation of the method of collecting suspended sediment from large rivers by discharge-weighted pumping and separating by continuous-flow centrifugation. *Hydrological Processes* 8, 513–530.
- Moore, W.S., 1967. Amazon and Mississippi River concentrations of uranium, thorium, and radium isotopes. *Earth and Planetary Science Letters* 2, 231–234.
- Palmer, M.R., Edmond, J.M., 1993. U in river water. *Geochimica et Cosmochimica Acta* 57, 4947–4955.
- Pande, K., Sarin, M.M., Trivedi, J.R., Krishnaswami, S., Sharma, K.K., 1994. The Indus River system (India-Pakistan): major-ion chemistry, uranium and strontium isotopes. *Chemical Geology* 116, 245–259.
- Plater, A.J., Ivanovich, M., Dugdale, R.E., 1992. Uranium disequilibrium in river sediments and waters: the significance of anomalous activity ratios. *Applied Geochemistry* 7, 101–110.
- Porcelli, D., Andersson, P.S., Wasserburg, G.J., Ingri, J., Baskaran, M., 1997. The importance of colloids and mires for the transport of uranium isotopes through the Kalix River watershed and Baltic Sea. *Geochimica et Cosmochimica Acta* 61, 4095–4113.
- Pourmand, A., Marcantonio, F., Schulz, H., 2004. Variations in productivity and eolian fluxes in the northeastern Arabian Sea over the past 110 ka. *Earth and Planetary Science Letters* 221, 39–54.
- Riotte, J., Chabaux, F., 1999. ($^{234}\text{U}/^{238}\text{U}$) activity ratios in freshwaters as tracers of hydrological processes: the Strengbach watershed (Vosges, France). *Geochimica et Cosmochimica Acta* 63, 1263–1279.
- Riotte, J., Chabaux, F., Benedetti, M., Dia, A., Gérard, M., Boulègue, J., Etamé, J., 2003. Uranium colloidal transport and origins of the ^{234}U – ^{238}U fractionation in surface waters: new insights from Mount Cameroon. *Chemical Geology* 202, 365–381.
- Robinson, L.F., Henderson, G.M., Hall, L., Matthews, I., 2004. Climatic control of riverine and seawater uranium-isotope ratios. *Science* 305, 851–854.
- Sarin, M.M., Krishnaswami, S., Somayajulu, B.L.K., Moore, W.S., 1990. Chemistry of U, Th, and Ra isotopes in the Ganga–Brahmaputra river system: weathering processes and fluxes to the bay of Bengal. *Geochimica et Cosmochimica Acta* 54, 1387–1396.
- Shiller, A.M., Boyle, E.A., 1987. Variability of dissolved trace metals in the Mississippi River. *Geochimica et Cosmochimica Acta* 51, 3273–3277.
- Shiller, A.M., 1997. Dissolved trace elements in the Mississippi River: seasonal, interannual, and decadal variability. *Geochimica et Cosmochimica Acta* 61, 4321–4330.
- Scott, M., 1982. The chemistry of U- and Th-series nuclides in rivers. In: Ivanovich, M.I., Harmon, R.S. (Eds.), *Uranium Series Disequilibria: Applications to Environmental Problems*. Clarendon, Oxford, pp. 181–201.
- Snow, D.D., Spalding, R.F., 1994. Uranium isotopes in the Platte River drainage basin of the North American High Plains region. *Applied Geochemistry* 9, 271–278.
- Swarczewski, P.W., McKee, B.A., 1998. Seasonal uranium distributions in the coastal waters off the Amazon and Mississippi Rivers. *Estuaries* 21, 379–390.
- Swarczewski, P., Campbell, P., Porcelli, D., McKee, B., 2004. The estuarine chemistry and isotope systematics of U-234 U-238 in the Amazon and Fly Rivers. *Continental Shelf Research* 24, 2357–2372.
- Thurber, D., 1962. Anomalous $^{234}\text{U}/^{238}\text{U}$ in nature. *Journal of Geophysical Research* 67, 4518–4520.