Size-fractionated uranium isotopes in surface waters in the Jiulong Estuary in China

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Abstract

Surface water was collected from the Jiulong Estuary for determination of activity concentrations of uranium isotopes in different size fractions, namely, greater than 53, 10 – 53, 2 – 10, 0.4 – 2 μm, 10 000 u – 0.4 μm and less than 10 000 u fractions by microfiltration and cross-flow ultrafiltration technologies. Results indicated that most of the dissolved uranium (<0.4 μm) existed in the low molecular mass fraction (<10 000 u), and the colloidal uranium-238 (10 000 u – 0.4 μm) only contributed less than 1% of the dissolved uranium-238. The fractions of colloidal uranium in the dissolved phases decreased with the increasing salinity. A positive linear relationship between uranium-238 activities and salinities was observed for the dissolved, colloidal and low molecular mass fractions, indicating a conservative behavior of uranium in the Jiulong Estuary. In the particulate phases (>0.4 μm), the partitioning of uranium isotopes among different size fractions was controlled by the partitioning of particle concentrations. In the regions with salinities below 20, the partitioning of uranium-238 among different size fractions was as follows: 10 – 53 μm > 2 – 10 μm > 0.4 – 2 μm greater than above 53 μm. However, the order at the offshore station with salinities above 30 changed as follows: 0.4 – 2 μm > 10 – 53 μm > 2 – 10 μm greater than above 53 μm. The fraction of the 0.4 – 2 μm particles increased at the offshore station, suggesting the increased contribution of the authigenic uranium. The activity ratio of uranium-234 to uranium-238 in the dissolved phases, including the low molecular mass fraction and the colloidal fraction, was larger than unity, showing the occurrence of excess uranium-234. In contrast, the activity ratio of uranium-234 to uranium-238 in all size fractions of the particulate phase was close to the equilibrium value (1.0). The observed different values of the activity ratio of uranium-234 to uranium-238 in the dissolved phase and the particulate phase were ascribed to the preferential leaching of uranium-234 and the small amount of the leaching particulate uranium. The mass ratio of thorium-232 to uranium-238 also showed different values between the dissolved phase and the particulate phase. Mass ratio of thorium-232 to uranium-238 in the dissolved, colloidal and low molecular mass fractions was less than unity, while those in the different size fractions of particulate phases were larger than unity, reflecting a different behavior between uranium and thorium during their transport into the ocean.

Key words: uranium isotopes, size fractionation, Jiulong Estuary in China


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1 Introduction

Rivers carry the products of continental weathering, and continuously supply the oceans with various chemical constituents. This erosional signature is, however, uniquely moderated by biogeochemical processes within estuaries. Estuaries are commonly described as filters at land–sea margins, where significant transformations occur. These changes differ for different classes of elements. Uranium- and thorium-series nuclides include a range of elements with vastly different characteristics and behaviors within such environment, and the isotopic system provide ideal tracers for investigating the transport of various chemical constituents across estuaries.

Rivers are the principal pathway by which natural uranium is discharged into the open ocean (Cochran, 1982; Scott, 1982), and the knowledge of uranium geochemical behavior in estuaries and coastal seas will lead to a better understanding of the chemical mass balance of uranium in marine environments. The extensive reviews by Cochran (1982) and Moore (1992) documented uranium data from estuaries and coastal zones in the world, and pointed out that uranium behaves differently in different estuarine systems and that geochemical reactions in the estuary may affect the flux of uranium into the ocean. Early reports of uranium concentrations in several estuaries characterized this element as conservative across a salinity gradient (Toole et al., 1987; Borole et al., 1982; Cochran, 1982; Scott, 1982; Martin, Meybeck et al., 1978; Martin, Nijampurkar et al., 1978). More recently, non-conservative behavior was observed in the Amazon and the Ganges/Brahmaputra estuarine systems. Uranium input/removal from the sediments was considered as the processes affecting the transport of uranium in these estuaries (Swarzenski et al., 1991; Carroll and Moore, 1994; Mckee et al., 1987). Presently the role of colloids and particles in controlling uranium cycling in estuarine systems is still unclear. To our knowledge, colloidal uranium concentrations were only reported for three estuarine and coastal zones, that is, the Amazon Estuary, the Kalix Estuary, and the Xiamen Bay in China. Moore et al. (1996) and Swarzenski et al. (1995) showed that colloidal uranium (10 000 u ~ 0.4 μm) comprised up to 92% of the dissolved uranium at the Amazon River mouth and in the productive, biogenic region of the Amazon shelf (salinities above approximately 20), and the colloidal fraction decreased to 15% at salinities approaching 35. Andersson et al. (2001, 1998) studied the colloidal uranium behavior in the low salinity zone in the Kalix Estuary. At the river mouth, more than 90% of the uranium in the filtered water was associated with the colloidal phase (3 000 u ~ 0.2 μm). Upon entering the estuary, the colloidal fraction rapidly becomes less significant and at salinities of about 3 the colloid-bound uranium contributed less than 5% of the dissolved phase. In contrast, Chen et al. (1999) determined the colloidal uranium-238 activity concentration (10 000 u ~ 0.2 μm) in the Xiamen Bay, and found that colloidal uranium-238 activity concentration was as low as 0.073 Bq/m³ and contributed only less than 1% of the dissolved phase. Until now, few data have been reported for the partitioning of uranium on different size particles in the estuarine zone.

In this study, surface water was collected at five stations along a salinity gradient section in the Jiulong Estuary in Fujian Province, China. The phase partitioning of uranium among different size fractions, namely, >53 μm, 10–53 μm, 2–10 μm, 0.4–2 μm, 10 000 u ~ 0.4 μm and less than 10 000 μm, was examined. The objective was to understand the geochemical behavior of size-fractionated uranium isotopes in the estuarine waters.
2 Materials and methods

2.1 Study area

The Jiulong River is the second largest river in Fujian Province. The river has a catchment area of 11,909 km$^2$, and an annual average river discharge of 117.5 x 10$^8$ m$^3$, which flows into the coastal region of Xiamen and further into the Taiwan Strait. The lithology of the drainage area consists largely of granite. The river runoff flows into the coastal zone of the Xiamen Bay via two inlets in the southern part of the estuary. The mixing of freshwater and seawater results in a salinity gradient in the estuarine mixing zone.

2.2 Sample collection

Surface water was collected from about 0.5 m depth at five stations in the Jiulong Estuary using a peristaltic pump on 12 March 2002 onboard the R/V Ocean No. 1. Sampling stations were designed to cover different salinities along a transect from the river estuary to offshore (Fig. 1). About 500 dm$^3$ of seawater at each station was pumped through a clean tubing and directly passed through a 300 mm diameter stainless steel filter holder with a 53 μm nylon screen. The prefILTERED seawater (<53 μm, 120 dm$^3$) and the screen with being greater than 53 μm particles were taken back to the laboratory for further treatment. The containers were rinsed with prefILTERED seawater three times before collecting the samples. Temperature and salinity were measured onboard ship using a thermometer and a refractometer (ATAGO, S -10E), respectively. The data were listed in Table 1.

![Fig. 1. Sampling locations in the Jiulong Estuary.](image)

<table>
<thead>
<tr>
<th>Station</th>
<th>T/°C</th>
<th>S</th>
<th>&gt;53 μm</th>
<th>10–53 μm</th>
<th>2–10 μm</th>
<th>0.4–2 μm</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>JL1</td>
<td>17.0</td>
<td>31.4</td>
<td>0.06</td>
<td>4.15</td>
<td>2.41</td>
<td>0.31</td>
<td>6.93</td>
</tr>
<tr>
<td>JL2</td>
<td>18.8</td>
<td>18.5</td>
<td>0.33</td>
<td>72.72</td>
<td>7.02</td>
<td>1.22</td>
<td>81.29</td>
</tr>
<tr>
<td>JL3</td>
<td>19.1</td>
<td>12.4</td>
<td>0.60</td>
<td>117.88</td>
<td>8.00</td>
<td>1.18</td>
<td>127.66</td>
</tr>
<tr>
<td>JL4</td>
<td>19.5</td>
<td>5.8</td>
<td>0.14</td>
<td>39.24</td>
<td>6.43</td>
<td>1.27</td>
<td>47.08</td>
</tr>
<tr>
<td>JL5</td>
<td>19.8</td>
<td>1.1</td>
<td>0.31</td>
<td>36.97</td>
<td>7.84</td>
<td>0.85</td>
<td>45.97</td>
</tr>
</tbody>
</table>

Once in the laboratory, the screens were sonically cleaned for 2 min in 200 cm$^3$ of filtered seawater (<0.4 μm) to resuspend the large particles. The resulting solution was filtered through a 0.4 μm polycarbonate membrane for collecting greater than 53 μm particles. Subsamples of the prefILTERED seawater (<53 μm) were sequentially passed through a series of polycarbonate filters with nominal pore sizes of 10, 2 and 0.4 μm, respectively. The three filters resulted in three different size fractions, namely, 10–53, 2–10, 0.4–2 μm. As for the colloidal uranium isotopes analysis, a large volume of seawa-
ter was needed due to the low concentration of uranium isotopes in the colloidal fraction. About 100 dm$^3$ of being less than 53 $\mu$m seawater was first filtered through a 0.4 $\mu$m polypropylene cartridge. The resulting less than 0.4 $\mu$m solution was further size-fractionated into the colloidal (10 000 u - 0.4 $\mu$m) and the low molecular mass fractions (< 10 000 u) by a cross-flow ultrafiltration system with a 10 000 NMW hollow fiber cartridge (H10P10, Millipore) (Chen et al., 2000). The system was cleaned by soaking in 20 cm$^3$ 0.2 mol/dm$^3$ HCl and then thoroughly rinsed with Milli-Q water before sampling and between samples. The concentration factors for ultrafiltration were 31 - 44. The colloidal uranium activity concentration ($C_u$) was calculated as follows:

$$C_u = \frac{R_u - U_u}{C_r},$$

where $R_u$ and $U_u$ are the uranium activity concentrations (Bq/m$^3$) measured in the retentate and the integrated permeate samples, respectively; and $C_r$ is the concentration factor.

In the following discussion, according to the traditional definition, greater than 0.4 $\mu$m and less than 0.4 $\mu$m fractions were defined as particulate and dissolved phases, respectively. The 10 000 u - 0.4 $\mu$m fraction was defined as the colloidal phase, and less than 10 000 u fraction was called the low molecular mass (LMM) phase. Various size particles in the particulate phase were expressed as their size ranges.

2.3 Measurement of uranium isotopes

For the uranium analysis in solution samples (i.e., LMM and 10 000 u < 0.4 $\mu$m colloidal fraction), uranium-232 - thorium-228 yield tracer and 60 mg of iron carrier were added to the samples after acidification. The samples were thoroughly mixed by bubbling with nitrogen gas for about 10 min, and then allowed to stand for about 6 h for spikes to equilibrate with seawater. About 40 cm$^3$ of concentrated NH$_4$OH was added to precipitate Fe(OH)$_3$, which co-precipitate with uranium. The resultant Fe(OH)$_3$ was dissolved in the concentrated HCl to make a 9 mol/dm$^3$ HCl solution for further separation by two anion resin columns. Uranium after chromatography work was extracted into a TTA - benzene solution and deposited on a stainless steel disk for measurement. Radioactivities of uranium-238, uranium-234 and uranium-232 in the stainless steel disk were measured by an alpha spectrometer with silicon surface barrier detectors (EG & G) (Chen et al., 1997). The particulate samples were transferred to teflon beakers for spiking and digestion using the concentrated HNO$_3$, HF and HClO$_4$ mixed solution. After digestion, the above procedure for dissolved uranium was used for uranium purification (Chen et al., 1997).

All of the reported data in this study were corrected for equipment background and procedure blank. The errors were propagated from one sigma counting uncertainty.

2.4 Measurement of total suspended matter concentration (TSM)

For TSM analysis, seawater was sequentially passed through a series of pre-weighted polycarbonate filters with nominal pore sizes of 10, 2 and 0.4 $\mu$m, respectively. After filtration, the filters were rinsed with distilled water to remove sea salts and dried to constant mass at room temperature in a vacuum desiccator. For being greater than 53 $\mu$m particles in the screen, filtered seawater (< 0.4 $\mu$m) was used to resuspend the large particles. The resulting solution was filtered through a 0.4 $\mu$m polycarbonate membrane for collecting greater than 53 $\mu$m particles and weighting. Suspended particle concentration was calculated by dividing the particle mass by the water volume filtered. The concentrations of TSM in different size fractions were listed in Table 1.
3 Results and discussion

The activity concentrations of uranium-238 in different size fractions in the Jiulong Estuary were listed in Table 2. The concentration, distribution and geochemical behavior of each size fraction were depicted below.

<table>
<thead>
<tr>
<th>Station</th>
<th>&gt;53 μm</th>
<th>10 - 53 μm</th>
<th>2 - 10 μm</th>
<th>0.4 - 2 μm</th>
<th>10 000 u - 0.4 μm</th>
<th>&lt;10 000 u</th>
<th>Dissolved</th>
<th>Particulate</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>JL1</td>
<td>0.011 ± 0.003</td>
<td>0.11 ± 0.06</td>
<td>0.06 ± 0.01</td>
<td>0.24 ± 0.02</td>
<td>0.18 ± 0.07</td>
<td>34.56 ± 1.73</td>
<td>34.74 ± 1.73</td>
<td>0.42 ± 0.06</td>
<td>35.16 ± 1.73</td>
</tr>
<tr>
<td>JL2</td>
<td>0.018 ± 0.002</td>
<td>3.33 ± 0.23</td>
<td>0.47 ± 0.04</td>
<td>0.10 ± 0.01</td>
<td>0.13 ± 0.05</td>
<td>23.95 ± 1.54</td>
<td>24.08 ± 1.54</td>
<td>3.92 ± 0.23</td>
<td>28.00 ± 1.56</td>
</tr>
<tr>
<td>JL3</td>
<td>0.056 ± 0.004</td>
<td>5.26 ± 0.31</td>
<td>0.34 ± 0.02</td>
<td>0.11 ± 0.02</td>
<td>0.10 ± 0.03</td>
<td>17.86 ± 0.81</td>
<td>17.96 ± 0.81</td>
<td>5.77 ± 0.31</td>
<td>23.73 ± 0.87</td>
</tr>
<tr>
<td>JL4</td>
<td>0.007 ± 0.001</td>
<td>2.53 ± 0.11</td>
<td>0.45 ± 0.05</td>
<td>0.15 ± 0.02</td>
<td>0.07 ± 0.02</td>
<td>8.48 ± 0.48</td>
<td>8.55 ± 0.48</td>
<td>3.14 ± 0.12</td>
<td>11.69 ± 0.49</td>
</tr>
<tr>
<td>JL5</td>
<td>0.015 ± 0.002</td>
<td>1.87 ± 0.10</td>
<td>0.54 ± 0.04</td>
<td>0.07 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td>3.46 ± 0.14</td>
<td>3.49 ± 0.14</td>
<td>2.50 ± 0.11</td>
<td>5.99 ± 0.18</td>
</tr>
</tbody>
</table>

3.1 LMM phase

The volume activity concentrations of uranium-238 in the LMM fraction (<10 000 u) ranged from 3.46 to 34.56 Bq/m³ in the estuarine surface water, which increased with the increasing salinity. The LMM uranium-238 was the main species in the dissolved phase, which accounts for 99.1% - 99.5% of the dissolved uranium-238 with an average of 99.3%.

A good linear relationship between the volume activity concentrations of the LMM uranium-238 and salinities was observed (Fig. 2a), indicating the conservative behavior of LMM uranium-238 in the study estuarine surface water. Considering the high share of the LMM uranium-238 in the dissolved phase, it is not surprising that the activity concentrations of dissolved uranium-238 increased linearly with the increasing salinity in the study estuary (Fig. 2b). On the basis of the regression equation in Fig. 2b, the volume activity concentration of dissolved uranium-238 in the offshore seawater with a salinity of 35 was estimated as 41.8 Bq/m³, which was well consistent with the reported value (41.4 Bq/m³) for open oceans (Chen et al., 1986). The conservative behavior of dissolved uranium observed here was consistent with previous reports (Cai et al., 1996; Chen et al., 1999), demonstrating that chemical reactions may not affect the flux of uranium through the Jiulong River – estuarine system.

![Fig. 2. Activity concentrations of the LMM (a) and dissolved (b) uranium-238 across a salinity gradient in the Jiulong Estuary.](image-url)
Uranium in different estuarine systems may behave differently. Previous studies of uranium behavior from the Zaire (Martin, Meybeck et al., 1978), Gironde (Martin, Nijampurkar et al., 1978) and Seine (Schmidt, 2005) Estuaries in France, the Narbada, Tapti and Godavari Estuaries in India (Borole et al., 1977; Borole et al., 1982), the Clyde and Tamar Estuaries in UK (Toole et al., 1987), the Mahandi Estuary in India (Ray et al., 1996), and the Fly Estuary in Papua New Guinea (Swarzenski et al., 2004) suggested that the dissolved uranium behaves conservatively at these locations. In contrast, examples of substantial removal were found in the Oggeechee and Savannah Estuaries in USA (Maeda and Windom, 1982), and were attributed to the precipitation of iron and manganese and/or flocculation of organic matter during low river discharge. In the Delaware and Chesapeake Estuaries in USA, uranium showed a distinct removal behavior at salinities below 5, which was suggested to be due to sedimentary redox processes in the extensive salt marshes (Sarin and Church, 1994; Church et al., 1996). Non-conservative behavior, with removal of uranium during low discharge, was reported in the low salinity region, with salinity below 12, of the Ganges–Brahmaputra mixing zone (Carroll and Moore, 1994). It was suggested that uranium removal occurs in the organic-rich sediments of the mangrove forest due to redox processes (Carroll and Moore, 1994). In the Amazon Estuary, uranium showed elevated concentrations compared with simple mixing (McKee et al., 1987). Release of uranium from bottom sediments on the shelf was suggested to be a source of dissolved uranium. However, subsequent studies in the Amazon Estuary also demonstrated that uranium removal occurred at salinities below 12 (Swarzenski et al., 1995; Swarfenski et al., 2004). Swarfenski and Baskaran (2007) reported that the dissolved uranium showed both removal and enrichment across the Alafia River/estuarine salinity gradient, removal from the water column was evidenced by a salinity of 1–9, and enrichment was observed beyond a salinity of 15.

3.2 Colloidal phase

The activity concentrations of colloidal uranium-238 (10,000 u ~ 0.4 μm) in the Jiulong Estuarine surface water were low with a range of 0.03 ~ 0.18 Bq/m³ (Table 2). The colloidal fractions only contributed 0.5% ~ 0.9% of the dissolved phases, and decreased with the increasing salinity (Fig. 3). The decrease of the colloidal percentages in the mixing zone suggested that uranium desorbed from the aquatic colloids due to the decreasing colloid concentration and the stabilization of dissolved uranyl carbonate complexes. The low activity concentrations of colloidal uranium-238 in the estuary were consistent with the soluble property of uranium in seawater. In the oxygenated seawater, uranium exists as the soluble and low molecular mass uranyl-carbonate complexes \( \text{UO}_2^+ (\text{CO}_3)^{4-} \) and \( \text{UO}_2^+ (\text{CO}_3)^{3-} \). The percentages of the colloidal uranium-238 in the dissolved phases in this study were consistent with those previously reported for the Xiamen Bay (Chen et al., 2000), but lower than those in the Amazon Estuary (Swarzenski et al., 1995; Moore et al., 1996) and the Kalix Estuary (Andersson et al., 2001). Chen et al. (2000) reported that the activity concentration of colloidal uranium-238 (10,000 u ~ 0.4 μm) in the Xiamen Bay seawater was 0.07 Bq/m³, which contributed only 0.2% of the dissolved phase. In contrast, Swarfenski et al. (1995) and Moore et al. (1996) suggested that up to 92% of the uranium in the filtered water was transported in the colloidal phases (10,000 u ~ 0.4 μm) in the Amazon Estuary, and even in the regions with a salinity of 35, the fraction of colloidal uranium-238 in the dissolved phase was as high as 15%. The results obtained from the Kalix Estuary showed that being greater than 90% of the uranium in the filtered water was
associated with the colloidal phase (3 000 u - 0.2 μm) at the river mouth. Upon entering the estuary, the colloidal fraction still dominated at low salinities, with 80% at a salinity of about 1, and decreased rapidly to being less than 5% at salinities of about 3 (Andersson et al., 2001). Apparently, colloidal uranium activity concentrations and their fractions in the dissolved phases in the Jialon Estuary were low compared with those in the Amazon and Kalix Estuaries, which may be ascribed to the difference of colloidal organic matter concentrations among them. Mann and Wong (1993) suggested that a significant fraction of uranium in coastal waters with relatively high concentrations of DOC was associated with organic matter.

A good linear relationship between colloidal uranium-238 activity concentrations and salinity was also observed in the Jialon River estuarine surface water (Fig. 3), indicating that colloidal uranium behaves conservatively in the estuary. This phenomenon was contrary to those observed in the Amazon and Kalix estuaries. In the Amazon Estuary, the distribution of colloidal uranium (10 000 u - 0.4 μm) within surface waters was highly nonlinear, reflecting both removal and input processes across the entire salinity regime. In the terrigenous region at salinities below 10, colloidal uranium concentrations were deficient relative to the expected values for conservative mixing, while in the biogenic zone at salinities above 15, colloidal uranium concentrations exceed the conservative mixing line (Swarzenski et al., 1995). In the Kalix estuary, colloidal uranium removal was also observed at salinities below 1 (Andersson et al., 2001).

3.3 Particulate phases

The volume activity concentrations of particulate uranium-238 (> 0.4 μm) ranged from 0.42 to 5.77 Bq/m³, with a magnitude of 14-folds. The maximum of the particulate uranium-238 concentrations existed at Sta. JL3 with the maximal TSM, while the minimum of the particulate uranium-238 concentrations corresponded to the minimum of TSM at Sta. JL1 (see Table 2). It was evident that the volume activity concentrations of particulate uranium-238 were controlled by the suspended particle concentrations (see Tables 1 and 2). A good positive linear relationship between both was observed, that is, the volume activity concentrations of particulate uranium-238 equaled 0.539 plus 0.042 multiplied by the concentration of TSM (n = 5, r² = 0.96, P = 0.003). Although the volume activity concentrations of particulate uranium was controlled by suspended particle concentrations, the fractions of particulate uranium-238 in the total phase decreased with the increasing salinity, from 41.7% at the river mouth (Sta. JL5) to 1.2% at Sta. JL1 with high salinity. The decrease of the particulate fractions with the increasing salinity was consistent with the previous reports for this estuary (Chen et al., 1999), reflecting the increasing stabilization of dissolved uranyl carbonate complexes along a salinity gradient.

Within the particulate pool, the partitioning of uranium among different size fractions was controlled by the partitioning of particle concentrations. At all stations except Sta. JL1, the 10 – 53 μm fractions
Fig. 4. Size-fractionated suspended particle concentrations (a, c, e, g, i) and uranium-238 activities (b, d, f, h, j) in the Jiulong Estuarine surface waters. a and b. Sta. JL1, c and d. Sta. JL2, e and f. Sta. JL3, g and h. Sta. JL4, i and j. Sta. JL5.
had the largest share of particulate uranium-238 (75% ~ 91%), followed by 2 ~ 10 μm fractions, the 0.4 ~ 2 μm fractions and greater than 53 μm fractions (see Figs 4d, f, h, j). This was in agreement with the size-fractionated patterns of the corresponding suspended particle concentrations (see Figs 4c, e, g, i). At Sta. JLI, the partitioning of uranium among different size fractions changed although the partitioning of TSM was similar to that at the low salinity regime (see Fig. 4a). At this station, the 0.4 ~ 2 μm fractions had the largest share of particulate uranium-238, followed by 10 ~ 53 μm fractions, 2 ~ 10 μm fractions and greater than 53 μm fractions (see Fig. 4b). The increase of the small size fraction in the particulate phase at the offshore station indicated the enhanced contribution of authigenic uranium. Compared with the low and middle salinity regime with high terrigenous input, the authigenic uranium produced by marine organisms in the high salinity regime was comparatively important.

In order to better understand the impact of different size particles on the uranium geochemical behavior in the estuary, the mass activity concentration was adopted to represent their concentrations in the particulate phases. Figure 5 showed the mass activity concentrations of uranium-238 across the salinity gradient in the Jiulong Estuary. At salinities below 20, the order of the mass activity concentrations of uranium-238 was as follows: 10 ~ 53 μm ≈ 2 ~ 10 μm > 0.4 ~ 2 μm greater than above 53 μm. The mass concentration of uranium-238 in the medium size particles were higher than those in the small and large particles. At Sta. JLI with high salinity, the order of the mass activity concentrations of uranium-238 changed as; 0.4 ~ 2 μm > 10 ~ 53 μm ≈ 2 ~ 10 μm approximately equaling above 53 μm. The increase of the uranium-238 mass concentration in the smallest size fraction (0.4 ~ 2 μm) further demonstrated the enhanced contribution of authigenic uranium at the offshore regime. In the study estuary, the mass concentrations of uranium-238 in greater than 53 μm fractions were constantly the lowest across the entire salinity regime (Fig. 5), suggesting that most of the uranium-238 associated with the largest particles was released into the dissolved phases before its transportation into the estuary. In contrast, the mass concentrations of uranium-238 in the 10 ~ 53 and 2 ~ 10 μm fractions decreased with the increasing salinity, indicating that the release from both size particles was occurring. Considering the conservative behavior of dissolved uranium in this estuary, it was reasonable to speculate that the flux of uranium released from the 10 ~ 53 and 2 ~ 10 μm fractions should be close to the uranium removal flux via the precipitation/aggregation of colloidal materials.

![Fig. 5. The mass activity concentrations of uranium-238 across a salinity gradient in the Jiulong Estuary. Greater than 53 μm fraction corresponds to the right axis, and the other fractions correspond to the left axis.](image)

3.4 Size-fractionated activity ratio of uranium-234 to uranium-238

Table 3 showed the ratio of uranium-234 to uranium-238 in the LMM, colloidal and different size particle fractions in the Jiulong Estuary. The ratio of uranium-234 to uranium-238 in the dissolved phases, including the LMM fraction and the colloidal fraction was higher than 1, while the ratio of uranium-234 to uranium-238 in different size particle frac-
tions was close to the equilibrium value (1.0). These values indicated that uranium-234 was excess relative to its parent uranium-238 in the dissolved phase, and was in near-equilibrium with uranium-238 in the particulate phase. The excess uranium-234 in the LMM and the colloidal fractions was ascribed to the preferential uranium-234 release from the host minerals and rocks by weathering. Uranium-234 was produced from uranium-238 by alpha decay. The alpha recoil process results in uranium-234 resident in damaged lattice locations, it is more vulnerable to leach from the lattice locations by fluids (Kigoshi, 1971). According to the processes described above, the ratio of uranium-234 to uranium-238 in the particulate phases should be lower than 1 due to the preferential uranium-234 release. However, our results showed that the ratio of uranium-234 to uranium-238 in the particulate phases was close to the equilibrium value (1.0). This disagreement may be due to the following: (1) Uranium amount in the minerals and rocks is significantly higher than that in the freshwater; the preferential uranium-234 release from the hosts only induces a tiny change of uranium activity ratios in the host particles; (2) particles in the estuary are relatively fresh compared with the soils and rocks on land; the short leaching time cannot result in significant disequilibrium between uranium-234 and uranium-238; (3) there is only a small difference between uranium-234 release rate and that of uranium-238. Uranium-234 deficiency in the host particles was insignificant during the short leaching time. Scott (1982) documented the ratio of uranium-234 to uranium-238 in the suspended particles in river waters in the world, and found that most of the ratio of uranium-234 to uranium-238 in the suspended particles was close to 1 and only a few were higher than 1. The authors argued that high ratio of uranium-234 to uranium-238 in the suspended particles was due to the high content of organic matter or carbonate. Chen et al. (1999) determined the ratio of uranium-234 to uranium-238 in the Jiulong Estuary surface water during the spring season, and found that the ratio of uranium-234 to uranium-238 in the suspended particles ranged from 1.04 to 1.17, slightly lower than that in the dissolved phases.

Table 3. The ratio of uranium-234 to uranium-238 in different size fractions in the Jiulong Estuary surface water

<table>
<thead>
<tr>
<th>Station</th>
<th>&gt;53 μm</th>
<th>10–53 μm</th>
<th>2–10 μm</th>
<th>0.4–2 μm</th>
<th>10 000 μ–0.4 μm</th>
<th>&lt;10 000 μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>JL1</td>
<td>0.83 ±0.16</td>
<td>1.02 ±0.08</td>
<td>1.02 ±0.20</td>
<td>1.00 ±0.17</td>
<td>1.09 ±0.05</td>
<td>1.12 ±0.02</td>
</tr>
<tr>
<td>JL2</td>
<td>0.89 ±0.15</td>
<td>1.03 ±0.08</td>
<td>0.96 ±0.10</td>
<td>1.16 ±0.19</td>
<td>1.16 ±0.05</td>
<td>1.16 ±0.04</td>
</tr>
<tr>
<td>JL3</td>
<td>1.18 ±0.13</td>
<td>1.20 ±0.08</td>
<td>0.89 ±0.07</td>
<td>1.19 ±0.16</td>
<td>1.20 ±0.05</td>
<td>1.11 ±0.02</td>
</tr>
<tr>
<td>JL4</td>
<td>1.00 ±0.14</td>
<td>1.06 ±0.05</td>
<td>1.23 ±0.18</td>
<td>1.01 ±0.17</td>
<td>1.10 ±0.06</td>
<td>1.11 ±0.04</td>
</tr>
<tr>
<td>JL5</td>
<td>1.12 ±0.20</td>
<td>1.05 ±0.07</td>
<td>0.99 ±0.09</td>
<td>1.14 ±0.18</td>
<td>1.13 ±0.08</td>
<td>1.14 ±0.03</td>
</tr>
<tr>
<td>Average</td>
<td>1.00 ±0.07</td>
<td>1.07 ±0.03</td>
<td>1.02 ±0.06</td>
<td>1.10 ±0.08</td>
<td>1.14 ±0.03</td>
<td>1.13 ±0.01</td>
</tr>
</tbody>
</table>

The ratio of uranium-234 to uranium-238 in the LMM and the colloidal fractions showed no isotopic difference between both fractions (Table 3). The lack of significant variation in isotopic composition demonstrated that substantial and rapid isotope exchange must have occurred between uranium in colloids and low molecular weight species. For comparison, Andersson et al. (2001) found no isotopic difference between LMM fractions (<3 000 μ) and colloidal fractions (3 000 μ~0.2 μm) in the Kalix Estuary.

3.5 Mass ratio of thorium-232 to uranium-238

Since the size-fractionated thorium isotopes
(thorium-232, thorium-230, thorium-228) were contemporarily determined at the same cruise (Zhang et al., 2005), it is possible to calculate the mass ratios of thorium-232 to uranium-238 in different size fractions. Our results showed that the mass ratios of thorium-232 to uranium-238 in the dissolved phases, including the LMM and the colloidal fraction, were lower than 1, while those in the different size particles were higher than 1 (Table 4). The partitioning characteristics of the mass ratios of thorium-232 to uranium-238 among various size fractions reflected the difference of geochemical behavior between uranium and thorium. It is well known that thorium is a particularly insoluble element in natural waters and it is usually found associated with solid matter. Thus, the mass ratios of thorium-232 to uranium-238 are typically much below unity in waters and above unity in particles.

<table>
<thead>
<tr>
<th>Table 4. Mass ratios of thorium-232 to uranium-238 in different size fractions in the Jiujiang Estuary surface water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Station</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>JL1</td>
</tr>
<tr>
<td>JL2</td>
</tr>
<tr>
<td>JL3</td>
</tr>
<tr>
<td>JL4</td>
</tr>
<tr>
<td>JL5</td>
</tr>
</tbody>
</table>

In the dissolved phases, the mass ratios of thorium-232 to uranium-238 in the colloidal fractions were around ten times higher than those in the LMM fractions, indicating the scavenging of thorium by aquatic colloids (Table 4). The mass ratios of thorium-232 to uranium-238 in the particulate phases ranged from 7.1 to 8.4. They were significantly higher than the typical values for surface rocks (3 - 4) (Andersson et al., 1995), and close to those for granite (3.5 - 6.5) (Wang, 1998). The high mass ratios of thorium to uranium in the particulate phases may probably be attributed to two reasons. One was the high mass ratios of thorium to uranium in the tetrigenous minerals/rocks. Most of the soils in the Jiujiang River come from the weathering of granite, a rock with high mass ratio of thorium to uranium and consists of 35% of the drainage area (The Guiyang Institute of Geochemistry of Chinese Academy of Sciences, 1979). The other was related to the difference of geochemical behavior between uranium and thorium. During the river transportation, thorium was scavenged onto the particles while uranium was released from them, which further resulted in the high mass ratios of thorium to uranium in the particulate fractions. Different mass ratios of thorium to uranium were observed for different size fractions, with the order as: $0.4 - 2 \, \mu m < 2 - 10 \, \mu m < 10 - 53 \, \mu m$ greater than above $53 \, \mu m$ (Table 4). This partitioning pattern of mass ratios of thorium to uranium was ascribed to the different surface areas of different size particles. Small particles have large surface areas, and will adsorb more thorium than the large one, which induced the high mass ratios of thorium to uranium in the particles.

4 Conclusions

The size-fractionated uranium isotopes and their geochemical behaviors in the Jiujiang Estuary surface water were studied. On the basis of our results, the following conclusions and implications can be drawn.

(1) The low molecular mass uranium-238 ($< 10,000 \, \mu m$) was the dominative species ($<0.4 \, \mu m$)
in the dissolved phase, and colloidal uranium-238 (10 000 u ~ 0.4 μm) contributed the only being less than 1% of the dissolved phase. This situation was different from that observed in the Amazon and Kalix Estuaries, where the colloidal phase was an important fraction in the dissolved phases.

(2) The dissolved, low molecular mass and colloidal uranium-238 all increased linearly with the increasing salinity, demonstrating the conservative behavior of uranium in the Jiulong Estuary.

(3) At salinities below 20, the partitioning of uranium among different size particles was controlled by the partitioning of particle concentrations. In contrast, the fractions of the 0.4 ~ 2 μm particles increased in the offshore regime, indicating the enhanced contribution of authigenic uranium.

(4) The activity ratio of uranium-234 to uranium-238 in the dissolved, low molecular mass and colloidal phases were higher than 1 while those in different size particles were close to 1, reflecting the preferential uranium-234 release from the host minerals and rocks by weathering.

(5) The mass ratios of thorium-232 to uranium-238 in the dissolved, low molecular mass and colloidal phases were lower than 1 while those in different size particles were higher than 1, reflecting more particle reactive to thorium over uranium in aquatic systems.

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