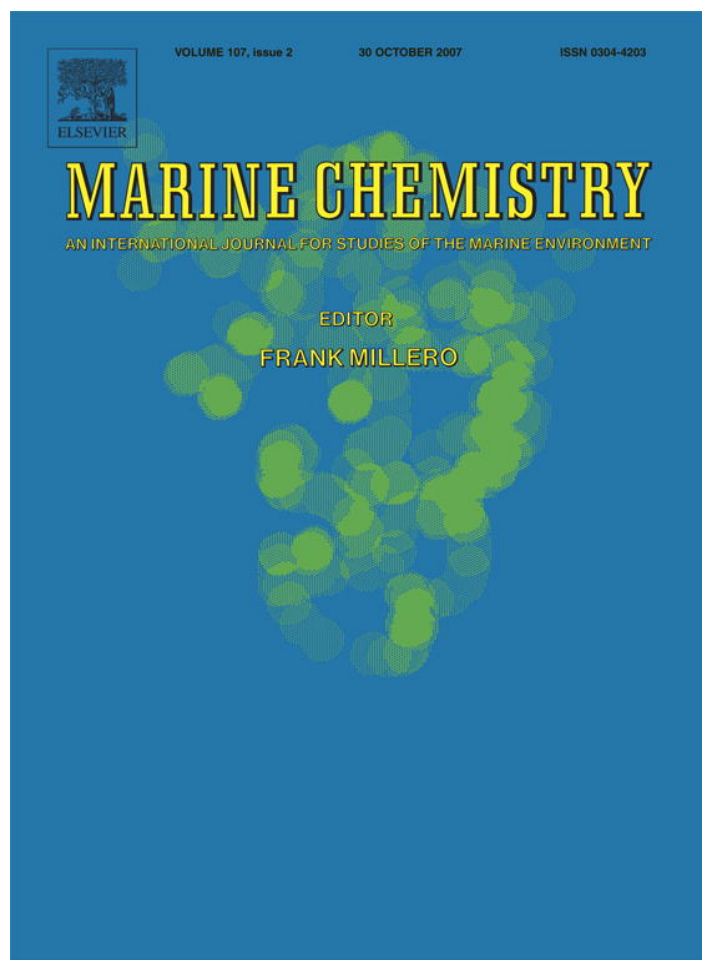


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article was published in an Elsevier journal. The attached copy is furnished to the author for non-commercial research and education use, including for instruction at the author's institution, sharing with colleagues and providing to institution administration.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Retention behavior of dissolved uranium during ultrafiltration: Implications for colloidal U in surface waters

Laodong Guo^{a,*}, Kent W. Warnken^b, Peter H. Santschi^c

^a Department of Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529, USA

^b Department of Environmental Science, Lancaster University, Lancaster, LA1 4YQ, UK

^c Dept. of Marine Science and Oceanography, Texas A&M University, 5007 Avenue U, Galveston, TX 77551, USA

Received 29 January 2007; received in revised form 12 June 2007; accepted 13 June 2007

Available online 4 July 2007

Abstract

While uranium (U) in natural waters is very soluble and highly mobile as U(VI), a colloidal, ultrafilterable, form of U was, at times, reported to be important. Laboratory experiments were thus carried out to examine the behavior of dissolved U during ultrafiltration (1 kDa, Amicon S10Y1) of both natural (containing colloids) and spiked artificial river waters (containing no colloids). In addition, the distribution of dissolved and colloidal U was determined for samples collected across a salinity gradient in Galveston Bay (Texas, USA) using ICP-MS. Results of laboratory experiments showed that the constant permeation model can be used to predict the ultrafiltration behavior of U in both natural and synthetic river waters. Most importantly, we found that low molecular weight (< 1 kDa) U can indeed be retained by a 1 kDa membrane by as much as 30–60%. This behavior is similar to that previously reported for SO₄, a major anion in sea water, and suggests an artifactual retention of dissolved U through preferential rejection by negatively charged membranes. Concentrations of total dissolved U increased from 2.9±0.9 nmol kg⁻¹ in the Trinity River freshwater endmember to 8–9 nmol kg⁻¹ in higher salinity estuarine waters of Galveston Bay. The annual export flux of dissolved U from the Trinity River was estimated to be 6.3 × 10⁴ moles, corresponding to a weathering rate of 0.75 moles-U/km²/yr in the Trinity River basin. Colloidal U, derived using the ultrafiltration permeation model, accounted for ~ 15% of the total dissolved U in river waters but was negligible in the higher salinity coastal waters. Therefore, apparent colloidal U concentrations calculated from the concentration difference between initial and permeate solutions, or measured directly from the retentate solution under low concentration factors (ratio of initial volume to final volume of retentate), can be significantly overestimated compared with truly colloidal U concentrations derived from the ultrafiltration permeation model. The association of dissolved U with nanoparticles and macromolecular organic matter in higher salinity seawater seems minimal and most dissolved U in seawater should be in the form of anionic U with a molecular weight < 1 kDa.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Dissolved uranium; Colloids; Ultrafiltration; Estuary; Galveston Bay; Trinity River

1. Introduction

Aquatic colloids, including organic biopolymers and inorganic nanoparticles, are abundant in natural waters (e.g., Buffle and Leppard, 1995; Guo and Santschi,

1997a; Gustafsson and Gschwend, 1997; Wells, 2002), and play a crucial role in regulating the speciation, bioavailability, and mobility of many trace metals, radionuclides and trace organic contaminants in aquatic environments (Honeyman and Santschi, 1989; Sigleo and Means, 1990; Wang and Guo, 2000; Santschi et al., 2002; Lead and Wilkinson, 2006). Due to the presence and significance of colloids in aquatic environments,

* Corresponding author. Tel.: +1 228 688 1176.

E-mail address: Laodong.Guo@usm.edu (L. Guo).

much work has been focused on their isolation, characterization and biogeochemical cycling (e.g., Guo and Santschi, 2007 and references therein). One of the most commonly used techniques in isolating colloids from natural waters is cross-flow ultrafiltration (Bueseler et al., 1996; Guo and Santschi, 2007). However, while the retention and permeation behavior of chemical species during ultrafiltration remains poorly understood, this information is vital to understanding of the ultrafiltration process in general and to correct interpretation of the size fractionation data obtained (Guo and Santschi, 1996; Gustafsson et al., 1996; Guo et al., 2000, 2001; Wilding et al., 2004).

Uranium (U) is a soluble element although its concentrations in natural waters are generally low, with increasing concentration from river water to seawater. The geochemical behavior of dissolved U seems to vary from one estuary to another (Carroll and Moore, 1993; Ingri et al., 2004; Swarzenski et al., 2003 and references therein). The partitioning of U between dissolved and colloidal phases may affect its geochemical behavior, especially at the freshwater/seawater interface, thereby altering fluxes of U from rivers to the ocean. While several recent investigations of colloidal U in natural waters have been carried out using ultrafiltration (e.g., Swarzenski et al., 1995; Chen et al., 2000; Zänker et al., 2000; Andersson et al., 2001; Singhal et al., 2004; Lu et al., in press), the extent to which U associates with colloidal macromolecules and nanoparticles remains poorly quantified. As shown in Table 1, the variability in the partitioning of U to the colloidal fraction may depend

on specific water chemistry parameters, U concentrations and composition and/or concentration of organic matter, as well as the rejection characteristics of the ultrafiltration membranes. From these limited colloidal U data that resulted from studies using different ultrafiltration membranes, any conjecture or generalized conclusions regarding the phase fractionation of U in natural waters becomes difficult.

Using a 10 kDa ultrafiltration membrane, Tanazaki et al. (1992) reported an average colloidal U percentage of $12 \pm 9\%$ for two Japanese rivers. Swarzenski et al. (1995) measured colloidal U in the Amazon River and its shelf waters and observed significant U removal during early estuarine mixing (salinity = 15). They found a high percentage of colloidal U in the Amazon River fresh water end-member ($\sim 90\%$ in the > 10 kDa fraction), decreasing colloidal U with increasing salinity in the shelf area, and 14% colloidal U in the seawater end-member. Andersson et al. (2001) also reported colloidal U abundances in the Kalix River estuary with a 3 kDa ultrafiltration membrane, ranging from less than 10% to $\sim 90\%$. In the Jiulong River estuary, however, very low colloidal U percentages of $< 1\text{--}2\%$ were measured using a 10 kDa ultrafiltration membrane (Chen et al., 2000; Lu et al., in press). Similarly, Harnish et al. (1996) reported low colloidal U concentrations (a few percent of the total U activity) in surface and ground waters at the Rocky Flats Environmental Technology Site in Colorado using 10 and 100 kDa membranes (Table 1).

Recent studies have shown that a significant fraction of low molecular weight (LMW, < 1 kDa) materials can

Table 1
Comparison of the reported colloidal uranium fractions in natural waters

Location	Salinity	U (n-mol/kg)	Size fraction	Colloidal U (%)	Reference
River waters	–	0.076 ± 0.043	0.5 kDa–10 kDa	53 ± 10	Tanazaki et al. (1992)
River waters	–	0.076 ± 0.043	10 kDa– $0.45 \mu\text{m}$	12 ± 9	Tanazaki et al. (1992)
Amazon River	0.31	0.504	10 kDa– $0.45 \mu\text{m}$	83	Swarzenski et al. (1995)
Amazon River	9.74	1.85	10 kDa– $0.45 \mu\text{m}$	34	Swarzenski et al. (1995)
Amazon Shelf	35.44	13.8	10 kDa– $0.45 \mu\text{m}$	14	Swarzenski et al. (1995)
Surface and ground waters	–	–	10 kDa– $5 \mu\text{m}$	< 3	Harnish et al. (1996)
Kalix River	–	0.46–0.75	10 kDa– $0.45 \mu\text{m}$	20–90	Porcelli et al. (1997)
Lake Pavin	–	0.17	> 1 kDa	78	Alberic et al. (2000)
Lake Pavin	–	0.17	> 10 kDa	18	Alberic et al. (2000)
Jiulong River estuary	29.6	12.8	10 kDa– $0.22 \mu\text{m}$	< 2	Chen et al. (2000)
Kalix River estuary ^a	~ 3	1.37	3 kDa– $0.2 \mu\text{m}$	4–6	Andersson et al. (2001)
Kalix River estuary	~ 2	0.99	3 kDa– $0.2 \mu\text{m}$	19–41	Andersson et al. (2001)
Kalix River estuary	0.8–1.4	0.66	3 kDa– $0.2 \mu\text{m}$	33–88	Andersson et al. (2001)
Groundwater	< 0.2	0.004–0.05	10 kDa– $0.45 \mu\text{m}$	47–94	Tricca et al. (2001)
Coastal seawater	–	29.1 ± 13.0	0.5 kDa– $0.22 \mu\text{m}$	~ 80	Singhal et al. (2004)
Jiulong River estuary	1.1–31	1.19 – 11.8	10 kDa– $0.45 \mu\text{m}$	< 1	Lu et al. (in press)

^a Low numbers of colloidal U in the Kalix River estuary are from the direct measurements in the retentate and the high numbers are from the concentration difference between initial solution and permeate (< 3 kDa).

be retained by a 1 kDa ultrafiltration membrane, which included organic molecules such as 0.59 kDa raffinose (Guo and Santschi, 1996) and 0.49 kDa rhodamine 6G (Guo et al., 2000), and major anionic species such as SO_4^{2-} (Guo et al., 2001). In addition, LMW complexed metals can also be retained to different extents (Guo et al., 2000). Similarly, Favre-Réguillon et al. (2005) also reported a selective rejection of dissolved U from seawater using cross-flow ultrafiltration.

The objective of this study was thus to examine the permeation and retention characteristics of U in contrasting mediums, i.e., natural vs. artificial river waters, and to quantify the colloidal U in estuarine waters of Galveston Bay. Our hypothesis is that anionic U species, present in most natural waters, may exhibit a similar ultrafiltration behavior as that previously described for SO_4^{2-} (Guo et al., 2001). It is expected that during ultrafiltration under low concentration factors (CF, the ratio of initial water volume divided by the volume of final retentate), artifactual retention of dissolved U species could result in higher apparent colloidal U concentrations. In addition, the annual export flux of dissolved U from the Trinity River was also estimated based on a year long biweekly sampling.

2. Experimental

2.1. Sampling of waters from the Trinity River and Galveston Bay

Water samples were collected from the Trinity River, as well as from Galveston Bay (Texas, USA). Immediately after collection, samples were filtered through a pre-cleaned 0.2 μm Nuclepore cartridge into a pre-washed 20 L Nalgene container. A filtered river

Table 2
Salinity and dissolved U concentrations in Galveston Bay waters used for ultrafiltration

Sample #	Salinity	U (n-mol/kg)	Ultrafiltration
1	~ 0	3.36±0.047	Time series
2	~ 0	2.980±0.042	Conventional
3	3.0	3.417±0.049	“
4	4.4	3.669±0.049	“
5	6.9	4.705±0.001	“
6	8.6	4.761±0.121	Time series
7	12.2	6.092±0.001	Conventional
8	17.5	8.122±0.243	“
9	19.4	8.962±0.243	“
10	21.6	8.122±0.243	Time series

Sample #1 was collected from the Trinity River in October 2000 while other samples are collected from Galveston Bay during April 2001. Ultrafiltration was carried out using both spiral wound cartridge (sample #1) and stirred cell membrane (sample #2–10).

Table 3
Uranium concentrations and other hydrographic parameters in the Trinity River^a

Date	Q (m ³ /s)	Conductivity (μS cm ⁻¹)	DOC (μM)	U (nmol kg ⁻¹)
06-Sep-00	32.0	454	350	2.69±0.024
06-Nov-00	617.3	413	370	4.33±0.042
11-Nov-00	591.8	390	382	4.62±0.084
21-Nov-00	308.7	369	392	3.24±0.042
09-Dec-00	63.7	365	454	2.61±0.042
18-Dec-00	247.8	360	461	3.74±0.084
28-Dec-00	671.0	358	425	4.16±0.084
02-Jan-01	742.0	353	429	3.91±0.084
16-Jan-01	436.1	332	430	3.99±0.084
20-Jan-01	1008.0	272	557	0.71±0.001
12-Feb-01	189.4	293	479	2.14±0.042
22-Feb-01	557.8	291	462	2.35±0.042
28-Feb-01	1138.0	290	534	2.27±0.042
04-Mar-01	1699.0	288	559	2.27±0.001
16-Mar-01	1781.0	285	534	1.93±0.042
21-Mar-01	1531.9	269	552	2.69±0.042
26-Mar-01	1282.8	276	519	3.07±0.042
09-Apr-01	821.2	293	511	2.98±0.042
23-Apr-01	267.9	316	484	2.52±0.042
09-May-01	258.8	336	457	3.28±0.042
11-Jun-01	2033.1	329	444	4.20±0.084
24-Jun-01	60.6	294	444	2.02±0.042
17-Jul-01	62.3	320	452	2.65±0.042
06-Aug-01	41.6	292	450	2.31±0.042
Average±SD	–	327±48	464±59	2.94±0.94

^a Data of DOC concentrations from Warnken and Santschi (2004). Alkalinity of Trinity River water ranges between 1.8 and 2.2 meq/L.

water sample (pH=7.7; Conductivity=326 μS cm⁻¹; DOC=375 μM) was used for testing the permeation behavior of U during ultrafiltration, while a suite of estuarine water samples were collected from Galveston Bay, during April 2001, to investigate changes in the phase fractionation of U with changes in salinity (Table 2). In addition, river water samples were also collected from the Trinity River during September 2000 to August 2001, to examine the seasonality of dissolved U and its riverine export flux to Galveston Bay. Concentrations of dissolved U, along with other hydrographic parameters, are listed in Table 3. Detailed water chemistry and fluxes of DOC and trace metals have been published elsewhere (Warnken and Santschi, 2004, 2007).

2.2. Cross-flow ultrafiltration of large volume river water and spiked samples

In order to examine the retention behavior of dissolved U during ultrafiltration, both Trinity River water, containing natural DOC, and artificial river water, with only background DOC, were used. Artificial river

water was prepared with nanopure water (background DOC concentration of $\sim 2 \mu\text{M}$) based on averaged major element composition of river waters (Martin and Whitfield, 1983; Berner and Berner, 1987). Major cations and anions are K^+ (0.03 mM), Na^+ (0.23 mM), Ca^{2+} (0.33 mM), Mg^{2+} (0.15 mM), Cl^- (0.16 mM), HCO_3^- (0.86 mM) and SO_4^{2-} (0.069 mM). The artificial river water (with a conductivity of 130 $\mu\text{S}/\text{cm}$ and alkalinity of 0.86 meq/L) was then spiked with a 1000 ppm U-salt standard (in 2% HNO_3) to a final concentration that is similar to that found in Trinity River water. The very small volume U solution added did not significantly change the pH. However, it is likely that the added chemicals may have also introduced ultratrace amounts of DOC and other impurities such as trace metals in the artificial river water, which were, however, not measured.

A spiral-wound 1 kDa Amicon S10Y1 cross-flow ultrafiltration cartridge (with regenerated cellulose as the membrane material) was used for the ultrafiltration of both Trinity River water and U-spiked artificial river water samples. To minimize sorptive losses and possible contamination from the apparatus, a Teflon[®] diaphragm pump head, with all associated fittings and tubings also being made of Teflon, was used (Guo et al., 2000). Calibration of the membrane cutoff was performed with a 1.3 kDa vitamin B₁₂ solution and showed a rejection rate of 0.94 for this specific cartridge.

Prior to use, the ultrafiltration cartridge was sequentially cleaned using 1–2% Micro[®] detergent solution, 0.05 M NaOH and 0.02 M HCl (Guo and Santschi, 1996). Each solution was recycled for 20–30 min and the membrane was allowed to soak for additional 20–30 min. Between each solution, ~ 40 l of nanopure water was flushed through the ultrafiltration system with the permeate and retentate lines going directly to a waste container. After cycling the HCl solution, 40 l of nanopure water was flushed through the system under normal operating conditions. The now clean membrane was preconditioned by cycling ~ 1 l of prefiltered water for 10–20 min. For the U-spiked sample, membrane pre-conditioning was carried out with un-spiked artificial river water. For these large volume ultrafiltration experiments, about 20 l of water was used and discrete permeate samples were collected at different CFs in a time series fashion.

2.3. Ultrafiltration of estuarine waters using stirred cell

Estuarine water samples were ultrafiltered through a stirred cell membrane disk with a molecular weight cutoff of 1 kDa (Millipore YM1) using a small volume

(500 ml). Before use, each ultrafilter membrane was soaked in nanopure water overnight and precleaned by ultrafiltering 200–300 ml of nanopure water before sample processing. From the onset of the experiment to its conclusion, permeate samples were collected from the stirred cell permeate line at increasingly higher CFs for selected samples.

2.4. Determinations of uranium

Concentrations of U were measured using a VG Plasma Quad 2 inductively coupled plasma mass spectrometer (ICP-MS) at the Laboratory for Oceanography and Environmental Research (LOER) at Texas A and M University at Galveston (Warnken et al., 1999) and a Thermo Fisher Scientific X7 Series ICP-MS at Lancaster University (UK). Both instruments were equipped with Pt-tipped sampler and microskimmer cones and a high-performance interface was used for improved sensitivity. Instrument optimization was performed by tuning the instruments for In/Cu ratios, while keeping the oxide levels $< 2\%$ and the doubly charged species $< 5\%$. To verify instrument stability, a 10 min short term stability test was carried out.

Accuracy and precision of the instruments was verified by the analysis of the standard reference material SLRS-4, a riverine water sample (National Research Council of Canada) and a value of $0.210 \pm 0.004 \text{ nmol kg}^{-1}$ was obtained. In addition, NASS-5, a certified seawater reference material with a salinity of 30.4 was analyzed after a dilution of 100 times, to verify that dilution was adequate for matrix free analysis, and a value of $10.92 \pm 0.004 \text{ nmol kg}^{-1}$ was obtained. The obtained U concentrations for SLRS-4 and NASS-5 were in agreement with their certified values, i.e. the 95% confidence limit (SLRS-4) and information only value (NASS-5), respectively, indicating analysis was without interference. Thus, samples collected from Galveston Bay were appropriately diluted from 2 times (freshwater end member) to 100 times (seawater end member), with analytical precisions of $< 2\%$.

2.5. Ultrafiltration permeation model

According to the ultrafiltration permeation model (Logan and Jiang, 1990; Kilduff and Weber, 1992), the relationship between LMW (or permeable) solute concentration, C_p , and the concentration factor, CF (the ratio of initial water volume divided by the volume of final retentate) can be described in Eq. (1):

$$\ln(C_p) = (1 - P_c)\ln(\text{CF}) + \ln(C_L^0 \times P_c) \quad (1)$$

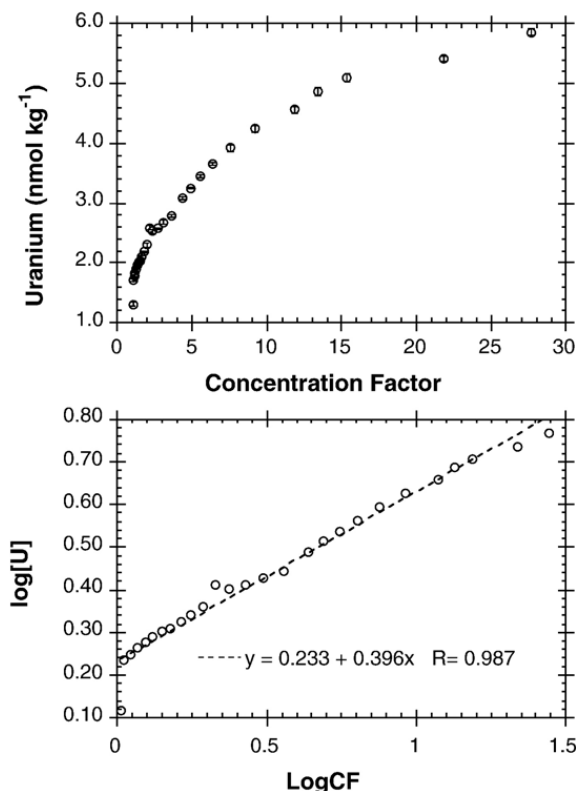


Fig. 1. Uranium concentrations in the permeate solution as a function of concentration factor (CF) (upper panel) and the relationship between $\log C_p$ and $\log CF$ (lower panel) for a Trinity River water sample.

where P_c is the permeation coefficient of LMW U, defined here as the fraction < 1 kDa, and C_L^0 is the initial LMW U concentration in the sample. A linear relationship between $\ln(C_p)$ and $\ln(CF)$ (or; $\log(C_p)$ and $\log(CF)$) indicates constant permeation (constant P_c) of LMW or permeable species (Guo and Santschi, 1996). Based on the constant permeation model, values of P_c and C_L^0 can be calculated from the values of the slope (m) and y intercept (b) of the linear relationship between $\ln(C_p)$ and $\ln(CF)$, as in Eq. (2):

$$P_c = 1 - m, \text{ and } C_L^0 = \exp(b)/P_c. \quad (2)$$

The concentration of colloidal U can then be calculated as the difference between C_L^0 and the initial dissolved U concentration (Guo and Santschi, 1996; Guo et al., 2000).

3. Results and discussion

3.1. Retention of dissolved U during ultrafiltration

Concentrations of U in the permeate solution, sampled at discrete time intervals during ultrafiltration, are plotted versus CF for a natural water sample collected

from the Trinity River (Fig. 1). Using the ultrafiltration permeation model to fit the data (see Section 2.5), one finds a linear relationship between $\log(C_p)$ and $\log(CF)$, indicating constant permeation of LMW U during ultrafiltration with a permeation coefficient of < 1 .

Previous studies have shown an increase in the permeate concentrations of LMW organic macromolecules, trace metals and major ions with increasing concentration factor (CF) (e.g., Guo and Santschi, 1996; Gustafsson et al., 1996; Guo et al., 2000, 2001; Wilding et al., 2004). Using model LMW organic compounds, this increase in the permeate solution concentration with increasing CF has been shown to be the result of the retention of LMW materials (e.g., Guo et al., 2000). Therefore, the observed relationship is, according to the permeation model, a logical consequence of the permeation/retention process of LMW molecules through membranes.

Ultrafiltration of an artificial river water sample spiked with U (containing no organic or colloidal particles) was used for comparison with the Trinity River water sample containing natural colloids. In a similar manner, permeate samples were collected at discrete time intervals during ultrafiltration to examine the retention behavior of dissolved U (Fig. 2). As shown in Fig. 2, spiked U in the

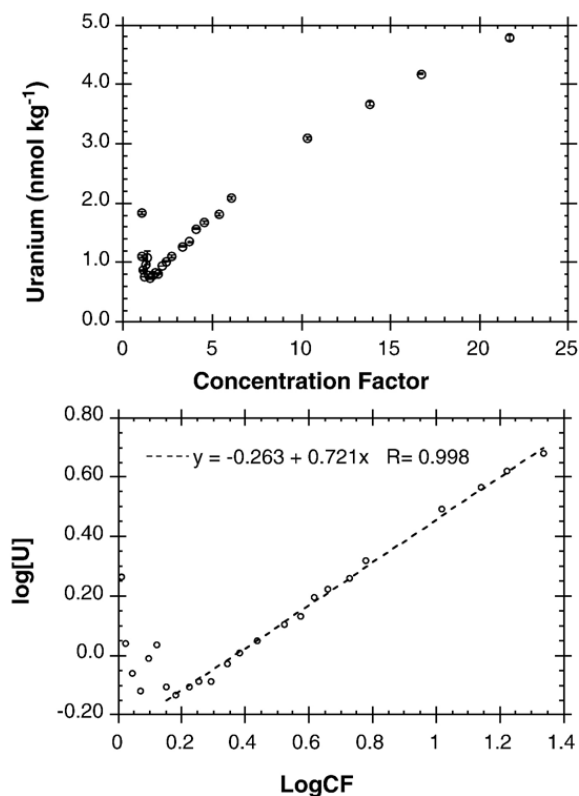


Fig. 2. Variations of U concentrations in the permeate solution with concentration factor (CF) (upper panel) and the relationship between $\log C_p$ and $\log CF$ (lower panel) for an artificial river water spiked with U.

artificial river water (without colloids) demonstrated the same ultrafiltration behavior as natural U in the Trinity River sample, although values of the permeation coefficient (P_c) are slightly different. As ultrafiltration progressed, the U concentration in the retentate solution increased with increasing CF due to partial retention of LMW U, which led to an increase in permeate U due to a constant permeation of LMW U. The constant permeation rate of LMW U species in the artificial river water has again been indicated by a linear relationship between $\log [U]$ and $\log CF$ (Fig. 2).

The same ultrafiltration behavior of dissolved U in both natural and artificial river waters indicates that the increase in U concentration in the permeate with increasing CF is indeed due to the permeation of LMW-U species but not any HMW or colloidal U. This is consistent with findings for major ions such as SO_4^{2-} (Guo et al., 2001) and model LMW organic compounds (Guo et al., 2000; Wilding et al., 2004). Because of the retention of dissolved U, lower CFs will give rise to a higher fraction of LMW materials (i.e., [LMW-U]/[dissolved U]) in the retentate solution and thus higher apparent colloidal U concentrations measured from the retentate. This ultrafiltration artifact has mostly been ignored in the literature, not only for organic but also for inorganic chemical species (Guo and Santschi, 2007).

Interestingly, the model derived permeation coefficient for natural river water ($P_c=0.604$; see also Fig. 1) is higher than that of artificial river water ($P_c=0.279$, Fig. 2), suggesting differences between these two waters. It is likely that the complexation of U with riverine DOM rather than with carbonate, which gives the complex a higher ratio of charge to radius, could cause the lower retention and thus the higher permeation of LMW-U. Thus, the artificial river water without the presence of natural DOM could result in a higher retention rate and lower permeation coefficient for LMW-U species. In general, many ultrafiltration membranes, including the one we used during this study, are negatively charged (Buffle et al., 1992). Hence, the retention of U during ultrafiltration would largely depend on chemical forms of dissolved U in the solution (Favre-Régouillon et al., 2005), but not as much on the sign of the charge, since positively charged

membranes show similar effects for major cations due to maintenance of electroneutrality (Buffle et al., 1992).

In surface waters, major inorganic and organic complexed U species include uranyl carbonate species, such as $(UO_2)(CO_3)_2^{2-}$, $(UO_2)(CO_3)_3^{4-}$, uranyl phosphate, and uranyl fulvates and humates (Markich, 2002; Favre-Régouillon et al., 2005). Therefore, dissolved U species in pure inorganic solutions largely exist as anionic complexes, resulting in a higher rejection rate or larger retention of dissolved U by ultrafiltration membranes (Fig. 2), similar to the retention behavior of SO_4^{2-} , a major anion in natural waters (e.g., Guo et al., 2001).

3.2. Colloidal U as quantified by ultrafiltration permeation model vs. conventional calculations

As shown in our previous studies (Guo and Santschi, 1996; Guo et al., 2000; Belzile and Guo, 2006), the colloidal fraction of a chemical species in natural waters can be quantitatively determined by application of an ultrafiltration permeation model. Fitting the time series data, values of the model derived parameters such as the LMW-U permeation coefficient (P_c), ambient LMW-U concentration and colloidal U fraction, are listed in Table 4. Interestingly, albeit it only for three samples, the difference in the model derived LMW-U concentrations and the initial dissolved U concentrations increased with decreasing salinity. This is a strong indication that erroneously high retentate U concentrations result largely from artifactual retention of LMW-U by ultrafiltration membranes, and that truly colloidal fractions of U in estuarine waters are indeed very low. This conclusion is consistent with the fact that U is a highly soluble element with a long residence time in the ocean (e.g., Ku et al., 1977). Association of dissolved U with HMW DOM and colloidal macromolecules and nanoparticles appears to be low, leaving dissolved U as mostly LMW ionic complexes (Djogic et al., 1986; Markich, 2002) although a significant fraction of dissolved U could still be mistakenly classified as colloidal due to anionic retention.

In general, apparent colloidal U concentrations decreased with increasing salinity, a trend similar to that reported for the Amazon River plume (Swarzenski et al.,

Table 4
Model parameters and colloidal U fraction derived from time series permeate data from selected samples

Salinity	U (nmol kg ⁻¹)	Slope	P_c	Intercept	LMW-U (nmol kg ⁻¹)	Colloidal fraction
0	3.36	0.396	0.604	0.233	2.83	0.15
8.6	4.76	0.643	0.357	0.174	4.18	0.12
21.6	8.12	0.678	0.322	0.422	8.20	~ 0

Table 5

Comparisons between colloidal fractions (F_C) derived from the permeation model (F_{C-M}), concentration difference between initial solution and permeate (F_{C-P}), and measurement in the retentate solution (F_{C-R})

S#	Salinity	Dissolved U (n-mol/kg)	F_{C-R}	F_{C-P}	F_{C-M}
1 ^a	0	3.36±0.047	0.59	0.38	0.15
2	0	2.980±0.042	0.56	0.46	–
3	3.0	3.417±0.049	0.46	0.42	–
4	4.4	3.669±0.049	0.45	0.44	–
5	6.9	4.705±0.001	0.48	0.41	–
6	8.6	4.761±0.121	0.49	0.38	0.12
7	12.2	6.092±0.001	0.40	0.45	–
8	17.5	8.122±0.243	0.55	0.40	–
9	19.4	8.962±0.243	0.48	0.50	–
10	21.6	8.122±0.243	0.53	0.34	0

F_{C-R} : colloidal U fraction derived from direct measurement of retentate and permeate solutions and CF (i.e., $F_{C-R}=(C_R-C_{IP})/CF/C_0$).

F_{C-P} : colloidal U fraction derived from concentration difference between initial solution and integrated permeate (i.e., $F_{C-P}=(1-C_{IP}/C_0)$).

F_{C-M} : colloidal U fraction derived from time series data and ultrafiltration permeation model (i.e., $F_{C-M}=C_L^0/C_0=10^{(\text{intercept})}/P_c/C_0$).

^a Sample #1 was collected at a different season from the Trinity River.

1995). However, the model-derived colloidal U fractions reported here are considerably lower than those reported previously (Table 1), but are consistent with studies which based their results on either the permeation model (Chen et al., 2000) or the use of high concentration factors (30–40) (Lu et al., in press) considering the different molecular weight cut-off membranes that were used.

In order to examine quantitatively the discrepancy in the colloidal U fractions (F_C), model-derived values (F_{C-M}) were compared to conventionally calculated values from single point measurements in permeate (F_{C-P}) and/or retentate (F_{C-R}). The calculated colloidal U fractions for the three different methods of calculation are listed in Table 5. The two conventional methods include a) estimation from CF, initial dissolved U concentration (C_0), U concentration in the retentate (C_R), and U concentration in the integrated permeate (C_{IP}), using $F_{C-R}=(C_R-C_{IP})/CF/C_0$ (see also Buesseler et al., 1996), and b) estimation from the U concentration difference between initial (C_0) and integrated permeate (C_{IP}) solutions (i.e., $F_{C-P}=(1-C_{IP}/C_0)$) at the same final CF. The permeation model derived method uses $F_{C-M}=C_L^0/C_0=\exp(\text{intercept})/P_c/C_0$ (Guo and Santschi, 1996). Indeed, one finds that the colloidal U fractions calculated using conventional methods are considerably higher than those derived from the permeation model (Table 5), although the difference between the two conventional methods, i.e., $F_{C-P}=(1-C_{IP}/C_0)$ or $F_{C-R}=(C_R-C_{IP})/CF/C_0$, is relatively small. Higher colloidal U fractions estimated from conventional methods are

again mostly the result of ultrafiltration artifacts due to the retention of LMW materials, in particular when negatively charged complexed ionic species are investigated (Guo et al., 2001; Favre-Réguillon et al., 2005). These results further support the notion that quantitative determination of the colloidal concentration (or percentage) of an ionic chemical species can only be achieved by time series sampling coupled with the use of an ultrafiltration permeation model (Guo and Santschi, 1996, 2007).

High percentages of colloidal U reported for natural waters are thus likely the result of the preferential retention of dissolved U through its interactions with the ultrafiltration membrane. In addition, colloidal fractions conventionally calculated from concentration differences between initial solution, integrated permeate, and retentate solution can be greatly overestimated, especially at low concentration factors (e.g., Guo and Santschi, 1996; Belzile and Guo, 2006). Taken together, these two factors are likely the main reasons for the variability in the reported fractions of colloidal U (Table 1). Further studies are needed to examine quantitatively the distribution of colloidal U concentrations and fractions in different aquatic environments.

3.3. Distributions of dissolved and colloidal U in Trinity River and Galveston Bay waters

Concentrations of dissolved U in the Trinity River ranged from 0.71 nmol kg⁻¹ in Jan. 2001 to 4.62 nmol kg⁻¹ in Nov. 2000, with a yearly average of 2.94±0.94 nmol kg⁻¹ (Table 3), which is significantly higher than the world average concentration of 0.7–1.4 nmol kg⁻¹ (Cochran, 1982; Palmer and Edmond, 1993; Windom et al., 2000) and likely the result of the large number of uranium strip mines operating in the upper reaches of the Trinity River drainage basin. Dissolved U concentrations in Trinity River waters were negatively correlated with DOC concentration, but positively correlated with conductivity (Fig. 3); correlations that are similar to those found for vanadium in the Trinity River sampled at the same time (Warnken and Santschi, 2007). These different relationships indicate that dissolved U and DOC in the Trinity River have different source terms, i.e. dissolved U being derived mostly from the leaching and weathering of exposed continental crust, with a dilution effect by rainwater runoff (negatively correlated with river discharge), and DOC largely derived from the leaching of surface soils (Warnken and Santschi, 2004). Based on results from biweekly sampling, the annual export flux of dissolved U from the Trinity River was estimated to be 6.3×10⁴

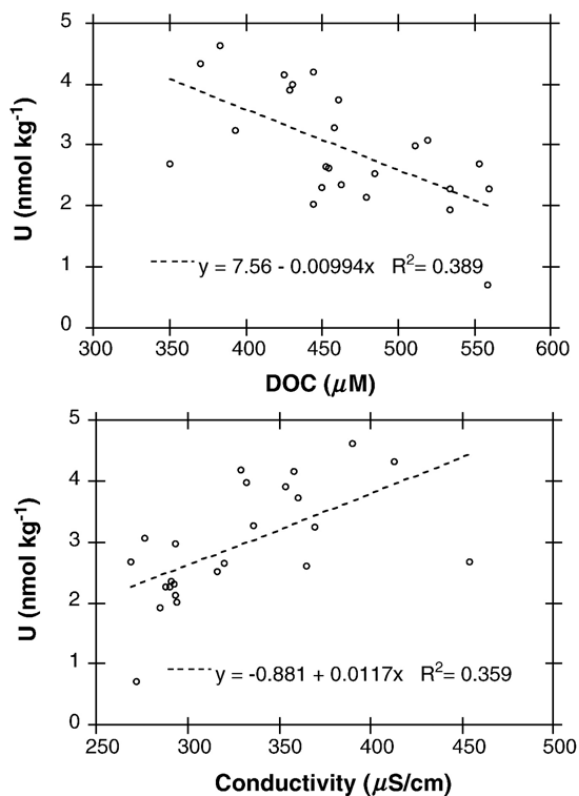


Fig. 3. Relationship between dissolved U (nmol kg^{-1}) and dissolved organic carbon (DOC, upper panel) concentrations or conductivity (lower panel) in Trinity River waters during September 2000–August 2001.

moles-U during Sept. 2000–Aug. 2001, compared to a global river U flux of $3\text{--}6 \times 10^7$ mol-U/yr (Palmer and Edmond, 1993). This annual flux from the Trinity River corresponds to a dissolved U yield (or weathering rate) of 0.75 moles U/ km^2 /yr from the Trinity River Basin, which is again substantially higher than the world average of $0.17\text{--}0.34$ moles-U/ km^2 /yr (Cochran, 1982; Palmer and Edmond, 1993), but significantly lower than those ($0.38\text{--}3.7$ moles-U/ km^2 /yr) of the rivers of India (e.g., Rengarajan et al., 2006).

Concentrations of dissolved U in Galveston Bay waters varied from ~ 3 nmol kg^{-1} in the lower salinity waters to concentrations of $8\text{--}9$ nmol kg^{-1} in the higher salinity coastal waters, and showed a linear increase with increasing salinity in Galveston Bay waters (Fig. 4). This linear trend, indicative of conservative estuarine mixing, is consistent with previously reported relationships between dissolved U and salinity (e.g., Borole et al., 1977; Toole et al., 1987; Lu et al., in press), although the geochemical behavior of dissolved U in river and estuarine waters could vary among estuaries (Carroll and Moore, 1993; Swarzenski et al., 2003 and references therein).

Concentrations of dissolved U showed a general increase with increasing salinity, whereas DOC concentrations decreased with increasing salinity (Fig. 4; Table 2; Guo and Santschi, 1997b). However, the apparent colloidal U fraction (not truly colloidal) did not show a consistent trend with salinity or dissolved U concentration (Table 5). The averaged apparent colloidal U percentage calculated from concentration differences between initial solution and the integrated permeate solution was $42 \pm 5\%$, while it was $50 \pm 6\%$ calculated from the concentration in the retentate solution and the CF (Table 5). In other words, $42\text{--}50\%$ of the total dissolved U was measured as the apparent colloidal fraction (not truly colloidal) in Galveston Bay waters. These apparent colloidal U results appear to be similar to those reported for natural waters using conventional calculation methods (Table 1), and they are greatly overestimated, and are largely the result of misinterpreting ultrafiltration data.

Again, high apparent colloidal fractions are largely the result of artifactual retention of dissolved U by the ultrafiltration membrane. Indeed, time series ultrafiltration data gave rise to a colloidal U percentage of $\sim 15\%$ for the Trinity water sample compared to an apparent colloidal U percentage of $38\text{--}59\%$ in freshwater or low salinity water samples estimated from conventional methods (Table 5). Furthermore, these model-derived colloidal U percentages show a decrease with increasing salinity and decreasing DOC concentration in Galveston Bay waters, consistent with the change of a strongly bound U with DOM in marine environments (Mann and Wong, 1993).

Higher colloidal U fractions in river waters could be the result of complexation of U with natural organic matter. As salinity increased, DOC concentration generally decreases in Galveston Bay waters (e.g., Guo and

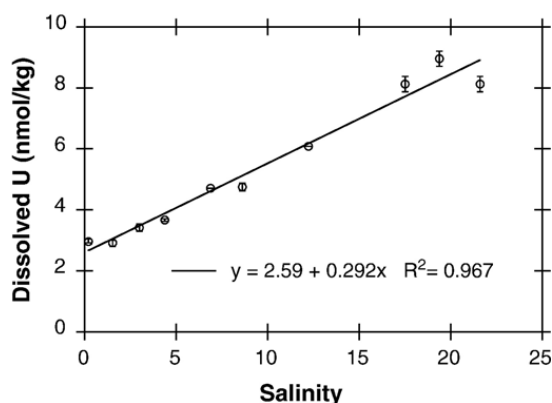


Fig. 4. Relationship between dissolved U concentrations (nmol kg^{-1}) and salinity in Galveston Bay waters.

Santschi, 1997b) and the speciation of U in seawater is likely significantly affected by lower DOC concentrations (Djogic et al., 1986). Decreased DOC concentration and changes in U speciation could result in a progressively lower colloidal U fraction as salinity increased (Table 5).

Under a high concentration factor or diafiltration conditions, the retained dissolved U will eventually permeate through the membrane resulting in a low colloidal fraction of U in seawater, like the case for the ultrafiltration of major ions such as SO_4^{2-} , Ca^{2+} and Mg^{2+} (Guo et al., 2001). The discreet sampling and model approach, on the other hand, minimizes the effects of this artifactual retention of LMW fractions under low ionic strength conditions and low CFs. Therefore, the permeation model should be used to derive truly colloidal chemical species when the ultrafiltration method is used.

It seems that binding of dissolved U to organic macromolecules (e.g., humic or fulvic acids) or inorganic nanoparticles (e.g., iron oxides) occurs to a greater extent in freshwater, groundwater or soil environments (Table 1, Ivanovich et al., 1996; Moulin et al., 1996). As salinity and U concentration increase and DOC concentration decrease from river to sea, association of dissolved U with colloids seems to be reduced, as also demonstrated by Mann and Wong (1993). Our results suggest caution when interpreting colloidal U results when conventional ultrafiltration approaches are used.

4. Summary and conclusions

Ultrafiltration of dissolved U in natural and artificial river waters revealed considerable retention of LMW-U by a 1 kDa membrane, likely due to the interactions of anionic U with the negatively charged ultrafiltration membrane, resulting in a preferential rejection of dissolved U, which caused a significant overestimation of the apparent colloidal U fraction in these waters. This overestimation of the colloidal U fraction for large anions, such as the uranium carbonate complexes and SO_4^{2-} , is much higher than for other ions and molecules such as dissolved organic matter species.

Comparisons of colloidal U fractions estimated from the ultrafiltration permeation model with those estimated by more conventional calculation methods, such as the concentration difference between U concentrations in initial solution and retentate/permeate solutions, further confirmed the artifactual retention of LMW-U species by the membrane. We have shown that the effect of this ultrafiltration artifact on colloidal U can be minimized by discreetly sampling the permeate solution during UF and using the ultrafiltration permeation model to model the results. It is thus highly recom-

mended that the ultrafiltration permeation model be used to derive the LMW fraction and thus, the colloidal fraction, of any chemical species in natural waters.

The concentration of dissolved U in Galveston Bay waters increased linearly from $\sim 3 \text{ nmol kg}^{-1}$ in the Trinity River and low salinity waters to $8\text{--}9 \text{ nmol kg}^{-1}$ in higher salinity waters, indicative of conservative estuarine mixing. The annual export flux of dissolved U from the Trinity River Basin was estimated to be 6.3×10^4 moles-U during 2000–2001, corresponding to a U weathering rate of $0.75 \text{ moles-U/km}^2/\text{yr}$. Colloidal U fractions derived from the ultrafiltration permeation model ranged from $\sim 15\%$ in Trinity River to ~ 0 in higher salinity coastal waters. Low colloidal U concentrations/fractions in seawater are consistent with the chemical properties of U and its relatively low association with colloidal nanoparticles, which is in stark contrast to highly particle-reactive and positively charged ionic species of trace metals such as Fe(III) and Th(IV).

Acknowledgments

We thank Jennifer Haye, Becky Hunt and Kim Roberts for their assistance during sampling and laboratory experiments, Associate Editor, Billy Moore, and two anonymous reviewers for constructive comments. This study was supported, in part, by the NSF (OCE0351559 and OCE0627820), Texas SeaGrant, and the Texas Institute of Oceanography.

References

- Alberic, P., Viollier, E., Jezequel, D., Grosbois, C., Michard, G., 2000. Interactions between trace elements and dissolved organic matter in the stagnant anoxic deep layer of a meromictic lake. *Limnol. Oceanogr.* 45, 1088–1096.
- Andersson, P.S., Porcelli, D., Gustafsson, O., Ingri, J., Wasserburg, G.J., 2001. The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary. *Geochim. Cosmochim. Acta* 65, 13–25.
- Belzile, C., Guo, L., 2006. Optical properties of low molecular weight and colloidal organic matter: application of the ultrafiltration permeation model to dom absorption and fluorescence. *Mar. Chem.* 98, 183–196.
- Berner, E.K., Berner, R.A., 1987. *The Global Water Cycle*. Prentice-Hall, New Jersey.
- Borole, D.V., Krishnaswami, S., Somayajulu, B.L.K., 1977. Investigations on dissolved uranium, silicon and on particulate trace elements in estuaries. *Estuar. Coast. Mar. Sci.* 5, 743–754.
- Buesseler, K.O., Bauer, J., Chen, R., Eglinton, T., Gustafsson, O., Landing, W., Mopper, K., Moran, S.B., Santschi, P.H., Vernon-Clark, R., Wells, M., 1996. An intercomparison of cross-flow filtration techniques used for sampling marine colloids: overview and organic carbon results. *Mar. Chem.* 55, 1–32.
- Buffle, J., Leppard, G.G., 1995. Characterization of aquatic colloids and macromolecules. *Environ. Sci. Technol.* 29, 2169–2175.

- Buffle, L., Perret, D., Newmann, M., 1992. The use of filtration and ultrafiltration for size fractionation of aquatic particles, colloids and macromolecules. In: Buffle, J., van Leeuwen, H.P. (Eds.), *Environmental Particles*, Col., vol. 1. Boca Raton, Lewis, pp. 171–230.
- Carroll, J., Moore, W.S., 1993. Uranium removal during low discharge in the Ganges–Brahmaputra mixing zone. *Geochim. Cosmochim. Acta* 57, 21–22.
- Chen, M., Guo, L., Huang, Y., Gao, Z., Cai, Y., Cai, M., 2000. Application of the cross-flow ultrafiltration technique to examining colloidal uranium, thorium, radium isotopes and organic carbon in seawater. *Acta Oceanol. Sin.* 22 (5), 51–59.
- Cochran, J.K. 1982. The oceanic chemistry of the U- and Th-Series Nuclides. In: Ivanovich, M., and Harmon, R.S., eds., *Uranium Series Disequilibrium: Applications to Environmental Problems*. Clarendon Press, Oxford University Press, New York, pp.384–430.
- Djogic, R., Sips, L., Branica, M., 1986. Characterization of uranium (VI) in seawater. *Limnol. Oceanogr.* 31, 1122–1131.
- Favre-Réguillon, A., Lebusit, G., Foos, J., Guy, A., Sorin, A., Lemaire, M., Draye, M., 2005. Selective rejection of dissolved uranium carbonate from seawater using cross-flow filtration technology. *Sep. Sci. Technol.* 40, 623–631.
- Guo, L., Santschi, P.H., 1996. A critical evaluation of the cross-flow ultrafiltration technique for sampling colloidal organic carbon in seawater. *Mar. Chem.* 55, 113–127.
- Guo, L., Santschi, P.H., 1997a. Composition and cycling of colloids in marine environments. *Rev. Geophys.* 35, 17–40.
- Guo, L., Santschi, P.H., 1997b. Isotopic and elemental characterization of colloidal organic matter from the Chesapeake Bay and Galveston Bay. *Mar. Chem.* 59, 1–15.
- Guo, L., Santschi, P.H., 2007. Ultrafiltration technique and its applications to sampling and characterization of aquatic colloids. In: Wilkinson, K., Lead, J. (Eds.), “Environmental Colloids and Particles” Chapter 4, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems. John Wiley, pp. 159–221.
- Guo, L., Hunt, B.J., Santschi, P.H., 2001. Ultrafiltration behavior of major ions (Na, Ca, Mg, F, Cl, and SO₄) in natural waters. *Water Res.* 35, 1500–1508.
- Guo, L., Wen, L., Tang, D., Santschi, P.H., 2000. Re-examination of cross-flow ultrafiltration for sampling aquatic colloids: evidence from molecular probes. *Mar. Chem.* 69, 75–90.
- Gustafsson, O., Gschwend, P.M., 1997. Aquatic colloids: concepts, definitions, and current challenges. *Limnol. Oceanogr.* 42, 519–528.
- Gustafsson, O., Buessler, K.O., Gschwend, P.M., 1996. On the integrity of cross-flow filtration for collecting marine organic colloids. *Mar. Chem.* 55, 93–111.
- Hamish, R.A., McKnight, D.M., Ranville, J.F., Stephens, V.C., Orem, W.H., 1996. Particulate, Colloidal and Dissolved-phase Associations of Plutonium, Americium, and Uranium in Water Samples from well 1587 and Surface-water Sites SW-51 and SW-53 at the Rocky Flats plant, Colorado, Water-Resources Investigations Report, 96-4067 (43pp).
- Honeyman, B.D., Santschi, P.H., 1989. Brownian-pumping model for oceanic trace metal scavenging: evidence from Th isotopes. *J. Mar. Res.* 47, 951–992.
- Ingri, J., Nordling, S., Larsson, J., Ronnegard, J., Nilsson, N., Rodushkin, I., Dahlqvist, R., Andersson, P., Gustafsson, O., 2004. Size distribution of colloidal trace metals and organic carbon during a coastal bloom in the Baltic Sea. *Mar. Chem.* 91, 117–130.
- Ivanovich, M., Wolf, M., Geyer, S., Fritz, P., 1996. Isotopic characterization of humic colloids and other organic and inorganic dissolved species in selected groundwaters from sand aquifers at Gorleben, Germany. In: Gaffney, J.S., Marley, N.A., Clark, S.B. (Eds.), *Humic and Fulvic Acids*, ACS Symp. Series 651, Am. Chem. Soc., Washington, DC, pp. 220–243.
- Kilduff, J., Weber Jr, W.J., 1992. Transport and separation of organic macromolecules in ultrafiltration processes. *Environ. Sci. Technol.* 26, 569–577.
- Ku, T., Knauss, K.G., Mathieu, G.G., 1977. Uranium in open ocean: concentration and isotopic composition. *Deep-Sea Res.* 24, 1005–1017.
- Lead, J.R., Wilkinson, K.J., 2006. Natural aquatic colloids: current knowledge and future trends. *Environ. Chem.* 3, 159–171.
- Logan, B., Jiang, Q., 1990. Molecular size distributions of dissolved organic matter. *J. Environ. Eng.* 116, 1046–1062.
- Lu, E., Zhang, L., Chen, M., Xing, N., Yang, W.F., Li, Y.P., Huang, Y.P., in press. Size-fractionated uranium isotopes in surface waters of the Jiulong River estuary. *Acta Oceanol. Sin.*
- Mann, D.K., Wong, G.T.F., 1993. “Strongly bound” uranium in marine waters: occurrence and analytical implications. *Mar. Chem.* 42, 25–37.
- Markich, S.J., 2002. Uranium speciation and bioavailability in aquatic systems: an overview. *Sci. World J.* 2, 707–729.
- Martin, J.M., Whitfield, M., 1983. The significance of the river inputs to the ocean. In: Wong, C.S., Boyle, E.A., Bruland, K.W., Burton, J.D., Goldberg, E.D. (Eds.), *Trace Metals in Seawater*. Plenum, New York, pp. 265–284.
- Moulin, V.M., Moulin, C.M., Dran, J.-C., 1996. Role of humic substances and colloids in the behavior of radiotoxic elements in relation to nuclear waste disposal: confinement or enhancement of migration. In: Gaffney, J.S., Marley, N.A., Clark, S.B. (Eds.), *Humic and Fulvic Acids*, ACS Symp. Series 651, Am. Chem. Soc. Washington, DC, pp. 259–271.
- Palmer, M.R., Edmond, J.M., 1993. Uranium in river water. *Geochim. Cosmochim. Acta* 57, 4947–4955.
- Porcelli, D., Andersson, P.S., Wasserburg, G.J., Ingri, J., Baskaran, M., 1997. The importance of colloids and mires for the transport of uranium isotope through the Kalix River watershed and Baltic Sea. *Geochim. Cosmochim. Acta* 61, 4095–4113.
- Rengarajan, R., Sarin, M.M., Krishnaswami, S., 2006. Dissolved Uranium and ²³⁴U/²³⁸U in the Yamuna and the Chambal Rivers, India. *Aquat. Geochem.* 12, 73–101.
- Santschi, P.H., Roberts, K.A., Guo, L., 2002. The organic nature of colloidal actinides transported in surface water environments. *Environ. Sci. Technol.* 36, 3711–3719.
- Sigleo, A.C., Means, J.C., 1990. Organic and inorganic components in estuarine colloids: implications for sorption and transport of pollutants. *Rev. Environ. Contam. Toxicol.* 112, 123–147.
- Singhal, R.K., Joshi, S.N., Hegde, A.G., 2004. Association of uranium with colloidal and suspended particulate matter in Arabian sea near the west coast of Maharashtra (India). *J. Radioanal. Nucl. Chem.* 261, 263–267.
- Swarzenski, P.W., McKee, B.A., Booth, J.G., 1995. Uranium geochemistry on the Amazon shelf: chemical phase partitioning and cycling across a salinity gradient. *Geochim. Cosmochim. Acta* 59, 7–18.
- Swarzenski, P.W., Porcelli, D., Andersson, P.S., Smoak, J.M., 2003. The behavior of U- and Th-series nuclides in the estuarine environment. *Rev. Mineral. Geochem.* 52, 577–606.
- Tanazaki, Y., Shimokawa, T., Nakamura, M., 1992. Physicochemical speciation of trace elements in river waters by size fractionation. *Environ. Sci. Technol.* 26, 1433–1444.
- Toole, J., Baxter, M.S., Thomson, J., 1987. The behavior of uranium isotopes with salinity change in three U.K. estuaries. *Estuar. Coast. Shelf Sci.* 25, 283–297.
- Tricca, A., Wasserburg, G.J., Porcelli, D., Baskaran, M., 2001. The transport of U- and Th-series nuclides in a sandy unconfined aquifer. *Geochim. Cosmochim. Acta* 65, 1187–1210.

- Wang, W., Guo, L., 2000. Influence of natural colloids on metal bioavailability to two marine bivalves. *Environ. Sci. Technol.* 34, 4571–4576.
- Warnken, K.W., Santschi, P.H., 2004. Biogeochemical behavior of organic carbon in the Trinity River downstream of a large reservoir lake in Texas, USA. *Sci. Total Environ.* 329, 131–144.
- Warnken, K.W., Santschi, P.H., 2007. Attenuation of sediment and trace metal delivery from the Trinity River watershed to Galveston Bay and the Gulf of Mexico. *Environ. Pollution* (in review).
- Warnken, K.W., Gary, G.A., Wen, L., Griffin, L., Santschi, P.H., 1999. Trace metal analysis of natural waters by ICP-MS with on line preconcentration and ultrasonic nebulization. *J. Anal. At. Spectrom.* 14, 247–252.
- Wells, M., 2002. Marine colloids and trace metals. In: Hansell, D.A., Carlson, C.A. (Eds.), *Biogeochemistry of Marine Dissolved Organic Matter*. Elsevier, USA, pp. 367–404.
- Wilding, A., Liu, R.X., Zhou, J.L., 2004. Validation of cross-flow ultrafiltration for sampling of colloidal particles from aquatic systems. *J. Colloid Interface Sci.* 280, 102–112.
- Windom, H., Smith, R., Niencheski, F., Alexander, C., 2000. Uranium in rivers and estuaries of globally diverse, small watersheds. *Mar. Chem.* 68, 307–321.
- Zänker, H., Richter, W., Brendler, V., Nitsche, H., 2000. Colloid-borne uranium and other heavy metals in the water of a mine drainage gallery. *Radiochim. Acta* 88, 619–662.