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Geochimica et Cosmochimica Acta 141 (2014) 303–313

Geochimica et Cosmochimica Acta

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Dissolved barium behavior in Louisiana Shelf waters affected by the Mississippi/Atchafalaya River mixing zone

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Received 2 January 2014; accepted in revised form 19 June 2014; Available online 28 June 2014

Abstract

In order to better understand the constraints on the use of barium as a coastal paleo-freshwater tracer, we surveyed the dissolved Ba distribution in Louisiana Shelf waters, including the Mississippi (MR) and Atchafalaya (AR) River plumes, during May and November 2008, and June/July 2009, which represent high, low and intermediate river discharges, respectively. Dissolved Ba was found dominantly in the <0.02 μm fraction, with no significant contribution from the 0.02–0.45 μm colloidal size fraction. Although apparent non-conservative surface water Ba behavior was observed during all three sampling periods, there were significant differences among the distribution patterns. River–seawater mixing experiments were supportive of substantial desorptive Ba addition only during the high discharge survey. At other times, input of Ba-enriched shelf bottom water as well as river endmember variability contributed to the apparent non-conservative behavior. During at least two of our surveys (high and intermediate river discharge), shelf bottom waters were significantly enriched in dissolved Ba relative to surface waters. While the cause of this enrichment (e.g., submarine groundwater discharge, dissolution/diffusion from the sediment, and/or an anthropogenic source such as drilling muds) could not be determined, we did observe that bottom Ba enrichment correlated with diminishing dissolved oxygen during summertime shelf bottom water hypoxia. Another interesting observation was Ba depletion in some high-salinity surface waters associated with a diatom bloom during June/July 2009. In addition, different Ba concentrations in the MR and AR appear related to inputs to the AR from the Red River as well as from the wetlands in the Atchafalaya River Basin.

Overall, our study of the Ba distribution in Louisiana Shelf waters implies that the seasonal variation of the surface water Ba–salinity relationship could lead to a considerable uncertainty in salinity prediction when using Ba as a proxy for paleosalinity changes. Barium input to bottom waters and the extent to which this is natural or anthropogenically-affected is a particular source of uncertainty. Thus, as is the case with nearly all paleoceanographic proxies, the planktonic foraminiferal Ba/Ca ratio should be used in conjunction with other constraining proxies.

1. INTRODUCTION

Barium is an important ocean geochemical tracer that has been used in several specific ways: (a) as a paleoproductivity tracer in the form of barite preserved in marine sediments (e.g., Dymond et al., 1992), (b) as an indicator of paleoceanographic changes in ocean circulation as recorded in the Ba/Ca ratio of benthic foraminifera (Lea and Boyle, 1989), (c) as a stable analogue for radium (Chan et al., 1976), and (d) as a tracer of fresh water influence in the coastal ocean both through direct measurement of seawater concentrations (Guay and Falkner, 1997, 1998) as well as

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http://dx.doi.org/10.1016/j.gca.2014.06.021
0016-7037/

by proxy measurement of Ba/Ca ratios in corals (Alibert et al., 2003) and foraminifera (Williams et al., 2010). The use of Ba as a coastal fresh water indicator has also been applied to fisheries research wherein changes in Ba/Ca ratios in fish otoliths help reveal migration and spawning patterns (e.g., Thorrold et al., 1997).

In order to fully exploit Ba as a coastal fresh water tracer, it is necessary to understand the fresh water source composition, how this composition might be changed in the estuarine environment, and what might be the temporal variability of the input as well as of the influencing estuarine processes. In rivers, geology (i.e., rock type) appears to be the major influence on dissolved Ba concentrations (Dalai et al., 2002) with changes in tributary flow contributions being an important control on seasonal variability in Ba concentrations in a large floodplain river (Shiller, 1997).

In estuaries, Hanor and Chan (1977) first reported non-conservative behavior of Ba, which they attributed to Ba desorption from clays. This was experimentally confirmed via sediment desorption experiments (Li and Chan, 1979) and seawater-fresh water mixing experiments (Li et al., 1984). While salinity-induced desorption may be the dominant process affecting the dissolved Ba flux through estuaries (Coffey et al., 1997), it is not the only process that can affect this element's distribution. In particular, there can be seasonal productivity-related depletion of Ba (Guay and Falkner, 1998; Stecher and Kogut, 1999) and there is some evidence suggesting removal associated with co-precipitation in Fe oxyhydroxides and subsequent flocculation of this material (Coffey et al., 1997). Perhaps of more importance in coastal and estuarine environments is the influence of benthic inputs, either from submarine groundwater discharge (Shaw et al., 1998), benthic dissolution of marine barite (Falkner et al., 1993; Colbert and McManus, 2005), or from desorption from river sediments deposited at high discharge in estuarine swamps/marshes (Carroll et al., 1993).

Herein, we report our studies of the dissolved Ba distribution in the mixing zone of the Mississippi River (MR) and Atchafalaya River (AR) including Louisiana Shelf waters. The Atchafalaya is a major distributary of the Mississippi River, mandated to contain 30% of the combined flow of the Mississippi and Red Rivers. While the mainstem of the Mississippi River enters the northern Gulf of Mexico through a birdfoot delta that extends to nearly the shelf break, the Atchafalaya enters the Gulf through a broad shallow bay. Thus, nearly the same river endmember mixes with seawater in two very different physiographic areas (Shiller, 1993). Furthermore, the Louisiana Shelf, where much of the extended mixing of these river waters takes place, is a region of high primary productivity and seasonal bottom water hypoxia, resulting from high anthropogenic fluvial nutrient fluxes combined with significant vertical stratification (Rabalais et al., 2010). This region therefore serves as a unique testbed to examine estuarine Ba geochemistry and our results may be pertinent to the interpretation of foraminiferal Ba/Ca ratios as a proxy for meltwater input to the northern Gulf (e.g., Williams et al., 2010).

2. METHODS AND MATERIALS

Sample collection was conducted on the Louisiana Shelf including the MR and AR plumes during three cruises in May and November 2008, and June/July 2009, which represent high, low, and intermediate Mississippi River water discharges, respectively (Figs. 1 and 2 and S1). Samples were also collected from the Atchafalaya River Basin (ARB) including the Red River (RR), Mississippi River (Knox Landing) and swamp waters. The ARB sampling campaigns were conducted in April and November 2010, and June 2011, which represent intermediate, low, and high river discharges.

Samples were collected at different depths on the shelf, but only surface samples were taken in the lowest salinity regions of the two river plumes. For May and November 2008, surface waters were taken using a clean underway pumping system that was driven by an air-powered plastic diaphragm pump. Acid-cleaned Teflon-lined polyethylene tubing was attached to a non-metallic tow-fish which was towed just below the surface, several meters off the side of the ship. Water from this system was sampled in a small plastic enclosure in the ship's lab. These surface water samples were taken after flushing the pumping system about 10 min while the ship was moving. During June/July 2009, the surface samples were collected using a grab sampler which consisted of a non-metallic PVC pole with polycarbonate bottle holder attached at the end of the pole. This was also carried out while the ship was slowly moving. For deep water samples, acid-cleaned Teflon-coated tubing was attached to a non-metallic cable holding an epoxy-coated weight at the end, and this tube was connected to the same pump system as the surface water collection. This pumping system was used to collect deep water samples during the first cruise. For the two later cruises, an external spring, Teflon-coated Niskin bottle was used. The Niskin bottle was mounted on a PVC frame extending ~1 m below the bottle and which automatically closed the bottle when the frame hit the bottom.

Soon after the water samples were collected, they were filtered using acid-cleaned 25 mm × 0.45 μm pore size polyethylene (Whatman Puradisc PP) and 25 mm × 0.02 μm pore size alumina (Whatman Anotop) syringe filters, providing us with operationally-defined "total" and "truly dissolved" fractions, respectively. The colloidal phase (0.02–0.45 μm) was defined by the difference between the two fractions. Details of the sample processing can be found elsewhere (Shiller, 2003). The filtered water samples were brought to our shore-based clean lab and acidified to pH < 2 by adding 70 μl and 140 μl of 6 M ultrapure hydrochloric acid (Seastar Baseline) for the 15 ml and 30 ml samples, respectively.

Barium was determined with a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, ThermoFisher Element 2) using an isotope dilution method (Shim et al., 2012). In this study, Ba was calibrated by adding a known amount of ^{135}Ba enriched isotopic spike obtained from Oak Ridge National Laboratory and measuring the $^{135/138}$Ba ratio. Samples were diluted 20-fold by the addition of 0.3 M of ultrapure dilute nitric acid (Seastar Baseline) prior to analysis. For verifying the accuracy of

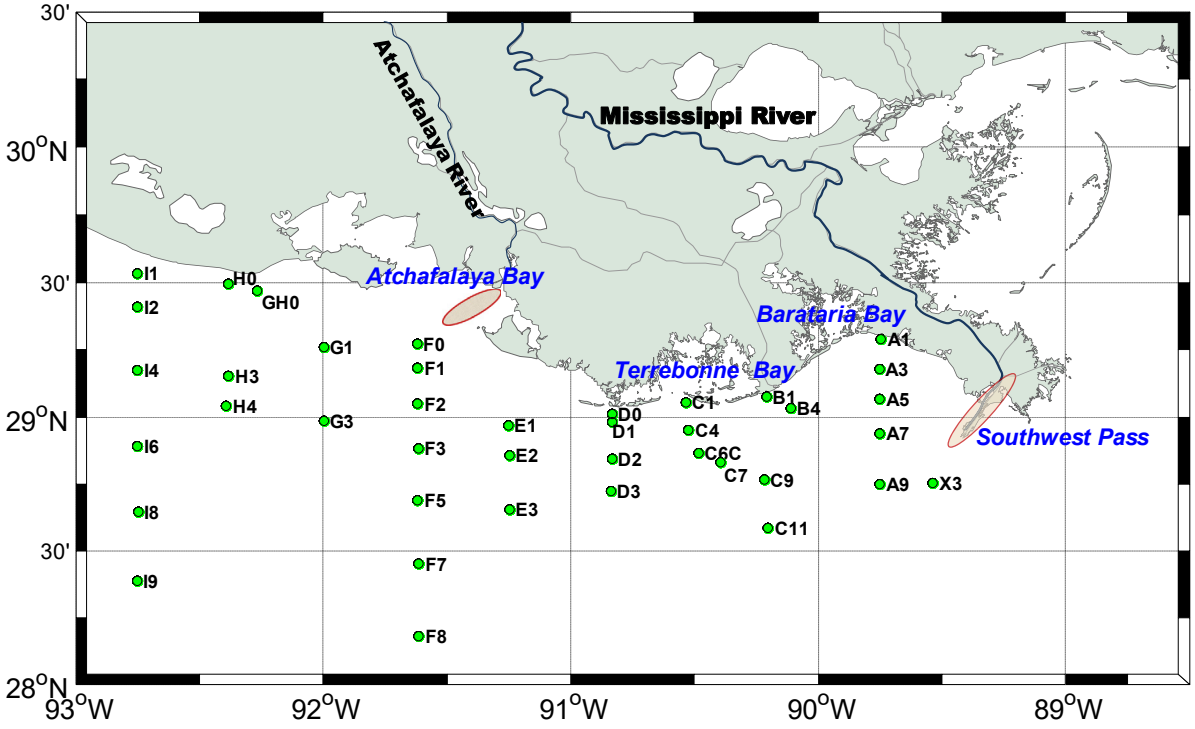

Fig. 1. Louisiana Shelf sampling stations during May 2008, November 2008, and June/July 2009. Shaded areas by Southwest Pass and Atchafalaya Bay show the general location of low salinity sampling (see Supplementary Fig. S1 and Tables S1–S3 for specific locations).

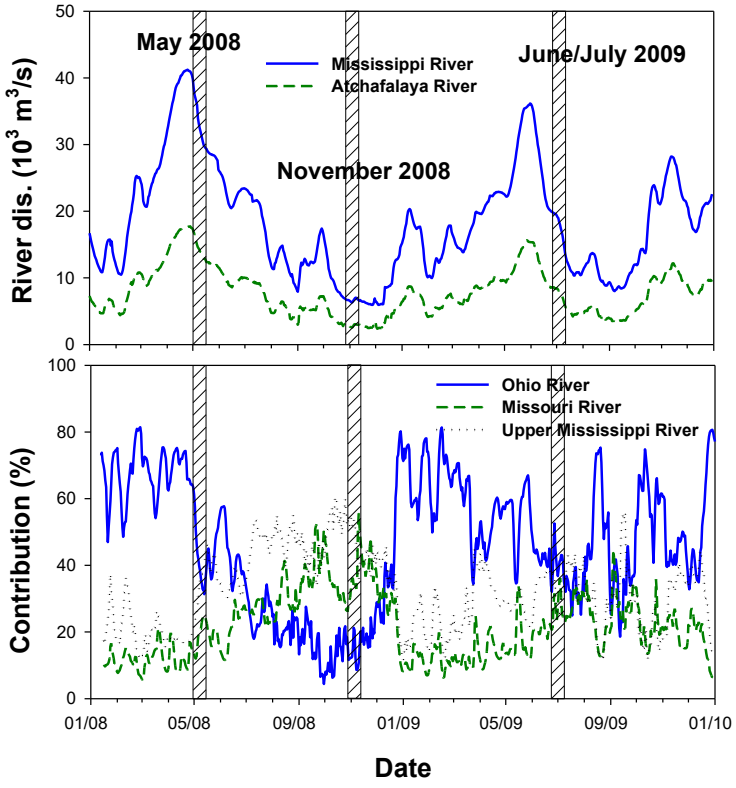

Fig. 2. Discharge and relative contributions of major Mississippi River tributaries to the total discharge.

analysis, the certified reference seawater NASS-5 (NRC-Canada) was measured during all analytical runs. Our NASS-5 result (37.3 ± 1.1 nM, $n = 40$) agrees well with previous results (37.0 nM, Field et al., 2007 and 37.5 nM, Shim et al., 2012). The detection limit of the method was estimated to be 1.2 nM.

Mixing experiments were conducted at sea using river water and seawater. Unfiltered river water and seawater were mixed in varying proportions and held in the dark for overnight, with the ship's motion providing constant sample mixing. The mixed samples were filtered in the same way as the field samples. The lowest salinity waters we obtained from the MR and AR were used as the river endmembers. The MR mixing experiment was conducted only during June/July 2009.

Ancillary data such as salinity, temperature and dissolved oxygen (DO) were obtained from instruments mounted on the ship's CTD-rosette system. The DO sensor calibration was calibrated by Winkler titrations. The oxygen isotope composition of the water was measured using isotope ratio infrared spectroscopy (L2120i cavity ring-down spectrometer, Picarro, Inc.) and the raw isotope data correction and calibration were made using the method of van Geldern and Barth (2012).

The Mississippi River discharge was obtained from the US Army Corps of Engineers discharge records from the gage at the Tarbert Landing, MS (http://rivergages.mvr.usace.army.mil). This gage is below the diversion of water into the Atchafalaya River. Major tributary contributions to the mainstem flow were estimated from USGS discharge data from the Ohio River at Metropolis, IL, the Missouri River at Hermann, MO, and the Mississippi River at Grafton, IL for Ohio, Missouri and Upper Mississippi Rivers, respectively (http://water.usgs.gov). To adjust approximately for the travel time of water from these tributaries to the sampling sites, about 15 days and 12 days were applied for the Upper Mississippi and Missouri Rivers, and the Ohio River, respectively. These travel times were adjusted by adding 2 days to the times used by Shiller (1997) in consideration of the extended distance from Baton Rouge to the birdfoot delta. For the Atchafalaya River Basin, discharges were also obtained from the US Army Corps of Engineers from the gages at Simmesport, Acme, Alexandria, Wax Lake, and Morgan City, LA.

Mississippi River discharge and major tributary contributions to the river are shown in Fig. 2. During May 2008, the MR discharge from the gage at Tarbert Landing, MS, was about 35×10^3 m^3/s while this was about 8×10^3 and 15×10^3 m^3/s during November 2008 and June 2009, respectively. Note that the Tarbert Landing gage is below the Old River Control Structure (where some MR water is diverted into the AR) and thus represents approx. 70% of the total flow of the river. During our high discharge sampling (May 2008), the MR mainstem was dominated by contributions from the Ohio River. However, the Upper Mississippi and Missouri Rivers were the primary MR contributors during low river discharge (November 2008), and all three tributaries had very similar contributions during the intermediate discharge period (June/July 2009).

3. RESULTS AND DISCUSSION

Results from the three field surveys and the mixing experiments are shown in Supplementary Tables S1–S4. Concentrations of Ba in the <0.02 μm and <0.45 μm filtrates were almost always within analytical error of each other. That is, there was no significant colloidal Ba, at least by the definition of the colloidal phase we use here (0.02–0.45 μm). We thus focus only on the <0.45 μm results.

Surface water Ba distributions and the associated mixing experiments (Figs. 3 and S2) show some distinct as well as subtle differences between our three sampling campaigns. During high discharge (May 2008), there is obvious non-conservative behavior at lower salinities in the immediate vicinity of the mouths of both the MR and AR, with conservative behavior at higher salinities. The mixing experiment at that time likewise shows low-salinity non-conservative behavior suggestive of Ba desorption from the suspended load as previously reported for this system by Hanor and Chan (1977). Also, the fluvial endmember Ba concentration for the AR is nearly 100 nM higher than for the MR, though the desorption humps for both distributaries are similar in magnitude as is the salinity of maximum Ba.

During low discharge (November 2008) the field data show apparent non-conservative behavior somewhat different from the high discharge distribution. While there might be a small abrupt increase in Ba at the very lowest salinities, there is also a broad upward curvature throughout the entire distribution which was not observed at high discharge. There are also some high salinity surface water samples that appear distinctly above the overall trend in Ba versus salinity. The mixing experiment in this instance is conservative, again contrasting with the high discharge behavior. Also at this time, the MR outflow appears to have slightly higher Ba than the AR outflow, again in contrast with high discharge (though we were unable to sample the true MR endmember in November 2008).

At intermediate discharge during summer hypoxia (June/July 2009), there again appears to be an abrupt jump in Ba at the lowest salinities, though both mixing experiments show conservative behavior. At higher salinities, Ba is more scattered than during the other sampling periods. In part, between salinities 15 and 30 the Ba distribution might be described by two different conservative trends with some additional scatter (e.g., the low Ba at stations C9 and C11). Similar to low discharge, the MR outflow appears to have higher Ba than the AR outflow at the lowest salinities.

During at least the high flow and hypoxia surveys, bottom water Ba appears to be enriched compared to surface and mid-depth waters (Figs. 3 and S2), suggesting Ba input to the shelf bottom. This effect was most pronounced during the June/July 2009 cruise which occurred when we observed the most depleted bottom water oxygen conditions (Fig. 4).

The questions raised by these distributions are severalfold. First, why is it only during high discharge that the mixing experiments support desorptive input of dissolved Ba? If desorption is not occurring during the low and intermediate discharge surveys, then what explains the

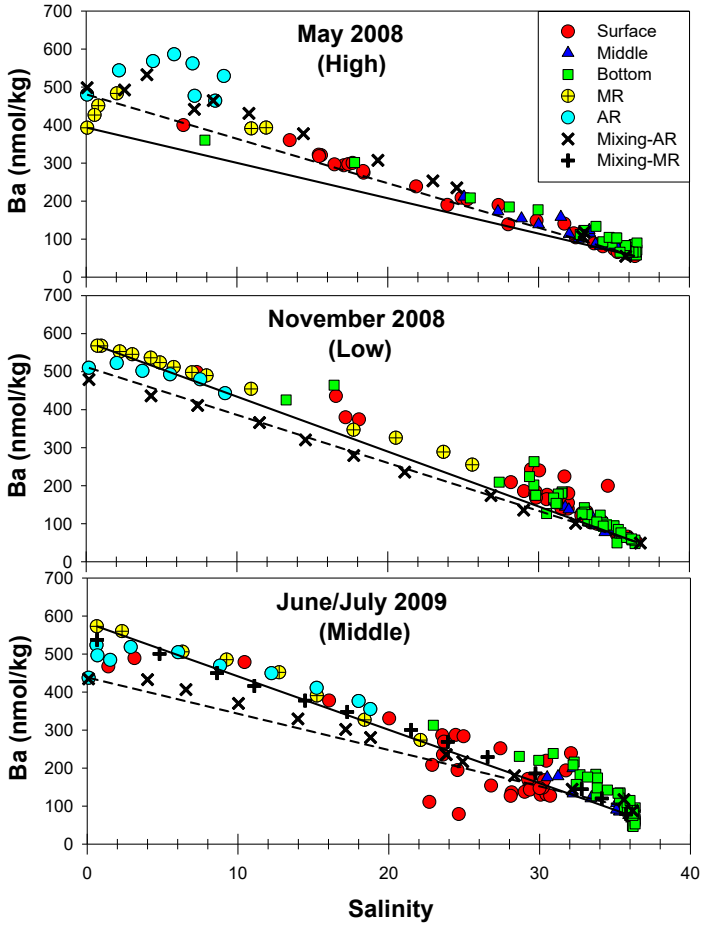

Fig. 3. Total dissolved Ba (<0.45 μm) distributions for three cruises. High, low and middle in parentheses indicate river stage. Mixing experiments are also plotted. For the Mississippi River endmember, the mixing experiment was only conducted during June/July 2009. Theoretical Ba dilution lines from the lowest to high salinities are also plotted for MR (solid line) and AR (dashed line).

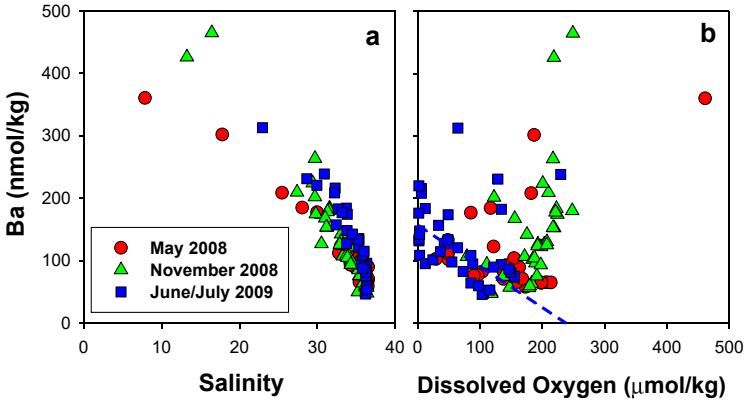

Fig. 4. Bottom water Ba versus (a) salinity and (b) dissolved oxygen (DO). For the June/July 2009 Ba–DO regression (dashed blue line), several stations of higher DO and low salinity (indicating substantial mixing with surface waters) were excluded. The regression was $Ba = -0.66 \times DO + 157$ ($r^2 = 0.53$, $n = 33$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

non-conservative behavior in those distributions? What accounts for the behavior of Ba in shelf bottom waters? And, finally, why are there differences between the MR and AR endmembers? We consider these questions below and then discuss the implications for paleoceanographic use of Ba as a freshwater proxy.

To begin with, there are several possible factors that are unlikely to be substantial influences on variation of the

fluvial input of Ba or desorptive inputs in the mixing regime. These include temperature, anthropogenic inputs, and variation in the composition of the fluvial suspended load. The issue of temperature effects on Mississippi River trace elements has been discussed (Shiller, 1997) and dismissed as being unimportant for most elements. Also, we didn't observe a large temperature range in our samples (Supplementary Tables S1–S3). We know of no evidence supporting substantial anthropogenic Ba input from New Orleans and our endmember Ba concentrations do not appear substantially different from dissolved Ba concentrations above New Orleans and Baton Rouge (Shiller, 1997). Limited data from Piper et al. (2006) on Mississippi River SPM suggests limited variability in the lower river's particulate Ba content. Thus, we focus on the amount of suspended material rather than these other likely less-important factors.

3.1. Ba input to shelf bottom waters

As noted above, Ba appears to be enriched in shelf bottom waters for at least two of our cruises. This is not simply a consequence of upwelling of deeper Ba-enriched offshore waters onto the shelf: Ba does not increase strongly with depth in the northern Gulf of Mexico. For instance, even at 1600 m, dissolved Ba is only ~60 nM (Joung and Shiller, 2013).

Input of Ba to shelf bottom waters should not be surprising in this environment, however. Krest et al. (1999) observed excess Ra in Louisiana Shelf bottom waters and suggested submarine groundwater discharge (SGD) or release of formation waters associated with oil/gas drilling as the source. McCoy et al. (2007) likewise suggested formation water input and/or seawater recirculation as minor fluid inputs to the shelf bottom, though they still measurably contribute to isotopic inputs to these waters. Kolker et al. (2013) more recently provided evidence for SGD input to the delta and coastal bays in this region based partly on the distribution of ^{222}Rn, the daughter product of ^{226}Ra. These processes are also likely to be sources of Ba in this environment given the chemical similarity of Ba to Ra. Drilling activities under some circumstances may also result in the release of Ba-enriched drilling muds (e.g., Joung and Shiller, 2013). Additionally, dissolution of barite in reducing shelf sediments is another possible dissolved Ba source (Falkner et al., 1993; Colbert and McManus, 2005). For the June/July 2009 cruise, which occurred during summertime shelf hypoxia, dissolved Ba in shelf bottom waters varied inversely with dissolved oxygen (Fig. 4). While this is compatible with anoxic barite dissolution being a significant source of bottom water barium, we note that this Ba–oxygen relationship could simply reflect the dual role of summertime water stratification both in inhibiting re-oxygenation of bottom waters as well as trapping benthic-sourced Ba (regardless of input mechanism).

Also of some relevance to this discussion of bottom input is how much particulate Ba is supplied by the river. Shiller (1997) found that the lower Mississippi River carried 5 μmol/g particulate Ba, or close to 1200 nM Ba at typical suspended loads. While it is unclear how much of this is either desorbable or able to be regenerated in the sediments, certainly there is significant fluvial particulate Ba for these processes. That is, while we cannot dismiss possible Ba input from oil and gas operations on the Louisiana Shelf, there is not necessarily a mass-balance requirement for it. Nonetheless, our data do not allow us to distinguish the particular source/mechanism of Ba input to shelf bottom waters. Clearly, though, benthic input is an important component of the Ba mass balance in this system just as it is in others (e.g., Colbert and McManus, 2005).

3.2. Ba input to surface waters

As described above, the high discharge (May 2008) Ba distribution is non-conservative, along with its associated mixing experiment, in a manner generally consistent with previous observations and experiments indicating salinity-induced desorption of Ba from the fluvial suspended load at low salinity (Hanor and Chan, 1977; Li and Chan, 1979; Li et al., 1984). This process is generally viewed as the dominant modifier of the Ba flux through estuaries (Coffey et al., 1997). Despite this "classic" picture, the high discharge Ba distribution is odd in that at a salinity of 10, Ba concentrations in the AR outflow suddenly drop and converge with the MR outflow trend in a single conservative distribution out to high salinity (Fig. 3). A related phenomenon is observed in the distribution of the δ^{18}O of the water versus salinity (Fig. 5), where the trend for the AR outflow also converges into a main δ^{18}O–S trend that is largely defined by the MR and offshore high salinity Gulf endmembers. This is not surprising given that during fall through spring, outflow waters are generally directed towards the west via the Louisiana Coastal Current (Cochrane and Kelly, 1986). Indeed, even when river discharge is exceptionally high, the influence of AR water on our sampling grid is likely be confined to the more landward stations south and west of Atchafalaya Bay (Falcini et al., 2012). In other words, for most of our shelf stations MR outflow should be the dominant freshwater influence and this is borne out by both the Ba and δ^{18}O data.

We also note that despite the enrichment of Ba in bottom waters during May 2008 (Figs. 3 and S2), there seems to be minimal influence of the bottom Ba input on the surface water Ba distribution. During this high flow survey, the surface-bottom salinity difference averaged 8. Thus, vertical stratification appears to have limited the upward mixing of Ba-enriched bottom waters.

In contrast to high discharge, the low discharge (November 2008) Ba distribution shows only a small, low-salinity concentration increase associated with the AR outflow. Possibly, the lack of low-salinity Ba increase in the MR outflow at this time is an artifact of our only being able to sample that outflow down to a salinity of 1, and thus missing the desorption hump almost entirely. However, a lower amount of desorption (relative to high discharge) is to be expected at this time as USGS data for Tarbert Landing, MS (water.usgs.gov), indicate that the low discharge suspended matter concentration of the river was more than twofold lower than the high discharge suspended matter concentration. Nonetheless, because there

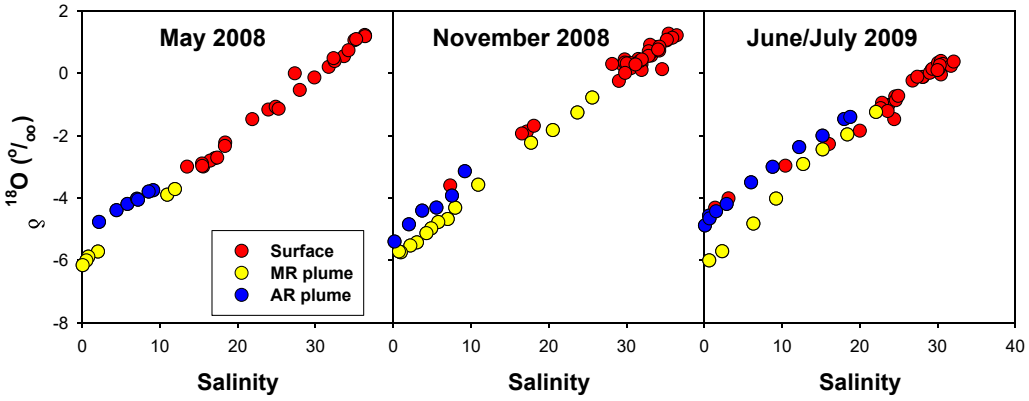

Fig. 5. Distribution of $\delta^{18}O$ of the water versus salinity in surface waters.

was broad upward curvature in the Ba distribution throughout the salinity range during November 2008, extrapolation of the high salinity surface water Ba data yields an effective river endmember of >800 nM Ba, suggesting substantial Ba input during river–seawater mixing.

Dion (1983) suggested that similar differences in the low/high discharge Ba distributions in the Amazon River plume might be explained through a kinetic/hydrodynamic mechanism. The concept is simply that at low discharge (as compared with high) a given suspended particle is likely to travel further through the salinity gradient before its Ba is desorbed, leading to a broader, more extended desorption maximum during low discharge. Coffey et al. (1997) likewise adapted this concept to explain differences in the location of Ba release among various estuaries. We feel that this mechanism is unrealistic. First, our mixing experiment shows scant evidence for Ba input, though one might argue that our surface grab sample under-sampled the suspended load. Second, it is difficult to explain why there would be desorption over a broad salinity range while the field data still show a small low-salinity jump in Ba (presumably indicative of desorption). More important, however, is that the Dion/Coffey mechanism requires that desorption be slow relative to mixing. However, as was pointed out by Coffey et al. (1997), most Ba desorption occurs within 60 min. of mixing; yet, the process of transporting MR and AR waters through the shelf mixing zone takes days (Moore and Krest, 2004) if not months (Dinnel and Wiseman, 1986). Thus, desorption is too fast for the kinetic/hydrodynamic mechanism to be relevant to our situation, nor do we think it likely to be a factor globally in any but the smallest mixing zones.

Another possible explanation for the November 2008 surface water Ba distribution is that the upward curvature of the field data represents a change in the river Ba concentration over the timescale of mixing (Loder and Reichard, 1981; Officer and Lynch, 1981). For the plume of the MR, mixing times can be a number of months at low discharge (Dinnel and Wiseman, 1986). While the more Ba-rich Missouri River was indeed the dominant major source of water to the lower Mississippi a month before our sampling (Fig. 2), the Missouri River's Ba concentration was probably not high enough to be the dominant cause of the upward curvature in our November surface water distribution (e.g., Shiller, 1997); i.e., it could not explain an extrapolated river endmember of >800 nM Ba.

We thus conclude that the non-conservative Ba input to the surface waters during November 2008 was simply from upward mixing of Ba-enriched shelf bottom waters. That is, the surface water distribution reflects mixing of more than just two endmembers, resulting in an appearance of non-conservative behavior (Shiller, 1996). In contrast to high discharge, the surface-bottom salinity difference averaged only 2 during our low flow survey (with a median difference of only 0.7). With vertical stratification low at this time of year (i.e., in November or fall/winter periods in general) due to the decreased fresh water input and increased mixing by winter fronts, such upward mixing would occur readily. Indeed, bottom and surface water samples fall on the same Ba–salinity trend, consistent with this sort of vertical exchange. This process also likely explains a similar broad Ba–salinity curvature observed in this system by Shim et al. (2012).

In the June/July 2009 Ba distribution, we again see the low-salinity jump in Ba concentration in the AR outflow (Fig. 3). However, we note that a plot of salinity versus the $\delta^{18}O$ of the water shows some curvature at low salinity in the AR plume, reflecting a recent change to an isotopically-lighter AR endmember (Fig. 5). This is consistent with the fact that during June/July 2009, the RR contribution to the AR decreased from 42% to 29% two weeks prior to our AR plume sampling (i.e., the RR is isotopically heavier than the MR water). Thus, endmember variability likely explains the scatter in the low salinity Ba distribution at this time. Beyond this initial curvature, the AR outflow Ba–salinity trend continues towards a high-Ba, high-salinity bottom water endmember, intersecting inshore surface water samples (e.g., A1, C1, E2, H0). In high-salinity bottom waters at this time, not only was the Ba enrichment related to bottom water oxygen depletion (Fig. 4) but also the most Ba-enriched bottom waters were the most inshore (i.e., shallowest) waters as evidenced by a plot of bottom Ba versus bottom depth (Fig. S3). This makes sense since the most inshore bottom waters are likely to have spent the most time traversing the shelf and interacting with the bottom. Although stratification was high at this time (average

surface-bottom salinity difference of 10), upward mixing of Ba-enriched bottom water is also supported by observation of high dissolved Co, Cu, Fe and Mn in these inshore waters (Joung and Shiller, in prep.). We note that this contrasts with the situation in May 2008 when we observed scant evidence of upward mixing of Ba-enriched bottom waters. This difference likely results both from the greater bottom Ba enrichment during summer hypoxia as well as the seasonal change in circulation on the shelf wherein summer winds become more upwelling-favorable (Cochrane and Kelly, 1986).

For the MR outflow during the June/July 2009 hypoxia survey, there is no apparent low-salinity jump in Ba, but there is a slight upward curvature out to mid-salinity (S ~ 17 to 30). As was the case in the low discharge survey, we were not able to sample quite as low a salinity in the MR outflow as the AR outflow and thus might have missed some very low salinity desorption input of Ba. The MR outflow Ba–salinity trend intersects offshore surface water stations (e.g., X3, A7, A9, C7, F8) continuing towards complete Ba depletion by salinity 35 (Fig. 3). Two offshore stations (C9 and C11) fall well below the trend, showing very significant Ba depletion. While Ba depletion in this region has not been reported before, in the Delaware estuary Stecher and Kogut (1999) reported rapid, episodic Ba removal which they attributed to barite precipitation during late stages of a diatom bloom. For the MR plume, Lohrenz et al. (2008) found that productivity tends to peak in April/May coinciding with high discharge and we also observed that chlorophyll a in surface waters was higher during our May 2008 survey (6–30 μg/kg) than during the June/July 2009 survey (1–6 μg/kg). Interestingly, Flow Cam data (J. Paul, USF, pers. comm.) indicates that surface water diatom abundance was comparatively high during June/July 2009 at the most Ba-depleted stations (C9 and C11). Our observations are thus consistent with the Stecher and Kogut (1999) Ba removal mechanism.

3.3. Seasonal variation of salinity of the peak Ba desorption

There is one final difference among our three surveys to consider. For the May 2008 survey, the apparent desorption hump spans a salinity range of 0–10 whereas the small increases we observe in the AR outflow in the other two surveys occur at a salinity below 2. This stands in contrast to the Dion/Coffey hydrodynamic mechanism (discussed above) which predicts the broadest desorption hump at low discharge rather than high as we observe. We suggest that the difference observed in this study does have a hydrodynamic component. Specifically, during May 2008, discharge was great enough so that the distributary channels were completely fresh and mixing of river and seawater began in open waters beyond the river channels. In contrast, during the other two surveys, mixing began within the channels of the MR and AR. At high discharge, fresh water rapidly spreads out from the river mouths, potentially mixing with estuarine waters of a variety of salinities thereby broadening the desorption maximum. But, when the initial mixing occurs within the distributaries, the constriction of the channels and the nature of gravitational circulation result in a simpler mixing regime and hence a much sharper and quicker desorption maximum.

3.4. Ba in the MR and AR endmembers

Another important aspect regarding the Ba distribution in the Louisiana Shelf is the different Ba endmembers of the MR and AR. At high discharge (May 2008), Ba was ~100 nmol/kg higher in the AR than in the MR. In contrast, at low and intermediate discharges (November 2008 and June 2009, respectively), Ba in the MR was generally higher than in the AR. As mentioned above, the AR water is derived mostly from the MR with a variable addition of water from the RR. Also, while the lower MR is highly channelized, the AR flows through the extensive wetlands of the Atchafalaya River Basin (ARB). During our ARB study, Ba concentrations in the RR were 480, 580 and 270 nmol/kg for April and November 2010, and June 2011, respectively. At the same time, Ba concentrations in the MR were 447, 546 and 456 nmol/kg, respectively (Table 1). The dissolved Ba concentrations in ARB swamp waters were found to be ~3 μmol/kg during intermediate (April 2010) and low (November 2010) river discharges. But, during high river flow (June 2011), the Ba concentration of the swamp water was 0.5 μmol/kg, similar to the MR Ba concentration, likely because opening of the

Table 1
Results of dissolved Ba from the Red River (RR), Mississippi River (MR) and Atchafalaya basin swamp waters (ARS).

Stations	Date	Discharge* (m^3/s)	Contribution to the AR** (%)	Ba (nmol/kg)
MR	Apr-10	8.7E+03	86	447
RR		1.2E+03	14	481
ARS				2802
MR	Nov-10	2.7E+03	95	546
RR		2.8E+02	5	583
ARS				3387
MR	Jun-11	13.5E+03	74	456
RR		1.9E+03	26	271
ARS				530

* River discharges were obtained from USGS and the US Army Corps Engineers river monitoring sites at Alexandria and Acne, LA for the Red River and at Tarbert Landing for the Mississippi River.
** Atchafalaya River.

Morganza Spillway during the lower MR flood that year inundated the ARB with MR water. Clearly our limited sampling of the RR and ARB was not sufficient to provide us with a predictive capability for the difference between the AR and MR endmembers, but nonetheless provides insight into how the AR can be either higher or lower in Ba than the MR.

3.5. Implications for paleoceanographic applications of Ba as a coastal salinity proxy

Ample studies have used the planktonic foraminiferal Ba/Ca ratio as an indicator of paleo-freshwater input because other proxies (e.g., oxygen isotopes) are affected by additional factors such as temperature (e.g., Flower et al., 2004; Hall et al., 2004; Hill et al., 2006). However, the foraminiferal Ba/Ca ratio appears to be affected dominantly by only the Ba/Ca ratio of seawater (Lea and Spero, 1994; Hönisch et al., 2011); and thus, it should reflect the salinity of the water at the time of foraminiferal calcite formation. Using a contemporary Ba–salinity relationship from a given coastal region, thus provides a means for inferring past salinities or freshwater inputs from planktonic foraminiferal Ba/Ca. Our work on the Louisiana Shelf Ba distribution suggests possible caveats in this approach due to changing Ba–salinity surface water relationships including seasonal changes in the endmember composition (including desorbable suspended Ba), seasonal changes in stratification resulting in variation of bottom inputs, long-term changes in distributary systems or the river system itself, and possible anthropogenic effects on coastal hypoxia, submarine groundwater discharge, and oil drilling operations. The Louisiana Shelf system today is, perhaps, uniquely complicated in these various factors and thus might be viewed as a worst-case scenario. Nonetheless, a better understanding of the extent of and controls on benthic inputs (natural and otherwise) in this system and others is likely a key factor for the coastal Ba mass balance and hence improved paleoceanographic application.

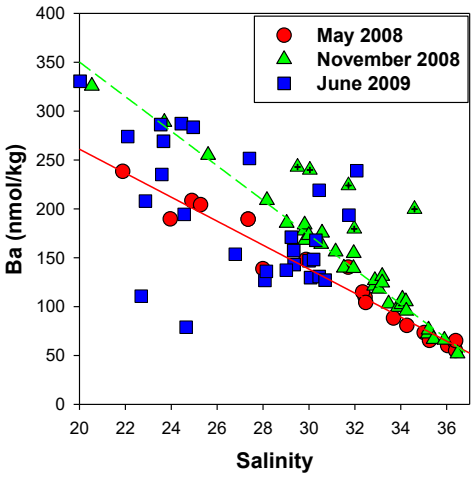

Fig. 6. Surface Ba distribution versus salinity (>20). Regressions for May (red solid) and November (green dashed) 2008 are $y = -12.4x + 506$ ($r^2 = 0.96$, $p < 0.0001$) and $y = -17.7x + 704$ ($r^2 = 0.98$, $p < 0.0001$), respectively. For the November 2008 regression, 5 data points (triangle with cross) were not considered (see text). The regression for June/July 2009 was not generated due to scatter in the data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To better demonstrate the potential paleoceanographic uncertainty, Fig. 6 provides an expanded view of our high salinity surface water Ba–salinity relationships. As an example, at a salinity of 30, there is a seasonal uncertainty of ~40 nmol/kg in dissolved Ba on the Louisiana Shelf which translates to a change of 0.68 μmol/mol in the foraminiferal Ba/Ca ratio when using the distribution coefficient of Lea and Spero (1994). Stated the opposite way, an uncertainly of 0.68 μmol/mol in the foraminiferal Ba/Ca ratio, would lead to an uncertainty in predicted salinity of 2–3. Clearly, this uncertainty would be reduced if a Ba–S relationship representative of the time of year of predominant calcification were used. Nonetheless, as is the case with nearly all paleoceanographic proxies, the planktonic foraminiferal Ba/Ca ratio should be used in conjunction with other constraining proxies and with an eye towards possible coastal oceanographic and geochemical confounding factors.

4. SUMMARY AND CONCLUSIONS

Significant spatial and temporal variations in the dissolved Ba distribution on the Louisiana Shelf were observed during our three surveys. During high discharge (May 2008), both field data and a mixing experiment indicate non-conservative behavior consistent with salinity-induced desorption of Ba from the fluvial suspended load. The desorption humps for the MR and AR outflows are similar even though the AR Ba concentration was substantially higher than the MR concentration. Shelf bottom water Ba during the high discharge survey also appeared to be enriched relative to surface waters, though there was little evidence of significant input of this bottom Ba to surface waters.

At low discharge (November 2008), there was scant evidence of Ba desorption, likely because of the lower fluvial suspended load. However, a broad upward curvature was observed in the Ba–salinity distribution which was not observed during high discharge. This broad upward curvature appears to be due to upward mixing of Ba-enriched shelf bottom waters, which occurs more readily at this time of year due to lessened freshwater inflow and hence diminished vertical stratification as well as to mixing due to the passage of fall/winter storm fronts.

At intermediate discharge during summer hypoxia season (June/July 2009), evidence for desorption was again limited. Bottom water Ba enrichment at this time appears to be related to oxygen depletion. Significant scatter in the high salinity surface water Ba distribution may appear to result from episodic input of enriched bottom waters. We also observed some Ba depletion associated with a diatom bloom.

These contrasting Ba distributions appear to reflect seasonal changes in suspended matter input, benthic inputs,

and stratification/vertical mixing. The origin of the benthic inputs, whether from SGD input, sediment regeneration, or anthropogenic inputs, remains unresolved. However, this is clearly a question of importance for understanding the Ba distribution in this and other coastal/estuarine systems. Benthic inputs influenced at least two of our Ba surveys as much if not more than desorptive input.

Our study of Ba distribution in the Louisiana Shelf implies possible caveats in the utilization of Ba as a proxy for paleo-salinity changes due to the contemporary seasonal variation of surface Ba–salinity relationships, which could lead to a considerable uncertainty in predicted salinity. The Louisiana Shelf, however, may prove a worst-case scenario due to its multiple endmembers and possible influences of anthropogenic hypoxia as well as inputs from oil/gas drilling operations. Clearly, though, a better understanding of benthic inputs of Ba is an important key in tying down the coastal/estuarine Ba mass balance.

ACKNOWLEDGEMENTS

We thank P. van Erp, X. Wang, B. Stolpe, and V.J. Shiller for assistance at sea and in the laboratory. S. Lohrenz (USM/UMass) provided the chlorophyll data. We thank the captains and crew of the R/V Pelican for assistance at sea and J. Krest and K. Park for collaborative planning of this work. D.J.J. also acknowledges support from the USM Dept. of Marine Science. This work was funded by the National Science Foundation Chemical Oceanography Program (OCE-0728775).

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2014.06.021.

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Associate editor: Robert H. Byrne

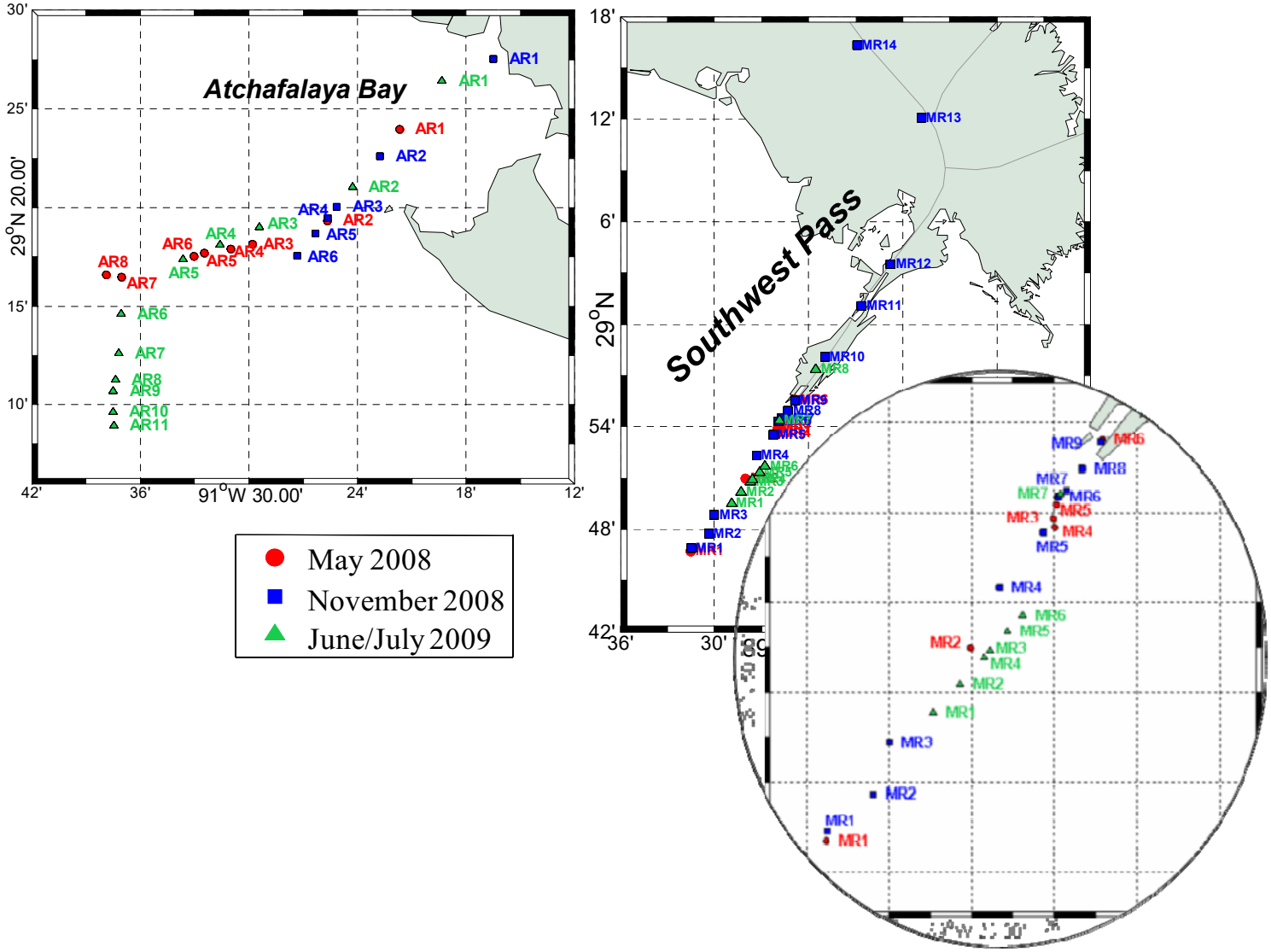

Fig S1. Sampling locations of the two river plumes.

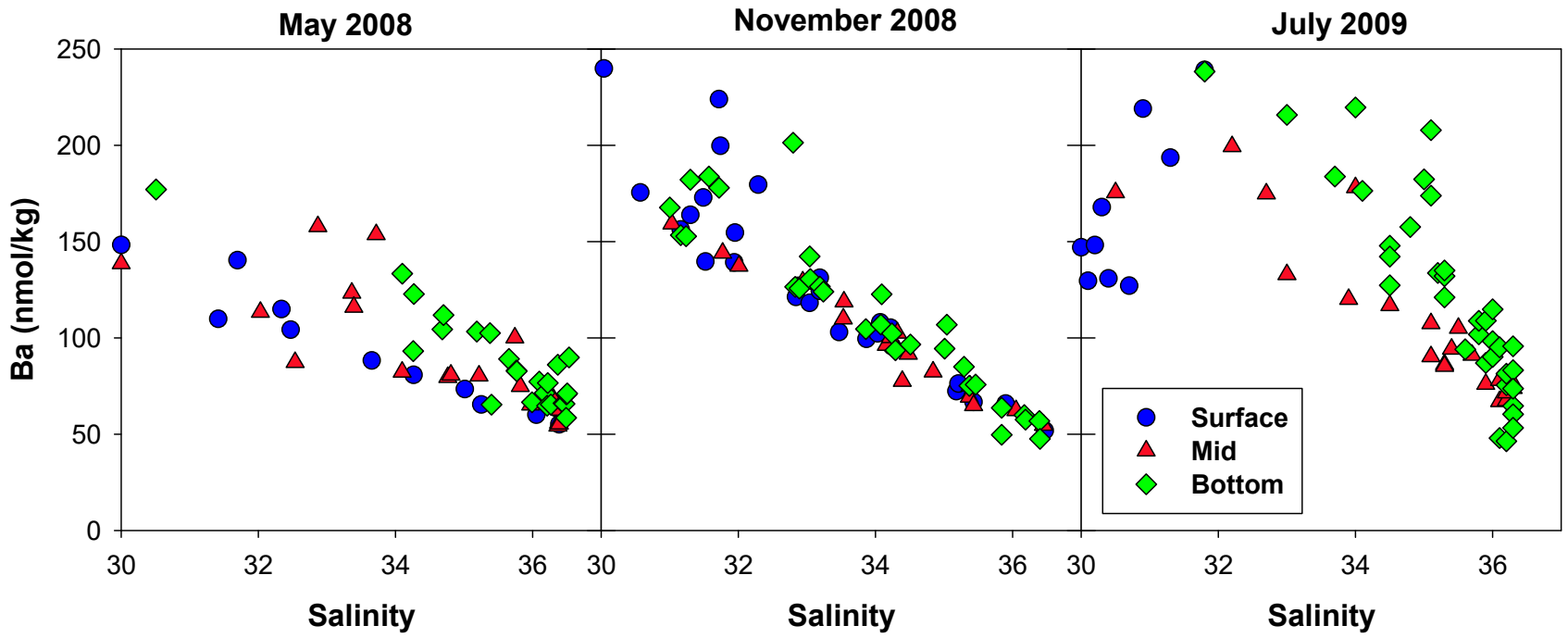

Fig. S2. High salinity (>30) Ba distribution.

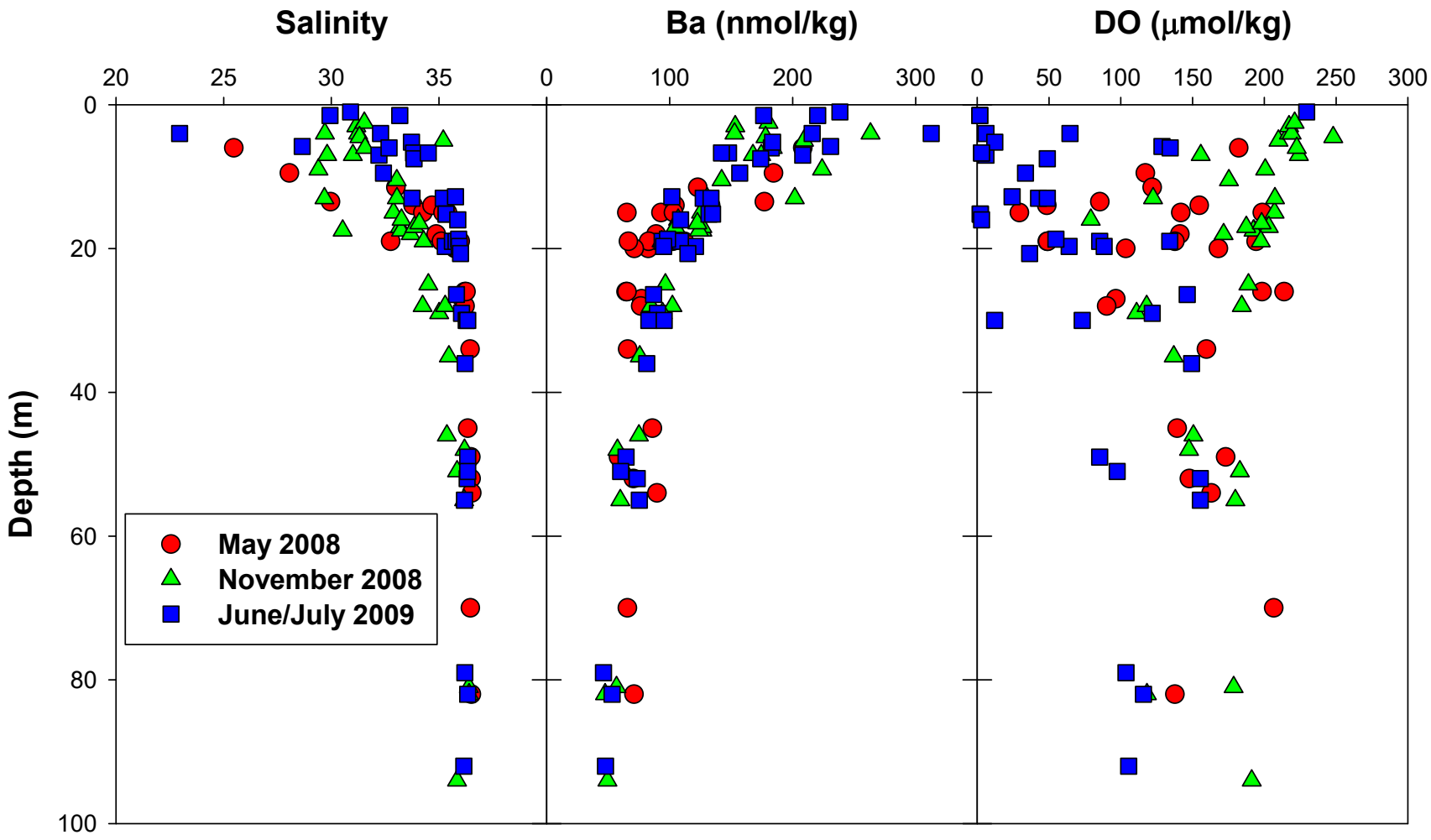

Fig S3. Bottom water salinity, Ba concentration, and dissolved oxygen (DO) with depth for samples with salinity > 20.

Table S1. Results from samples during May 2008.

Station	Date	Bottom Depth (m)	Sample Depth (m)	Latitude	Longitude	Salinity	Temperature (°C)	DO* (μmol/kg)	SPM* (mg/kg)	Chl a (μg/kg)	Ba (nmol/kg) 0.45 μm	Ba (nmol/kg) 0.02 μm	$\delta^{18}O$ (‰)
X3	5/1/08	90	0	28.758	89.537	22.3	22.8	245.2	4.1	5.0			
			80			36.5	20.1	170.1		0.2			
MR1	5/1/08	0	0	28.778	89.525	11.0			143.6	2.1	391	392	-3.9
MR2	5/2/08	0	0	28.850	89.467	11.9			6.3		393	386	-3.7
MR3	5/2/08	0	0	28.898	89.434	2.0					483	473	-5.7
MR4	5/2/08	0	0	28.894	89.433	0.8					451	438	-5.9
MR5	5/2/08	0	0	28.903	89.433	0.6					426	419	-6.0
MR6	5/2/08	0	0	28.927	89.414	0.1					393	370	-6.2
A9	5/2/08	82	0	28.751	89.750	28.0	23.1	419.6	1.9	14.0	139	137	-0.5
			20			30.0	23.1	325.3	2.1		139	136	-0.5
			70			36.5	20.4	206.6	2.5	0.4	66	64	1.1
A7	5/2/08	50	0	28.945	89.760	15.6	22.7	192.3	3.4	22.2	321	315	-3.0
			18			32.7	22.3	160.9			100	99	0.3
			45			36.3	20.9	139.3	1.4	0.5	86	89	1.1
A5	5/2/08	30	0	29.074	89.757	17.1	23.3	597.9	4.3	38.8	294	290	-2.7
			15			36.0	22.9	311.4			65	59	1.1
			26			36.2	22.3	198.4		0.6	65	62	1.1
A3	5/2/08	17	0	29.186	89.758	16.5	24.0	542.8	6.3	29.7	296	290	-2.8
			14			33.8	21.9	48.6		1.4	133	134	0.5
A1	5/3/08	5	0	29.292	89.753	6.4	22.8	428.6	12.6	7.7	400	396	
			4			7.9	23.3	461.5		11.1	360	353	
C1	5/3/08	5	0	29.057	90.532	17.4	23.8	329.4	27.1	26.0	297	293	-2.7
			3.5			17.4	23.8	325.8		38.5			
C4	5/3/08	13	0	28.951	90.533	17.7	23.8	336.0	5.0	30.5	300	297	
			6			27.3	23.3	279.1	5.8		173	173	-0.8
			11.5			33.0	23.1	121.9	11.5	5.9	123	121	
C6	5/3/08	20	0	28.843	90.497	18.4	23.3	267.0	3.0	18.5	274	275	-2.2
			8			33.8	23.3	240.5	1.4		87	87	0.7
			18			34.9	22.4	141.3	20.0	1.4	89	90	1.1
C7	5/3/08	20	0	28.827	90.396	18.4	23.8	335.2	1.7	29.6	279	276	-2.3
			10			33.4	23.1	204.0	2.3		116	95	0.6
			20			35.7	22.6	103.5	14.0	1.2	83	83	1.2
C9	5/3/08	27	0	28.768	90.225	24.0	23.8	304.2	1.8	16.2	190	190	-1.2
			10			34.8	23.2	218.5	0.4		80	81	0.8
			27			36.1	21.9	96.6	6.2	0.7	77	77	1.0
C11	5/4/08	51	0	28.587	90.207	32.4	23.4	244.3	1.4	6.1	110	110	
			18			36.3	23.2	209.6	1.3		68	67	1.0
			49			36.5	20.4	173.1	2.4	0.2	58	60	
F0	5/3/08	3.5	0	29.275	91.618	13.8	22.8	202.2	28.2	6.6			
			2.2			17.8	24.0	187.0	25.2	9.1	302	305	-1.8
AR1	5/4/08	0	0	29.400	91.362	0.1					480	466	
AR2	5/4/08	0	0	29.323	91.429	2.2					544	544	-4.8
AR3	5/4/08	0	0	29.303	91.497	4.4					568	555	-4.4
AR4	5/4/08	0	0	29.299	91.517	5.8					586	591	-4.2
AR5	5/4/08	0	0	29.295	91.542	7.1					562	565	-4.0
AR6	5/4/08	0	0	29.293	91.551	9.1					529	533	-3.8
AR7	5/4/08	0	0	29.275	91.618	8.6					464	465	-3.8
AR8	5/4/08	0	0	29.277	91.632	7.2					477	483	-4.1
F2	5/4/08	8.4	0	29.517	91.620	21.9	24.7	258.8	3.6	8.7	238	248	-1.5
			6			25.5	23.6	182.2	5.3	16.5	208	209	-1.0
F3	5/5/08	20	0	28.887	91.618	27.3	24.6	275.4	5.1	7.3	190	194	
			10			33.4	23.2	181.1	4.3		123	123	0.3
			19			35.1	22.8	49.2	22.6	3.5	103	104	

F5	5/5/08	30	0	28.699	91.621	31.7	23.7	204.5	8.8	3.4	140	126	0.2
			10			35.2	22.5	147.2	1.4		80	75	1.1
			28			36.2	21.9	90.2	8.8	0.5	77	77	1.2
F7	5/5/08	57	0	28.451	91.619	36.4	23.3	174.2	2.2	0.1	65	55	1.2
			28			36.4	22.5	178.4	1.1		63	56	1.2
			52			36.5	21.1	147.8	4.4	2.2	71	70	1.2
F8	5/5/08	82	0	28.178	91.620	36.4	23.6	173.7	0.3	0.1	64	56	1.2
			28			36.4	23.0	176.8	2.3		54	56	1.1
			82			36.5	19.9	137.8	4.8	0.9	71	70	1.3
I9	5/6/08	57	0	28.384	92.753	36.0	23.3	175.9	3.0	0.1	60	59	
			28			36.4	22.0	180.5	1.2		56	56	1.2
			54			36.5	20.2	163.0	3.2	1.5	90	74	
I8	5/6/08	37	0	28.648	92.759	36.4	22.9	176.6	1.8	0.1	55	55	1.2
			15			36.4	22.9	176.0	0.6		55	56	1.3
			34			36.5	21.9	159.7	1.5	1.5	66	62	1.3
I6	5/6/08	28	0	28.889	92.762	35.0	23.0	221.6	3.0	1.3	73	74	1.1
			13			35.8	22.9	217.7	2.4		75	69	1.1
			26			36.3	22.6	213.8	7.3	1.2	65	60	1.2
I4	5/6/08	20	0	29.031	92.761	33.7	23.6	232.3	15.8	2.4	88	89	0.5
			12			34.8	23.2	222.7	2.1		81	80	0.8
			19			36.0	22.8	194.4	2.7	1.1	67	66	1.2
I2	5/6/08	15	0	29.413	92.751	24.9	24.3	277.3	1.8	12.8	209	206	-1.1
			7			25.1	23.7	236.9	5.3		211	210	-1.1
			13.5			30.0	23.2	85.4	4.1	4.7	177	174	-0.3
I1	5/6/08	11	0	29.536	92.754	13.5	24.4	260.1	3.3	6.8	360	359	-3.0
			9.5			28.1	23.0	117.1	2.1	2.0	185	183	-0.5
H3	5/7/08	14	0	29.167	92.403	25.3	24.8	287.9	4.5	14.4	204	202	-1.1
			9			31.5	23.3	95.4	3.9		158	153	-0.2
			15			34.3	23.4	141.9	1.8	4.0	93	92	0.8
H4	5/7/08	22	0	29.040	92.391	34.3	24.2	234.1	2.1	1.6	81	82	0.7
			20			35.8	22.7	168.0	1.9	1.2	71	70	1.1
G3	5/7/08	21	0	28.974	92.007	32.5	23.8	220.5	2.2	3.8	104	100	0.4
			10			34.1	23.6	205.4	2.6		82	81	0.8
			19			35.8	23.0	137.8	5.3	1.0	83	82	1.1
F3(2)	5/7/08	20	0	28.893	91.623	29.9	24.1	252.7	3.8		148	149	-0.1
			11			32.0	23.9	223.2	2.3		113	112	0.4
			19			32.8	22.9	48.9	5.7		112	107	0.7
E2	5/7/08	16	0	28.745	91.254	32.3	24.3	254.2	1.5	3.7	115	103	0.5
			14			34.7	23.3	154.7	2.0	4.5	104	102	0.8
D3	5/8/08	18	0	28.725	90.837	35.3	23.9	199.0	1.5	0.7	65	66	1.1
			15			35.4	23.7	198.7	2.3	0.8	65	64	1.2
B4	5/8/08	16	0	29.035	90.120	15.4	24.0	265.9		6.5	322	324	-2.9
			0			15.4	24.0	265.9	2.0		318	321	-3.0
			9.5			28.9	22.6	186.7	1.2		154	153	-0.4
			15			35.2	22.3	29.5	1.9	0.7	103	102	0.9

(*: DO = dissolved oxygen, SPM = suspended particulate matter)

Table S2. Results from samples during November 2008.

Station	Date	Bottom Depth (m)	Sample Depth (m)	Latitude	Longitude	Salinity	Temperature (°C)	DO* (μmol/kg)	Chl a (μg/kg)	Ba (nmol/kg) 0.45 μm	Ba (nmol/kg) 0.02 μm	$\delta^{18}O$ (‰)
X3	10/31/08	95	0	28.758	89.537	34.6	23.4	211	3.3	199	201	0.1
			20			34.8	25.0	187		82	89	1.0
			94			35.2	18.3	118	0.2	50	50	1.0
MR 1	10/31/08	0	0	28.782	89.525	25.6				255	253	-0.8
MR 2	10/31/08	0	0	28.796	89.506	23.7				289	286	-1.3
MR 3	10/31/08	0	0	28.815	89.500	20.5				326	324	-1.8
MR 4	10/31/08	0	0	28.872	89.456	17.7				347	377	-2.2
MR 5	10/31/08	0	0	28.893	89.438	10.9				455	454	-3.6
MR 6	10/31/08	0	0	28.906	89.432	8.0				490	481	-4.3
MR 7	10/31/08	0	0	28.908	89.429	7.0				498	495	-4.7
MR 8	10/31/08	0	0	28.999	89.422	5.8				512	509	-4.8
MR 9	10/31/08	0	0	28.926	89.415	4.9				524	522	-5.0
MR 10	10/31/08	0	0	28.969	89.383	4.3				537	534	-5.1
MR 11	10/31/08	0	0	29.018	89.344	3.1				545	538	-5.4
MR 12	10/31/08	0	0	29.058	89.313	2.2				553	548	-5.5
MR 13	10/31/08	0	0	29.202	89.281	1.0				568	551	-5.7
MR 14	10/31/08	0	0	29.272	89.349	0.8				568	557	-5.7
A1	11/1/08	7	0	29.287	89.752	30.0	21.2	227	5.9	173	182	0.3
			6			31.6	21.3	223	6.0	184	201	0.5
A3	11/1/08	16	0	29.170	89.762	30.6	21.9	233	4.4	175	169	0.2
			8.3			31.8	22.6	217		144	142	0.4
			16			33.3	26.3	79	1.1	107	118	0.8
A5	11/1/08	30	0	29.067	89.752	31.9	22.7	230	3.8	139	139	0.3
			12			32.0	22.7	225		137	141	0.2
			29			35.0	26.1	111	0.8	94	96	0.7
A7	11/1/08	47.5	0	28.937	89.758	29.0	22.1	257	5.8	185	203	-0.2
			9.8			31.0	22.4	226		159	173	0.1
			46			35.4	26.3	137	0.3	75	79	0.9
A9	11/1/08	83	0	28.744	89.776	32.0	23.7	228	4.0	155	164	0.1
			20			34.4	27.6	203		78	83	0.8
			82			36.4	18.9	118	0.3	48	48	1.0
C11	11/2/08	52	0	28.576	90.214	35.4	25.2	188	0.3	67	71	1.3
			19.8			35.4	25.1	191		65	69	1.0
			48			36.2	23.4	148	0.2	58	57	1.0
C9	11/2/08	31	0	28.763	90.225	33.9	24.1	207	3.2	99	105	0.8
			15.3			34.5	25.0	164		92	97	0.8
			28			35.3	25.8	151	1.0	85	84	1.0
C7	11/2/08	21	0	28.830	90.395	33.5	23.7	211	3.3	103	108	0.7
			10			33.5	23.7	211		110	107	0.6
			18			33.7	23.9	172	2.8	107	107	0.8
C6	11/2/08	20	0	28.860	90.498	34.0	23.5	202	1.2	102	104	0.8
			16.5			34.1	23.6	198	1.4	123	130	1.0
C4	11/2/08	13	0	28.943	90.533	31.5	22.2	207	2.3	140	154	0.5
			10.5			33.0	23.3	175	1.3	142	140	0.6
C1	11/2/08	5	0	29.055	90.533	29.5	20.5	230	5.5	243	262	0.3
			4			29.7	20.5	217	5.5	263	262	0.2
D3	11/2/08	18	0	28.713	90.839	33.2	23.0	209		131	131	0.6
			17			33.2	23.0	203		127	126	0.8
			0							124	128	0.7
E2	11/3/08	16.5	0	28.743	91.255	33.0	22.7	208		118	129	0.9
			13			33.1	22.7	207		131	138	0.7
F0	11/3/08	3	0	29.784	92.033	7.3	19.1	312	13.0	499	502	-3.6
			2			13.3	19.5	219	5.2	426	429	-2.5

F1	11/3/08	6	0	29.185	91.618	17.2	21.1	269	4.4	380	376	-1.9
			5			27.4	21.1	210	3.4	209	219	-0.1
AR 1	11/3/08	0	0	29.626	91.257	0.2	19.1			510	513	-5.4
AR 2	11/3/08	0	0	29.377	91.379	2.0	19.7			523	521	-4.8
AR 3	11/3/08	0	0	29.334	91.420	3.7	20.6			502	498	-4.4
AR 4	11/3/08	0	0	29.325	91.428	5.6	20.6			493	497	-4.3
AR 5	11/3/08	0	0	29.311	91.439	7.6	20.7			480	485	-3.9
AR 6	11/3/08	0	0	29.293	91.456	9.2	20.9			443	469	-3.1
F2	11/3/08	8	0	29.053	91.619	29.8	21.6	224	1.8	178	184	0.4
			7			29.8	21.6	224	1.9	174	192	0.0
F3	11/4/08	18.5	0	28.884	91.618	30.5	22.0	210	1.3	164	172	0.3
			17.5			30.5	22.7	193	1.2	127	138	0.6
F5	11/4/08	29	0	28.688	91.629	34.2	23.9	186		105	105	0.7
			15.3			34.2	23.9	185		100	102	0.8
			28			34.2	23.9	184		102	102	1.0
F7	11/4/08	52	0	28.449	91.617	35.2	24.7	189	0.8	72	72	1.1
			20.3			35.4	24.9	189		69	75	1.1
			51			35.8	25.6	183	0.4	64	64	1.1
F8	11/4/08	82	0	28.180	91.622	36.5	25.8	189	0.3	52	51	1.2
			30			36.5	25.8	189		55	55	1.2
			81			36.4	25.3	179	0.4	57	58	1.2
I9	11/4/08	56	0	28.392	92.764	35.9	25.3	192	0.2	66	65	1.1
			19.8			36.1	25.4	190		62	62	1.0
			55			36.2	25.3	180	0.8	60	59	1.1
I8	11/5/08	36	0	28.641	92.764	35.2	24.6	191	0.7	76	75	1.1
			20.7			35.4	24.8	193		75	82	1.1
			35			35.5	24.9	191	0.5	76	77	1.0
I6	11/5/08	26	0	28.893	92.762	34.2	23.8	192	0.7	96	106	0.9
			12.1			34.3	23.9	190		103	103	0.9
			25			34.5	24.0	189	0.6	97	98	1.0
I4	11/5/08	19	0	29.181	92.761	32.9	23.0	202	0.9	127	128	0.7
			10.3			32.9	23.0	200		129	131	0.7
			17.5			33.2	23.2	192	0.7	124	127	0.7
I2	11/5/08	14	0	29.411	92.756	29.8	21.8	208	1.3	184	199	0.3
			13			29.7	23.8	123	1.0	202	206	0.3
I1	11/5/08	10	0	29.539	92.759	28.2	21.5	223	1.6	209	207	0.3
			9			29.4	21.3	201	1.0	224	227	0.2
H0	11/5/08	3	0	29.492	92.388	16.6	21.1	249		436	454	-1.9
			2			16.4	21.1	249		464	461	-1.9
GH0	11/6/08	3.5	0	29.470	92.268	18.1	20.8	251		374	362	-1.7
			2.5			31.5	20.8	248		180	184	0.5
E1	11/6/08	5.5	0	28.968	91.252	31.7	21.5	221		224	245	0.4
			4.5			31.3	21.5	221		178	181	0.5
D0	11/6/08	4	0	29.016	90.833	30.0	20.6	226		240	239	0.3
C6-1	11/6/08	18	0	28.872	90.493	32.8	23.4	223		121	123	0.6
			11.3			33.5	23.9	200		119	118	0.6
			17			33.9	24.2	187		105	106	0.6
C7-1	11/6/08	20	0	28.837	90.398	34.1	24.4	209		108	106	0.8
			12.3			33.7	24.2	203		96	96	0.8
			19			34.3	24.2	198		94	94	0.8
B4	11/6/08	16	0	29.032	90.111	32.0	23.6	226		180	136	0.4
			15			32.9	23.6	207		126	125	0.6
B1	11/6/08	8	0	29.077	90.208	29.8	22.6	247		168	170	0.0
			7			31.0	22.7	156		168	164	0.1
C1-1	11/7/08	5	0	29.059	90.549	31.2	22.5	219		156	159	0.3
			4			31.2	22.6	219		153	151	0.4
C1W	11/7/08	5	3	29.058	90.533	31.2	22.5	217		153	155	0.3

(*: DO = dissolved oxygen)

Table S3. Results from samples during June-July 2009.

Station	Date	Bottom Depth (m)	Sample Depth (m)	Latitude	Longitude	Salinity	Temperature (°C)	DO* (µmol/kg)	Chl a (µg/kg)	Ba (nmol/kg) 0.45 µm	Ba (nmol/kg) 0.02 µm	$\delta^{18}O$ (‰)
X3	6/28/09	93	0	28.753	89.534	26.8	30.4	200	0.8	154	151	-0.2
			40			36.3	23.4	192	0.4	63	63	1.2
			92			36.2	16.4	106	0.0	48	48	1.0
MR 1	6/28/09	0	0	28.826	89.482	22.1				274	269	-1.2
MR 2	6/28/09	0	0	28.837	89.471	18.4				327	324	-2.0
MR 3	6/28/09	0	0	28.846	89.462	15.2				391	395	-2.4
MR 4	6/28/09	0	0	28.849	89.459	12.7			18.0	452	452	-2.9
MR 5	6/28/09	0	0	28.856	89.452	9.2				485	484	-4.0
MR 6	6/28/09	0	0	28.862	89.446	6.3				506	502	-4.8
MR 7	6/28/09	0	0	28.907	89.431	2.3				560	544	-5.7
MR 8	6/28/09	0	0	28.956	89.392	0.6			1.9	573	559	-6.0
A1	6/29/09	6.8	0.3	29.290	89.745	23.5	29.7	142	6.5	286	283	-1.0
A1			5.8			28.7	28.5	129	1.3	231	229	-0.5
A3	6/29/09	15.5	0	29.177	89.751	23.7	30.1	182	5.1	269	265	-1.0
			7			32.8	25.2	64	0.8	175	172	0.0
			16			35.9	24.4	3	0.2	109	109	0.9
A5	6/29/09	31	0	29.068	89.750	24.4	30.0	194	4.8	287	286	-1.5
			13.5			35.7	24.8	116	0.1	91	92	1.0
			20			36.2	24.4	146		67	68	1.0
			30			36.3	22.1	12	0.2	96	96	1.0
A7	6/29/09	50	0	28.940	89.749	24.6	30.6	197	1.7	194	194	-0.7
			20			35.9	24.9	162	0.4	76	76	1.2
			49			36.3	18.9	85	0.2	65	65	1.0
A9	6/29/09	80	0	28.750	89.749	22.9	31.3	200	0.9	208	205	-0.9
			14			35.5	25.6	107		117	116	0.9
			30			36.1	24.7	189	0.1	67	66	1.1
			40			36.3	21.8	119	0.3	74	73	1.1
			79			36.2	16.8	104	0.0	46	45	0.9
C11	6/30/09	52	0	28.587	90.201	22.7	30.3	212	2.1	111	36	-1.1
			30			36.3	21.8	128	0.3	76	76	1.2
			51			36.3	19.3	98	0.1	60	60	1.1
C9	6/30/09	31	0	28.767	90.216	24.6	30.1	224	5.2	79	52	-0.9
			20			36.1	24.5	149	0.2	78	78	1.1
			30			36.3	22.7	73	0.5	83	83	1.0
C7	6/30/09	20.7	0	28.830	90.392	23.6	30.4	237	6.5	235	210	-1.2
			9.5			35.1	24.8	61	1.2	107	107	0.6
			19.7			35.9	24.3	88	1.2	95	94	1.0
C6C	6/30/09	19.7	0	28.866	90.483	20.0	30.6	238	6.4	331	323	-1.8
			10			35.4	25.0	92	1.1	94	95	0.8
			18.7			35.9	24.4	55	0.9	98	97	1.0
C4	6/30/09	13.8	0	28.950	90.523	25.0	30.1	157	8.8	284	281	-0.7
			5.3			31.2	25.6	58	0.5	178	180	-0.1
			12.8			35.8	24.4	24	1.5	102	101	0.9
C1	6/30/09	6.2	0	29.055	90.533	30.4	27.7	181	9.7	219	218	0.0
			5.2			33.7	25.6	12	6.1	184	184	0.5
D2	6/30/09	16.2	0	28.843	90.833	16.0	30.3	223	7.5	377	383	-2.3
			15.2			35.3	24.5	2	0.9	132	133	0.8
			15.2			35.3	24.5	2		135	134	0.8
AR 1	7/1/09	0	0	29.440	91.322	0.1				437	421	-4.9
AR 2	7/1/09	0	0	29.351	91.405	0.6				523	495	-4.6
AR 3	7/1/09	0	0	29.317	91.490	0.7				496	512	-4.7
AR 4	7/1/09	0	0	29.302	91.527	1.5				484	490	-4.4
AR 5	7/1/09	0	0	29.290	91.561	2.9				518	526	-4.2

AR 6	7/1/09	0	0	29.244	91.618	6.0				505	500	-3.5
AR 7	7/1/09	0	0	29.211	91.620	8.8				469	469	-3.0
AR 8	7/1/09	0	0	29.188	91.623	12.2				449	450	-2.4
AR 9	7/1/09	0	0	29.178	91.625	15.2				411	409	-2.0
AR 10	7/1/09	0	0	29.161	91.625	18.0				376	372	-1.5
AR 11	7/1/09	0	0	29.149	91.625	18.8				355	363	-1.4
F0	7/1/09	5	0	29.272	91.619	3.1	30.0	137	26.3	489	482	-4.0
			4			23.0	29.1	65	5.0	313	316	-1.1
F1	7/1/09	5	0	29.181	91.618	1.4	30.2	210	3.5	467	472	-4.3
			4			32.3	26.8	6	6.1	216	214	0.5
F2	7/1/09	7	0	29.050	91.617	10.4	31.1	218		478	478	-3.0
			6			32.7	26.3	134		183	184	0.5
F3	7/1/09	20	0	28.883	91.616	29.3	30.7	199	0.5	157	154	0.1
			6.5			30.5	28.5	150	1.0	175	177	0.1
			19			35.6	25.7	134	1.6	94	96	1.1
F5	7/1/09	30	0	28.691	91.617	29.2	31.2	196	0.3	171	174	0.1
			10			35.5	34.1	195	0.5	105	104	0.5
			29			36.1	24.0	122	0.9	90	90	1.0
F7	7/2/09	53	0	28.464	91.612	28.1	30.5	193	0.3	136	129	-0.1
			20			35.3	27.1	198	0.2	86	87	0.9
			40			36.2	22.8	201	0.4	72	74	1.0
			52			36.3	21.2	155	1.1	74	75	1.2
F8	7/2/09	84	0	28.181	91.613	28.1	31.0	193	0.3	127	125	-0.1
			20			35.3	26.7	204	0.3	85	85	1.0
			82			36.3	18.8	116	0.2	53	53	1.1
I9	7/2/09	56	0	28.391	92.752	29.0	31.0	196	0.2	137	136	0.0
			20			35.1	26.6	201	0.4	90	92	1.0
			55			36.2	20.9	155	0.5	75	78	1.3
I8	7/3/09	37	0	28.646	92.748	29.4	30.9	193	0.4	143	144	0.1
			12.5			32.2	27.4	153	0.5	133	133	0.5
			36			36.2	22.2	149	0.7	81	82	1.3
I6	7/3/09	27.4	0	28.892	92.750	30.1	30.9	193	0.3	130	131	0.3
			18.5			33.4	26.9	144	0.8	120	119	0.8
			26.4			35.8	24.9	146	1.3	87	88	1.4
I4	7/3/09	20.7	0	29.174	92.750	30.4	32.0	193	0.3	131	126	0.4
			19.7			35.3	26.1	64		121	121	1.0
I2	7/3/09	14	0	29.409	92.750	30.7	31.9	196	1.0	127	126	0.3
			13			33.8	26.9	43		127	129	1.0
I1	7/3/09	10.4	0	29.532	92.750	31.7	32.1	208	1.9	193	197	0.2
			5.7			32.2	28.5	107		199	200	0.3
			9.5			32.4	33.8	34		157	155	0.5
H0	7/3/09	2	0	29.494	92.385	32.1	31.9	229	8.0	239	237	0.4
			1			30.9	31.9	230		238	237	0.4
H3	7/3/09	14	0	29.154	92.382	30.2	31.7	193	0.3	148	148	0.2
			13			35.2	26.0	49		134	134	0.8
G1	7/4/09	8	7	29.260	91.998	32.2	26.1	6		208	205	0.3
G3	7/4/09	20	0	28.983	91.998	30.3	31.1	196		168	155	0.3
			19			35.8	25.6	85		109	106	1.0
E2	7/4/09	8.5	0	28.857	91.248	27.4	31.3	206		252	246	-0.1
			7.5			33.8	25.7	49		174	166	0.8
E3	7/4/2009	21.7	0	28.656	91.248	30.0	31.4	196		147	143	1.0
			20.7			36.0	24.2	37		115	112	0.9
D1	7/4/2009	7.7	6.7	28.982	90.833	33.8	24.9	3		148	144	0.7
			6.7			34.5	24.9	3		142	138	0.8
D0	7/4/09	7.8	1.5	29.013	90.833	33.2	25.3	2		176	174	0.6
D0(W)	7/4/09	6.5	1.5	29.018	90.833	29.9	25.5	2		220	217	0.3

(*: DO = dissolved oxygen)

Table S4. Results from mixing experiments during May and November 2008 and June-July 2009. MR mixing experiment was conducted only during June/July 2009.

May 2008			November 2008			June/July 2009	MR		AR		
Salinity	Ba (nmol/kg)		Salinity	Ba (nmol/kg)		Salinity	Ba (nmol/kg)		Salinity	Ba (nmol/kg)	
	0.45 µm	0.02 µm		0.45 µm	0.02 µm		0.45 µm	0.02 µm		0.45 µm	0.02 µm
0.1	498	466	0.2	479	512	0.7	537	517	0.1	435	418
2.5	492	470	4.3	436	478	4.8	501	485	4.0	433	421
4.0	533	521	7.4	411	446	8.6	450	440	6.5	406	400
7.2	441	431	11.5	366	391	11.1	416	409	10.0	370	363
8.4	464	465	14.5	320	342	14.4	378	372	14.0	329	326
10.8	431	425	17.7	279	299	17.2	348	339	17.1	302	295
14.4	377	374	21.1	236	252	21.5	300	295	18.8	280	275
19.3	307	309	26.9	174	192	23.9	269	261	23.8	235	233
23.0	253	254	29.0	136	144	26.6	229	227	24.9	217	213
24.6	235	232	32.5	101	108	29.7	186	183	28.3	180	176
32.9	107	106	36.7	49	51	32.8	144	143	32.2	145	141
33.0	118	101				34.1	120	119	35.6	117	114
35.8	55	54				35.7	79	78	36.2	88	86