



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

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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 $<0.02 \mu\text{m}$ fraction, with no significant contribution from the $0.02\text{--}0.45 \mu\text{m}$ 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.

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1. INTRODUCTION

Barium is an important ocean geochemical tracer that has been used in several specific ways: (a) as a paleo-

productivity 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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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 tributary 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 ¹³⁵Ba 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

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