



Temporal and spatial variations of dissolved and colloidal trace elements in Louisiana Shelf waters



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ABSTRACT

Selected trace elements (TEs), dissolved organic carbon and nutrients were studied in Louisiana Shelf waters including the low salinity Mississippi (MR) and Atchafalaya (AR) River plumes during periods of high, intermediate and low river discharge in 2008–2009. The dissolved phase ($<0.02 \mu\text{m}$) was predominant for Cs, Cu, Mo, Ni, and U, while Fe was mainly in the colloidal phase ($0.02\text{--}0.4 \mu\text{m}$). Cobalt, Cr and Mn existed mainly in the dissolved phase but sometimes showed significant colloidal concentrations in low (Cr, Mn) and middle (Co) salinity. In the shelf surface waters, dissolved Cs, Cu, Mo, Ni, and U showed conservative as well as non-conservative behaviors relative to salinity gradients, with vertical mixing the main cause for apparent non-conservative behavior. However, the other TEs showed consistently non-conservative behavior during all sampling campaigns. Through examination of associated mixing experiments, nutrient and chlorophyll distributions, and surface-bottom concentration contrasts, the non-conservative behavior of TEs was variously related to colloidal flocculation (Fe, Cr), biological activity (Fe, Mn), desorption (Co), photochemical reaction (Cr) and benthic mobilization (Co, Cu, Ni, Mn). During the June/July 2009 bottom hypoxia season, TE concentrations in bottom waters were greatly enriched (Co, Cu, Ni, Mn, Fe) and depleted (Cr, V), probably due to particulate or sedimentary dissolution and/or diffusion for the enrichment, and diffusion into sediment and/or adsorptive removal onto particles for the depletion under prolonged reducing conditions. We also observed seasonal variations of TEs and nutrients in the two river plumes as well as in shelf waters. These seasonal variations appear to be related to the variation of mixing ratios of MR tributaries for the MR plume as well as inputs from the Red River and wetlands in the Atchafalaya Basin for the AR plume and contribute to observed variability of shelf TE distributions. More importantly, evidence of considerable vertical mixing, even during strong stratification associated with bottom water hypoxia, suggests that vertical mixing of bottom recycled nutrients may be an important mechanism for sustaining shelf biological production. Bottom-enriched (or depleted) TEs and nutrients that are not mixed upwards likely flow off the shelf delivering these materials offshore to the open Gulf of Mexico. Given the predicted rapid growth of coastal eutrophication and bottom water hypoxia under current global climate change scenarios, a better understanding of these recycled vertical and offshore fluxes is required for proper implementation in modeling studies and management strategies.

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1. Introduction

Estuaries are the interface between rivers and the ocean, and play an important role in controlling the flux of trace elements to the ocean via intense chemical, physical, biological, and geological processes. The study of trace elements in estuaries is of importance because of their bioavailability and toxicity (Wen et al., 1999a), as well as their ability to be tracers of key biogeochemical processes. However, biogeochemical characteristics and distributions of trace metals in estuaries are

complicated due to temporal and spatial variability of sources and sinks including river input, atmospheric deposition, groundwater input, mixing with ocean water, input from the bottom, and biological productivity (Breuer et al., 1999; Tovar-Sánchez et al., 2004).

The Louisiana Shelf receives fresh water dominantly from the Mississippi and Atchafalaya Rivers (MR and AR, respectively). The AR is a major tributary of the MR, carrying 30% of the combined flow of the MR and the Red River (RR). While the main channel of the MR enters the northern Gulf of Mexico through the birdfoot delta that extends to nearly the shelf break, the AR enters the shelf through the largest freshwater wetlands basin in the United States (Ford and Nyman, 2011) and a broad shallow bay. That is, nearly the same river endmember mixes with seawater in two very different physiographic areas (Shiller, 1993a). Furthermore, the Louisiana Shelf is well known for experiencing

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bottom water hypoxia, occurring annually from spring to late fall, due to the combined effects of anthropogenic fluvial nutrient input together with strong vertical stratification (e.g., Rabalais et al., 2010).

Various prior trace element studies have been conducted in Louisiana Shelf waters including the low salinity waters of the MR and AR plumes (e.g., Hanor and Chan, 1977; Shiller and Boyle, 1991; Shiller, 1993a; Shiller and Mao, 1999; Shim et al., 2012; Joung and Shiller, 2014). For example, Shiller and Boyle (1991) observed largely conservative behavior of dissolved Cu, Fe, Mo, Ni and Zn in the MR plume during high river discharge, whereas Cd, Cr and V showed non-conservative behavior. Similarly, Shim et al. (2012) reported conservative behavior of Cu. Rapid removal of Ni was observed at low salinity, and was suggested to result from biological uptake (Shiller, 1993a) as well as adsorption onto suspended particles (Shim et al., 2012). Shim et al. (2012) reported conservative behavior of Re and Cs, and desorption of Co in the MR delta outflow region. For Fe, Shim et al. (2012) observed rapid removal at low salinity in the MR plume, whereas Shiller and Boyle (1991) reported less intensive Fe removal at low salinity due to the alkaline nature of MR water (Shiller, 1997). This discrepancy may have resulted from the different filtration procedures between these two studies (Shim et al., 2012). Powell and Wilson-Finelli (2003) observed that a substantial fraction of the Fe in the MR plume was organically complexed. The observed non-conservative behavior of Cr in the MR outflow region suggested a temporal variability of the river endmember concentration (Shiller and Boyle, 1991), or photo-reduction of Cr(IV) to more particle-reactive Cr(III) (Shim et al., 2012). Non-conservative V behavior was observed in the surface waters in the MR plume area, and has been suggested to result from biological uptake (Shiller and Boyle, 1991) or, more likely, from mixing with V-depleted bottom water (Shiller and Mao, 1999). In contrast, a nearly conservative dissolved V distribution was observed in the MR plume area following the passage of a hurricane (Shim et al., 2012). Desorption of Ba from fluvial suspended particles has been commonly observed at low salinity during mixing of Mississippi plume waters (Hanor and Chan, 1977; Shim et al., 2012; Joung and Shiller, 2014). From the same surveys as this study, Joung and Shiller (2014) found slightly enriched Ba in shelf bottom waters due to an apparent Ba flux from the sediments on the Louisiana Shelf, which led them to suggest caution in the application of Ba as a paleo-salinity proxy. For Mn, a rapid increase was found at low salinity on the shelf near the delta and was suggested to result from desorption from the fluvial suspended matter (Shim et al., 2012). Mallini (1992) reported that surface and bottom water enrichment of dissolved Mn in Louisiana Shelf waters was related to reductive dissolution and inhibited vertical mixing during summer stratification and bottom water hypoxia. In general, U has been found to behave conservatively (Swarzenski and McKee, 1998; Shim et al., 2012), although removal was observed during unusually high river flow (Swarzenski and McKee, 1998). In addition, Shiller (1993a) reported contrasting behavior of Cd between the MR delta plume and the extended mixing zone of the Louisiana Shelf, and suggested that the Cd behavior likely resulted from Cd desorption from suspended particles in the low salinity MR delta plume and subsequent biological uptake in the shelf waters.

Overall, these previous studies paint a complex picture of potential seasonal and spatial variability of trace element behavior in this system. Herein, we report our studies of dissolved and colloidal trace elements together with nutrient and dissolved organic carbon (DOC) distributions in Louisiana Shelf waters including the low salinity mixing zones of the MR and AR. The ultimate goals of this study were to identify the sources and sinks of trace elements in the Mississippi/Atchafalaya mixing zones, to compare trace element distributions in different tributary mixing zones during different seasons, and to investigate the origin of the different element distributions in the two mixing zones. The results can potentially provide critical information on environmental issues such as hypoxia on the Louisiana Shelf as well as pollutant source tracking. Moreover, the results should deliver crucial knowledge

of the consequences of globally expanding human induced environmental disturbances on coastal and thus, oceanic ecosystems.

2. Methods and materials

Trace element, nutrient and dissolved organic carbon (DOC) samples were collected on the Louisiana Shelf, including the low salinity MR and AR plumes, during three cruises in May and November 2008 and June 2009 aboard the R/V Pelican (Fig. 1 and S1). These cruises represent high, low, and mid-range Mississippi River water discharges, respectively (Fig. 2). All trace element apparatus including syringes, filters, Teflon tubing, sample bottles, Niskin bottles and tubing connectors were acid cleaned as described by Shim et al. (2012) and Joung and Shiller (2013).

For the MR and AR plumes (i.e., the lowest salinity regions near or in the river mouths, depending on season), only surface samples were collected and this was done using a small boat moving forward slowly. For the shelf, samples were collected at different depths including surface, near bottom and middle depths. For the earlier two cruises (May and November 2008), a clean underway pumping system, driven by an air-powered plastic diaphragm pump, was employed for surface waters. A non-metallic, tow-fish was towed just below the surface, several meters off the side of the ship. One end of acid-cleaned Teflon-lined polyethylene tubing was attached to and extended in front of the tow-fish running to the pump; from the pump, tubing was then run into a small plastic enclosure in the ship's lab where surface waters were sampled. These surface water samples were collected after allowing about 10-minutes flushing of the pumping system while the ship was moving. For the June 2009 sampling, a grab sampler was used. An acid-cleaned bottle was attached at the end of PVC pole (~5 m length), and the bottle was rinsed with ambient water three times before collecting the sample while the ship was moving slowly forward. For deep water, a clean pumping system was used during the first cruise. This system was similar to the surface water sampling at this time, but the acid-cleaned tubing was connected to a Kevlar cable, which held a non-metallic weight at the end. 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. This system was also used for mid-depth sampling by using a plastic messenger to trigger the closing of the Niskin bottle.

Trace element samples were filtered using acid-cleaned 25 mm × 0.45 μm pore size polypropylene (Whatman Puradisc) and 25 mm × 0.02 μm pore size alumina (Whatman Anotop) syringe filters, allowing us to separate operationally-defined "total" and "dissolved" fractions, respectively. The colloidal phase (0.02–0.45 μm) is defined by the difference between the two fractions. Details of the sample processing can be found elsewhere (Shiller, 2003). Nutrient and DOC samples were also collected at the same time, but these samples were filtered using only 0.45 μm pore size filters. The trace element filtrates were then tightly capped and kept in clean double zippered plastic bags. Nutrient and DOC samples were kept frozen until analysis.

Mixing experiments were conducted at sea using river water and seawater endmembers. Unfiltered river water and seawater were mixed in varying proportions and held at room temperature in the dark overnight. The experiments were done at sea and it was assumed that the ship's motion provided adequate mixing of the samples. The mixed samples were filtered in the same way as the field samples. The lowest salinity waters for the mixing experiment were collected from the AR (i.e., Stn. AR1) for all our study periods, and additionally from the MR (i.e., Stn. MR8) only for June/July 2009. An overnight mixing time was chosen as being sufficient for chemical reactions such as flocculation or desorption to occur (Boyle et al., 1977; Hanor and Chan, 1977; Sholkovitz, 1978; Li et al., 1984; Hatje et al., 2003), but not so long that biological processes are likely to be dominant influences.

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