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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 μm) was predominant for Cs, Cu, Mo, Ni, and U, while Fe was mainly in the colloidal phase (0.02–0.4 μm). 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.

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 distributary 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 photoreduction 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 distributary 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.

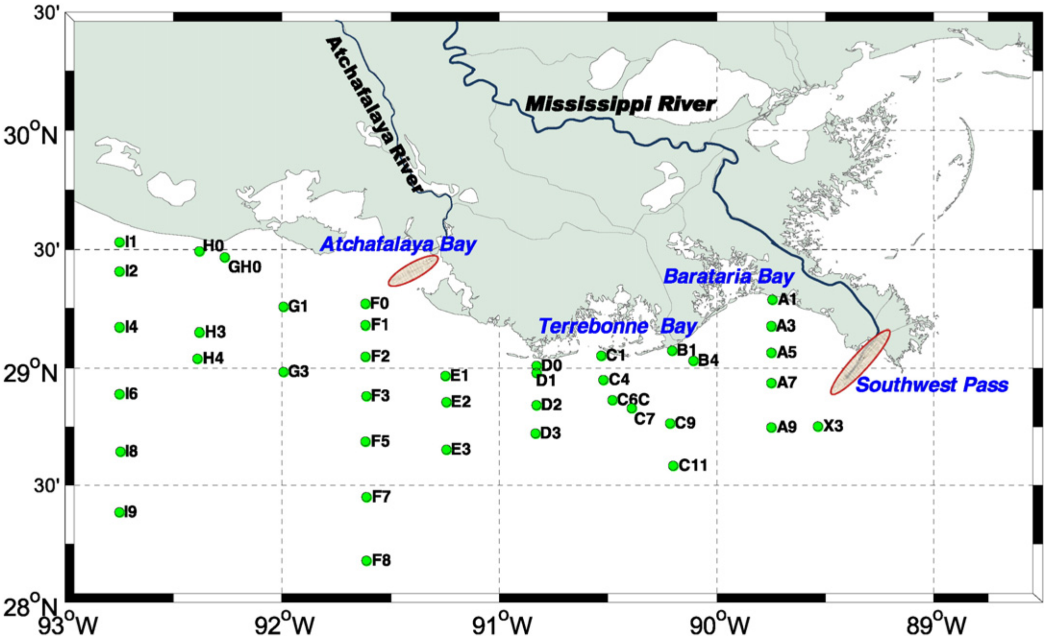

Fig. 1. Louisiana Shelf sampling stations May 2008, November 2008, and June 2009 (green circles). Shaded areas by Southwest Pass and Atchafalaya Bay show general location of river endmember sampling (see Fig. S1 and Tables S2–S4 for specific locations).

Nonetheless, some biological effects on these mixing experiments cannot be ruled out.

Ancillary data such as salinity, temperature, and dissolved oxygen (DO) were obtained from a separate CTD cast. The DO sensor calibration was checked by Winkler titration. Nutrient analyses were performed at the University of South Florida or by the Geochemical & Environmental Research Group (Texas A&M). The oxygen isotope composition of the water was determined 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). Standardization was accomplished using in-house standards calibrated to the VSMOW scale.

The Mississippi River discharge was obtained from US Army Corps of Engineers' (http://www.mvn.usace.army.mil/eng/edhd/wcontrol/discharge.asp) discharge records from the gage at Tarbert Landing, Mississippi. Relative major tributary contributions to the MR mainstem discharge were estimated from USGS 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://usgs.gov/water/). To adjust approximately for the travel time of water from these tributaries to the delta, the estimation of relative contributions used Upper Mississippi River, Missouri River and Ohio River discharges from 15, 15, and 12 days, respectively, prior to our sampling. 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, discharge was also obtained from the US Army Corps of Engineers from the gage at Simmesport, LA.

2.1. Nutrient, DOC, chlorophyll a and trace element analysis

The frozen nutrient and DOC samples were thawed overnight at room temperature just before analysis. Nutrients were analyzed using a nutrient auto-analyzer applying standard methods. Detection limits of nutrient analysis were 0.1, 0.02 and 0.1 μmol/L for nitrate, phosphate and silicate, respectively. The DOC samples were analyzed using a Shimadzu TOC-V total organic carbon analyzer employing the high temperature combustion method (Guo et al., 1995). For DOC measurements, samples were acidified with concentrated HCl to pH < 2 before analysis. Concentrations of DOC were automatically calculated using the calibration curves generated at the beginning of the analytical run. Certified DOC standards (University of Miami) were measured frequently during the run to check the performance of the instrument. The variation of three to five measurements of each sample was less than 2%. Chlorophyll *a* measurements were conducted by High Performance Liquid Chromatography (HPLC). Detailed descriptions of sample processes can be found elsewhere (Chakraborty and Lohrenz, 2015).

For trace element analysis, the filtered samples were acidified to pH < 2 by addition of 140 and 70 μL of clean 6 M HCl (Seastar Baseline) for 30 (<0.45 μm) and 15(<0.02 μm) mL samples, respectively, to prevent trace element loss onto the bottle wall, precipitation, or biological interaction. Trace elements were measured using a sector field-inductively coupled plasma–mass spectrometry (SF-ICP-MS; Thermo-Fisher Element 2). Analysis of seawater was performed either by diluting the sample 20-fold with 0.3 M ultrapure HNO_3 (Seastar Baseline) for Ba, Cs, Mo, Re, and U or by using a magnesium hydroxide co-precipitation technique for Fe, Cu, Ni, Mn, Co, Cr, and V (e.g., Shim et al., 2012; Wu and Boyle, 1997). In both cases, calibration was performed by isotope-dilution using enriched isotopic spikes obtained from Oak Ridge National Laboratory with exception of Co, Cs, Mn and U which were calibrated using external standards (see Shim et al., 2012, for details). Samples were prepared for analysis without UV oxidation. As noted by Shim et al. (2012), this yields reliable results for all trace elements with the possible exception of Co for which there may be a fraction that is not labile even after sample acidification (Saito and Moffett, 2001). However, given the high (compared with open ocean) Co values we report here, it is likely that we are recovering the substantial portion of the total dissolved Co. To verify the accuracy of the analysis, the certified reference seawater NASS-5 (NRC-Canada) was measured at the beginning and end of each analytical run. Analytical performance was checked by measuring a standard and blank after every 8 sample measurements. The detection limits and recoveries for the certified reference material are shown in Table S1.

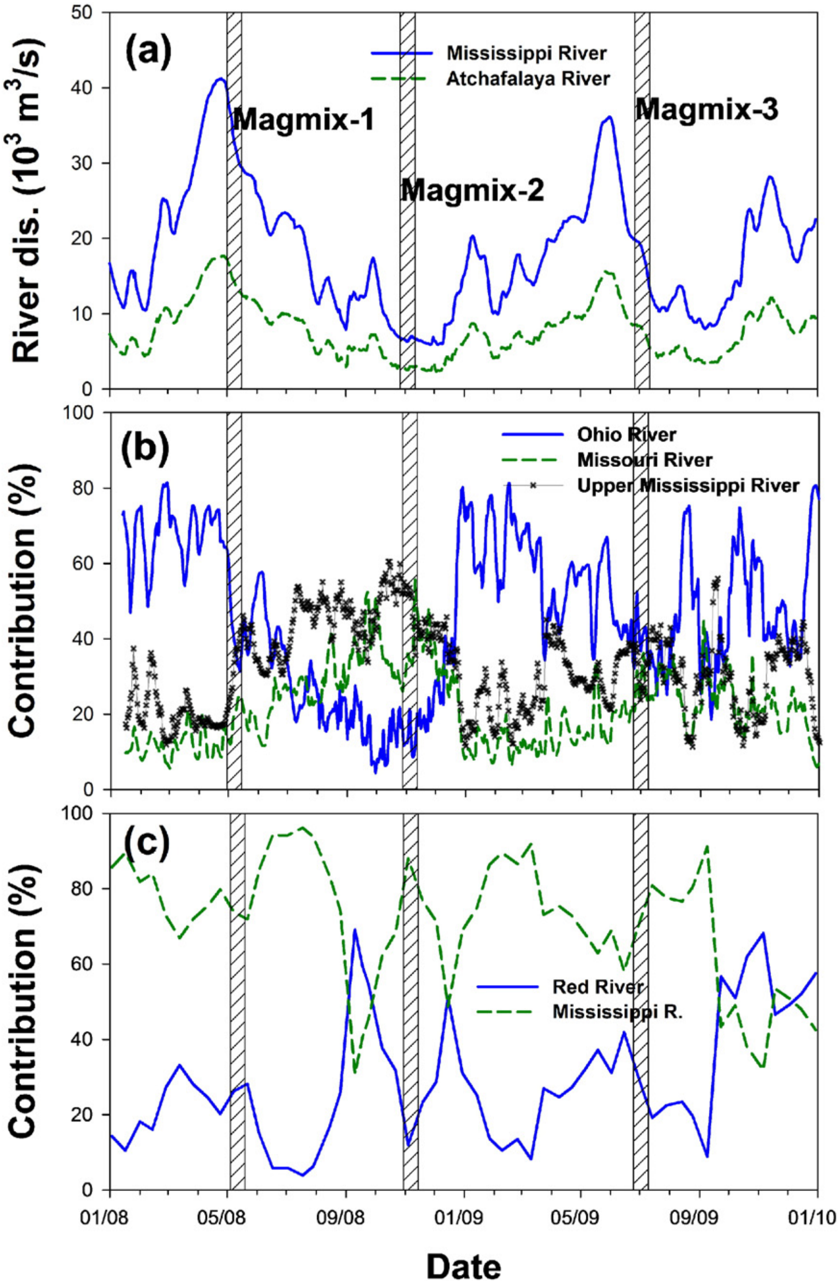

Fig. 2. a) Discharges of Mississippi (MR) and Atchafalaya (AR) Rivers; b) relative contributions of major MR tributaries to the lower river; and, c) relative contributions of the MR and Red River (RR) to the AR discharge.

3. Results and discussion

3.1. DOC and nutrients in river water

The MR discharge and major tributary contributions to the river are shown in Fig. 2. During our high discharge sampling, the main water contributor was the Ohio River, which accounted for more than 50% of the flow in the lower river. However, the Missouri and Upper Mississippi Rivers were the primary contributors during low river discharge, and all three tributaries had very similar contributions during the intermediate river discharge period.

The DOC and nutrient distributions are shown in Fig. 3. The DOC and nutrient endmember concentrations varied seasonally in both the MR and AR, but the concentration range was similar to previously reported values (Shen et al., 2012; Duan and Bianchi, 2006; Bianchi et al., 2004; Dubois et al., 2010). These seasonal variations likely resulted from hydrologic factors such as changes in tributary mixing ratios (Duan et al., 2010) as well as inputs from the Red River (RR) and wetlands in the Atchafalaya River Basin (ARB) (Shen et al., 2012).

Different distributions of DOC and nutrients were observed between the low salinity AR and MR plumes. The distribution of DOC showed relatively higher concentrations in the AR than MR plume, while nutrient concentrations were higher in the MR than AR plume, with the exception of phosphate and silicate during May 2008 when the concentrations were similar between the two plumes (Fig. 3). Similar observations of nutrient and DOC distributions were reported previously in this system and were suggested to result from different conditions of suspended loads, mixing rates, and marsh interactions (Shen et al., 2012; Lohrenz et al., 2008; Shiller, 1993a) and different turbidities which affect chlorophyll concentration by controlling light availability and species of phytoplankton (Pakulski et al., 2000). Total chlorophyll *a* concentrations showed maximum concentrations in low-middle

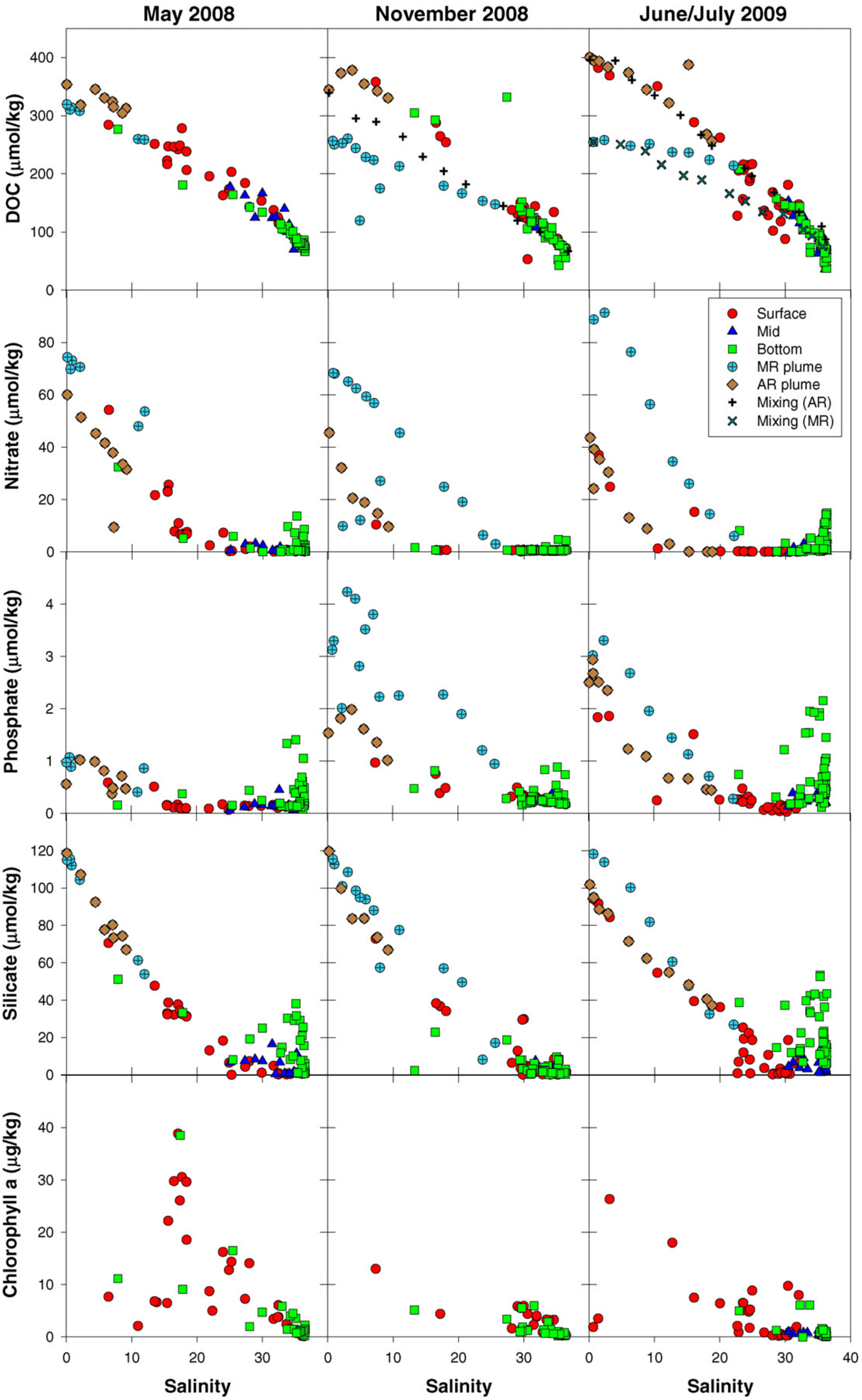

Fig. 3. Distributions of DOC, nutrients, and total chlorophyll *a*.

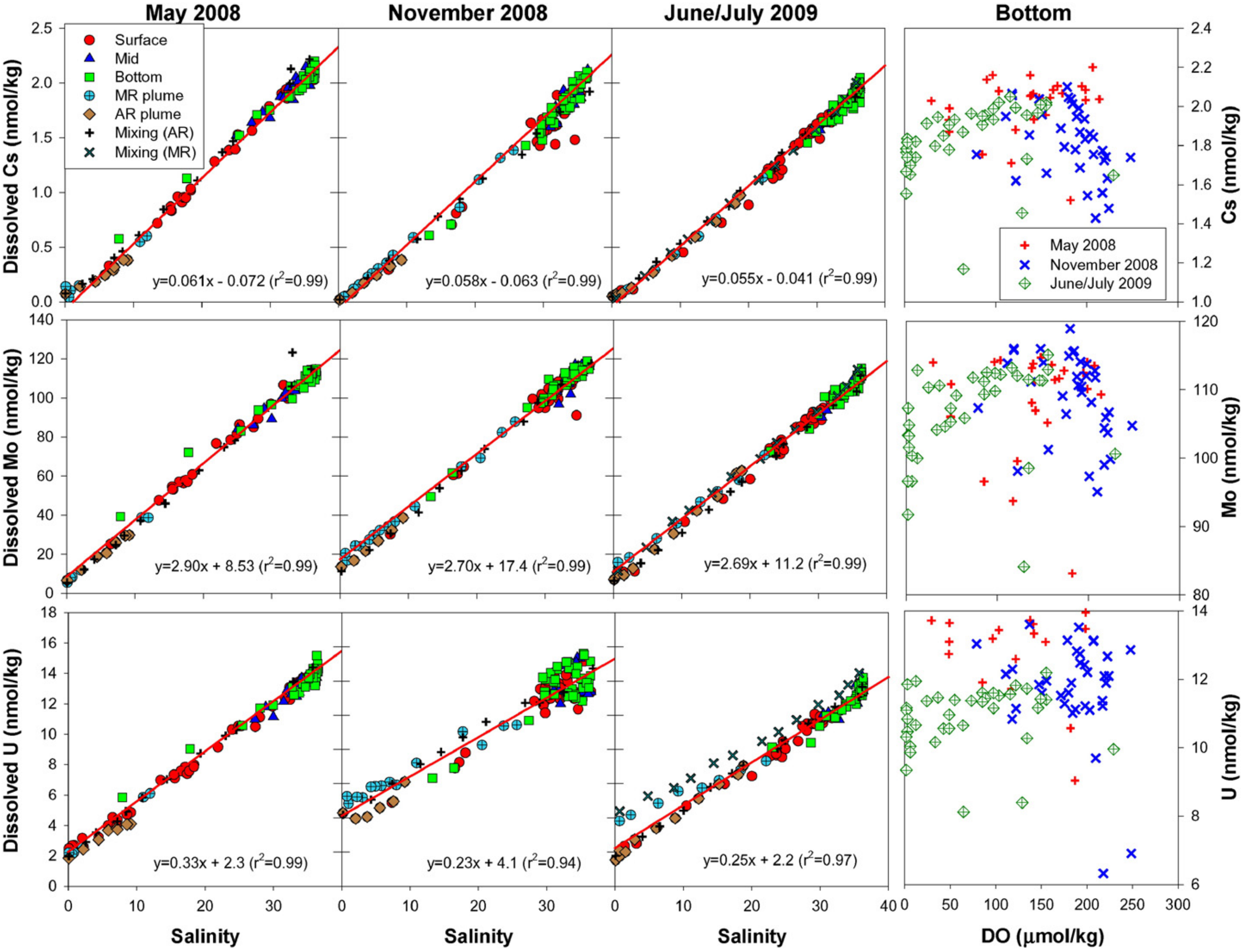

Fig. 4. Distributions of dissolved Cs, Mo and U. The left three columns show concentrations versus salinity for each survey; the rightmost column of figures shows bottom water DO versus concentration for all surveys. Regressions were generated for surface water data including the low-salinity river plumes (n = 44, 57 and 50 for May and November 2008, and June/July 2009), and p values for all regressions were <0.0001).

salinity regions (Fig. 3). These nutrient and total chlorophyll *a* distributions are similar to other studies in this system (Lohrenz et al., 1990, 2008; Shim et al., 2012) and suggest that the enhanced light availability with diminishing suspended load (Lohrenz et al., 1990), as well as increasing residence time with increasing salinity (Shiller, 1993b) in these regions are the main reasons for increasing biological uptake of nutrients.

3.2. Distribution of trace elements in the shelf waters

Most of the trace elements in river waters showed seasonal variations, having higher concentrations of both dissolved and colloidal Fe, Mn, Cr, and Co during high river discharge (May 2008), while the concentrations of Cu, Mo, Re, U and V were high at low river flow (November 2008) (Figs. 4–11). Previously, Shiller (1997, 2002) found distinctive differences of dissolved trace element concentrations in the major tributaries of the MR and suggested that the observed seasonal variations of some trace elements in the lower MR (at Baton Rouge, LA) resulted from seasonal variations of the tributary mixing ratios as well as redox chemistry within the river system. During our shelf studies, the mixing ratios of the major MR tributaries varied significantly (Fig. 2). With the exception of Mn, a simple estimation of the MR trace element concentration based on Shiller's (1997) tributary endmembers and their mixing ratios during our studies showed general agreement with the observed concentrations in the MR endmember (Table S2). During high and intermediate river flow, Mn was about 50-fold higher in the observed MR endmember than the estimated, possibly due to seasonal variation in the rate of microbial Mn oxidation (Shiller and Stephens, 2005).

As mentioned above, the AR is composed of part of the MR and all of the RR discharge and it flows through the ARB, which is the largest wetland in North America. During our sampling periods, the RR contributed 23% (Apr. 24–May 8, 2008), 22% (Oct. 22–Nov. 4, 2008) and 35% (Jun. 15–Jul.1, 2009) of the water in the AR (Fig. 2), suggesting that the additional inputs as well as interaction with floodplains in the ARB may have considerably affected the AR trace element concentrations (Joung and Shiller, in prep.). During June/July 2009, the RR contribution to the AR decreased from 42% to 29% two weeks prior to our AR plume sampling (Fig. 2). A plot of salinity versus the δ^{18}O of the water for the AR plume in June/July 2009 showed upward curvature below a salinity of 5, reflecting the more recent increased MR contribution to the AR as evidenced by the change to isotopically lighter values (Joung and Shiller, 2014). This change of the RR contribution may have influenced the Co, Fe and Mn distributions in the AR plume, which showed a low-salinity change at that time (June/July 2009; Figs. 7, 8).

3.2.1. Distributions of Cs, Mo, and U

The dissolved (<0.02 μm) phase was the dominant fraction for Mo, Cs, and U (Tables S2–S4), accounting for typically >90% of the total dissolved fraction (dissolved + colloidal) (Fig. S2). However, at low salinity, there was a considerable colloidal fraction of Cs, even though concentrations were still low (Figs. S2 and S3). As this was observed in all seasons and in both the MR and AR plumes, it is clearly a consistent feature. Because the dissolved Cs distribution shows no evidence of addition at low salinity (see below), Cs desorption from colloidal clay minerals or oxides seems an unlikely explanation for the removal of colloidal Cs despite recent evidence of estuarine Cs desorption (Bera et al., 2015). Thus, the likely explanation for the removal of colloidal Cs is salt-induced coagulation of Cs-adsorbing colloids and the correlation between colloidal Cs and Fe (Fig. S4) tends to support this idea.

Dissolved Cs and Mo in surface waters of the shelf showed generally conservative behavior in the field data regardless of season with some minor exceptions discussed below (Fig. 4). Likewise, in the mixing experiments these elements also showed conservative behavior. This generally conservative behavior was previously observed for Mo (Shim et al., 2012; Shiller and Boyle, 1991) and Cs (Shim et al., 2012) in this area. In the low salinity of the river plumes, Cs showed similar concentrations between the MR and AR plumes, while Mo showed slightly higher concentration in the MR than AR plume during November 2008 and June/July 2009, probably due to input of Mo-depleted water in the ARB. This depletion results from either Mo removal under reducing conditions in the ARB wetlands (see below) or from low-Mo RR water.

Despite the generally conservative Cs behavior, in May 2008 during high river flow, low salinity dissolved Cs, in both the field data and mixing experiment, showed a slight removal, possibly due to adsorption onto riverine particulate material during estuarine mixing (James and Palmer, 2000). Interestingly, low salinity colloidal Cs was highest at that time, too (Fig. S3). Thus, the removal of dissolved and colloidal Cs was probably due to adsorption as well as flocculation at low salinity estuarine mixing. This low salinity dissolved Cs removal was not clear during the other two sampling times, which may be due to lower fluvial suspended particulate matter during mid-low river discharge (http://waterdata.usgs.gov/nwis).

Bottom water dissolved Mo and Cs distributions generally agree well with the surface metal-salinity trend for all of our study periods. We do note, however, that high salinity bottom waters showed more scatter in dissolved Cs and Mo than can be accounted for by analytical uncertainty (Figs. 4 and S5). Furthermore, during June/July 2009, the lowest oxygen samples were generally slightly depleted in dissolved Cs and Mo (Fig. 4, left panels). Note that bottom DO was not correlated with salinity, so these Cs and Mo depletions with DO do not appear to be due simply to dilution with river water. For Mo, our observation in low DO bottom water is comparable to previous observations of diffusive Mo loss into anoxic sediments in oxygen-depleted waters (Emerson and Huested, 1991; Crusius et al., 1996; Morford et al., 2005, 2007) as well as removal via adsorption onto particles as a result of reduction of soluble Mo(VI) to reactive Mo(IV) in natural anoxic waters (Helz et al., 1996). In contrast, however, anthropogenic radio-Cs (Cs-137) has been observed to be released from anoxic sediments (Davison et al., 1993; Comans et al., 1989; Evans et al., 1983), and thus, an explanation of apparent bottom water Cs removal at low DO remains unclear. Nonetheless, the shelf bottom acted as a sink for Cs and Mo, at least in June/July 2009 during bottom water hypoxia.

For U, previous studies in this system reported both conservative (Swarzenski and McKee, 1998; Shim et al., 2012) and non-conservative (Swarzenski and McKee, 1998) distributions, with the non-conservative behavior attributed to adsorption onto settling particles and/or interaction of water with salt marshes at low salinity (Swarzenski and McKee, 1998; Sarin and Church, 1994; Church et al., 1996). Our observations point to largely conservative U behavior, with some important exceptions. Slight removal of dissolved U in our field data relative to the mixing experiment was observed at low salinity in the AR plume during November 2008. Because this U removal was observed in the AR plume but not the MR plume, the removal may thus have resulted from interactions with the extensive salt marshes surrounding the micro-tidal Atchafalaya Bay system as has been observed in the lower Delaware salt marshes (Church et al., 1996). During June/

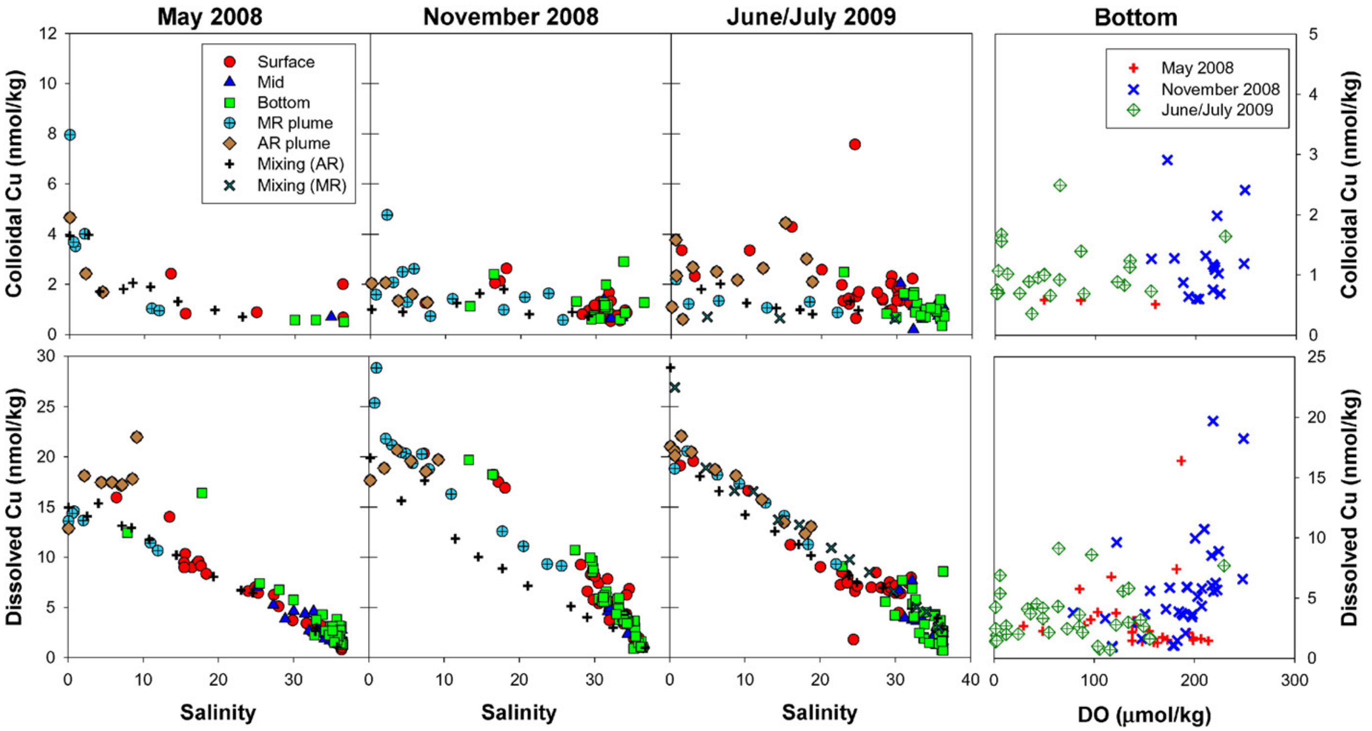

Fig. 5. Distribution of colloidal (0.02–0.45 μm; upper panel) and dissolved (<0.02 μm; lower panel) Cu are shown. The left three columns show concentrations versus salinity for each survey; the rightmost column of figures shows bottom water DO versus concentration for all surveys.

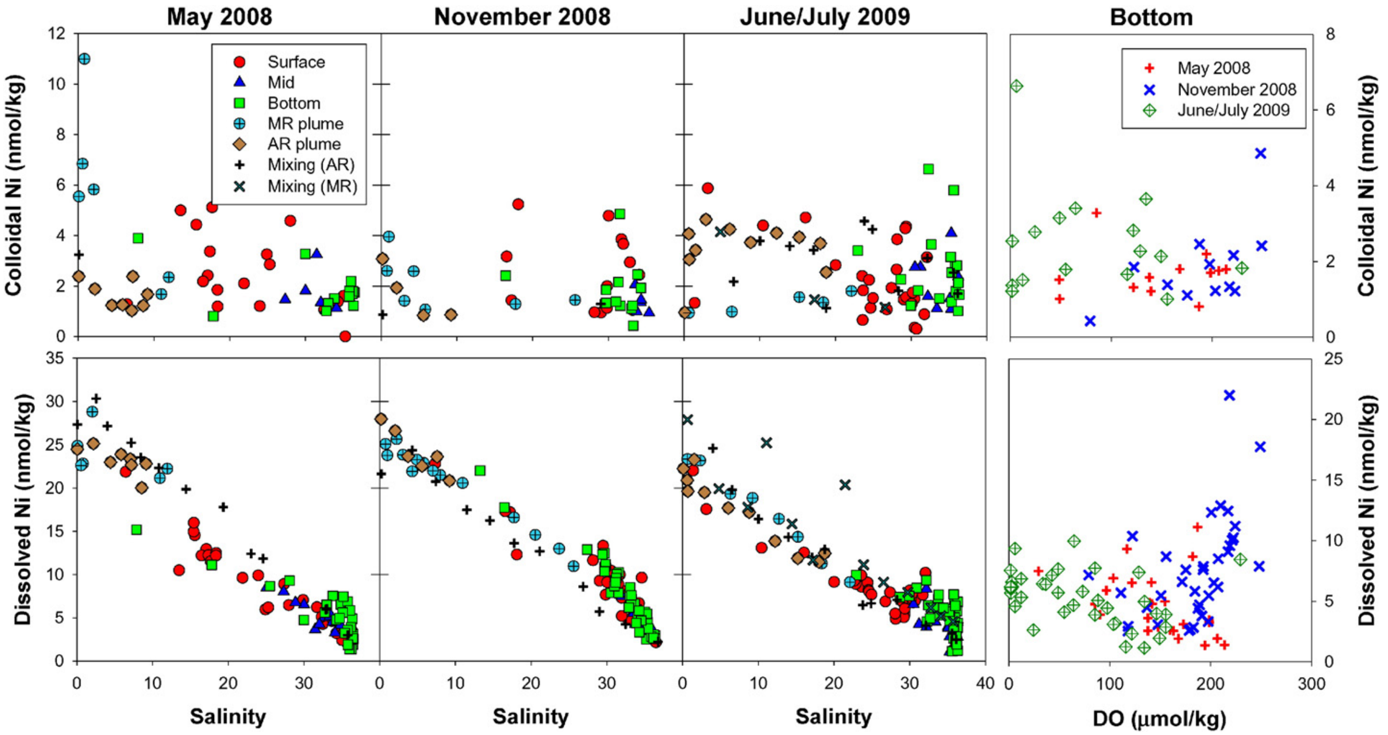

Fig. 6. Distribution of colloidal (0.02–0.45 μm; upper panel) and dissolved (<0.02 μm; lower panel) Ni are shown. The left three columns show concentrations versus salinity for each survey; the rightmost column of figures shows bottom water DO versus concentration for all surveys.

July 2009, variation of dissolved U in the low salinity MR and AR plumes may reflect the temporal change in the river endmember as evidenced by non-linearity of the δ^{18}O-salinity relationship of the water (Joung and Shiller, 2014). Slightly higher dissolved U concentration in the MR than AR plume during June/July 2009 may be related to input of U-depleted waters in the ARB, similar to Mo. In June/July 2009 during bottom water hypoxia, the surface dissolved U distribution showed slightly lower concentrations in the field data than in the mixing experiment, particularly in some high salinity waters as compared to the MR mixing experiment. This is probably due to episodic vertical mixing as additionally evidenced by other elements (Co, Mn, Cu, Ni; see below). During November 2008, a group of samples showed relatively low

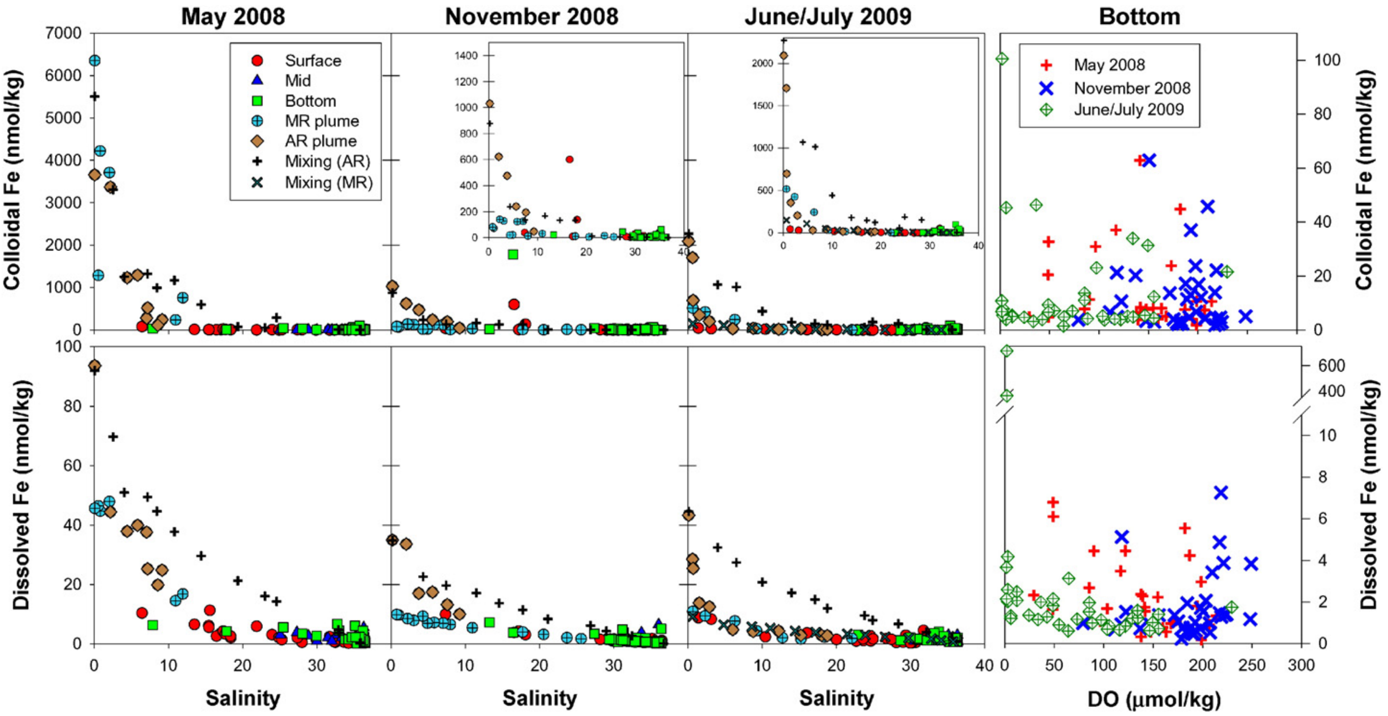

Fig. 7. Distribution of colloidal (0.02–0.45 μm; upper panel) and dissolved (<0.02 μm; lower panel) Fe are shown. The left three columns show concentrations versus salinity for each survey; the rightmost column of figures shows bottom water DO versus concentration for all surveys.

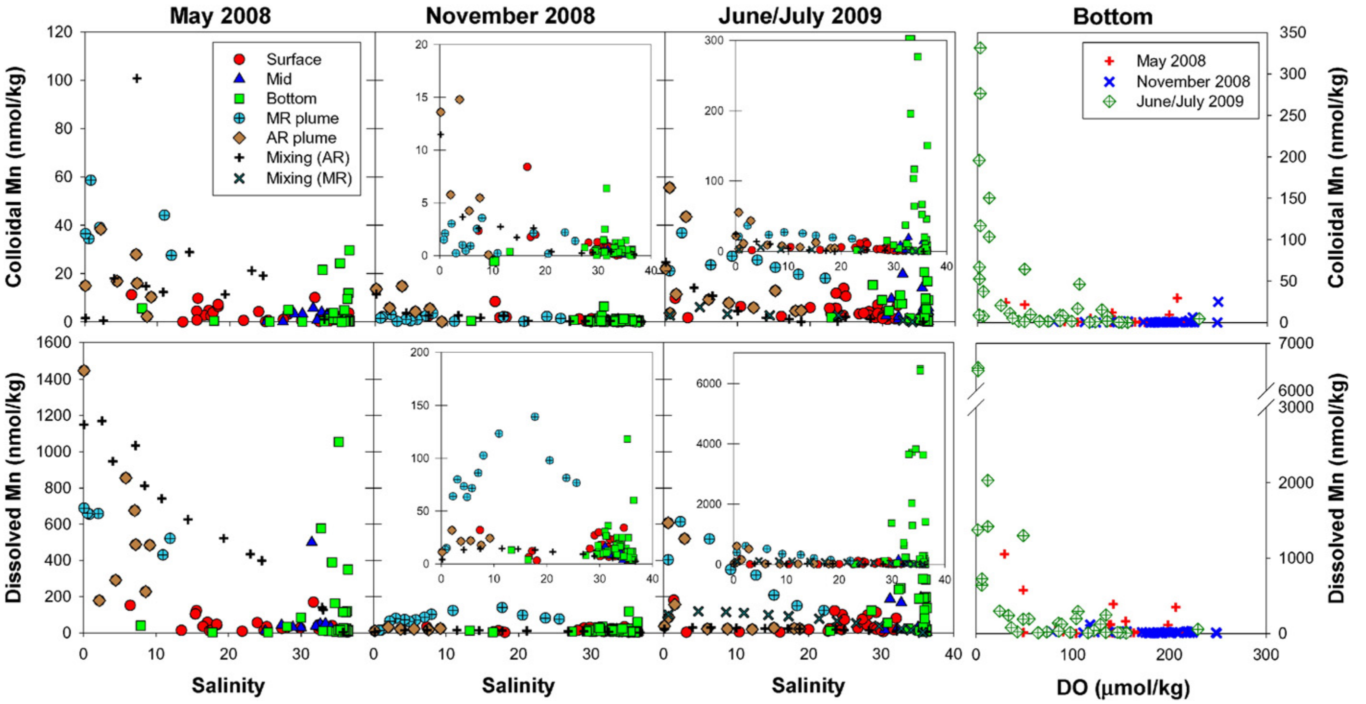

Fig. 8. Distribution of the colloidal (upper panel) and dissolved (bottom panel) Mn. The left three figures show concentrations versus salinity for each survey; the rightmost figure shows bottom water DO versus concentration for all surveys. Inset for November 2008 shows expanded scale while inset for June/July 2009 shows very high Mn bottom water samples; units are the same as the original figures.

concentrations of dissolved U in some of high salinity surface waters (e.g., C6, D3, F5, F7, F8, I4, I8, I9 and X3) compared to other regions similar in salinity (Figs. 4 and S5). Because relatively low U concentrations were found in the bottom and middle depths of these stations, vertical exchange may also have affected the surface U distribution at this time. That is, bottom water that became U-depleted during bottom water hypoxia (see below) may have mixed with surface water under weak water stratification conditions in November.

Bottom water U concentrations showed seasonal variations having concentrations in the order June/July 2009 < November 2008 < May 2008. In June/July, during bottom water hypoxia, the bottom water U at high salinity showed slight removal (Figs. 4 and S5), which may

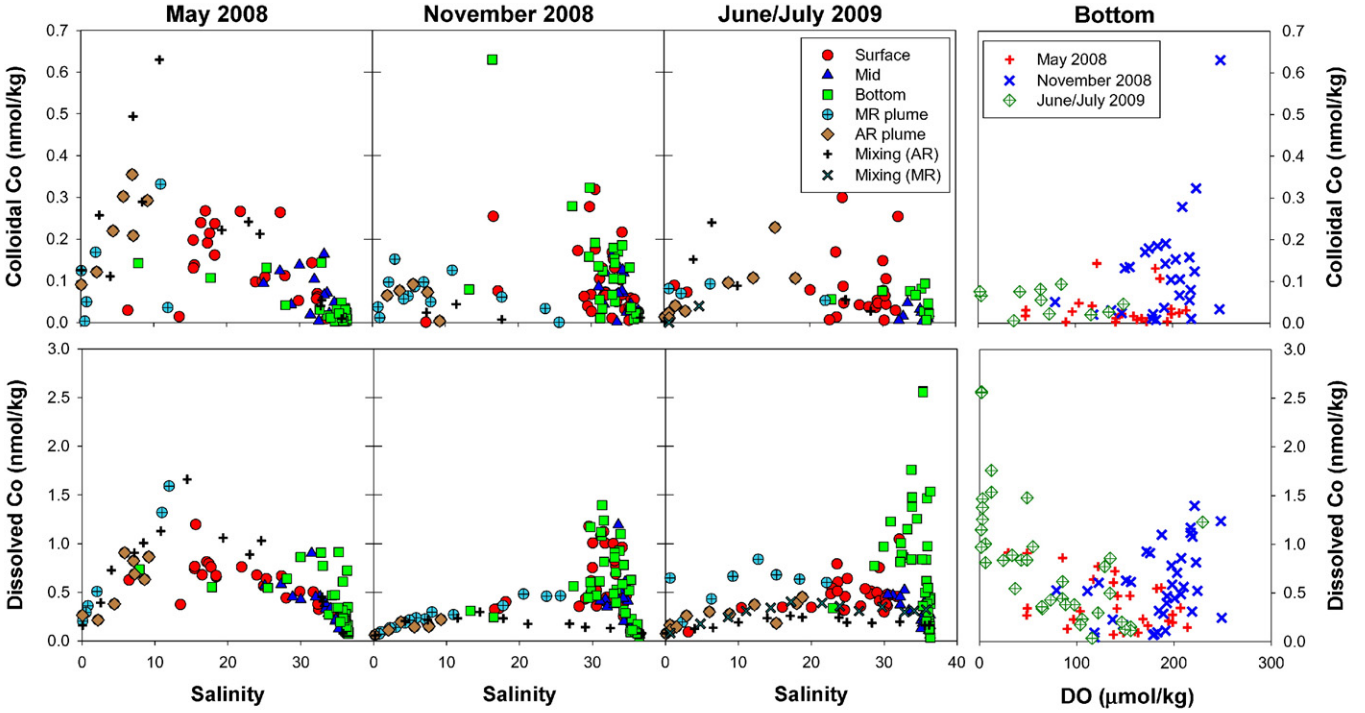

Fig. 9. Distribution of the colloidal (upper panel) dissolved (bottom panel) Co. The left three figures show concentrations versus salinity for each survey; the rightmost figure shows bottom water DO versus concentration for all surveys.

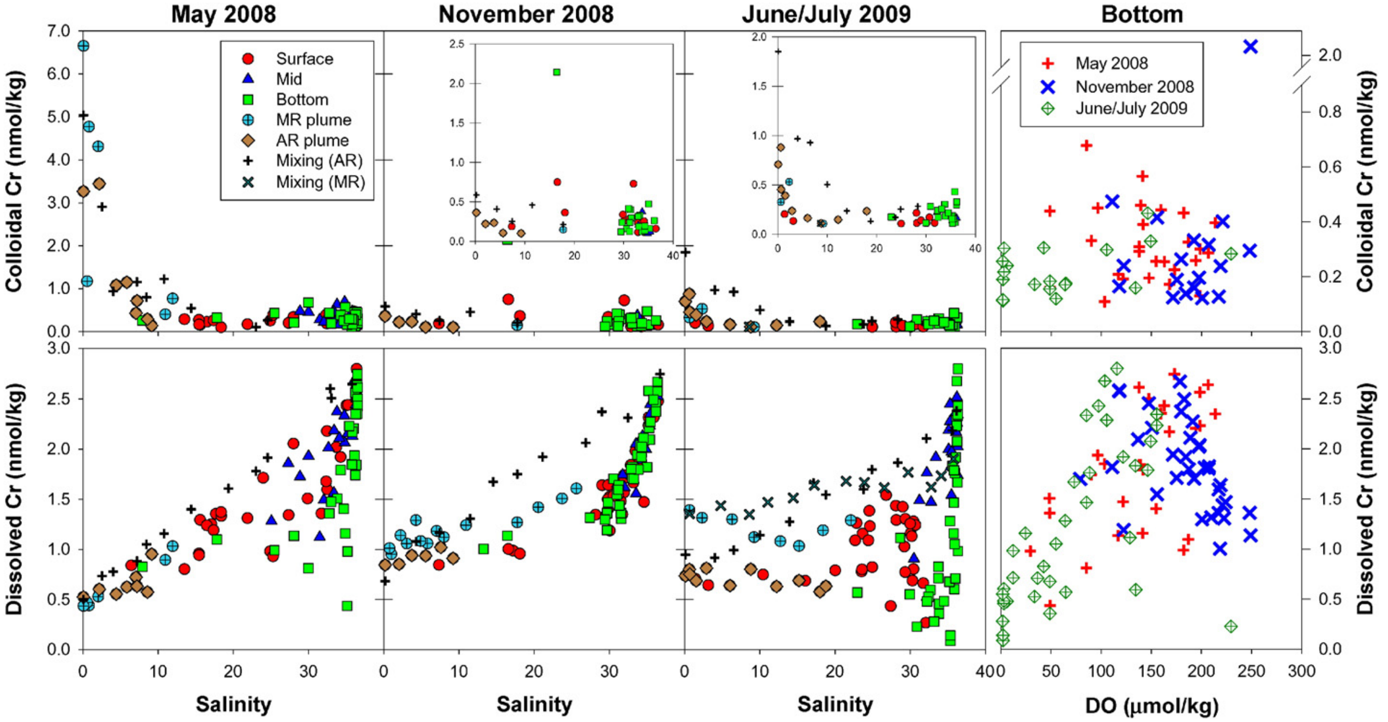

Fig. 10. Distribution of colloidal (0.02–0.45 μm; upper panel) and dissolved (<0.02 μm; lower panel) Cr along the salinity gradient. The left three columns show concentration versus salinity for each survey; the rightmost column of figures shows bottom water DO versus concentration for all surveys.

have led to lower U concentrations than during the other two times. Thus, the shelf sediments may act as a sink for U during bottom water hypoxia, which is compatible with previous reports of U removal in oxygen-depleted waters (Klinkhammer and Palmer, 1991; McManus et al., 2006; Morford et al., 2005, 2007). During November 2008, bottom water U concentrations were intermediate compared to the other two periods, probably due to vertical mixing. The scenario, again, is that bottom water which became U-depleted during hypoxia subsequently mixed with surface water, resulting in higher bottom water U in November compared to the June/July bottom water, as well as relatively lower U in some high salinity surface waters compared to the other surface waters of similar salinity during November 2008.

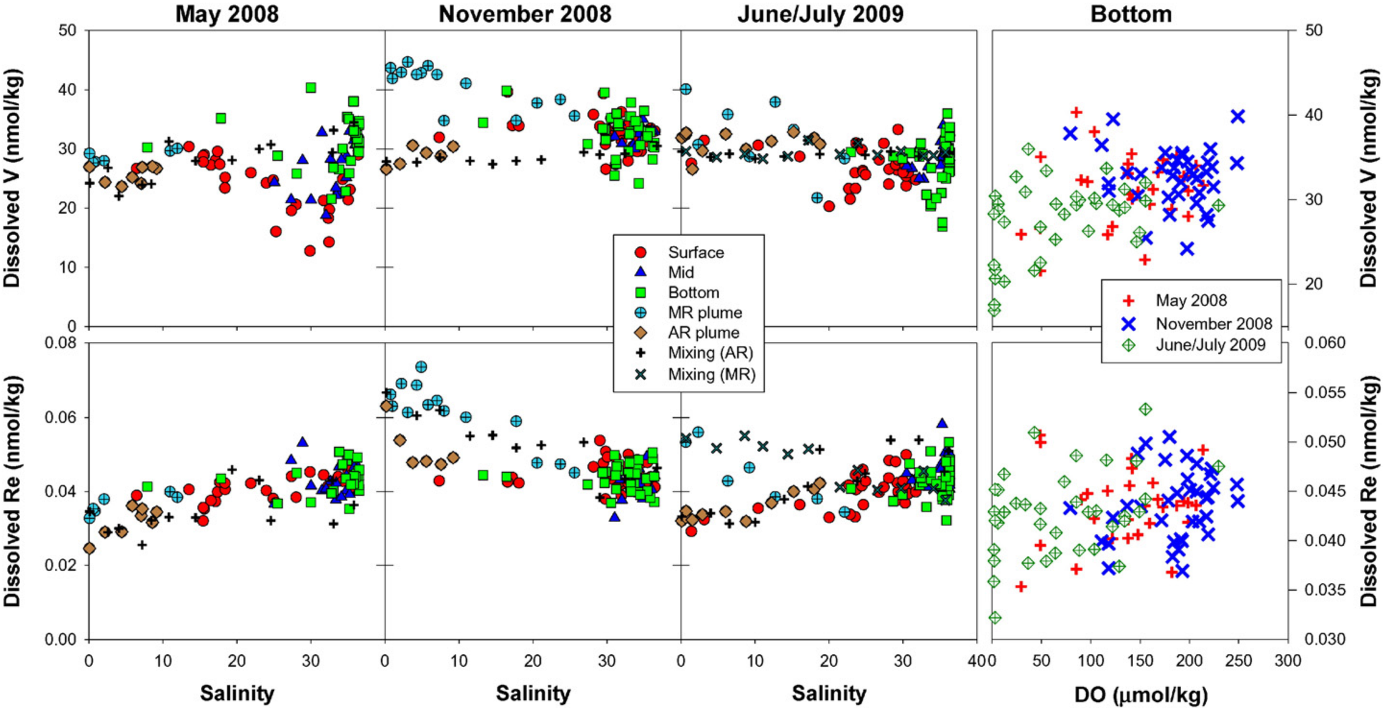

Fig. 11. Distribution of dissolved (<0.02 μm) V and Re are shown. The left three columns show concentrations versus salinity for each survey; the rightmost column of figures show bottom water DO versus concentration for all surveys.

3.2.2. Distributions of Cu and Ni

Dissolved (<0.02 μm) phases were the dominant size for Ni and Cu in both the field data and the mixing experiments, generally accounting >70% of the total dissolved (<0.45 μm) fractions (Fig. S2). This dissolved dominance is seemingly somewhat different from other systems where considerable colloidal fractions of Ni and Cu have been reported (e.g., Wen et al., 1999b). This is probably due to the difference in operationally-defined "dissolved" sizes, i.e., with <0.02 μm in our study compared with a much smaller <1 kD cut-off for others (Wen et al., 1999b). This led to the low colloidal concentrations in our study. Additionally, these low (near detection) colloidal concentrations in our study may have resulted in poor correlations with other elements (Fe, Mn), chlorophyll *a*, or the dissolved concentrations of these two elements. Thus, colloidal (0.02–0.45 μm) Ni and Cu distributions showed scatter in both the field data and the mixing experiments. In May 2008, during high river discharge, colloidal Cu and Ni concentrations were slightly higher at low salinity (Figs. 5 and 6), likely reflecting association with fluvial colloidal Fe oxides (see below). Also, during Nov. 2008, colloidal Cu and Ni concentrations in some surface and bottom water samples were elevated primarily at shallow stations (H0, GH0, D0, E1, B4), which were probably related to benthic input under typically weak water column stratification in November on the shelf.

The behaviors of dissolved Ni and Cu were complex (Figs. 5 and 6), but the concentrations and distributions of these elements were nonetheless similar to the previous studies in this system (Shim et al., 2012; Shiller, 1993a; Shiller and Boyle, 1991; Wen et al., 2011). In the associated mixing experiments, dissolved Cu and Ni showed largely conservative behavior, implying that any non-conservative behavior of these elements in the field data is not likely the result of flocculation or adsorption reactions.

In bottom waters, we observed slightly elevated concentrations of dissolved Ni and Cu relative to surface and middle depths during May 2008 and June/July 2009 (Figs. 5, 6 and S6). The bottom water enrichment of Cu and Ni is not surprising given that these elements are known to be mostly organically complexed and tend to be preferentially remineralized in reducing environments (Petersen et al., 1995; Waeles et al., 2005; Baeyens et al., 1998; Martino et al., 2004). Likewise, the bottom water dissolved Ni and Cu during May and June/July showed negative correlations with DO, suggesting either dissolution and/or diffusion from reducing sediments. During November 2008, bottom water dissolved Cu and Ni showed non-conservative behavior, probably due to the mixing of Cu and Ni enriched bottom water with surface waters.

At low salinity, dissolved Cu in the AR plume showed upward curvature indicative of Cu addition, while Cu in the MR plume was generally conservative. This difference, therefore, most likely resulted from sedimentary inputs in the shallow Atchafalaya Bay. Generally, dissolved Ni in both river plumes showed conservative behavior. Surface water concentrations of dissolved Ni and Cu in the field data were commonly higher than in the mixing experiments (Figs. 5 and 6). In part, we suggest that this phenomenon reflects the different freshwater endmembers for the mixing experiment and field data as evidenced by changes in the δ^{18}O values at salinity ~5 in June/July 2009 (Joung and Shiller, 2014). During November 2009, dissolved Cu and Ni in high salinity surface and bottom waters were enriched relative to the mixing experiment. Because the mixing experiment was conservative, this enrichment is not likely derived from desorption in surface waters. One might argue that the elevated surface as well as bottom water dissolved Cu and Ni may be derived from different freshwater sources in November when the freshwater residence time on the shelf is a few months (Dinnel and Wiseman, 1986). However, extrapolating the high salinity trend of dissolved Cu and Ni to zero salinity yielded to river endmembers of over 40 and 50 nmol/kg, respectively, which is greater than has been previously observed in the lower MR (Shiller, 1997). Thus, the elevation of Cu and Ni was derived from processes on the shelf rather than from changes in the river concentration. We conclude that the enriched surface water concentrations of Cu and Ni likely reflect benthic input as evidenced also by elevated Mn, Co, and Fe (see below).

During June/July 2009, the concentrations of dissolved Ni and Cu in surface waters from some shallow stations (e.g., E2, F3, F5, H0, H3, I1, and I2) were elevated relative to the conservative mixing trend. Surface waters Mn, Co, and Fe at these stations were also high, indicative of episodic vertical exchanges in relation to the seasonal changes in circulation on the shelf in which summer winds become more upwelling-favorable (Cochrane and Kelly, 1986). Thus, the episodic addition of the elements found in our study reflects somewhat different distributions than those found in previous studies, which reported fairly conservative mixing of Cu and low salinity removal of Ni (Shim et al., 2012; Shiller, 1993a; Shiller and Boyle, 1991). This difference probably results from our greater spatial/temporal coverage of the study area as compared with previous work. Our observation of elevated surface water dissolved Cu and Ni concentration even during strong water stratification (average surface-bottom salinity difference of 10) implies that episodic upward mixing may be an important process altering the shelf surface water Cu and Ni distributions.

3.2.3. Distribution of Fe

Mostly, Fe was in the colloidal phase (0.02–0.45 μm), typically accounting for over 80% of the total dissolved phase (<0.45 μm) in all samples (Figs. 7 and S2). However, there were significant dissolved Fe fractions at mid-high salinity in surface waters as well as in a few deep water samples. We note again that our low end cutoff for the colloidal fraction is larger than the 1 or 10 kDa cutoff commonly used by other workers (e.g., Guo et al., 2000; Wen et al., 1999b), and that very little organic matter is retained by the 0.02 μm filters (Shiller, 2003). Thus, most of the organically-complexed and bioavailable Fe was likely in our dissolved (<0.02 μm) fraction, and the colloidal fraction in our study was mainly composed of suspended nanoparticles including Fe hydroxides (Shim et al., 2012; Stolpe et al., 2010). Throughout our sampling campaigns, we did not observe correlations between DOC and either phase of Fe, probably because organic complexes represent only a very small fraction of the total DOC. Because we did not observe an increase of dissolved Fe concentrations at the mid-high salinity where low colloidal percentage were observed, it is unlikely that the low colloidal fractions were derived from an increase in Fe-organic matter complexes at that salinity. Instead, faster removal of colloidal Fe compared with dissolved Fe (Fig. S7) may simply explain the lower colloidal Fe fractions at mid-high salinity.

In bottom waters, we observed elevated dissolved and colloidal Fe relative to surface and middle depths (Figs. 7 and S8). The dissolved (<0.02 μm) Fe showed an inverse correlation ($r^2 = 0.39$, $n = 33$, $p = 0.0003$, excluding D2, F0 and H0) with DO during June/July 2009 (Fig. S9). For May 2008, excluding some low salinity samples (A1, F0 and F2), we also observed a negative correlation ($r^2 = 0.33$, $n = 26$, $p = 0.0021$) between dissolved Fe and DO. This suggests particulate or sedimentary Fe dissolution under reducing conditions for these two surveys. Generally, the bottom water increase in Fe concentration in both phases was not as great as the Mn concentration increases at low DO (see Fig. 8 and next section), possibly due to the more rapid oxidation of Fe than Mn, the deeper (i.e., more reducing) sedimentary conditions needed for Fe reduction, and the possible incorporation of reduced Fe into sulfides. A bottom water Fe-DO relationship was not observed in the November study, probably due to generally higher bottom DO concentrations at this time of vertically well-mixed conditions. During these conditions the high DO at the bottom may limit reductive Fe dissolution and diffusion from the sediments. Thus, the increase of dissolved Fe in November was probably due to resuspension under weak-stratification conditions (Almroth et al., 2009).

The surface water distributions of dissolved and colloidal Fe in all seasons were non-conservative in both the field data and mixing experiments (Fig. 7), showing rapid removal at low salinity with low Fe concentrations (<10 nmol/kg) at high salinities (S > 20). This Fe removal behavior is typical in estuarine systems (e.g., Powell et al., 1996; Shim et al., 2012) and mainly reflects colloidal flocculation/coagulation during estuarine mixing (Sholkovitz, 1976; Boyle et al., 1977). In the two low salinity river plumes, Fe (both phases) was higher in the AR than MR plume with the exception of slightly higher colloidal Fe in the MR than AR plume during May 2008. Again, this is probably due to Fe inputs from the RR and wetland waters in the ARB resulting in higher AR Fe concentrations. The colloidal Fe in the MR in May 2008 was much greater than during the other two study periods as well as previous studies (Shim et al., 2012; Shiller and Boyle, 1991). In June/July 2009, the Fe distributions in the field and the mixing experiments were not closely matched, probably due to the change of river endmember evidenced by the $\delta^{18}O$ distribution at this time (Joung and Shiller, 2014).

For dissolved Fe (<0.02 μm), the field data showed a consistently lower concentration than the mixing experiments when plotted versus salinity (Fig. 7). One might argue that the higher dissolved Fe in the mixing experiments resulted from not enough time for Fe-flocculation/coagulation and thereby less Fe removal in our mixing experiment compared to the field. However, in their laboratory experiments of sea- and river water mixing, Boyle et al. (1977) reported that the kinetics of the Fe precipitation were extremely rapid with a time scale of a few minutes. Thus, our overnight mixing experiments should have allowed for sufficient time for Fe removal in the mixing experiment samples. Therefore, the deviation between the field data and mixing experiments likely resulted from other processes in the field rather than the artifacts of our mixing experiments.

We suggest that biological removal of dissolved (<0.02 μm) Fe (Ho et al., 2003; Powell et al., 1996; Shim et al., 2012) is the likely cause of the lower concentrations in the field data relative to the mixing experiments. The nitrate vs. salinity distribution showed an almost identical pattern of removal as the dissolved Fe distribution, similar to the observation of Shim et al. (2012). During May 2008, the salinity where nitrate and dissolved Fe approached zero, and the peak of the chlorophyll *a* distribution coincided (Fig. 3). Based on a cellular Fe:N ratio of 0.47 nmol/μmol (Ho et al., 2003), if we assume that the decrease of nutrients is due to biological uptake, then the observed decrease of nitrate from 80 μmol/kg to 0.1 μmol/kg during May 2008 yields about 35 nmol/kg of potential Fe removal. Similarly, the potential Fe removal was found to be about ~33 and ~42 nmol/kg during November 2008 and June/July 2009, respectively. These potential Fe removals were of similar magnitude to the fluvial dissolved Fe concentrations, suggesting that biological activity may indeed greatly influence the surface Fe distribution of the shelf. Obviously, these estimates are crude and do not account for differences in the regeneration of nutrients and Fe or other sources of these materials.

The surface water Fe distribution also appears to have been affected by input from below at certain stations during November and June/July. At these times, surface Fe (both colloidal and dissolved) at shallow, inshore stations (e.g., H0, GH0, D0, E1) was higher than at other offshore surface waters with similar salinity (Fig. S8). During low river flow in November, the water stratification was much weaker than during the other seasons due to the thinner buoyant freshwater layer at the surface and mixing due to passage of fall atmospheric fronts (Dagg et al., 2007). The average salinity difference between the surface and the bottom was smaller in November 2008 (~2) than in May 2008 (~7) and June/July 2009 (~9), suggesting conditions more conducive to vertical mixing. Other dissolved trace elements (e.g., Mn, Co, Ni, Cu) were elevated as well, suggesting that vertical mixing altered the surface Fe distribution in November 2009.

During June/July, despite significant stratification, several stations (mostly inshore shallow, but also one offshore: A1, H0, I1, I8) showed elevated dissolved and colloidal Fe relative to other offshore surface samples with similar salinities. This was probably due to episodic vertical exchange in these shallow waters and was also evidenced by increased concentrations of dissolved Mn, Cu, and Ni at the surface. Also, the salinity difference between surface and bottom at stations H0 and I1 was very weak (<2), and the surface DO at A1 was 145 μmol/kg (about 50 μmol/kg lower than other surface waters), indicative of recent vertical mixing. For station I8, which had a 37 m water depth, it is unlikely that the surface increase of Fe originated from direct vertical mixing at this location due to the high surface-bottom water salinity and temperature differences (7 and 8 °C, respectively) and the much lower total (colloidal + dissolved) dissolved Fe at the middle depth (12.5 m) than at the surface and bottom. Surface water Fe (both phases) concentrations at nearby stations were lower than the surface Fe concentration at I8, and thus, we suspect that the increased Fe at I8 may have resulted from lateral inflow of water from another location on the shelf which had already experienced vertical mixing input. Regardless of the exact source, these stations with high surface Fe (both phases) suggest that there can still be localized episodic vertical mixing even when the shelf is overall strongly stratified. Recently, based on high frequency meteorological observations for a year as well as modeling studies, Wang and Justić (2009; see their Fig. 3) showed frequent wind and current direction changes on the LA Shelf, similar to the observations of Cochrane and Kelly (1986), suggesting that wind direction change is a consistent phenomenon during summer. Additionally, Hetland and DiMarco (2008) reported that changing of wind stress during summer could occur with timescales of a few days to week, which alters the position of river plumes and subsequently affects shelf water column stratification. Thus, these studies suggest that episodic vertical mixing on the shelf may occur often during summer despite water column stratification being generally strong, and this is likely what is observed in our data set. Typically, shelf surface nutrient concentrations are very low during summer, and thus episodic vertical mixing as a means of nutrient supply during summer may play an important role on surface water biological activity as well as bottom water hypoxia in this region and may well need to be accounted for in shelf bottom water hypoxia modeling studies.

3.2.4. Distribution of Mn

The distribution of Mn is shown in Fig. 8. The dissolved (<0.02 μm) phase Mn was dominant except for a few samples (9 out of 314 samples) having colloidal fractions over 30% (Fig. 8 and S2). This size distribution is similar to other estuarine systems (e.g., San Francisco Bay and Texas coast, Sanudo-Wilhelmy et al., 1996; Benoit et al., 1994), though those studies have different operationally-defined colloid and dissolved sizes (e.g., 10 kDa–0.2 μm for colloid and <10 kDa for dissolved; Sanudo-Wilhelmy et al., 1996 or 10 kDa–0.5 μm and <10 kDa for colloid and dissolved; Benoit et al., 1994). Although the colloidal fractions were low relative to the dissolved fraction throughout the salinity range, surface waters generally showed higher colloidal Mn concentrations at low salinity, suggesting a fluvial source. We also note that the dissolved and colloidal Mn concentrations were higher in May 2008 and June/July 2009 than in November 2008. This is somewhat surprising given previous work on the Mississippi River showing higher fluvial dissolved Mn in winter (Shiller, 1997), which has been attributed to the temperature dependence of fluvial microbial Mn oxidation rate (Shiller and Stephens, 2005). In June/July 2009, the colloidal Mn concentrations were high in some bottom waters where there were high dissolved Mn and low DO. Positive correlation between colloidal and dissolved Mn in bottom waters was observed during June/July 2009 and, to a lesser extent, May 2008, probably due to benthic reductive remobilization of dissolved Mn from sediments with slow reprecipitation in the bottom waters (Fig. S10).

Higher bottom water dissolved (<0.02 μm) Mn relative to surface and middle depths was observed in all of our surveys. In particular, bottom water Mn was the highest at low DO. This is consistent with other estuarine observations and likely results from reductive dissolution of Mn oxides in the sediments (Almroth et al., 2009; Colbert and McManus, 2005). Interestingly, for the most Mn-enriched bottom waters, there was a positive correlation between dissolved and colloidal Mn (Fig. S10), suggesting either a source of colloidal Mn from the sediments or increased precipitation of colloidal Mn with higher dissolved Mn. During November 2008, concentrations of Mn in the bottom waters were not elevated as much as the other two periods, reflecting several processes: lower flux of Mn from the sediments due to higher bottom water DO, precipitation of dissolved Mn due to the higher bottom DO, and greater mixing of bottom water with lower Mn surface waters due to diminished stratification (Shim et al., 2012). Overall, the seasonal variation of bottom water Mn appears to be controlled by oxygenation of the bottom waters, which in turn is controlled by respiration and stratification.

Also, in the bottom waters during the June/July hypoxia season survey, we observed that the highest dissolved Mn concentrations were correlated with high concentrations of dissolved phosphate and silica (Fig. S11). Inorganic nitrogen components as well as total dissolved inorganic nitrogen did not correlate with bottom water Mn, probably because of removal of N via denitrification. Because regeneration of dissolved Si is largely inorganically driven and unlikely to be substantially affected by direct or indirect redox processes, we interpret these correlations of Mn, P, and Si to be driven by trapping and accumulation of these elements in strongly stratified bottom waters (Redfield et al., 1963; Shiller, 1996).

During all sampling periods, surface dissolved Mn showed nonconservative behavior, with rapid removal at mid-salinity (S–15) during May 2008 and upward curvature at mid-salinity in November 2008 and low salinity in June/July 2009. The field Mn data showed lower concentrations than the associated mixing experiment during May 2008, whereas the Mn concentrations were higher in the field than the mixing experiments during November 2008 and June/July 2009. During November 2008, dissolved Mn, especially in the low salinity MR plume, showed maximum concentrations at low and mid-salinity, and this has been commonly observed in other estuarine systems (e.g., Roitz et al., 2002; Yang and Sanudo-Wilhelmy, 1998) as well as in this system during a previous fall survey (Shim et al., 2012). Although Mn can be added by desorption from fluvial suspended sediments in estuarine mixing of fresh- and seawater (Li et al., 1984), Hatje et al. (2003) reported that the desorption peak is generally placed at very low salinity due to a rapid desorption time (~0.5 h). Thus, the peak of Mn at around salinity 15 during November 2008 seems too high (i.e., too slow of a reaction) for Mn desorption. Therefore, the increase of Mn at mid-salinity likely originated from benthic inputs under vertically well-mixed conditions during November, similar to the Ba distribution at the same time (Joung and Shiller, 2014). Whatever the cause, overall dissolved and colloidal Mn at low to mid-salinity was lower in November than during the other periods.

During June/July 2009, there was much higher Mn in the field data at low to intermediate salinity than in the mixing experiments (Fig. 8). Although we noted above a change in the AR endmember at this time, low salinity samples in the MR plume were much higher than previously reported for the MR (Shiller, 1997) suggesting that the elevation in Mn at low-intermediate salinity is indicative of another source. Clearly the mixing experiment results argue against Mn desorption from the fluvial suspended load in June/July. We were not able to obtain near-bottom samples in the low salinity regions. However, given the very high Mn enrichment of low DO bottom waters (Fig. 8), it would seem that mixing with those waters is the most likely source of the low-salinity surface water Mn enrichment. In June/July despite increased water stratification, some high salinity surface samples also showed increased dissolved Mn relative to the mixing experiment and other high salinity surface waters (Fig. S12). At these stations, elevated Ba (Joung and Shiller, 2014), Co, Cu, Fe, and Ni were also observed in the surface waters. Thus, the increase of Mn in some high salinity surface waters was probably due to episodic vertical exchange when summer winds become more upwelling favorable (Cochrane and Kelly, 1986) even though average shelf vertical stratification was high.

During high river flow (May 2008), Mn in the two rivers was much higher than during the other two study periods as well as compared with Shiller's (1997) lower MR temporal study. Shiller's (1997) river samples were collected in Baton Rouge, well upstream of any possible estuarine influence. In contrast, due to the high discharge in May 2008, relatively unmixed river water was pushed out of the distributary channels and hence our fluvial endmember samples at that time were collected in more estuarine than fluvial environments. Mn at low salinity in the AR plume showed sharply fluctuating concentrations with salinity. A likely explanation for these fluctuations is that different parcels of water we sampled were on slightly different river-seawater mixing trajectories, as evidenced by slightly lower salinity at AR8 than at AR5 even though AR8 was further from the AR mouth than AR5. This is likely the simple result of significant quantities of AR water entering Atchafalaya Bay both through the mouth of the AR as well as through the Wax Lake Delta ~15 km NW of the AR mouth, Additionally, inflow of water from or interaction of AR water with surrounding bays (e.g., Fourleague Bay, West Coat Blanche Bay, Vermilion Bay) (Walker and Hammack, 2000) with different Mn inputs (including sedimentary input) may have affected the AR plume.

We also note that during May 2008, dissolved Mn concentrations declined more rapidly with salinity than the conservative results of the mixing experiment. Sinks for dissolved Mn include precipitation by formation of Mn-oxides or adsorption onto particles (Fe-hydroxides; Millward and Moore, 1982, and organic matter; Roitz et al., 2002; Moffett and Ho, 1996) and biological activity including uptake (Bruland et al., 1991; Sunda and Huntsman, 1997) and microbial oxidation (Shiller and Stephens, 2005). The distribution of Mn was somewhat different from Fe distributions in our study, indicative of other removal processes rather than adsorption onto Fe-hydroxides.

Biological assimilation of Mn by phytoplankton could have been considerable at mid-salinity where high chlorophyll *a* (~40 μg/kg) was observed. Based on a ratio of chlorophyll *a* to carbon of 125 (g C/g chl *a*) in this area (the highest value from Lohrenz et al., 1992) and a Redfield-type elemental ratio of Mn:C ($3.8–25.9 \times 10^{-6}$:1) in phytoplankton (Ho et al., 2003), phytoplankton uptake could have accounted for removal of up to 40% of the observed Mn in the water during May 2008. The uptake estimates during the other two periods, however, were generally less than 10%. Due to a much longer residence time during low river flow, one might expect a greater total Mn removal via biological uptake in November than in May. But, the biological production (as reflected by chlorophyll *a*) in November was much lower than in May, and we observed an increase at low-mid salinity in November. Thus, although we cannot entirely rule out biological uptake of Mn during November, it is less likely that the biological removal was a predominant factor for the November Mn distribution.

Microbial Mn oxidation has also been found to be an important process for Mn removal in river and estuarine waters with the oxidation rates 10–84 nM/day (Shiller and Stephens, 2005; Sunda and Huntsman, 1987). Although different bacterial species may have different Mn oxidation rates (Tebo et al., 2005), bacterial production (depth integrated) in the MR/AR plumes was found to be much higher than in other river plumes (e.g., Hudson, Chesapeake, & Fly River plumes; Amon and Benner, 1998). Thus, taking the maximum oxidation rate and the freshwater residence time of 10 days during high river flow, Mn removal via microbial oxidation alone could account for more than 60% of the ~1400 nmol/kg change in Mn concentration in May 2008. Considering the residence time of Louisiana Shelf water of a few days to months (Dinnel and Wiseman, 1986; Moore and Krest, 2004), microbial Mn oxidation thus may also play an important role in the surface water Mn removal. Because of a much longer residence time during low river flow, one might expect a greater total Mn removal via microbial oxidation as well as biological uptake in November than in May. However, as discussed above, we observed an addition of dissolved Mn in the surface water in November due to intensive vertical mixing. Thus, although we cannot rule out any removal of Mn via microbial oxidation, the removal may be much less significant than vertical mixing during November.

3.2.5. Distribution of Co

The dissolved (<0.02 μm) phase of Co was predominant, though ~10% of the samples had colloidal (0.02–0.45 μm) Co fractions that accounted for over ~30% of the total dissolved Co (colloid + dissolved) (Figs. 9 and S2). It is difficult to compare this with other estuarine colloidal Co distributions due to differences in the operationally defined dissolved sizes, such as <1 kDa (Wen et al., 1999b) or <0.2 μm (Takata et al., 2010). In general, though scattered (due to low, near-detection concentrations), the surface water colloidal Co distributions were similar to the dissolved phase distributions, having upward curvature at mid-salinity as well as additional scatter at high salinity (Fig. 9).

Enrichment of bottom water dissolved (<0.02 μm) Co relative to surface and middle depths was observed during all our surveys. During hypoxic conditions in June/July 2009, bottom water dissolved Co was negatively correlated with DO, suggesting that the Co increase was probably due to diffusion from anoxic sediments and/or dissolution from particles (Takata et al., 2010). At this time, bottom water dissolved Co was also positively correlated with dissolved Mn (Fig. S13), indicating a similar behavior of Co and Mn and suggesting that the release of Co occurs concomitantly with the reductive dissolution of Mn oxides as has been observed in other systems (Santos-Echeandia et al., 2009; Shaw et al., 1990). During November 2008, elevated dissolved Co was observed in some bottom waters (e.g., A1, C1, E1, F1, F2), and the increase also may have originated from benthic mobilization of Co (Takata et al., 2010; Chiffoleau et al., 1994).

During all our sampling periods, dissolved Co showed non-conservative behavior, with maximum surface water concentrations generally at intermediate salinity. This behavior has been observed in other estuarine systems (Tovar-Sánchez et al., 2004; Takata et al., 2010) as well as previously in this system (Shim et al., 2012) and appears to be partly due to Co desorption from riverine SPM (Takata et al., 2010; Hatje et al., 2003; Li et al., 1984). In the low salinity river plumes, the field dissolved Co data was generally similar to the mixing experiments, consistent with the idea of Co desorption. The low salinity AR plume dissolved Co showed sharp changes during May 2008, which probably reflects different low salinity water sources and mixing trajectories similar to the dissolved Mn distribution at this time, in that both Mn and Co went up and down at the same time (Fig. S14).

At intermediate to high salinity, the field dissolved Co concentrations were higher than the associated mixing experiments in at least two of our studies (November and June/July) (Fig. 9). As discussed in previous sections (e.g., Cu, Ni, Mn, Fe), upward mixing of Co-enriched bottom waters likely affected the surface water dissolved Co distributions. During November 2008, in addition to broad upward curvature, surface water Co concentrations were the highest at shallow, high salinity stations (i.e., <20 m; stations A1, C1, C4, C6, C7, D0, E1, F2, and F3). It seems likely that Co-enriched bottom water, left over from the summer hypoxia period, was vertically mixed into surface waters during November when stratification was reduced and mixing increased due to passage of cold fronts at that time of year. This is similar to the situation discussed above for Cu and U. It also makes sense that the shallow stations would be most susceptible to this mixing effect. We thus conclude that the benthic flux of Co is one of the dominant processes affecting the surface water dissolved Co distribution, especially during times of diminished vertical stratification. During high river flow (May 2008), concentrations of dissolved Co were slightly lower in the field data than in the mixing experiment, which contrasts with the other two periods. Biological assimilation of Co, based on a chlorophyll *a* to carbon ratio of 125 (g C/g Chl a) in this area and a Redfield-type elemental ratio of Co:C (1.3×10^{-7}:1) in phytoplankton (Bruland et al., 1991; Ho et al., 2003), suggests that phytoplankton assimilation of Co could account for uptake of up to 50% of the observed dissolved Co during May 2008, but generally less than 10% of the Co during the other sampling periods. Thus, phytoplankton activity also likely plays an important role on the surface Co distribution, at least during bloom conditions in May.

3.2.6. Distribution of Cr

For Cr, the colloidal (0.02–0.45 μm) phase was dominant at low salinity, and the dissolved phase (<0.02 μm) was dominant at intermediate to high salinity (Figs. 10, S2 and S15). The distribution of colloidal Cr showed non-conservative behavior in both the field data and the associated mixing experiments, showing a downward curvature during all our surveys. Dissolved (<0.02 μm) Cr showed a different distributions in the field data from the mixing experiments. In the mixing experiments, dissolved Cr showed fairly conservative behavior during all our studies. In the field data, the dissolved Cr distributions showed downward curvature in all our studies.

Bottom waters commonly showed dissolved Cr depletion relative to surface and middle depths. Additionally, bottom water dissolved Cr was depleted relative to the conservative trend in the mixing experiments. When plotted versus DO (Fig. 10, bottom right), bottom waters show clear depletion of dissolved Cr with diminished oxygen. This is not surprising given that soluble Cr(VI) can be reduced to particle-reactive Cr(III) in reducing environments (Richard and Bourg, 1991 and references therein). Note that one could also hypothesize that bottom water dissolved Cr would be high due to oxidation of Cr(III) to soluble Cr(VI) during Mn reduction (Eary and Rai, 1987; Richard and Bourg, 1991). However, given that we have already demonstrated that with diminished bottom DO, Mn increases and Cr decreases, this is clearly not the case (Fig. S16). This is consistent with the major locus of reduction for both Mn and Cr being in the sediments with the resulting dissolved Mn diffusing out from sediments into the water column, while oxidized Cr diffuses into sediments to be reduced therein at the same time. During November, bottom and surface water Cr showed similar distributions. This makes sense in the context of increased vertical mixing with reduced stratification at that time, as we have discussed above for several other elements.

Surface water colloidal Cr showed removal at low salinity, particularly in May 2008. The associated mixing experiments also showed similar distributions, supporting the idea that colloidal flocculation/coagulation is responsible for low salinity Cr removal (Fig. 10). The colloidal Cr distributions were very similar to colloidal Fe (Fig. S15b), suggesting that the Cr removal was probably due to the adsorption of Cr onto Fe-hydroxides (Richard and Bourg, 1991). The low salinity MR plume showed higher colloidal Cr concentrations than in the low salinity AR plume during May and June/July, possibly due to variation of the inputs from the RR and wetlands in the ARB.

In addition to low salinity colloidal Cr removal, dissolved Cr at intermediate to high salinity in the field was lower than in the mixing experiments. This is a similar observation to previous studies in this area (Shim et al., 2012; Shiller and Boyle, 1991). Shiller and Boyle (1991) suggested that variation of Cr in the river endmember could explain this observation. However, as was noted by Shim et al. (2012), this removal seems to occur regardless of the river stage, making such an explanation unlikely. Thus, in situ processes such as biological uptake (Wang and Guo, 2000; Wang and Dei, 2001), photoreduction (Kieber and Helz, 1992) and vertical mixing with Cr-depleted bottom water are more likely responsible for the Cr removal from shelf surface waters. Also, the fairly conservative behavior of the dissolved Cr in the mixing experiment discounts the idea that the removal in the field is derived from flocculation at mid-high salinity.

Biological uptake has been suggested as a process for Cr removal in the water column (Wang et al., 1997; Wang and Guo, 2000; Wang and Dei, 2001). However, our dissolved Cr distribution showed no similarities to the distributions of chlorophyll *a* or nutrients. We also note that during May 2008, for example, the plankton Cr/Fe ratio reported by Martin and Knauer (1973) suggests that our estimated 35 nmol/kg Fe removal would have been accompanied by <0.1 nmol/kg Cr removal. Thus, biological uptake (or removal) in our study may not be particularly important for Cr removal.

Photochemical reduction of Cr(VI) to the more particle-reactive Cr(III) in surface water has been suggested as a removal process in other estuaries (Kieber and Helz, 1992; Abu-Saba and Flegal, 1995) and in this system (Shim et al., 2012). Shim et al. (2012) found that Cr removal appeared to occur in less turbid surface waters away from the most immediate river influence. Similarly, in our studies, the sharpest removal of surface Cr (or the largest difference between the field and the mixing experiment) occurred at mid-high salinity, suggesting that light-induced Cr reduction and removal by adsorption onto particles may play an important role in the apparent Cr removal from surface waters during all of our studies (Kieber and Helz, 1992). This process should occur widely except in light-limited low salinity regions as well as in high salinity regions lacking sufficient electron donors (e.g., dissolved organic matter and Fe(II); Kieber and Helz, 1992). Thus, while we lack supporting experimental evidence for photoreduction and removal of Cr in this system, it remains a plausible mechanism of significance.

In addition to possible photochemical dissolved Cr removal, vertical mixing will result in apparent Cr removal from surface waters. As discussed above, we observed bottom water depletion of dissolved Cr, and thus upward mixing of these Cr-depleted waters would result in apparent Cr removal from the surface waters. During November 2008, the similar Cr concentrations described above for the surface and bottom waters are suggestive of vertical mixing. Bottom water that was depleted of Cr during the time of low DO may have mixed with surface water around our November sampling time. During June/July 2009, surface water Cr at high salinity (>25) was found to be very low at some stations with low bottom water Cr concentrations (e.g., C1, E2, F3, G3, H0, and I1), suggesting episodic vertical exchanges affecting the surface Cr distribution as also evidenced by elevated concentrations of Co, Cu, Fe, Mn and Ni. Many of the low-intermediate salinity surface water samples at that time also appear to lie on a mixing trend with the most Cr-depleted bottom waters (Fig. 10). Interestingly, during May 2008, when other elements showed little evidence of vertical exchanges, the surface water Cr distribution is the closest to conservative of our three surveys. Circumstantially, therefore, it seems that surface water Cr removal via mixing with Cr-depleted bottom water is of substantial importance in affecting the dissolved Cr distribution on the Louisiana Shelf.

3.2.7. Distributions of Re and V

Distributions of V and Re are shown in Fig. 11. The V distributions showed non-conservative behavior in both the field and the associated mixing experiments. Distributions of Re were largely conservative, though the concentrations were close to the detection limit, which may result in scattered distributions along the salinity gradients. The dissolved (<0.02 μm) phase was the main form of these elements, accounting for typically over 80% of total dissolved (colloidal + dissolved) phases (Figs. S2 and S17). But, there were a few exceptions for V at low salinity and some high salinity. Generally, colloidal V concentrations were higher at low salinity than high salinity, reflecting a riverine source of colloidal V. Some high salinity surface and bottom waters showed high colloidal V concentrations, probably due to benthic remobilization of colloidal V under well-mixed conditions in November (as seen in, e.g., Co, Ni, Fe, and Mn) and through episodic vertical mixing during the other two periods as seen in the other metals (e.g., Co, Cu, Fe, Mn and Ni).

Bottom water dissolved V showed variability indicative of non-conservative behavior, especially in May and June/July. Because the bottom V concentrations scattered below typical seawater values (~35 nmol/kg; Shiller and Mao, 1999), this behavior is indicative of V removal, most likely removal into reducing shelf sediments (Emerson and Huested, 1991). Shiller and Mao (1999) previously observed V depletion in Louisiana Shelf bottom waters during summertime and found that V correlated well with DO in those waters in agreement with removal to reducing shelf sediments. Our results are also consistent with this, though the relationship between bottom water V and DO is more scattered in this work. In the June/July hypoxia season cruise, V showed a negative correlation with Mn when the DO was <65 μmol/kg, probably due to diffusion into the overlying water column for Mn and into sediments for V (Fig. S18) and perhaps resulting from a "negative recycling trap" for V. Thus, bottom water hypoxia appears to have a significant impact on the shelf distribution and flux of V through this coastal zone, just as we have observed for a number of other elements (Cr, Mo, U).

Seasonally, the dissolved V distribution in the surface water was somewhat scattered in both the field data and associated mixing experiments. This stems partly from the high standard error of our analytical method for V. Distributions of V in the field and the mixing experiments showed an initial decrease as salinity increased in both the low salinity MR and AR plumes during May 2008 and June/July 2009. Adsorption of V onto particulate matter and thereby removal from the water column may contribute to this trend (Prange and Kremling, 1985; Yeats, 1992; Auger et al., 1999; Takematsu et al., 1985). The V distributions were similar to colloidal Fe at the low salinity (S < 8) in May 2008 (compare Figs. S17 and 7), suggesting that the V removal at low salinity may have been associated with adsorption onto the Fe-colloidal flocculants (Auger et al., 1999). In June/July 2009, changes of freshwater sources as evidenced by the δ^{18}O-salinity plot (Joung and Shiller, 2014) may have resulted in a rapid decrease of V in the AR plume. Interestingly, during November 2008, there was a significant difference in the dissolved V in the MR and AR endmembers, resulting in distinct mixing trends for the two low-salinity plumes, though both trends were largely conservative.

At intermediate to high salinity, surface water dissolved V was depleted relative to the mixing experiments, particularly in the May and June/July studies (Fig. 11). Shiller and Boyle (1987) suggested biological removal of V from Louisiana Shelf surface waters based on the similarity between V and phosphate. However, we did not observe correlations of dissolved V with nutrients or total chlorophyll *a*, consistent with previous observation in this system (Shiller and Mao, 1999) and in Long Island Sound (Wang and Sanudo-Wilhelmy, 2009). We note, however, that V-depleted surface waters can be interpreted as being on a mixing trend with V-depleted bottom waters. Thus, as suggested previously by Shiller and Mao (1999), the mid-salinity surface water V depletion probably results from vertical mixing of V-depleted bottom waters into the surface. Our data do not directly tell us when the vertical mixing occurred relative to when we sampled; however, we note that Mn (which was enriched in bottom waters) was slightly elevated in V-depleted surface waters. Considering the rapid Mn-oxidation rate in natural waters (Sunda and Huntsman, 1986; Shiller and Stephens, 2005), vertical mixing likely occurred nearly contemporaneously with our sampling (i.e., within days). In any event, episodic vertical mixing appears to be an important process for the dissolved V distribution, as well as the distributions of other trace elements, even during times of strong vertical stratification.

The November V distribution is more difficult to interpret due to the significant difference between MR and AR V concentrations at that time. There is some slight upward curvature of the AR plume mixing trend, consistent with the suggestion of Shiller and Mao (1999) of benthic V input during this time of year. Benthic inputs of dissolved V and desorption of V from resuspended particulate matter have also been suggested as sources of V in Long Island Sound (Wang and Sanudo-Wilhelmy, 2009). Clearly the Louisiana Shelf is a sink for V during times of low oxygen and possibly it may be a source at some other times.

In contrast to V and Mo, we did not observe depletion of Re nor a relationship with DO in the bottom water (Fig. 11), even though each of these elements can be removed under reducing conditions (e.g., Morford et al., 2005, 2007). This contrasting behavior may be related to the sulfide content of the water column or sedimentary pore waters (Helz and Dolor, 2012). Helz and Dolor (2012) reported that Re(VII) could be reduced to insoluble Re(IV) in the presence at least $10^{-3.0}$ M of sulfide, whereas Mo could be reduced at $10^{-4.9}$ M sulfide. Although we did not measure the sulfide content in the water column or sedimentary pore waters, the different reaction of Mo and Re to S may result in the removal of Mo, but not for Re in this system during bottom water hypoxia. Also, stronger reducing conditions are needed for Re reduction than V reduction. For example, Crusius et al. (1996) reported that Re enrichment in sediments occurred at depths below Fe and U reduction. In our study, particularly in June/July with oxygen-depleted bottom waters, the release of Fe was not as prominent as Mn, though U and V removal was apparent. Thus, the system was not sufficiently reducing in either the bottom waters or near the sediment–water interface to lead to Re reduction and removal.

Surface Re distributions were broadly conservative along the salinity gradient (Fig. 11). Note that the high uncertainty of our Re measurements at these low concentrations results in significant analytical scatter in our results. In previous work, others have occasionally observed non-conservative estuarine Re behavior which has been suggested to result from desorption from fluvial SPM (Colodner et al., 1993), vertical exchange of Re-depleted bottom water with the surface, remobilization of Re from the sediment to the water column during oxic conditions (Morford et al., 2009; Rahaman and Singh, 2010), and possible incorporation of Re in sulfide minerals (Miller et al., 2011; Xiong, 2003). Nonetheless, the concentrations of Re we observed were within the range previously reported in this system (Shim et al., 2012), and the conservative Re distributions are similar both to the previous study in this area and other estuaries in India and the Amazon plume (Shim et al., 2012; Rahaman and Singh, 2010; Colodner et al., 1993).

3.3. Implications for trace element and nutrient fluxes as well as for the maintenance of hypoxia

Our trace element distributions reveal clear bottom water removal of dissolved Cr and V with perhaps more limited removal of Cs, Mo, and U. On the other hand, dissolved Co, Cu, Fe, Mn, and Ni increased in bottom waters, suggesting a flux from the shelf sediments. These bottom water changes tended to be strongest during the June/July hypoxia period. Correlation of the changes in bottom water trace element concentrations with dissolved oxygen during the hypoxia period could suggest a relationship between bottom oxygen and sedimentary trace element fluxes. However, our data offer an alternative interpretation. First, we note that bottom removal of V was also significant during May while bottom removal of Cr was significant during all sample periods and with no apparent correlation with oxygen during non-hypoxia periods. Second, during the hypoxia period, dissolved Si accumulated in bottom waters even though its regeneration should not be strongly linked to oxygen depletion. We suggest, therefore, that to some extent these benthic fluxes are always occurring, and that it is the high stratification during spring and summer that allows clear observation of the effects of these fluxes on bottom water composition. Hypoxia likely still has a significant relationship to these benthic fluxes, however, as suggested by modeling studies of the shelf (e.g., Eldridge and Morse, 2008). This could come about through seasonal alteration of the depth of sedimentary redox transitions which thereby alters the extent of diffusive fluxes into or out of the sediments. Additionally, since hypoxia is partly driven by a high flux of autochthonous organic matter, this organic matter undoubtedly drives the shelf sediments overall more reducing throughout the year than they would be without the autochthonous organic matter input. That high organic matter input, in turn, is driven by the flux of anthropogenic fluvial nutrients (e.g., Rabalais et al., 2007).

One interesting outcome of the importance of stratification on bottom water trace element and nutrient concentrations is that greater stratification will tend to lead to increased bottom water accumulations (or depletions in the case of V and Cr) but a diminished flux of bottom regenerated materials into the surface waters. Nonetheless, our trace element distributions, especially those of Cr and V (see also Shiller and Mao, 1999), clearly demonstrate that signals generated in the shelf bottom waters affect surface water distributions and that this occurs even during times of significant stratification. Knowledge of that flux of materials from the shelf bottom to the surface, especially for nutrients, is a key area of uncertainty in our understanding of the maintenance of hypoxia on the Louisiana Shelf (Dagg et al., 2007; Eldridge and Roelke, 2010).

That surface water depletions of V and Cr are similar to bottom water depletions (Figs. 10 and 11), suggests that most of the salty water mixing with river water on the shelf has interacted with the shelf bottom, i.e., it is mixing upwards. The maximum surface water depletions are observed at a salinity of ~30, which is a mixture of ~17% river water with seawater of $S = 36.3$, or, stated another way, a flux of 4.8 times more seawater than river water at that salinity of 30. Given that bottom water nutrient concentrations can at times be an appreciable fraction of the river nutrient concentrations (Fig. 3), it becomes clear that the upward flux of bottom-regenerated nutrients can be an important or even dominant component of nutrient fluxes to surface waters at high salinity, in agreement with modeling results (Eldridge and Roelke, 2010).

There are two other important implications of our observations. First, some of our data suggests episodic vertical mixing of shelf bottom waters into the surface waters. If this process is of a similar or greater significance to upward diffusive fluxes, then some adjustment of approaches to hypoxia modeling may be required. Second, it is likely that some of the shelf bottom waters with altered chemical composition do not mix upwards and flow off the shelf bringing nutrients offshore to the open Gulf of Mexico. Indeed, Trefry and Presley (1982) suggested this as a mechanism for bringing “excess Mn” to Gulf of Mexico sediments. Quantifying this offshore flux of altered shelf bottom water remains an important unresolved problem (Shiller, 1996).

4. Conclusions

This new survey, with greater spatial/temporal resolution than previously, has allowed an improved understanding of trace element and nutrient behavior in the outflow regions of the Mississippi/Atchafalaya River. With these data, we found that, first, the size distributions of trace elements in shelf waters were quite different among metals as well as salinity ranges. In the shelf waters, Fe was mostly in the colloidal phase (0.02–0.45 μm) through the salinity range, and colloidal Cr was significant at low salinity, but dissolved Cr was the predominant form at mid-high salinity regions. The proportion of the colloidal fraction was typically less than 30% (Co, Cu, Mn, Ni, V) and 10% (Cs, Mo, U, Re) of the total dissolved concentrations (<0.45 μm). A few exceptional samples of high colloidal Co, Cu, Mn, Ni and V were likely associated with river inputs and benthic remobilization. Second, during all our sampling campaigns, we observed that dissolved Mo, Cs, U, Ni and Cu showed conservative as well as apparent non-conservative behaviors, with the apparent non-conservative behavior derived mainly from vertical mixing in November 2008. However, the other trace elements consistently showed non-conservative behavior during our samplings. Through examination of the associated mixing experiments, nutrient and chlorophyll distributions, and surface-bottom concentration contrasts, the non-conservative behaviors were variously related to colloidal flocculation (Fe, Cr), biological activity (Fe, Mn), desorption (Co), photochemical reaction (Cr) and benthic mobilization (Co, Cu, Ni, Mn). In bottom waters, particularly during hypoxic conditions in June/July 2009, certain trace elements were greatly altered showing enrichment (Co, Cu, Ni, Mn, Fe) or depletion (Cr, V). This behavior undoubtedly results from particulate or sedimentary dissolution and/or diffusion for the enrichment, and diffusion into sediment and/or adsorptive removal onto particles as result of reduction for the depletion. Lastly, we observed seasonal variations of trace elements and nutrients in the low salinity waters of the two river plumes as well as in shelf waters. At low salinity, the observed seasonal variations appear to be related to seasonal changes in the river water endmembers, which themselves are associated with variation of mixing ratios of MR tributaries as well as inputs from the Red River and wetlands in the Atchafalaya Basin.

Subsequently, this seasonal river endmember variability together with the above listed biogeochemical factors to different degrees affect seasonal variations of trace elements and nutrients in the shelf waters. Overall, the observed concentration (and hence flux) differences between the two low salinity river plumes suggest another aspect of fluvial input that should be accounted for in modeling studies of LA Shelf biogeochemistry and hypoxia.

Importantly, particularly in June/July 2009 during bottom water hypoxia, we observed evidence of considerable vertical mixing even during times of significant stratification. This could be a key process for maintaining the shelf biological production and thus, bottom water hypoxia during summer low discharge and in areas of the shelf further away from the locus of river input. As noted by others (e.g., Bianchi et al., 2010), this flux needs better quantification. And, it should be incorporated into shelf hypoxia modeling. It is also likely that the bottom enriched (or depleted) trace elements that are not mixed upwards flow off the shelf bringing nutrients and trace elements offshore to the open Gulf of Mexico. Alterations of trace elements and nutrients in bottom waters are at least partly related to anthropogenic eutrophication/oxygen depletion. With continued exacerbation of coastal eutrophication and bottom water hypoxia especially in association with global climate change (e.g., Rabalais et al., 2009), the alteration of chemical fluxes to the ocean could be even more significant in the near future.

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Appendix A. Supplementary data

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