Geotraces and Beyond: Studies of Trace Elements in Coastal and Open Ocean Waters with an Emphasis on the Effects of Oxygen Depletion and Hydrothermal Plumes

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GEOTRACES AND BEYOND: STUDIES OF TRACE ELEMENTS IN COASTAL AND OPEN OCEAN WATERS WITH AN EMPHASIS ON THE EFFECTS OF OXYGEN DEPLETION AND HYDROTHERMAL PLUMES

by

Peng Ho

A Dissertation
Submitted to the Graduate School, the College of Arts and Sciences and the School of Ocean Science and Engineering at The University of Southern Mississippi in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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ABSTRACT

We investigated various dissolved trace element (dTE) distributions in two distinct areas: the coastal northern Gulf of Mexico and the eastern tropical Pacific Ocean.

A multi-year (2007–2011) chemical time series of eight stations in the western Mississippi Sound (MS) and northwestern Mississippi Bight (MB) was undertaken to examine the factors affecting chemical distributions in this dynamic region. Key findings include the frequent development of bottom water hypoxia in MB during late spring-summer, the likely contribution of submarine groundwater discharge (SGD) to the material flows, and observation of effects of episodic events including tropical storms and the opening of the Bonnet Carré Spillway. In hypoxic bottom waters, enriched nutrients, Mn, and Ba as well as depleted V and Cr were commonly observed.

Contrasting with the northern Gulf section, we also examined dTE distributions in the eastern tropical Pacific Ocean in late 2013. Generally, a conservative dissolved Mo (dMo) distribution and surface dissolved V (dV) depletion were observed in the East Pacific Zonal Transect (EPZT) from Peru to Tahiti. Depleted dMo and dV in the oxygen deficient zone (ODZ) coincided with the nitrite maximum, suggesting association of these elements with the nitrogen cycle. Particulate Mo (pMo) and V (pV) enrichments in the ODZ indicate scavenging by Fe oxyhydroxides and/or biogenic particles. Depleted dMo and dV in hydrothermal plumes suggest a sink for Mo and V. Within the plumes, pV and pMo are adsorbed onto Fe oxyhydroxide and Fe/Mn (oxy)hydroxides, respectively.

Low surface water dissolved Ga and Al, as well as high and variable surface Ga/Al ratios along the EPZT reflect low aeolian input and a longer Ga residence time.
than Al. Intermediate water dissolved Ga (removal) and Al (addition) behaved non-conservatively in the EPZT, having contrasting behaviors that remain to be explained. Generally, elevated Ga and Al concentrations were observed in deep water, indicating inputs from hydrothermal activity and resuspended sediments. Hydrothermal flux estimates for Ga and Al showed that hydrothermal inputs of these elements are likely to be of local, not global importance, with dust input still the likely major influence on the distributions of these elements.
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DEDICATION

I dedicate this dissertation to my family and friends.
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CHAPTER I - INTRODUCTION

Studies of trace element biogeochemistry in the hydrologic cycle are critical and valuable to other disciplines in marine sciences. For instance, various trace elements (e.g., Fe, Cu, Co, Mn, Zn) are essential for the phytoplankton growth (Morel et al., 2014). Trace elements can be used not only as tracers to provide information on dust deposition (e.g., Al, Ga, Mn and Th) and anthropogenic inputs (e.g., Pb and Hg) but also as paleoproxies (e.g., Ba, Mo, Nd, U, Zn, etc.) for the reconstruction of paleoenvironment conditions (Bruland et al., 2014; Lynch-Stieglitz and Marchitto, 2014). The biogeochemical cycles of trace elements in aquatic environments are regulated by various processes (e.g., dilution, redox, complexation, coagulation/aggregation, adsorption/desorption, scavenging, regeneration/remineralization, etc.) (Bruland et al., 2014). It is necessary to elucidate the processes controlling the distributions of trace elements in various aquatic environments to provide a better understanding of the trace elements cycling on the Earth.

This dissertation includes studies of trace element distributions in two contrasting environments: (1) a river-dominated estuarine-coastal system (Mississippi Sound and Mississippi Bight) in the northern Gulf of Mexico and, (2) a section in the Eastern Tropical Pacific Ocean extending from the wind-driven coastal upwelling system off Peru toward the oligotrophic open ocean in mid-South Pacific Ocean (Peru-Tahiti).

It is important to study the biogeochemistry of trace elements in estuarine-coastal systems, regions which are characterized with strong gradients in biogeochemical and physical properties. For instance, riverine input is a dominant source of freshwater, chemical constituents, and particles to estuaries and coastal regions to form rivers plumes
extending offshore (Muller-Karger et al., 1988; Walker, 1996; Hickey et al., 1998; Kang et al., 2013). Riverine inputs of macronutrients and micronutrients enhance primary production in estuarine and coastal waters (Lohrenz et al., 1990). Within such a dynamic system, the coupling of physical and biogeochemical processes can result in the riverine fluxes of chemical constituents being significantly modified in the estuarine-coastal system before it reaches the open ocean. In contrast, some coastal regions receive very limited riverine inputs but are still highly productive due to the supply of nutrient-rich upwelling water (e.g., California and Peruvian coastal upwelling regimes; Bruland et al., 2001, 2005; Lachkar and Gruber, 2012). In eastern boundary upwelling regimes, shelf sediments play an important role in the source and sink of elements (Johnson et al., 1999; Codispoti et al., 2001; Friederich et al., 2002; Böning et al., 2004; Bruland et al., 2005; Scholz et al., 2011; Noffke et al., 2012).

Low-oxygenated waters have been observed in the Mississippi Bight (e.g., Brunner et al., 2006; Rakocinski and Menke, 2016) and along the Peruvian continental margin (e.g., Gutiérrez et al., 2008). However, the mechanisms and causes of the development of the oxygen deficient zone is somewhat different between river-dominated coastal regions (Mississippi Bight) and oceanic coastal upwelling regions (Peruvian coast).

Coastal hypoxia (dissolved oxygen \(< 63 \, \mu \text{M or } 2 \, \text{mg/L}\)) development is the synergistic effects of eutrophication driven by excess nutrients from rivers and stratification due to salinity or temperature gradients. Hypoxia in the Mississippi Bight is potentially influenced by anthropogenic activities (Rabalais et al., 2010). It is known that the Mississippi River and other local rivers are important fluvial sources to the
Mississippi Sound and Bight. Highly developed catchments in the Mississippi River Basin associated with fertilizer used in the watershed drain excess nutrients to rivers which finally discharge into the Louisiana and Mississippi coastal regions. High levels of riverine nutrients feed into coastal waters and stimulate phytoplankton growth which can result in coastal eutrophication. Given the significant difference in temperature and salinity between surface and bottom layers under specific circumstances (i.e., high river discharge and summer heating), strong stratification in the coastal water column prevents the supply of oxygenated waters from the surface to the bottom. Thus, increasing biological respiration and organic matter oxidation consume large amounts of oxygen in the stratified bottom water and finally lead to hypoxic or anoxic conditions. The extensive “dead zone” on the Louisiana Shelf is a typical example of seasonal hypoxia caused by human activities (Rabalais et al., 2002) with an average volume of 45 km$^3$ (Rabalais et al., 2007). The extent and area of hypoxia have been aggravated and spreading since 1950’s due to anthropogenic inputs (Diaz and Rosenberg, 2008). Hypoxia causes changes in benthic community structure (e.g., Rabalais et al., 2001a, b) and decreases in the capture of fish, shrimp, and crabs by trawls (Renaud, 1986). The Mississippi coastal region provides important fisheries resources (fisheries loading of $1.3\times10^5$ metric tons annually during 1950–2016, NOAA Office of Science and Technology, National Marine Fisheries Service) in the northern Gulf of Mexico, and this production can potentially be affected by Mississippi Bight hypoxia.

Coastal hypoxia occurs seasonally, driven by increased springtime river discharge and ameliorated by fall storm-induced mixing (Rabalais et al., 2007; Zhang et al., 2010). Contrastingly, the oxygen minimum zone (OMZ) off Peru, one of the most intensive
OMZs in the world (Stramma et al., 2008), persists year-round and extends into the ocean basin. The volume of the OMZ core (dissolved oxygen < 20 μM) off the Peru coast (0°–18°S) is 1.8–55 × 10^4 km^3 (Paulmier and Ruiz-Pino, 2009). This Peruvian upwelling system is one of the most productive regions of the ocean (Pennington et al., 2006) and supports the largest pelagic fishery (mainly anchovy, 4.3×10^6 metric tons of anchoveta annually during 1950–2015, FAO) in the world. The upwelling of cold and nutrient-rich waters fuels the productivity at the surface to produce a high flux of organic matter to the continental margin (Jahnke et al., 1990; Jahnke, 1996) which consumes dissolved oxygen during the decomposition of the organic matter. The Peruvian OMZ is a result of high productivity induced by wind-driven coastal upwelling and sluggish ventilation (Fuenzalida et al., 2009; Karstensen et al., 2008). The variability of the Peruvian OMZ is regulated by mesoscale activities (e.g., Bettencourt et al., 2015; Duteil and Oschlies, 2011; Vergara et al., 2016) and currents (Peru-Chile Current System and Equatorial Undercurrent System; Vergara et al., 2016).

As noted above, the mechanisms and spatial-temporal scales of oxygen-depleted waters in these two study areas are very distinct. Contrasting with seasonal hypoxia in the Mississippi Bight, the Peruvian OMZ are larger and persists year-round. There are several other contrasting features in two regions. Fluvial inputs are very limited along the Peruvian coast in comparison to the Mississippi coast. Large-scale oceanic currents (i.e., Eastern Boundary Current and Peru-Chile Undercurrent) are dominant in the Peruvian continental margin (Wyrtki, 1966, 1967; Kessler, 2006) while small-scale alongshore and tidal currents are prevailing in the Mississippi coastal region (Keen, 2002; Walker et al., 2005; Dzwonkowski and Park, 2010). This dissertation provides an opportunity to
understand the biogeochemical cycling of trace elements in these two contrasting environments.

1.1 Background

1.1.1 Temporal and spatial distributions of trace elements (Ba, Cs, Cr, Fe, Mn, Mo, U, V and Re) in Mississippi coastal waters: influence of hypoxia, submarine groundwater, and episodic events in a river-dominated system (CHAPTER II)

There are several riverine sources in the western Mississippi Sound and Mississippi Bight, including the Mississippi and Pearl Rivers, as well as St. Louis Bay. Mobile Bay outflow is also a major freshwater source to the Mississippi Bight, especially on the Mississippi-Alabama Shelf (Dzwonkowski et al., 2014; Greer et al., 2018). During the opening of the Bonnet Carré Spillway, a flood control structure at the Lower Mississippi River operated by the U.S. Army Corps of Engineers, Mississippi River water is redirected into Lake Pontchartrain and discharged into the western Mississippi Sound. The influences of the Pearl River plume and St. Louis Bay waters are mostly observed in nearshore western Mississippi Sound waters (Eleuterius, 1976; Orlando et al., 1993; Bera et al., 2015). The Mississippi River plume direction varies throughout the year depending on the prevailing winds (Walker, 1996) but tends to be westward from fall through early spring and eastward during summer (Morey et al., 2003).

Conventionally, riverine inputs are considered the main pathway to deliver terrestrial materials into the coastal region. Moreover, benthic inputs are mostly attributed to chemical constituents (e.g., reduced N species, Mn$^{2+}$, Fe$^{2+}$, S$^{2-}$) regenerated in the sediments and that then diffuse into overlying water. In last two decades, the significance of chemical constituents transported via submarine groundwater discharge (SGD, which
includes fresh groundwater discharge and recirculated saline water discharge through coastal aquifers; Burnett et al., 2006; Mulligan and Charette, 2006; Moore et al., 2008) to the coastal region has been emphasized (Moore, 1996, 1997; Krest et al., 1999; Moore and Krest, 2004). Several studies have found the presence of SGD along the Louisiana, Alabama, and Florida coasts with high nutrient loads from SGD contributed to coastal regions (Cable et al., 1996; Krest et al., 1999; Moore and Krest, 2004; Thompson et al., 2007; Su et al., 2012). Paleochannels or buried sand deposits are potential pathways for SGD to flow into the coastal zone (Kolker et al., 2013). The advection of SGD in coastal regions provides low oxygen waters, excess nutrients as well as ammonium and sulfide which further deplete bottom oxygen (Slomp and Van Cappellen, 2004; Burnett et al., 2006; Moore, 2010; McCoy et al., 2011; Rodellas et al., 2015; Peterson et al., 2016). Evidence of paleochannels extending from the Mississippi coast to the barrier islands (e.g., Oivanki and Otvos, 1994) and artesian wells on the barrier islands, suggest SGD may be a potential cause for hypoxia in the Mississippi Bight.

The distribution of trace elements in estuarine-coast systems is regulated by the variability of riverine sources, benthic inputs, biogeochemical processes (e.g., redox, biological uptake, adsorption/desorption, aggregation/disaggregation, etc.) and physical processes (e.g., currents, tides, upwelling, eddies, etc.). As noted above, our study area is characterized with strong gradients of physical and chemical properties. We conducted a time-series survey from the mouth of St. Louis Bay, MS and through the western end of Mississippi Sound and into the northwestern corner of the Mississippi Bight (“NGI transect”) and investigated the behaviors of various trace elements (Ba, Cs, Cr, Fe, Mn, Mo, U, V and Re) in the Mississippi Sound and Bight.
Previous work has recognized that Ba enrichment in groundwaters provides an additional Ba source on the shelf (Moore, 1997; Shaw et al., 1998; Windom and Niencheski, 2003; Charette and Sholkovitz, 2006; Moore and Shaw, 2008; Santos et al., 2011). Barium also can be used as a tracer of river waters (Guay and Falkner, 1997, 1998). The behavior of Ba in estuaries and coastal regions is controlled by the variability in riverine Ba concentration, desorption from fluvial particles, coprecipitation with Mn/Fe oxides, biological uptake and benthic inputs (Coffey et al., 1997; Shaw et al., 1998; Stecher and Kogut, 1999; Moore and Shaw, 2008; Santos et al., 2011; Shim et al., 2012; Joung and Shiller, 2014). In the lower Mississippi River, the seasonal variability of dissolved Ba is largely controlled by changing proportions of water derived from the major tributaries (Shiller, 1997a). In the Mississippi outflow, the seasonal variation of dissolved Ba in the endmember is strongly affected by changes in hydrodynamic conditions (Joung and Shiller, 2014). On the Louisiana Shelf, Joung and Shiller (2014) found that a significant depletion of Ba in surface waters was associated with a diatom bloom and enriched Ba in shelf waters was due to benthic inputs (i.e., SGD and/or dissolution/diffusion from sediments/drilling muds). The determination of Ba concentration in the NGI transect might be helpful to elucidate the contributions of rivers, SGD, sediment inputs in this river-dominated system.

Dissolved Cs concentration in seawater is about 2 nM and it behaves conservatively (Spencer et al., 1970; Brewer et al., 1972). Cs levels are extremely low in Mississippi (0.09 nM) and Pearl River (< 0.27 nM) waters (Shim, 2011; Shim et al., 2012; Joung and Shiller, 2016). However, very high dissolved Cs concentrations (up to 148 nM) have been measured in St. Louis Bay, which is likely caused by the outflow of
the DuPont titanium dioxide (TiO$_2$) plant (Shim, 2011; Bera et al., 2015). Cesium salts can be used as a nucleant substance during TiO$_2$ manufacturing process (Allen and Evers, 1993). Therefore, Cs can be an indicator to assess the contribution of bay water to the Mississippi Sound and Bight.

Dissolved Fe and Mn are typically non-conservative in estuarine/coastal systems which means their riverine fluxes can be largely modified in the coastal region. From nearshore to pelagic regions, dissolved Fe and Mn concentrations decrease with increasing distance from the coast (Landing and Bruland, 1987; Shiller, 1997b). Estuaries can be a sink of Fe by flocculation, coagulation, precipitation and scavenging during mixing (Boyle et al., 1977; Sholkovitz et al., 1978; Vuori, 1995). The inventory of Mn in the coastal region is regulated by river discharge, sediment diffusion and resuspension, and redox potential in the aqueous system (Yeats et al., 1979; Sundby and Silverberg, 1981; Ponter et al., 1992; Paucot and Wollast, 1997). Dissolved Fe and Mn concentrations are significantly higher in the Pearl River than in the Mississippi River (Shiller, 2003; Shiller and Stephens, 2005; Stolpe et al., 2010; Shim, 2011) and this difference is associated with the presence of a significant amount of colloids and dissolved organic carbon in the Pearl River compared with the Mississippi River (Duan et al., 2007; Stolpe et al., 2010). The solubility of dissolved Fe and Mn are sensitive to dissolved oxygen concentration. Under reducing conditions, Mn and Fe are dominantly in the dissolved phase (Berner, 1978; Wedepohl, 1978; Stumm and Morgan, 1996) while dissolved Mn is retained in waters longer than dissolved Fe (Landing and Bruland, 1987) due to faster oxidation rate of Fe than Mn (Stumm, 1992). A study of a subterranean estuary showed increased dissolved Fe and Mn in porewaters due to the reduction of Fe
and Mn (Charette and Sholkovitz, 2006). Based on these observations and mechanisms, dissolved Fe and Mn measurements will provide information on riverine influences (from Pearl River or other rivers of low-Fe and low-Mn concentrations), SGD input, and reducing conditions in our study area.

The biogeochemical cycle of Cr in aquatic environments is controlled by complexation, adsorption/desorption, dissolution/precipitation, biological and redox processes (Richard and Bourg, 1991). The temporal variation of riverine Cr concentration might be a potential factor to cause the observation of Cr removal in the outflow of the Mississippi River (Shiller and Boyle, 1991). However, considerable removal of Cr was observed in high salinity water on the Louisiana Shelf which could be a result of photoreduction of Cr(VI) and the reduction of Cr (Shim et al., 2012; Joung and Shiller, 2016).

The concentration of V ranges from 30‒45 nM in oxic seawater with a slight depletion in surface waters, possibly due to biological utilization (Collier, 1984; Jeandel et al., 1987). Previous studies observed that V was depleted in surface waters off the Mississippi Delta due to biological uptake (Shiller and Boyle, 1987, 1991). However, Shiller and Mao (1999) suggested V-depleted surface water was caused by upward mixing of low-V hypoxic shelf bottom waters.

As noted above, the distributions of trace elements are affected by riverine inputs and biogeochemical processes in the estuarine-coastal system. Various factors (rivers, hypoxia and SGD) can alter the behaviors of trace elements in the Mississippi Sound and Bight. In this study, we investigated the factors in regulating the distribution of trace
elements in the Mississippi Sound and Bight and the influences of episodic events (tropical storms and the opening of Bonnet Carré Spillway) on their distributions.

1.1.2 The distribution of trace elements (Mo, V, Ga and Al) in the eastern tropical Pacific Ocean and the controlling processes of their distributions (CHAPTER III and CHAPTER IV)

The U.S. GEOTRACES GP16 East Pacific Zonal Transect (EPZT) was executed from 25 October to 20 December 2013 aboard R/V Thomas G. Thompson from Manta, Ecuador to Papeete, Tahiti. There are a wide variety of biogeochemical features across the section. (1) The upwelling of nutrient-rich waters enhances primary production which results in an extreme OMZ (Brink et al., 1983; Helly and Levin, 2004; DiTullio et al., 2005). (2) Hydrothermal plumes originating from hydrothermal fields on the East Pacific Rise (EPR) are sources or sinks of various elements (Von Damm et al., 1985; Sarradin et al., 2008; German and Seyfried, 2014). (3) Compared with the Peruvian coastal upwelling region and the EPR, the waters near Tahiti are a pelagic environment with low primary productivity, low nutrients and little coastal influence (Grob et al., 2007; Bonnet et al., 2008). Compiling trace element data from these features will allow us to examine the processes that regulate their distributions and to evaluate the sources and sinks of trace elements from the continental shelf to the open ocean.

Near-coastal circulation along the Peruvian coast is mainly dominated by the equatorward Peru Coastal Current (Wyrtki, 1966, 1967). Meanwhile, the Peruvian coastal regime is subject to a wind-driven upwelling system. The main source of upwelled waters off Peru originates from the Equatorial Subsurface Water which feeds into the Peru-Chile Undercurrent (Wyrtki, 1963; Brink et al., 1983; Huyer et al., 1987; Albert et al., 2010).
About 150 km off Peru, the Peru Oceanic Current (i.e., eastern boundary current) flows equatorward in near-surface layers and veers northwestward around 0°–12°S which feeds into the South Equatorial Current (Strub et al., 1998; Kessler, 2006).

The GP16 section provides an excellent opportunity to study the biogeochemical cycle of trace elements in the Peruvian upwelling system and its OMZ. High primary production in the Peruvian upwelling system (e.g., Pennington et al., 2006) increases the export of biological particles to create a scavenging boundary across the continental margin (e.g., Bruland et al., 2005) where trace elements can be removed either by active/passive biological uptake or adsorption onto biogenic particles. In the Peruvian OMZ, extensive reducing shelf sediments can be a source or a sink of redox-sensitive elements (Böning et al., 2004; Bruland et al., 2005; Scholz et al., 2011; Noffke et al., 2012). The mobilization and partitioning of redox-sensitive trace elements across the seawater-sediment interface are strongly influenced by the resuspension of Fe-rich sediments on the continental shelf (Johnson et al., 1999; Böning et al., 2004; Morford et al., 2005).

The EPR, a fast spreading ridge, has a hydrothermal vent system characterized by high temperature and acidic fluids. Hydrothermal vents can be sources or sinks of trace elements in the ocean (Von Damm et al., 1985; Sarradin et al., 2008; German and Seyfried, 2014). For instance, high levels of dissolved Fe and Mn are released from hydrothermal vents (e.g., Tagliabue et al., 2010; Nishioka et al., 2013; Fitzsimmons et al., 2014; Hatta et al., 2015; Resing et al., 2015) and then authigenic Fe and Mn (oxy)hydroxides are formed as reduced Fe and Mn are oxidized by ambient seawater (e.g., Von Damm et al., 1985; Field and Sherrell, 2000; Fitzsimmons et al., 2017; Lam et
Authigenic Fe and Mn particles or minerals will also alter the partitioning and cycling of other trace elements (e.g., Mo, V) by adsorption and complexation processes in seawater (Morford et al., 2005). The emission of hydrogen sulfide from hydrothermal activities can affect the distributions of other elements (e.g., Cd, Cu, Mo, Fe) by co-precipitation, complexation and adsorption (Trefry et al., 1985; Von Damm et al., 1995; Helz et al., 1996; Shooter, 1999; Field and Sherrell, 2000; Audry et al., 2006; Sarradin et al., 2008). The GP16 cruise logistics also provided an opportunity to examine the sources and sinks of trace elements from hydrothermal activities on the EPR.

Our group collected dissolved seawater samples at 35 stations along the EPZT and determined the concentrations of dissolved Mo, V and Ga in our laboratory. We acquired hydrographic data and other supporting trace element data from other groups who participated in the GP16 cruise. In Chapter III, we investigate the distributions of two redox-sensitive elements (Mo and V) in the EPZT and evaluate the influences of the OMZ and hydrothermal plumes on their distributions. In Chapter IV, we focus on the distributions of dissolved Ga and Al and examine the importance of atmospheric deposition, particle scavenging, sediment resuspension and hydrothermal process in their distributions in the EPZT.

1.1.2.1 The distribution of dissolved and particulate Mo and V along the U.S. GEOTRACES East Pacific Zonal Transect (GP16): The roles of oxides and biogenic particles in their distributions in the oxygen deficient zone and the hydrothermal plume (CHAPTER III)

The distribution of Mo is generally thought to be conservative in the ocean (Bruland, 1983; Collier, 1985). However, both slight depletion and enrichment of Mo
was observed in the Eastern Tropical Pacific by Tuit (2003). Dissolved V behaves fairly conservatively in the ocean with ~10% depletion at the surface (Collier, 1984; Jeandel et al., 1987).

Both Mo and V serve as micronutrients and enzymatic co-factors. For Mo, it plays an important biological role in the nitrogen cycle as a co-factor in nitrogenase, nitrate reductase, and nitrite oxidoreductase (Stiefel, 1996; Moreno-Vivián et al., 1999; Maia et al., 2017) as well as in DMSO reductase (Schindelin et al., 1996). V has been identified as a cofactor in V-nitrogenases and V-haloperoxidases (Crans et al., 2004; Rehder, 2008). Specifically, V-haloperoxidases are commonly found in marine macroalgae (Crans et al., 2004).

Mo and V are redox-sensitive elements, with decreased solubility in oxygen-depleted water. Based on thermodynamics, Mo is predominantly present as the MoO$_4^{-}$ species (Baes and Mesmer, 1976; Manheim, 1978). Under reducing conditions, Mo(VI) is reduced to Mo(IV) and then preferentially removed to the particulate phase. Small amounts of the more particle-reactive Mo(V), which should be thermodynamically stable in reducing waters (Bertine, 1972; Brookins, 1988), have been reported in low-oxygen estuarine waters (Wang et al., 2009). Furthermore, when a threshold of sulfide concentration (~11 μM H$_2$S$_{(aq)}$) is reached, molybdate can be sulfidized to more readily scavenged thiomolybdates without Mo reduction (Erickson and Helz, 2000; Dahl et al., 2010; Vorlicek et al., 2015). For V, its predominant species in oxic seawater is H$_2$VO$_4^{-}$ (Baes and Mesmer, 1976; Wang and Sanudo-Wilhelmy, 2008). V can be removed from the water column through the scavenging of vanadate onto particles and the reduction of vanadate to vanadyl (i.e., a more particle-reactive species) (Wehrli and Stumm, 1989).
Under extremely reducing conditions, V(IV) could be further reduced to V(III) by humic acid or sulfides, and be present as $\text{V}_2\text{O}_3$ or $\text{V(OH)}_3$ (Goodman and Cheshire, 1975; Breit and Wanty, 1991).

With respect to the influence of hydrothermal vents on the distributions of Mo and V, there is still no clear conclusion about the source and/or sink of Mo and V in hydrothermal systems. Jeandel et al. (1987) suggested that the hydrothermal flux of V is insignificant even though V is enriched in hydrothermal vent fluids (German and Seyfried, 2014). Further work by Trefry and Metz (1989) showed that hydrothermal process could be a significant sink of V due to scavenging by iron oxides near hydrothermal vents. The sources and sinks of Mo in hydrothermal vents are probably negligible. For instance, in the Reykjanes thermal brine area Mo concentration in the vent fluid is similar to ambient seawater (Bjornsson et al., 1972). However, Mo is depleted in hydrothermal vent fluids on the Southern Juan-de-Fuca Ridge (Trefry et al., 1994).

As noted above, Mo and V distributions can be affected by redox process, biological utilization, adsorption onto particles, remobilization/diffusion from sediments, hydrothermal process. The biogeochemical and physical features across the EPZT allows for a better understanding of the processes affecting oceanic Mo and V distributions. We present the first detailed oceanic section of Mo and V distribution in the eastern tropical Pacific Ocean and examine the processes controlling their distributions.

1.1.2.2 Processes affecting the distributions of dissolved Al and Ga along the U.S. GEOTRACES East Pacific Zonal Transect (Chapter IV)

Ga is in the same group as Al in the Periodic Table which causes these two elements to behave similarly (Orians and Bruland, 1988a). In the ocean, Al speciation is
dominated by hydrolysis species, mostly Al(OH)$_4^-$ and Al(OH)$_3^0$ (Stumm and Morgan, 1996). Ga is readily hydrolyzed as well and mostly present as Ga(OH)$_4^-$ (Bruland, 1983; Diakonov et al., 1997). Although Ga exhibits behavior similar to Al, Al appears to be scavenged faster than Ga due to a combination of preferential adsorption of Al(OH)$_3^0$ species onto net negatively charged particle surfaces (Orians and Bruland, 1988a). A surface ocean Ga residence time of decades (Orians and Bruland, 1988b) is an order of magnitude longer than the surface Al residence time (2 – 6.5 yrs; Orians and Bruland, 1986; Jickells et al., 1994; Measures and Brown, 1996). In deep water, Ga has residence time of ~100–750 years based on vertical advection/diffusion results (Orians and Bruland, 1988a) while Al residence time estimates is 100–200 years (Orians and Bruland, 1985, 1986), depending on locations. The difference in Ga and Al residence times is reflected in higher surface water Ga/Al ratios (Orians and Bruland, 1988a; Shiller, 1988, 1998), relative to the crustal ratio (Rudnick and Gao, 2014), and lower intra-basin fractionation of Ga than that of Al (Orians and Bruland, 1985, 1988a). Additionally, the combination of larger ionic radius of trivalent Ga relative to Al and the longer and more covalent Ga-O bond than Al-O bond (Burton and Culkin, 1972) suggests Ga is more readily leached from solid phases where it substitutes for Al and results in high dissolved Ga/Al ratios. As noted above, lower reactivity and a longer residence time of Ga than Al can provide us more detailed insight into the processes controlling the dissolved Al distribution in surface waters (Orians and Bruland, 1988a, b; Shiller, 1988; Shiller and Bairamadgi, 2006).

Al and Ga are particle-sensitive elements and exhibit a scavenged-type profile in the ocean. The sources of dissolved Al and Ga to the surface ocean include atmospheric
deposition (Hydes, 1979, 1983; Measures et al., 1984; Orians and Bruland, 1985, 1986, 1988a; Shiller, 1998; Shiller and Bairroadig, 2006) and fluvial inputs (Kremling, 1985; Measures et al., 1984; Shiller and Frilot, 1996; McAlister and Orians, 2012); however, riverine Al and Ga are mostly scavenged in river plumes (Brown and Bruland, 2009; McAlister and Orians, 2012). Mid-depth minima of dissolved Al and Ga are associated with the advection of low-Ga and low-Al waters (Measures and Edmond, 1990; Measures, 1995; Shiller, 1998; Shiller and Bairroadig, 2006; Middag et al., 2015) and particle scavenging (Hydes, 1979; Moran and Moore, 1988, 1992; Orians and Bruland, 1988b; Gehlen et al., 2002; Koning et al., 2007; Li et al., 2013). Earlier studies observed a subsurface Ga/Al maximum in the Pacific Ocean with elevated Ga that was attributed to remineralization (Orians and Bruland, 1988a, b). However, the absence of a subsurface Ga/Al maximum in the Atlantic Ocean suggested that Ga distribution in the upper water column was controlled by advection (Shiller, 1998). The benthic sources of Ga and Al are likely to be sediment flux and shelf processes (Orians and Bruland, 1986, 1988a, b; Measures, 1995; Shiller, 1998; Grand et al., 2015; Middag et al., 2015). Increased Al and Ga in deep waters can be attributed to resuspended particles, especially in regions where strong boundary currents occur (Orians and Bruland, 1986; Shiller, 1998; Moran and Moore, 1991; Measures et al., 2015).

For Al, the removal mechanism involves passive and active biological scavenging, possibly associated with biogenic silica (Hydes, 1979; Moran and Moore, 1988, 1992; Gehlen et al., 2002; Koning et al., 2007; Li et al., 2013), while Ga removal is mostly by passive scavenging. Low surface water dissolved Ga and Al concentrations in highly productive waters, relative to open gyre waters, are caused by intensive
scavenging by biogenic particles (Orians and Bruland, 1986, 1988b; Shiller, 1998; Brown and Bruland, 2009). Shiller and Bairamadgi (2006) found that the surface water Ga/Al ratio correlated with chlorophyll-a in North Pacific Ocean, probably due to a faster uptake rate of Al than Ga, and suggested that a possible means for adjusting surface Al residence time estimates in the Al-based dust deposition models.

With respect to the role of biological scavenging in the cycling of Al, the Al distribution may be partially associated with the Si cycle by the incorporation of Al in diatoms and/or preferentially scavenging onto biogenic siliceous particles (e.g., Van Bennekom et al., 1991; Van Beusekom et al., 1997; Gehlen et al., 2002; Han et al., 2008; Middag et al., 2009). Various studies have examined the Si-Al relationship throughout the water column in different ocean basins. A well-correlated Si-Al relationship was found in the North Atlantic and Arctic Ocean (e.g., Kremer et al., 2004; Middag et al., 2009), as well as Mediterranean Sea (e.g., Chou and Wollast, 1997; Hydes et al., 1988). However, this positive correlation sometimes is collapsed in the North Atlantic and Mediterranean (e.g., Stoffyn and Mackenzie, 1982; Measures et al., 2015) and even is absent in the Pacific and Southern Oceans (e.g., Orians and Bruland, 1985; Middag et al., 2011). Possibly, the Si-Al correlation is regulated by the supply and export of Al and Si, as well as deep ocean circulation (Middag et al., 2011, 2015). Unlike Al, there is no study of Ga removal mechanisms by particle scavenging in the aqueous systems. However, it is known that Ga is the only element which competes with Fe for binding to siderophores (Emery and Hoffer, 1980; Emery, 1986; Gascoyne et al., 1991), suggesting Ga could be removed via active scavenging.
Combined with Al and Ga enrichments in hydrothermal vent fluids (German and Seyfried, 2014), elevated Al and Ga in the deep water near the mid-ocean ridges (Stoffyn and Mackenzie, 1982; Shiller et al., 2014; Measures et al., 2015; Resing et al., 2015) suggest that hydrothermal inputs are sources of deep water Al and Ga. However, Middag et al. (2015) argued that hydrothermal source for Al is minor on the basin wide scale, supported by the reports of insignificant hydrothermal Al sources (Lunel et al., 1990; Elderfield and Schultz, 1996).

It is known that the atmospheric sources of Ga and Al at the surface are limited in our study area due to low dust deposition in the South Pacific Ocean (Mahowald et al., 2005). A gradient in chlorophyll-a concentration across the EPZT allows for the examination of the correlation between surface water Ga/Al molar ratio and chlorophyll-a so that we can evaluate the possible means of correcting mixed layer Al residence time used in the Al-based dust deposition model (Shiller and Bairamadgi, 2006). Coupled with other particle-sensitive elements (e.g., Th and Pa), the investigation of dissolved Ga and Al distributions in the EPZT allows us to examine the roles of particle scavenging and benthic inputs in their distributions in the eastern tropical Pacific Ocean. As described above, the importance of hydrothermal sources of Al and Ga is still obscure depending on the locus of vent fields. The processes and mechanisms controlling Al and Ga distributions in the water column can be further elucidated by the studies of the 2013 U.S. GEOTRACES EPZT.
CHAPTER II – TEMPORAL AND DISTRIBUTIONS OF TRACE ELEMENTS (Ba, Cs, Cr, Fe, Mn, Mo, U, V AND Re) IN MISSISSIPPI COASTAL WATERS: INFLUENCE OF HYPOXIA, SUBMARINE GROUNDWATER, AND EPISODIC EVENTS IN A RIVER-DOMINATED SYSTEM

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2.1 Introduction

Estuarine systems, where the mixing of river water and seawater mainly takes place, are characterized with strong gradients in physical and biogeochemical properties. The behavior and distribution of trace metals in estuaries and coasts are regulated by temporal and spatial variations in riverine sources, benthic sources (e.g., sediment resuspension, submarine groundwater discharge, diffusion at the sediment-water interface), primary production, and circulation patterns. Thus, the fluvial fluxes of trace metals to the ocean can be modified in estuarine-coastal systems. In order to evaluate the magnitude and mechanism of trace element input to the coastal ocean, it is necessary to investigate the physical and biogeochemical processes controlling the distribution and partitioning of trace metals in estuarine-coastal systems.

The Mississippi Sound and Bight is a shallow estuarine-coastal system (average depth of ~3 m in the Mississippi Sound and < 20 m on the inner shelf of the Mississippi Bight) in the northern Gulf of Mexico. The Mississippi Sound receives various fluvial inputs (i.e., Mississippi River, Pearl River, St. Louis Bay outflow, Biloxi River, Pascagoula River, and Mobile Bay outflow) and is separated from the Mississippi Bight by barrier islands. Freshwater influences on the Mississippi Bight are mostly from the Mississippi River and Mobile Bay outflows. Evidence of the influence of the various
fluvial sources on our sampling sites in the western Mississippi Sound and northwestern Mississippi Bight comes from various studies. For instance, Cs-rich St. Louis Bay outflow has been observed in the western Mississippi Sound but not further into the Bight (Bera et al., 2015). However, freshwater input to the western Sound is generally dominated by the Pearl River plume during times of high Pearl River discharge (Orlando et al., 1993) which diminishes the relative influence of St. Louis Bay outflow. The influence of Mississippi River outflow on the western Mississippi Sound and northwestern Bight was suggested by the similar size fractionation of chromophores in Mississippi River water and Mississippi coastal waters (Stolpe et al., 2010). Mobile Bay outflow (which has a discharge equal to about 10% of the discharge of the lower Mississippi River) also brings substantial fresh water to the western Mississippi Bight. This is based on satellite-derived data and in situ observation (water levels, salinity, velocity, and temperature), showing that the Mobile Bay outflow tends to extend westward due to the Coriolis force, downwelling winds, high river discharges, and along-shelf westward-flowing currents (e.g., Dzwonkowski et al., 2015, 2017).

In addition to the river influences, bottom hypoxia (defined here as dissolved oxygen < 63 μM or < 2 mg/L) has been reported in the Mississippi Bight (Brunner et al., 2006; Shim, 2011). Processes controlling bottom water hypoxia development and its influence on chemical constituents in the water have been studied on the Louisiana Shelf west of the Mississippi River Delta (Shiller and Mao, 1999; Rabalais et al., 2002; Cai and Guo, 2009; Duan et al., 2010; Justic and Wang, 2014; Joung and Shiller, 2014, 2016). However, hypoxia on the eastern side of Mississippi River Delta has been studied far less than in the “dead zone” on the Louisiana Shelf. Mississippi River outflow mostly flows
westward driven by the prevalent westward winds from fall through spring (Walker et al., 2005). However, during summer, Mississippi River water and plumes are more likely to be transported east of the birdfoot delta by persistent southwest, west and south winds (Morey et al., 2003; Walker et al., 2005). Given that hypoxia on the Louisiana Shelf is related to the increased nutrient loading and strong stratification from the Mississippi River (Rabalais et al., 2010), it is worthwhile to evaluate the possible role of the Mississippi River in the Mississippi Bight hypoxia (Rabalais et al., 2002).

Additionally, the possible role of submarine groundwater discharge (SGD) in affected the chemical mass balance of the Mississippi Sound/Bight is uncertain. SGD has been shown to be globally important (Moore, 1996, 2010; Burnett et al., 2006) and can also contribute low oxygen to bottom waters (Peterson et al., 2016). Likewise, the delivery of ammonium (Windom and Niencheski, 2003; Santos et al., 2008) and possibly sulfide from the SGD to bottom waters could further deplete bottom oxygen as well as alter chemical distributions.

Various trace metal studies have been conducted on the Louisiana Shelf and have shown non-conservative behavior in a variety of trace elements when shelf water was hypoxic. For instance, previous work observed dissolved V depletion in low-oxygen bottom waters which resulted in V-depletion in surface waters by upward mixing (Shiller and Mao, 1999; Joung and Shiller, 2016). The dissolved Cr distribution on the Louisiana Shelf appears to be similarly affected (Joung and Shiller, 2016). Dissolved Mn enrichment in surface and bottom waters on the Louisiana Shelf was associated with MnO2 dissolution and enhanced trapping of enriched Mn at the bottom by strong stratification (Mallini, 1992; Joung and Shiller, 2016) whereas less enrichment of
dissolved Fe was seen in oxygen-depleted shelf waters (Joung and Shiller, 2016) due to the faster oxidation rate of Fe than Mn (Stumm, 1992). Dissolved Ba enrichments in low-salinity surface waters and salty bottom waters were attributed to desorption from fluvial particles (Hanor and Chan, 1977; Shim et al., 2012; Joung and Shiller, 2014) and benthic inputs (Joung and Shiller, 2014), respectively. Despite these previous studies, only limited work has addressed trace element distributions on the eastern side of the Mississippi River Delta, where other coastal water sources may also be important. Thus, the response of various trace metals (Ba, Cs, Cr, Fe, Mn, Mo, Re, U and V) in Mississippi coastal waters under hypoxic and non-hypoxic conditions is investigated in this manuscript.

Hypoxia significantly affects the biogeochemistry of trace elements, the structure of ecosystems in coastal waters, and the harvest of commercial fisheries (Leming and Stuntz, 1984; Renaud, 1986; Riedel et al., 1999; Rabalais and Turner, 2001a; Middelburg and Levin, 2009; Rakocinski and Menke, 2016). Investigating the causes of hypoxia is necessary for the development of policies for alleviating it. A time-series survey, conducted from the mouth of St. Louis Bay, MS and through the western end of Mississippi Sound and into the northwestern corner of the Mississippi Bight (“NGI transect”), provided an opportunity to understand seasonal and spatial variations of hypoxia in the Mississippi Sound and Bight system. This study investigates the causes of hypoxia and the factors controlling the distribution of various trace elements in this region from late 2007 through 2011.
2.2 Methods and Materials

2.2.1 Study area

The NGI transect of eight stations extended southeastward from the Mississippi coast into the Mississippi Sound and Bight (Fig. 2.1). This transect receives material from various sources which include fresh waters from the Mississippi River and other local rivers, seawater from the Gulf of Mexico, and possibly SGD from the bottom.

Figure 2.1 Map of sampling locations along the NGI transect.

Note: Red dots labeled with station names. Contour lines show 10, 20, and 30 m isobaths.

2.2.1.2 Riverine sources

Major sources of freshwater to the western Mississippi Sound and northwestern corner of Mississippi Bight are from the Mississippi and Pearl Rivers, as well as St. Louis Bay (Fig. 2.1). The watersheds of three fluvial sources are distinctly different.

The Mississippi River is known to carry high nutrients, low salinity, and high sediment loads to the Louisiana and Mississippi coastal regions (Jochens et al., 2002). The Mississippi River water enters the northern Gulf of Mexico through the birdfoot delta. The plume direction varies throughout the year depending on the prevailing winds,
typically westward from fall through spring and eastward in summer (Morey et al., 2003). The Mississippi River outflow creates strong stratification and brings high levels of anthropogenic nutrients to the Louisiana Shelf which results in bottom hypoxia in that region during spring and summer (Rabalais et al., 2010).

The Pearl River drains central and southern Mississippi and southeastern Louisiana and finally enters into the west end of Mississippi Sound. The watershed is mostly covered by upland forest (43%) while agriculture and urban areas accounting for 28% of watershed in the Pearl River (MDEQ, 2007a). The Pearl River is a relatively pristine environment, compared with the Mississippi River system and St. Louis Bay.

St. Louis Bay, a shallow (~1.5 m) estuary, mainly receives freshwater from the Jourdan and Wolf Rivers and connects to the Mississippi Sound through a narrow passage (~3 km wide). Both local rivers have relatively small watersheds in comparison to the Mississippi River and Pearl River. Similar to the Pearl River Basin, more than half of the St. Louis Bay watershed is covered in forest (MDEQ, 2007b). However, a DuPont titanium dioxide refinery is located at the northern of St. Louis Bay and appears to be the source of elevated dissolved Cs in the Bay (Bera et al., 2015) since Cs salts can be used as a nucleant substance in titanium dioxide refineries (Allen and Evers, 1993). The influence of nutrient input is mostly limited inside the bay while increased phosphate (0.03–1.8 μM) concentration toward the mouth of bay may be caused by sediment resuspension, anthropogenic inputs, and mixing with phosphate-enriched seawater from the Mississippi Sound (Shim, 2011; Cai et al., 2012).

The Mississippi Sound also receives freshwater from the Pascagoula River and Mobile Bay outflow; however, influences of these rivers are more significant in the
central and eastern Sound and less important in the western Sound. Similar to the Pearl River, the watershed of Pascagoula River is mostly covered by forest (MDEQ, 2000). Fluvial inputs to Mobile Bay are mainly from the Alabama and Tombigbee Rivers, located within the Mobile River system, which has the fourth largest discharge in the USA (ADEM, 2010). Most of Mobile Bay outflow (~64 %) empties to the Alabama continental shelf through Main Pass, and is considered as a major freshwater source to the Mississippi Bight, and the remaining outflow enters into the eastern Mississippi Sound via Pass-aux-Herons (Kim and Park, 2012).

2.2.1.3 Bonnet Carré Spillway

The Bonnet Carré Spillway is a flood control structure in the lower Mississippi River system, operated by the U.S. Army Corps of Engineers. With an approaching flood stage of the Mississippi River, the operation of spillway relieves pressure of levees and lessens threat of flooding in New Orleans by diverting a portion of Mississippi River water flow into Lake Pontchartrain, finally entering into the northern Gulf of Mexico in our study region. The spillway is opened to keep the discharge above New Orleans at or below $3.54 \times 10^4 \text{ m}^3/\text{s}$. During the study period, the Bonnet Carré Spillway was opened in April 2008 and May 2011. The spillway was partially opened on April 11, 2008 and continued for 19 days with 160 of 350 of its bays opened at peak (max. flow: $4.5 \times 10^3 \text{ m}^3/\text{s}$). In 2011, the spillway was opened on May 19 and closed 43 days later with 330 bays opened at peak (max. flow: $9.0 \times 10^3 \text{ m}^3/\text{s}$).

2.2.1.4 Mississippi Sound and Bight

The Mississippi Sound is an elongated and shallow (average depth < 3 m) basin along the Alabama-Mississippi coast in the northern Gulf of Mexico, extending from
Lake Borgne to Mobile Bay and partially enclosed with barrier islands to the south. Mississippi Sound exchanges water with the Mississippi Bight via the passes between the barrier islands. In the Mississippi Sound, current patterns are complicated by tidal currents through the passes and the variation of river discharge in local rivers (Boone, 1973). A 180-day flow field time-series observation from spring to fall showed the mean surface flow (30–60 cm/s) is mostly eastward in the western Mississippi Sound and the mean bottom flow is deviated slightly left relative to mean surface flow (Kjerfve, 1983), whereas a wave-driven longshore westward current (40 cm/s) was seen along the Mississippi coastline (Boone, 1973).

The Mississippi Bight, within the Alabama-Mississippi continental shelf, extends seaward from the barrier islands. The western Mississippi Bight is bounded to the west by the Chandeleur Islands and Breton Sound. In the Mississippi Bight, the seasonal current circulation showed eastward-flow in late spring and westward-flow in late fall along the shelf, with strong association to wind directions (He and Weisberg, 2003; Morey et al., 2003; Dzwonkowski and Park, 2010). Core, drill hole, and seismic data indicate the existence of paleochannels extending from the Mississippi coast to at least the barrier islands (Oivanki and Otvos, 1994). There are also buried paleochannels within the Mississippi River system (e.g., Kolker et al., 2013), though the extent of these into the Mississippi Bight is unclear. These paleochannels or buried sand depositions are potential pathways for SGD to flow into the coastal zone (Kolker et al., 2013).

2.2.2 Sample collection

Monthly or bimonthly sample collection was carried out at eight stations (Stns. 1–8) along the NGI transect from late 2007 through 2011 (Fig. 2.1). A package of sensors (a
Seabird SBE 49 CTD, a Seabird SBE 43 sensor (dissolved oxygen sensor) and a WetLabs ECO Puck (optical sensor) mounted within a frame was deployed at all stations to obtain vertical hydrographic profiles. Water samples were collected only at the surface in the Mississippi Sound (nearshore stations, Stns. 1–4) whereas both surface and bottom water samples were collected in the Mississippi Bight (offshore stations, Stns. 5–8). For trace metal samples, surface waters were collected in an acid-cleaned polyethylene [PE] sample bottle attached to a metal-free submerged rod. Surface nutrient and chlorophyll a [Chl-a] samples were obtained by leaning over the boat and filling a brown Nalgene bottle which was rinsed with Nanopure water followed by 10% HCl rinse before cruises. Bottom samples were collected by pumping bottom waters to the surface and filling an acid-cleaned PE bottle for trace metal samples and an acid-cleaned brown Nalgene bottle for nutrient and Chl-a samples, respectively. The pump consisted of C-flex tubing attached to a peristaltic pump and other sections were connected with Teflon-lined polyethylene tubing. Some parameters were not collected throughout the entire study period, such as dissolved oxygen (sensor deployed after June 2008), discrete Chl-a samples (collected after June 2009) and oxygen isotope ratio of water samples (collected during June–November 2011). All samples were returned to the laboratory and further processes as soon as possible.

2.2.3 Ancillary Data

Ancillary data (salinity, temperature, pressure, dissolved oxygen [DO], Chl-a fluorescence) were obtained from the deployment of a package of sensors mounted within a frame. The DO sensor was calibrated by Winkler titration of discrete water samples. The optical sensor determined Chl-a fluorescence with excitation (EX) and
emission (EM) wavelengths at 470 and 695 nm. The optical sensor was sent back to the WetLabs in June 2006, October 2008 and February 2011 for the manufacturer’s calibration of chlorophyll concentration which was performed in both a proxy solution (uranine) and by a serial dilution (µg/L) of *Thalassiosira weisflogii*. A dark count was conducted in the laboratory to check the offset of the fluorometer before cruises.

2.2.4 Analytical Methods

2.2.4.1 Nutrient, chlorophyll a and the oxygen isotope composition (δ¹⁸O) of water

Nutrient samples were filtered through 47 mm diameter GF/F filters (Whatman, 0.7 µm nominal pore size) and frozen until analysis. Dissolved nutrient concentrations were determined by an Astoria 2 segmented flow nutrient analyzer (Astoria-Pacific). Additional discrete Chl-a samples, only collected from June 2009 to November 2011, were retained on 25 mm diameter GF/F filters (Whatman, 0.7 µm). After the methanol extraction of Chl-a, extracted Chl-a was measured using a Turner Designs 10AU fluorometer in the laboratory. In our results and discussion section, measured Chl-a refers to Chl-a concentration in these discrete samples. The δ¹⁸O of water samples, only collected from June-November 2011, was determined using isotope ratio infrared spectroscopy (L2120-i cavity ring-down spectrometer, Picarro Inc.). The procedure for raw data correction and calibration of oxygen isotope data is described in van Geldern and Barth (2012). Calibration of the isotope data to the VSMOW scale was done by measuring in house standards that had been cross-calibrated with VSMOW-2 and SLAP-2.
2.2.4.2 Dissolved trace metals

For dissolved trace metal samples, water was filtered through pre-cleaned 0.45 and 0.02 µm pore size syringe filters (Shiller, 2003). Below, we refer to the < 0.45 µm filtrate as the total dissolved fraction and the < 0.02 µm filtrate as the dissolved fraction, with the understanding that these are somewhat arbitrary operational definitions. The colloidal fraction is thus the difference between these two fractions (< 0.45 µm and < 0.02 µm). Filtered samples were brought back to the laboratory and acidified to pH < 2 with 6 N ultra clean HCl (Seastar Baseline). After acidification, samples were stored in a clean space at room temperature until analysis. Total dissolved and truly dissolved trace metals (Ba, Cs, Cr, Fe, Mn, Mo, Re, U and V) in surface and bottom waters were determined using a sector-field inductively coupled plasma-mass spectrometer (ICP-MS, Thermo-Fisher Element 2). Since most elements were dominantly in the dissolved fraction (except for Fe) in our samples, we focus on the total dissolved trace element concentrations in this manuscript except where the colloidal fraction (i.e., Fe) becomes important.

For samples collected before November 2008, trace elements were analyzed by both a simple dilution method and a variant of the Magnesium-Induced Co-precipitation method (MagIC) (Wu and Boyle, 1997; Shim et al., 2012). We report Fe, Mn and V concentrations analyzed using the MagIC method due to higher precision of these elements with the MagIC method, compared with the dilution method. For other elements (Ba, Cs, Cr, Mo, Re and U), reported concentrations were analyzed by the dilution method because these elements were not targeted (Ba, Cs, Mo, Re and U) or had low recovery (Cr) with the MagIC method. For samples collected after November 2008, all
trace element concentrations were only determined using the dilution method. Thus, after November 2008 reported trace metal concentrations were obtained from the dilution method.

2.2.4.2.1 Dilution method

In the dilution method, samples were diluted 20-fold with 0.3 M ultrapure HNO₃ (Seastar Baseline) which contained a known amount of In and isotopically-enriched ⁵⁰V, ⁵⁷Fe, ⁹⁵Mo, ¹³⁵Ba and ¹⁸⁵Re. The In response was used for an initial instrumental drift correction and sensitivity check. The concentrations of V, Fe, Mo, Ba and Re are calculated from their isotope ratios and the known isotope spike. For Cs and U, determined in low resolution, the instrumental drift was corrected by a response factor, which is derived from the instrumental response (cps/nM) of ⁹⁵Mo and ¹³⁵Ba (low resolution). A response factor derived from the instrumental response (cps/nM) of ⁵⁷Fe (medium resolution) was applied in the instrumental drift correction for Cr and Mn, which were determined in medium resolution. For Cs, Mn, Cr and U, the calibrations were performed by standard additions to a seawater sample (see details in Shim et al., 2012).

2.2.4.2.2 Magnesium-Induced Co-precipitation (MagIC) method

In the MagIC method, a small amount of ultrapure 7 M NH₄OH was added into the equilibrated mixture of enriched isotope (⁵⁰V and ⁵⁷Fe) and sample to form a small amount of Mg(OH)₂ precipitate which contains the target elements. After centrifugation and pouring off the supernatant, the precipitates were dissolved in a small amount of 0.3 M HNO₃ (Seastar Baseline) and analyzed by ICP-MS. The concentration of Mn in this method was derived from the intensity factor of ⁵⁷Fe in the same way as was described in
the dilution method. To verify the accuracy of trace metal analysis, a seawater standard reference material (NASS-5, NRC-Canada) was measured at the beginning and end of each run. For Fe, the recovery was examined by standard additions to an in-house reference solution. The recoveries are shown in Table 2.1.

The NGI data can be found at the GRIIDC data repository (doi: 10.7266/N77M06C6).

Table 2.1

<table>
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<tr>
<th></th>
<th>V(^a)</th>
<th>Fe(^*)</th>
<th>Mn</th>
<th>Cs(^b)</th>
<th>Ba(^c)</th>
<th>Cr</th>
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<tr>
<td>NASS-5 (nM)</td>
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<td>1.91</td>
<td>37.1</td>
<td>2.1</td>
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<tr>
<td>Average (nM)</td>
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<td>18.3</td>
<td>1.88</td>
<td>37.7</td>
<td>2.4</td>
<td></td>
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<tr>
<td>Standard deviation</td>
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<td>1.6</td>
<td>0.09</td>
<td>3.0</td>
<td>0.4</td>
<td></td>
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<td>Recovery (%)</td>
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<td>99±13%</td>
<td>109%</td>
<td>99%</td>
<td>103%</td>
<td>116%</td>
</tr>
<tr>
<td>n</td>
<td>17</td>
<td>9</td>
<td>21</td>
<td>20</td>
<td>19</td>
<td>15</td>
</tr>
</tbody>
</table>

Note: \(^a\) NASS-5 concentration was used uncertified informative concentration listed on the NASS-5 certification sheet. \(^b\) NASS-5 concentration was estimated from average oceanic Cs concentration (2.0) adjusted to the NASS-5 salinity of 30.4. \(^c\) NASS-5 concentration was taken from Field et al. (2007). * The recovery of Fe was derived from the standard addition of in-house solution at each run.

2.3 Results and Discussion

2.3.1 Hydrology and precipitation

During the study period, the annual cycle of the Mississippi River showed peak flow in spring and low flow in the fall, with an exception in 2009 (Fig. 2.2a). In 2009, the peak of flow \((3.4 \times 10^4 \text{ m}^3/\text{s})\) occurred in June, later than the observed maximum flow in other years. Also, the discharge stayed within a range of \(1.4–3.0 \times 10^4 \text{ m}^3/\text{s}\) between mid-November 2009 and June 2010, which is different from the observation of a consistent increasing discharge from late fall to spring in other years. Two peak discharges in late-
April 2008 (3.7 × 10^4 m^3/s) and mid-May 2011 (4.1 × 10^4 m^3/s) caused the opening of the Bonnet Carré Spillway in April 2008 and May 2011 (see section 2.1.2). In contrast, the Pearl River and Wolf River discharges were commonly low in summer and variable in other seasons (Fig. 2.2b). The highest flows in the Pearl River (2.0 × 10^3 m^3/s) and Wolf River (3.9 × 10^2 m^3/s) were observed in April 2009. Both rivers generally showed a similar variation in discharge during our time series, except for early 2009. Monthly precipitation data showed no specific wet or dry seasons in this local area (Fig. 2.2c), but a record high precipitation for local regions near the Mississippi and Louisiana coasts (Waveland, MS; Lakefront, LA) in December 2009 (Fig. 2.2c) corresponded with relatively high flows in the Mississippi, Pearl and Wolf Rivers (Fig. 2.2a, b).

The meteorological data, provided by the NOAA National Data Buoy Center (NDBC, http://www.ndbc.noaa.gov/), was used to calculate the frontal index which is a composite of barometric pressure (p), air temperature (T) and wind stress (τ) that can be used to identify the intensity and strength of a cold front (Perez et al., 2000). The definition of a cold front is that the wind direction shifts from southerly to northerly (Perez et al., 2000). A significant cold front event is recognized by exceeding the threshold of three factors (\( \frac{dp}{dt} > 0.3 \text{ mbar}, \frac{dT}{dt} < 0.2 \degree \text{C}, \tau > 0.10 \text{ N/m}^2 \)) (Perez et al., 2000). The results of our calculated frontal index at two buoy sites (Station SHBL1–8761305–Shell Beach, Louisiana; Station GPOM6–8744707–Gulfport Outer Ranger, Mississippi) from mid-2008 through 2011 indicate that cold fronts rarely pass this area in late spring and summer (frontal index of 2009 and 2011 shown in Fig. A.1). Tropical Storm Lee on 2–5 September 2011 brought enhanced precipitation to the local area and increased Pearl River and Wolf River flows (Fig. 2.2b, c), compatible with an increasing
frontal index (Fig. A.1). Temporal variability of flows in these rivers indicates that the discharge in the Mississippi River is regulated by the melting snow in the upper Mississippi River basin while the Pearl River and Wolf River discharges are predominantly influenced by local precipitation (Fig. 2.2).
Figure 2.2 Temporal variability of discharge in (a) the Mississippi River at Baton Rouge, LA, (b) the Pearl River at Bogalusa, MS and the Wolf River at Landon, MS during late 2007 through 2011. (c) Monthly accumulated precipitation at local areas during 2008 and 2011

Note: In Fig. 2.2 (b), black line shows Pearl River discharge on the left axis and red line shows Wolf River discharge on the right axis. River discharge data from US Geological Survey: https://waterdata.usgs.gov/nwis. Open circles indicate our sampling dates. Gray shaded areas indicate periods of Bonnet Carré Spillway opening. Precipitation data from National Climatic Data Center, NOAA: http://www.ncdc.noaa.gov/cdo-web/)

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2.3.2 Ancillary Data

2.3.2.1 Salinity and Temperature

Temporal and spatial patterns of surface salinity, as shown in Fig. 2.3a, indicate fresh water was transported further offshore in spring and summer, consistent with increased freshwater discharge of Mississippi River at that time of year. However, the seaward extent of freshwater signals varied each year. Two distinct freshwater signals in April 2008 and May 2011 were caused by the opening of the Bonnet Carré Spillway (Fig. 2.3). The spillway operation discharges Mississippi River water into Lake Pontchartrain and finally into the northern Gulf of Mexico. Low-salinity water was transported further offshore along the sampling line in May 2011 compared with April 2008 due to more open days and open bays of the spillway in May 2011 than in April 2008. In August 2009, saline water (S = 25.1‒30.7) was observed at the surface in the Mississippi Sound (Fig. 2.3a), corresponding with relatively low Mississippi River discharge in spring, low local river influxes (Pearl, Wolf, Jourdan, Biloxi, Pascagoula Rivers) and low Mobile Bay outflow in summer. Indeed, the sampling trip in August 2009 was conducted three days after Tropical Storm Claudette made landfall at Fort Walton Beach, Florida (~90 miles west of Mobile Bay). Although three was no increase in precipitation or wind speeds in our study area during mid- and late August 2009, offshore saline water was likely transported onshore due to wind forcing by this tropical storm. A similar case of an onshore transport of saline water in the Mississippi Sound and Bight due to a storm passage was observed by Cambazoglu et al. (2017) and Dzwonkowski et al. (2017).

Previous studies observed that water exchange in Louisiana bays can be caused by meteorological flushing events, as related to cold fronts and storms (Feng and Li, 2010).
A similar meteorological flushing event was observed in fall 2015 on the Mississippi-Alabama shelf, followed by an inflow of saline shelf water toward to the shore (Cambazoglu et al., 2017; Dzwonkowski et al., 2017). We observed similar phenomena during our time series study. With regard to meteorological flushing events, low-salinity water (S = 3.6) was observed at Stn. 1 in January 2010 and its influence extended across the Mississippi Sound (Stn. 4, S = 16). This was related to high precipitation and increasing front index in December 2009 in the local area (Figs. 2c, 3a and A.1; see section 2.3.1). Also, the inflow of offshore water toward the coast was seen in August 2009 (mentioned earlier) and September 2011. In September 2011, there was a very low salinity of 8.8 and a δ¹⁸O signature influenced by the Mississippi River at Stn. 3 which was associated with increased precipitation due to Tropical Storm Lee (discussed below; Figs. 2.2c and 2.3a).

Salinity data in bottom water, provided by the CTD sensors, showed fresher water in spring/summer and saltier water in fall/winter (Fig. 2.3b). Low-salinity bottom water was restricted to the Mississippi Sound (Fig. 2.3b) while low-salinity surface water extended further offshore in spring and summer (Fig. 2.3a). During the periods when the freshwater plume extended offshore, mostly in spring and summer, the difference between surface and bottom salinity is smaller in the Mississippi Sound than in the Mississippi Bight. This reflects that the Sound water column is easily mixed due to its shallow depth (3–5 m). During fall and winter, less difference between surface and bottom salinity through the NGI transect suggests the water column was well-mixed in fall and winter, compared with spring and summer conditions.
The temporal and spatial temperature distribution in surface water shows that temperature varied greatly with season with the coldest temperatures (5.1°C) in winter and the warmest temperatures (32.5°C) in summer (Fig. 2.3a). The coldest temperature was observed at the mouth of St. Louis Bay and propagated over the shelf in January 2010, coupled with observed low salinity in the Mississippi Sound, due to increased local precipitation in December 2009. The bottom temperature distribution is similar to the distribution of surface temperature (Fig. 2.3).
Figure 2.3 Temporal and spatial distributions of salinity and temperature in (a) surface waters and (b) bottom waters.

Note: Sampling sites/dates are shown by black dots. The numbers on the right axis are station number. Arrows indicate periods of the Bonnet Carré Spillway opening.
2.3.2.2 Chlorophyll a fluorescence and measured chlorophyll a concentration

In order to evaluate the representativeness of Chl-a fluorescence measurement, we examined the correlation between Chl-a fluorescence and measured Chl-a concentration. Chl-a fluorescence is well-correlated with measured Chl-a in 2010 and 2011, with similar slopes of the regression lines in both years, although there are a few scattered points at high Chl-a (Fig. A.2). In 2009, excluding a few outliers of low measured Chl-a concentration but high Chl-a fluorescence, the slope of the linear regression line is similar to that of 2010 and 2011 (Fig. A.2). Scattered points and outliers can be caused by the vertical variability of phytoplankton. Note that the in situ discrete Chl-a sampling method was different from the deployment of optical sensors (see section 2.2.2), and it is possible that the depth where the reading of Chl-a fluorescence was taken from was not the same sampling depth as in situ Chl-a samples. In general, a well-correlated relationship between Chl-a fluorescence and measured Chl-a in our dataset suggests that Chl-a fluorescence data was a representative but semi-quantitative indicator for the phytoplankton biomass.

Both Chl-a fluorescence and measured Chl-a data show low Chl-a in winter and increased Chl-a in summer at the surface (Fig. 2.4a, c), with a gradient of increasing Chl-a concentration from offshore toward the coast. In bottom waters, measured Chl-a concentration decreased offshore, consistent with Chl-a fluorescence data (Fig. 2.4b, d). However, no clear seasonal pattern of bottom Chl-a was found in fluorescence nor in discrete samples. We focus our attention on measured Chl-a concentration below since measured Chl-a concentration is a quantitative analysis. In the Mississippi Bight, surface Chl-a was generally higher than bottom Chl-a, except for March 2010 (Fig. 2.4d).
Relatively high Chl-a concentrations (32–95 µg/L) were seen in surface waters (Stns. 1–6, Fig. 2.4c) in June 2011, which might have resulted from the Bonnet Carré Spillway opening the previous month. That is, diversion of Mississippi River water into Lake Pontchartrain has been observed to cause algal blooms in the lake (e.g., Mishra and Mishra, 2010) which could then export the Chl-a to the Mississippi Sound and Bight and leave the waters of our study area relatively nutrient-poor as we observed (see section 2.3.2.5). The observation of high suspended particulate matter [SPM] concentrations in June 2011 provides additional evidence of the influence of the spillway opening on the Mississippi Sound and Bight (Vandermeulen, 2012). That is, that the SPM in the Mississippi Sound and Bight in June was the highest observed that year suggests the transport of high river-borne suspended particles from the Mississippi River (Turner et al., 2007) and/or increased sediment resuspension in Lake Pontchartrain during the opening of the Bonnet Carré Spillway in 2011. Unfortunately, discrete Chl-a samples were not collected in April/May 2008 and the SPM data was not available before 2011; thus, we cannot make a comparison of the Spillway openings in 2008 and 2011.
Figure 2.4 Temporal and spatial variations of Chl-α fluorescence in (a) surface waters at Stns. 1–8 and (b) bottom waters at Stns. 5–8 during late 2007–2011. The temporal and spatial variations of measured Chl-α concentration (c) in surface water at Stns. 1–8 and (d) in both surface and bottom water at Stns. 5–8 from June 2009–2011.
2.3.2.3 Dissolved Oxygen (DO)

The DO data show that bottom water hypoxia extended from Stn. 4 to Stn. 8 in late spring and summer during the study period, except for 2009 (Fig. 2.5a). DO profiles (Fig. 2.5b) reveal that hypoxia was confined between mid-depth and the bottom. The presence of a strong pycnocline in summer (Fig. A.3) prevented oxygen-rich surface water from mixing with oxygen-depleted bottom water. In order to estimate water column stratification, the potential energy anomaly (\(\phi\)) (i.e., the energy required to mix the water column) is used for the evaluation of stratification, with higher values representing a more stable water column (Simpson and Bowers, 1981). The potential energy anomaly is calculated from:

\[
\phi = \frac{1}{h} \int_{z=0}^{h} (\rho_{avg} - \rho(z))g z \, dz \quad (J/m^3)
\]

where \(h\) is water column depth, \(g\) the gravitational acceleration, and \(\rho_{avg}\) the depth averaged density.

The seasonal pattern of \(\phi\) reveals that summertime stratification persisted offshore (Fig. 2.5b), suggesting the importance of stratification for hypoxia formation in Mississippi Bight bottom water. Bottom oxygen depletion was relatively weak in summer 2009 and that year also showed the lowest summertime \(\phi\) of our time series. Multiple factors including low local river flows in summer, closure of the Bonnet Carré Spillway, and Tropical Storm Claudette (August 16–17, 2009) resulted in relatively weak stratification in summer 2009.
Figure 2.5 (a) Temporal and spatial distributions of dissolved oxygen concentration in bottom waters. (b) Temporal variability of potential energy anomaly ($\phi_i$) and dissolved oxygen profiles at Stns. 4–8.

Note: White contour lines indicate dissolved oxygen of 63 µM (i.e., 2 mg/L, the local hypoxia limit)
2.3.2.4 The δ\textsuperscript{18}O of water

Water samples for δ\textsuperscript{18}O analysis were only collected from June through November 2011. Plots of δ\textsuperscript{18}O versus salinity show that the Mississippi Sound and Mississippi Bight waters were characterized by two mixing lines in summer 2011 (Fig. 2.6a). Specifically, samples collected within the Sound extrapolate to a zero-salinity δ\textsuperscript{18}O of -2.6 to -4.4‰ while samples collected in the Bight extrapolate to a zero-salinity δ\textsuperscript{18}O of -5.3 to -6.5‰. This suggests different freshwater endmembers dominated the mixing with seawater in these two regions in summer 2011. This is reasonable given that fluvial δ\textsuperscript{18}O measurements reported by Coplen and Kendall (2000) indicate that the Wolf River (a major source of fresh water to St. Louis Bay) is considerably isotopically heavier (-2.66 to -4.09 ‰) than the Mississippi River (-5.99 to -7.54 ‰, near Arkansas City). The Pearl River, a major freshwater source to the western Mississippi Sound, has a similar δ\textsuperscript{18}O signature (-3.78 to -4.38 ‰) (Sanial et al., submitted.) as the Wolf River. We also expect that δ\textsuperscript{18}O signatures in other rivers (Pascagoula and Mobile River systems) and local rivers (Pearl and Wolf Rivers) are alike since the latitude of their meteoric source is similar. In other words, our data indicate that waters in the northwestern part of the Mississippi Bight were predominantly affected by mixing of Mississippi River water and seawater during the 2011 hypoxic periods. Note, however, that 2011 was a high discharge year for the Mississippi River, which resulted in the opening of the Bonnet Carré Spillway and thus we cannot be sure that our conclusions here are generally true regardless of discharge. Indeed, a comprehensive physical/biogeochemical study of the Mississippi Bight showed limited influence from Mississippi River on the northwestern Mississippi Bight in various seasons (Greer et al., 2018; Sanial et al., submitted.). Thus,
we the influence of the Mississippi River on the western Mississippi Sound and Bight observed during the 2011 hypoxia might be an unusual episodic consequence of the opening of spillway due to the high Mississippi discharge.

Interestingly, the lightest $\delta^{18}$O was observed at Stns. 3 and 4 in September 2011, and plotted on a trend suggesting mixing with fresh water predominantly from the Mississippi River (Fig. 2.6b). Low Cs concentrations at these stations (Fig. 2.8; see below) help confirm this. This pulse of low salinity water near the barrier islands was likely caused by a tropical storm (Lee) during September 2–5, 2011, coincident with increased precipitation (mentioned in section 2.3.1). In October and November, the effective $\delta^{18}$O in the zero-salinity endmember became progressively more positive than the September endmember, suggesting a relaxation to conditions wherein the local rivers became the dominant freshwater source for the study region during fall 2011.

Figure 2.6 Plots of $\delta^{18}$O of water versus salinity during June–November 2011.

Note: $\delta^{18}$O in nearshore surface (Stns. 1–4, open circles), offshore surface (Stns. 5–8, solid circles) and bottom waters (Stns. 5–8, triangles) in (a) June (black), July (purple), August (red), (b) September (grey), October (green) and November (magenta). The dashed lines and solid lines in Fig. 2.6 (a) show the linear regressions of $\delta^{18}$O in Mississippi Sound waters and in Mississippi Bight waters, respectively. The solid lines in Fig. 2.6 (b) represent the linear regression of $\delta^{18}$O in Mississippi Sound and Bight waters. Note that the lowest salinity and the lightest $\delta^{18}$O versus in September 2011 was found at Stn. 3.
2.3.2.5 Nutrients

Figure 2.7 shows the basic concentration levels and variations of the macro-nutrients. Surface water concentrations of dissolved inorganic N (DIN = NO₃ + NO₂ + NH₄) and PO₄ were detectable but typically sub-micromolar and with a low (~1) DIN/PO₄ molar ratio (Table 2.2), even at the lower salinities. This suggests that DIN was generally more limiting in surface waters than PO₄. We also cannot exclude a source of PO₄ to the Mississippi Sound from the Superfund site at the former Mississippi Phosphates Corporation (Pascagoula, MS) operation (e.g., Eleuterius, 1976; U.S. EPA) that might be responsible for replete PO₄, relative to DIN, in our study area. In contrast, dissolved Si was high in surface waters of the transect as compared with typical open ocean surface waters, due to the influence of high fluvial Si concentrations and apparent limited removal in St. Louis Bay and the Sound. This resulted in a high surface water Si* (Si* = Si - DIN).

We note that low-Si surface water was usually observed at Stns. 7 and 8 within a salinity range of 20–30 (Fig. 2.7b), mostly in late spring and summer, accompanied occasionally with depleted Ba, except for 2009 (discussed below; Fig. A.4). This also reflects on relatively low Si* (median values: ~3) in surface waters at Stns. 7 and 8, in comparison to Si* values in nearshore surface waters, and was likely caused by diatom uptake.

In the bottom waters, nutrient levels contrasted spatially with surface water concentrations as well as temporally between hypoxic and non-hypoxic conditions (Fig. 2.7, Table 2.2). During well-oxygenated periods, bottom PO₄ and Si concentrations were generally similar to concentrations in surface waters of similar salinity, though DIN was
often significantly higher in bottom water than surface waters. This resulted in a higher bottom molar DIN/PO$_4$ ratio (~12) and a lower (though still elevated) Si* (~6) in non-hypoxic bottom waters as compared with surface waters. During periods of bottom water hypoxia, however, all three of the macro-nutrients in the salty bottom waters became significantly elevated relative to both surface waters and non-hypoxic bottom waters (Table 2.2). These elevated nutrient concentrations during periods of hypoxia are higher than can be accounted for by fluvial input (diluted to high salinity) or upwelling of off shelf waters and thus are likely derived from the sediments through diffusion or input of SGD. Note that while dissolved organic nitrogen (DON) was not measured in our study, it was also likely enriched in inputs from the sediments (e.g., Santos et al., 2009; Couturier et al., 2017). We also note that the Si increase in typical hypoxic bottom waters (compared to non-hypoxic bottom waters) is about twice that of the DIN increase (Table 2.2). Since biogenic silica tends to be less efficiently remineralized than organic nitrogen, one possible explanation for this observation is that Si-rich SGD is a significant source of nutrients to the bottom water. Supporting this is the observation of dissolved Ba concentrations (discussed below) in salty bottom waters that are significantly higher than dissolved Ba found in typical shallow North Atlantic waters (Chan et al., 1977; Shaw et al., 1998). However, we can’t eliminate the possibility that DIN is consumed faster than Si by benthic organisms as evidenced by increased bottom Chl-a fluorescence in spring (Fig. 2.4b).
Figure 2.7 The distributions of nutrients in Mississippi Sound surface waters and Mississippi Bight waters under (a) non-hypoxic and (b) hypoxic conditions. (c) The concentrations of dissolved nitrogen species in offshore bottom waters during late 2007 through 2011.

Note: In Fig. 2.7 (a and b), open circles represent Mississippi Sound surface waters. Mississippi Bight surface and bottom waters are shown in solid circles and triangles, respectively. Note that not all but most bottom samples shown in Fig. 2.7 (b) were oxygen-depleted (DO < 63 μM or < 2 mg/L). Figure 2.7 (c) is shown in next page. In Fig. 2.7 (c), black colors represent ammonium. White and red colors represent nitrite and nitrate, respectively.
Table 2.2

Median values of chemical properties in surface waters, bottom oxic waters, and bottom hypoxic waters.

<table>
<thead>
<tr>
<th></th>
<th>S (µM)</th>
<th>DIN (µM)</th>
<th>PO₄ (µM)</th>
<th>Si (µM)</th>
<th>Mn (nM)</th>
<th>Fe (nM)</th>
<th>Ba (nM)</th>
<th>Chl-a (µg/L)</th>
<th>DIN/PO₄</th>
<th>Si* (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>22.1</td>
<td>0.4</td>
<td>0.4</td>
<td>16</td>
<td>22</td>
<td>14</td>
<td>245</td>
<td>7.2</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>Bottom (&gt; 63 µM DO)</td>
<td>33.6</td>
<td>3.7</td>
<td>0.3</td>
<td>9</td>
<td>23</td>
<td>13</td>
<td>110</td>
<td>4.9</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Bottom (&lt;63 µM DO)</td>
<td>34.7</td>
<td>13.6</td>
<td>1.3</td>
<td>38</td>
<td>612</td>
<td>15</td>
<td>153</td>
<td>4.6</td>
<td>12</td>
<td>23</td>
</tr>
</tbody>
</table>
During March 2010 and September 2011, both of which were non-hypoxic periods, elevated bottom DIN relative to other non-hypoxic periods was observed (Fig. A.5). In March 2010, there was also an elevation in dissolved Mn and Fe in the bottom waters (discussed below) and the potential energy anomaly (Fig. 2.5b) and density profiles showed a stratified layer below 6.5 m in the offshore stations (Fig. A.5). Bottom DO at the offshore stations was 95–127 µM at this time and was hypoxic during our next sampling in May 2010. It thus appears that March 2010 was at the beginning of the hypoxia initiation period, with bottom water DO decreasing but not yet hypoxic. Interestingly, this period also showed the highest bottom water Chl-a concentrations among all bottom water samples over our time series, suggesting that the bottom-derived nutrients may fuel early spring benthic primary production at least until DO is depleted.

For September 2011, rather than the initiation of bottom hypoxia, we appear to be observing its termination. Besides DIN (mostly ammonia), dissolved Ba was also elevated in the bottom waters and DO was below 127 µM at two of the offshore stations whereas conditions had been hypoxic at three of the four offshore stations the previous month. Ten days before our September 2011 sampling, Tropical Storm Lee made landfall in south-central Louisiana, passing 350 km southwest of our study area before landfall and 180 km north afterwards, thus providing the energy for the partial mixing and infusion of oxygen into the bottom waters.

Examination of the distribution of DIN species in hypoxic bottom waters is also instructive (Fig. 2.7c). Closer inshore (Stns. 5 and 6), NH₄ dominates, while at the more offshore stations (7 and 8), nitrate dominates, despite similar concentration levels in the bottom waters of these stations. This suggests the possibility of input of reduced species
such as NH$_4$ close to the barrier islands and gradual oxidation as the bottom water moves further offshore. Based on the observation of artesian springs and brackish ponds on the barrier islands as well as seismic data indicative of buried river channels beneath the Sound (Oivanki and Otvos, 1994), it is certainly possible that the islands could be a locus of SGD inputs and that reduced SGD inputs could drive an oxygen demand in the bottom waters (e.g., Peterson et al., 2016).

2.3.3 Temporal and spatial variabilities of trace metals

2.3.3.1 Cs, Mo, U and Re

Dissolved Cs is conservatively distributed in seawater with a concentration of 2.2 nM (Spencer et al., 1970; Brewer et al., 1972). In local river waters, Cs concentrations are sub-nanomolar (Shim, 2011; Joung and Shiller, 2016) and the dissolved Cs distribution in Mississippi River plume waters is generally conservative (Shim et al., 2012; Joung and Shiller, 2016). However, St. Louis Bay is a source of comparatively high Cs concentrations, apparently derived from the outfall of a TiO$_2$ refinery (Bera et al., 2015). Bera et al. (2015) examined part of our time series (six samplings from September 2010–November 2011) and concluded that the high Cs from St. Louis Bay was observable in the Sound but not in the Bight. The more complete time series (Fig. 2.8) largely confirms this but adds some additional pertinent detail. Enriched Cs (5–40 nM) at nearshore stations (Stns. 1–3) decreased dramatically to the normal seawater level of Cs (2.2 nM) heading offshore, confirming that the main influence of St. Louis Bay water on our transect is limited to the Sound. This is not surprising given the comparatively low fluvial discharge to the bay (Fig. 2.2b) as well as mean surface currents in the western Mississippi Sound that direct St. Louis Bay outflow towards the east (Kjerfve, 1983). The
lowest Cs concentrations at nearshore stations (Stns. 2–4) occurred during April–May 2008 and May–June 2011, both periods in which the opening of the Bonnet Carré Spillway directed low Cs Mississippi River into the west end of the Sound. The greater discharge through the spillway in 2011 than 2008 also resulted in comparatively low surface water salinity and Cs throughout the transect. At Stns. 3 and 4, we also observed comparatively low Cs in January 2010 and September 2011. As we discussed previously in section 2.3.2.1, high local precipitation and river discharge in December 2009 probably resulted in low Cs Pearl River water diminishing the high Cs St. Louis Bay signal that it is a relaxation of Pearl River plume toward shelf regions one month later after a cold front passage. In contrast, during September 2011 the passage of Tropical Storm Lee appears to force Mississippi River influenced waters towards the Mississippi Bight and Sound, as evidenced by the δ¹⁸O data discussed previously.

Figure 2.8 Temporal and spatial distributions of surface Cs during late 2007 through 2011.

Note: Arrows indicate the opening of the Bonnet Carré Spillway.

Dissolved Mo and U behaved largely conservatively, as they do in seawater. For Re, which also behaves conservatively in seawater (41 pM; Anbar et al., 1992), there was significant scatter in the trend with salinity. While this may be due partly to the
concentrations being close to our detection limit, it also likely reflects the fluvial sources. In particular, Re concentrations in the Mississippi River vary temporally (Joung and Shiller, 2016) and range from below to above seawater concentrations while Pearl River and St. Louis Bay have very low dissolved Re (~10 pM; Shim, 2011; Shim et al., 2017). In any event, these elements, which can be removed from seawater during highly reducing conditions, showed no evidence of substantial redox effects on their distributions during our study.

2.3.3.2 Ba

Dissolved Ba distributions in our transects show several interesting characteristics (Fig. 2.9). In general, concentrations are highest at low salinity, consistent with a fluvial source enriched in Ba. However, we also observed some surface water samples at mid-salinity that appear to be depleted in Ba, particularly during late spring and summer, generally corresponding to Si-depleted water (see section 2.3.2.5 and Fig. A.4). Similar observations of Ba depletion have been attributed to removal in association with diatom blooms (Coffey et al., 1997; Stecher and Kogut, 1999; Sternberg et al., 2005) and was also reported west of the Mississippi River delta on the Louisiana Shelf (Joung and Shiller, 2014).

Most importantly, we note that bottom water samples were often enriched in Ba relative to surface waters at similar salinities and that this enrichment was most evident during periods of hypoxia (Fig. 2.9a, b). A similar observation was made by Joung and Shiller (2014) for bottom waters of the Louisiana Shelf. For the seven surveys where we had three or more bottom hypoxic samples, extrapolation of the bottom Ba-salinity relationship to zero salinity leads to micro-molar Ba concentrations (Table 2.3), far
higher than can likely be accounted for from fluvial input even when Ba desorption from the suspended load is accounted for (Joung and Shiller, 2014). Likewise, we doubt that an anthropogenic Ba source from drilling muds can account for our observations. Joung and Shiller (2013) did observe an input of Ba to deep waters affected by the injection of drilling muds used in an attempt to cap the blown out Deepwater Horizon drill rig. However, the Ba enrichments they observed were on the order of 10’s of nM as opposed to the 100’s of nM enrichments observed here. Shelf edge upwelling is also unlikely to account for the benthic Ba enrichment since Ba does not increase strongly with depth here (Joung and Shiller, 2013).

![Figure 2.9](image)

**Figure 2.9** The distribution of Ba in Mississippi Sound surface waters and Mississippi Bight waters along the salinity gradient under (a) non-hypoxic and (b) hypoxic conditions. (c) Plots of dissolved trace metals (Ba, Fe and Mn) and nutrients in surface waters and bottom waters versus salinity in August 2009 and August 2011.

Note: In Fig. 2.9 (a and b), open circles represent Mississippi Sound surface waters. Mississippi Bight surface and bottom waters are shown in solid circles and triangles, respectively. Note that not all but most bottom samples shown in Fig. 2.9 (b) were oxygen-depleted (DO < 63 μM or < 2mg/L). Figure 2.9 (c) is shown in next page. In Fig. 2.9 (c), surface and bottom waters are shown in circles and triangles, respectively. Red and green colors represent August 2009 and August 2011, respectively.

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Table 2.3

Extrapolated zero-salinity Ba based on bottom hypoxic samples.

<table>
<thead>
<tr>
<th>Date</th>
<th>Ba (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jun-08</td>
<td>2200</td>
</tr>
<tr>
<td>Aug-08</td>
<td>3280</td>
</tr>
<tr>
<td>May-10</td>
<td>930</td>
</tr>
<tr>
<td>Jul-10</td>
<td>1080</td>
</tr>
<tr>
<td>Jun-11</td>
<td>1950</td>
</tr>
<tr>
<td>Jul-11</td>
<td>1760</td>
</tr>
<tr>
<td>Aug-11</td>
<td>2150</td>
</tr>
</tbody>
</table>
We thus conclude that a source of Ba from the sediments affects the bottom water Ba distribution. If we assume the bottom stratified layer in the Bight is ~5 m thick (based on our salinity data) and bottom water has a 14-day residence time (based on short-lived Ra isotope distributions; Shiller et al., 2017), then to accumulate an extra 100 nM Ba in the bottom waters would take a flux from the sediment of ~35 µmol/m²/d. We can compare this with estimates of Ba fluxes from potential benthic sources. McManus et al. (1998) reported diffusive fluxes of Ba from California continental margin sediments on the order of 1 µmol/m²/d, making this process likely too small to account for our bottom water Ba enrichment. Likewise, estimated resuspension fluxes of Ba in both the Bay of Bengal (Moore, 1999) and the Tillamook Bay estuary (Colbert and McManus, 2005) are similar in magnitude (~2 µmol/m²/d) to the diffusive Ba fluxes. Thus, our conclusion is that an advective flux from the sediments (i.e., SGD) is the most likely explanation for the benthic Ba enrichment. Similar shelf Ba enrichments due to SGD have also been observed on the South Atlantic Bight (Shaw et al., 1998).

Finally, we also note that for some of the surface water transects, extrapolation of dissolved Ba to zero salinity also yielded very high effective endmember concentrations. For instance, in August 2009 (non-hypoxia) and August 2011 (hypoxia), surface waters extrapolated to Ba > 1.2 µM at zero salinity (Fig. 2.9c). Surface waters at these times also showed enrichments in dissolved Mn, Fe, and nutrients which suggests the influence of benthic inputs even in the surface waters. Given the shallowness of the water column in this transect (< 20 m), this should not be surprising.
2.3.3.3 Mn

One of the most evident aspects of the dissolved Mn distribution is its inverse relationship with oxygen in the bottom waters (Fig. 2.10a). The most Mn-enriched bottom waters were also high in Ba, Si, PO$_4$, and NH$_4$, but low in NO$_3$ and V (Fig. A.6). These observations are all compatible with a benthic reducing source, perhaps augmented by SGD, for high bottom water Mn concentrations. Interestingly, in surface waters an opposite relationship for Mn concentrations is seen with hypoxia (Fig. 2.10b, c). That is, when bottom waters are hypoxic, surface water Mn is almost always < 100 nM and often < 10 nM, whereas when bottom waters are not hypoxic, surface water dissolved Mn is often > 100 nM and usually > 10 nM. This inverse relationship between surface and bottom Mn probably stems from the stratification associated with hypoxia. That is, high stratification prevents reoxygenation of bottom waters, promotes/preserves reduced inputs, but limits the amount of benthic Mn that can mix upward into surface waters. When stratification is low and bottom oxygen is high, benthic Mn input is lower and/or more rapidly oxidized, but what input there is can more readily be mixed into the surface waters. A similar phenomenon was noted for surface and bottom waters on the Louisiana Shelf (Mallini, 1992).
Figure 2.10 (a) The relationship between dissolved Mn and DO in hypoxic waters during 2008 and 2011. The distribution of Mn concentrations in Mississippi Sound surface waters and Mississippi Bight waters along the salinity gradient under (b) non-hypoxic and (c) hypoxic conditions. (d) The relationship between dissolved Mn and water temperature in surface water at Stns. 1 and 2 from late 2007 to 2011.

Note: In Fig. 2.10 (a-c), dissolved Mn is shown in log scale. In Fig. 2.10 (b and c), open circles represent Mississippi Sound surface waters. Mississippi Bight surface and bottom waters are shown in solid circles and triangles, respectively. Note that not all but most bottom samples shown in (b) were oxygen-depleted (DO < 63 μM or < 2 mg/L).

Two times when we observed low dissolved Mn in hypoxic bottom water occurred at Stns. 5 and 7 in summer of 2008 and 2011; however, enriched Ba, nutrients, and depleted V were observed in these samples. In other words, we saw all the signs of reducing bottom input, except for increased Mn. We note that in both of these years the
Bonnet Carré Spillway had been opened in the spring. We can only speculate on the relationship, but suggest that the spillway opening and input of nutrient- and organic-rich Mississippi River water into the western Sound and Bight may have exacerbated hypoxia and depleted the sediment reservoir of reducible Mn before the end of the hypoxic period.

In the most inshore surface waters (Stns. 1 and 2), we also observed a distinct inverse trend between dissolved Mn and water temperature (Fig. 2.10d), which is not evident further offshore. The salinity distribution (Fig. 2.3a), makes it clear that these two stations are most influenced by fluvial input. Furthermore, examination of dissolved Mn in the Mississippi and Pearl Rivers as well as St. Louis Bay (Shiller, 1997a; Shiller and Stephens, 2005; Shim, 2011) suggests that the Pearl River is far and away the fluvial source with the highest dissolved Mn (typically low µM) and the nearshore current in the Sound should bring Pearl River outflow towards the mouth of St. Louis Bay (i.e., towards Stns. 1 and 2). Since the Pearl River discharge typically peaks during late winter/early spring and water temperature is typically low during this period, the inverse Mn-temperature relationship might be a coincidence of the seasonality of local fluvial Mn supply. Additionally, the effect of temperature on the rate of microbial Mn oxidation (Shiller and Stephens, 2005) results in slower oxidative removal of dissolved Mn at lower temperatures.

We also note that two periods, October 2007 and September 2011, fall off the Mn-temperature trend for Stns. 1 and 2. As we have noted above, the September 2011 transect occurred shortly after the passage of Tropical Storm Lee. Thus, the high surface Mn at these stations may have resulted either from wind induced nearshore sediment resuspension or enhanced fluvial Mn. In October 2007, elevated Cs (49–99 nM) in the
most inshore surface waters (Stns. 1 and 2) with a salinity range of 21–26 indicates the influence of St. Louis Bay input overwhelms that of the Pearl River. Discharge data (Fig. 2.2b) indicates low flows in the Pearl (< 44 m³/s) and Wolf (< 2 m³/s) Rivers prior to our sampling. Thus, we speculate that the source of elevated dissolved Mn (0.3–1.5 μM) in the nearshore surface waters in October 2007 might be from benthic inputs (i.e., sediment resuspension and/or SGD), instead of fluvial influx. Indeed, we did observe relatively high Ba (423–475 nM) in these Mn-rich waters, an indicator of SGD input (see section 2.3.3.2).

2.3.3.4 Fe

Unlike dissolved Mn, an inverse relationship between dissolved Fe and DO was not evident in the hypoxic bottom waters, likely due to the faster oxidation rate of Fe than that of Mn (Stumm, 1992). Additionally, reduced Fe might precipitate with sulfide and remain in the sediment when sulfate reduction occurs, thereby limiting the Fe flux to the overlying bottom water. Thus, enriched dissolved Fe (both dissolved (< 0.02 μm) and colloidal (0.02–0.45 μm) fractions) was only seen in a few low-oxygen samples (Fig. 2.11b), and was two orders of magnitude lower than the dissolved Mn enrichment (Fig. 2.10c) in hypoxic bottom waters.

Taking a closer look at Fe in just the offshore stations, highly variable Fe concentration in surface and bottom waters was observed throughout the study, with no clear temporal or spatial trends. However, a difference in colloidal percentage between hypoxic and non-hypoxic periods was observed (Fig. 2.11), indicating that Fe was dominant in the colloidal fraction during hypoxic periods while the colloidal percentage was highly variable during non-hypoxic periods. The high colloidal percentage during
hypoxic periods might have resulted from ferric hydroxide precipitation due to rapid oxidation of reductively dissolved Fe coming from the sediments.

In surface waters during periods of non-hypoxia, dissolved Fe was usually > 10 nM and mostly dominated by the colloidal fraction, though with frequently elevated Fe (> 100 nM) at the nearshore stations (Stns. 1 and 2) (Fig. 2.11a). Published dissolved Fe data in the Mississippi and Pearl Rivers, as well as St. Louis Bay (Shiller, 1997a; Stolpe et al., 2010; Shim, 2011) suggests that increased dissolved Fe in nearshore surface waters is likely derived from the Pearl River, as also seen in elevated dissolved Mn at nearshore stations. In general, decreased dissolved Fe with increasing salinity of the transect is likely due to the aggregation and settling of colloidal Fe (Sholkovitz, 1976; Sholkovitz et al., 1978). We note that in January 2010 total dissolved Fe concentrations were very high (83–1153 nM) in Mississippi Sound waters, as was dissolved Mn (60–563 nM). As we discussed in previous sections, this was a result of enhanced fluvial influence and/or sediment resuspension due to an episodic event, evidenced with high precipitation in December 2009 (Fig. 2.2c).
Figure 2.11 The distributions of dissolved Fe (< 0.02 μm) and colloidal Fe (0.02–0.45 μm) in Mississippi Sound surface waters and Mississippi Bight waters, and the variability of colloidal fraction in Mississippi Bight waters along the salinity gradient under (a) non-hypoxic and (b) hypoxic conditions.

Note: In Fig. 2.11 (a and b), open circles represent Mississippi Sound surface waters. Mississippi Bight surface and bottom waters are shown in solid circles and triangles, respectively. Dissolved and colloidal Fe concentrations are shown in log scale. Note that not all but most bottom samples shown in (b) were oxygen-depleted (DO < 63 μM or < 2 mg/L).

Contrastingly, during periods of hypoxia, surface water Fe was usually < 10 nM although elevated Fe was seen in a few surface samples from 2010 and 2011 (Fig. 2.11b). This generally low surface water Fe suggests limited influence of the Fe-rich Pearl River. However, during May–July 2011, increased Fe (53–543 nM), mostly colloidal, in
nearshore surface waters (Stns. 1 and 2) might have been caused by sediment resuspension. Specifically, we speculate that the opening of the Bonnet Carré Spillway in May 2011 resulted in an influx of suspended material from the Mississippi River (Waters et al., 2009; Fabre, 2012) as well as possible increased turbulent resuspension of sediments in Lake Pontchartrain. Supporting this explanation is that elevated SPM was observed throughout the transect in May and June 2011 (note: SPM data is only available for 2011), with a higher SPM in the Mississippi Sound than in the Bight (Vandermeulen, 2012). During two sampling trips in May 2010, increased Fe was observed in some offshore surface waters (Stn. 6: 331 nM and Stn. 8: 103 nM and 187 nM; Fig. 2.11b) that is unlikely to have been contributed by benthic sources due to lower bottom water Fe than surface water. However, we can’t exclude the advection of higher Fe water from an adjacent area.

2.3.3.5 Cr

Dissolved Cr in seawater is typically a few nM in concentration (Bonnand et al., 2013 and references therein) and thus, much of our high salinity data appears to be depleted in Cr (Fig. 2.12). Overall, surface dissolved Cr concentrations were constant throughout low- and mid-salinity (5-25) and gradually increased at high-salinity, showing a downward curvature (Fig. 2.12). Similar observation of dissolved Cr depletion in mid- and high-salinity waters in the Mississippi River outflow (e.g., Shiller and Boyle, 1991; Shim et al., 2012) and on the Louisiana Shelf (e.g., Joung and Shiller, 2016) have been attributed to photoreduction and also the upward mixing of Cr-depleted bottom water.

Most importantly, Cr was depleted in hypoxic bottom waters relative to Cr in oxic surface and bottom waters (Fig. 2.12c). This suggests reduction of Cr to the more
adsorption-prone Cr(III) species (Richard and Bourg, 1991) at or near the sediment-water interface. These low-Cr hypoxic bottom waters can mix upward and slightly deplete surface water Cr at mid-salinity, similar to what was observed in oxygen-depleted water on the Louisiana Shelf (Joung and Shiller, 2016). Figure 2.12c shows the relationship between bottom Cr and DO was generally positive, although this correlation is scattered, perhaps due to the influence of other processes (Richard and Bourg, 1991). Given that Cr(VI) reduction can be mediated by Fe(II), S(II), organic matter, and MnO₂ (Schroeder and Lee, 1975; Eary and Rai, 1987; Richard and Bourg, 1991), we plotted Cr against other parameters to evaluate the factors affecting the Cr-DO correlation. No strong colloidal Fe-Cr or Mn-Cr correlations in low-oxygen waters were observed, suggesting that the co-precipitation of colloidal Fe and the reduction of MnO₂ do not appear to be important factors regulating Cr solubility in this area. Since we didn’t measure organic matter, we cannot evaluate the importance of organic complexation in increasing solubility of Cr.
Figure 2.12 The distribution of Cr concentrations in Mississippi Sound surface waters and Mississippi Bight waters along the salinity gradient under (a) non-hypoxic and (b) hypoxic conditions. (c) The relationship between Cr and DO in bottom waters.

Note: In Fig. 2.12 (a and b), open circles represent Mississippi Sound surface waters. Mississippi Bight surface and bottom waters are shown in solid circles and triangles, respectively. Note that not all but most bottom samples shown in (b) were oxygen-depleted (DO < 63 μM or < 2 mg/L).
2.3.3.6 V

Dissolved V in normal seawater is ~32–36 nM (e.g., Ho et al., 2018). However, in coastal environments, both depletions and enrichments in dissolved V have been observed in previous work as well as in our results here (Fig. 2.13). For instance, on the Louisiana Shelf, Shiller and Mao (1999) and Joung and Shiller (2016) observed dissolved V removal in bottom water in association with oxygen depletion. These V-depleted bottom waters could subsequently be mixed into the shelf surface waters to provide an apparent surface V-depletion. However, Shiller and Mao (1999) also found evidence of V input from sediments into shallow waters of Atchafalaya Bay. Enriched dissolved V associated with SGD has also been reported (Beck et al., 2010; Riedel et al., 2011).

With this possible mix of input and removal processes, it is not surprising that our V data at first glance appear somewhat scattered (Fig. 2.13a, b) and with no clear relationship between DO and dissolved V in the bottom waters (Fig. 2.13c). However, when plotted versus time (Fig. 2.13d), consistent patterns emerge, lending confidence to the data. Surface dissolved V concentrations were low (~5 nM) in winter and high (50–65 nM) in summer and fall (Fig. 2.13d). These high values are surprising given that they are higher than normal seawater as well as values previous reported for the Mississippi River (Shiller, 1997 a), the Pearl River (Shim et al., 2017), and St. Louis Bay (Shim, 2011). This strongly suggests that the sediments must play an important role as a source of high dissolved V. Furthermore, the low winter values of dissolved V are too low to have been caused by mixing of even zero V river water with normal seawater and thus are indicative of removal either by biological uptake, adsorption on particles, or uptake by the sediments. Since the low V occurred during winter when surface water chlorophyll a (and
by implication plant productivity) was comparatively low, we discount biological uptake as a factor. Likewise, we see no relationship between V and colloidal Fe, which would be expected to be a strong adsorbent for vanadate ions. Although we have no data on the overall SPM concentrations, we tentatively accept the lack of a V-colloidal Fe relationship as indicative of adsorptive removal being a minor issue in this system.

To further tease apart the processes affecting the dissolved V distribution, we examined the difference between surface and bottom water V at our four offshore stations as a function of DO. When binned in 1 mg/L (32 µM) DO intervals, it is clear that surface waters are slightly depleted in V relative to bottom waters when the bottom is well-oxygenated (Fig. 2.13e). However, as the bottom water becomes hypoxic, dissolved V becomes depleted in the bottom water relative to the surface waters. Bottom water depletion of V during hypoxic conditions is consistent with the findings of Shiller and Mao (1999) and Joung and Shiller (2016) for the Louisiana Shelf. However, that bottom water V is higher than the surface water concentration when the water is well-oxygenated, also lends credence to our suggestion of a bottom source of V.
Figure 2.13 The distribution of V in Mississippi Sound surface waters and Mississippi Bight waters along the salinity gradient under (a) non-hypoxic and (b) hypoxic conditions. (c) The relationship between DO and bottom water V. (d) The temporal variability of dissolved V and salinity in surface waters at Stns. 1-6. (e) The difference between surface and bottom water V as a function of bottom water DO in the Mississippi Bight.

Note: In Fig. 2.13 (a and b), open circles represent Mississippi Sound surface waters. Mississippi Bight surface and bottom waters are shown in solid circles and triangles, respectively. Note that not all but most bottom samples shown in Fig. 2.13 (b) were oxygen-depleted (DO < 63 µM or < 2 mg/L). Figure 2.13 (d and e) are shown in next page. In Fig. 2.13 (d), filled circles and crosses represent dissolved V and salinity, respectively.
Why the sediments in our study area switch from V source to sink seasonally is uncertain. Clearly bottom hypoxia plays some role but other potential factors include changes in organic complexation (Beck et al., 2008) or changes in the rates of microbial processes affecting V speciation (e.g., Huang et al., 2015). In fact, water temperature does correlate with V in our data, thus suggesting a temperature effect on the rates of microbial processes affecting V speciation. Also, O’Conner et al. (2015) note that V speciation in sediments of the York River estuary may be affected by changes in pH. Indeed, the E\text{H}-pH diagram for V shows the V(V)-V(IV) transition moving to sharply lower E\text{H} as pH increases (e.g., Huang et al., 2015). Thus, seasonal pH changes could affect V speciation and hence mobility from the sediments.

### 2.4 Conclusions

A multi-year chemical time series of eight stations in the western Mississippi Sound and northwestern Mississippi Bight has provided insight into chemical transport and processing in this coastal transition zone. Key findings include the frequent development of bottom water hypoxia in this part of the Bight during late spring and summer, the likely contribution of submarine groundwater discharge (SGD) to the material flows, and observation of effects of episodic events including tropical storms and the opening of the Bonnet Carré Spillway. Rivers are an important material source to the study region. Analysis of the $\delta^{18}\text{O}$ of the water, available only for a small fraction of the time series, indicates that rivers draining local coastal basins (i.e., Pearl, Wolf, and Jourdan Rivers) are major contributors of fresh water to the western Sound except in the aftermath of a tropical storm which pushed Mississippi River influenced waters into the Sound. In the Bight, contributions from the Mississippi River become more important,
especially during summer. If generally true, this may imply an influence of the nutrient-rich Mississippi River on summertime development of hypoxia in the Bight.

The distributions of Si and a variety of trace metals (i.e., Ba, Mn, Fe, V and Cs) in Mississippi Sound surface waters were largely regulated by the temporal and spatial variations of riverine sources. For instance, in fall and winter, high concentrations of dissolved Mn and dissolved Fe (mostly colloidal) at the most nearshore stations followed by a sharp decline in concentrations offshore, are indicative of Pearl River influence in the Mississippi Sound. Cs-rich water coming from St. Louis Bay is evident in the Mississippi Sound, but not observable in Mississippi Bight.

During the study period, the Bonnet Carré Spillway was opened in April 2008 and May 2011. The spillway discharges Mississippi River to Lake Pontchartrain and ultimately to our study area, which is supported by the observation of an extended freshwater signal and low Cs across the Mississippi Sound and Bight during these two spillway openings. It is plausible that Mississippi Bight hypoxia was more severe due to increased nutrients and intense stratification induced by Mississippi River input following the opening of Bonnet Carré Spillway.

Based on our observations of increased nutrients, Ba, Mn, Fe and V, SGD appears to be an important source for various chemical constituents in this region. Consideration of the mass balances of Ba and V, in particular, supports this conclusion. Seasonal change in the direction of the V flux from the sediments suggests that the chemical conditions (i.e., pH, E<sub>H</sub>) of the groundwater are changing, too. Given that anoxic groundwater has the potential to contribute to hypoxia both through the input of oxygen-depleted water (e.g., Peterson et al., 2016) as well as through the oxygen demand of
reduced substances such as ammonium and sulfide, the effect of SGD on hypoxia in this region needs further consideration.

We also observed the influence of hypoxia on the distribution of chemical constituents in this study. Enriched nutrients, Mn and Ba as well as depleted V and Cr were commonly observed in hypoxic bottom waters in the study region. Interestingly, although dissolved Mn was often enriched to micromolar levels in hypoxic bottom waters, Fe concentrations (both truly dissolved and colloidal) were rarely over 100 nM, likely due to rapid oxidation and removal of the Fe. Similar to previous observations of Cr and V depletion in Louisiana Shelf waters, we observed that the signal of bottom depletion of V and Cr during hypoxia periods, is at times mixed upwards into surface waters.

Important remaining questions from this study include the extent to which SGD and/or Mississippi River water are necessary for establishment and maintenance of hypoxia in the Mississippi Bight and the reasons for the seasonal change in the direction of the sedimentary V flux.

Note: The text of this chapter was published on Marine Chemistry 201, 2018.

3.1 Introduction

Molybdenum and vanadium both occur as oxyanions in oxic waters and have somewhat similar geochemical behaviors in the ocean. For instance, both elements are redox-sensitive, with decreased solubility in oxygen-depleted water. Also, Mo and V are micro-nutrients, although their biochemical functions and uptake differ. Conventionally, Mo is thought to be conservative in seawater (Bruland, 1983; Collier, 1985) and V nearly so, with only a ~10% depletion in the shallow ocean relative to deep waters (Collier, 1984; Middelburg et al., 1988; Sherrell and Boyle, 1988). Thus, the distributions of these elements have tended not to be studied in detail in the open ocean and the possibility remains that interesting aspects of their oceanic geochemistries have been overlooked.

The distribution of dissolved Mo is generally thought to be essentially conservative in the open ocean (Morris, 1975; Bruland, 1983; Collier, 1985). Likewise, the uniform distribution of Mo stable isotope ratios in the ocean (Nakagawa et al., 2012) also suggests the relative unreactivity of oceanic Mo. However, a number of studies have reported non-conservative behavior of dissolved Mo in coastal and estuarine waters (e.g., Dalai et al., 2005; Dellwig et al., 2007; Joung and Shiller, 2016; Wang et al., 2016). The reasons for this non-conservative behavior are varied and likely relate to biological
processes, organic complexation, redox processes, scavenging, and sedimentary interactions. For example, scavenging of Mo by ferromanganese oxides appears to be a mechanism of importance for removal of Mo from the water column (Goldberg et al., 2009; Kashiwabara et al., 2011) and the diagenesis of these oxides plays a role in the enrichment of Mo in reducing sediments (Scholz et al., 2011). Also, the formation of Mo-enriched organic aggregates has been observed to deplete coastal water dissolved Mo (e.g., Dellwig et al., 2007; Kowalski et al., 2013). Mo plays an important biological role in the nitrogen cycle as a co-factor in nitrogenase, nitrate reductase, and nitrite oxidoreductase (Stiefel, 1996; Moreno-Vivián et al., 1999; Maia et al., 2017) as well as in DMSO reductase (Schindelin et al., 1996). Based on thermodynamics, Mo is present in the +VI oxidation state in seawater, predominantly as the highly soluble MoO$_4^{2-}$ species (Baes and Mesmer, 1976; Manheim, 1978). However, small amounts of the more particle-reactive Mo(V), which should be thermodynamically stable in reducing waters (Bertine, 1972; Brookins, 1988), have been reported in low-oxygen estuarine waters (Wang et al., 2009). Furthermore, when there is sufficient sulfide present (~11 μM H$_2$S$_{(aq)}$), molybdate can be sulfidized to more readily scavenged thiomolybdates without reduction of the Mo (Erickson and Helz, 2000; Dahl et al., 2010; Vorlicek et al., 2015). Helz et al. (2011) proposed that the Mo scavenging in sulfidic water is controlled not only by H$_2$S concentration but also by pH and the availability of reactive Fe(II). This may account for the high levels of Mo found in sediments and pore waters of anoxic depositional environments (e.g., Emerson and Huested, 1991).

As outlined above, the utilization of Mo as an enzymatic co-factor, the interaction of Mo with organic matter, the change of Mo speciation in redox gradients and
association with Fe/Mn cycling along with the diagenesis of Mo in sediments/pore waters supports the prior observations of non-conservative Mo behavior in various marginal environments. In the open ocean, however, the limited observations of the Mo distribution are more equivocal. Both slight depletion and enrichment of Mo concentration were reported in the eastern tropical Pacific Ocean by Tuit (2003). However, no significant depletion of Mo was observed either in the extreme oxygen minimum zone (OMZ) of the Arabian Sea (Goswami et al., 2012) or in the eastern tropical North Pacific OMZ (Nameroff et al., 2002). In oceanic hydrothermal systems, Elderfield and Schultz (1996) suggested there was no direct hydrothermal source/sink of Mo, but that scavenging removal in hydrothermal plumes did remove Mo from seawater, albeit at a rate of only ~1% of the fluvial input. However, Mo depletion was observed in vent fluids from the Southern Juan de Fuca Ridge (Trefry et al., 1994). Thus, hydrothermal effects on the oceanic Mo distribution may be variable.

Dissolved V concentrations are generally found to be ~35 nmol/kg in the deep ocean with a slight reduction in concentration in the upper water column (e.g., Collier, 1984; Middelburg et al., 1988; Sherrell and Boyle, 1988). There is one report suggesting deep Pacific concentrations might be 10-15 nmol/kg higher than this (Jeandel et al., 1987), though their intercalibration effort showed somewhat variable results and Middelburg et al. (1988) showed only a few nmol/kg inter-basin increase. Thermodynamically, the predominant species of V in oxic seawater should be $\text{H}_2\text{VO}_4^-$ (Baes and Mesmer, 1976; Wang and Sanudo-Wilhelmy, 2008), which has similar chemical characteristics as phosphate. Thus, the slight V depletion in surface waters has been attributed to biological uptake of V(V) (Collier, 1984).
V is used as a nutrient by some species (Taylor and van Staden, 1994) and is found in some enzymes (Antipov et al., 1998; Rehder, 2000; Butler and Carter-Franklin, 2004). More specifically, V is found in V-nitrogenases and V-haloperoxidases (Crans et al., 2004). Observation of V-nitrogenase in the ocean may not be likely, since its expression seems to require Mo-limitation (Rehder, 2000). V-haloperoxidases are commonly found in marine macroalgae (Crans et al., 2004). Additionally, previous studies have hypothesized that the intracellular V enrichment in Trichodesmium colonies is related to the V-haloperoxidases (Tovar-Sanchez and Sañudo-Wilhelmy, 2011; Nuester et al., 2012). High concentrations of V(III) are also found in certain tunicates (Michibata et al., 2003). While the effect of these types of biological V uptake may be limited, Klein et al. (2013) has speculated on an unknown mechanism of biological V uptake from surface waters based on correlations between intracellular V, biogenic Si, and total chlorophyll a and Osterholz et al. (2014) presented evidence that diatoms are a major factor in oceanic V depletion.

In contrast to the biological uptake hypothesis for surface ocean dissolved V depletion, Shiller and Mao (1999) found no evidence of biological V removal in productive waters of the Louisiana Shelf and suggested that V depletion in those shelf waters resulted from V reduction and removal to the sediments. While the details of this mechanism were not specified, it likely involves adsorption of V onto ferromanganese oxide particles, possibly with water column reduction of V(V) to the more readily scavenged V(IV) (Wehrli and Stumm, 1989), and removal to and incorporation into reducing sediments (e.g., Scholz et al., 2011). Thus, an alternative or additional mechanism for surface ocean V depletion might involve V redox chemistry along the
continental margins. Other studies have also found dissolved V is lower in concentration in suboxic/anoxic water columns than in oxic waters (Emerson and Huested, 1991; Shiller and Mao, 1999; Wang and Sanudo-Wilhelmy, 2008). Similarly, it has been shown that V is enriched in the solid phase of anoxic and organic-rich sediments (Lewan and Maynard, 1982; Holland, 1984; Breit and Wanty, 1991). Under extremely reducing conditions, V(IV) could be further reduced to V(III) by humic acid or sulfides, and be present as V$_2$O$_3$ or V(OH)$_3$ (Goodman and Cheshire, 1975; Breit and Wanty, 1991).

Jeandel et al. (1987) suggested that hydrothermal processes are a minor factor in the cycling of vanadium. However, V has been characterized as an enriched element in hydrothermal vent fluids relative to seawater (German and Von Damm, 2006). Nonetheless, several studies have demonstrated that V is scavenged from seawater and adsorbed onto iron oxyhydroxides within rising hydrothermal plume waters, which is supported by evidence of particulate V enrichments in hydrothermal particles (Trefry and Metz, 1989; Feely et al., 1994; Edmonds and German, 2004). Thus, Elderfield and Schultz (1996) concluded that there is no significant direct hydrothermal input of V to the ocean and that the scavenging removal flux of V from the hydrothermal plumes is roughly equal to the river input flux of V.

Clearly the past work on Mo and V has demonstrated the basics of their oceanic distributions, but uncertainties remain in some of the details. Understanding these details may aid both in understanding modern ocean processes as well as in the interpretation of paleo-environmental data on the ocean’s Mo (e.g., Anbar, 2004; Tribovillard et al., 2006; Scott et al., 2008) and V composition (e.g., Hastings et al., 1996; Tribovillard et al., 2006). In this study, we present the first detailed oceanic sections of dissolved Mo and V,
obtained along the US GEOTRACES East Pacific Zonal Transect (EPZT). This transect (Fig. 3.1a) crossed a variety of contrasting oceanic regimes including an extreme OMZ, hydrothermal plumes, and the pelagic realm, thus providing an opportunity to more thoroughly examine the distributions of these two elements.

3.2 Methods

3.2.1 Seawater sampling

The U.S. GEOTRACES EPZT was conducted during 25 October–20 December 2013 aboard R/V Thomas G. Thompson from Manta, Ecuador to Papeete, French Polynesia (GEOTRACES section GP16; Fig. 3.1a). Samples were collected at four shelf stations (1-2 casts), 13 full depth stations (3 casts), 13 shallow stations (1 cast, depth ~1000 m) and five super-stations (3-4 casts) by use of 12-L Teflon-coated GoFlo bottles deployed on the trace metal clean GEOTRACES carousel (Cutter and Bruland, 2012).

Water samples were filtered through 0.2 µm capsule filters (Pall Acropak Supor capsule) and collected by an ultra-clean sampling technique which was previously deployed during CLIVAR (Measures et al., 2008b) and US GEOTRACES intercalibration and North Atlantic cruises (Cutter et al., 2014). In addition, surface water samples (~2 m depth) were taken from an underway towed-fish system (Bruland et al., 2005) and filtered through a 0.45 µm Osmonics and a 0.2 µm polycarbonate cartridge filter.

The filtered samples (~125 mL) collected from the GoFlo bottles were stored in pre-cleaned HDPE bottles and shipped back to the laboratory for acidification and analysis. Ancillary data (e.g., salinity, temperature, nutrients, oxygen) was provided by the cruise management team (http://www.bco-dmo.org/project/499723). After samples...
were transported to the laboratory, an aliquot of ultrapure 6 N HCl (Seastar Baseline) was added to each sample to reduce the pH to ~1.8 and the samples were then stored at room temperature.

Figure 3.1 (a) Cruise track of the US GEOTRACES East Pacific Zonal Section (GP16). (b) The distribution of dissolved oxygen in the upper water column along the EPZT. (c) The distribution of total chlorophyll a in the upper 200 m of the water column along the EPZT.

Note that station 1 (Peru-Chile Trench) is out of numerical order and is located between stations 5 & 6. In Fig. 3.1b, purple color indicates the ODZ.

3.2.2 Particle sampling

Particle samples were collected at four shelf stations, 13 full depth stations and five super-stations. Here, we briefly describe particle sampling protocols. Two particle fractions (small size fraction: 0.8-51 μm; large size fraction: >51 μm) were collected using McLane WTS-LV in-situ battery powered pumps that were deployed on a metal-free hydrowire (Hytrel-jacketed Vectran). Filters were loaded in two mini-MULVFS
filter holders (‘QMA’ and ‘Supor’) (Bishop et al., 2012) which were configured with each pump. All filters were acid leached (Cutter et al., 2014) in a HEPA-filtered clean environment prior to use. Each filter holder held a 142 mm-diameter, 51 µm pore-size polyester pre-filter, and either a pair of Whatman QMA quartz fiber filters or a pair of 0.8 µm pore-size Pall SuporTM polyethersulfone filters. In each cast, blank filters (both “QMA” and “Supor”) that were not connected to the pumps were deployed together with the pumps, and these dipped blank filters were treated as procedure blanks. After the pumps were recovered, the filter holders were brought into a shipboard HEPA-filtered clean environment for rinsing, subsampling and drying procedures and then stored in particle-free cleanroom polyethylene bags. More detailed particle sampling protocols are described in Heller et al. (2017), Lam et al. (2018), Lee et al. (2018) and in on-line documentation (http://www.bco-dmo.org/project/499723).

3.2.3 Analytical methods

3.2.3.1 Dissolved Mo and V

Both dissolved Mo and V were determined using a ThermoFisher Element XR sector field inductively coupled plasma-mass spectrometer (ICP-MS) with a PFA microflow nebulizer (Elemental Scientific, Inc.). Quantification used the isotope dilution method. We obtained enriched $^{95}$Mo (96.45%) and $^{50}$V (44.30%) from Oak Ridge National Laboratories. In general, we sought to spike the samples with an amount of enriched isotope such that measured isotope ratios in the spiked sample were close to the geometric mean of the natural isotope ratio and the isotope ratio of the enriched spike.

For Mo, ~50 µL of seawater was spiked with $^{95}$Mo and diluted 30-fold with ultrapure water prior to ICP-MS analysis using a PFA spray chamber (Shim et al., 2012).
The intensities of $^{95}\text{Mo}$ and $^{98}\text{Mo}$ were determined in low resolution on the ICP-MS. We measured Br during analyses to check the interference of $^{79}\text{Br}^{16}\text{O}^+$ and $^{81}\text{Br}^{17}\text{O}^+$ on $^{95}\text{Mo}$ and $^{98}\text{Mo}$, respectively. The correction for BrO$^+$ was usually less than 1% (1.1 nmol/kg) and no more than 2.5% (2.7 nmol/kg). The reproducibility of this method was estimated by comparing samples collected at the same depth on different casts at the same station. For 32 pairs of these replicate samples, the average absolute deviation was 2.3 nmol/kg or typically 2.1% (Table 3.1). Repeated runs of US GEOTRACES intercalibration samples (GS and GD; Table 3.1) and in-house reference solutions suggest a precision of ±2.3% (Table 3.1); the limit of detection for Mo was ~1 nmol/kg. Average Mo of GS and GD in our analyses were comparable to reported Mo values (GS: 116 nmol/kg; GD: 113 nmol/kg) by Goswami et al. (2012).

For V, 14-mL samples were spiked with a $^{50}\text{V}$-enriched solution and extracted/preconcentrated in 1 mL of eluate (10% HNO$_3$, Seastar Baseline) by using an Elemental Scientific (ESI) seaFAST system. Multiple elements can be simultaneously extracted using the chelating resin Nobias PA-1 (Sohrin et al., 2008; Biller and Bruland, 2012) which is the extraction material used in the seaFAST system. This system removes the matrix effect caused by seawater major ions while a buffered (NH$_4$Ac) sample passes through the Nobias PA-1 extracting many trace metals but excluding major seawater ions. The seaFAST also avoids the problem of ICP-MS interface clogging caused by sea salt or Mg(OH)$_2$ precipitates. A similar online seaFAST extraction procedure is described by Hathorne et al. (2012) for rare earth elements. Eluates from the seaFAST system were analyzed in medium resolution on the ICP-MS using an Apex-FAST high efficiency sample introduction system with Spiro desolvator (Elemental Scientific, Inc.) to obtain
the intensities of $^{50}\text{V}$ and $^{51}\text{V}$. Additionally, $^{47}\text{Ti}$ and $^{52}\text{Cr}$ were monitored to correct for any $^{50}\text{Ti}$ or $^{50}\text{Cr}$ isobaric interference on $^{50}\text{V}$; the correction was generally <1%. The reproducibility of this method was estimated by comparing samples collected at the same depth on different casts at the same station. For 32 pairs of these replicate samples, the average absolute deviation was 0.7 nmol/kg or typically 2% (Table 3.1). Repeated runs of US GEOTRACES intercalibration samples (GS and GD; Table 3.1) and in-house reference solutions suggest a precision of ±1.5%; the limit of detection for V was ~0.5 nmol/kg. Recovery of the method, as determined by repeated analysis of a spiked and unspiked seawater sample was 99.5 ± 2.8% (Table 3.1).

Because dissolved Mo and V are conservative or nearly so, much of the variability in the concentrations of these elements is caused by changes in salinity. We thus normalized our concentrations to constant salinity for this presentation by dividing by the in situ salinity and multiplying by 35. To present the spatial distribution of dissolved Mo (dMo) and V (dV), we used the Ocean Data View software package (Schlitzer, 2015).

Table 3.1
Reproducibility of dissolved Mo and V in GEOTRACES reference waters and detection limits for Mo and V. The recovery of V was calculated by a standard addition method.

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS (nmol/kg)</td>
<td>115.3±2.2 (N = 17)</td>
<td>34.5±0.5 (N = 16)</td>
</tr>
<tr>
<td>GD (nmol/kg)</td>
<td>111.4±2.3 (N = 18)</td>
<td>32.9±0.5 (N = 16)</td>
</tr>
<tr>
<td>*Avg. replicate deviation (nmol/kg)</td>
<td>2.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td></td>
<td>99.5 ± 2.8 (N = 31)</td>
</tr>
</tbody>
</table>

Note: *Average absolute deviation in 32 pairs of replicates.
3.2.3.2 Particulate Mo and V

Methodological details for particulate trace element analysis are in Lee et al. (2018) and Heller et al. 2017. Briefly, subsamples of small (0.8-51 μm) and large (>51 μm) size fraction particulate samples collected by in-situ filtration were digested using a two-step digestion method that first fully dissolved the polyethersulfone filter using the strongly oxidizing Piranha reagent (75% H₂SO₄/25% H₂O₂), and then fully dissolved particles in a strong mineral acid mixture of 4 M each of HCl, HNO₃, and HF (Ohnemus et al., 2014). Digest solutions were diluted and analyzed for a suite of elements on an ElementXR sector field ICP-MS in the UCSC Plasma Analytical Facility. To verify the accuracy of analytical procedures, two certified reference materials (CRMs), BCR-414 (freshwater plankton) and PACS-2 (coastal marine sediment), were digested and analyzed using the same procedures as for samples. The average recoveries of BCR-414 for Mo and V were 110 ± 10% and 112 ± 11%, respectively. The average recoveries of PACS-2 for Mo and V were 89 ± 13% and 92 ± 8% respectively.

Reported particulate Mo and V concentrations in this manuscript were corrected with the median of all dipped blanks, filtered seawater volume and the filter area used in digestion. The median dipped blank values and the detection limits for Mo and V are shown in Table 3.2. The uncertainty of particulate Mo and V concentrations can be attributed to the dipped blank correction, heterogeneity in particle distribution, and variation in digestion. The uncertainty for most samples was mainly from the blank correction. For the large size particulate Mo (pMo), most samples were below detection and thus only the small size fraction pMo is discussed here, with the exception of ridge crest hydrothermal samples where the large fraction pMo was significant. In contrast, for
particulate V (pV) the large size fraction accounted for a wide range of the total particulate V (0.7-82%) but was typically only 16% (median) of the total across the section (Lee et al., 2018). Thus, in general, particulate V in our discussion refers to the small particulate fraction; where necessary, we do distinguish the behavior of large particulate V when its contribution becomes significant.

Table 3.2

The median and standard deviation of dipped blanks and detection limit for both small and large fractions of particulate Mo and V.

<table>
<thead>
<tr>
<th></th>
<th>Small size fraction</th>
<th>Large size fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
<td>V</td>
</tr>
<tr>
<td>Median of dipped blank (pmol)</td>
<td>308</td>
<td>178</td>
</tr>
<tr>
<td>s.d. of dipped blank (pmol)</td>
<td>65</td>
<td>52</td>
</tr>
<tr>
<td>Approx. dipped blank (pM)</td>
<td>0.76</td>
<td>0.44</td>
</tr>
<tr>
<td>Approx. detection limit (pM)</td>
<td>0.48</td>
<td>0.38</td>
</tr>
</tbody>
</table>

There were 46 blank filters for small size fraction and 44 blank filters for large size fraction. The dipped blank values are for the entire area of the filters (active area = 125 cm²). The detection limit was defined as three times the standard deviation of the dipped blank filters. Dipped blanks and detection limits in pM were derived by assuming seawater volumes filtered through small size filters (470 L) and large size filters (1,100L).

In order to help identify the composition/origin of particulate trace elements, we calculated their non-lithogenic fractions. This was done by assuming that all particulate Al was lithogenic in origin. We then used element/Al ratios for upper continental crust (Rudnick and Gao, 2014) to estimate the amount of a particulate element likely to be of lithogenic origin. Non-lithogenic fractions were then estimated by subtracting the lithogenic estimate from the total particulate elemental concentration.
All original data, ancillary data (salinity, nitrite, density, total chlorophyll a and dissolved oxygen) and total particulate elements data are available online at 

3.2.4 Reanalysis of depleted dissolved Mo and V samples

Lower than expected dMo and dV concentrations were measured in a few samples. Because of the large number of samples in the EPZT section, we only re-analyzed dMo when the initial sample analysis was more than two standard deviations (5 nmol/kg) from the section salinity-normalized mean. For dV, we chose samples with dV <30 nmol/kg for re-analysis. Low dV in these samples was reproducible in the re-analysis. In order to verify that the dMo depletions were real, the Mo-depleted samples were re-analyzed a number of times (2-5 times) over 19 months. An additional reanalysis was performed if the first two results disagreed by more than two standard deviations. In general, we averaged all results except when one of the three analyses was more than three standard deviations away from the other two. An interesting phenomenon was found in many of these Mo-depleted samples. We observed that dMo in most of the Mo-depleted samples increased with sample storage time (~19 months). This observation is discussed in more detail below in Section 3.2. For the samples with slowly changing concentrations, the values reported here are averages of all replicate analyses of that sample since we do not know what the initial depleted value was. In other words, our presentation of those depleted concentrations is necessarily semi-quantitative. Acknowledging the imprecision of our terminology, we will refer to these samples as “Mo-depleted.” When the salinity-normalized Mo was more than 3 standard deviations
from the section mean dMo (i.e., <101.1 nmol/kg), the depletion was viewed as
significant.

3.3 Results and Discussion

3.3.1 Oceanographic setting and ancillary data

Peters et al. (2018) reported nutrients, hydrographic data, and the distribution of
water masses in the EPZT. We review here a few of their most pertinent conclusions
relating to hydrographic and nutrient features. The lowest surface water temperature
(~15°C) was found near the Peruvian coast, indicating upwelling of offshore cooler
waters. A pool of high salinity water at ~100 m depth in the mid-section originated from
subtropical gyre water. A salinity minimum in the mid-water column (600-800 m) reveals
the influence of Antarctic Intermediate Water in this region. Warmer and slightly fresher
depth waters (>3000 m) east of the East Pacific Rise (EPR) reflect the signature of Pacific
Deep Water (PDW). West of the EPR, slightly cooler and saltier deep water was
influenced by Antarctic Bottom Water. More detailed hydrographic data are presented in
the Water Mass Analysis manuscript (Peters et al., 2018).

Typical nutrient profiles were observed in the EPZT (Peters et al., 2018). Nitrate
and phosphate were low in the upper water column and reached maximum concentrations
at ~800 m, then, slowly decreased with depth. Silicic acid increased with depth, except
for a slight decrease in bottom waters in the western part (Stns. 32-36) and eastern part
(Stns. 1-9) of the transect. An extreme OMZ (dissolved oxygen <2 µmol/kg) was
observed from the Peruvian coast to at least 100°W (Stns. 1-13) (Fig. 3.1b), which can be
attributed to weak ventilation and consumption by intense biological activity (Karstensen
et al., 2008; Peters et al., 2018). For clarity and to distinguish the normal oceanic oxygen
minimum zone from this extreme zone, we use the term oxygen deficient zone (ODZ) to refer to the region of the water column with essentially anoxic conditions. In the case of the EPZT, the ODZ was found from Stn. 13 east to the Peru margin. Nitrite enrichments in the ODZ have previously been mainly attributed to nitrate reduction and ammonia oxidation (Lam et al., 2009). In deep water (> 3000 m), lower oxygen and higher silicic acid east of the EPR than to the west suggests the influence of PDW on the tropical eastern Pacific deep basin. More detailed nutrient results were discussed in the water mass analysis manuscript (Peters et al., 2018).

High total chlorophyll a (Chl a) concentration was seen in surface waters (0-25 m) near the Peruvian coast (Stns. 1-5) (Fig. 3.1c), implying high primary productivity in that region. Pigment composition showed macroplankton dominance at coastal stations (Stns. 1-5) which shifted to picoplankton dominance in the open ocean (Ohnemus et al., 2017). Heading to the open ocean (west of 100°W), the total Chl a maximum occurred at depths of 75-100 m (Fig. 3.1c; Ohnemus et al., 2017). The depth of the total Chl a maximum was tilted slightly upward toward the coast (east of 100°W) where the region was more influenced by the upwelling.

3.3.2 Description of Mo and V distributions

Without salinity normalization, slightly elevated dMo was commonly seen in the upper 200 m water column west of 100°W (Fig. B.1). After the dMo concentration was normalized to salinity 35 (dMo\(^n\)), the distribution was generally invariant across the EPZT (Fig. 3.2a), with an average dMo\(^n\) concentration of 108.2 ± 2.7 nmol/kg. However, a significant depletion of Mo in a few samples was observed within the ODZ and the hydrothermal plume (Fig. 3.2a).
Figure 3.2 (a) The distribution of dissolved Mo (normalized to salinity 35) along the EPZT. (b) The distribution of particulate (0.8 – 51 µm) Mo along the EPZT.

Note: In both graphs, white contours indicate dissolved nitrite concentration (µmol/kg).
As was mentioned earlier, in most of our dMo-depleted samples, the dMo\(^n\) concentration actually increased slowly over at least 19 months (Fig. 3.3). Indeed, only three samples in the section showed unchanging, low dMo\(^n\). Those three unchanging samples were a) Stn. 2 at 3.5 m (dMo\(^n\) = 97.8 ± 0.7 nmol/kg), which was the station closest to the coast and the sample with the highest total Chl \(a\); b) Stn. 6 at 125 m (dMo\(^n\) = 82.1 ± 2.0 nmol/kg), which was the depth of maxima in both nitrite (4.3 µmol/kg) and dissolved Mn (3.3 µmol/kg) for that station (though not for the entire ODZ); and, c) Stn. 20 at 2500 m (dMo\(^n\) = 94.2 ± 1.9 nmol/kg), which was the depth of the dissolved Mn maximum at this station and was immediately west of the crest of the EPR.
Figure 3.3. Salinity-normalized dissolved Mo values as a function of sample storage times from (a) St.18, (b) St. 26, and (c) the OMZ.

Note: Dashed lines show the trends of Mo increase with time.
For the samples that did change with time, it would seem that Mo was slowly converted from a form not determined by our ICP-MS analysis back to molybdate. However, since the Mo ICP-MS analysis is a “dilute-and-shoot” method that does not involve an extraction step, it seems unlikely that even a colloidal Mo species would be analytically invisible. We hypothesize that the missing Mo is in a form that was adsorbed to the sample container (acid-washed high-density polyethylene) walls even when the sample was acidified. For instance, Wang et al. (2009) developed a method in which what is thought to be Mo(V) is complexed with tartrate and extracted onto a non-ionic acrylic resin, thus suggesting that at least some organic Mo complexes might adsorb onto the walls of our sample containers. We are unaware of other reports of this sample storage phenomenon, though its transient nature might result in it being overlooked.

Although we cannot explain this phenomenon, we infer that it represents a real change in Mo speciation since it was only observed in a limited number of samples and, as we shall show, those samples might reasonably be expected to have some change in Mo concentration or speciation. Therefore, we suggest that previous studies reporting conservative dMo behavior in other OMZs (Nameroff et al., 2002; Goswami et al., 2012) might have missed the observation of the unknown transient species depending on their sampling, sample processing, and analytical methods. Again, in our discussion here, we refer to all samples that showed either consistent or transient low dMo\textsuperscript{n} concentrations as being Mo-depleted.

Anomalously low dMo\textsuperscript{n} was observed in several parts of the section. In the upper part of the ODZ (Fig. 3.1b), low dMo\textsuperscript{n} was observed in several offshore samples in the secondary nitrite maximum (Stns. 6 and 9; Fig. 3.2a), including one sample mentioned
above where the low dMo\textsuperscript{n} was not transient. Also, in some shallow (<200 m) samples along the Peru margin (Stns. 1-5) depleted dMo\textsuperscript{n} (98.5-104.6 nmol/kg) was observed (Fig. 3.4a). Salinity normalized dMo was also significantly depleted (4-8 s.d.) in a number of samples in the general depth range of the hydrothermal plume (Fig. 3.2a). The magnitude of dMo\textsuperscript{n} depletion was higher off-axis (Stns. 25 and 26), compared with the depletion above the ridge crest (Stn. 18) (Fig. 3.2a).

Figure 3.4 The vertical distributions of (a) dissolved Mo (normalized to salinity 35), (b) dissolved V (normalized to salinity 35) and (c) total chlorophyll a in the upper 100 m on the Peru margin.

The maximum pMo (16.8 ± 2.6 pmol/L at Stn. 4) in the section was observed in the ODZ (Fig. 3.2b). Particulate Mo data showed that most of the pMo (80-100%) was non-lithogenic across the EPZT (Figs. 2b and B.2). Enriched pMo in the ODZ corresponded both with elevated nitrite concentrations (Fig. 3.2b) and with elevated particulate Fe (pFe) (Fig. B.3).

The salinity-normalized dV\textsuperscript{n} EPZT section, which shows slight depletion in near surface waters and then relative constancy at depth (Fig. 3.5a), agrees with earlier observations in the open ocean (Collier, 1984; Jeandel et al., 1987; Middelburg et al., 1988). Without salinity normalization, the dV distribution shows the same basic trend
(Fig. B.4), though details are less clear. Previously reported average $dV^n$ concentrations are $32.4 \pm 2.7$ and $32.0 \pm 0.4$ nmol/kg in Atlantic and Pacific surface water, respectively (Collier, 1984; Jeandel et al., 1987). In deep water, average $dV^n$ appears to vary in different ocean basins (Atlantic Ocean: 32.0-35.3 nmol/kg; Pacific Ocean: 35.3 nmol/kg; Indian Ocean: 36.0 nmol/kg) (Collier, 1984; Middelburg et al., 1988), though intercalibration of these data sets is lacking. In our data, average $dV^n$ was $32.6 \pm 1.0$ nmol/kg in the upper water column (<450 m). Below 1000 m depth, average $dV^n$ was $34.9 \pm 1.8$ nmol/kg.
Figure 3.5 (a) The distribution of dissolved V (normalized to salinity 35) along the EPZT. Black dashed lines indicate neutral density surfaces ($25 \text{ kg m}^{-3} \leq \gamma_n \leq 27 \text{ kg m}^{-3}$). (b) The distribution of particulate (0.8 – 51 µm) V along the EPZT.

Note: In both graphs, white contours indicate dissolved nitrite concentration (µmol/kg).
As was the case with dMo\textsuperscript{n}, anomalously low dV\textsuperscript{n} (relative to the rest of the section) was found in several places in the EPZT. However, in contrast to dMo\textsuperscript{n}, depleted dV\textsuperscript{n} concentrations were stable; that is, they did not change with sample storage time. Low dV\textsuperscript{n} at Stn. 9 (~28.6 nmol/kg at 154 m) corresponded with the nitrite maximum (Fig. 3.5a). Here, the depletion of dMo\textsuperscript{n} and dV\textsuperscript{n} was mostly found in the same samples (Figs. 3.2a and 3.5a). This tends to confirm our observed Mo-depletion in the ODZ as more than simply an analytical artifact. Note that some other dissolved trace elements we determined in these samples (e.g., Ba, Ni) were not depleted; thus, the samples do not appear to be generally anomalous. Dissolved V depletion greater than the usual surface water depletion was also observed in near surface waters across the Peruvian continental shelf where dV\textsuperscript{n} concentrations ranged from 29.7-32.0 nmol/kg (Fig. 3.4b). The lowest dV\textsuperscript{n} in the coastal upwelling region was observed near the surface at Stn. 2 (the station closest to shore), and also corresponded with the lowest dMo\textsuperscript{n} at the coastal stations (Figs. 3.4a and b). Depleted dV\textsuperscript{n} was also found in some samples in association with the hydrothermal plume (Fig. 3.5a). As with dMo\textsuperscript{n}, off-axis dV\textsuperscript{n} was more depleted (to as low as 17 nmol/kg at Stn. 26) than in the ridge crest (Stn. 18) samples. Additionally, a few V-depleted samples were found deeper in the water column (>3000 m, Stns. 26 and 28) (Fig. 3.5a), along the boundary of elevated dissolved Fe in the off-axis hydrothermal plume (Resing et al., 2015).

In the particulate phase, elevated pV concentrations were seen in the ODZ and the hydrothermal plume. Non-lithogenic (average 92%) pV was dominant across the EPZT (Figs. 3.5b and B.5). This pV behavior is similar to that of pMo, discussed above. West of Stn. 13, pV additionally shows an enrichment in the mixed layer and then a slight
minimum in the 100-300 m depth range coincident with the nitrite maximum and where suspended particulate matter concentrations typically decrease and the nutricline begins. The mixed layer $pV$ enrichment is reflected both in the small and large particulate fractions and, in contrast to most of the rest of the section, large particulate $V$ is generally the dominant $pV$ mixed layer fraction, averaging 59% of the total. Lee et al. (2018) attributed the elevated large $pV$ concentrations in the mixed layer to $V$ uptake by diatoms, as evidenced by the fact that biogenic Si is the only carrier phase similarly showing elevated large particulate fractions in the mixed layer (Lam et al., 2018). The slight $pV$ minimum below the mixed layer (where the small particulate fraction dominates), however, is due solely to changes in the small particulate fraction. Close to the Peru margin, upper water column $pV$ concentrations are generally higher than further west and the $pV$ minimum is no longer apparent.

### 3.3.3 Mo and V behavior in the hydrothermal plume

The depletions in $dMo^n$ and $dV^n$ in the hydrothermal plume are both apparent in our sections (Figs. 3.2a and 3.5a) and, as we shall show, puzzling aspects of our distributions. At the ridge crest (Stns. 18 and 20), these depletions in $dV^n$ and $dMo^n$ corresponded to enrichments in $pV$ and $pMo$ associated with $pFe$ enrichments (Fig. 3.6) while off-axis (Stns. 26 and 28) larger patches of $dV^n$ and $dMo^n$ depletion are observed towards the boundaries of $pFe$-enriched waters (purple patches in Figs. 3.2a and 3.5a). We note that Mo and V were analyzed by different methods and that other elements analyzed at the same time (e.g., Ba with Mo; Ni with V) showed no anomalous behavior. Thus, we view these $dMo^n$ and $dV^n$ depletions as being robust and not indicative of generally anomalous samples. Because no significant sulfide was observed in the water
formation of thiomolybdate or particulate sulfides seem unlikely factors in the Mo and V removal. Adsorption of these elements onto hydrothermal Fe and Mn oxides is thus the most likely possibility for removal of these elements (e.g., Trefry and Metz, 1989; Kashiwabara et al., 2011) and we explore this further with the particulate data.

Figure 3.6 The relationships between small fraction (0.8 – 51 μm) particulate elements and (a) particulate Fe/ (b) particulate Mn in the ridge-crest plumes.

Note: V: light blue at Stn.18/dark blue at Stn. 20; Mo: yellow at Stn. 18/green-grey at Stn. 20; P: red at Stn. 18/brown at Stn. 20

We initially confine our consideration of hydrothermal oxide scavenging of Mo and V to waters 2300 m and deeper at Stns. 18 and 20, i.e., waters at the ridge crest with pFe concentrations > 1 nM. Since pFe was typically 10-fold greater in concentration than particulate Mn (pMn), it is tempting to focus just on pFe as the adsorbing phase. Note, however, that there is evidence that δ-MnO₂ more strongly adsorbs Mo than Fe oxyhydroxides (e.g., Kashiwabara et al., 2011). Based on pAl concentrations, lithogenic pMo, pV, pMn, and pFe were generally <1% of the total particulate concentrations in these hydrothermally-influenced waters (Lam et al., 2018) and are thus ignored. Figure 3.6 shows that in the small particulate fraction both pV and pMo are significantly
correlated with both pFe and pMn in the ridge crest plume. Note that the concentrations of the large particulate V were also greatly increased in the ridge crest plume (Stns. 18 and 20), even though the small fraction was still the majority of the total particulate concentrations. The large particulate pV/pFe ratio in these plume samples was statistically the same as the small particulate ratio. Lee et al. (2018) noted that hydrothermal pFe and pMn at Stns. 18 and 20 show different size partitioning, with pFe mostly (~80%) occurring in the small particulate fraction, while pMn occurring almost evenly between small and large particulate fractions. Interestingly, the fractions of total pV and total pFe of these hydrothermal samples that were in the large size particles were similar (median 27% and 24%, respectively; Fig. B.6). In contrast, the fraction of total pMo of these samples that was in the large size particles (median 34%; Fig. B.6) was midway between the large fraction percentages for pFe and pMn (median 24% and 49%, respectively; Fig. B.6). These observations are compatible with pFe being the main scavenger for pV while pMo may well be scavenged by both pFe and pMn.

Using an estimated global hydrothermal Fe input of ~10 Tg/yr (Poulton and Raiswell, 2002) and assuming most of this Fe precipitates and is removed to the sediments, then the EPZT hydrothermal pMo/pFe molar ratio of 6.4 x 10^{-5}, yields a Mo removal rate of ~10^7 mol/yr or ~5-10% of the estimated fluvial dissolved Mo flux (Gaillardet et al., 2014). Similarly, the EPZT hydrothermal pV/pFe molar ratio of 5.1 x 10^{-3}, yields a V removal rate of ~10^9 mol/yr or about twice the estimated fluvial dissolved V flux (Gaillardet et al., 2014). Similar calculations can be made using the estimated 1-2 x 10^{10} mol/yr global accumulation of Mn in metalliferous sediments (Elderfield and Schultz, 1996) and these yield similar results for hydrothermal Mo and V removal. While
there is considerable uncertainty in all of the numbers used for these estimates, the results are nonetheless in general accord with the conclusion of Trefry and Metz (1989) who suggested that adsorption onto hydrothermal precipitates was a major mechanism of removal of dV from the ocean as well as the similar conclusion for dMo removal (Kashiwabara et al., 2011 and references therein).

In order to understand whether hydrothermal pFe adsorption of V (and possibly Mo) should affect their dissolved distributions, we next consider phosphate, which has previously been shown to be adsorbed onto hydrothermal pFe (e.g., Wheat et al., 1996; Feely et al., 1998). Close inspection of the dissolved phosphate distribution in the hydrothermal plume (Fig. 3.7a) suggests adsorptive removal of ~100-150 nM PO$_4^{3-}$ in the most pFe-rich waters at Stns. 18 and 20. For the particulate phosphorus (pP) in the hydrothermal plume, lithogenic corrections are again trivial and ignored. Also, assuming a C/P Redfield Ratio of 117, the POC data suggests that biological contributions to pP in the hydrothermal plume are likewise trivial (i.e., the median POC/pP molar ratio in the plume waters is 10) (Lam et al., 2018). The hydrothermal pP-pFe relationship (Fig. 3.6) shows a good correlation and indicates a pP/pFe molar ratio of 0.29, which is about 50% higher than the P/Fe ratio Ohnemus et al. (2017) estimated for EPZT hydrothermal particles from particles filtered from GoFlo bottles. Taking the 100-150 nM estimate of hydrothermal PO$_4^{3-}$ adsorptive removal and the hydrothermal pV/pP molar ratio (0.016), thus suggests we should expect a 2-3 nM dV removal onto hydrothermal pFe. For Mo, the pMo/pP molar ratio (1.8 x 10$^{-4}$) indicates an insignificant dMo removal of only a few pM. These crude calculations indicate that we might see some dV removal at the ridge crest but not in the extended plume and we should not see any dMo removal. This
conclusion is clearly at odds with our observations and indicates that something else must be responsible for the significant dMo\textsuperscript{n} and dV\textsuperscript{n} depletions at Stns. 26 and 28.

Figure 3.7 (a) The distribution of dissolved phosphate along the EPZT. The distributions of (b) phosphate and (c) silicate (µmol/kg) in the upper 1000 m of the water column along the EPZT.

Note: In Fig. 3.7a, expanded concentration scale which emphasizes the range of concentrations associated with waters affected by the hydrothermal plume. Black dashed contours indicate neutral density surfaces (25 kg m\textsuperscript{-3} ≤ γ\textsuperscript{n} ≤ 27 kg m\textsuperscript{-3}).
We briefly consider several other possibilities for the hydrothermal dissolved Mo and V removal. First, more depleted dMo$^{n}$ and dV$^{n}$ in the off-axis plume than in the ridge-crest plume might be a result of different hydrothermal sources in the off-axis plumes (Stns. 25 and 26) from the ridge-crest plumes (Stns. 18-21), as evidenced by the $^{228}$Ra measurements in hydrothermal plume waters (e.g., Stn. 20: 3.2-5.5 yr; Stn. 25: 2.7-5.4 yr old) (Kipp et al., 2018). Likewise, Resing et al. (2015) suggested that off-axis hydrothermal samples (Stns. 20-36) were derived from vent fields south (~17°S-18.5°S) of the EPZT section while anomalously low excess $^{3}$He at Stn. 18 was likely a signal from local hydrothermal activity (Jenkins et al., 2018). Certainly, this observation is not surprising since various hydrothermal vent sites are distributed along the EPR and the EPR plumes are not restricted to the axial valley (German and Von Damm, 2006; Wu et al., 2011; Resing et al., 2015). Thus, the different extent of dMo$^{n}$ and dV$^{n}$ depletion between the ridge-crest plume and the off-axis plume may well reflect different vent sources. In contrast, the $^{3}$He data (Jenkins et al., 2018) and positive linear correlations between excess $^{3}$He with dissolved Fe and dissolved Mn from the first off-axis station (Stn. 20) of the EPR to the westernmost station (Stn. 36) (Resing et al., 2015) indicate that the off-axis samples form a continuous plume. However, the locale of additional hydrothermal sources across the EPZT suggested by the $^{228}$Ra data (Kipp et al., 2018) is incompatible with that suggested by other data ($^{3}$He, dissolved Fe and dissolved Mn; Resing et al., 2015). Thus, the extent to which the extended hydrothermal plume observed during the EPZT reflects one or many sources is unresolved.

A change in competition for adsorption sites due to concentration changes in another element is another possible explanation for our observations that seems unlikely.
Phosphate is likely the highest concentration strongly competing element (Feely et al., 1998; Brinza et al., 2008) and its dissolved concentration varies minimally and, in fact, increases slightly off-axis (Fig. 3.7a) where we see the highest dMo$^n$ and dV$^n$ removal.

Alteration of the structure of hydrothermal particles during off-axis transport (Fitzsimmons et al., 2017) and thus alteration of their adsorption capacity is another possibility. Indeed, at the ultramafic-hosted Rainbow hydrothermal site on the Mid-Atlantic Ridge, Edmonds and German (2004) did observe progressive increases in particulate V/Fe ratios going from young buoyant plumes to neutrally buoyant plumes, and ultimately to the highest V/Fe ratios in the underlying hydrothermal sediments. Likewise, Brinza et al. (2015) found that as ferrihydrite ages to hematite, sorbed V and Mo become incorporated into the hematite structure while Kashiwabara et al. (2011) found that molybdate adsorbs to ferrihydrite as an outer sphere complex but to hematite and goethite as an inner sphere complex. These observations and experiments are thus compatible with increased removal of V and Mo from the water with plume particle age. We note that from $^{228}$Ra measurements in the EPZT hydrothermal plume samples, Kipp et al. (2018) estimated a significantly greater age for samples at Stn. 20 (2.4-5.5 yrs) than for the axial Stn. 18 (~1 mo.).

Since pV in the EPZT extended hydrothermal plume was significantly greater than the deep water background concentrations, we can at least partially test this idea. If we confine our analysis to hydrothermally-influenced samples with pV > 9 pM (i.e., about 3x greater than the pelagic deep water background in the EPZT of 2 - 4 pM), then non-lithogenic pV/pFe molar ratios cluster around 5.3 ± 0.8 x $10^{-3}$ and show no relationship with distance from the ridge crest (Fig. B.7). Thus, this provides no evidence
of significantly changing pV/pFe with particle ageing. Interestingly, the one dV-depleted plume sample where we have both dissolved and particulate data (Stn. 20, 2500 m, dV\textsuperscript{n} = 19 nmol/kg) had the highest non-lithogenic pV/pFe molar ratio (8.1 x 10\textsuperscript{-3}) of these samples. This is, of course, scant evidence on which to build a hypothesis as well as only a relatively modest pV enrichment. In any event, we find no support for large changes in V adsorption in the EPZT hydrothermal particle data. Given that the hydrothermal dV\textsuperscript{n} depletions are at the edges of the pFe plume, we can only speculate that breakdown of the organic matrix associated with hydrothermal pFe (Fitzsimmons et al., 2017) might result in more exposed pFe surface area and ultimately aggregation and removal by sinking.

3.3.4 Mo and V in shallow waters

Through most of the section, the transition from slightly dV-depleted shallow waters to higher dV\textsuperscript{n} deep waters occurs in the neutral density range $\gamma$\textsuperscript{n} = 25.5-26.5 kg/m\textsuperscript{3} which is also where the sharpest gradients in phosphate and silica concentrations occur (Fig. 3.7b,c). Enrichment of pV in surface waters with dominance in the large particulate fraction suggests that V was taken up by biogenic particles (likely diatom) (Lam et al., 2018; Lee et al., 2018; Osterholz et al., 2014), which is compatible with the observation of surface water dV\textsuperscript{n} depletion. Our observations thus suggest that the dV\textsuperscript{n} gradient in the water column (200-400 m) in the pelagic region is mostly controlled by shallow biological removal and deeper regeneration.

Near the Peru margin, nutrient gradients still follow the density gradient; however, the relationship between dV\textsuperscript{n} and density weakens (Fig. 3.5a), suggesting additional processes influencing the dV\textsuperscript{n} distribution in this environment. Given the removal of dV in hypoxic Louisiana Shelf waters (Shiller and Mao, 1999) and the slight
Mo depletion in those same waters (Joung and Shiller, 2016) as well as the low oxygen water impinging on the Peru margin in the EPZT, we more closely examined our dMo$^n$ and dV$^n$ profiles across that margin (Stns. 1-5; Fig. 3.4). We do indeed observe some shallow (<200 m) samples with depleted dMo$^n$ (98.5-104.6 nmol/kg). Again, those samples with slightly or moderately depleted Mo (1.5-4 s.d.) were reanalyzed to validate the depletion. We do not see high nitrite or dissolved/particulate Fe or Mn in these Mo-depleted samples relative to other shallow samples in the margin stations. Thus, there is no evidence of a recent, substantially different, impact of scavenging, denitrification, or sediment interaction.

Similar to our observations of Mo, dV$^n$ depletion greater than the usual surface water depletion was observed in near surface (< 50 m) waters of Stns. 1-5 across the Peruvian continental shelf where concentrations ranged from 29.7-32.0 nmol/kg. The lowest dV$^n$ in the coastal upwelling region was observed near the surface at Stn. 2 (the station closest to shore), and also corresponded with the lowest dMo$^n$ and the highest total Chl $\alpha$ in the coastal stations (Fig. 3.4). Other dV$^n$- and dMo$^n$-depleted samples in this part of the section were also generally in the shallowest waters of the three most inshore stations. Given that dMo and dV were analyzed by different methods at different times, we view this as a robust observation, despite the concentration changes being close to our analytical precision. Since nearshore pFe enrichment was coincident with the high nitrite plume below 100 m (i.e., well below where we observe shallow dV$^n$ and dMo$^n$ depletion), adsorptive removal or removal associated with denitrification seems unlikely. However, apparent biological uptake of Mo from surface waters has been reported by Wang et al. (2016) who observed non-conservative dMo behavior in the Taiwan Strait.
Likewise, Osterholz et al. (2014) observed significant dV removal in diatom cultures. Surface waters of the inshore EPZT stations had the greatest amount total Chl a and the protective pigments diadinoxanthin, diatoxanthin, and β-carotene of the entire section (Moffett et al., 2015) as well as the highest amount of opal (Lam et al., 2018). Taken together, our observations thus suggest biological uptake and/or adsorption onto organic particles as the likely cause of the shallow inshore dV\textsuperscript{n} and dMo\textsuperscript{n} depletions in the EPZT section.

The V section also allows us to revisit the issue of whether coastal shelf redox processes play a significant role in overall surface ocean V depletion as suggested by Shiller and Mao (1999). We do note that the expansion of the upper ocean dV\textsuperscript{n} depleted depth range east of Stn. 13 (99° W) may relate to both biological and redox processes (see next section). However, the pelagic vertical dV\textsuperscript{n} gradient still tends to follow the nutricline and thus occurs slightly shallower than might be expected from the OMZ dV depletion along the margin. In contrast to the Louisiana Shelf observations (Shiller and Mao, 1999; Joung and Shiller, 2016), we did not observe dV\textsuperscript{n} (or dMo\textsuperscript{n}) depletions in oxygen-depleted bottom waters on the Peru margin. Also, there was no significant horizontal gradient in upper water dV\textsuperscript{n} depletion away from the margin as would be expected if margin processes dominated shallow V removal. Thus, the EPZT data seem to argue against a large redox effect on the pelagic dV distribution. Nonetheless, we cannot rule out a margin effect elsewhere in the ocean where, for example, an extreme oxygen minimum intersects a wider margin than occurs off the west coast of Peru.
3.3.5 Mo and V in the offshore OMZ

As noted above, significant dV\textsuperscript{n} and dMo\textsuperscript{n} depletion was observed in a few samples in the offshore ODZ (Figs. 3.2a and 3.5a). This is especially apparent at Stn. 9 where several samples in the 150 - 200 m depth range are depleted in both elements and which corresponds to a pool of water with high nitrite as well as high I\textsuperscript{−} and low IO\textsuperscript{3−} (Cutter et al., 2018), high dissolved and labile Co (Hawco et al., 2016) and elevated pFe (Heller et al., 2017). That said, there is higher nitrite water (also with high I\textsuperscript{−} and low IO\textsuperscript{3−} as well as high Co and high pFe; Cutter et al., 2018; Hawco et al., 2016; Heller et al., 2017) close to the coast at Stns. 2-5 which does not show significant dMo\textsuperscript{n} depletion and which has a dV\textsuperscript{n} depletion similar to the typical upper water column depletion.

No significant dissolved sulfide was observed in these Mo and V depleted waters (Cutter et al., 2018) and only low pM amounts of acid volatile sulfides were detected (Ohnemus et al., 2017). Thus, formation of thiomolybdate or particulate sulfides seem unlikely factors in the Mo and V removal. Likewise, Scholz et al. (2017) summarize observations for this region and discount sulfide as a factor in Mo cycling. Recent work suggests two other possible processes that might explain the dMo and dV depletions. Scholz et al. (2011, 2017; see also Heller et al., 2017) proposed that Fe oxides that are reductively dissolved in the anoxic benthic boundary layer re-precipitate at the oxycline or below to scavenge Mo and V and then ultimately settle to the sediments for burial at the boundaries of the ODZ. Since the Fe can cycle through this process repeatedly, Fe oxides can be viewed as shuttling the Mo and V to the sediments. An alternative mechanism, discussed by Ohnemus et al. (2017) using other EPZT data, involves denitrifying prokaryotes taking up various trace elements, including V, in the ODZ. This
is also consistent with the utilization of Mo in bacterial nitrate reductase (Tsementzi et al., 2016). For V, there are some reports of nitrate reductases that lack Mo and contain V instead (Rehder, 2008 and references therein), though the presence of V nitrate reductase in the ocean is, as yet, unknown.

Confounding any attempt to deconvolve the effects of redox shuttling versus heterotrophic uptake on Mo and V cycling in the ODZ is the fact, noted by Ohnemus et al. (2017), that pFe is enriched in ODZ waters roughly coincident with the enrichment in nitrite. Indeed, Heller et al. (2017) observed oxidation of dissolved Fe(II) to particulate Fe(III) in the upper ODZ of the EPZT section. Heller et al. (2017) and Scholz et al. (2016) further suggested coupling between the Fe and N redox cycles. To help resolve this overlap of processes, we examine the particulate data to see if it might shed further light on ODZ Mo and V cycling. We note that the pump particles considered here include pMo and particulate organic carbon (POC) data that were not available to Ohnemus et al. (2017) in their consideration of bottle particulates in the EPZT.

We first plot pMo and pV versus the non-lithogenic pFe in ODZ, upper oxycline, and mixed layer samples from the upper 500 m of Stns. 1-36 (Fig. 3.8). If we compare element-Fe relationships in the ODZ with those same relationships for ridge crest particles under the assumption that adsorption onto Fe oxyhydroxides controls pMo and pV concentrations in both regions, then inshore ODZ Fe particles (Stns. 1-5; green circles in Fig. 3.8) would need to sorb >10x more Mo per mole of pFe and 3x more V than hydrothermal pFe. For the offshore ODZ (Stns 7-13; red circles in Fig. 3.8), Fe precipitates would need to sorb ~80x more Mo and >10x more V per mole pFe than hydrothermal precipitates. Certainly, adsorption capacities of Fe oxyhydroxides can vary
substantially and are likely to be affected by pH, organic matter, and competing ions. Additionally, evidence suggests that the precipitation of ODZ Fe oxyhydroxides occurs in the absence of dissolved oxygen (Scholz et al., 2016; Heller et al., 2017), which is not likely the case for ridge crest precipitates, which may result in different scavenging characteristics for these oxyhydroxides. Indeed, Heller et al. (2017) reported at least some lepidocrocite in the ODZ while Hoffman et al. (2017) found ferrihydrite-like oxyhydroxides in the hydrothermal plume of the EPZT section. This mineralogical difference could also contribute to differences in scavenging removal by pFe in the ODZ versus the hydrothermal plume (e.g., Kashiwabara et al., 2011). Thus, using ridge crest precipitate composition to correct for Fe oxyhydroxide adsorption onto ODZ Fe precipitates is potentially problematic (Ohnemus et al., 2017). Furthermore, while the pMn concentration was typically <1% that of pFe in the upper ODZ, above the ridge crest pMn was typically 8% of pFe concentration. As was discussed in the hydrothermal section, above, particulate MnO₂ may well be an important or even dominant Mo adsorbing phase above the ridge crest, complicating the application of hydrothermal element-Fe relationships to the ODZ. Thus, compositionally, it is difficult to rule out adsorption onto Fe precipitates as a significant factor affecting Mo and V in the ODZ.

Figure 3.9 shows pMo and pV plotted versus POC (Lam et al., 2018) for small particulate fraction samples in the ODZ, upper oxycline above the ODZ, and the mixed layer throughout the transect. Plotting versus particulate nitrogen or phosphorus shows similar trends. Corrections for lithogenic contributions are minor, typically 3% of pV and <1% for pMo, and were not made to the data. For Mo, the Fe correction based on the hydrothermal pMo-pFe relationship affects pMo concentrations in the ODZ, oxycline and
mixed layer trivially, typically only 2%. For pV, the Fe correction is larger, typically 21%; however, making the correction does not change the trends in Fig. 3.9. Because of the trivial nature of the lithogenic correction and the uncertain nature of the Fe adsorption correction (which is small if we use hydrothermal element-Fe relationships), we therefore show the original, uncorrected data. For pV, our results are in general agreement with those of Ohnemus et al. (2017). That is, ODZ particles are clearly enriched in pV relative to the mixed layer and oxycline and there is a general trend of increasing pV with POC. Similar trends are also observed for pMo. Thus, the ODZ cycling of V and Mo could well involve biotic incorporation into organic matter and/or removal by adsorption onto organic particles.
Figure 3.8 The relationships of small (0.8 – 51 µm) (a) particulate Mo (left) and (b) particulate V (right) with and non-lithogenic Fe in the upper 500 m of the water column along the EPZT.

Note: For clarity, only ODZ, mixed layer and upper oxycline samples in the upper 500 m are shown here.

Figure 3.9 The relationships of small (0.8 – 51 µm) (a) particulate Mo and (b) particulate V with POC in the upper 500 m of the water column along the EPZT.

Note: For clarity, only ODZ, mixed layer and upper oxycline samples in the upper 500 m are shown here.
Scant data on cellular V and Mo quotas is available to test this idea that the ODZ pV and pMo enrichments are biogenic. Much of the available data for Mo and V relates to diazotrophs and not to the heterotrophic prokaryotic community of the ODZ. In an N\textsubscript{2}-fixing soil bacterial mutant that expresses only V-nitrogenase, Bellenger et al. (2008) found cellular V/P molar ratios of ~1.5 \times 10^{-4} at seawater concentrations of dV. Tovar-Sanchez and Sañudo-Wilhelmy (2011) measured metal:P cellular quotas in Trichodesmium colonies in subtropical Atlantic waters influenced by the Amazon plume and found V/P molar ratios of 5-11 \times 10^{-3} and Mo/P molar ratios of 1-10 \times 10^{-3}. Osterholz et al. (2014) reported cellular V/P molar ratios of 4-11 \times 10^{-3} for two diatom cultures. Ho et al. (2003) suggested an average oceanic phytoplankton Mo/P molar ratio of 3 \times 10^{-5}. Tuit et al. (2004) examined Mo quotas in two N\textsubscript{2}-fixing cyanobacteria and reported Mo/C molar ratios of 0.7 \pm 0.3 \times 10^{-6}. For the EPZT ODZ samples, Ohnemus et al. (2017) estimated a V/P molar ratio of 3 \times 10^{-3} and our data indicate molar ratios of V/P = 4 \times 10^{-3}, Mo/P = 5 \times 10^{-4}, and Mo/POC = 5 \times 10^{-6}. Thus, while the available biological data are scattered and not necessarily applicable to the relevant ODZ biota, they nonetheless indicate that the necessary cellular element ratios are within reasonable biological possibility. However, seeing that particulate metal/C ratios in ODZ waters are higher than in the mixed layer (Fig. 3.9) does require significantly increased metal quotas for the ODZ heterotrophic biota as compared with mixed layer phytoplankton, as was noted by (Ohnemus et al., 2017).

Note that inclusion of the large particulate fraction in this discussion does not significantly alter our conclusions. While the large size pV in the oxycline often was greater than small pV (presumably because the oxycline is shallow and receives large
size $pV$ from the mixed layer), large $pV$ was generally less than a third of the total $pV$ in the ODZ. More details of processes controlling $pV$ size partitioning in the ODZ are discussed by Lee et al. (2018). However, for the inshore stations (Stns. 1-5), the $pV/POC$ ratios were typically 3 times higher in the large particles than the small. Furthermore, there was no clear correlation in the large fraction between $pV$ and POC across the ODZ. These observations make sense both in the context of heterotrophic metal uptake more likely involving small (i.e., <51 µm) cells thereby leading to a lack of $pV$-POC relationship in large particles as well as small FeOOH precipitates aggregating to form larger particles leading to a similar $pV$-pFe relationship in small and large particles.

Despite the fact that there are potential mechanisms for removing $dMo$ and $dV$, we note that the highest ODZ $pV$ and $pMo$ concentrations are found at the most inshore stations. Indeed, that is where the Fe oxide shuttling mechanism is most likely to be relevant (Scholz et al., 2011, 2017). Thus, we are still left with the puzzle of why we don’t see even greater dissolved phase Mo and V depletions nearshore than offshore at Stn 9. We note, however, a slight upward doming of isopycnals in the upper few hundred meters at Stn. 9 (Fig. 3.5a) which is possibly indicative of a cyclonic eddy. Eddies can be important in offshore transport of waters along eastern upwelling margins (Pegliasco et al., 2015). Although the sampling period of the cruise was during the annual minimum of eddy activity along the Peruvian coast (Chaigneau et al., 2008), the occurrence of an eddy is still possible and supported by a relatively weak seasonal variation (~10 %) of the surface eddy kinetic energy observed around 10°S off the Peru coast (Colas et al., 2012). Additionally, subsurface anticyclonic eddies generated at the bottom boundary layer of the continental slope in the Peru-Chile Undercurrent can transport low oxygen and
elevated nitrite waters offshore (Thomsen et al., 2016). Because of persistent cloud cover during the EPZT transect, daily satellite imagery is not available. However, monthly composites for November 2013 (Fig. B.8) show dynamic features in the chlorophyll imagery trending southwestward away from the coast as well as a surface temperature front where the Peru Coastal Current likely bifurcates (Penven et al., 2005). Thus, the cruise track passed through a clearly dynamic region and the waters at Stn. 9 may well have come from the northeast where the shelf is somewhat broader and the ODZ also extends further offshore. This may well explain the discontinuous nature of nitrite and some other chemical distributions and suggests the offshore ODZ dMo and dV depletions are remnant signals of more intense removal near the coast.

3.4 Conclusions

Our presentation of the first detailed oceanic sections of dissolved Mo and V largely confirms past interpretations of the distributions of these two elements (Morris, 1975; Collier, 1984; Collier, 1985; Middelburg et al., 1988; Sherrell and Boyle, 1988; Tuit, 2003). In the broad picture, Mo behaves conservatively while V is nearly so, with only a ~5% increase in concentration with depth. However, some interesting details emerge from the sections.

For dissolved Mo, a small number of samples showed significantly depleted concentrations which, in most cases, gradually increased with time. We hypothesize that the original sample had experienced a change in speciation of dissolved Mo from the predominant molybdate to another, as yet, unknown form. Because these Mo depletions were not randomly scattered but instead corresponded with other factors including low oxygen, high nitrite, depleted V, and/or the hydrothermal plume, along with the
observation of pMo and pV enrichments in the OMZ and the hydrothermal plume, these Mo depletions (or speciation changes) cannot be dismissed as random analytical artifacts. However, full understanding or exploitation of this information necessarily awaits further analytical development. Note that due to lack of observable sulfide in the section, formation of thiomolybdates is probably not a factor.

For dissolved V, the transition from slightly V-depleted surface waters to slightly V-enriched deeper waters generally occurs in the same density range as the most rapid increase in nutrients. Closer to the Peru margin, this relationship between the V gradient, pycnocline and nutricline is less clear. Depleted dV\(^n\) (and dMo\(^n\)) were found in a few samples within the ODZ, generally associated with the nitrite maximum. Increased non-lithogenic pV (and pMo) were also observed in these upper ODZ waters and correlated with pFe. These results, along with the reported oxidation of dFe(II) to pFe(III) in the upper ODZ of the EPZT section (Heller et al., 2017), are supportive of the mechanism proposed by Scholz et al. (2011) for the adsorption of these oxyanions onto reprecipitated Fe (oxy)hydroxides in the upper ODZ resulting in a shuttling of V and Mo to the sediment surface. There may also be some additional dV and dMo removal in the ODZ due to biological uptake, presumably in association with nitrogen cycling (Crans et al., 2004; Maia et al., 2017). This is supported both by correlations between POC and pV or pMo as well as reasonable requirements for V and Mo biological uptake.

Particulate Mo and V are mostly found in non-lithogenic phases across the section. Enriched pMo and pV in the ODZ were well-correlated with both pFe and POC and found in association with the nitrite maximum, which implies that Mo and V in the ODZ are likely scavenged by Fe (oxy)hydroxides as well as taken up by the biota.
Slightly increased \( p\text{Mo} \) was seen in the ridge-crest plume near the EPR while elevated \( p\text{V} \) was observed in both the ridge-crest plume and the off-axis plume. Both \( p\text{Mo} \) and \( p\text{V} \) were well correlated with \( p\text{Fe} \) and \( p\text{Mn} \) in the hydrothermal plume, suggesting the scavenging removal of \( \text{Mo} \) and \( \text{V} \) onto hydrothermal \( \text{Fe/Mn} \) (oxy)hydroxide precipitates.

Additional slight depletions of \( d\text{V}^n \) and \( d\text{Mo}^n \) in nearshore surface waters, relative to offshore surface water, and coincident with higher total Chl \( a \) concentrations toward the Peruvian coast, suggests removal by biological activity. Due to the absence of low \( \text{V} \) and/or \( \text{Mo} \) in the shelf bottom waters, the removal of these elements to anoxic sediments did not appear to be significant, at least in this section. Thus, our data do not support the proposal that incorporation of \( \text{V} \) into reducing shelf sediments contributes to the overall oceanic shallow water \( d\text{V} \) depletion (Shiller and Mao, 1999).

Depleted \( d\text{V}^n \) and \( d\text{Mo}^n \) were also seen in association with the hydrothermal plume emanating from the EPR. Non-lithogenic \( p\text{V} \) and \( p\text{Mo} \) correlated with \( p\text{Fe} \) in plume waters and suggests adsorption onto hydrothermal \( \text{Fe} \) oxyhydroxides are a dominant oceanic sink for \( \text{V} \) and a minor one for \( \text{Mo} \), in agreement with previous observations (e.g., Trefry and Metz, 1989). Greater depletion of the dissolved concentrations of these elements in some off-axis samples than in ridge crest samples as well as in samples from the plume margins remains an enigma, possibly relating to different hydrothermal vent sources, particle ageing, or breakdown of hydrothermal plume particles increasing the scavenging of these two oxyanions.

While the sections presented here do not substantially change our picture of the distributions of dissolved \( \text{V} \) and \( \text{Mo} \) in the ocean, they do provide constraints on these elements’ cycles and provide guidance for future work. In particular, highly reducing
environments, not considered in this section, remain important regions for the removal of V and Mo. Further development of methods for determining the speciation of these elements as well as more detailed studies of shelf and hydrothermal regions will likely improve our understanding of the oceanic cycling of V and Mo as well as potentially provide improved insight into their roles in biological and redox cycles.
CHAPTER IV – PROCESSES AFFECTING THE DISTRIBUTIONS OF DISSOLVED ALUMINUM AND GALLIUM ALONG THE U.S. GEOTRACES EAST PACIFIC ZONAL TRANSECT

4.1 Introduction

Gallium (Ga) is one position below aluminum (Al) in the Periodic Table, which suggests they have similar chemical behaviors. Previous studies have indeed shown that Ga in seawater behaves geochemically in manner akin to Al (e.g., Orians and Bruland, 1988a, b; Shiller, 1988). Dissolved Al exhibits a typical scavenged-type distribution in the open ocean (Bruland et al., 2014) and is controlled by various processes including aeolian inputs, particle scavenging, regeneration/remineralization, hydrothermal activities, sediment resuspension and advection (Hydes, 1979, 1983; Measures et al., 1984, 2015; Orians and Bruland, 1985, 1986; Measures and Edmond, 1990; Measures, 1995; Middag et al., 2012, 2013, 2015; Hatta et al., 2013; Grand et al., 2015). Analogous to Al, the oceanic distribution of dissolved Ga is also affected by most, if not all, of these processes; however, Ga is generally less reactive than Al and also less well-studied (Orians and Bruland, 1988 a, b; Shiller, 1998; Shiller and Bairamadgi, 2006).

Although both dissolved Ga and Al are particle reactive and hydrolyzed in seawater, there are key differences in their behaviors resulting from the small differences in their chemistry. In particular, at the pH of seawater, Ga should be dominantly present as Ga(OH)$_4^-$ (Bruland, 1983) while the dominant forms of Al are Al(OH)$_3^0$ and Al(OH)$_4^-$ (Stumm and Morgan, 1996). Because neutral species should be more favored for adsorption onto the net negatively charged surfaces of oceanic particles, it follows that Al should be more readily sorbed by oceanic particle surfaces than Ga (Orians and Bruland,
This results in the shorter residence time of Al in seawater as compared with Ga. For instance, Orians and Bruland (1988a) suggested that in surface waters, dissolved Ga has a residence time of ~decades, which is an order of magnitude longer than the surface water dissolved Al residence time (2–6.5 yrs; Orians and Bruland, 1986; Jickells et al., 1994; Measures and Brown, 1996). In deep waters, Ga has a residence time of ~100–750 years based on simple vertical advection/diffusion modeling (Orians and Bruland, 1988b) while the Al residence time is estimated to be 100–200 years (Orians and Bruland, 1985, 1986), depending on location. Additional chemical factors affecting the two elements are the larger ionic radius of trivalent Ga relative to Al and the longer and more covalent Ga-O bond than Al-O bond (Burton and Culkin, 1972). These two factors suggest that Ga will be more readily leached from solid phases where it substitutes for Al. Both the hydrolysis difference (affecting relative removal of the two elements) and the structural differences (affecting relative input), therefore combine to result in the observed distribution differences of dissolved Ga and Al. Specifically, the high dissolved Ga/Al ratio in surface waters (Orians and Bruland, 1988b; Shiller, 1988, 1998) relative to the crustal ratio (Rudnick and Gao, 2014), and the lower inter-basin fractionation of Ga than of Al (Orians and Bruland, 1985, 1988b), suggest the interplay of these chemical factors.

Major sources for dissolved Al and Ga in surface water include dust deposition and fluvial input. Surface water distributions of Al and Ga suggest that the major source of these elements is aeolian input (Hydes, 1979, 1983; Measures et al., 1984; Orians and Bruland, 1985, 1986, 1988a; Shiller, 1998; Shiller and Bairamadgi, 2006). Higher surface water dissolved Al and Ga concentrations in a regime where a high atmospheric dust
input occurs (e.g., Hydes, 1989; Shiller, 1998; Kramer et al., 2004; Measures et al., 2008a; Middag et al., 2015) reflect the implication of both elements as tracers for dust deposition to the surface ocean. The importance of fluvial inputs for Ga and Al also have been recognized in previous studies (Measures et al., 1984; Kremling, 1985; Shiller and Frilot, 1996; McAlister and Orians, 2012). However, fluvial Al fluxes are commonly removed in river plumes and estuaries (Van Bennekom and Jager, 1978; Morris et al., 1986; Takayanagi and Gobeil, 2000; Brown and Bruland, 2009). In the one study of its estuarine behavior, significant Ga removal was also observed (McAlister and Orians, 2012), though how common this is and the relative estuarine removal of Ga versus Al is not known. Anthropogenic Ga input to the surface ocean both through dust (Shiller, 1998; Shiller and Bairamadgi, 2006) and fluvial input (Shiller, 1988; Shiller and Frilot, 1996) appears to be minor. Possible sources for Al and Ga throughout the water column include reversible exchange, regeneration, and remineralization (Orians and Bruland, 1985, 1986, 1988a, b). Since Ga and Al have hydrolysis chemistry similar to that of thorium (Th), reversible exchange on particles in the water column was suggested as a source of deep Ga and Al; however, no direct evidence has been found for this mechanism (Orians and Bruland, 1988a, b; Bruland et al., 2014). Middag et al. (2015) proposed that the well-correlated Si-Al relationship in some basins is due to regeneration/remineralization from settling biogenic particles. They also observed a positive correlation between Al and apparent oxygen utilization (AOU) in the oxygen minimum zone (OMZ) in the western equatorial Atlantic Ocean (between the equator and 10°N), indicating Al release from remineralization. However, Measures et al. (2015) did not observe this positive relationship in the OMZ off the northwest African coast, instead
finding that Al minimum corresponded with the oxygen minimum. Like Al, regenerated Ga from settling particulate matter and remineralization at the sediment-water interface were suggested as sources for Ga to the water column (Orians and Bruland, 1988a, b). The bottom sources for Ga and Al can be sediment fluxes (i.e., pore water, remobilization at the sediment surface) and sediment resuspension (Orians and Bruland, 1986, 1988a, b; Measures, 1995; Shiller, 1998; Hatta et al., 2013; Middag et al., 2012, 2013, 2015; Grand et al., 2015). Increased dissolved Al and Ga in the deep water have been attributed to resuspended sediments and subsequent dissolution of Al and Ga (e.g., Orians and Bruland, 1986; Moran and Moore, 1991; Shiller, 1998; Measures et al., 2015) and/or the release of diagenetically Al-enriched porewaters (e.g., Middag et al., 2012, 2013; Hatta et al., 2013). Along with Al and Ga enrichments in hydrothermal vent fluids (German and Seyfried, 2014), elevated dissolved Al and Ga in the deep water near the mid-ocean ridges (Stoffyn and Mackenzie, 1982; Shiller et al., 2014; Measures et al., 2015; Resing et al., 2015) suggests hydrothermal inputs for Al and Ga in the deep water. However, Middag et al. (2015) argued that hydrothermal source for Al is minor on the basin-wide scale, which is supported by reports of insignificant hydrothermal Al fluxes (Lunel et al., 1990; Elderfield and Schultz, 1996).

Evidence of Al and Ga removal by particle scavenging has been seen throughout the water column (Hydes, 1979; Orians and Bruland, 1985, 1986, 1988a, b; Shiller, 1998; Middag et al., 2015). For Al, the removal mechanism probably involves both passive and active scavenging by biogenic particles, likely associated with silica (Hydes, 1979; Moran and Moore, 1988, 1992; Gehlen et al., 2002; Koning et al., 2007; Li et al., 2013). In contrast, the understanding of Ga scavenging removal has not received much attention.
Given that Ga competes with Fe for binding to siderophores (Emery and Hoffer, 1980; Emery, 1986; Gascoyne et al., 1991), Ga could be removed via active scavenging. Low surface water dissolved Ga and Al concentrations in high productivity waters, relative to their concentrations in open gyre waters, are likely caused by intensive scavenging by biogenic particles (Orians and Bruland, 1986, 1988a; Shiller, 1998; Brown and Bruland, 2009).

The advection of low or high dissolved Ga and Al from areas of low or high dust input also affects the distributions of these elements. For example, minima of Ga and Al at mid-depth observed in the Atlantic and North Pacific are indicative of the advection of low-Ga and low-Al waters from higher latitudes where there is lower dust deposition (Measures and Edmond, 1990; Measures, 1995; Shiller, 1998; Shiller and Bairamadgi, 2006; Middag et al., 2015). Likewise, dissolved Al characteristic of Subtropical Mode Water has been observed advected away from source regions (Measures et al., 1986, 2008a, 2015; Middag et al., 2015). Maxima of Ga and Al have been observed in waters influenced by the Mediterranean Outflow Water (Measures, 1995; Shiller, 1998; Shiller et al., 2014; Measures et al., 2015). Additionally, Shiller and Bairamadgi (2006) suggested that a Ga maximum in subsurface waters in the northeast Pacific Ocean (Orians and Bruland, 1988a, b) was likely caused by transport of high Ga waters rather than from in situ Ga regeneration.

Given the differing reactivities of these two similar elements, examination of dissolved Ga/Al ratios in the water column can reveal the effect of biogeochemical and physical processes on their distributions. Shiller and Bairamadgi (2006) found that the dissolved Ga/Al ratio varied with chlorophyll a (Chl a) in northwest Pacific surface
waters, probably because of a faster scavenging removal of Al than Ga. An implication of this relationship is that the Ga/Al ratio might be used to minimize the uncertainty of surface Al residence time used in Al-based dust deposition models (Shiller and Bairamadgi, 2006). In deep waters, the change of dissolved Ga/Al ratio between different water masses (e.g., Ga/Al ratio in North Atlantic Deep Water: ~2 mmol/mol; Ga/Al ratio in Antarctic Bottom Water: ~4 mmol/mol) suggests the possibility of different enrichment mechanisms causing differing ratios in these water masses (Shiller and Bairamadgi, 2006).

Despite the knowledge of oceanic dissolved Ga and Al distributions outlined above, distributions of these two elements in the southeastern tropical Pacific Ocean are largely unknown. We present here dissolved Al and Ga data collected from the U.S. GEOTRACES GP16 East Pacific Zonal Transect (EPZT). A variety of biogeochemical and physical processes (i.e., Peru upwelling, extreme OMZ, and hydrothermal plumes) in our study area provide an opportunity to further examine the processes and mechanisms that control oceanic Al and Ga distributions. Although the dust deposition in the South Pacific Ocean is not as significant as in the North Atlantic Ocean, biogenic removal and shelf sediment input might be important sinks/sources for Al and Ga in the Peru upwelling region. This transect also showed a strong westward transport of hydrothermal plume waters from the East Pacific Rise (EPR) and a hydrothermal dissolved Al signal was observed as far as ~3000 km west of the EPR (Resing et al., 2015; Jenkins et al., 2018). Thus, hydrothermal activity might be a potential source for Ga as well. Benthic nepheloid layers were commonly observed near the bottom across the transect (Lee et al., 2018; Ohnemus et al., 2018) providing an opportunity to evaluate the role of resuspended
sediments for deep Al and Ga. The correlation between Ga/Al ratios and Chl \( \alpha \) concentration in surface water is examined here to test the possibility of using Chl \( \alpha \) and Ga to adjust surface Al residence time which is used in Al-based dust deposition estimates, as Shiller and Bairamadgi (2006) proposed previously.

4.2 Methods

4.2.1 Seawater sampling

Water samples were collected at 35 stations from the R/V Thomas G. Thompson during the U.S. GEOTRACES GP16 EPZT expedition (Fig. 4.1), conducted October 25–December 20, 2013 from Manta, Ecuador to Papeete, French Polynesia. Various station types were occupied in the EPZT: four shelf stations (1–2 casts), 13 full depth stations (3 casts), 13 shallow stations (1 cast, depth ~1000 m) and 5 super-stations (3–4 casts).

Figure 4.1 Cruise track of the U.S. GEOTRACES GP16 East Pacific Zonal Transect (EPZT).

Note: station 1 (Peru-Chile Trench) is out of numerical order and is located between stations 5 & 6.

Water column samples were obtained using 12-L Teflon-coated GoFlo bottles deployed on the trace metal clean GEOTRACES carousel (Cutter and Bruland, 2012). Water samples were filtered through 0.2 \( \mu \)m capsule filters (Pall Acropak Supor capsule)
and collected using trace-metal-clean protocols (Measures et al., 2008b; Cutter et al., 2014). Surface water samples (~2 m depth) were obtained using an underway towed-fish system (Bruland et al., 2005) and filtered through a 0.45 µm Osmonics and a 0.2 µm polycarbonate cartridge filter.

For Ga samples, the filtered samples (~125 mL) collected from the GoFlo bottles were stored in pre-cleaned HDPE bottles and shipped back to the laboratory for acidification and analysis. After samples were transported to the laboratory, an aliquot of ultrapure 6 N HCl (Seastar Baseline) was added to the sample to reduce the pH to ~1.8 and the sample was then stored at room temperature. For Al samples, filtered samples were stored in 100-mL LDPE bottles and were acidified with 12 N ultrapure HCl (Fisher Optima) to pH ~1.7 at sea. Note that surface towed-fish samples were not available for Al. Ancillary data (e.g., salinity, temperature, nutrients, oxygen) was provided by the cruise management team and can find at the BCO-DMO (http://www.bco-dmo.org/project/499723).

4.2.2 Analytical methods

4.2.2.1 Ga

Ga was concentrated using an isotope dilution, magnesium hydroxide co-precipitation method (Shiller and Bairamadgi, 2006 as modified from Wu and Boyle (1997, 1998)) and analyzed using ThermoFisher Element XR sector field inductively coupled plasma-mass spectrometer (ICP-MS) with a PFA microflow nebulizer (Elemental Scientific, Inc.).

Briefly, acidified seawater samples (7 mL) were spiked with a known amount of enriched isotope of 99.8% $^{71}$Ga (Oak Ridge National Laboratory), following by adding an
aliquot of clean ammonia to form a small amount of magnesium hydroxides precipitate. Centrifugation allowed removal of the interfering, salty supernatant. Trial results showed an interference of doubly charged $^{138}$Ba on $^{69}$Ga. In order to minimize the Ba$^{2+}$ inference, precipitates were rinsed three times with purified 0.1% NH$_4$OH (Seastar Baseline), centrifuging the sample and removing the supernatant between each rinse. The final, washed precipitate was then dissolved in 275 µL ultrapure 3% HNO$_3$ and analyzed in low resolution on the ICP-MS, monitoring $^{69}$Ga, $^{71}$Ga, and $^{138}$Ba. The interference of Ba$^{2+}$ was generally less than 0.2%. A minor correction for residual Ba was made based on the ratio of $^{138}$Ba$^{++}$/$^{138}$Ba$^+$ counts in a Ba standard solution. For data points that did not fit in the vertical profile shape, we prepared another fresh sample to reanalyze. When the re-analyzed value fit the vertical profile, we reported the results from the reanalysis. Otherwise, we averaged all results when the re-analyzed value agreed with the original values (the difference is mostly less than 2 s.d. = 3.0 pmol/kg).

Repeated runs of US GEOTRACES intercalibration samples (GS and GD) and in-house reference solutions suggest a precision of ± 4.0%; the limit of detection for Ga was 1.5 pmol/kg. Recovery of the method, as determined by repeated analysis of a spiked and unspiked seawater sample was 101.3 ± 4.7%.

4.2.2.2 Al

Dissolved Al was measured on board ship using a modified Flow Injection Analysis (FIA) method with in-line preconcentration and fluorometric detection (Resing and Measures, 1994). In the modified FIA method, Toyopearl AF-Chelate 650M was used to preconcentrate Al and acidified deionized water was the carrier (Resing et al., 2015). Repeated runs of internal and primary standards suggest a precision of ± 4.2%. 126
Additionally, two internal reference standards and SAFe reference samples were analyzed as well. The two internal reference standards had precisions of ± 14% (n = 101) and ± 3.4% (n = 75). The results of SAFe reference standards showed that shipboard Al has unidentified blank (~0.6 nM) (see additional details in Resing et al., 2015). The dissolved Al detection limit is 0.3 nM. Note that there was an offset issue of Al measurement (high by about 0.1–0.3 nmol/kg) during the transit from east to west which might affect Al values above the mixed layer.

4.2.2.3 Conservative Ga estimates

Water mass analysis combined with published Ga data allows for the estimation of a ‘conservative’ Ga distribution in this section. Through comparisons between our observed Ga concentrations and the conservative Ga estimates, we can evaluate the extent to which observed changes in Ga concentrations resulted from simple mixing versus biogeochemical processes in this transect. An Optimum Multiparameter Analysis (OMPA) of tracer distributions in the GP16 section was previously conducted by Peters et al. (2018). Along the EPZT, Peters et al. (2018) divided the water column into three discrete zones: thermocline (26.0 kg m\(^{-3}\) ≤ \(\sigma_0\) ≤ 27.0 kg m\(^{-3}\)), intermediate (27.0 kg m\(^{-3}\) < \(\sigma_0\) ≤ 27.72 kg m\(^{-3}\)) and deep water (\(\sigma_0\) > 27.72 kg m\(^{-3}\)). Thermocline water masses include the Equatorial Subsurface Water (ESSW), Eastern South Pacific Intermediate Water (ESPIW) and South Pacific Central Water (SPCW). Intermediate water masses include Antarctic Intermediate Water (AAIW), Equatorial Pacific Intermediate Water (EqPIW), Upper Circumpolar Deep Water (UCDW) and Pacific Deep Water (PDW). Deep water masses include UCDW, PDW, Lower Circumpolar Deep Water (LCDW) and Antarctic Bottom Water (AABW). More details of this OMPA analysis are described in Peters et
al. (2018). Because data on the distribution of dissolved Ga are limited, we were not able to determine the dissolved Ga concentration of all of the exact water types chosen by Peters et al. (2018). Thus, in some instances, we present a range of possible endmember Ga concentrations and then construct several scenarios of the likely conservative Ga distribution.

For AAIW, AABW, UCDW and PDW, Ga endmember estimates in these water masses were reported previously (Shiller, 1998; Shiller and Bairamadgi, 2006). Although their sampling stations were located in the South Atlantic and North Pacific Oceans, not close to the GP16 stations, we selected the closest locations to the geographic regions of water masses defined by Peters et al. (2018). Additionally, we compared previously reported characteristics (i.e., potential temperature, salinity, dissolved oxygen, or nutrients) in these water masses (where available) with those of the water masses selected by Peters et al. (2018) to help verify our selection (see details in the Supplementary Materials).

There were no reference values for Ga endmembers in the ESSW, ESPIW, SPCW, EqPIW and LCDW. However, our Ga data allows for Ga endmember estimates in EqPIW, ESSW and SPCW since the Peters et al. (2018) analysis results in some GP16 samples having a 100% contribution of these water types. Thus, we plotted Ga concentration versus water mass fraction (EqPIW, ESSW, SPCW) to find Ga endmembers in these water masses (Figs. C.1 and C.2). Although the contribution of ESPIW in samples ranged from 0% to 76%, only a small variation (± 2 pmol/kg) of Ga concentration was observed in ESPIW-dominant (> 40 %) samples (Fig. C.2). Thus, the ESPIW Ga endmember estimate was obtained by extrapolation of the Ga vs %ESPIW
relationship. The lack of dominant LCDW in samples (LCDW contribution < 54%) and no reported LCDW Ga in previous studies make LCDW Ga estimates difficult. However, based on its origin and flow path (Talley et al., 2011), we assumed that Ga in LCDW is somewhere between that of AABW and North Atlantic Deep Water. Our selection of Ga endmember concentrations for each water type are listed in Table 4.1; further detail on the endmember Ga concentration selection can be found in the Supplementary Material.

The ‘conservative’ Ga estimate is a sum of the contribution of Ga from each water mass:

\[
\text{conservative Ga} = \sum_{i=1}^{n} Ga_i \times \text{fraction}_i
\]

Here \(Ga_i\) is the Ga endmember in water type \(i\) and \(\text{fraction}_i\) is the percent contribution of water type \(i\) to the samples. The difference of conservative Ga from observed Ga can thus be an indicator of the extent of non-conservative Ga behavior. Ga is removed from the water column when conservative Ga is higher than observed Ga. Lower conservative Ga than observed Ga suggests additional sources for Ga in the water column.

Because we could only provide estimated ranges for some of the Ga endmember concentrations, different scenarios (i.e., different values used for endmembers; shown in Table C.1) are presented here (Fig. C.4), which illustrate the uncertainty, to some extent, of conservative Ga.
Table 4.1

Ga endmember estimates in water masses of GP16 OMPA.

<table>
<thead>
<tr>
<th>Water Mass</th>
<th>Ga endmember (pmol/kg)</th>
<th>Reference Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermocline Layer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ESSW</td>
<td>7-10</td>
<td>EPZT</td>
<td>this study</td>
</tr>
<tr>
<td>ESPIW</td>
<td>6-8</td>
<td>EPZT</td>
<td>this study</td>
</tr>
<tr>
<td>SPCW</td>
<td>7-9</td>
<td>EPZT</td>
<td>this study</td>
</tr>
<tr>
<td><strong>Intermediate Layer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EqPIW</td>
<td>7-9</td>
<td>EPZT</td>
<td>this study</td>
</tr>
<tr>
<td><strong>Intermediate/Deep Layers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDW</td>
<td>22-28</td>
<td>near Hawaii (22°45’N, 158°W)</td>
<td>Shiller and Bairamadgi (2006)</td>
</tr>
<tr>
<td><strong>Deep Layer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCDW</td>
<td>30-35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: These Ga endmembers were used for estimating conservative Ga concentrations in GP16 samples. There are no available published Ga data for LCDW and no means for directly estimating Ga in LCDW from our data. Ga in LCDW was roughly estimated by assuming a concentration range between that of AABW and NADW.
4.3 Results and Discussion

4.3.1 Overview of dissolved Ga and Al distributions across the transect

Dissolved Ga concentration was generally low (< 12 pmol/kg) in the upper water column (0–1000 m) and increased with depth between 1000 and 3500 m (Fig. 4.2a, b). Below this, Ga was nearly constant in the deep water (starting at 2500–3500 m), with the exception of hydrothermal plume waters near the EPR and deep waters at the westernmost stations (Stns. 32–36) (Fig. 4.2a, b).

In shallow waters (150–300 m) of the North Pacific, Orians and Bruland (1988a) found a dissolved Ga maximum in subsurface water which they attributed to reversible exchange of Ga with particle surfaces (Bacon and Anderson, 1982). However, little evidence of this subsurface Ga maximum was seen in the Atlantic Ocean or the northwest Pacific Ocean (Shiller, 1998; Shiller and Bairamadgi, 2006) nor is it observed in our eastern tropical Pacific Ocean section. Thus, the subsurface Ga maximum in the North Pacific Ocean is likely caused by advection, as Shiller and Bairamadgi (2006) suggested.

The absence of a dissolved Ga minimum at mid-depth in the EPZT section (Fig. 4.2a, b) differs with previously published Ga profiles in other ocean basins (Orians and Bruland, 1988a, b; Shiller, 1998; Shiller and Bairamadgi, 2006). Specifically, an intermediate water Ga minimum was observed in the Atlantic (700–1000 m) and the North Pacific Oceans (~500–1000 m) (Orians and Bruland, 1988a, b; Shiller and Bairamadgi, 2006). While Orians and Bruland (1988b) argued that the intermediate water Ga minimum was caused by Ga scavenging, Shiller and Bairamadgi (2006) suggested it resulted from advection of low Ga intermediate waters formed in low dust surface outcrops.
Figure 4.2 (a) The distribution of dissolved Ga concentration along the EPZT. (b) Ga profiles at various stations (Stns. 1, 13, 18, 21, 32 and 36). (c) The difference between observed Ga and conservative Ga shown is an average of all the scenarios here (see text).

Note: Stn. 18 was located near the crest of the East Pacific Rise. Dashed lines show isopycnal surfaces ($\sigma_0 = 26.0$ kg m$^{-3}$, $\sigma_0 = 27.0$ kg m$^{-3}$ and $\sigma_0 = 27.2$ kg m$^{-3}$). Yellow contours indicate where the greatest Ga depletion was observed. The results of individual scenarios can be found in Fig. C.4.
The steady depth increase of dissolved Ga in the mid-water column and relatively constant concentrations in the deep water across most of the transect (Fig. 4.2a, b) is similar to some of the Ga profiles previously reported in the Atlantic and Pacific Oceans (Shiller and Bairromadgi, 2006). A slight increase in dissolved Ga was seen in the hydrothermal plume near the EPR (Fig. 4.2a). Likewise, additional Ga from the Mid Atlantic Ridge (MAR) was observed in the North Atlantic Ocean during the GEOTRACES GA03 North Atlantic Zonal Transect cruise in 2011 (Shiller et al., 2014).

In spite of limited Ga data in hydrothermal plume waters, our results combined with enriched Ga in hydrothermal vent fluids (German and Seyfried, 2014) suggest a small but noticeable hydrothermal source for Ga in the deep water.

As we described earlier (Section 4.2.3), the difference between observed and conservative Ga distributions can help us evaluate dissolved Ga behavior in the EPZT. Most scenarios showed that the difference between observed and conservative Ga was very small in the thermocline layer while conservative Ga differed significantly from observed in the intermediate and deep waters (Fig. C.4; an average of all the scenarios is shown in Fig. 4.2c). In the intermediate layer, observed Ga was lower than conservative, indicating Ga is removed from the water (Figs. 4.2c and C.4). However, in deep waters, the observed Ga was higher than conservative at most stations, except at the western-most stations (Stns. 32 and 36; Figs. 4.2c and C.4) where the observed Ga was slightly lower than conservative. Only Scenario 2 (Fig. C.4), which used high Ga values for the endmember concentrations of each water type (Table C.1), showed Ga removal in the thermocline and intermediate layers and conservative behavior in most of the deep waters, with a slight addition of Ga in the hydrothermal plume near the EPR. Despite the
slight deviations among the different endmember scenarios, all of the scenarios suggest that Ga behaves non-conservatively throughout most of water column in the EPZT (Figs. 4.2c and C.4), in general agreement with the prevailing view of the oceanic Ga distribution.

Dissolved Al (dAl) results for the EPZT were presented by Resing et al. (2015), with a focus on the hydrothermal plume. In this manuscript, we describe the dAl distribution across the entire transect and investigate possible mechanisms controlling its distribution. Dissolved Al was commonly low (< 3 nmol/kg) in the upper and middle layers in the EPZT (Fig. 4.3). Three areas of increased dAl were observed in the section (Fig. 4.3): (1) abnormally high dAl (4–32 nmol/kg) in subsurface waters (20–150 m) at Stns. 16–18, (2) hydrothermal plume waters from Stn. 18 to Stn. 26 and (3) deep waters near the bottom (east of the EPR: ~800–1500 m above bottom; west of the EPR: ~1000–2400 m above bottom). Dissolved Al profiles in the Atlantic and Pacific Ocean have been classified as showing a scavenged-type distribution, with high surface dAl, a mid-depth dAl minimum and increased bottom dAl (Hydes, 1979; Orians and Bruland, 1985, 1986; Measures et al., 1986, 2005; Measures, 1995). In contrast, the dAl minimum was absent in the intermediate water in the EPZT (Fig. 4.3). Instead, dAl concentrations were generally homogeneous (~1–2 nmol/kg) between 500 and 2000 m, except for slowly increasing dAl with depth at Stn. 36 (Fig. 4.3). Elevated dAl was observed in the hydrothermal plume and extended westward > 3000 km (Fig. 4.3; Resing et al., 2015). In general, a small increase in dAl near the bottom (Fig. 4.3) was coincident with bottom nepheloid layers across the transect (Ohnemus et al., 2018), except in the bottom waters at Stns. 15–17 (immediately east of the EPR). At almost all stations, the bottom layer also
showed increased dissolved $^{232}$Th (d$^{232}$Th) (Pavia et al., 2018) as well as particulate Ti (pTi) and Al (pAl) (Lee et al., 2018), all lithogenic elements suggestive of sedimentary sources. Moreover, resuspended sediments in bottom nepheloid layers also resulted in the intensive scavenging of d$^{230}$Th and dissolved $^{231}$Pa (Pavia et al., 2018), especially east of the EPR. This suggests that resuspended sediment is a source of deep Al in the EPZT, in agreement with previous observations (Orians and Bruland, 1986; Moran and Moore, 1991; Measures et al., 2015).

Figure 4.3 The distribution of dissolved Al concentration along the EPZT.

Similar to previously reported Ga profiles, a dAl minimum has been observed in intermediate waters in various ocean basins, and could be caused by either scavenging (e.g., Hydes, 1979; Orians and Bruland, 1986, 1988a; Bruland et al., 1994) or advection of low-Al water masses (Measures, 1995). However, a dAl minimum was not distinct in intermediate waters of the EPZT. In EPZT intermediate waters, dAl ranges from 1–3 nmol/kg, similar to intermediate water dAl in the North Pacific (0.5–2 nmol/kg; Orians and Bruland, 1985, 1986, 1988a; Measures et al., 2005) and South Atlantic (2–6 nmol/kg; Measures and Edmond, 1990; Middag et al., 2015) Oceans, but an order of magnitude
lower than in North Atlantic intermediate waters (10–20 nmol/kg; Measures et al., 2015; Middag et al., 2015). This suggests the homogeneous dAl concentration in the upper water column (500–2000 m) along the EPZT might be a result of low dust deposition in the South Pacific Ocean (Mahowald et al., 2005; Grand et al., 2014; Zhang et al., 2015). In the upper intermediate layer (500–1000 m) of the EPZT section, waters consisted of a mixture of AAIW (~40%) and EqPIW (~60%) (Peters et al., 2018). Previously, it has been shown that AAIW is characterized with low Al due to low dust deposition in high-latitude regions (Van Beusekom et al., 1997; Middag et al., 2011, 2015). Transport of low-Al AAIW in the South Atlantic has been observed at mid-depth (Measures, 1995). For the origin of EqPIW, Peters et al. (2018) selected a location near the equator (at 829m, 5°S, 110°W) where dust deposition also appears to be low (Mahowald et al., 2005). We thus suspect that Al in EqPIW is fairly low as well. Low Al was expected in both water masses (AAIW and EqPIW) due to their origins in low dust deposition regions. However, low Al was not distinct in the intermediate water across the transect (Fig. 4.3). We suspect that a combination of low scavenging rate and low dust deposition in this region might be responsible for the absence of Al minimum in the intermediate waters.

Given that the spatial (horizontal and vertical) variations of dissolved Ga/Al ratios reflect differential input and/or removal of Ga and Al, their ratio also can be a proxy to identify what processes control their behaviors. In the EPZT, a distinct feature is a mid-depth belt of elevated Ga/Al ratio across the transect (Fig. 4.4), in the depth range of the mid-water Ga gradient and relatively low dAl (Figs. 4.2 and 4.3; see also Section 4.3.3).
Decreased Ga/Al ratios near bottom across the transect likely reflects increased bottom dAl due to sediment resuspension (Figs. 4.3 and 4.4).

![Graph showing Ga/Al ratios in the EPZT](image)

**Figure 4.4** The distribution of dissolved Ga/Al ratios in the EPZT.

### 4.3.2 Dissolved Ga and Al in the upper water column

#### 4.3.2.1 Surface waters

Surface water dissolved Ga ranged from 4 to 11 pmol/kg, with decreasing Ga from the central gyre toward the Peru coast (Fig. 4.5). A similar horizontal gradient in the surface Ga distribution was observed in the northeast subtropical Pacific as well, with a range of 2–12 pmol/kg (Orians and Bruland, 1988a). Relatively low Ga (generally 4–6 pmol/kg) in the upper 50 m at the coastal stations (Stns. 1–6) coincided with elevated total Chl $a$ concentration (Fig. 4.6a, c).

Surface water Al (< 3.6 m) concentrations ranged from 0.6 to 1 nmol/kg (Fig. 4.5) which is close to the average dAl (0.7–2 nmol/kg) in the mixed layer at most stations, and these concentrations are similar to the range predicted from dust deposition by Han et al. (2008). However, mixed layer dAl at Stns. 16 and 18, with average dAl concentrations of 17 nmol/kg at Stn. 16 and of 15 nmol/kg at Stn. 18, deviated significantly from the very surface dAl concentrations (0.8 and 0.9 nmol/kg, respectively). Since most stations
showed insignificant differences (<2 nmol/kg) between surface and mixed layer Al, we discuss here just the surface dAl (returning to the subsurface enrichment in Section 4.3.2.2, below). Note that there is an offset issue of Al measurements, high by 0.1–0.3 nmol/kg, moving from east to west that Al measurements within the mixed layer can be problematic due to this offset issue.

Figure 4.5 The distributions of dissolved Ga and Al in surface waters along the EPZT.

Note: Red circles and black diamonds represent dissolved Ga and Al, respectively.

Figure 4.6 Vertical distributions of dissolved (a) Ga and (b) Al in the upper 200 m near the Peru coasts (Stns. 1–6). (c) Total Chl a concentration distribution in upper 100 m at Stns. 1–5.

Note: pigment samples were not collected at Stn. 6.
Surface dAl values were relatively low in the Eastern Tropical Pacific Ocean, compared with surface dAl in the North Atlantic Ocean (average mixed layer dAl: 9–43 nmol/kg) where high dust input contributes to elevated surface water Al (Measures et al., 2015). Likewise, surface Ga in the Eastern Tropical Pacific Ocean (this study) was lower than published surface Ga (28-59 pmol/kg) in the Atlantic Ocean (Shiller, 1998; Shiller and Bairamadgi, 2006). It does make sense that we observed relatively low Ga and Al in surface waters along the EPZT due to low dust input in this study area (Mahowald et al., 2005). This observation is also supported by observation of low pAl concentrations in the EPZT (Lee et al., 2018) relative to pAl in the North Atlantic Ocean (Ohnemus and Lam, 2015). Again, the concentrations of dissolved Ga and Al in surface waters reflect the amount of dust deposition, consistent with the observations in previous studies (Orians and Bruland, 1988a, b; Hydes, 1989; Measures and Edmond, 1990; Shiller, 1998; Kramer et al., 2004; Shiller and Bairamadgi, 2006; Measures et al., 2008a; Middag et al., 2011, 2015). In comparing the surface water dissolved Ga and Al concentrations between the EPZT section and the North Atlantic (GEOTRACES GA03), we note the greater relative inter-ocean difference for Al versus Ga, which is consistent with a shorter residence time of Al than Ga.

Low surface Al (0.3–0.8 nmol/kg) was seen in the high productivity waters off the California coast, with a gradient of increasing Al concentration toward the North Pacific subtropical gyre region (Orians and Bruland, 1986; Measures and Edmond, 1990; Johnson et al., 2003; Measures et al., 2005; Brown and Bruland, 2009). In contrast, a surface Al gradient was not observed in the tropical southeastern Pacific Ocean (this study; Fig. 4.5). An obvious question is why we don’t observe diminished dAl near the
Peru margin especially given the high productivity of upwelled margin waters.

Furthermore, as was mentioned earlier, low surface Ga was commonly seen in the upper 50–100 m at Stns. 1–6 and coincident with elevated total Chl a (Fig. 4.6a, c), suggesting that the less reactive Ga is removed by biogenic particles. Below, we examine several explanations for the apparent disconnect between Ga and Al removal in these margin waters, including: a) low coastal Ga is actually a result of advection rather than local removal, b) lack of apparent Al removal is due to an additional source of Al, and c) lack of Al removal reflects its physical-chemical speciation.

Regarding a possible advective source of the low dissolved surface water Ga near the Peru margin, our discussion is limited by the lack of dissolved Ga measurements in the South Pacific. However, along the Peru margin, there is an equatorward surface current related to the Peru Coastal Current and Peru Oceanic Current (Wyrtki, 1966; Strub et al., 1998) that deliver cold water from the south (Chaigneau et al., 2013). Although dust deposition models (e.g., Jickells et al., 2005) show some localized increase in dust deposition to the coastal waters along the northern Chilean margin, predicted Al for those waters is still low and thus we assume that the dissolved Ga is also low.

Upwelling is another factor that could influence the Ga distribution in our margin stations; however, increasing Ga with depth in the upper 200 m at Stns. 1–6 (Fig. 4.6a) suggests that low Ga at the surface was not derived from upwelled water. Despite not being able to pinpoint a source of low Ga water for the Peru margin, we do note that there was a linear correlation between salinity and surface Ga at Stns. 1–15 ($R^2 = 0.6$, $p < 0.0001$; Fig. 4.7), suggesting a contribution of physical mixing for the observed surface water Ga gradient in on the first half of the transect.
Figure 4.7 Surface water dissolved Ga concentration in the first half of the EPZT section (Stns. 1‒15) as a function of salinity.

With regard to the lack of dissolved Al depletion in Peru margin surface waters relative to the rest of the surface waters in the EPZT section (Figs. 4.5 and 4.6b), we note two things. First, there is a small increase in dAl (~1–2 nmol/kg) with depth at these stations along with a large increase in pAl (Lee et al., 2018), suggesting that there could be a source of Al from the margin sediments. Second, previous studies found that dAl is potentially present in the colloidal fraction as organic complexes and/or inorganic precipitates (Perdue et al., 1976; Hydes and Liss, 1977; Sholkovitz, 1978; Tipping et al., 2002). Buck et al. (2018) found low concentration of dissolved organic carbon in shelf waters of the EPZT, implying only limited formation of Al-organic complexes. If the very low dAl in surface waters of the EPZT is thus mainly inorganic colloids, then perhaps these colloids are less available for biological removal.

A previous study found that surface water Ga/Al ratios correlated with chlorophyll concentrations in the northwest Pacific Ocean (Shiller and Bairamadgi, 2006). They proposed that if this relationship is valid in most surface waters, that one
could then use Ga or Chl \( a \) to adjust the surface ocean \( dAl \) residence time in Al-based models of global dust deposition. Here, we examine the variation in surface water Ga/Al ratios and further look into the relationship between this ratio and total Chl \( a \) in the EPZT. Surface water Ga/Al ratios range from 4–8 mmol/mol at the upwelling-influenced stations (Stns. 1–8). Beyond the upwelling region, Ga/Al ratios increased to a range of 8–13 mmol/mol (Stns. 10–36). Note that a constantly low surface Al and a gradient of surface water Ga were observed in our section (Fig. 4.5), indicating the variation of Ga/Al ratios in surface waters was regulated by the surface water Ga gradient. High and variable surface water Ga/Al ratios in our Eastern Tropical Pacific section contrast with the low and more constant Ga/Al ratios (0.9–1.7) in the North Atlantic Ocean (Shiller et al., 2014; Measures et al., 2015) and suggest two possibilities: (a) the input is a more important factor than the removal in a low dust deposition area; (b) a residence time effect. That is, in a low dust deposition region, very low Al input results in a high and variable Ga/Al ratio which de-emphasizes the importance of preferential Al scavenging on this ratio. Additionally, if other factors are constant, then the Ga/Al ratio will be proportional to the Ga residence time (Shiller, 1988).

In the surface mixed layer, a positive correlation between the dissolved Ga/Al ratio and total Chl \( a \) concentration was observed at the coastal stations (Stns. 1–5; Fig. 4.8a). Increasing surface water Ga/Al ratio with increasing Chl \( a \) concentration reflects that Al is more readily scavenged by biogenic particles (Measures et al., 1984; Moran and Moore, 1988; Hydes, 1989) than Ga (Shiller and Bairamadgi, 2006). We do note that there was no apparent Al longitudinal gradient in surface waters across the EPZT while a surface water longitudinal Ga gradient was observed east of Stn. 15 (section 4.3.2.1; Fig.
4.5). This suggests that the Ga/Al-total Chl \( a \) correlation in coastal surface waters (Stns. 1-5) might be a coincidence. This relationship between Ga/Al ratios and total Chl \( a \) concentrations was absent in offshore surface waters (on west of Stn. 7). Since particulate phosphorus (pP) can be an indicator for biomass abundance as well, we examined the relationship between pP (Ohnemus et al., 2017) and Ga/Al ratios in surface water and showed no apparent correlation between Ga/Al ratios and pP in surface waters. Again, the lack of correlation between surface Ga/Al ratios with total Chl \( a \) and pP in our section implies that limited Al input results in the variation of surface water Ga/Al ratios here.

Amounts of dust deposition to the ocean can affect the Ga/Al ratios as well. We used the modelled dust deposition (Mahowald et al., 2005) to look at the correlation between dust deposition and surface water Ga/Al ratios (Fig. 4.8b). It seems the variation of surface Ga/Al ratios is not associated with the dust deposition. Although there is no significant correlation between surface Ga/Al ratios with biogenic indicators and dust deposition across the EPZT, the Ga/Al ratio in coastal waters increased toward the pelagic region, suggesting a) the effect of higher dust input and more intense particle scavenging near the Peru coast relative to open ocean waters and b) a longer residence time beyond coastal region. In spite of the absence of a linear Ga/Al ratio-Chl \( a \) correlation from our results, to some extent, the variation of surface water Ga/Al ratios somehow provides insights on the dust deposition estimates on a global (or intra-basin) scale and a changing residence time of mixed layer dAl away from high dust deposition regions.
Figure 4.8 (a) The relationship between the dissolved Ga/Al ratio and total Chl \(a\) concentration in surface waters. (b) Modeled dust deposition at our sampling stations are shown in red bars. The variations of surface Ga/Al ratios and mixed layer Ga/Al ratios in the EPZT.

Note that Ga/Al ratios and total Chl \(a\) shown in this graph are average concentrations in the mixed layer. In Fig. 4.8 (b), modeled dust deposition was taken from Mahowald et al., 2005. Open and solid circles represent surface Ga/Al ratios and mixed layer Ga/Al ratios.
4.3.2.2 Ga and Al between subsurface and intermediate water ($\sigma_0 \leq 27.72 \text{ kg m}^{-3}$)

The dissolved Ga and Al distributions from the near surface through the intermediate waters show several interesting features (Fig. 4.9). First, in the offshore part of the transect beyond the coastal upwelling, there is no evidence of Ga removal associated with the Chl $a$ maximum, in accord both with previous observations elsewhere as well as the presumed limited reactivity of Ga relative to other strongly hydrolyzed elements. Similarly, we didn’t observe a minimum in Al associated with the Chl $a$ maximum such as that seen in the Atlantic Ocean (Kramer et al., 2004; Dammshäuser et al., 2013). This suggests that the removal of Al and Ga by biological scavenging is not significant in the oligotrophic gyre waters in the EPZT, consistent both with the oligotrophic nature of these waters and the low dust input.

Next, in general correspondence with the westward increase in surface dissolved Ga, there is an expanding shallow pool ($< 200 \text{ m}$) of Ga-enriched water starting around $105^\circ W$ (Stn. 15/16; Fig. 4.9a) and roughly corresponding to the waters above the $\sigma_0 = 24.8 \text{ kg m}^{-3}$ isopycnal, which might be classified as waters of the South Pacific gyre. Interestingly, dissolved Al shows a no such gyral enrichment pool though there is the very obvious high Al patch in the upper $200 \text{ m}$ at three stations from $106^\circ–113^\circ W$ (Stns. 16–18) which we discuss below. We suspect, therefore, that the Ga-enriched pool of gyre water reflects slow accumulation of Ga within gyre surface waters; i.e., a residence time effect (Shiller, 1998).
Figure 4.9 The distributions of dissolved (a) Ga and (b) Al in the upper 2000 m of the water column along the EPZT.

Note: Black dashed lines (a) show the Chl a (µg/L) maxima. White dashed lines (a) show PO₄ (µmol/kg) contours. Black solid lines (b) show the small sized fraction of pAl (pM) contours.
Below the Ga-enriched pool, there is a dissolved Ga minimum centered within the nutricline, that outcrops in the vicinity of 90°W (Fig. 4.9a). This is at shallower depths than the intermediate water Ga minimum observed in other basins (e.g., 500–1000 m; Orians and Bruland, 1988a, b; Shiller, 1998; Shiller and Bairamadgi, 2006) and which appears to be related to advective transport of Ga-depleted waters from high latitude. The minimum starts above the upper boundary of the Peters et al. (2018) water mass analysis, so it is problematic to use the water mass analysis to interpret this feature. One possibility is that the minimum is simply the result of advectively-transported low Ga water being sandwiched between the Ga-enriched near surface pool and the higher Ga waters deeper in the thermocline. Alternatively, the Ga minimum may reflect scavenging removal in the mesopelagic realm. Indeed, Hawco et al. (2016) recently suggested that scavenging of Co onto Mn oxides in the mesopelagic plays a major role in the oceanic Co distribution and the EPZT particulate data (Lam et al., 2018). However, as is discussed below (Section 4.3.3.1), we did not observe evidence of scavenging removal of Ga in the hydrothermal plume where particulate Mn oxides are even more prevalent.

The distribution of dAl showed generally little variability in the upper 1000 m of the water column across the EPZT (Fig. 4.9b). However, several exceptions to this were observed, specifically: subsurface water at Stns.16–18, water at 400–2000 m depth at Stns. 32–36, and water near the Peru margin. We discuss these areas below.

The small patch of highly dissolved Al-enriched water in the upper 200 m in the middle of the section (Stns. 16–18) is a distinct and unusual feature of the section. This does not appear to be an artifact of contamination since the same GoFlo bottles were used for the deep casts at these stations and showed no artifacts. Additionally, the first two Al-
enriched stations occurred before the hydrothermal plume was sampled and thus the bottles would not have been exposed to the Al-enriched hydrothermal waters. Other dust-derived elements, such as Ga and Fe, do not show a dissolved enrichment in these waters, nor is there an enrichment in particulate Al or Fe (Lee et al., 2018), nor in Chl a. However, John et al. (2018) do show a similar small patch of high δ⁵⁶Fe water at the same place. This high δ⁵⁶Fe is compatible with dust input. We speculate that there had been a brief dust event that resulted in rapid biological Fe uptake from these oligotrophic waters and which left the Al and δ⁵⁶Fe as the only evidence of the event. A rapid response of surface water dissolved Al to dust input has been observed before in the Sargasso Sea (Jickells et al., 1994) as well as in mesocosm experiments (Wuttig et al., 2013). The oligotrophic nature of these waters may also limit the rate of scavenging removal of dAl.

Near the Peru margin, slightly elevated dAl was observed ~20–100 m below the surface east of Stn. 9 (Fig. 4.9b), corresponding with increased total pAl (small + large fractions) (Lee et al., 2018). Higher lithogenic particulate materials were seen in the coastal upwelling region which was a result of dust deposition and lateral advection from shelf sediments (Lam et al., 2018). Anomalies in various chemical properties in the mid-depth range along the continental slope include relatively high dissolved Fe (John et al., 2018), d²³²Th (Schlitzer et al., 2018) and ²²⁸Ra (Sanial et al., 2018), as well as the highest lithogenic material concentration at a slope station (Stn. 5; Lam et al., 2018) suggesting a potential source of dAl from the margin. In other words, the slight increase in dAl in Peru margin waters suggests a mechanism of increased dust input (relative to the rest of the section) along with scavenging removal in productive upwelled waters followed by
sinking and remineralization of dAl from sinking particles and margin sediments. In contrast, there was no evidence of Al release from shelf/margin sediments off the northwest African coast (Measures et al., 2015) although many lithogenic material tracers (e.g., d$^{232}$Th, dissolved Fe) also showed a source from sediments there (Hatta et al., 2015; Revels et al., 2015). Furthermore, previous work has shown variable Al solubility in aerosols from different dust sources (Baker et al., 2006; Shelley et al., 2018) as well as a function of the dust load (Shelley et al., 2018).

Above, in our description of the apparent non-conservative Ga distribution (Fig. 4.2c), we mentioned that Ga removal was commonly observed in the intermediate waters, especially near the Peru margin. This is opposite from the observation of slightly increased Al in these waters (see above), which raises the question of why Ga and Al have contrasting behaviors in intermediate waters. We rule out the possibility of this being an artifact of our Ga endmember selection for the conservative distribution. First, we note that the depth of the most depleted Ga does not coincide with the contour of any particular water type. The most depleted mid-depth Ga appears to be on the first half of the transect (mostly at Stns. 1–15). We thus examined the relationship between dissolved Ga and salinity in the intermediate layers ($27 \text{ kg m}^{-3} < \sigma_0 \leq 27.72 \text{ kg m}^{-3}$) at Stns. 1–15 to evaluate the role of a simple mixing between different water masses in these waters. Briefly, the composition of water masses in the intermediate layer at Stns. 1–15 mainly included EqPIW, AAIW and PDW, while UCDW was a minor component (range: 0–34 %; average: 6%; median: 0%; the most UCDW influenced waters are below 1500 m at Stns. 13 and 15 where less Ga depletion was seen) (Peters et al., 2018). Note that Ga endmember estimates for UCDW are not very different from those of in other
intermediate water masses (Table 4.1). Thus, the influence of the UCDW fractions must be limited in these Ga-depleted samples. At these stations (Stns. 1–15), in the upper intermediate layer (500–1000 m), a combined fraction of EqPIW and AAIW accounts for more than 50% of the water. Below 1000 m, PDW becomes a dominant water mass (Peters et al., 2018). In Fig. 4.10, we plotted dissolved Ga versus salinity of intermediate water samples below 1000 m depth at Stns. 1–15 in which the pronounced Ga anomaly was seen. If we assumed these waters at 1000 m represent the mixture of EqPIW and AAIW, a linear mixing trend between the EqPIW-AAIW mixture and PDW can be drawn. We found that Ga, in many samples, falls below this mixing trend, suggesting intermediate water Ga removal near the Peru margin is not an artifact. However, it is unclear why we didn’t see a stronger removal for Al in these waters.

Figure 4.10 Dissolved Ga versus salinity in the 1000-2500 m water column at Stns. 1–15.

Note: A purple circle with black outline represents an average from all samples of 1000 m at Stns. 1–15. Black circles show the range of Ga endmember values for PDW. Triangles and squares show a range of Ga endmembers in EqPIW and AAIW, respectively. Black solid line is a mixing trend between an average value of 1000 m samples and a low-Ga PDW endmember (22 pmol/kg).
Increased dAl (> 2 nmol/kg) at 400–2000 m at Stns. 32–36 partially overlapped with slightly elevated pAl (Fig. 4.9b) (Lam et al., 2018; Lee et al., 2018). Since the distributions of dAl and pAl respond at different time scales, the lack of complete overlap of their distributions is not exceptional. Dissolved Al samples represent a decadal time-scale while pAl responds on a time scale of weeks to months in the water column. In other words, particulate samples show a relatively instant picture compared to dissolved samples. It is surprising, however, that this dAl enrichment on the western, open ocean boundary of the EPZT section is more prominent than the dAl enrichment observed along the Peru margin. This may result from greater biological removal along the margin as well as different sources of the Al. For instance, Lam et al. (2018) pointed out that lateral inputs of lithogenic particles from volcanic islands (i.e., Marquesas Islands and Tuamotu Archipelago) and submarine plateaus (i.e., Tuamotu Plateau) in the upper 2000 m of the western part of the transect could be potential sources for lithogenic materials in this region. Furthermore, previous work has shown variable Al solubility in aerosols relating to differing dust loads and dust (Baker et al., 2006; Shelley et al., 2018).

4.3.3 Ga and Al in the deep and bottom water ($\sigma_n > 27.72 \text{ kg m}^{-3}$)

Deep water dissolved Ga and Al in the EPZT ranges from 19–35 pmol/kg and 1–12 nmol/kg, respectively. This is lower than the concentration range of both elements in the deep Atlantic Ocean which is influenced by the Al- and Ga-rich NADW (Measures and Edmond, 1990; Measures, 1995; Shiller, 1998; Shiller and Bairamadgi, 2006; Measures et al., 2015; Middag et al., 2015). Excluding the area influenced by the EPR hydrothermal plume, low Al (generally < 4 nmol/kg) in deep water is in agreement with the range of Al previously reported in deep North Pacific, Indian and Southern Oceans.
Compared with deep water Ga (12–30 pmol/kg) in the North Pacific (Orians and Bruland, 1986a; Shiller and Bairamadgi, 2006), slightly increased deep water Ga in our section might be caused by the accumulation of Ga during the southward flow of PDW (Peters et al., 2018) and/or from local sediment inputs.

Various interesting features in deep water dissolved Ga and Al distributions were observed in the EPZT. Elevated deep water Ga and Al concentrations were commonly observed in this section, relative to the rest of water column. First, the depth of chemocline (i.e., the sharpest increases in dissolved Ga and Al) is below the potential density $\sigma_0 = 27.72$ kg m$^{-3}$ (a boundary between intermediate and deep layers defined by Peters et al. (2018)) at Stn. 11 and deepened toward the Peru margin. Second, the high Al concentrations across the deep waters are abruptly interrupted at Stn. 15 (~930 km east of the EPR) where bottom water Al concentrations are relatively low at this station compared with most deep waters in the transect. Third, at the westernmost part of the transect (Stns. 32 and 36), dissolved Ga decreased and dAl increased toward the bottom, respectively. Based on the results of OMPA, the influence of AABW is most pronounced in these western deep waters, relative to deep waters in the rest of section (Peters et al., 2018). Lastly, the two most striking EPZT deep water features for Ga and Al are the enrichments in these elements in the hydrothermal plumes and nepheloid layers. We discuss these features further in the next two sections below.

4.3.3.1 Ga and Al in the EPR hydrothermal plumes

A remarkable extended hydrothermal plume, ranging from the EPR at Stn. 18 westward for thousands of kilometers was previously reported for this section (Resing et
al., 2015) and our Al data was originally reported therein. The dissolved Ga section (Fig. 2a) suggests that Ga is likewise affected by hydrothermal input. However, the extent of Ga enrichment is somewhat obscured by the fact that waters east of the EPR (which were not observed to be hydrothermally influenced; Resing et al., 2015) are also high in dissolved Ga and show a similar “excess” dissolved Ga (Fig. C.4). In contrast, increased dAl (up to 12 nmol/kg at Stn. 18, 2625 m) in the hydrothermal plumes clearly extended westward ~3000 km in the EPZT (Fig. 4.2b), and this was also seen in other dissolved trace elements (Fe, Mn) (Resing et al., 2015; Fitzsimmons et al., 2017) and $^3$He ex (Jenkins et al., 2018). Increased dAl has been observed in the hydrothermal plume in the MAR as well (Lunel et al., 1990; Measures et al., 2015). Higher hydrothermal dAl in the MAR plume than in the southern EPR is thought to be due to the effect of the axial valley of the MAR (Resing et al., 2015) in that axial rift-valley walls in the MAR confine the movement of buoyant hydrothermal plumes. Resing et al. (2015) inferred that the larger dAl source from hydrothermal vents along the southern EPR caused the extended dAl plume seen in the far field. More active eruptions on the sea floor in the southern EPR (Gamo et al., 1993) could be a possible source for dAl in the southern EPR hydrothermal plume, as proposed by Resing et al. (2015).

In Figures 4.11a and b, we show the inventories of dissolved Ga and Al in the depth range of the hydrothermal plume (2200–2640 m) plotted versus the inventory of excess $^3$He (from Jenkins et al., 2018). This diagram shows several interesting things: a) Stn. 18 at the ridge crest falls on a different trend, in agreement with the suggestion (Resing et al., 2015; Jenkins et al., 2018) that the extended hydrothermal plume is actually sourced from elsewhere on the EPR; b) for the other stations, the Ga and Al
trends versus $^3$He$_{ex}$ are linear, suggesting conservative dilution of these elements within the extended plume; and, c) there is a far greater relative change in Al than Ga.

Figure 4.11 The relationship of dissolved (a) Ga and (b) Al with $^3$He$_{ex}$, integrated concentration within a depth of 2200-2800 m on west of the EPR.

Red symbols show Ga and Al integrated from 2200–2640 m at Stn. 18. Black symbols are integrated Ga and Al concentration at Stns. 20–36. (c) The relationship between Ga/Al ratio and $^3$He$_{ex}$ at 2500 m, west of the EPR. The dashed line represents simple mixing between Stn. 20 and Stn. 36. Note abnormally low $^3$He$_{ex}$ at Stn. 18.

Earlier (Section 4.3.2.2), we suggested the possibility of Ga scavenging by Mn oxides in the subsurface Ga minimum. In the hydrothermal plumes, however, the dissolved Ga concentration is largely controlled by dilution. There is no evidence of Ga or Al scavenging by hydrothermal particles in our section. That is, there is no correspondence of depleted Ga (or Al) and increased Mn oxides in the hydrothermal
plumes. Thus, Ga and Al scavenging appears to be limited and fairly slow and the particulate Ga and Al enrichments in these hydrothermal particles are suppressed by highly enriched particulate Mn and Fe concentrations. This would seem to rule out mid-depth Ga scavenging by Mn oxides unless the structure of Mn oxides in subsurface waters is significantly different from those in the hydrothermal Mn oxides and thus has a very different ability for Ga scavenging.

We can also examine the variation of dissolved Ga/Al ratios in these hydrothermally influenced waters. A decreased Ga/Al ratio was observed in the hydrothermal plume, compared with the Ga/Al ratio in ambient deep water (Fig. 4.4). Low dissolved Ga/Al ratios would be expected close to the ridge crest due to the dissolution of basalt under acidic, high-temperature conditions and since the crustal Ga/Al ratio (0.084 mmol/mol; Rudick and Guo, 2014) is low compared to seawater. Since a mid-depth (~2500 m) hydrothermal $^3$He tongue was observed in the EPR and extending westward ~4000 km (Resing et al., 2015; Jenkins et al., 2018), we focus on the variation of Ga/Al ratios at 2500 m on west of the EPR (Fig. 4.11c). An inverse correlation between the Ga/Al ratio and $^3$He$_{ex}$ in hydrothermal plume waters, along with the positive linear correlations between each of the two elements and $^3$He$_{ex}$, suggests this is a result of simple mixing between high (Stn. 36) and low (Stn. 20) Ga/Al ratios endmembers. Lee et al. (2018) do note slightly increased pAl near the ridge crest, so there is at least some limited scavenging of Al on hydrothermal particles. But, overall, the behavior of dissolved Ga and Al in the EPR extended hydrothermal plumes is dominated by dilution.
We can make an estimate of the global hydrothermal Ga flux by using the slope of the Ga-\(^3\)He\(_\text{ex}\) linear regression (1.9 × 10\(^4\) mol Ga/mol \(^3\)He\(_\text{ex}\)) and the global \(^3\)He hydrothermal flux (450±50 mol/yr, Schlitzer, 2016). This results in a global dissolved Ga flux from hydrothermal activity of 8.6±1.0 × 10\(^6\) mol/yr. Applying the same method to dAl (i.e., a slope of 1.6 × 10\(^7\) mol Al/mol \(^3\)He\(_\text{ex}\)), we estimate a global hydrothermal dAl flux of 8.2±0.8 × 10\(^9\) mol/yr, which is an order of magnitude higher than previous reports (axial high temperature fluxes: 1.2–6 × 10\(^8\) mol/yr, Elderfield and Schultz, 1996).

We can compare these estimates of hydrothermal Ga and Al input with estimates of their aeolian and fluvial inputs. For Al, the aeolian source of dAl can be derived from global dust deposition (450 Tg/yr; Jickells et al., 2005) with 8% Al in the UCC (Rudick and Guo, 2014) and Al solubility of 5% (Measures et al., 2010). This yields a dAl input from dust dissolution in the surface ocean 6.7 × 10\(^{10}\) mol/yr. Gaillardet et al. (2014) estimated the fluvial flux of dAl to be 4.0 × 10\(^{10}\) mol/yr, though the actual flux to the ocean is likely much lower due to estuarine removal of colloidal/organic fluvial Al.

For Ga, there is a lack of reported solubility from aerosol/dust samples. We thus estimate a likely range for aeolian Ga input by choosing a probable range in Ga/Al input ratios. We can choose a low Ga/Al input ratio of 0.1 mmol/mol based on both crustal Ga/Al ratios and ratios from uncontaminated streams (Shiller, 1988; Shiller and Frilot, 1996). Likewise, we can choose a high estimate of 1 mmol/mol from dissolved Ga/Al ratios in surface waters of high dust input regions of the North Atlantic (Shiller, 1988; Shiller et al., 2014). With the aeolian dAl input, this yields a probable input range of 0.7–7 × 10\(^7\) mol/yr Ga from dust dissolution. For rivers, the review of Gaillardet et al. (2014) suggests a fluvial dissolved Ga input of 1.4 × 10\(^7\) mol/yr. Here again, this ignores likely
estuarine removal of Ga (McAlister and Orians, 2012) and may also be biased high due to inclusion of some unusually high Ga rivers in the fluval average.

While our estimates above are crude, they nonetheless both emphasizes that hydrothermal inputs of Ga and Al are likely to be of local, not global importance and also restates the overall importance of aeolian inputs for Ga and Al to the ocean. Note that previous studies showed variable Al/\(^{3}He_{ex}\) ratios in different hydrothermal systems (Jenkins et al., 2015; Measures et al., 2015; Resing et al., 2015). This probably results in the higher hydrothermal Al flux estimates derived from the Al/\(^{3}He_{ex}\) ratio in the EPR than previously reported for global hydrothermal Al flux estimates. Thus, the EPR data likely overestimates the global impact of hydrothermal input for Ga and Al.

4.3.3.2 Ga and Al in the bottom nepheloid layer

Although Ga profiles showed no increase in bottom waters at most stations (Fig. 2a), the difference between observed and conservative Ga suggests that dissolved Ga has additional inputs to the bottom waters, with the exception of the westernmost part of the section (Stns. 32–36) (Fig. C.4). There are two possible explanations for why near bottom waters at Stns. 32–36 don’t show the apparent Ga input that other bottom waters in the section do. We note first that the bottom waters at Stns. 32–36 were the only waters in the section having a significant AABW component and they also had a significant LCDW component rather than being dominantly PDW. It is possible that the PDW in the EPZT shows more apparent Ga input than AABW/LCDW due to its longer transit/exposure to bottom inputs. Alternatively (or additionally), it is possible that we overestimated the endmember Ga concentrations of AABW and/or LCDW. Indeed, while Shiller and Bairamadgi (2006) provided the 25–30 pmol/kg estimate for AABW used here, Shiller
(1998) suggested an AABW Ga concentration < 17 pmol/kg. For Al, its concentration increased from 4.2 to 5.6 nmol/kg below 4000 m depth at Stns. 32–36. In the South Atlantic basin, Middag et al. (2015) observed fairly low Al in the AABW (mostly < 2 nmol/kg), with slightly increased Al (but still < 5 nmol/kg) near the bottom. Thus, the increased bottom water dAl at Stns. 32 and 36 is likely an indication of Al accumulation (either by remineralization of sinking particles or from sediment resuspension) during the northward transit of AABW.

For most of bottom waters, higher observed than conservative Ga in bottom water suggests additional Ga inputs from sediment resuspension and accumulated Ga during advection. There was also increased dAl in the bottom water across the transect. Previous studies have observed elevated dAl in bottom waters elsewhere and attributed this to input from sediment resuspension (Moran and Moore, 1991; Measures et al., 2015). Benthic nepheloid layers were generally observed ranging 600–750 m above the bottom at Stns. 1, 6–36 (Ohnemus et al., 2018). Dissolved $^{232}$Th also showed increases in bottom waters (Pavia et al., 2018). All these observations imply a source of dissolved Ga and Al in the bottom waters in the EPZT from resuspended sediments. Furthermore, the dissolved Ga/Al ratio (Fig. 4.4) in these bottom waters is generally lower than the waters above. Given that other sources of Ga and Al (i.e., aeolian, fluvial, and hydrothermal) tend to show comparatively low Ga/Al ratios, this bottom decrease in the ratio is also compatible with the idea of benthic input of these two elements, though certainly the decrease in the ratio could be accomplished with just an Al input.

In contrast to the near-bottom increase observed (Al) or inferred (Ga) for most of the section, there was slightly decreased dissolved Al in the bottom waters at Stn. 15,
relative to deep waters in the rest of transect (Figs. 4.2 and 4.3). This is puzzling given
the near-bottom increase in suspended particulate matter for this station (Ohnemus et al.,
2018). For instance, particulate trace element data showed that benthic nepheloid layer
particles (mostly present in small size fraction) at Stns. 13–17 were characterized with
low pAl, pTi and pFe but high pFe/pAl and pMn/pAl ratios (Lam et al., 2018; Lee et al.,
2018). These samples also showed significant excess Fe and Mn (oxyhydr)oxides near
the bottom, suggesting these benthic particles were associated with hydrothermal
particles (Lam et al., 2018; Lee et al., 2018). Lee et al. (2018) suggested that
hydrothermal particles could be delivered from the nearby Bauer Basin (see Fig. 4.1)
where ferromanganese sediments have been found and are likely transported by eastward
bottom currents from the ridge crest of the EPR through transform fault troughs (3°–5° S)
(Lonsdale, 1976; Reid, 1997). The GP16 OMPA results showed that PDW accounted for
up to 70% of deep water samples at Stns. 13–17, suggesting mainly southward flow in
this region (Peters et al., 2018). Thus, it is possible that fine ferromanganese materials
were carried by southward flows from the Bauer Basin to these stations (Stns. 13–17).
Lee et al. (2018) also suggested that additional sources of the excess pFe and pMn in
small size fractions at Stns. 13–17 could be hydrothermal particles derived from low
temperature hydrothermal activity in the Bauer and Peru Basins (McMurtry and Burnett,
1975; Marchig et al., 1999). As mentioned above (Section 4.3.3.1), dAl and Ga mainly
show dilution in the hydrothermal plume, suggesting limited Al and Ga scavenging by
hydrothermal particles (Fe and Mn (oxyhydr)oxides). Thus, the low Al content in the
hydrothermal particles is unlikely to supply a significant dissolution of Al and/or Al-rich
porewater (or Ga) from sediment resuspension. However, the observation of increased
dissolved $^{231}$Pa/$^{230}$Th ratios at these stations below 3000 m (Pavia et al., 2018) is likely caused by suspended particles preferentially scavenging of dissolved $^{230}$Th relative to dissolved $^{231}$Pa (Anderson et al., 1983; Hayes et al., 2015). This implies a higher affinity of $^{230}$Th and $^{231}$Pa onto Fe and Mn oxyhydroxides than that of Ga and Al. This is accord with the greater first hydrolysis constant of Th(IV) than those of Ga(III) and Al(III) (Stumm and Morgan, 1996).

We also note, however, that the high fraction of PDW in the bottom waters at Stns. 13–17 (Peters et al., 2018) and the comparatively low Ga and Al in PDW (e.g., waters at ~2500 m along the Peru margin are dominantly PDW; see Figs. 4.2 and 4.3) suggests another contribution to the low near bottom Al at Stn. 15. That is, the advection of low-Ga and low-Al PDW by southward bottom currents (Reid, 1997; Peters et al., 2018) should result in lower Ga and Al at stations east of the EPR.

4.3.4 The relationship of Al and Silica

A well-correlated Al-Si relationship was observed in the Arctic and North Atlantic Oceans (Middag et al., 2009, 2011), suggesting release of Si and Al from the remineralization of biogenic particles. However, the breakdown of this correlation in other oceanic regions (Hydes, 1979; Stoffyn and Mackenzie, 1982; Measures et al., 2015) argues that the remineralization of Si-phase particle is not a factor of increased Al in the water column. In our dataset, we didn’t observe an Al-Si correlation, in agreement with previous observations in the central North Pacific Ocean (Orians and Bruland, 1985) and implying that Al is not significantly released from those biogenic particles. Middag et al. (2015) suggested that the absence of the positive Al-Si correlations could be caused by
the influence of old water masses having high Si and low Al, and a decreased Al/Si ratio in diatom opal due to very low Al in surface waters (Collier and Edmond, 1984).

4.4 Conclusions

Here we have reported high-resolution dissolved Al and Ga distributions in the Eastern Tropical South Pacific Ocean. Key features that were observed in this section include: a) relatively low dissolved Ga and Al concentrations at the surface; b) a noticeable dissolved Al and Ga input from the hydrothermal plumes; and, c) a bottom source of deep water Al and Ga from sediment resuspension.

In the surface water, there was relatively low dissolved Ga and Al with high and variable Ga/Al ratios across the transect, as compared with previously reported values in the North Atlantic Ocean. This suggests that low dust input and increased residence times due to the oligotrophic nature of the gyre waters affect these elements in the Eastern Tropical South Pacific Ocean. Surprisingly, no significant dAl removal was observed in upwelled coastal surface waters. A gradient of Ga was observed in surface water with increasing concentration towards the open ocean but not in dAl. Possible reasons for this observation include: (1) additional dAl inputs from shelf sediments, evidenced by increased pAl (Lee et al., 2018), (2) dissolved Al might be present as inorganic complexes and thus less reactive to scavenging, or (3) the horizontal gradient in surface dissolved Ga is a result of advectively-transported low-Ga water, though from an unidentified origin, instead of biological scavenging.

Our results showed no correlation between surface water Ga/Al ratios with biogenic particle indicators (total Chl a and pP) or dust deposition in our study area. Nonetheless, lower surface water Ga/Al ratios in coastal waters relative to oligotrophic
gyre waters, still suggests at least a broad scale effect of dust input balanced by biological scavenging as a control on the surface water dAl residence time and hence the Ga/Al ratio.

Various interesting features of dissolved Ga and Al were observed between surface and intermediate layers. Beyond the coastal upwelling zone, the absence of Ga and Al removal associated with the Chl $a$ maximum suggests that the removal of Al and Ga by biological scavenging is not significant in the oligotrophic gyre waters in the EPZT. West of $105^\circ W$, an expanding shallow pool ($< 200$ m) of Ga-enriched water, recognized as South Pacific gyre water, suggests slowly accumulated Ga within the gyre circulation. However, we did not observe dissolved Al enrichment in this Ga-enriched pool. West of $90^\circ W$, a dissolved Ga minimum centered within the nutricline, right below the Ga-enriched pool, is coincident with a Mn oxide maximum (Lee et al., 2018). This could be simply the result of the advection of low Ga water or Ga removal by Mn oxides. However, the later explanation seems less likely due to the lack of Ga scavenging in the hydrothermal plume.

Besides the hydrothermal dAl plume, several other regions with elevated dAl were observed in the EPZT: a) subsurface water at Stns.16‒18, b) water near the Peru margin, and c) water at 400‒2000 m depth at Stns. 32‒36. Anomalously high dAl water in the upper 200 m at Stns. 16‒18 does not appear to be an artifact of contamination. A similar small patch of high $\delta^{56}$Fe water, compatible with dust input, was observed at the same place (John et al., 2018). We speculate that this observation is resulted from after a brief dust event. Near the Peru margin, slightly elevated dAl below the surface suggests a potential source of dAl from the margin, evidenced by increased $^{228}$Ra, dissolved Fe and
other lithogenic elements (pAl, pTi, d\textsuperscript{32}Th) (John et al., 2018; Lam et al., 2018; Lee et al., 2018; Sanial et al., 2018; Schlitzer et al., 2018). Increased dAl (> 2 nmol/kg) was observed at 400–2000 m at Stns. 32–36, partly associated with increased pAl. It is surprising, however, that this dAl enrichment on the western, open ocean boundary of the EPZT section is more prominent than the dAl enrichment observed along the Peru margin. This may result from greater biological removal along the margin as well as different sources of the Al with differing Al solubility. For Ga, a depletion was commonly observed in the intermediate waters, especially near the Peru margin. This is opposite from the observation of slightly increased Al in these waters and still remains to be explained.

Elevated deep water Ga and Al concentrations were commonly observed in this section, relative to the rest of water column. The two most striking EPZT deep water features for Ga and Al are the enrichments in these elements in the hydrothermal plumes and nepheloid layers. However, at Stn. 15, bottom water Al concentrations are relatively low compared with most deep waters in the transect, even in the nepheloid layer. Lee et al. (2018) observed fine hydrothermal particles in these bottom waters at Stns. 15–17 (immediately east of the EPR). We speculate low dAl at Stn. 15 is explained by limited Al dissolution from these resuspended hydrothermal particles and/or the advection of low-Al PDW from north. At the westernmost part of the transect (Stns. 32 and 36), decreased Ga and increased dAl near the bottom indicate AABW influence.

We observed pronounced hydrothermal Al and to a lesser extent hydrothermal Ga signals in the EPZT. We estimated a global hydrothermal flux of dissolved Ga (8.6±1.0 × 10\textsuperscript{6} mol/yr) and Al (8.2±0.8 × 10\textsuperscript{9} mol/yr), derived from the slopes of Ga/\textsuperscript{3}He\textsubscript{ex} and
Al/$^3$He$_{ex}$ relationships in the extended EPR plume. These fluxes are still an order of magnitude less than aeolian inputs of both elements. We also note that the global hydrothermal Al fluxes estimated from our EPR data are much higher than previous estimates. Within the hydrothermal plumes, relatively low Ga/Al ratios, relative to the rest of the transect, suggests a source that is more similar to UCC material. A linear correlation between Ga/Al ratio and $^3$He$_{ex}$ indicates preferential Al removal or mixing of low hydrothermal-derived Ga/Al and high Ga/Al in background seawater.

Our study again demonstrates the importance of aeolian inputs and sediment resuspension in dissolved Ga and Al distribution in the ocean. This work also suggests areas of emphasis for future research. Specifically, the speciation (organic, inorganic, and colloidal) of Al at low concentrations may provide further insight to its reactivity. The determination of Ga solubility in dust will be an aid to the application of the surface water Ga/Al ratio. Studies of Ga input from sediments and via estuaries are also needed. Further work on the oceanic Ga distribution will also aid in the application of conservative mixing models to better resolving locations of Ga input and removal.
Figure A.1 The variations of hourly wind stress and the changing rate of barometric pressure (dP) and air temperature (dT) calculated over a 24 hours period in 2009 and 2011.

Note: Data was provided by the National Oceanic and Atmospheric Administration NDBC buoy stations (Shell Beach, LA: 29°52'5" N 89°40'24" W and Gulfport Outer Range, MS: 30°13'48" N 88°58'55" W).
Figure A.2 The relationship between measured Chl-α concentration (discrete samples) and Chl-α fluorescent (WetLab, ECO Puck).

Note: Dashed lines indicate linear regressions for 2009 (green), 2010 (red) and 2011 (black). Linear regression equations are shown in the graph. Note that the linear regression line and equation of 2009 do not include three points (marked with circle) of high Chl-α fluorescence with low measured Chl-α.
Figure A.3 The temporal variation of the density (kg/m³) profiles at Stns. 4-8.

Figure A.4 The distributions of Ba and SiO₄ along the salinity gradients from late spring through summer during 2008-2011.
Figure A.5 (Left) The distributions of nitrate, ammonia, dissolved Mn and dissolved Fe along the salinity in March 2010 and September 2011. (Right) The density and DO profiles along the transect in March 2010 and September 2011.

Note: In Fig. A.5 (left), red and green colors represent March 2010 and September 2011, respectively.
Figure A.6 The relationships between trace elements (Ba and V), NH$_4^+$, and nutrients (NO$_3^-$, PO$_4^{3-}$ and SiO$_4^{2-}$) with Mn concentrations in hypoxic bottom waters.

Note: Dissolved Mn concentration is shown in log scale.
Figure B.1 The distribution of dissolved Mo (without salinity normalization) along the EPZT.

Note: White contours indicate nitrite concentration (μmol/kg).
Figure B.2 The distribution of non-lithogenic particulate (0.8–51 μm) Mo along the EPZT.

Note: White contours indicate nitrite concentration (μmol/kg). The concentration of non-lithogenic Mo was obtained by the difference between total particulate Mo and lithogenic Mo. Lithogenic Mo (pmol/L) = lithogenic material (μg/L) × UCC Mo (1.1 μg/g) (Rudnick and Gao, 2014) / 95.94 (g/mol). Lithogenic material (μg/L) = Al (pmol/L) × 27 (pg/pmol) × 10− 6 (μg/pg) / 0.0804 (μg Al/μg UCC).
Figure B.3 The distribution of particulate Fe (0.8–51 μm) in the upper 1000 m along the EPZT.

Note: Black dashed contours indicate dissolved oxygen concentration (μmol/kg).

Figure B.4 The distribution of dissolved V (without salinity normalization) along the EPZT.

Note: Black dashed lines indicate neutral density surfaces (25 kg m$^{-3}$ ≤ γn ≤ 27 kg m$^{-3}$). White contours indicate nitrite concentration (μmol/kg).
Figure B.5 The distribution of non-lithogenic particulate (0.8–51 μm) V along the EPZT.

Note: White contours indicate nitrite concentration (μmol/kg). The concentration of non-lithogenic V was obtained by the difference between total particulate V and lithogenic V. The derivation of lithogenic V is the same as for non-lithogenic Mo, which was described in the caption of Fig. B.2. Here UCC V content (97 μg/g) was taken from Rudnick and Gao (2014).
Figure B.6 The fractions of large size (fLSF) pFe (upper left), pMn (upper right), pV (lower left) and pMo (lower right) of the total particulate concentrations between 2200 and 3000 m at Stns. 18–21.

Note: fLSF = LSF / (SSF + LSF). Here, LSF and SSF are large size (> 51 μm) particulate concentration and small size (0.8–51 μm) particulate concentration, respectively.
Figure B.7 The variation of non-lithogenic particulate (0.8–51 μm) pV/pFe molar ratios in hydrothermal plume waters at depth 2500 m against the distance from the EPR.

Figure B.8 November 2013 monthly mean (a) sea surface temperature and (b) chlorophyll $a$ image retrieved from MODIS-Aqua.
C.1 Details of Ga endmember selection in the thermocline layer (26.0 kg m\(^{-3}\) \(\leq \sigma_0 \leq 27.0\) kg m\(^{-3}\))

The thermocline layer was typically present at the depth range of 250-500 m in the western half of the transect; closer to the Peru margin, the upper boundary of the thermocline shallowed due to upwelling (Peters et al., 2018).

A small variation of Ga concentration and a comprehensive range of thermocline water mass contribution in our samples allow for Ga endmember estimates for SPCW, ESSW and ESPIW. When SPCW accounted for more than 80 % in the samples, the observed constant Ga concentration suggests SPCW Ga estimates of 7-9 pmol/kg (Fig. C.2). We defined the ESSW Ga endmember of 7-10 pmol/kg since Ga concentrations varied from 7 to 10 pmol/kg in samples with 90-100 % ESSW fraction (Fig. C.2). Although there were no 100% ESPIW samples, we chose 6-8 pmol/kg for ESPIW Ga due to fairly constant Ga in samples of >40% ESPIW (Fig. C.2). In summary, Ga endmembers of thermocline water masses didn’t differ significantly from each other. It is not surprising that there was such a small variation in Ga endmembers of these thermocline water masses due to low dust deposition in the South Pacific Ocean (Mahowald et al., 2005). Although there is slightly elevated modeled dust deposition near the Chile coast, the amount of dust deposition and the area of increased dust deposition are still minor compared to the North Atlantic Ocean (Mahowald et al., 2005).
**C.2 Details of Ga endmember selection in the intermediate (27.0 kg m\(^{-3}\) < \(\sigma_0\) ≤ 27.72 kg m\(^{-3}\)) and deep (\(\sigma_0 > 27.72\) kg m\(^{-3}\)) layers**

For intermediate water masses, Ga endmembers in AAIW, UCDW, PDW were reported earlier by Shiller (1998) and Shiller and Bairamadgi (2006). Previous studies found the Ga minimum at 700 – 970 m in the south and central Atlantic Ocean (IOC1996 and IOC-90), with a range of 7.0 to 14.8 pmol/kg (Shiller, 1998; Shiller and Bairamadgi, 2006), coincident with waters of the low salinity AAIW. Salinity and nutrients at the southmost station in the South Atlantic Ocean during the IOC1996 (Stn. 10: 33°S, 40°W at 700 m; Ga = 12.7 pmol/kg) were fairly in agreement with these characteristics of AAIW endmember chosen by Peters et al. (2018). With a consideration of removal/addition during the transit of AAIW in different basins (i.e., Atlantic and Pacific), we chose an entire range of Ga that was reported in previous study. Thus, we used a Ga endmember range of 7-15 pmol/kg for AAIW.

The EqPIW endmember selected by Peters et al. (2018) is water at 829 m near the equator (5°S, 110°W). There are no published Ga data in the equatorial Pacific Ocean. However, the fraction of EqPIW in our samples ranged from 0-100% and Ga remained at 6.6-9.3 pmol/kg in samples of more than 40 % EqPIW (Fig. C.1). The Ga endmember of EqPIW was assumed as 7-9 pmol/kg in a ‘conservative’ Ga estimates.

During the IOC 1996 cruise, hydrographic data showed that UCDW was observed in the central and south Atlantic Ocean (Cutter and Measures, 1999). A distinct characteristic of UCDW, oxygen minimum and nutrient maximum, was seen at the depth of ~1500 m at a South Atlantic station (Stn. 10: 33°S, 40°W) where salinity and nutrients (nitrate and phosphate) were comparable to that of the UCDW endmember chosen by
Peters et al. (2018). At the same station, Ga data (23.1 pmol/kg) was collected by Shiller (1998). There was a linear relationship between salinity and Ga concentration (Ga = 36.2 x Salinity - 1229.7, R² = 0.95, p<0.0001; shown in Fig. C.3) in samples at 700-3100 m, suggesting that the Ga distribution was controlled by physical mixing of different water masses (AAIW, UCDW and NADW). Plugging the salinity in UCDW and AAIW (defined by Peters et al. (2018)) into the linear regression equation, Ga in UCDW and in AAIW are 22.1 pmol/kg and 10.6 pmol/kg, respectively. AAIW Ga estimates derived from the linear regression fall within the range of 7-15 pmol/kg reported in the literature (Shiller, 1998; Shiller and Bairamadgi, 2006). We feel that UCDW Ga derived from this linear regression is reliable. Additionally, UCDW is a mixture of PDW, Indian Deep Water and NADW, and is also affected by adiabatic upwelling of LCDW (Talley et al., 2011). We expect the UCDW Ga has a slightly higher Ga endmember, relative to AAIW Ga. Thus, UCDW Ga was selected as a range of 20-25 pmol/kg. Noted that silicate in the UCDW endmember at Stn. 10 during the IOC 1996 was ~20 \( \mu \)mol/kg less than UCDW silicate endmember in the GP16 OMPA. To ensure our selection of UCDW Ga is appropriate, we examined the difference between observed and conservative Ga in the region where UCDW has most influences in the GP 16 section. Based on OMPA results, the strongest influence (> 40 – 60 %) of UCDW was seen between 1500 and 2000 m west of 120°W (Stn. 23) in the EPZT and the other water contribution in these samples is PDW. In the most UCDW influenced region, observed Ga was lower than conservative Ga, indicative of Ga removal in these waters. If this anomaly is caused by an artificial selection of Ga endmembers, Ga in the UCDW must be 6-10 pmol/kg (depending on the selection of Ga PDW (22-28 pmol/kg)) to maintain a conservative Ga distribution in this
mostly UCDW influenced region. The UCDW Ga estimates by this means is close to AAIW Ga and lower than previously reported UCDW Ga in the South Atlantic Ocean (33°S, 40°W) and AABW/NADW Ga endmembers (Shiller and Bairamadgi, 2006). In other words, Ga in the UCDW endmember selected by Peters et al. (2018) has to be removed during the transit (from its formation region (50-70 °S) to the location (47°S, 100°W) chosen by Peters et al. (2018). It is doubtful that there is strong Ga scavenging in this location due to low dust deposition and low productivity in the South Pacific and the Pacific sector of Southern Oceans. Therefore, the selection of a range of 20-25 pmol/kg for Ga UCDW should be reliable.

It is known that PDW is formed in deep water near the equator and observed the farthest near 40°N in the Pacific Ocean by upwelling and diapycnal diffusion from the northward-flow LCDW/AABW (Talley et al., 2011). PDW is generally present below 3500 m north of 20°N (Talley et al., 2011). The closest station to the geographic definition of PDW (at 3126 m, 21°N, 110°W) by Peters et al. (2018) is a station near Hawaii (22°45’N, 158°W) during the IOC 2002 cruise (Shiller and Bairamadgi, 2006). At this station, PDW is a main water mass in the deep layer and Ga data was available. Additionally, salinity, temperature and dissolved oxygen at the station near Hawaii (IOC 2002) are comparable with that of PDW endmember selected by Peters et al. (2018). Thus, Ga concentration at 3000-4500 m at 22°45’N, 158°W near Hawaii is used for PDW Ga endmember (22-28 pmol/kg; Shiller and Bairamadgi, 2006).

Ga in AABW was reported by Shiller and Bairamadgi (2006); however, no available Ga data has been reported for LCDW. A Si-Ga correlation in deep Atlantic water indicated AABW Ga of 25-30 pmol/kg (Shiller and Bairamadgi, 2006) that was used to calculate
‘conservative’ Ga estimates here. Note that salinity and nutrients in the deepest sample (5155 m) in the South Atlantic Ocean (Stn 8: 17°S, 25°W), indicative of AABW influenced water in the IOC 1996 cruise, were similar to that of the AABW endmember defined by Peters et al. (2018), except for lower silicate endmember (116 umol/kg) in the IOC 1996 than silicate AABW endmember (144 umol/kg) used in the GP16 OMPA. In our data, LCDW Ga is difficult to estimate due to its low fractional range (0-54 %) in our samples. LCDW is formed as NADW flows into the Circumpolar Current. Subsequently, LCDW is upwelled in the subpolar region and participates in the formation of AABW (Talley et al., 2011). Finally, LCDW flows northward into the Pacific Basin (Talley et al., 2011). Based on the formation and circulation path of LCDW, we expect Ga in LCDW should be in a range between AABW Ga (25-30 pmol/kg; Shiller and Bairamadgi, 2006) and NADW Ga (30-40 pmol/kg; Shiller and Bairamadgi, 2006). We chose the range of 30-35 pmol/kg as LCDW Ga endmember.

Figure C.1 Dissolved Ga concentration versus the fraction of EqPIW in the intermediate layer (27.0 kg m\(^{-3}\) < \(\sigma_0\) ≤ 27.72 kg m\(^{-3}\)).
Figure C.2 Ga versus the fractions of thermocline water masses.

Note: Red triangles represent ESSW. Purple crosses represent ESPIW. Grey circles represent SPCW. Samples presented here are within the thermocline layer ($26.0 \text{ kg m}^{-3} \leq \sigma_0 \leq 27.0 \text{ kg m}^{-3}$).

Figure C.3 The distribution of Ga from 700 to 3100 m in the South Atlantic Ocean (33°S, 40°W) versus salinity.

Note: Data presented here was taken from the IOC 1996 cruise (Shiller, 1998).
Figure C.4 The deviations of predicted Ga from observed Ga in ten scenarios.

Note: Color bar represents the results of observed Ga minus predicted Ga. Ga endmembers of water masses used in scenarios are listed in Table C.1. Dashed lines represent isopycnal surfaces ($\sigma_0 = 26.0$ kg m$^{-3}$, $\sigma_0 = 27.0$ kg m$^{-3}$ and $\sigma_0 = 27.2$ kg m$^{-3}$).
Table C.1

Ga concentrations (pmol/kg) for endmembers in GP16 OMPA water masses used for estimating conservative Ga concentrations in ten scenarios.

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