Tungsten-molybdenum fractionation in estuarine environments

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Abstract – Dissolved tungsten (W) and molybdenum (Mo) concentrations were measured in surface waters and sediment pore waters of Terrebonne Bay, a shallow estuary in the Mississippi River delta, to investigate the biogeochemical processes that fractionate these Group 6 elements relative to one another during transit from weathering to sedimentary environments. Although many of the chemical properties of W and Mo are similar, the two elements behave autonomously, and the fractionation mechanisms are only partly understood. In sulfidic pore waters, dissolved Mo is depleted relative to river water-seawater mixtures, whereas dissolved W is >10-fold enriched. Reductive dissolution of poorly crystalline phases like ferrihydrite, which is a preferential host of W relative to Mo in grain coatings on river-borne particles, can explain the dissolved W enrichment. Dissolved W becomes increasingly enriched as $\text{H}_2\text{S}(\text{aq})$ rises above about $60\ \mu\text{M}$ due to transformation of WO_4^{2-} to thiotungstates as well as to additional reductive dissolution of phases that host W. In contrast, as rising sulfide transforms MoO_4^{2-} to thiomolybdates in pore waters, dissolved Mo is suppressed, probably owing to equilibration with an Fe-Mo-S phase. This putative phase appears to control the aqueous ion product, $Q = [\text{Fe}^{2+}][\text{MoS}_4^{2-}]^{0.6} [\text{H}_2\text{S}^{0.4}]/[\text{H}^+]^{0.8}$, at a value of $10^{-7.78}$. Concentrations of dissolved W and Mo in pore waters bear no relation to concentrations in surface waters of the same salinity. In surface waters, dissolved Mo is nearly conserved in the estuarine mixing zone. Dissolved W appears also to be conserved except for several cases where W may have been enhanced by exchange with underlying, W-rich pore waters. With increasing salinity, the molar Mo/W ratio rises from about 10 to about 1000 in surface waters whereas it is mostly <10 in underlying pore waters and in highly sulfidic pore waters is mostly near 1. Differences in two chemical properties may account for this fractionation of Mo with respect to W; Mo^{VI} is more susceptible to reduction than W^{VI} , but the latter is more prone to adopting octahedral coordination. We propose that the first difference facilitates Mo but not W precipitation in sulfidic sediments, whereas the second explains tungsten's proportionately greater sequestration on river-borne particles and its subsequent release to sulfidic pore waters after the particles are deposited in the delta and become subject to reductive dissolution during diagenesis.

1. Introduction

In the aquatic environment, greater similarities than differences exist in the geochemical properties of the Group 6 elements, Mo and W. These elements exist in oxic natural waters as tetrahedral oxyanions, $\text{Mo}^{\text{VI}}\text{O}_4^{2-}$ and $\text{W}^{\text{VI}}\text{O}_4^{2-}$. Both oxyanions are conservative components in the ocean (Sohrin et al. 1987; 1999), although WO_4^{2-} has a mean residence time appreciably shorter than MoO_4^{2-} (14,000 vs. 740,000 y according to Firdaus et al. 2008). In sulfidic waters, both MoO_4^{2-} and WO_4^{2-} become thiolated, forming a series of thioanions, $\text{MO}_x\text{S}_{4-x}^{2-}$ (M = Mo or W and $x=0-4$; Erickson and Helz, 2000; Mohajerin et al. 2014a); however considerably higher sulfide concentrations are needed for this transition in the case of W. Both Mo and W have nearly matching ionic radii, and therefore compositionally comparable Mo and W minerals are usually isomorphs. Protonation near pH 4 converts both tetrahedral anions to octahedral species, possibly $\text{Mo}(\text{OH})_6^0$ and $\text{W}(\text{OH})_6^0$. This transition occurs at slightly higher pH for W, indicating that W has a greater inclination toward octahedral coordination (Cruywagen, 2000). On most Fe and Mn oxyhydroxides, both Mo and W adsorb as octahedral, inner-sphere complexes, although Mo on ferrihydrite is an important exception, as discussed later (Kashiwabara et al. 2010; 2011; 2013). Both oxyanions form oligomers containing hexavalent Mo and W (e.g. $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{W}_6\text{O}_{20}(\text{OH})^{5-}$). However, these species form only when total MoO_4^{2-} and WO_4^{2-} concentrations in mildly acidic solutions exceed about 10^{-4} M (Baes and Mesmer, 1976; Cruywagen, 2000), which is orders of magnitude higher than usual in nature. Both elements are employed in enzymes that catalyze redox reactions (Pilato and Stiefel, 1999; Andreessen and Makdessi, 2008; Gonzalez et al. 2013). Consistent with a general trend that W species are harder to reduce than analogous Mo species, W-based enzymes catalyze redox reactions at roughly 300 mV lower potential than structurally similar Mo-based enzymes (Kletzin and Adams, 1996; Stewart, et al. 2000). Molybdenum, but not tungsten, is an essential trace element for humans. Tungsten sometimes acts as a Mo antagonist in biology (Andreessen and Makdessi, 2008), and apprehensions have arisen recently about possible human health threats from W in the environment (Koutsospyros, et al. 2006).

Considering their many similar characteristics, it is surprising that Mo and W are strongly fractionated relative to one another in the weathering, fluvial, and marine environments. Recent estimates give $\text{Mo}/\text{W} \approx 1$ in upper continental crust (range 0.8 to 1.4; see Table EA1 in the electronic annex; all Mo/W ratios in this paper are

atomic, not mass ratios). Natural waters almost invariably have Mo/W ratios much higher than this, indicating preferential solid-phase retention of W during transit from the weathering to the sedimentary environments. For example, river waters are characterized by wide ranges of Mo/W, probably related to lithologic variations in their watersheds; they have an average Mo/W on the order of 8 (Gaillardet et al. 2005; see Table EA2 for a compilation of some river water data). In seawater, Mo/W is still higher (≈ 1800 ; Sohrin et al. 1987, 1999; Firdaus et al. 2008). Icelandic surface waters extract Mo and W from basalt nearly congruently (Mo/W ≈ 6.4 in local basalt and ≈ 6.3 in water), but local peat soil waters are depleted in W relative to Mo (Mo/W = 18), which implies selective retention of W by insoluble components of peat (Arnórsson and Óskarsson, 2007). A recent estimate suggests that three-fourths of the Mo, but nine-tenths of the W transported by rivers is particle-bound (Viers et al. 2009). Furthermore, a significant fraction of the nominally dissolved (i.e. filter passing) W is in fact associated with Fe^{III} oxyhydroxide colloids, whereas Mo is carried mainly as truly dissolved $\text{MoO}_4^{2-}(\text{aq})$ (Pokrovsky and Schott, 2002; Stolpe et al. 2005; Taylor et al. 2012).

Reflecting the large enrichment of Mo relative to W in seawater compared to continental crust, marine sinks for these elements are also characterized by relatively high Mo/W ratios. In marine ferromanganese deposits, which are one of the largest sinks for Mo (Brucker et al. 2009), average Mo/W in a worldwide database is about 12 (Hein et al. 2013; see Table EA 1 in the electronic annex). Sediments forming in euxinic basins, another important sink for Mo, also are characterized by elevated Mo/W ratios. For example, in Black Sea sapropels, average Mo/W ≈ 130 (Baturin et al. 2011), but in black shales a more modest value of about 14 is representative (Ketris and Yudovich, 2009). In suspended particulate matter at the top of the intensely sulfidic, hypersaline water pools in the Tyro and Bannock Basins of the Mediterranean Sea, both Mo and W are highly enriched relative to continental crust, with Mo/W ≈ 20 (van der Sloot et al. 1990). Relative to seawater, high temperature deep-sea hydrothermal fluids have lower dissolved Mo and greater dissolved W (Kishida et al. 2004), implying that high temperature hydrothermal circulation increases the Mo/W ratios of oceanic crust relative to unaltered crust. This notion is supported by reports of sediments near hydrothermal vents in the Okinawa Trough that have a higher Mo/W ratio compared to both continental sediment and China Shelf Sea sediments (Zhao et al. 1995; Table EA-1).

However, farther from mid-ocean ridge crests, where circulating water is cooler and more alkaline, the pattern for Mo reverses and the fluid phase is enriched in Mo relative to seawater (McManus et al. 2002; Wheat et al. 2002).

Mo-isotope evidence indicates that nearly half of the dissolved Mo entering the sea is trapped in estuarine and continental margin sediments (Brucker et al. 2009). Owing to high organic carbon production and deposition in these regions, the sediments are usually characterized by shallow O₂ penetration, with biologically driven manganese, iron and sulfate reduction processes occurring a few centimeters or less below the sediment-water interface (Morford and Emerson, 1999; Zheng et al. 2000; Böning et al. 2004, 2005, 2009; Morford et al. 2005). Sulfide produced by sulfate reduction is believed to play a key role in fixing Mo in these environments (Adelson et al. 2001; Helz and Adelson, 2013). As yet, little is known of the corresponding behavior in these sediments of W, which is less sulfide-reactive than Mo (Mohajerin et al. 2014a).

In this study, we present new data for W and Mo in surface waters and underlying sediment pore waters in Terrebonne Bay, located about 100 km southwest of New Orleans on the outer margin of the Mississippi River delta. This estuarine locality affords an opportunity to investigate W and Mo behavior over a wide range of salinity and pore water sulfide concentrations. To the best of our knowledge, our data represent the first reported estuarine pore water data that include W concentrations.

2. Study Area

Terrebonne Bay is a shallow, well-mixed estuary that consists of a network of open channels and ponds between emergent marshes. Salinities in the channels are vertically homogeneous, and the water column, typically 1 – 3 m deep, is usually oxic to the sediment-water interface. Within the sediments, however, pore waters are intensely sulfidic owing to an abundant supply of organic carbon exported from the nearby marshes. As an abandoned outlet of the Mississippi River, active delta development in this basin last occurred between 800 to 1200 years ago (Penland et al. 1987). Today, fresh water is supplied predominantly from local precipitation and runoff, with only minor contributions from the Mississippi-Atchafalaya River system. Residence time of the fresh-water fraction of Terrebonne Bay is estimated to be 125 days (Solis and Powell, 1999). Circulation in Terrebonne

Bay is primarily controlled by wind-driven flow and to a lesser degree by daily tidal events (i.e., 0.2 m - 0.4 m tides with currents of 0.01 m/s and 0.025 m/s, respectively; Prager, 1992; Adams et al., 1997; Solis and Powell, 1999). Vegetation in the marshes of Terrebonne Bay is dominated by *Spartina alterniflora* and *Spartina patens*.

3. Methods

3.1 Sample collection

Surface waters and pore waters were collected on 8 August 2013 and 30 April 2014 along a 35 km traverse shown in Figure 1. Surface water samples were collected in HDPE (August) or Teflon (April) bottles cleaned using procedures described in Johannesson et al. (2004). Trace metal clean sampling and handling techniques including wearing polyethylene gloves, conditioning each bottle 3 times with sample water before collection, double bagging all water samples in clean zip-lock style polyethylene bags, and handling the samples under a class 100, laminar flow clean bench and/or within a class 100 cleanroom, were employed for sample collection and processing. Surface water samples were collected about 5 cm below the water surface using a peristaltic pump with acid-cleaned Teflon® tubing attached to a 0.45 µm in-line filter (Gelman Sciences, Pall Corp. polyethersulfone membrane). The filtered water samples were stored in a cooler on ice in the field and acidified with ultrapure (Fisher Optima) nitric acid within a class 100 laminar flow clean bench after returning to the lab.

In August, temperature and pH were measured in the field for surface water samples using an Oakton pHTestr 30 meter calibrated with NIST certified pH 4, 7, and 10 buffers. For the August collection, one aliquot of surface waters was used to measure chloride concentrations using a chloride ion selective electrode (accumet®). Salinity was calculated as $S\text{‰} = 1.81 \text{ Cl}\text{‰}$ (Millero, 2001). In April, a calibrated YSI multiprobe sonde was employed to measure pH, dissolved oxygen, temperature, and salinity (measured via conductivity) at the surface (0.25 m) and 0.5 m depth intervals.

Sediment cores were collected in small, natural channels and ponds away from the dredged canals. The cores were collected using a push core sampler and clean acrylic tubes (I.D. 6.8 cm, 2 mm thick walls). Although this salt marsh is known to be habitat for various macrofauna (Lindstedt, 2005; Fry, 2008), no evidence of

bioturbation was observed in our samples. Some vegetation (roots and buried shoots), however, were observed in the collected sediment cores. Recovered cores were capped and immediately sealed in O₂-impermeable Remel® bags (Mitsubishi Gas Chemical Co., Remel®; Cat. No. 2019-11-02) anaerobic bags that were previously flushed with N₂ and subsequently kept anaerobic by addition of an O₂ absorber pouch (Mitsubishi Gas Chemical Co., AnaeroPouch® Anaero; Cat. No. 23-246-379; Sankar et al., 2014). The sediment cores were stored on ice for transport back to the laboratory at Tulane University, where the sealed cores were transferred into a nitrogen-filled glove box the same day they were collected. Cores were sectioned into 50 mL polyethylene tubes within the glove box. Pore waters were obtained by centrifugation of sediment core sections under nitrogen.

Pore water pH was measured on recovered pore water inside the glove box. Pore water sulfide concentrations were determined using the methylene blue method (i.e., Cline, 1969; Eaton et al., 1995) in which sealed cuvettes were measured spectrophotometrically outside the glove box and diluted as needed with deoxygenated doubly distilled (Milli-Q 18.2 MΩ cm) water. Because of the small sample volumes available, a refractometer was used to estimate pore water salinity. In the glove box, remaining interstitial waters were filtered (0.45 μm polyethersulfone Whatman syringe filters) and collected in trace metal clean HDPE bottles or trace metal clean 50 mL polyethylene centrifuge tubes. The filtered pore waters were then removed from the glove box and acidified with ultra-pure nitric acid (Fisher Optima) at a class 100, laminar flow clean bench for subsequent trace metal analysis. Processing of the August 2013 sediment cores took place within 2, and at most, 7 days after sample collection. During this time, the unprocessed, sealed cores were stored in an N₂ atmosphere at room temperature. In April, processing of a smaller number of samples was completed on the day after collection. Because of the longer processing time of the August 2013 core, the resulting data are possibly less robust than the April 2014 data. Nevertheless, the pore water data from both sampling campaigns exhibit similar trends, which suggests any affects from the longer processing time in August were minor.

3.2 Trace metal analysis

Tungsten, Mo, Fe, and Mn concentrations were quantified in surface and pore waters from the Terrebonne Bay study site using high resolution (magnetic sector) inductively coupled plasma mass spectrometry (HR-ICP-MS, Thermo Fisher Element II) following procedures described previously (Clausen et al., 2010; Johannesson et al., 2013; Mohajerin et al., 2014b; Yang et al., 2015). Here, all sample handling was conducted in a class 100 cleanroom, before introduction to the HR-ICP-MS for quantification. To minimize matrix effects the water samples were first diluted 1.5- to 20-fold with a 2% (v/v) ultra-pure nitric acid (Fisher Optima grade) solution made up in ultra-pure Milli-Q water (i.e., 18.2 MΩ cm; Millipore Corporation) within the class 100 cleanroom. The HR-ICP-MS was calibrated and the sample concentrations verified using a series of W, Mo, Fe, and Mn calibration standards of five to seven known concentrations prepared from NIST traceable High Purity (Charleston, SC, USA) single element standards (e.g., Johannesson et al., 2013; Yang et al., 2015; Electronic Annex). The National Research Council Canada (Ottawa, Ontario, Canada) Standard Reference Material (SRM) for trace metals in river waters (SLRS-4) and estuarine waters (SLEW-3) were routinely analyzed for Mo, Fe, and Mn to ensure accuracy. The accuracy for Mo, Fe, and Mn following this approach was generally within 10% (Tables EA-3 and EA-4) for the majority of the analyses conducted by means of external calibration curves. No certified reference waters could be found for W, although Yeghicheyan et al (2001) report a value of 0.07 nM for W in SLRS-4. We note that our measurements of W in SLRS-4 using the external calibration curve approach agreed well (i.e., 0.065 ± 0.011 nM; Table EA-5) with the value reported by Yeghicheyan et al (2001). Detection limits reported in Tables EA-3 and EA-4 represent concentrations detectable in 1.5- to 20-fold diluted water samples. Thus, the actual detection limit for each sample was dependent on the dilution factor as shown in Tables EA-3 and EA-4.

For the August 2013 sampling campaign we also analyzed the surface water and pore water samples collected from Terrebonne Bay by isotope dilution mass spectrometry (IDMS) to check the results of the external calibration curve approach (Tables EA-5 and EA-6). Because the external calibration curve approach yielded data in better agreement with the SLEW-3 certified values for Mo, Fe, and Mn compared to the IDMS analyses (Tables EA-3 – EA-6), we chiefly focus in this contribution on the Mo, W, Fe, and Mn concentration data that were determined by means of the external calibration curves (see Mohajerin, 2014). Nevertheless, we point out two exceptions to this where IDMS data are employed to supplement the database. First, the high Mn concentrations measured in

pore waters from the August 2013 sampling strongly suggests that ^{55}Mn ^{40}Ar may have interfered with the quantification of Mo using ^{95}Mo . Consequently, the Mo concentrations data for pore water collected in August 2013 that are discussed herein, were determined by IDMS. Second, the surface water W concentration data for August 2013 were also supplemented by IDMS measurements because many of the samples yielded W concentrations below detection for the calibration curve approach (Electronic Annex for details).

4. Results

4.1 Surface waters

Concentrations of W, Mo, Fe, and Mn in surface waters along with pH, salinity, dissolved O₂, and temperature are presented in Table 1. The dissolved Mo and W concentrations in surface waters are plotted versus salinity in Figure 2. The dashed reference lines in this figure trace the hypothetical compositions of conservative mixtures of Mississippi River water (based on our measurements reported in Table 1) and seawater (Sohrin et al. 1987). Seawater contains much more dissolved Mo than river water, whereas seawater contains much less dissolved W than river water; thus the conservative mixing lines have opposite slopes.

Molybdenum concentrations adhere closely to the conservative mixing line (Figure 2; $r = 0.99$, $p < 0.0001$). Extrapolating from these Mo data to a seawater salinity of 35‰ results in projected Mo concentrations of about 95 nM for the April data and about 116 nM for the August data, both values being similar to measured values of Mo in 35‰ seawater (100–110 nM: Collier, 1985; Sohrin et al. 1987, 1999; Firdaus et al. 2008) and in the Gulf of Mexico (95 nM: Yao and Byrne, 1999). Extrapolation to $S = 0\text{‰}$ results in a freshwater endmember with Mo = 9–12 nM, which compares reasonably well with our direct measurements of Mo in the Mississippi River (12–14 nM, Table 1), and with published estimates of the world average river water Mo concentration (4–8 nM: Gaillardet et al. 2005, Archer and Vance, 2008; Miller et al. 2011; see Table EA-2).

On the other hand, variation of W concentration with salinity seems to change seasonally. In the April sampling, W concentrations vary linearly with salinity, but the implied concentration in the locally derived freshwater endmember (0.080 ± 0.007 nM) is about one-third of the Mississippi River value. Extrapolating the

linear regression line to 35‰ salinity yields a W concentration in seawater of 0.04 ± 0.03 nM, broadly consistent with accepted values in seawater (0.05 to 0.06 nM; Sohrin et al. 1987). In contrast, the August data include three samples with W concentrations greatly in excess of linear trends (Figure 2). Probably these samples have gained dissolved W from underlying sediments. All three samples occur in the higher salinity realm where underlying pore waters can be expected to be highly sulfidic and rich in dissolved W (see below).

4.2 Pore waters

Concentrations of dissolved W, Mo, Fe, and Mn in pore waters are presented in Table 2 along with corresponding dissolved sulfide concentrations, salinity, and pH values. The August and April samplings provide snapshots of pore waters in two different stages of an annual redox cycle. Estuarine sediment pore waters in temperate climatic zones are subject to a redox cycle that is controlled by the interaction between downward diffusing O_2 with upward diffusing microbial metabolic products such as species of Mn^{II} , Fe^{II} , and S^{II} . In winter, when microbial metabolic rates are at a minimum, O_2 penetration is maximal (e.g., Marvin-DiPasquale et al. 2003; Helz and Adelson, 2013; Kalnejais et al. 2015). As temperatures rise in spring and fresh, highly reactive organic matter produced by the spring plankton bloom settles to the sediment surface, microbial production of reducing agents accelerates. In consequence, O_2 consumption accelerates, and O_2 penetration depths shoal.

In our data set, all pore waters are found to be entirely anaerobic and sulfidic already in April at the level of depth resolution of our core sectioning. Even low-salinity pore waters (e.g., TBW1.1, TBW4.1, TBW4.2, 1A14, 1A15), which are probably influenced by SO_4^{2-} limitation, contain $\Sigma S^{II} > 1$ μM ; in higher salinity samples, where SO_4^{2-} is more plentiful, $\Sigma S^{II} > 100$ μM in almost all cases and > 1000 μM in many cases. By August, sulfidic conditions have become more intense. For example, the average sulfide concentration in the top 5 cm of Core 9 is 40 μM in April but nearly 1300 μM in August; salinity is similar at both times. Probably reflecting these changes in redox conditions, the W concentration in the top 5 cm of Core 9 is eight times higher in August than in April, whereas the Mo concentration is slightly lower. Dissolved Mn is 20-40% lower in August than in April in Core 9, probably reflecting reductive dissolution of Mn oxyhydroxides followed by diffusive loss of Mn to overlying waters.

Dissolved Fe is nearly an order of magnitude lower in August, reflecting both diffusive loss of Fe to overlying waters and additional FeS precipitation in response to higher sulfide concentrations.

Figure 3 shows pore water concentrations of Mo and W plotted vs. salinity. Comparison with surface waters (Fig. 2) reveals limited communication between the pore waters and overlying surface waters. The excellent linear correlation of dissolved Mo with salinity in surface waters is not observed in the underlying pore waters. Instead, pore waters are mostly depleted in dissolved Mo relative to surface waters, although at salinities <5‰, both the August and April data reveal enrichment. Contrary to the depletion of Mo in most pore waters relative to surface waters, W is immensely enriched in the pore waters. In August, pore waters underlying low-salinity surface waters contain dissolved W concentrations nearly two orders of magnitude higher than typical river waters (compare with Table EA-2). They also exhibit Mo/W ratios approaching the low values in continental crust.

As shown in Figure 4, plots of dissolved Mo and W in pore waters vs. $H_2S(aq)$ suggest that both elements vary with this component systematically. (The non-ionized form of sulfide, $H_2S(aq)$, is equal to $\Sigma S^{-II} / [1 + K_{H_2S} / 10^{-pH}]$, where K_{H_2S} is the apparent ionization constant of H_2S). Except in the lowest $H_2S(aq)$ range, $H_2S(aq)$ has almost no effect on dissolved W until $H_2S(aq)$ exceeds about 60 μM , after which dissolved W rises with further increases in $H_2S(aq)$. For Mo, $H_2S(aq)$ suppresses solubility up to $H_2S(aq) = 20 \mu M$, above which the data are scattered and a trend is uncertain.

Dissolved Mn in the pore waters is uniformly much higher than in overlying surface waters owing to reductive dissolution of Mn oxyhydroxides (compare Tables 1 and 2). Exchange between pore waters and surface waters would result in transfer of Mn into the surface waters. Previously, Trefry and Presley (1982) have documented losses of Mn from Mississippi river suspended particles as they deposit in the Mississippi delta and become subject to diagenetic processes. Furthermore, laboratory experiments performed on Mississippi River water suggest that microbial Mn oxidation is likely a common and important process in Mn removal from fluvial systems (Shiller and Stephens, 2005).

5. Discussion

Like the Terrebonne Bay surface waters, dissolved Mo in most estuaries that are free of large anthropogenic sources varies near-conservatively with salinity (Audry et al. 2007; Rahaman et al. 2010; Scheiderich et al. 2010; Beck et al. 2012). This implies that the burial flux of authigenic Mo in estuarine sediments is small relative to the total flux of dissolved Mo passing through estuarine zones. Ultimately, continental margin sediments capture nearly half of the Mo delivered to the ocean by rivers (Brucker et al. 2009; O'Connor et al., 2015), but this happens mostly further offshore, where O₂ penetration into sediments becomes shallow beneath the O₂-depleted waters of the ocean's oxygen minimum zones. Nutrient upwelling along coasts and in estuaries also contributes to Mo trapping by fueling intense production of organic carbon, which leads to intense, microbial-driven reduction in underlying sediments.

Dissolved W, on the other hand, displays complex patterns vs. salinity in the few estuaries so far investigated. For example, in the lower salinity (less than 15‰) region of the Scheldt estuary in Belgium and the Netherlands, which commonly experiences low O₂ conditions, dissolved W is greatly in excess of what would be expected in a conservative mixture of river and seawater. On the other hand, at higher salinities W is depleted relative to such a mixture (van der Sloot et al. 1985). In the River Solo in Indonesia, dissolved W appears to be nearly conserved during the dry season, but not during the wet season (van der Sloot et al. 1989). These patterns imply that exchange of W between the water column and sediments in estuaries is substantial relative to the total flux of W through the estuarine zone.

Comparison of Figures 2 and 3 reveals that any exchange between pore waters and surface waters would raise the W concentration and lower the Mo concentration in surface waters, except in the lowest salinity realm, where exchange would elevate both elements in surface waters. However the effect of such exchange would be visible mainly in the dissolved W concentration in surface waters owing to tungsten's immense enrichment in pore waters relative to overlying waters. Possibly pore water-surface water exchange explains the high W values seen in August within the higher salinity surface waters of Terrebonne Bay (Fig. 2).

The surface waters and pore waters of Terrebonne Bay exhibit a large range of Mo/W ratios, from a high of 930 to a low of 0.34. Figure 5 shows that two general trends exist. In surface waters, Mo/W is primarily controlled simply by dilution of seawater by river water in the estuary. Three August surface water samples, which

are circled in Figure 5, fall substantially off the dilution line; these samples may have been enriched in W by exchange with underlying pore waters, as suggested above. On the other hand, Mo/W is low in pore waters. In the subset of pore waters that contain $>100\mu\text{M H}_2\text{S}_{(\text{aq})}$, three-fourths of the Mo/W ratios cluster around 1.0 ± 0.4 (see histogram in inset, Fig. 5). We have no chemical explanation for this Mo/W cluster in highly sulfidic pore waters. Waters with such low, continental crust-like Mo/W ratios are rare (see Table EA-2). Less sulfidic pore waters have Mo/W ratios that range widely, from 1.2 to 84.

One question raised by these data concerns the source of the remarkably high dissolved W in the pore waters. The most likely source is destruction during early diagenesis of poorly crystalline oxyhydroxide coatings on detrital particles, which were sourced originally from the Mississippi River but in modern Terrebonne Bay may originate mainly from resuspension. Ferrihydrite, a common component of such coatings, is likely to be an important host phase. Gustafsson (2003) shows that ferrihydrite adsorbs WO_4^{2-} much more strongly than MoO_4^{2-} . Kashiwabara et al. (2013) report that ferrihydrite's empirical partition coefficient for W (i.e. $W_{\text{ferrihydrite}}/\text{WO}_4^{2-}(\text{aq})$), is more than an order of magnitude larger than molybdenum's in the pH range 5 to 9. This difference must be one reason why W is carried in rivers primarily on Fe-rich particles and colloids, whereas Mo is to a great degree present as dissolved MoO_4^{2-} . The chemical reason for tungsten's greater affinity for ferrihydrite may lie in its greater tendency to adopt octahedral coordination; WO_4^{2-} sorbs to ferrihydrite as an inner sphere, octahedral complex, whereas MoO_4^{2-} sorbs as a chemically more fragile, outer sphere complex that retains tetrahedral coordination (Kashiwabara et al. 2011; 2013).

In the reducing sediments of estuaries, ferrihydrite is unstable. A plausible thermodynamic limit to ferrihydrite stability can be defined by the following reaction:

Using solubility constants of Hiemstra (2015) for 6-line ferrihydrite and Davison et al. (1999) for mackinawite, log K_1 for this reaction is found to be +9.28. The $\text{H}_2\text{S}_{(\text{aq})}$ threshold for sulfidation of 6-line ferrihydrite at $a_s^0 = 1$ thus is about $1 \mu\text{M}$. The threshold would be lower when $a_s^0 < 1$, representing solutions undersaturated with elemental sulfur (Helz, 2014). It must be recognized that ferrihydrite can decompose below this threshold, for example by

microbial dissimilatory iron reduction. However it, cannot long persist in environments that sustain $H_2S_{(aq)}$ above this threshold because ferrihydrite is highly reactive toward sulfide (Poulton et al. 2004; Peiffer et al. 2015).

In all of our pore water samples, the $H_2S_{(aq)}$ threshold for ferrihydrite decomposition was exceeded. Thus ferrihydrite would have decomposed, releasing its sorbed W and enhancing the dissolved W in Terrebonne Bay pore waters. Poulton and Raiswell (2002) point out that loss of highly reactive iron, an operationally-defined component that includes ferrihydrite, is a general process affecting river-borne particles worldwide as they enter coastal zones.

Because Mo, much more than W, is carried in the dissolved state in rivers, ferrihydrite destruction is expected to have much less effect on Mo in reducing pore waters. However the elevated Mo concentrations seen in Figure 3 in the lowest salinity samples may be due to a similar process involving Mn redox cycling. In reduced estuarine sediments, Mn oxyhydroxides also undergo reductive dissolution. The dissolved Mn^{2+} can escape to overlying, O_2 -bearing waters where it will be oxidized back to Mn-oxyhydroxide particles. These, in turn, will scavenge Mo as they settle back to the sediment surface. When the particles again become subject to reductive dissolution in the near-surface sediments, their adsorbed Mo will be released to pore waters, enriching them relative to overlying waters. Scheiderich et al. (2010) estimate from Mo isotope data that in a typical year, 60% of the authigenic Mo fixed in Chesapeake Bay sediments was collected by this Mn-refluxing mechanism. This mechanism is expected to operate at all salinities, but we observe its effect on dissolved Mo only in the lowest salinity pore waters because these are less sulfidic, allowing dissolved Mo to accumulate. Although W will also be scavenged in this Mn reflux cycle, tungsten's low concentration in surface waters make Mn refluxing relatively less effective for W.

Another question raised by our pore water data concerns the chemical mechanisms that account for the contrasting behavior of dissolved Mo and W as a function of $H_2S_{(aq)}$ as shown in Figure 4. For Mo, a plausible hypothesis is progressive precipitation with rising sulfide after pore waters have become saturated with a Fe-Mo-S phase. Helz et al. (2011) proposed that the following reaction controlled dissolved Mo in sulfidic natural waters:

where $\text{FeMo}_{0.6}\text{S}_{2.8}$ is an empirical formula of a precipitate inferred from the distribution of dissolved Mo in the sulfidic waters of Rogoznica Lake. Some recent work (Helz et al. 2014) hints that the hexavalent oxidation state of Mo in this formula may be incorrect and that at least partial Mo reduction occurs in the precipitate. This finding would imply that the activity product expression for reaction 2, Q_{FeMoS} , which is defined in Figure 6, must contain an additional term in the denominator for the activity of zero-valent sulfur. Nevertheless, assuming that departures from $a_{\text{S}}^0 = 1$ are not large in shallow sediment pore waters (Helz, 2014) and thus that a_{S}^0 variations can be neglected as a first approximation, we plot Q_{FeMoS} for the April cores in Figure 6. At 5 cm and below, $\log Q_{\text{FeMoS}}$ approaches -7.78 ± 0.14 (1σ , $n = 9$), which falls within the range of previous estimates of $\log K_{\text{FeMoS}}$ for reaction 2. The August data from depths greater than 5 cm in core TBW5 (not shown) yielded a similar average $\log Q_{\text{FeMoS}}$ but had much greater scatter ($1\sigma = 0.61$, $n = 8$), which we attribute to pH drift during the longer sample processing times for those samples. The tight constraint on the value of Q_{FeMoS} in the April dataset strongly supports a hypothesis that dissolved Mo in the deeper pore waters of Terrebonne Bay becomes controlled by saturation with an Fe-Mo-S phase.

The behavior of W in pore waters is different from the behavior of Mo. Between about 0.4 and 60 μM $\text{H}_2\text{S}_{(\text{aq})}$, dissolved W concentrations lie in the narrow range, 0.41 ± 0.09 nM ($\pm 1\sigma$; Fig. 4). The samples in this group have salinities as low as 2 and as high as 12, and have pH as low as 6.7 and as high as 7.3. If dissolved W concentrations are being controlled by a chemical mechanism in this $\text{H}_2\text{S}_{(\text{aq})}$ region, as the nearly constant dissolved W concentrations suggest, then the mechanism does not involve $\text{H}_2\text{S}_{(\text{aq})}$ and probably does not involve H^+ as either reactants or products. Geochemical modeling predicts that the stable dissolved W species throughout this region is WO_4^{2-} (Fig. 4). A plausible, $\text{H}_2\text{S}_{(\text{aq})}$ - and H^+ -independent control would involve ion exchange of WO_4^{2-} between the water and a solid-phase reservoir that is moderately unreactive to sulfide in this range.

Above about 60 μM $\text{H}_2\text{S}_{(\text{aq})}$, dissolved W concentrations begin to rise with increasing sulfide concentrations (Fig. 4). Transformation of WO_4^{2-} to thiotungstates in the aqueous phase begins in this sulfide range (Fig. 4). Reaction of aqueous WO_4^{2-} to thiotungstates would cause desorption of WO_4^{2-} from solid phase reservoirs, thus increasing total dissolved W. Additionally, gradual decomposition of more sulfide-resistant Fe oxyhydroxides, such as goethite and magnetite (Poulton et al. 2004), could provide a source of additional dissolved

W. The rise in total dissolved W, as $\text{WO}_4^{2-} \rightarrow \text{WO}_x\text{S}_{4-x}^{2-}$, suggests that thiotungstate formation may increase W solubility in sulfidic waters just as thioarsenate formation increases dissolved As (Lee et al., 2005; Mamindy-Pajany et al., 2013; Couture et al. 2013; Yang et al., 2015).

In earlier investigations (e.g., Goldschmidt, 1958; Szilágyi, 1967; Bertine, 1972), emphasis was placed on redox mechanisms to explain the behavior of Mo and W in reducing environments. One hypothesis (Piper and Isaacs, 1995) holds that these elements are reduced by sulfide to $\text{Mo}^{\text{IV}}\text{S}_2$ and $\text{W}^{\text{IV}}\text{S}_2$ (i.e., respectively, molybdenite and tungstenite). There seems to be no doubt that reactions of the form:

are favored thermodynamically. For the M = Mo case, $\log K_{\text{MoS}_2} = +44.98$ and for the M = W case, $\log K_{\text{WS}_2} = +42.83$ based on the thermodynamic data compilation of Brookins (1987). To illustrate the significance of these K values, consider a pore water that contains $\text{H}_2\text{S}_{(\text{aq})} = 10^{-4}$ M, $a_{\text{S}}^0 = 1$ and pH = 7.0. We note that these values are representative of pore waters in Terrebonne Bay (Table 2). The equilibrium concentration of MoO_4^{2-} in such pore waters would be 10^{-19} M and total dissolved Mo (i.e., including thiomolybdates) would be 10^{-15} M, whereas the equilibrium concentration of WO_4^{2-} , as well as the total concentration of W, would be 10^{-17} M (thiotungstates are minor at this $\text{H}_2\text{S}_{(\text{aq})}$ concentration; Mohajerin et al., 2104a). Contrary to observations in the current study, both Mo and W would be immeasurably small if sulfidic pore waters equilibrated with MS_2 phases. These observations suggest that reaction 3 must be kinetically inhibited at earth-surface temperatures. The same conclusion has been reached based on months-long laboratory experiments in which high degrees of supersaturation with respect to MoS_2 and WS_2 were sustained with no evidence of precipitation (Erickson and Helz, 2000; Vorlicek et al. 2004; Mohajerin et al. 2014a). Likewise this conclusion has been reached from x-ray spectrographic studies of the sulfidic sediments of Lake Cadagno (Dahl et al. 2013).

It is interesting that MoS_2 has been observed to form in a few days by an enzymatic mechanism in cultures of sulfate reducing bacteria (Tucker et al. 1997). These cultures contained 1 mM MoO_4^{2-} , which is in the concentration range where both MoO_4^{2-} and WO_4^{2-} become toxic to sulfate reducers (Oremland and Capone, 1988). It is possible that sulfate reducing bacteria have evolved this enzymatic mechanism for catalyzing

precipitation of MS_2 phases in order to protect themselves from MoO_4^{2-} and WO_4^{2-} toxicity. If so, then the enzymatic mechanism would be unnecessary and possibly would not be expressed in the estuarine environment, where dissolved Mo and W are many orders of magnitude below toxic levels.

Another microbially mediated reduction mechanism for MoO_4^{2-} involves formation of Mo blues (Sugio et al. 1988; Ghani et al. 1993; Shukor et al. 2009). This class of materials, and closely related W blues, are mixed-valence ($\text{Mo}^{\text{VI,V}}$ and $\text{W}^{\text{VI,V}}$) oligomers that may contain heteroatoms such as P or Si in addition to Mo or W. They are readily produced by adding a reducing agent to mildly acidic solutions containing $>10^{-4}$ M MoO_4^{2-} or WO_4^{2-} . In cultures, microbes supply the reducing agent. These materials tend to consist of large oligomers, such as $\text{Na}_{35}[\text{Mo}_{150}\text{O}_{451}(\text{OH})_5(\text{H}_2\text{O})_{61}] \cdot x\text{H}_2\text{O}$ (Miras et al., 2012), and are commonly described as colloids. The Law of Mass Action requires that their tendency to form will depend on MoO_4^{2-} or WO_4^{2-} concentrations raised by large exponents (i.e., $[\text{MoO}_4^{2-}]^{150}$ in the example given in the previous sentence). Thus they are very unlikely to form in coastal waters that contain $< 10^{-7}$ M dissolved Mo and $< 10^{-8}$ M dissolved W.

Curiously, Mo blue has been observed rarely in alteration zones associated with ore deposits where it has been given the mineral name, ilsemanite (Müller and Serain, 2000). It is undoubtedly favored in these environments by high dissolved Mo concentrations and low pH (e.g. in an extreme example, 10^{-4} M Mo, 10^{-5} M W and pH 0.82; Sánchez España et al. 2008). The W analog of ilsemanite has not been reported in nature.

Previous studies (e.g., Bertine, 1972; Brookins, 1987) also portrayed a large stability field in mildly acidic pH solutions for a different reduction product, MoVO_2^+ . However the stability data for this species were based on experiments that were conducted under high Mo, low pH conditions where Mo^{VI} oligomers would have been predominant. The existence of oligomers was not recognized, and instead the experiments were dubiously interpreted as giving evidence for MoO_2^+ despite the absence of a reducing agent (Titley, 1963). More recent work does not support a stability field for MoO_2^+ (Wang et al. 2010), and existence of this species, or its dimer, $\text{Mo}_2\text{O}_4^{2+}$, under conditions achievable in natural waters remains to be demonstrated.

Instead, the only dissolved reduction products of MoO_4^{2-} that are stable within the stability field of water are Mo^{3+} and its hydrolysis products; in near-neutral pH solutions, $\text{Mo}(\text{OH})_3^0$ predominates (Wang et al. 2010). In

this respect, the speciation of Mo is analogous to that of Cr, its Group 6 cohort. However reduction of MoO_4^{2-} to Mo(OH)_3^0 is only just possible within the stability field of water at near neutral pH, and Mo^{III} is not known to play a significant role in the aquatic geochemistry of Mo, unlike Cr^{III} . Tungstate forms no stable dissolved reduction products within the stability field of water at near-neutral pH.

Despite doubts that Mo or W disulfides or blue phases or MoO_2^+ or Mo(OH)_3^0 have roles in the fractionation of Mo relative to W in ordinary coastal environments, growing but still scanty evidence supports the presence of some kind of reduced Mo species in sulfidic environments. The evidence includes x-ray spectra of sediments from Lake Cadagno (Dahl et al. 2013) and extraction assays from the Peconic River estuary and Flax Pond (Wang et al. 2009; 2011). The molecular structure of the reduced Mo compounds has not been determined. In the Peconic River and Flax Pond cases, it appears that the assay could have determined any XAD-7 sorptive form of Mo, regardless of oxidation state. The assay was shown to recover Mo^{V} added to samples as Mo(V) chloride while rejecting MoO_4^{2-} , but the possibility remains that non- Mo^{V} analytes, including colloids, might also be recovered by XAD-7.

One redox mechanism that has been demonstrated in the laboratory to be feasible under conditions achievable in nature is ligand induced reduction of Mo^{VI} to Mo^{IV} or Mo^{V} species (Vorlicek et al. 2004). Again, the exact molecular composition of the product remains to be determined. In this mechanism, S^0 atoms are donated to thiomolybdate ions by inorganic polysulfides or organic di- or polysulfides. This step induces an electron rearrangement in which an S^{II} atom in the thiomolybdate transfers two electrons to the central Mo^{VI} atom, reducing it to Mo^{IV} . Although ligand induced reduction of W^{VI} is also possible, it is much more difficult (Stiefel, 1998), a manifestation of the general rule that W is harder to reduce than Mo.

If a ligand induced reduction step lies in the pathway that fixes Mo in sediments, as Dahl et al. (2013) suggest for Lake Cadagno, then this possibility offers an appealing hypothesis to explain why in our pore waters dissolved Mo and W behave oppositely. Dissolved Mo is suppressed by rising $\text{H}_2\text{S(aq)}$ in pore waters because ligand induced reduction opens a pathway to a precipitate, the Fe-Mo-S phase. In contrast, owing to tungsten's resistance to ligand induced reduction, no corresponding pathway to a Fe-W-S phase exists. Instead dissolved W simply accumulates in pore waters as its river-borne host phases are destroyed by reduction during diagenesis.

Our work has not established what ultimately happens to the high concentrations of dissolved W observed in Terrebonne Bay pore waters. Mohajerin (2014) reports that the sediments are commonly only mildly enriched in W relative to Earth's crust although some W appears to partition into diagenetic pyrite. However, some dissolved W must eventually escape from the sediments, as suggested by a few exceptionally high dissolved W concentrations in surface waters in August (Figure 2). The observation of Arnórsson and Óskarsson (2007) that components of peat selectively sequester W suggest that some missing W might be found in the nearby salt marshes.

6. Conclusions

Sulfidic conditions in the sediment pore waters of Terrebonne Bay have opposed effects on dissolved Mo and W concentrations. Dissolved Mo concentrations are suppressed relative to those in overlying waters, whereas dissolved W concentrations are enhanced. This behavior is contrary to that observed in oxic natural waters, where Mo almost always displays greater preference for the aqueous phase than W. Sulfide's enhancement of W solubility is attributed to reductive dissolution of carrier phases, like ferrihydrite, and to transformation of WO_4^{2-} to thiotungstates, which appear to desorb more readily than WO_4^{2-} from mineral substrates. Sulfide's transformation of MoO_4^{2-} to thiomolybdates suppresses Mo solubility by favoring formation of a precipitate of approximate composition, $\text{FeMo}_{0.6}\text{S}_{2.8}$. Values of $Q = [\text{Fe}^{2+}][\text{MoS}_4^{2-}]^{0.6}[\text{H}_2\text{S}^{0.4}]/[\text{H}^+]^{0.8}$ that are tightly constrained at $10^{-7.78 \pm 0.14(1\sigma)}$ in two widely separated cores are the evidence for existence of this phase. Evidence for the formation of an analogous solid W-bearing phase is currently lacking. The apparent greater stability of W in the highly sulfidic pore waters of Terrebonne Bay as compared to Mo suggests that W may persist in solution in euxinic waters where Mo is removed to the sediments. Consequently, W may prove to be a more powerful tracer of euxinia in the ancient ocean compared to Mo owing to the apparent greater stability of thiotungstate anions in sulfidic waters compared to thiomolybdate anions.

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Table 1. Surface water data from the Terrebonne Bay estuary system.

Sample	Dissolved O ₂ (μM)	Temp. (°C)	pH	Salinity ^a	W (nM)	Mo (nM)	Mn (μM)	Fe (μM)
August 8, 2013^b								
Mississippi River ^c	ND	ND	ND	ND	0.24±0.08	13±1	0.04±0.05	0.05±0.02
TBW-1	256	31.0	7.71	0.29	0.12±0.02	9.1±0.3	0.04±0.01	0.59±0.02
TBW-2	206	29.8	7.30	0.05	0.13±0.04	10.1±0.3	0.73±0.02	0.11±0.01
TBW-3	194	32.8	7.33	0.13	0.11±0.05	10.2±0.5	0.28±0.01	0.21±0.01
TBW-4	306	36.7	7.76	0.66	0.20±0.06	12.6±0.4	0.21±0.00	1.03±0.03
TBW-5	406	34.8	8.34	7.24	0.12±0.05	31.3±0.9	0.87±0.01	2.52±0.04
TBW-6	463	35.4	8.35	11.22	0.60±0.05	44.2±0.6	0.19±0.00	0.01±0.00
TBW-7	263	33.9	7.86	22.58	0.15±0.02	78±2	1.40±0.02	0.12±0.00
TBW-8	531	34.4	8.25	21.86	0.33±0.08	76±1	0.67±0.01	0.63±0.01
TBW-9	538	34.0	8.61	6.05	0.12±0.05	29.9±0.6	0.53±0.01	3.13±0.05
TBW-10	456	32.8	8.56	6.76	0.12±0.06	30±2	1.10±0.01	3.30±0.06
April 30, 2014								
TBW-1	509	24.4	7.59	1.27	0.06±0.00	12.7±0.5	1.39±0.04	0.42±0.01
TBW-2	361	24.6	7.30	4.04	0.09±0.01	21.5±0.7	3.0±0.1	0.29±0.01
TBW-3	412	24.4	7.26	5.30	0.07±0.01	25.0±0.8	3.2±0.1	0.39±0.01
TBW-4	384	25.7	7.27	7.37	0.07±0.01	29±2	2.11±0.06	0.137±0.004
TBW-5	454	27.4	7.53	12.5	0.07±0.01	40.2±0.7	0.93±0.03	0.39±0.01
TBW-6	454	27.4	7.51	12.5	0.07±0.01	43.9±0.8	0.48±0.01	0.29±0.01
TBW-7	566	26.8	7.78	12.1	0.05±0.01	44±1	0.165±0.005	0.037±0.001
TBW-8	572	26.4	7.95	20.57	0.06±0.01	56±2	0.122±0.004	0.020±0.001
TBW-9	365	28.6	7.45	10.28	0.06±0.01	40±1	1.0±0.1	0.21±0.01
TBW-10	384	26.7	7.39	10.34	0.06±0.01	40±1	0.89±0.03	0.108±0.004
TBW-11	379	24.8	7.39	3.95	0.07±0.01	20±1	3.4±0.1	0.37±0.02
TBW-12	409	25.1	7.54	2.39	0.10±0.01	17.3±0.4	2.1±0.2	0.25±0.02

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ND: not determined, ^a Salinity calculated from Cl⁻ concentration in August 2013; calculated from conductivity in April 2014. ^b W data in August obtained by isotope dilution analysis. ^c Two Mississippi River surface samples were collected, one in June and one in July, 2013. Concentrations represent the average ± half the range.

Table 2. Pore water data from the Terrebonne Bay estuary system.

Sample	Depth (cm)	Sulfide (μM)	Salinity	pH	W (nM)	Mo (nM)	Mn (μM)	Fe (μM)
August 8, 2013^a								
TBW-1.1	9.8-15.5	2.30	3	7.78	24.6 $\pm$ 0.4	30 $\pm$ 10	6.91 $\pm$ 0.08	3.95 $\pm$ 0.04
TBW-4.2	0-5.2	2.46	3	7.83	20.7 $\pm$ 0.4	33 $\pm$ 3	8.10 $\pm$ 0.07	1.62 $\pm$ 0.02
TBW-4.1	5.2-11.3	2.46	3	7.83	14.3 $\pm$ 0.5	45 $\pm$ 6	7.99 $\pm$ 0.08	2.06 $\pm$ 0.02
TBW-5.7	4.5-5.5	412	10	7.30	1.6 $\pm$ 0.1	1.0 $\pm$ 0.2	47.8 $\pm$ 0.7	0.7 $\pm$ 0.01
TBW-5.6	5.5-6.5	795	10	7.29	0.90 $\pm$ 0.07	1.2 $\pm$ 0.3	50.3 $\pm$ 0.9	0.19 $\pm$ 0.01
TBW-5.5	6.5-7.5	1173	11	7.08	0.74 $\pm$ 0.08	0.9 $\pm$ 0.2	47.1 $\pm$ 0.9	0.16 $\pm$ 0.01
TBW-5.4	7.5-9.8	746	12	7.25	0.79 $\pm$ 0.08	0.5 $\pm$ 0.1	46.1 $\pm$ 0.5	2.56 $\pm$ 0.03
TBW-5.3	9.8-12	1269	13	7.21	2.6 $\pm$ 0.2	0.9 $\pm$ 0.4	46.3 $\pm$ 0.8	1.99 $\pm$ 0.04
TBW-5.2	12-13	1750	14	7.32	1.1 $\pm$ 0.1	0.6 $\pm$ 0.1	43.1 $\pm$ 0.6	0.16 $\pm$ 0.01
TBW-5.1	13-14	1166	14	7.22	1.22 $\pm$ 0.07	1.2 $\pm$ 0.6	44.6 $\pm$ 0.7	1.03 $\pm$ 0.02
TBW-7.4	2.2-4.7	780	13	7.41	2.0 $\pm$ 0.2	2.0 $\pm$ 0.4	22.6 $\pm$ 0.3	1.55 $\pm$ 0.02
TBW-7.3	4.7-6	978	16	7.51	2.4 $\pm$ 0.2	1.3 $\pm$ 0.3	25.4 $\pm$ 0.5	0.82 $\pm$ 0.02
TBW-7.2	6-7.5	1388	15	7.61	1.8 $\pm$ 0.1	1.9 $\pm$ 0.3	30.3 $\pm$ 0.6	0.83 $\pm$ 0.02
TBW-7.1	7.5-9.3	761	14	7.37	2.3 $\pm$ 0.3	1.9 $\pm$ 0.3	40.8 $\pm$ 0.4	4.18 $\pm$ 0.06
TBW-9.4	0.5-2.2	1827	10	6.90	1.6 $\pm$ 0.1	<1	9.29 $\pm$ 0.09	0.32 $\pm$ 0.01
TBW-9.3	2.2-3.4	1806	11	6.89	4.3 $\pm$ 0.2	6.4 $\pm$ 0.6	5.04 $\pm$ 0.07	1.11 $\pm$ 0.02
TBW-9.2	3.4-4.5	202	12	6.83	5.9 $\pm$ 0.3	6.3 $\pm$ 0.9	4.94 $\pm$ 0.09	1.66 $\pm$ 0.03
April 30, 2014								
9A7	0-2	24.6	11	6.80	0.41 $\pm$ 0.03	9.4 $\pm$ 0.7	23 $\pm$ 1	15.8 $\pm$ 0.8
9A8	2-4.5	2.49	12	6.99	0.53 $\pm$ 0.06	17.4 $\pm$ 0.7	23 $\pm$ 1	12.7 $\pm$ 0.6
9A6	4.5-5.5	94.0	12	6.73	0.50 $\pm$ 0.04	7.8 $\pm$ 0.4	15.7 $\pm$ 0.5	1.34 $\pm$ 0.04
9A5	5.5-7	184	11	6.80	1.70 $\pm$ 0.07	8.6 $\pm$ 0.3	14.7 $\pm$ 0.5	0.46 $\pm$ 0.02
9A4	7-8	498	13	6.95	1.71 $\pm$ 0.1	7.1 $\pm$ 0.3	14.2 $\pm$ 0.7	0.35 $\pm$ 0.02
9A3	8-9.5	1609	12	6.94	4.0 $\pm$ 0.2	6.5 $\pm$ 0.4	15.9 $\pm$ 0.4	0.43 $\pm$ 0.01
9A2	9.5-11	1165	11	6.98	2.6 $\pm$ 0.1	6.7 $\pm$ 0.2	16.5 $\pm$ 0.4	0.41 $\pm$ 0.01
9A1	11-11.5	889	11	6.96	0.84 $\pm$ 0.05	7.2 $\pm$ 0.5	17.9 $\pm$ 0.5	0.53 $\pm$ 0.01
1A15	0-3	1.40	2	7.22	0.30 $\pm$ 0.02	25.3 $\pm$ 0.6	43 $\pm$ 2	6.6 $\pm$ 0.2
1A14	0-3	6.86	2	7.14	0.36 $\pm$ 0.02	13.3 $\pm$ 0.4	32 $\pm$ 1	2.4 $\pm$ 0.1
1A13	3-4.5	74.9	3	7.25	0.35 $\pm$ 0.05	3.0 $\pm$ 0.2	9.0 $\pm$ 0.6	2.1 $\pm$ 0.1
1A12	4.5-5.5	162	3	7.04	0.95 $\pm$ 0.06	3.7 $\pm$ 0.5	9.0 $\pm$ 0.3	0.66 $\pm$ 0.02
1A10	5.5-7.6	767	3	6.96	1.6 $\pm$ 0.1	4.0 $\pm$ 0.2	7.0 $\pm$ 0.5	0.32 $\pm$ 0.02
1A11	7.6-11	770	4	6.92	3.18 $\pm$ 0.09	3.8 $\pm$ 0.2	7.2 $\pm$ 0.3	0.35 $\pm$ 0.02

^a Mo data in August obtained by isotope dilution.

Figure Captions

Figure 1: Map of study area showing sample locations.

Figure 2. Variation with salinity of Mo and W concentrations in surface waters of Terrebonne Bay. The dashed lines are for reference and represent hypothetical conservative mixing of seawater (Mo = 105 nM, W = 0.055 nM) and Mississippi River water (Mo = 13 nM, W = 0.24 nM; see Table 1). The dash-dot line in the lower panel is a linear regression fit to the April dissolved W data. This fit implies a freshwater endmember concentration at this time of year of W = 0.080 ± 0.007 nM, about one-third the Mississippi River value.

Figure 3. Dissolved Mo and W in pore waters of Terrebonne Bay vs. salinity. Contrast this with surface waters in Figure 2. The dashed reference lines, representing hypothetical conservative mixing lines, are the same as in Figure 2. In this case, the conservative mixing line for W is near the baseline because it is necessary to extend the W concentration scale to much higher values than in Figure 2.

Figure 4. Upper panels: Dissolved W and Mo vs. $\text{H}_2\text{S}_{(\text{aq})}$ in sediment pore waters of Terrebonne Bay. Lower panels: Equilibrium speciation of dissolved W^{VI} and Mo^{VI} as a function of $\text{H}_2\text{S}_{(\text{aq})}$ concentration. Equilibrium speciation is based on data from Mohajerin et al. 2014a and Erickson and Helz, 2000.

Figure 5. Mo/W ratios in surface and pore waters of Terrebonne Bay. The surface waters approximately follow the dashed line trend, which represents seawater (Mo/W = 1800) diluted by river water (Mo/W = 54). The three surface water samples that fall distinctly below this trend (circled) are the three samples having high dissolved W from the August sampling (Figure 2). These samples are inferred to have experienced pore water-surface water exchange which has considerably enhanced their dissolved W concentrations and lowered their Mo/W ratios.

Figure 6. Saturation state of pore waters with respect to a hypothetical Fe-Mo-S phase. Helz et al. (2011) estimate that at equilibrium $\log Q_{\text{FeMoS}} = -8.3 \pm 0.7$, a range depicted by the hatched area. The two Terrebonne Bay cores studied herein (i.e., TBW-1 and TBW-9) are located 25 km apart (Fig. 1) and have pore water salinities differing by 6-fold. Below 5 cm, their pore water compositions cover a range of 17-fold in sulfide concentration and 27-fold in H^+ concentration, but their ion products, Q_{FeMoS} , are constrained by a putative solubility equilibrium (reaction 2, text) to a range of less than 3-fold.

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