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Molybdenum accumulation in sediments: a quantitative indicator of hypoxic water conditions in Narragansett Bay, RI

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Abstract

Authigenic molybdenum (Mo) accumulation in marine sediments has often been used as a qualitative indicator of hypoxic bottom water. To investigate its use as a quantitative indicator of hypoxic exposure, sediment cores were collected from water quality monitoring sites in Narragansett Bay (RI, USA) that experience varying periods of hypoxia. Total Mo concentrations in surficial (0–1 cm) sediments were determined by total digestion and ICP-MS analysis. Lithogenic contributions to total Mo concentrations were estimated by multiplying measured concentrations of aluminum (Al) by the mean crustal Mo:Al ratio and subtracting them from the total concentrations to yield the authigenic fraction. ²¹⁰Pb dating was used to determine sediment accumulation rates at each site. Mean annual periods of hypoxia in bottom waters were determined from continuous monitoring data for the years coinciding with the top 1 cm of sediment. Results indicated a linear relationship between authigenic Mo concentrations and frequency of hypoxia, although the relationships differed between different sampling periods. These results demonstrate the potential of sedimentary Mo as a tool for assessing the spatial and temporal extent of hypoxia in coastal waters.

Keywords

molybdenum; sediments; hypoxia; dissolved oxygen; monitoring

1.0 Introduction

Hypoxia (low concentrations of dissolved oxygen) is one of the most important stressors of estuarine and coastal fish populations. The spatial and temporal extent of hypoxia in coastal systems has increased rapidly, with seasonal or episodic hypoxia becoming more common

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and extensive in smaller coastal estuaries (Diaz, 2001; Rabalais et al., 2001; Suzuki, 2001; Diaz and Rosenberg, 2008; Breitburg et al., 2018). This phenomenon is often linked to anthropogenic input of excess nitrogen leading to eutrophication of marine ecosystems. These conditions have resulted in reduced biota growth and survival, increased susceptibility to predation, disruption of spawning and recruitment, reduction in suitable habitat, altering migration and distribution patterns and fish behaviors, disruption of fisheries food webs, and even increased oceanic fluxes of greenhouse gases (Diaz and Rosenberg, 1995; Diaz, 2001; Rabalais et al., 2001; CENR, 2003; De Jonge et al., 2009; Hale et al., 2016; Breitburg et al., 2018).

The spatial and temporal extent of hypoxia in coastal systems has proven difficult to quantify. While sensor technologies have made it easier to measure time series of dissolved oxygen (DO) or conduct spatial DO surveys, determining the extent of hypoxic conditions over large scales remains challenging. Dissolved oxygen concentrations are highly variable, requiring numerous measurements and thus significant expenditure of money and labor to characterize the extent and duration of hypoxia. Most importantly, DO sensors cannot be used to measure past DO conditions, limiting retrospective analyses to the relatively few locations where long-term time series are available.

To address these limitations, we examined the concentrations of molybdenum (Mo) in surficial marine sediments as a potential quantitative proxy for direct measurements of hypoxic conditions in overlying waters. Molybdenum has been of great interest in the geochemical studies because of its sensitivity to environmental redox conditions (Francois, 1988; Emerson and Husted, 1991; Calvert and Pedersen, 1993; Crusius et al., 1996; Morford and Emerson, 1999; Zheng et al., 2000; Nameroff et al., 2002; McManus et al., 2006a; Pearce et al., 2006; van der Weijden et al., 2006; McKay et al., 2007; Chappaz et al., 2008). Molybdenum concentrations in marine sediments are comprised primarily of a lithogenic fraction derived from tributaries and coastal weathering, and an authigenic fraction that is precipitated from overlying and interstitial waters of sediment by either of two primary mechanisms. In sediments with oxic bottom waters ($[DO] > 3.2 \text{ mg L}^{-1}$), dissolved manganese (Mn) diffusing to the surface from deeper reduced sediments can be oxidized to form manganese oxyhydroxides and build up in a shallow redox boundary layer near the surface. Molybdate (MoO_4^{2-}) in seawater readily adsorbs to manganese oxides (Morford and Emerson, 1999; Crusius and Thomson, 2000; Zheng et al., 2000; Müller et al., 2002), so these boundary layers can accumulate very high concentrations ($>100 \text{ } \mu\text{g g}^{-1}$) of Mo (Bertine and Turekian, 1973; Calvert and Price, 1977; Shimmield and Price, 1986). These accumulations of Mn oxide-associated Mo are generally transient in estuarine sediments, as the Mo is released when the Mn oxides are buried and subsequently dissolved in reducing sediments. Conversely, in reduced sediments with dissolved sulfide concentrations $>10 \text{ } \mu\text{M}$, molybdate (MoO_4^{2-}) present in seawater or interstitial waters reacts with HS^- to form thiomolybdates ($\text{MoS}_x\text{O}_{(4-x)}^{2-}$) that are readily adsorbed to particles containing iron or organic carbon and rapidly removed from interstitial waters (Helz et al., 1996; Dean et al., 1999; Crusius and Thomson, 2000; Zheng et al., 2000; McManus et al., 2006c). This scavenging process is enhanced when iron sulfide (FeS) minerals are present, particularly when elemental sulfur is also available (Helz et al., 2004; Vorlicek et al., 2004). Adsorption to iron oxide minerals can also be a significant sink for Mo in the

absence of sulfide or manganese oxides (Goldberg et al., 2009); in the near-coastal/estuarine environments under consideration in this study, precipitation and dissolution of these oxides and associated molybdenum are very similar to those of manganese. Molybdenum can also be adsorbed to marine organic matter (King et al., 2018), and be incorporated into surface sediments along with the organic matter. Again, a portion of that adsorbed Mo will be released as the organic matter is consumed in early diagenetic processes; if the diagenesis is sufficiently intense, the Mo released from the organic matter may be precipitated by sulfide generated by the same diagenesis.

This general model of Mo accumulation in sediments – adsorption to oxyhydroxides of Mn and Fe in surficial sediments, reaction with sulfide and scavenging by Fe minerals in deeper sediments - predicts a temporal link between transient oxygen depletion in the water column and Mo fixation in the underlying sediments (Adelson et al., 2001). When surface sediments are oxic, accumulation of Mo is limited by the rate at which MoO_4^{2-} diffuses through the oxic surface sediment layer to the depth at which dissolved sulfide is produced, often several centimeters below the sediment-water interface. When DO in overlying water is sufficiently low, sediment interstitial waters can become anoxic very close to the surface. With a thin oxic sediment layer, diffusion through the layer no longer limits the supply of Mo to react with sulfide in deeper sediments and the Mo accumulation rate increases greatly.

Laboratory experiments with tightly controlled DO concentrations showed that Mo accumulation in the top centimeter of sediment was linearly related to the length of time with DO below $\sim 3 \text{ mg L}^{-1}$, and that the rate of accumulation was independent of DO concentrations when $\text{DO} < 2.8 \text{ mg L}^{-1}$ (Boothman and Coiro, 2009). To evaluate how these laboratory results apply in a field setting, we analyze sediment core samples from sites in Narragansett Bay, RI, USA that experience varying periods of hypoxia and encompass multiple years exposure to determine Mo accumulation and relate it to the frequency of hypoxia in overlying bottom waters. The resulting relationship may be useful to assess the extent and prevalence of hypoxia in estuarine waters.

2.0 Methods

2.1 Sampling sites

Sediments were collected at seven sites where the Rhode Island Department of Environmental Management (RI DEM), with assistance from the University of Rhode Island Graduate School of Oceanography (GSO), maintains a network of water quality monitoring stations distributed throughout Narragansett Bay, with particular emphasis on the upper Bay where several rivers and wastewater treatments plants discharge into the bay (Figure 1). Narragansett Bay is a relatively saline estuary (i.e., mean salinity 29–31) with a mean flushing time of 26 days (Pilson, 1985), and is subject to episodic hypoxic events in summer months. Greenwich Bay, where 2 of the sites are located, is a sub-estuary off the main stem of Narragansett Bay with a mean flushing time of 7 days that experiences more prolonged periods of hypoxia each summer.

Instrumentation is deployed seasonally (generally late spring through late fall) at each station to monitor water quality; instrumentation is not deployed in winter, when low water

temperatures make hypoxia unlikely. Water quality data (temperature, salinity, chlorophyll, dissolved oxygen, pH) is collected for surface and bottom waters at 15-minute intervals from spring to late fall. The seven sites were selected for sediment sampling based on the availability of bottom water dissolved oxygen monitoring data for a minimum of 4 years (the period of time expected for deposition of the top 1 cm of sediment). The selected sites were all within the highly saline portion of the estuary and encompass a range of hypoxic exposures (Table S1).

2.2 Dissolved oxygen data

To assess the cumulative occurrence of hypoxic conditions at the monitoring sites, monitoring data from each of the sites for years 2003–2011 (Stoffel, 2003; Narragansett Bay Fixed-Site Monitoring Network, 2004–2011) were examined and the amount of time that DO concentrations in bottom waters were below 2.8 mg L^{-1} was summed for each year at each site. The 2.8 mg L^{-1} threshold was established by laboratory experiments where molybdenum accumulated in sediments under hypoxic bottom waters (Boothman and Coiro, 2009). This concentration threshold is also an approximate threshold for onset of deleterious effects of hypoxia (U.S. Environmental Protection Agency, 2000; Breitburg et al., 2001). Where gaps were found in the data sets, hypoxic periods during the gap were estimated using correlations of measured DO concentrations with contemporaneous measurements from nearby sites (when and where available) and temporal trends for that site in other years. The estimates of hypoxic periods during data gaps were added to the observed totals to provide an estimated annual duration of bottom-water hypoxia for each site and year. There is some question of whether to include all periods below 2.8 mg L^{-1} or to filter the data to remove very short periods, based on the reasoning that there may be a time lag before interstitial waters become sulfidic, leading to precipitation of Mo. We chose not to impose such a filter for two reasons: 1) we expect that as DO concentrations in bottom waters decrease, the redox boundary in the sediments will move closer to the sediment surface, even when bottom waters are not yet hypoxic, so the transition from oxic to sulfidic interstitial waters should happen quickly; and 2) although brief periods of hypoxia may contribute to the total, the great majority of the total derives from a number of longer events that make up the bulk of the total hypoxic duration.

From these data, the mean annual hypoxic duration was calculated for each site and sampling time frame. The sampling date and sedimentation rates derived from the ^{210}Pb data (described below) were used to estimate the time period corresponding to the surface (0–1 cm) sediment horizon for each site/core. The mean annual period of hypoxia for each site was then calculated using the annual hypoxic periods for the years between the core collection date and the date estimated for the bottom of the sediment horizon.

2.3 Sediment sampling

Short sediment cores (generally 24 – 45 cm penetration) were collected using a modified Benthos gravity corer at the seven sampling sites in early April 2008 and again in December 2011 / January 2012. Upon core retrieval, each core liner was capped at each end and stored vertically in ice for return to the laboratory. Three cores were collected at each site; two

were sectioned and analyzed, with the third available if large differences between cores were found.

Upon return to the laboratory, cores were frozen at -20°C with overlying water intact until sectioning. Replicate cores from each site were subsequently sectioned into 1-cm horizons distributed vertically through the length of each core. After slightly thawing the core and removing the plug of frozen overlying water, each core tube was placed on a polypropylene cutting board and a 1-cm length of sediment extruded from the core tube. Several millimeters of the exposed exterior layer of the sediment horizon were scraped off to prevent contamination by drag-down of overlying sediment, and the remaining portion of the horizon sliced off with plastic scraper/spatula. The sliced portion was placed into trace-metal free polypropylene jars and stored frozen until analysis.

2.4 Sediment accumulation rates

Sediment accumulation rates at the core sites were estimated from analysis of ^{210}Pb concentrations in cores from both 2008 and 2012 and calculated using two different models - the Constant Input Concentration (CIC) model and the Constant Rate of Supply (CRS) model. ^{210}Pb analyses were performed by gamma spectroscopy at the University of Rhode Island Graduate School of Oceanography. Methods for preparation of the samples and analysis of the counting data using the models are provided in the supplementary information.

2.5 Molybdenum and Aluminum

Concentrations of the metals Mo and Al in surficial (0–1 cm) sediments were determined by total digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis for Mo and inductively coupled plasma atomic emission spectrometry (ICP-AES) for Al (Boothman and Coiro, 2009). Aliquots of dry sediment (~ 0.25 g) and 10 mL of an acid mixture (30% nitric / 10% hydrochloric / 20% hydrofluoric) were digested in closed vessels by microwave heating (Milestone Ethos, 1 hour at $190\text{--}200^{\circ}\text{C}$), then diluted to 100 mL with deionized water. A procedural blank, a certified reference sediment (MESS-3, Marine Sediment, National Research Council of Canada), and one sample analyzed in triplicate were included in each batch of 24 samples. Digests were analyzed for Mo by ICP-MS (Perkin-Elmer ELAN 6000, peak-hopping mode, 97.91 isotope) and Al by ICP-AES (Horiba JY Ultima 2, peak max mode, 396.152 nm line). Analytical runs included initial / continuing calibration standards, duplicate analysis of one sample, and a spiked blank and spiked sample for every 20 samples. A summary of quality control results is given in Table 1. Although the instrumental analyses of Al were quantitative, the recovery of Al from the standard reference sediment MESS-3 were low, implying incomplete microwave digestion of the sediment or a loss of Al during dilution and filtration of the digestate

Only the authigenic Mo fraction is related to the duration of hypoxia, requiring the lithogenic fraction to be subtracted from the total concentration. This was done by multiplying the measured Al concentration in each sample by the mean Mo:Al ratio in continental crust to give the lithogenic fraction and subtracting that from the total concentration to yield the authigenic Mo concentration:

$$[\text{Mo}]_{\text{auth}} = [\text{Mo}]_{\text{total}} - [\text{Mo}]_{\text{lith}} = [\text{Mo}]_{\text{total}} - [\text{Al}]_{\text{total}} \times [\text{Mo}:\text{Al}]_{\text{crust}}$$

where $[\text{Mo}:\text{Al}]_{\text{crust}} = 1.8226 \times 10^{-5}$ (Taylor, 1964).

There is some uncertainty surrounding this ratio, as some evidence has indicated that granitic rocks, which contribute half of the input to Taylor's calculations, are depleted in Mo due to MoS_2 precipitation or loss of Mo during geologic processes (Greaney et al., 2018). Lacking the ability to determine the magnitude of that deficit in Narragansett Bay sediments, however, we utilize Taylor's ratio in our estimation of lithogenic Mo concentrations. In addition, the incomplete recovery of Al from reference sediments (Table 1) implies that measured Al concentrations were possibly low, resulting in underestimated lithogenic Mo concentrations.

3.0 Results

3.1 Hypoxia in Narragansett Bay

Hypoxic conditions in Narragansett Bay are generally associated with water column stratification created by river input and summer seasonal warming (Bergondo et al., 2005). A number of factors contribute to the magnitude of hypoxia in any year: meteorological conditions that enhance water column stratification through freshwater input and surface heating (e.g., precipitation, temperature, prevailing wind direction), variations in tidal amplitude, and nutrient availability in the euphotic zone supporting phytoplankton blooms (Bergondo et al., 2005; Codiga et al., 2009). Interannual variability of these contributing factors means that the frequency and severity of hypoxic events can vary substantially annually. This substantial spatial and temporal (diurnal, seasonal and annual) variation of dissolved oxygen concentrations is evident in the bottom waters of Narragansett Bay (Figure 2). During summer months, DO concentrations exhibit a large diurnal range (6.5 – 10.35 mg L⁻¹) in partially enclosed Greenwich Bay (GB), whereas at the more exposed Poppasquash Point site (PP) in the middle of the East Passage, diurnal variation of DO was seldom greater than 2 mg L⁻¹. Greenwich Bay also becomes hypoxic earlier in the year than Poppasquash Point and remains hypoxic for much of the summer, whereas PP dips below the hypoxic threshold only occasionally and generally not for more than a few hours to days. Annual differences at both sites are evident in the period of time below 2.8 mg L⁻¹ in 2004 (a “good” year) and 2006 (a “bad” year).

Trends of annual duration of hypoxia at the Narragansett Bay sites (Table 2, Figure 3) are similar to those seen in individual years. Periods of hypoxic bottom waters were longer and more consistent at the relatively enclosed Greenwich Bay and Sally Rock sites compared to sites near central Narragansett Bay; Greenwich Bay bottom waters were hypoxic for more than 25 days in 8 of the 9 years for which annual durations were calculated, as were those at Sally Rock once monitoring commenced at that site. A similar pattern of substantial periods of hypoxia in recent years was observed at Bullocks Reach, although less frequently in early 2000s. At the same time, waters south of the Providence River (e.g., Conimicut Point (CP), North Prudence (NP), and Poppasquash Point (PP)) are partially to well mixed (Kremer

and Nixon, 1975; Pilson, 1985) and consequently periods of hypoxic bottom waters vary substantially from year to year at these sites, with the annual cumulative periods of hypoxia varying by 67–130%. Overall, hypoxia was much more severe in 2003, 2006, 2008 and 2009 than in other years (Fig 3), illustrating the need for a marker that integrates over a time frame longer than a year.

3.2 Sediment accumulation rates

Sediment accumulation rates determined for both the 2008 and 2012 cores using the CIC model are presented in Table 3, along with rates determined in cores from nearby locations in 2008. The CIC model rates varied from 0.14 to 0.43 cm yr⁻¹; rates calculated using the CRS models were very similar (Figure S2, supplementary material), and are not shown. The 2008 and 2012 rates differed by <10% for every site except CP, where the rates calculated from 2008 and 2012 cores differed by ~20%, and also agreed within 4–8% with rates previously determined by Salacup et al. There was a discrepancy between the rates calculated for the replicate 2012 QP cores. The rate obtained from one core was close to that from the 2008 core from the same location (0.428 and 0.433 cm yr⁻¹), whereas the second core gave a rate similar to that obtained from a core from a nearby site sampled by Salacup et al (0.137 and 0.165 cm yr⁻¹, respectively). Due to the low frequency of hypoxia at QP, however, the difference in the mean annual duration of hypoxia calculated using either rate (1.5 versus 2.5 d yr⁻¹) was not particularly significant to the subsequent calculations.

3.3 Molybdenum in surficial sediments

Molybdenum was found in surface sediments throughout Narragansett Bay. Total Mo concentrations (Figure 4; total, lithogenic and authigenic concentrations and variabilities are given in Table S2 of the supplemental material) showed only slight spatial variation, varying by less than a factor of 2 from the more enclosed sites (BR, GB, SR) to those from the central part of Narragansett Bay. The lithogenic fraction was fairly consistent, ranging between 0.68 and 1.13 µg g⁻¹ dry sediment in 24 of 26 samples, with 2 other samples containing only ~0.3 µg g⁻¹. Concentrations in Greenwich Bay and Providence River / upper Bay sediments were 2 to 4 times higher than at the other sites. Within-site variability at the NP and GB sites was 2 to 5 times greater than at other sites; at the NP site, this was likely due to uneven bathymetry causing different sediment regimes to be sampled within a small area, whereas at the GB site, substantial amounts of shell fragments at the sediment surface probably led to the greater variability between samples. While there was little temporal difference at BR, PP, and QP, authigenic Mo concentrations at CP, NP, and GB were 30–50% lower in 2011 compared to 2008.

Consistent with laboratory and field data showing accumulation of molybdenum in surface sediments under hypoxic waters proportional to the duration of hypoxia rather than the intensity (Adelson et al., 2001; Boothman and Coiro, 2009), authigenic Mo concentrations in surface sediments at the monitoring sites correlated strongly with mean annual duration of hypoxia for both the 2008 and 2012 samples (Figure 5). The different dating models gave somewhat different ranges of dates to calculate the mean annual periods of hypoxia at some sites, but resulted in insignificant differences in the regression relationships. The relationship was linear across the full range of observed hypoxic durations, and data from the Sally Rock

site, which was not part of the 2008 sample analysis, fell in line with those of the other stations sampled in 2011–12.

4.0 Discussion

4.1 Mo-hypoxia relationship

The Mo accumulated in the 0–1 cm horizon integrates the occurrence of hypoxic bottom waters over multiple years (generally ~2–5 years), and thus provides a longer-term view of bottom water conditions. To some extent, this integration averages out factors such as precipitation and meteorology that contribute to interannual variability in the occurrence / prevalence of hypoxia in bottom waters. The strong relationship between concentrations of authigenic Mo in surface sediments and frequencies of hypoxia in the overlying water column shows the potential utility of Mo concentrations as a quantitative indicator of hypoxia. The relative ease of sampling and analysis can enable widespread and detailed spatial analysis of recent occurrences of hypoxia, providing the ability to conduct retrospective analyses of hypoxia when monitoring instrumentation was not deployed.

While the correlations of authigenic Mo concentrations with periods of hypoxia at the sample collection sites in this study were strong, the relationship differed between the two sampling periods. The slope of the Mo-DO regression, which represents the rate of Mo accumulation per day of hypoxia, is 2x higher in the samples encompassing the 2003–2007 period than in samples encompassing 2008–2011 (Figure 5). What factor(s) caused the differing authigenic Mo accumulation rates in the two periods is uncertain. Mo is a conservative element in seawater, therefore lower bottom water salinity could mean lower Mo concentrations in interstitial waters of surface sediments resulting in a slower rate of Mo accumulation during hypoxic conditions. However, inspection of buoy data show that hypoxic periods with lower salinity bottom waters were rare, but more frequent and severe, during the time frames encompassed by the earlier sampling. Warmer temperatures might be expected to increase rates of the reactions generating thiomolybdates or adsorption of them by Fe-S minerals, resulting in higher Mo accumulation rates, but we observed just the opposite: in three of the four years of the 2008–2011 samples, bottom waters were 1 to 4 °C warmer compared to the same time period in 2004–2007 (Narragansett Bay Fixed-Site Monitoring Network, 2004–2011). Greenwich Bay was approximately 2 to 4 °C warmer from early June into early July in 2008, 2010 and 2011 (Figure 6), while temperatures at other stations were elevated by 1 to 4 °C relative to 2004–2007, beginning in mid- to late-June through mid-July. Cooler temperatures at these sites in 2009 were similar to those in 2004–2007.

A more likely factor affecting authigenic Mo accumulation rates is sulfate reduction activity in the sediments. Because sulfate is a major ion in seawater, microbial oxidation of organic carbon using sulfate (SO_4^{2-}) as terminal electron acceptor is often the dominant metabolic process in coastal sediments, accounting for as much as 50% of the carbon oxidation in some sediments (Jorgensen, 1977; Valiela, 1995). This process, which produces the sulfide that reacts with MoO_4^{2-} to form the thiomolybdates scavenged by Fe-S minerals and accumulated in sediments, is thus strongly tied to the organic carbon cycle within the sediments. At sites in Buzzard's Bay and Hingham Bay (, MA, USA), high sulfate reducing

activity (annually averaged organic matter oxidation rates of 390 and 880 $\mu\text{mol C cm}^{-2} \text{ yr}^{-1}$) in sediments underlying normoxic bottom waters ($[\text{DO}] = 7.4 - 12.2 \text{ mg L}^{-1}$) have resulted in authigenic Mo accumulations of 60 to 131 $\text{nmol m}^{-2} \text{ day}^{-1}$ (Morford et al., 2007; Morford et al., 2009). Conversely, in some continental margin sediments, sulfate was not depleted in pore waters, indicating little to no sulfate reduction activity, and no accumulation of Mo was found, even within the oxygen minimum zone ($[\text{O}_2] \approx 0.9 \text{ mg L}^{-1}$) (McKay et al., 2007). This was attributed to the combination of low sedimentation rates on the slope (< 1 to 6 cm kyr^{-1}) and intense bioturbation maintaining suboxic conditions despite low bottom water oxygen concentrations and a high flux of organic carbon to the sediment. It has been posited that the accumulation rate of authigenic Mo is less sensitive to concentrations of sulfide in bottom waters than it is to the flux of carbon: because the organic carbon is a food source for the sulfate-reducing bacteria that reduce Mo(VI) to Mo(IV), it controls the activity of the bacteria and thereby determines the formation of authigenic Mo (Zheng et al., 2000). Given this wide range of influence on Mo accumulation related to sulfate reducing activity and organic matter oxidation rates, it is not surprising that a slight variation in those rates could result in a 2-fold difference in Mo accumulation rates. This emphasizes a need to quantitatively link sulfate reduction activity to Mo accumulation rate in order to improve the accuracy of the Mo-DO model.

4.2 Comparison of results with models of Mo accumulation

In most oceanic settings outside of basins with restricted water circulation, permanent fixation of molybdenum occurs not in surface sediments, but several to many centimeters deep into the sediments. The mechanisms of molybdenum accumulation in coastal marine sediments have been incorporated into a generalized model of accumulation and remobilization of redox-sensitive metals (Morford et al., 2007; Morford et al., 2009). In that model, Mo in overlying water may be adsorbed to manganese oxides accumulated at the sediment-water interface, but there is no subsurface removal of Mo from interstitial waters in the oxic layer below the sediment surface. Adsorbed Mo may be released to interstitial and overlying waters as $[\text{DO}]$ in overlying water decreases below 3.2 mg L^{-1} . Molybdenum removal from interstitial waters occurs below the oxic layer by reaction with dissolved sulfide or iron sulfide minerals (e.g., pyrite, greigite, amorphous FeS). The onset of removal varies seasonally from $\sim 2.5 \text{ cm}$ below surface in winter/spring to $\sim 1.5 \text{ cm}$ or less during summer months when sulfate reduction is active in sediments. In deeper sediments ($\sim 6 - 7 \text{ cm}$ and below), there is no further removal of Mo from pore waters. Bioirrigation may introduce oxygenated overlying water into deeper sediments, liberating some Mo into interstitial waters (Morford et al., 2009). Some of this released Mo may diffuse to deeper sediments where it can react with dissolved or mineral sulfides and accumulate.

Although the Morford model would seem to preclude accumulation of authigenic Mo in the top centimeter of marine sediments, the conditions in surface sediments underlying waters experiencing frequent or intermittent hypoxia may be very different from those in the sediment cores used to develop and parameterize the general model. Both coastal sites used to develop the Morford model had consistently high concentrations of DO ($\sim 7.5 - 12 \text{ mg L}^{-1}$) in bottom water and oxygen penetrated into the sediments to depths of $2 - 6 \text{ cm}$ or more. Under a hypoxic water column, these conditions can be quite different,

resulting in increased delivery of Mo to the sediments and increased retention of that Mo. With hypoxic bottom waters, the depth of O₂ penetration can decrease to less than 1 cm and dissolved and solid phase sulfides form in near-surface sediments (Jørgensen, 1977; Howarth and Jørgensen, 1984; Zheng et al., 2000; McManus et al., 2006b). With only a shallow oxic sediment layer, the rate of diffusion of MoO₄²⁻ into the sediments increases. In addition, the shallow redox boundary allows dissolved Mn⁺² and Fe⁺² to diffuse into overlying waters and be oxidized to particulate oxyhydroxides. These particulates can efficiently scavenge MoO₄²⁻ from the water column and deliver it to the sediments (Mn/Fe “shuttle”) (Scholz et al., 2011), where reducing conditions can dissolve the oxyhydroxides and associated Mo. The dissolved Mo reacts with sulfides and is removed to the solid phase, a process enhanced by the presence of iron sulfide minerals (e.g., amorphous FeS, mackinawite, greigite and pyrite) (Helz et al., 1996; Helz et al., 2004; Helz et al., 2011). In locations subject to cycling between oxic and suboxic/anoxic conditions, oxidation of reduced forms of sulfur leads to the formation of elemental sulfur and pyrite within the top few cm of sediment (Troelsen and Jørgensen, 1982; Howarth and Jørgensen, 1984), and elemental sulfur enhances the authigenic fixation of Mo from interstitial waters (Helz et al., 2004; Vorlicek et al., 2004; Dahl et al., 2013). Furthermore, such processes can trap sulfide-associated Mo in pyrite, making it resistant to remobilization during oxic periods and increasing its retention (Adelson et al., 2001). And as bottom waters become oxic, Mn oxyhydroxides can form in surface sediments, retaining Mo remobilized from underlying sulfide minerals (Scholz et al., 2013). As a result of these processes, Mo fixed in surface sediments below intermittently hypoxic waters may be retained to a greater extent than predicted by models developed using sediments from fully oxic waters (Helz and Adelson, 2013) and result in greater rates of accumulation in sediments that experience episodic rather than continuous hypoxia (Scholz et al., 2011; Scholz et al., 2013).

Other processes may complicate the use of sediment Mo concentrations to determine if the overlying water was hypoxic at time of deposition. Physical mixing of sediments (primarily via bioturbation) and diffusive transport are likely to broaden peaks within the sediment column to some extent. Of particular concern is the possibility of remobilization of authigenically fixed Mo when exposed to oxic waters. However, there is reason to believe that much of the authigenically fixed Mo may be retained in surface sediments. Reductive dissolution of Mn oxides begins to occur at DO concentrations below 100 μM (3.2 mg L⁻¹) (Calvert and Pedersen, 1993), very close to concentrations where Mo accumulates in surface pore waters (~2.8 mg L⁻¹) (Boothman and Coiro, 2009). As a result, much of the Mo remobilized from Mn oxides may become available for fixation by reaction with sulfide phases also present in surface or near-subsurface sediments. Conversely, subsequent oxidation of surface sediments can lead to the formation of Mn oxides that can retain Mo released from solid phases. Profiles of Mn in the cores sampled in 2011–2012 (Figure 7) show no surface maxima, implying that the Mo concentrations in those surface sediments are not due to adsorption from overlying water, but rather from lithogenic and authigenic sources.

The results presented here are limited to sites in Narragansett Bay. However, the processes that lead to the observed relationship(s) – sulfate reduction producing sulfide in near surface sediments under hypoxic waters and reaction of Mo with sulfide to form particle-active

thiomolybdates – are not unique to Narragansett Bay and occur in estuarine and coastal waterbodies elsewhere. Further sediment sampling and analysis in other estuaries or coastal embayments where detailed and extensive records of bottom water DO concentrations exist are needed to determine if similar relationships exist in other systems. Such relationships could be used to make inferences regarding oxygen status based on Mo measurements. The use of Mo isotopic ratios may help to remove questions regarding post-depositional diagenesis, as there is an apparent co-variation between the Mo isotope composition and the accumulation rate of authigenic Mo under reducing conditions, as well as a relationship between Mo accumulation, isotope signature and the rate of organic carbon oxidation and burial (Pearce et al., 2006; Siebert et al., 2006; Scheiderich et al., 2010; Kendall et al., 2017).

5.0 Conclusions

Through chemical analysis of sediments and numerical analysis of dissolved oxygen records from water quality monitoring sites, we have demonstrated a strong linear relationship between sediment concentrations of the element molybdenum and the mean annual periods of hypoxia in the overlying waters. The slope of the relationship, that is, the Mo accumulation rate, differed between the time periods encompassed by the samples, most likely due to varying rates of benthic sulfate reduction activity. However, the difference in accumulation rates was relatively narrow (~ factor of 2) and further investigation to determine prior rates of sulfate reducing activity may allow the differing slopes to be harmonized.

The strong correlation between hypoxia in bottom waters and authigenic Mo in surface sediments does not appear to hold up in either the oceanic or freshwater environment. In near-coastal and estuarine environments, however, the relationship holds promise as a quantitative indicator of hypoxia. The relative ease of sampling and analysis can enable widespread and detailed spatial analysis of occurrences of hypoxia and provides the ability to “look back” at hypoxia in places or times when monitoring instrumentation was not deployed. In addition, because sediment samples encompass accumulation over multiple years, the results would presumably be less subject to effects due to annually and seasonally variable factors, such as precipitation or winds. As a result, surveys of Mo in sediments may provide a useful tool for assessing the prevalence and extent of hypoxia in coastal waters and its relationship to input of nutrients, which can contribute to the development of limits / standards for nutrients to prevent or minimize the impacts of hypoxia in coastal waters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

References

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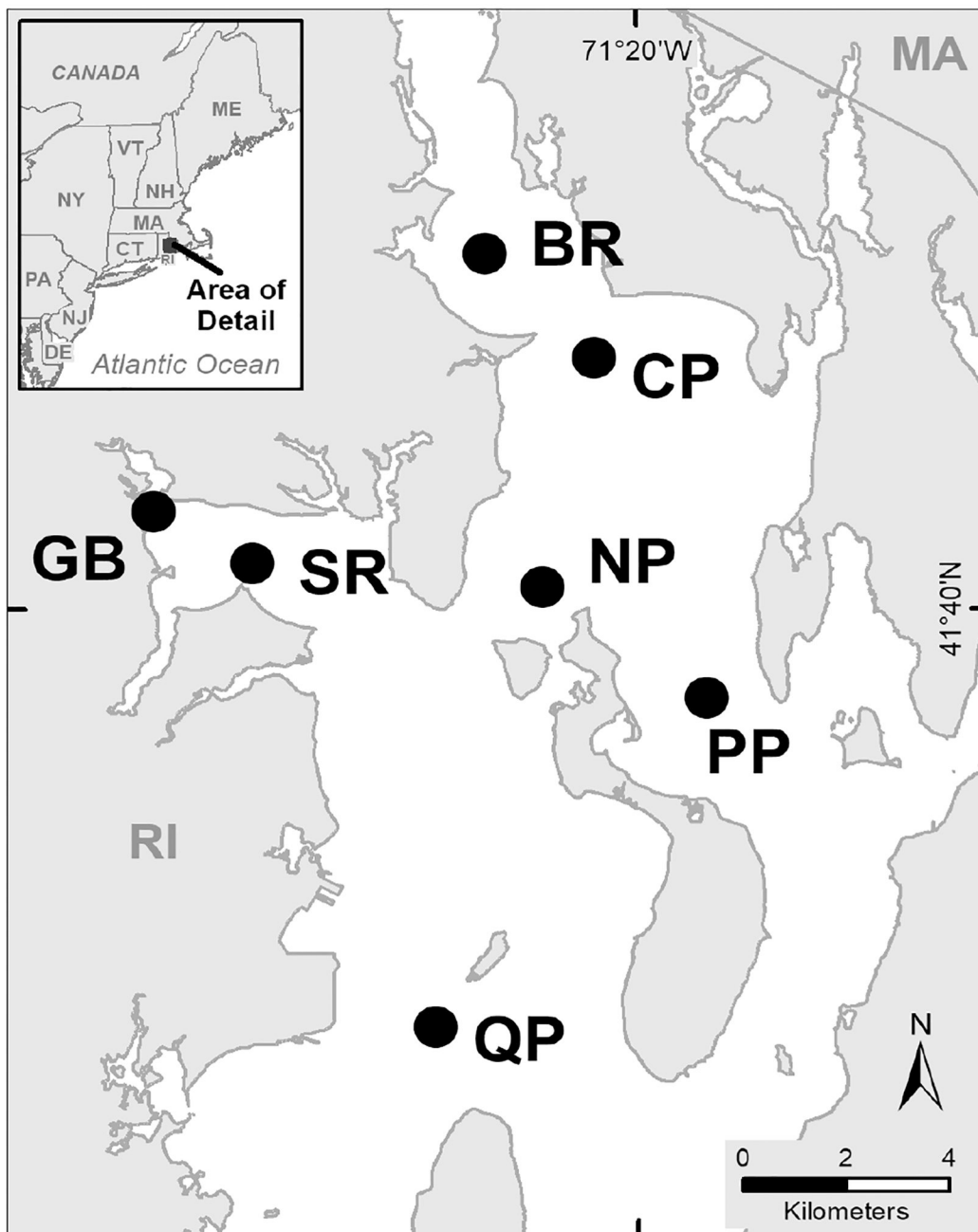


Figure 1. Water quality monitoring station in Narragansett Bay, RI, where sediment cores were collected. Site codes: BR - Bullock's Reach; CP - Conimicut Point; NP - North Prudence; PP - Poppasquash Point; GB - Greenwich Bay; SR - Sally Rock; QP - Quonset Point. Further information about sampling sites given in Table S1 of supplementary information.

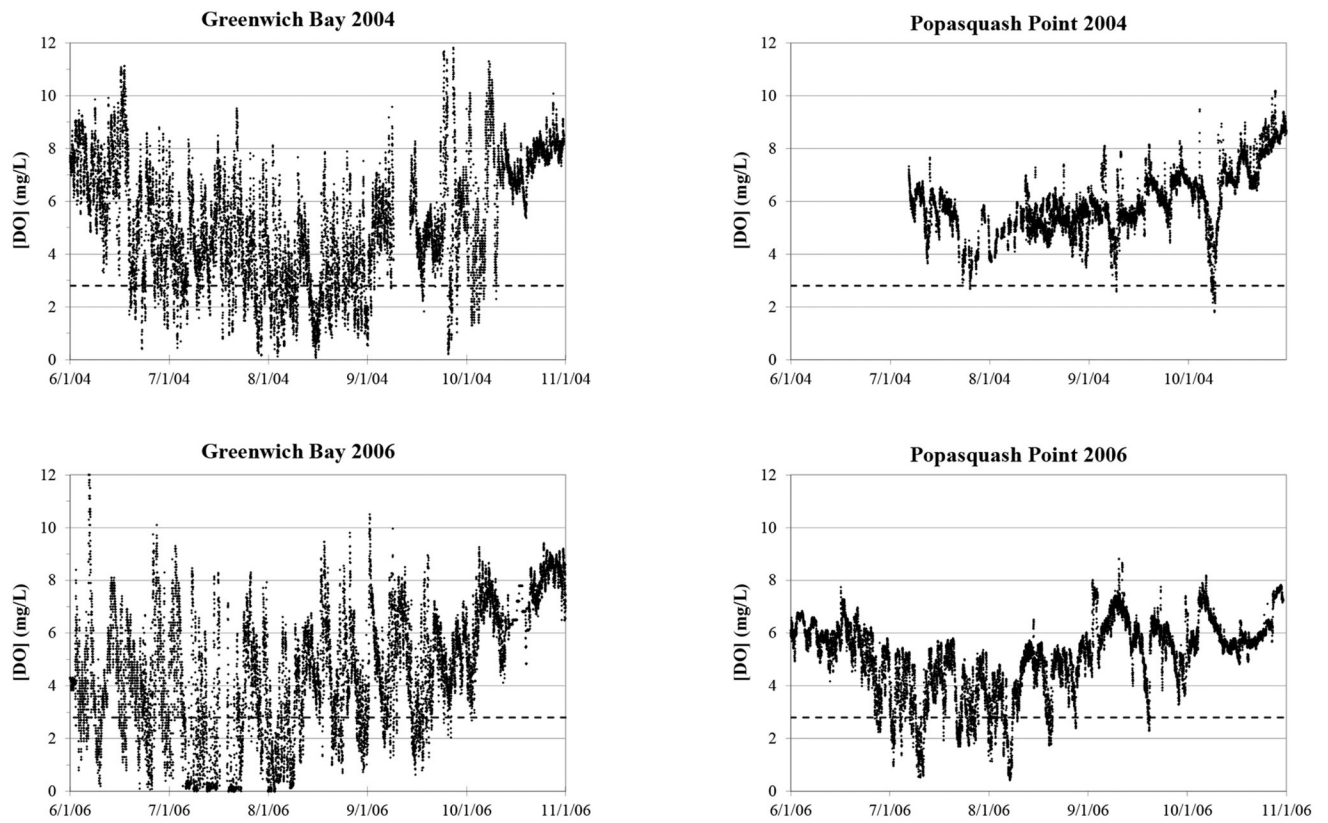


Figure 2. Dissolved oxygen concentrations in bottom waters at Greenwich Bay (GB) and Poppasquash Point (PP) monitoring sites in 2004 (a “good” year) and 2006 (a “bad” year). Dashed line indicates 2.8 mg/L hypoxic threshold.

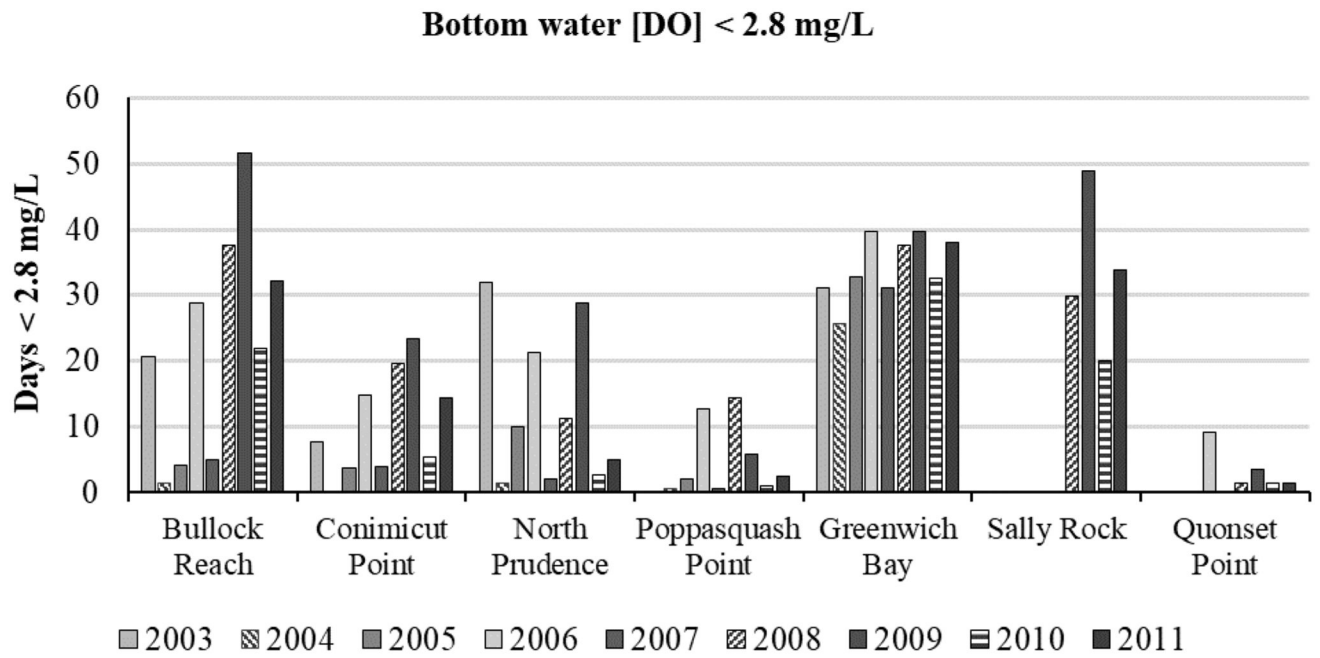


Figure 3.
Annual periods of hypoxia at Narragansett Bay monitoring stations.

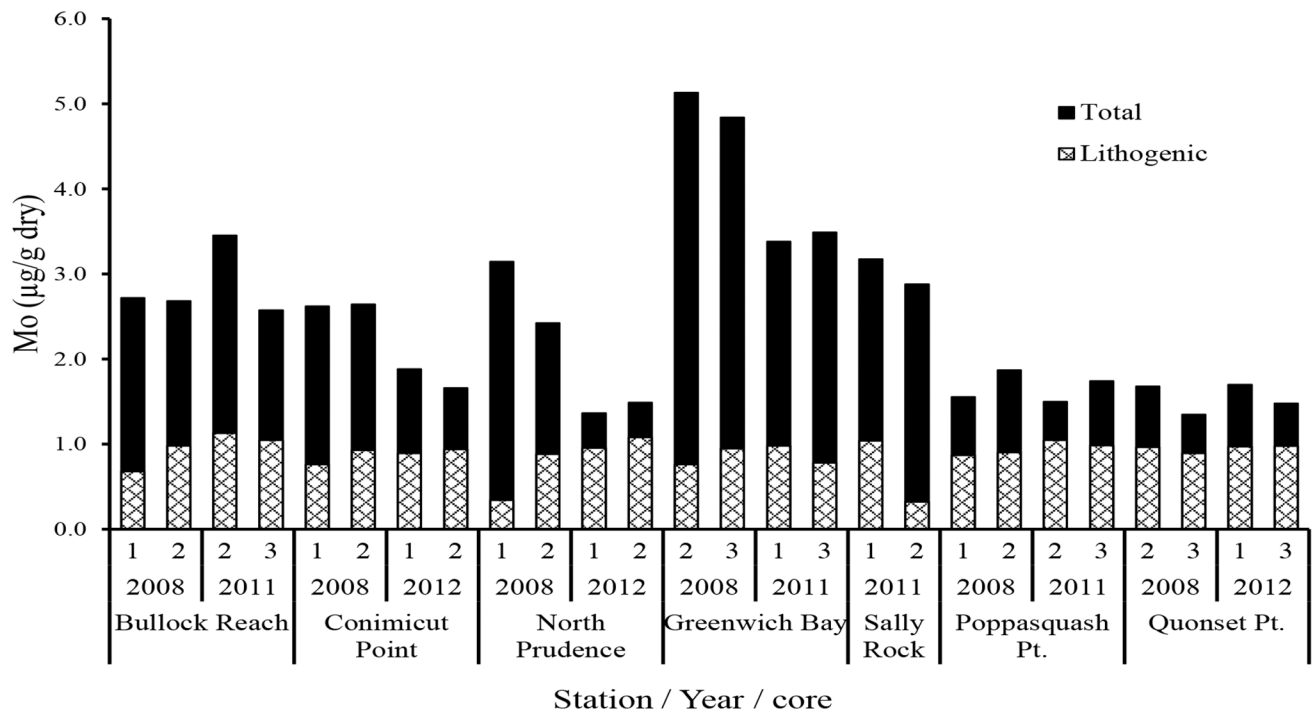


Figure 4. Concentrations of total and lithogenic Mo in Narragansett Bay sediments. Lithogenic fraction calculated as $Mo_{lith} = Al_{total} \times [Mo_{crust} / Al_{crust}] (= 1.8226 \times 10^{-5})$ (Taylor, 1964)

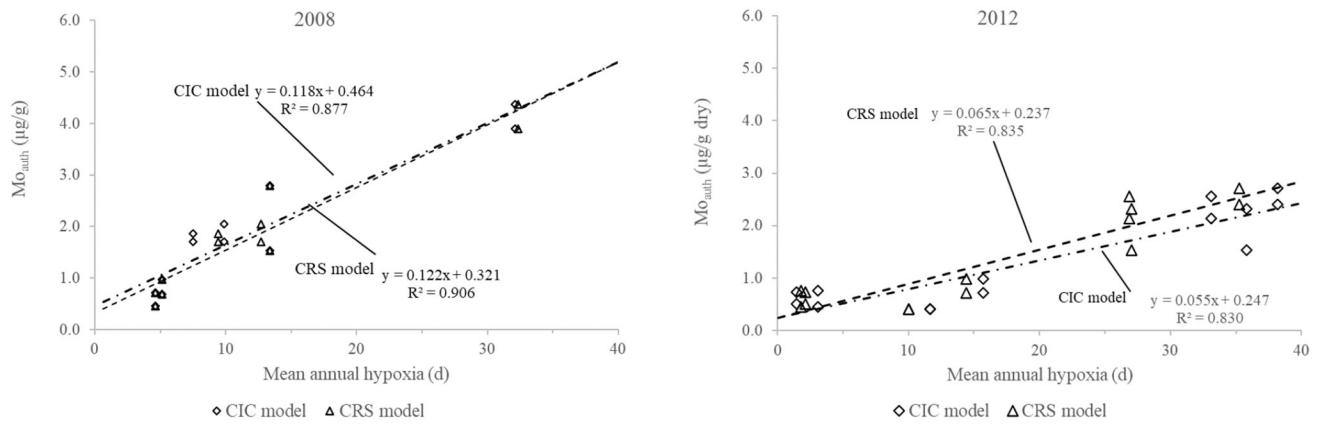


Figure 5. The relationship between mean annual periods of hypoxia and authigenic Mo in surface sediments collected at RI DEM/GSO monitoring sites in (a) 2008 and (b) 2012.

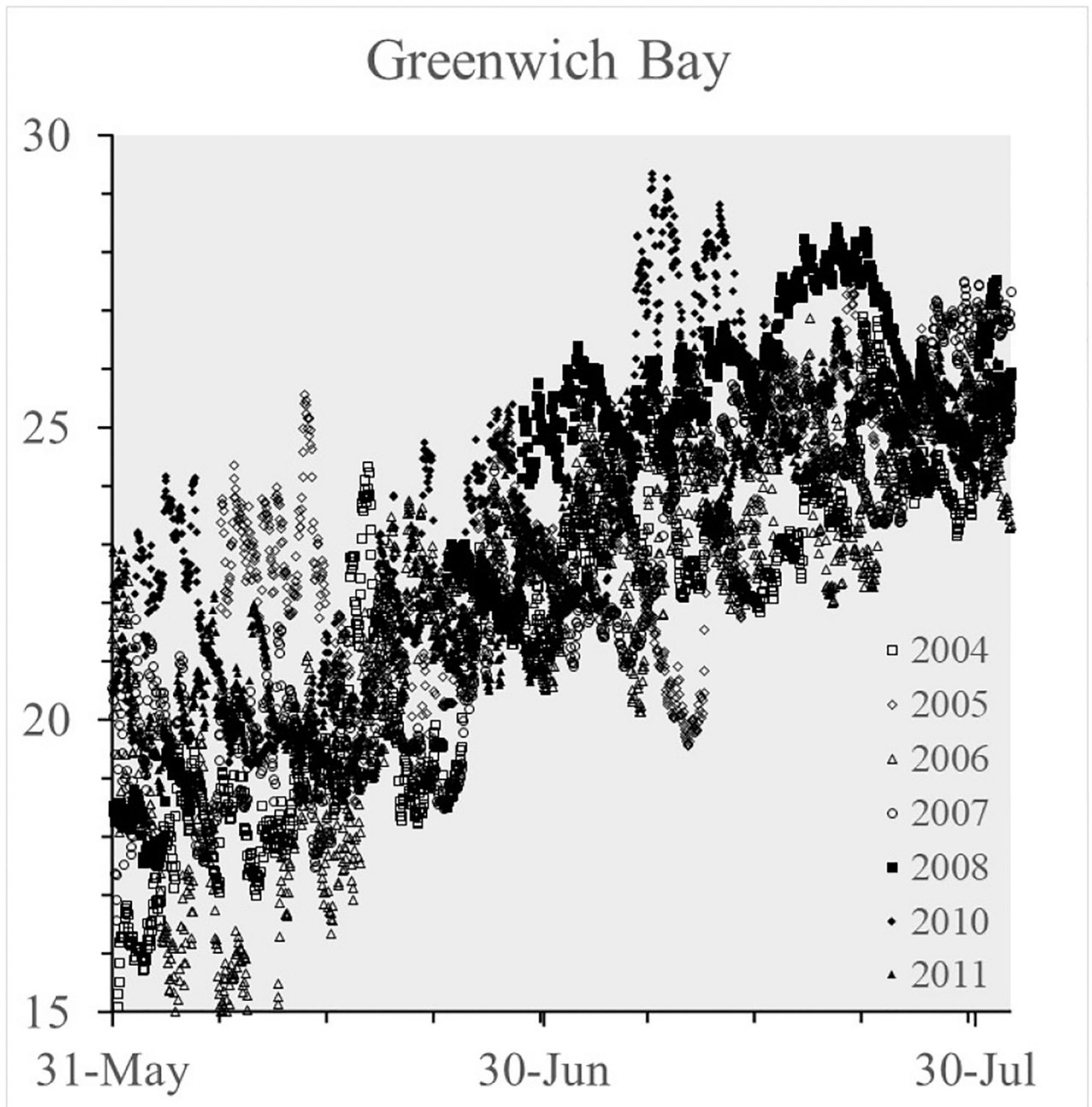


Figure 6. Bottom water temperatures at Greenwich Bay station, 2004–2007 (open symbols) and 2008–2011 (closed symbols)

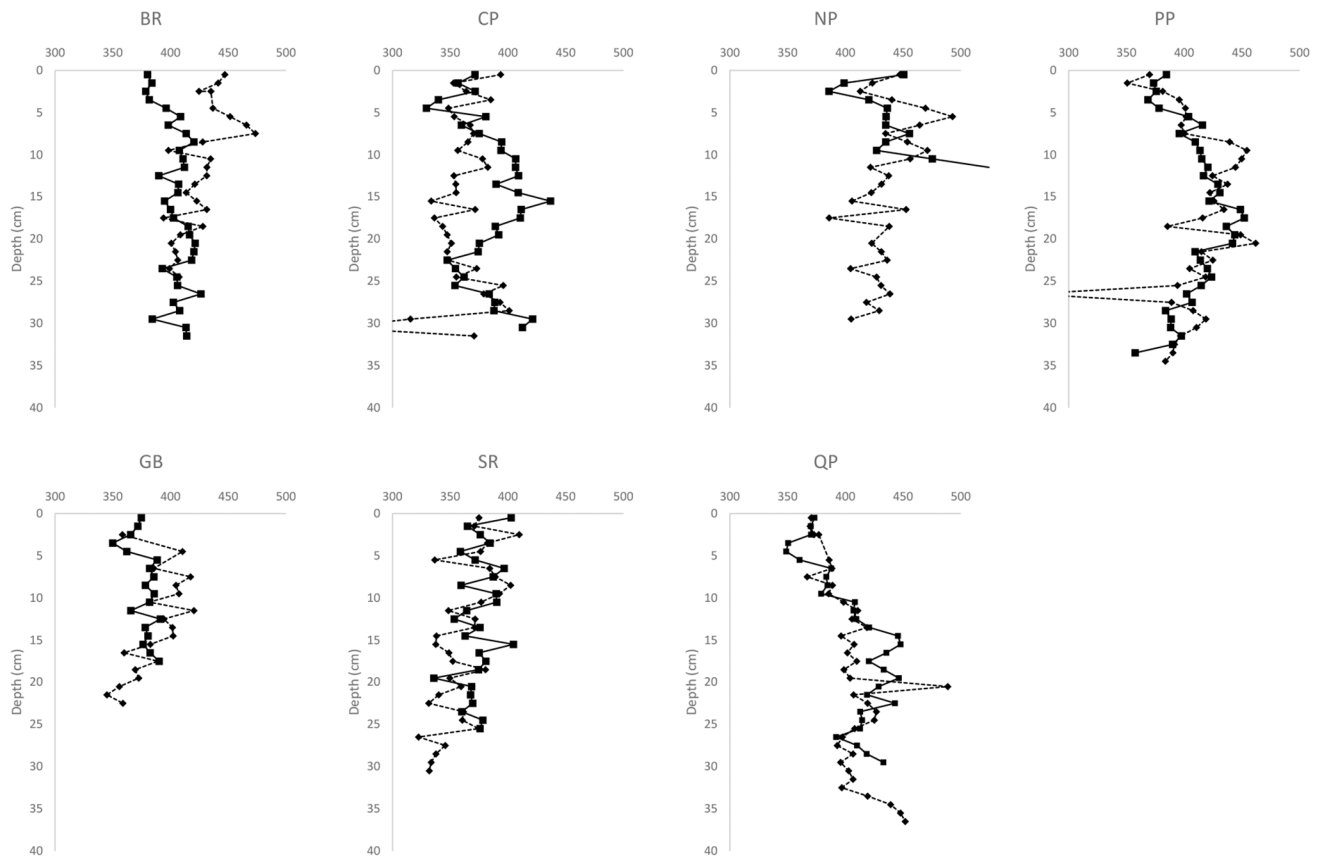


Figure 7. Profiles of manganese concentrations ($\mu\text{g Mn / g dry}$) in sediment cores from RI DEM monitoring buoy sites in Narragansett Bay. Symbols represent replicate cores.

Table 1.

Quality Control results for analyses of Mo and Al in Narragansett Bay sediments

Type	Measure		Mo	Al
Instrumental	Calibration verification	error	11 – 19%	6 – 15 %
	Duplicates	RPD	1 – 2%	0.1 – 2%
	Spike recovery	blanks	97% - 110%	87 – 113%
		samples	103 – 111%	77 – 103%
Analytical	procedural blanks	% of lowest measured concentration	< 1–10%	< 0.5 – 1.5%
	triplicate analyses	RSD	2 – 5%	4%
	Standard Reference Material (MESS-3 Marine sediment)	Recovery	98 – 114%	54 – 74%

Table 2.

Annual duration of time with bottom water [DO] < 2.8 mg L⁻¹ at Narragansett Bay monitoring sites. Values in bold were used to calculate mean annual values for the 2008 samples; values in italics were used for the 2012 samples. Values in parentheses give the estimated period of hypoxia during gaps in the collected data.

Station	Days < 2.8 mg/L									
	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Bullock Reach	20.7 (5.4)	1.5 (0.5)	4.3 (0.0)	28.8 (0.0)	5.0 (0.3)	<i>37.6</i> (0.0)	<i>51.5</i> (0.0)	<i>22.0</i> (0.0)	<i>32.1</i> (0.0)	
Conimicut Point	7.6 (1.9)	N/A	3.7 (0.6)	14.9 (0.0)	4.0 (0.0)	<i>19.6</i> (0.0)	<i>23.3</i> (0.0)	<i>5.5</i> (0.9)	<i>14.4</i> (1.1)	
North Prudence	31.9 (0.6)	1.5 (0.0)	10.0 (0.0)	21.3 (7.3)	2.1 (0.1)	<i>11.4</i> (0.0)	<i>28.8</i> (3.1)	<i>2.8</i> (0.3)	<i>5.1</i> (0.0)	
Greenwich Bay	31.1 (0.0)	25.7 (0.6)	32.7 (0.0)	39.7 (2.2)	31.1 (0.0)	<i>37.6</i> (5.7)	<i>39.7</i> (0.0)	<i>32.5</i> (1.8)	<i>38.0</i> (0.0)	
Sally Rock	N/A	N/A	N/A	N/A	N/A	<i>29.8</i> (0.3)	<i>48.9</i> (9.7)	<i>19.9</i> (2.2)	<i>33.8</i> (0.1)	
Poppasquash Point	N/A	0.5 (0.0)	2.1 (1.4)	12.7 (0.0)	0.5 (0.0)	14.4 (0.2)	<i>5.8</i> (0.0)	<i>1.0</i> (0.3)	<i>2.5</i> (0.0)	
Quonset Point	N/A	N/A	0.0 (0.0)	9.2 (0.0)	0.0 (0.0)	1.6 (0.0)	3.5 (2.8)	<i>1.5</i> (0.0)	<i>1.4</i> (0.0)	

Table 3.

Sediment accumulation rates (cm yr^{-1}) and correlation coefficients for exponential fit of $^{210}\text{Pb}_{\text{xs}}$ activities against depth (CIC model) determined from sediment cores collected at Narragansett Bay monitoring sites in 2008 and 2012 and nearby core sites. Values in the right hand column from Salacup et al (Salacup et al., 2019), except for station GB10 (Boothman, unpublished data).

Station	Depth range included in analysis	2008		2012		2008	
		cm yr^{-1}	r^2	cm yr^{-1}	r^2	core site	cm yr^{-1}
BR	4 to 27 cm	0.251	0.92	0.279	0.88		
CP	3 to 30 cm	0.298	0.98	0.241	0.92	3	0.254
NP	0 to 17 cm	0.136	0.99	0.140	0.94		
GB	0 to 21 cm	0.219	0.79	0.233	0.95	<i>GB10</i>	0.215
SR	2 to 25 cm	NA	-	0.228	0.98	12	0.237
PP	0 to 25 cm	0.325	0.94	0.347	0.97	8, 25	0.367
QP	0 to 30 cm	0.428	0.98	<i>0.433</i>	<i>0.90</i>		
	0 to 11 cm			<i>0.137</i>	<i>0.97</i>	44	0.165