Diel Biogeochemical Cycling in a Hyperventilating Shallow Estuarine Environment

NICOLE G. BECK¹ Earth Sciences Department University of California at Santa Cruz Santa Cruz, California 95064

KENNETH W. BRULAND Ocean Sciences Department University of California at Santa Cruz Santa Cruz, California 95064

ABSTRACT: A diel biogeochemical study was performed to assess the influence that periods of elevated biological activity have on the biogeochemical cycling of macronutrients and redox-sensitive elements in a natural estuarine environment. High-resolution data (15 min sampling) illustrates periodic extreme variations in dissolved oxygen (DO) in the shallow waters of Azevedo Pond, Elkhorn Slough, California. During periods of low tidal flushing, DO values can range from highly oxic (> 560 μ M O₂: > 250% saturation) during sunny days to suboxic conditions (< 5 μ M) at night. Nutrient cycling and redox-sensitive trace element biogeochemistry were evaluated in response to the extreme daily DO fluctuations. A diel sampling study was conducted over a 26-h period, where O₂ concentrations ranged from 346 µM to sustained. non-detectable levels in the night hours. In concert with the DO fluctuations, diel phosphate cycling was on the order of 4 μ M in response to tidal flushing events and biological assimilation and regeneration. The IO_3^-/I^- redox couple quickly responded to suboxic conditions in the water column by a marked increase in I- concentrations and corresponding depletion of IO_3^- . The extreme fluctuations of the p ϵ in the water column resulted in diel dissolved Mn²⁺ variations of nearly 5 µM, with observed dissolved Mn removal rates on the order of 1 µM h⁻¹. The elevated biogeochemical cycling of oxygen, nitrogen, phosphorus, iodine, manganese, and iron found in this shallow estuarine environment suggest that tidal restrictions and anthropogenic nutrient enrichments can amplify diel variations and potentially hinder the functional and ecological stability of these systems. These data suggest that accurate chemical monitoring of the health of an estuarine ecosystem must account for the diel variability inherent in these highly productive environments.

Introduction

Problems related to hypoxia/anoxia within U.S. estuarine waters appear to be increasing, and in many cases can be attributed to anthropogenic nutrient enrichment and/or tidal restrictions (Nixon 1995; Ansfield and Benoit 1997). In several studies of East Coast estuarine systems, excessive major nutrient enrichments lead to large seasonal increases in algal production in surface waters, followed by complete oxygen depletion in the bottom waters (Taft et al. 1980; Officer et al. 1984; Welsh and Eller 1991; Atwood et al. 1994; Cooper 1995). The increasing frequency of extreme seasonal phytoplankton blooms in South San Francisco Bay correlates with excessive anthropogenic inputs of nutrient concentrations, and physical and hydrological forcings that allow spring-time stratification of the water column (Cloern 1996). Alterations of the tidal flow regime in urbanized coastal zones may further exacerbate eutrophic conditions within

wetland ecosystems by decreasing mixing and creating stagnant water bodies. Circulation restrictions within the diked Herring River Estuary, Cape Cod, Massachusetts were shown to be responsible for periodic anoxic conditions in the bottom waters and associated fish kills (Portnoy 1991).

Photosynthetic organisms often exist in a static quasi-equilibrium, where primary productivity is balanced by grazing, respiration, and physical transport (Evans and Parslow 1985). Deviations from this balance occur when various physical forcings (e.g., tidal cycling and sunny, warm days) interact to provide conditions ideal for elevated photosynthetic biomass production. An increase in the rate of input and removal of dissolved oxygen (DO) to the system is one consequence of increased photosynthetic activity and biomass production in eutrophic systems. In many environments, the ratio of DO inventory to the diel oxygen flux (i.e., net input by photosynthesis during the daylight and respiratory output at night) is so large that variations in O_2 are relatively insignificant. For instance, O_2 fluxes to and from the ter-

¹ Corresponding author; e-mail: nbeck@earthsci.ucsc.edu.

^{© 2000} Estuarine Research Federation



Fig. 1. Site map of Azevedo Pond, located in Elkhorn Slough, California.

restrial biomass are negligible relative to the O_2 reservoir of the troposphere, and phytoplankton production is small relative to the O_2 reservoir of the upper 100 m of oceanic oligotrophic gyre waters. However, in shallow, productive, estuarine systems there can be extensive primary productivity and respiration confined to a small volume of water, creating marked diel changes in DO concentrations.

This study investigates the impact that major nutrient enrichment and tidal restrictions have on the diel biogeochemical cycling of an isolated estuarine salt marsh. The research site focuses on Azevedo Pond, a shallow (≤ 2 m) tidal salt marsh located within Elkhorn Slough, California (Fig. 1). Azevedo Pond receives nutrient-rich runoff from neighboring agricultural fields, and due to periodic tidal flow restrictions, can experience times of high tidal flushing, interspersed with relatively stagnant periods. High-resolution water quality data (15 min sampling) suggests that nutrient-induced eutrophication causes extreme diel oxygen fluctuations within the pond, when periods of restricted flow are incidentally coupled with clear sunny days. An event from October 1996 illustrates that DO can vary from $> 560 \mu M$ (> 250% saturation) to non-detectable levels, resulting in suboxic, or potentially anoxic, conditions within an 8-h



Fig. 2. Time series of dissolved oxygen variations as a result of increased biological activity in Azevedo Pond, October 1996. Photosynthesis = PS. Respiration = R. Periods of sustained DO levels below detection limits are referred to as suboxic events.

period (Fig. 2). Suboxic conditions during this 1996 event persisted up to 11 h. Biological metabolism can be inferred from these extreme diel DO variations, where it is assumed that increasing concentrations during the daylight are attributable to net photosynthesis (PS), while nighttime decreases are due to respiration (\mathbf{R}) . The balance of biomass productivity and consumption in this shallow system are amplified on very short time scales, where production of O_2 greatly exceeds losses by respiration and atmospheric exchange during the day, and consumption depletes the oxygen reservoir and exceeds atmospheric exchange at night. Azevedo Pond appears to hyperventilate during these time periods. These hyperventilation events are what prompted our investigation of the diel biogeochemical cycling of macronutrients and redoxsensitive element in Azevedo Pond.

In most estuarine environments previously investigated, a seasonal stratification of the water column exists, isolating oxygen-depleted bottom waters from the oxygen-rich waters above (Richard and Broenkow 1971; Officer et al. 1984; D'Avanzo and Kremer 1994). The research environment presented herein differs from many of the hypoxic/ anoxic estuarine systems, in that it appears that the entire water column of a shallow estuarine tidal marsh can hyperventilate on diel time scales. The occurrence of these extreme DO events provides an ideal natural laboratory to apply realistic open system methods to perform detailed measurements of biometabolism and its influence on redox-sensitive elements.

Acute DO variations can significantly affect redox cycling of some macronutrients and other trace elements. During times of oxygen depletion, respiring bacteria use other electron acceptors to continue oxidizing organic matter (Froelich et al. 1979). The excessive loading of organic carbon in



Fig. 3. Predicted thermodynamic sequence of the redox couples investigated in this study as a function of a range of $p \in$ values (modified from Rue et al. 1997).

eutrophic systems will increase the biogeochemical cycling of elements associated with anaerobic modes of respiration. The predicted thermodynamic order of oxidation/reduction reactions (Fig. 3) allows us to place reasonable bounds on the progress heterotrophic bacteria make through the alternate electron acceptors during a sustained suboxic event. Suboxic conditions are defined by the point where oxygen concentrations are below 5 μ M and SO₄²⁻ reduction does not yet occur (Cline and Richards 1972; Froelich et al. 1979). The initiation of suboxic conditions is indicated by the reduction of iodate (IO_3^-) to iodide (I^-) (Liss et al. 1973; Rue et al. 1997). In some suboxic systems, the dissimilatory reduction of nitrate can provide a large proportion of oxidizing energy for organic carbon. Concentrations of dissolved manganese also increase markedly in response to suboxic conditions (Martin and Knauer 1984; Landing and Bruland 1987; Rue et al. 1997). According to thermodynamics, the reduction of Mn oxides should occur at a similar $p \in as$ iodate reduction, but much earlier than the reduction of iron oxyhydroxides (Fig. 3). Variations in the dissolved Fe concentrations may also respond to reductions in the $p\epsilon$ of the environment, due to the reductive dissolution of Fe(III) oxyhydroxides, the dominant Fe species in oxygenated environments. Sulfate reduction is the next transformation in the redox sequence, and represents the complete depletion of oxygen and the presence of truly anoxic conditions.

We have investigated the influence that elevated levels of photosynthetic activity have on the diel biogeochemical cycling within a natural estuarine environment. This paper presents our interpretation of the physical forcing mechanisms controlling the timing of these hyperventilation events, and data for macronutrients (N, P) and a variety of redox-sensitive elements (I, Mn, and Fe) from a detailed 26-h biogeochemical study conducted during a 1998 extreme DO variation event in Azevedo Pond.

Methods

SITE DESCRIPTION

Elkhorn Slough (Fig. 1) is a shallow coastal estuary located near Moss Landing, California, halfway between Santa Cruz and Monterey on the Monterey Bay National Marine Sanctuary. Elkhorn Slough is composed of a main channel that extends inland approximately 7 km with associated tidal flats occupying approximately 10 km². Agriculture is the primary land use within the drainage basin. The majority of nutrient contributions to Elkhorn Slough and Azevedo Pond occur during the winter months of December and January, associated with increased runoff and freshwater inputs (Smith 1973). Azevedo Pond is part of the wetland system associated with Elkhorn Slough and is bordered on the west by a Pacific Railway track and on the east by an approximately 100 m long hill (15–20° slope). An active 20-acre agricultural farm is located at the top of the hill. The daily tidal flushing of the pond is controlled by the flow through a 1.5 m-diam culvert located beneath the railroad track, isolating Azevedo Pond from the main channel of Elkhorn Slough. An elevation gradient exists between the main channel and Azevedo Pond, which prevents any mixing until the tidal height at Moss Landing exceeds approximately 1.2 m. The deepest depth of Azevedo Pond is dependent upon the tidal heights, fluctuating from an average of 1.5 m in the wetter winter months to 1 m in the summer and fall.

SAMPLE COLLECTION AND ANALYTICAL PROCEDURES

Hydrographic data were provided by the Elkhorn Slough National Estuarine Research Reserve (ESNERR) from a YSI 6000 multiparameter instrument which recorded DO, pH, salinity, temperature, depth, and conductivity at 15-min intervals within Azevedo Pond. The hydrographic data collection by the ESNERR was initiated in September 1995 and continues in 2000. Weather data were provided by the University of California at Santa Cruz (UCSC) Real-time Environmental Information Network and Analysis System (REINAS) project, and collected by a meteorological station located approximately 18 km southwest of Azevedo Pond, at Fort Ord, California. We conducted three diel-sampling studies during 1998 in an attempt to evaluate the nutrient dynamics and redox chemistry associated with one of these extreme oxygen fluctuation events. The diel sampling studies were scheduled on days when early morning high tides

at Moss Landing were predicted to be below 1.2 m. Due to the elevation gradient at the culvert mouth, low amplitude early morning high tides result in the absence of flushing of the pond, allowing the microbial decay of organic matter to continue throughout the dark hours. DO, pH, and temperature values were calibrated using a Solomat Water Quality Monitoring System (WP4007) on shore during the sampling study. For the data presented herein, three water samples were collected at 0.5 to 1 h intervals from 0700 July 17, 1998 through 0900 July 18, 1998, using appropriate clean techniques (Bruland et al. 1979). Water samples were collected at the same water depth as the in situ sensor data collector (approximately 0.5 m above the sediments), passed through a $0.45 \ \mu m$ Gelman Sciences Aqua Prep 250 filter and immediately frozen on dry ice. The presence or absence of hydrogen sulfide was determined by the odor of each sample following collection. All of the frozen water samples were returned to the laboratory and kept frozen until analysis. One set of duplicates was quick-thawed and analyzed for nitrate, nitrite, ammonium, and phosphate using a peak area technique recommended for brackish waters on an automated spectrophotometric flow injection analysis system (Lachat, Quickchem 8000).

A BAS Controlled Growth Mercury Electrode system was used for the determination of iodate $[I(V), (IO_3^{-})]$ and iodide $[I(I), (I^{-})]$ concentrations in the estuarine samples by square wave cathodic stripping voltammetry following the method described by Lucia and Campos (1997). A 3-ml sample was filtered through an Analtech SPICE cartridge to remove any interferences that were presumed to be due to the high concentrations of dissolved organic matter (DOM). This cartridge did not remove either of the anionic iodate or iodide species. Three ml of sample were diluted to 10 ml with deionized water and 100 µL 1 M boric acid and 100 µL of 0.2% Triton X-100 were added to all iodine analyses. The sample was purged for 5 min with argon gas with a stir rate of 800 rev min⁻¹. The iodide was adsorbed onto the freshly formed hanging mercury drop electrode for 60 s followed by a 5 s quiescent period before initiating measurements as follows: 0-V deposition potential, 2-mV step potential, 20-mV wave amplitude, and 100-Hz frequency. The scanning potential was from -106 to -700 mV with the iodine peak potential at about -300 mV. The same procedure for total iodine was used with the inclusion of 50 μ L 0.1 M ascorbic acid, 50 μ L 6 M HCl, and 50 μ L 6 M NH₄OH. The concentration of iodate was determined by the difference between the concentration of total iodine and iodide concentrations. The detection limit for both the iodide and total iodine

was approximately 1 nM and the analytical precision was 5% (relative standard deviaiton).

Direct analyses of dissolved manganese (Mn(II)) and dissolved iron (Fe(II) or Fe(III)) were conducted utilizing standard procedures on a graphite furnace atomic adsorption spectrometer (Perkin Elmer 4100ZL). Manganese samples were diluted by a factor of five and the iron samples by ten-fold with 0.5 N trace-metal grade nitric acid prior to analysis to reduce the salt matrix effects. The detection limits for dissolved Mn and Fe samples were on the order of 0.04 μ M and 5 nM, respectively.

Results and Discussion

Physical Forcings

1996 Event

The oxygen fluctuation events in Azevedo Pond correlate to changing physical conditions such as irradiance intensity, air temperature, and tides. An example of the progression of Azevedo Pond into a typical hyperventilation event (Fig. 4) illustrates these relations. Figure 4a presents irradiance, air temperature, and wind speed collected by a nearby weather station from September 30 through October 5, 1996. Figure 4b shows the response of the depth of Azevedo Pond to the tidal cycle at Moss Landing, California, and Fig. 4c presents the DO concentrations and water temperatures recorded in Azevedo Pond for the same time period. Figure 4 has been divided into two physical regimes: a low irradiance, high tidal fluctuation period (LIHT period) and a high irradiance, low tidal fluctuation period (HILT period). During the LIHT period (October 30–November 1), coastal fog intrusions greatly reduced irradiance (Fig. 4a) and the DO concentrations within Azevedo Pond barely reached atmospheric equilibrium during the day (Fig. 4c). In addition, the extreme tidal cycle generated large depth fluctuations, increased mixing, and decreased water stagnation (Fig. 4b). A few days later, during the HILT period (November 3-5), increased offshore winds prevented fog migration into coastal areas, resulting in a substantial increase in irradiance intensity and daily maximum water temperatures. The lower magnitudes of the HILT daily tidal cycle decreased mixing (Fig. 4b), and did not alter the pond depth during the early morning hours. Dissolved oxygen data from Azevedo Pond during the HILT period displays a daily maximum of over 500 µM (approximately 240% saturation), followed by a 9.5 h suboxic event, and returning to supersaturated levels the following day (Fig. 4c). This diel hyperventilation can continue for a number of days, depending upon the duration of clear weather and low early morning spring tides (< 1.2 m) which do not breach the



Fig. 4. Time series of Azevedo Pond DO and water temperature (c) values as the system progresses into hyperventilation in October 1996. Also provided for the same time period, is the depth of Azevedo Pond as it responds to the Monterey Bay tidal cycle (b) and irradiance, air temperature, and wind speed data from a nearby weather station (a). LIHT (low irradiance high tidal fluctuations) periods display physical conditions that are not ideal for extreme DO fluctuations, in contrast to HILT (high irradiance, low tidal fluctuations).

mouth of culvert. This particular event persisted for a week, until October 10, 1996 (data not shown), after which the tidal cycle prevented sustained water stagnation in the morning hours.

The degree and timing of tidal flushing within Azevedo Pond has a profound effect on the structure of the DO curves. Inflow of water from the main channel of Elkhorn Slough contains DO levels near atmospheric equilibrium and produces a DO flushing peak signature of close to 220 μ M (approximately 100% saturation). During the LIHT periods, the flushing DO signature is the dominant peak during the day because of the light limitations on the photosynthetic organisms. During the HILT period, however, the peak signature due to flushing is only a small shoulder on the primary DO peak (Fig. 4c).

The hyperventilation events in Azevedo Pond



Fig. 5. Time series of DO and water temperature from Azevedo Pond as the system progress to hyperventilation in July 1998 (b). Figure 5a is the depth of Azevedo Pond as it responds to the Monterey Bay tidal cycle for the same time period.

are driven by elevated rates of PS and R. Photosynthetic rates in these nutrient-rich waters increase asymptotically with water temperature and irradiance (Wetzel 1975), and water temperature and biomass drive R rates. In nutrient enriched waters, the physical conditions become the main variables influencing biometabolic rates. A detailed analysis of the diel oxygen dynamics of the Waquiot Bay by D'Avanzo and Kremer (1994) suggest a correlation between the occurrence of major fish kills with unusually calm cloudy weather that followed peak summertime temperatures. The extreme photosynthetic activity of the previous days was greatly diminished by the cloud cover, but respiration rates remained elevated due to the excess biomass produced within the system. Respiration would rapidly deplete the O₂ reservoir of the water column, creating anoxic events within Waquiot Bay that were toxic to fish and many invertebrates.

July 1998

Diel sampling was conducted during the summer and fall of 1998 to evaluate the nutrient dynamics and redox chemistry associated with the extreme DO fluctuations within Azevedo Pond. This summertime series strongly illustrates the role of stagnation on the timing of hyperventilation events. Figure 5 shows the early morning tides on the 4 d prior to July 17 exceeding the height of the culvert (Fig. 5a), introducing oxygenated water and turbulence into Azevedo Pond and preventing (or in one case alleviating) the suboxic conditions (Fig. 5b). An examination of the tidal height data shows that when both high tides breach the culvert and flush the pond with oxygenated waters from the main channel, the DO is kept from undergoing extreme fluctuations (Fig. 5b). When the magnitude of a high tide diminishes so that it no longer breaches the culvert, the pond depth remains relatively constant, as shown by the depth data from Azevedo Pond (Fig. 5a). As the daily solo flushing event shifts to the later afternoon/early evening, it allows the midday peak in DO to reach levels well above saturation, followed by suboxic conditions during the pre-dawn hours when no flushing occurs. The influence of main channel flushing during a hyperventilation event can be seen as a secondary, early evening shoulder on the DO curve (Fig. 5b).

Yearly weather patterns have profound effects on these types of dynamic and productive coastal systems. The most influential physical conditions driving the biological metabolism of Azevedo Pond appear to be light intensity, water temperature, and tidal mixing. These diel hyperventilation or extreme DO fluctuation events do not occur in Azevedo Pond during the cooler months of November through April, during times of decreased light intensity and air temperatures, or during times of strong diurnal tidal mixing. Low light periods caused by heavy fog conditions in the late spring and early summer seem to prevent Azevedo Pond from experiencing extreme oxygen fluctuation events, even when the tidal cycles appear to be ideal. The 1998 diel-sampling event followed an unseasonably wet winter and cool spring brought on by El Niño conditions. In comparison to the previous years of DO data from Azevedo Pond, 1998 experienced only two hyperventilation events where the nocturnal suboxic conditions persisted for longer than 3 h. In contrast, the previous two warmer seasons each experienced four to five events, where oxygen fluctuations were over 650 μ M (approximately 300% saturation) and suboxic conditions persisted for as long as 11 h.

BIOGEOCHEMICAL CYCLING

Physical Parameters

A thermocline is created within Azevedo Pond during warm, sunny days. Thermal stratification within the pond is apparent (Fig. 6) approximately 45 min prior to the late afternoon flushing event, following which the thermal stratification is destroyed. The in situ sensor is located approximately 0.5 m above the bottom of the pond, and was poised at the top of the thermocline at this time.

A high tide of 1.68 m on July 17 breached the



Fig. 6. Vertical profile of temperature taken at 1500, July 17, 1998. Inflow of water from the main channel began at 1545.

culvert connecting Azevedo Pond at 1545, mixing the water column and eliminating thermal stratification. The inflow continued for nearly 3.5 h and resulted in a corresponding depth change from 0.76 to 1.12 m (Fig. 5a). During this flushing event the volume of water within Azevedo Pond more than doubled, introducing water from the main channel with relatively low nutrient concentrations and DO levels close to atmospheric equilibrium.

Biological Parameters

Dissolved oxygen reached a maximum value of 346 μ M (185% saturation) at approximately 1400 on July 17 (Fig. 7), and then began to drop, presumably due to the coupling of decreased photosynthetic oxygen production and high respiration rates. Dissolved oxygen values decreased to approximately 200 μ M (near saturation) in response to the mid-afternoon flushing event. The DO concentrations further declined to non-detectable levels and suboxic conditions were sustained for over 3.5 h (approximately 0320 to 0700) on the morning of July 18. Early in the sampling, pH values rose from 7.33 to 7.97 in less than 6 h (Fig. 7). This rapid pH change is in response to the intense photo synthetic CO_2 fixation and changes in the carbonate chemistry within the pond. At night, respiration reverses the process, subsequently decreasing pH. Seasonal increases in pH values have been correlated to dinoflagellate blooms in coastal environments (Hinga 1992), and this data illustrates the same pH trend on a daily cycle where the pho-



Fig. 7. DO and pH values at 15 min sampling resolution in Azevedo Pond during the diel sampling study of July 17 and July 18, 1998 (data provided by ESNERR).

tosynthetic organisms are a combination of phytoplankton, benthic algae, and macrophytes.

The two potential biolimiting macronutrients for cell growth (N and P) also exhibit marked diel cycling (Fig. 8). Ammonium exhibits maximum concentrations of over 7 μ M from approximately 0700 to 1400 on July 17 and again from 0430 to the end of the sampling period (0900) on July 18 (Fig. 8a). Phosphate displays a similar diel curve as ammonium, with maximum concentrations close to 5 μ M (Fig. 8b). The macronutrient minimums are associated with the flushing event at 1545, when the high tide on July 17 breached the culvert of Azevedo Pond, introducing over 10,000 m³ of nutrient-depleted water (Fig. 8a,b). The nutrients within Azevedo Pond have a fixed N:P ratio of approximately 2.8, a value far below the Redfield ratio required for photosynthetic growth, illustrating a large excess of P in this system.

Ammonium is the dominant N species in the system during this sampling period, and in fact historical data from a nearby site in 1971 (Smith 1973) and other 1998 data (Beck and Bruland unpublished data) also show ammonium concentrations exceeding those of nitrate and nitrite during the summer months. The variability of inorganic macronutrient concentrations in Azevedo Pond is the result of biological activity, coupled with the introduction of relatively nutrient-depleted water into the system during high tidal events. The variability is due to fluctuating uptake and assimilation



Fig. 8. (a) Time series of DO and ammonium, nitrate and nitrite in Azevedo Pond during the diel sampling study of July 17 and July 18, 1998. (b) Time series of DO and phosphate in Azevedo Pond during the diel sampling study of July 17 and July 18, 1998. A high tidal flushing event occurred at 1545, introducing nutrient deplete water with oxygen concentrations near atmospheric equilibrium.

of reactive inorganic substances during the hours of net primary production and regeneration of dissolved nutrients back into the water column during the times that respiration is dominant.

Nitrate and nitrite concentrations within the water column are at low levels ($\leq 2 \mu M$) (Fig. 8a). Nitrite levels slightly exceed NO₃⁻ during the morning and early afternoon on July 17. Shortly after tidal flushing, nitrate values are higher than nitrite and show a steady decrease throughout the night, possibly due to denitrification during suboxic periods. This data suggests that the flushing events and the sediments may be contributing to the flux of these species.

Redox Species

We investigated a sequence of redox-sensitive elements to examine changes in the chemistry associated with the sustained periods of suboxia in Azevedo Pond. Aerobic organisms (both eukaryotes and prokaryotes) remineralize organic matter under oxic conditions. Following the near depletion of DO, facultative anaerobic bacteria are able to utilize other energy yielding reduction reactions to continue the oxidation of photosynthetically derived organic material. Although denitrification and dissimilatory nitrate reduction have been found to be a significant source of electron acceptors for anaerobic bacteria (Fiaderiro and Strickland 1968; Cline and Richards 1972; Froelich et al. 1979) (Fig. 3), the low nitrate levels detected suggest that the reservoir of nitrate was insufficient to fuel metabolic activity within Azevedo Pond. The response to suboxic conditions of the compounds investigated here (iodate ((IO₃-) I(V)): iodide $((I^{-}) I(-I))$, Mn(IV) oxides: dissolved Mn²⁺, and Fe(III) oxides: dissolved Fe^{2+}) can be detected by marked increases in concentrations of the associated reduced species within the water column. Photosynthetic activity in the morning results in a net increase in DO levels and $p\epsilon$ of the water column, making the reoxidation of the reduced species thermodynamically favorable.

Iodine. The IO_{s}^{-} (I(+V))/I⁻(I(-I)) redox couple has been shown to be a powerful indicator of suboxic conditions for two main reasons. First, the high-energy yield associated with the transfer of the 6 electrons predicts that the conversion of IO_{3}^{-} to I⁻ will occur shortly following the onset of suboxic conditions, and second, the concentration fluctuations of the redox pairs are relatively conservative. This is due to negligible biological uptake, minimal particle scavenging (both oxidized and reduced forms are dissolved anions), and no significant intermediate species. Essentially all of the IO_{3}^{-} concentrations reduced will appear as I⁻ (Liss et al. 1973; Rue et al. 1997).

In Azevedo Pond, the total iodine concentration remains relatively constant at approximately 0.7μ M. The complete reduction of IO_3^- to I⁻ appears to occur within 3 h of the onset of suboxic conditions, illustrating the rapid response of this redox couple to the onset of suboxic conditions (Fig. 9a). The oxygen levels fall below 10 μ M at 0230, which results in a rapid decrease in IO_3^- and a corresponding increase in I⁻. The reduction rate of the iodine species was calculated to be on the order of 0.05 μ M h⁻¹. The initial response of the



Fig. 9. Time series of the iodate/iodide redox couple (a), dissolved Mn concentrations (b), and dissolved Fe concentrations (c) in Azevedo Pond during the diel sampling study of July 17 and July 18, 1998.

 IO_3^{-}/I^{-} couple to the oxygen depletion appears to take place at least 0.5 h prior to the initiation of Mn oxide reduction, consistent with the progression of pe and the associated elements (Fig. 3).

The oxidation of I⁻ to IO₃⁻ during the subse-

quent oxygenated period was markedly slower than the reduction of IO_3^- to I⁻ during the suboxic event. In the morning hours of July 17, 99% of iodine species are in the reduced form (I⁻), indicating the presence of suboxic conditions. The iodate concentrations show a small steady increase during the morning hours following the increasing DO levels, with the iodate fraction increasing from 1% to approximately 15% of the total iodine. The afternoon flushing event essentially equalizes the IO_{3}^{-}/I^{-} concentrations and they remain relatively balanced for over 9 h. The failure of the water column to oxidize nearly 0.3 µM of iodide during supersaturated oxygen conditions suggests that the oxidation kinetics were not fast enough to convert all of the I⁻ back to IO₃⁻ prior to the next suboxic event hours later. The oxidation rate limitation is further supported by the data collected towards the end of the sampling study on July 18, where the IO_3^- concentrations are still low, but the DO levels have reached 100 µM. These findings support previous research conducted in a reducing fjord (Emerson et al. 1979), which suggested that redox couples (including IO_3^-/I^-) in the anoxic bottom waters attained thermodynamic equilibrium, but that the relatively slow oxidation kinetics prevented the overlying oxygenated waters from reaching a steady state. These data suggest that the IO_3^-/I^- redox couple can be a strong indicator of decreases in p ϵ , but the ability of IO₃⁻/I⁻ to accurately indicate the timing of water column reoxidation on diel time scales is limited by the slow oxidation kinetics of iodide.

Manganese and Iron. Manganese and iron are micronutrients, as well as elements whose chemical speciation in natural waters is controlled by redox transitions between dissolved reduced forms and oxidized particulate forms. In oxygenated aquatic systems, manganese and iron exist primarily as precipitates (Mn(IV) and Fe(III) oxides), and at low $p\epsilon$ (suboxic conditions) can be reduced to dissolved Mn(II) and Fe(II).

The diel dissolved Mn concentrations during the July sampling study appear to respond to the oxygen concentrations within the pond (Fig. 9b), with maximum values corresponding to times of non-detectable DO levels. Prior to the tidal flushing of relatively Mn depleted water (1.13 μ M), the dissolved Mn removal rate in Azevedo Pond was approximately 1.0 μ M h⁻¹, resulting in a 5 μ M decrease in dissolved Mn. Dissolved Mn concentrations began to increase significantly when DO concentrations had been sustained below detection limits for nearly 1 h. The rate of dissolved Mn increase ranged from 0.5 to 0.7 μ M h⁻¹ during suboxic conditions.

Fe reduction is thermodynamically less favorable

than either iodate or Mn(IV) reduction reactions (Fig. 3), and previous investigations in oxygen minimum zones suggest that anoxic conditions may be necessary for the reductive dissolution of particulate iron (Landing and Bruland 1987; Lewis and Landing 1991; Rue et al. 1997). In contrast to other observations, Fig. 9c illustrates a 100 nM variation in dissolved Fe concentration in response to the changing oxidation/reduction potential of Azevedo Pond. The magnitude of dissolved Fe cycling was 40-fold less than that of dissolved Mn. In contrast to dissolved Mn, times of essentially complete removal of dissolved Fe from the water column corresponded to DO values above saturation (with the exception of the initiation of the flushing event). Dissolved Fe concentrations displayed a marked increase in response to the suboxic conditions until photosynthetic activity began to reintroduce DO into the water column the following morning.

In order for the water column to be in a truly anoxic state, the microbial community must begin to utilize SO_4^{2-} as a primary electron acceptor to oxidize organic matter. None of the samples collected during the suboxic event appeared to contain the reduced sulfide species (H₂S, HS⁻, or S²⁻). The lack of any distinct rotten egg odor (from H₂S) within the water samples collected leads us to believe that Azevedo Pond may have remained a suboxic water column during this particular sampling study.

The marked increase in dissolved Mn and Fe concentrations during the suboxic event may be explained by two possible mechanisms; reduction of Mn and Fe oxides associated with particulate organic carbon (POC) in the water column and surficial sediments (Johnson et al. 1992) and/or the diffusion of these dissolved ions from the underlying porewaters (Hunt and Kelly 1988). Figure 10 presents a theoretical illustration of the diel migration of the oxic/ suboxic boundary within the water column in Azevedo Pond. During times of non-detectable levels of oxygen, there would be no chemical barrier between the sediments and the water column, resulting in increased dissolved flux of reduced species from the sediments upward. As primary productivity increases oxygen concentrations, the oxic/suboxic boundary is suppressed to some depth in the water column, or even into the surface sediments. The positioning of the oxic/suboxic boundary at the sediment/water interface has been shown to suppress simple diffusion of dissolved species from the deeper, truly anoxic sediments into the overlying water column (Epping et al. 1998). We are unable to decipher the relative contribution of porewater diffusion and water column/surface sediment reduction on the marked increases of dissolved Mn and Fe measured



Fig. 10. A schematic illustrating the migration of the oxic/ suboxic boundary within Azevedo Pond on a diel time scale. When respiration dominates the oxygen concentrations in the early morning, the oxic/suboxic boundary is essentially eliminated. During these times, there may be an increased diffusive flux of dissolved ions from the sediments into the overlying water column. As photosynthetic rates increase during the daylight hours, oxygen production in the surface waters suppresses the oxic/suboxic boundary toward the sediments, potentially decreasing diffusion of dissolved compounds from the underlying pore waters.

in the water column. If we assume a diffusional coefficient of 1.5×10^{-6} cm² s⁻¹ (Bender 1971) for dissolved Mn and Fe, we can estimate the characteristic time required for the upward diffusion of dissolved trace metals over 1 cm of sediment to be on the order of 10^2 d. On diel time scales, the strict diffusional contribution of the increased concentrations of dissolved trace metals is limited to the upper few millimeters of the sediments, but the role of advective processes may provide an additional transport mechanism of dissolved trace metals from the porewaters into the overlying water column.

One of the most interesting geochemical observations to emerge from this study is the relatively rapid rate of dissolved Mn removal measured during the daytime oxygenated conditions within Azevedo Pond. Mn(II) is thermodynamically unstable in the presence of O_2 , but oxidation rates are considered to be relatively slow at the pH of most natural waters (Emerson et al. 1979; Stumm and Morgan 1996). Previous investigations have determined that Mn(II) oxidation in seawater is predominately microbially mediated (Sunda and Hunstman 1987; Tebo 1991) and as a result can be much faster. From a study in the coastal waters of the Bahamas, Sunda and Huntsman (1990) concluded that Mn-oxidizing bacteria are photoinhibited and oxidation rates in the surface photic zone are greatly reduced during the daylight hours. These high dissolved Mn removal rates observed in this study suggest that a different process may be occurring in wetland environments. Characterizing the mechanisms controlling the marked

degree of Mn cycling was beyond the scope of this project, but observations suggest that additional research on dissolved Mn removal processes occurring within shallow estuarine systems may be justified.

Conclusions

Shallow estuarine and wetland systems can be extremely dynamic, and any attempts to monitor the health of these environments need to assess the diel variations inherent in such ecosystems. As the data herein illustrate, extreme diel variations in dissolved oxygen, pH, temperature, nutrients, and redox-sensitive trace elements can exist in productive aquatic environments. Temporally variable water quality monitoring schedules will provide a more comprehensive data set when assessing the health of such systems. Using Azevedo Pond as an example, if water samples were collected at 0700 on a weekly basis, the data would suggest that the subject system be characterized as a hypoxic environment with elevated concentrations of reduced manganese and iron. If weekly water samples were collected at 1400, the data would suggest that Azevedo Pond is supersaturated with respect to oxygen, with relatively low dissolved Mn and Fe concentrations.

Future research of oxidation/reduction processes within estuarine ecosystems should focus on the mechanisms controlling iodate/iodide and Mn redox reactions. Are these processes microbially mediated, or are microbes gaining energy from these reactions as they proceed in response to the $p\epsilon$ of the water column? As we continue to gather knowledge about the cyclic nature of biogeochemistry, we should include shallow estuarine ecosystems in the array of natural environments investigated when pondering the mechanisms that control a significant portion of the aquatic inorganic chemical cycling.

Using an average DO increase of 500 µM from sunrise to midday during a typical hyperventilation event, a minimum estimate of net productivity in Azevedo Pond is 4.8 g C m⁻² d⁻¹ (the maximum productivity actually occurs during an 8-h period). This primary productivity value is consistent with other biomass estimates of wetland systems, including the value of 3.6 g C m^{-2} d⁻¹ proposed by Houghton and Skole (1990). The extreme oxygen fluctuations measured in Azevedo Pond would not be found in nutrient-limited systems. Nor would the hyperventilation events be detectable in relatively deep, well-mixed systems with a larger DO reservoir. The combination of anthropogenic nutrient enrichments and tidal flow alterations in shallow estuarine systems can severely impact the ability of wetland systems to function as productive, yet stable ecosystems.

The hyperventilation events occurring in Azev-

edo Pond are the result of a shallow water column, nutrient enrichments, and periodic decreases in water column mixing. These data bring to light the chemical and potential ecological implications associated with tidally-restricted and nutrient-enriched marsh areas. In the instance of Azevedo Pond, sustained periods of suboxia, coupled with elevated levels of various trace metals, may have detrimental effects on the local ecology. Species diversity must be adversely affected when resident organisms are forced to survive without DO for periods of up to 10 h. Management decisions concerning wetland restoration and mitigation need to consider the necessity of proper water circulation and decreased nutrient loading in order to maintain the functional health, and therefore the ecological diversity of these systems.

LITERATURE CITED

- ANSFIELD, H. C. AND G. BENOIT. 1997. Impacts of flow restrictions on salt marshes: An instance of acidification. *Environmental Science and Technology* 31:1650–1657.
- ATTWOOD, D. K., A. BRATKOVICH, M. GALLAGER, AND G. L. HITCH-COCK (EDS.). 1994. Papers from NOAA's Nutrient Enhanced Coastal Ocean Productivity Study. *Estuaries* 17:729–903.
- BENDER, M. L. 1971. Does upward diffusion supply the excess manganese in pelagic sediments? *Journal of Geophysical Research* 76:4214-4215.
- BRULAND, K. W., R. P. FRANKS, G. A. KNAUER, AND J. H. MARTIN. 1979. Sampling and analytical methods for the determination of copper, cadmium and nickel in seawater. *Analytica Chimica Acta* 105:233–245.
- CLINE, J. D. AND F. A. RICHARDS. 1972. Oxygen deficient conditions and nitrate reduction in the eastern tropical North Pacific. *Limnology and Oceanography* 17:885–900.
- CLOERN, J. E. 1996. Phytoplankton bloom dynamics in coastal ecosystems: A review with some general lessons from sustained investigation of San Francisco Bay, California. *Reviews* of *Geophysics* 34:127–168.
- COOPER, S. R. 1995. Chesapeake Bay watershed historical land use: Impact on water quality and diatom communities. *Ecological Applications* 5:703–723.
- D'AVANZO, C. AND J. N. KREMER. 1994. Diel oxygen dynamics and anoxic events in an eutrophic estuary of Waquoit Bay, Massachusetts. *Estuaries* 17:131-139.
- EMERSON, S., R. E. CRANSTON, AND P. S. LISS. 1979. Redox species in a reducing fjord; equilibrium and kinetic considerations. *Deep-Sea Research* 26:859–873.
- EPPING, E. H. G., V. SCHOEMANN, AND H. DE HEIJ. 1998. Manganese and iron oxidation during benthic oxygenic photosynthesis. *Estuarine, Coastal and Shelf Science* 47:753–767.
- EVANS, G. T. AND J. S. PARSLOW. 1985. A model of annual plankton cycles. Biological Oceanography 3:327–347.
- FIADERIRO, M. AND J. D. H. STRICKLAND. 1968. Nitrate reduction and the occurrence of a deep nitrite maximum in the ocean off the west coast of South America. *Journal of Marine Research* 26:187–207.
- FROELICH, P. N., G. P. KLINKHAMMER, M. L. BENDER, N. A. LUEDTKE, G. R. HEATH, D. CULLEN, P. DAUPHIN, D. HAMMOND, B. HARTMAN, AND V. MAYNARD. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochimica et Cosmochimica Acta* 43:1075–1090.
- HINGA, K. R. 1992. Co-occurrence of dinoflagellate blooms and high pH in marine enclosures, *Marine Ecological Progress Series* 86:181–187.

- HOUGHTON, R. A. AND D. L. SKOLE. 1990. Carbon, p. 393-408. In B. L. Turner, W. C. Clark, R. W. Kates, J. F. Richards, J. T. Mathew, and W. B. Meyer (eds.), The Earth as Transformed by Human Action. Cambridge University Press, Cambridge, Massachusetts.
- HUNT, C. D. AND J. R. KELLY. 1988. Manganese cycling in coastal regions: Response to eutrophication. *Estuarine, Coastal and Shelf Science* 26:527–558.
- JOHNSON, K. S., W. M. BERELSON, J. E. COALE, T. L. COLEY, V. A. ELROD, W. R. FAIRLY, H. D. IAMS, T. A. KILGORE, AND J. L. NOWICKI. 1992. Manganese flux from continental margin sediments in a transect through the oxygen minimum. *Science* 257:1242–1245.
- LANDING, W. M. AND K. W. BRULAND. 1987. The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. *Geochimica et Cosmochimica Acta* 51:29-43.
- LEWIS, B. L. AND W. M. LANDING. 1991. The biogeochemistry of manganese of iron in the Black Sea. *Deep-Sea Research* 38:S773– S804.
- LISS, P. S., F. R. HERRING, AND E. D. GOLDBERG. 1973. The iodide/iodate system in seawater as a possible measure of redox potential. *Nature Physical Science* 242:108–109.
- LUCIA, M. AND A. M. CAMPOS. 1997. New approach to evaluating dissolved iodine speciation in natural waters using cathodic stripping voltammetry and a storage study for preserving iodine species. *Marine Chemistry* 57:107–117.
- MARTIN, J. H. AND F. A. KNAUER. 1984. VERTEX: Manganese transport through oxygen minima. *Earth and Planetary Science Letters* 67:35–47.
- NIXON, S. W. 1995. Coastal marine eutrophication: A definition, social causes, and future concerns. *Ophelia* 41:199–219.
- OFFICER, C. B, R. B. BIGGS, J. L. TAFT, L. E. CRONIN, M. A. TYLER, AND W. R. BOYNTON. 1984. Chesapeake Bay anoxia: Origin, development, and significance. *Science* 223:22–27.
- PORTNOY, J. W. 1991. Summer oxygen depletion in a diked New England Estuary. *Estuaries* 14:122–129.
- RICHARDS, F. A. AND W. W. BROENKOW. 1971. Chemical changes, including nitrate reduction, in Darwin Bay, Galapagos Archipelago, over a 2-month period. *Limnology and Oceanography* 16: 758–765.
- RUE, E. L., G. J. SMITH, G. A. CUTTER, AND K. W. BRULAND. 1997. The response of trace element redox couples to suboxic conditions in the water column. *Deep-Sea Research Part I Oceano*graphic Research Papers 44:113–134.
- Sмтт́н, R. E. 1973. The hydrography of Elkhorn Slough a shallow California coastal embayment. Technical Publication 73-2, Annual Report, Part 2. Moss Landing Marine Laboratories, California.
- STUMM, W. AND J. J. MORGAN. 1996. Aquatic Chemistry; Chemical Equilibria and Rates in Nature Waters, 3rd edition. John Wiley & Sons, New York.
- SUNDA, W. G. AND S. A. HUNTSMAN. 1987. Microbial oxidation of manganese in a North Carolina estuary. *Limnology and Oceanography* 32:552–564.
- SUNDA, W. G. AND S. A. HUNTSMAN. 1990. Diel cycles in microbial manganese oxidation and manganese redox speciation coastal waters of the Bahama Islands. *Limnology and Oceanog*raphy 35:325–338.
- TAFF, J. L., E. O. HARTWIG, AND R. LOFTUS. 1980. Seasonal oxygen depletion in Chesapeake Bay. Estuaries 3:242–247.
- TEBO, B. M. 1991. Manganese (II) oxidation in the suboxic zone of the Black Sea. *Deep-Sea Research* 38:S883–S905.
 WELSH, B. L. AND F. C. ELLER. 1991. Mechanisms controlling
- WELSH, B. L. AND F. C. ELLER. 1991. Mechanisms controlling summertime oxygen depletion in western Long Island Sound. *Estuaries* 14:265–278.
- WETZEL, R. G. 1975. Limnology. W.B. Saunders Company, Philadelphia, Pennsylvania.

Received for consideration, May 11, 1999 Accepted for publication, October 7, 1999