Short-term and interannual variability of redox-sensitive chemical parameters in hypoxic/anoxic bottom waters of the Chesapeake Bay

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Abstract

A combination of CTD casts, discrete bottle sampling and *in situ* voltammetric microelectrode profiling was used to examine changing redox conditions in the water column at a single station south of the Bay Bridge in the upper Chesapeake Bay in late July/ early August, 2002–2005. Short-term (2–4 h) fluctuations in the oxic/suboxic/anoxic interface were documented using *in situ* voltammetric solid-state electrodes. Profiles of dissolved oxygen and sulfide revealed tidally-driven vertical fluctuations of several meters in the depth and thickness of the suboxic zone. Bottom water concentrations of sulfide, Mn^{2+} and Fe^{2+} also varied over the tidal cycle by approximately an order of magnitude. These data indicate that redox species concentrations at this site varied more due to physical processes than biogeochemical processes. Based on analysis of ADCP data, tidal currents at this station were strongly polarized, with the principal axis of tidal currents aligned with the mainstem channel. Together with the chemical data, the ADCP analysis suggests tidal flushing of anoxic bottom waters with suboxic water from north of the site. The present study is thus unique because while most previous studies have focused on processes across relatively stable redox interfaces, our data clearly demonstrate the influence of rapidly changing physical mixing processes on water column redox chemistry.

Also noted during the study were interannual differences in maximum bottom water concentrations of sulfide, Mn^{2+} and Fe^{2+}. In 2003, for example, heavy spring rains resulted in severe hypoxia/anoxia in June and early July. While reported storm-induced mixing in late July/early August 2003 partially alleviated the low-oxygen conditions, bottom water concentrations of sulfide, Mn^{2+} and Fe^{2+} were still much higher than in the previous year. The latter implies that the response time of the microbial community inhabiting the suboxic/anoxic bottom waters to changing redox conditions is slow compared to the time scale of episodic mixing events. Bottom water concentrations of the redox-sensitive chemical species should thus be useful as a tracer to infer prior hypoxic/ anoxic conditions not apparent from ambient oxygen levels at the time of sampling.
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1. Introduction

1.1. Background

The seasonal development of hypoxia/anoxia in the upper and middle regions of the Chesapeake Bay has been extensively documented. Low oxygen conditions in the bottom waters are produced and maintained during the summer months by salinity stratification of the water column (Officer et al., 1984; Boicourt, 1992) and microbial decomposition of organic matter in the water column and sediments (Jonas and Tuttle, 1990; Jonas, 1992, 1997; Kemp et al., 1992). Persistent low-oxygen conditions in the bottom waters generally occur from May–September with the most pronounced oxygen depletion in late July and August (Taft et al., 1980; Malone, 1991). The severity of bottom-water hypoxia/anoxia varies interannually with changes in the magnitudes of the spring freshet and nutrient inputs (Schubel and Pritchard, 1986; Malone et al., 1988; Harding et al., 1992; Smith et al., 1992; Hagy et al., 2004).

Superimposed on the general seasonal cycle of dissolved oxygen may be short-term variations dominated by advective mixing processes, which may include a strong tidally-driven semi-diurnal oscillation, lateral seiching, and/or episodic wind-forced pycnocline disruptions (e.g. storm mixing) (Itsweire and Phillips, 1987; Breitburg, 1990; Sanford et al., 1990; Luther et al., 2004). Sanford et al. (1990), for example, collected time series measurements of dissolved oxygen (DO) and salinity at several moorings along a cross-axial transect of the mid-Bay during the summer of 1987. The strongest observed response was that due to tidal forcing. Large changes in DO and salinity at semi-diurnal and diurnal frequencies (i.e. in phase with the surface tides) were attributed to vertical movement of the pycnocline, driven by surface-forced internal tides. Longer period (subtidal frequency) fluctuations in DO and salinity were correlated with wind-forcing.

1.2. The present study

In addition to changes in the vertical dissolved oxygen profile, the aforementioned physical mixing processes are expected to alter the vertical distributions of other redox-sensitive chemical constituents as well. The primary goal of the present study was to document vertical and temporal short-term (hours to days) variations in redox-sensitive chemical parameters across the oxic–anoxic interface in response to tidal forcing and other physical and biogeochemical processes. This study is in contrast to other east coast systems (e.g.

Narrangansett Bay and Long Island Sound), which exhibit episodic hypoxic events on monthly and near weekly time scales, respectively (Anderson and Taylor, 2001; Bergondo et al., 2005). These dynamic systems are also in contrast to relatively stable interfaces that experience less physical forcing, such as those found in the central regions of the Black Sea, which have been extensively studied (e.g., Konovalov et al., 2003, 2006), the Cariaco Trench (Scranton et al., 2001; Ho et al., 2004) and the Framvaren Fjord (Dyrssen, 1999). A combination of *in situ* voltammetric microelectrode profiling, CTD casts and discrete bottle sampling was used to examine changing redox conditions in the upper Chesapeake Bay in late July/early August, 2002–2005). The study documents short-term tidal fluctuations in the depth and thickness of the suboxic layer due to tidally-forced and episodic changes in the vertical distributions of dissolved oxygen, Mn^{2+}, Fe^{2+} and sulfide in the Chesapeake Bay water column. Because data were collected for four summer periods, interannual variations could also be assessed.

1.3. The study site

Ship-board and *in situ* measurements for chemical and physical parameters were collected from aboard the R/V Cape Henlopen at a single station (Fig. 1; Station 858; 38°58.8′ N; 76°22′ E) in the upper bay for one week periods in late July, 2002 (7/24–29) and early August, 2003 (8/2–7). To assess longer-term interannual differences in water column chemistry, the site was also re-occupied for several days in August 2004 and 2005. Station 858 is an ~25 m deep hole located just south of the Route 50 Bay Bridge. The hole is approximately 4.0 km long by 0.8 km wide. The site is bordered to the east by Kent Island and to the west by the main shipping channel. This region of the bay is one of the first areas to become strongly stratified in the spring, and low-oxygen conditions persist there well into the fall (Chesapeake Bay Program; http://www.chesapeakebay.net/wquality.htm). Although we chose to focus on the temporal changes at a single site, the bottom topography at this site is typical of the upper and mid-bay, with an approximate mid-channel depth of ~18 m and numerous deeper troughs to depths of some 25–30+ m (Bratton et al., 2003). During an October 2004 cruise, for example, bottom water samples collected from five holes in the upper to mid-bay region all displayed severe hypoxia (DO<2 mg/L; <~60 μM), despite the lateness of the season (Luther et al., unpublished data). The lowest DO concentrations were observed at Station 858, and the site appears to be typical of sub-pycnocline conditions of the upper bay.
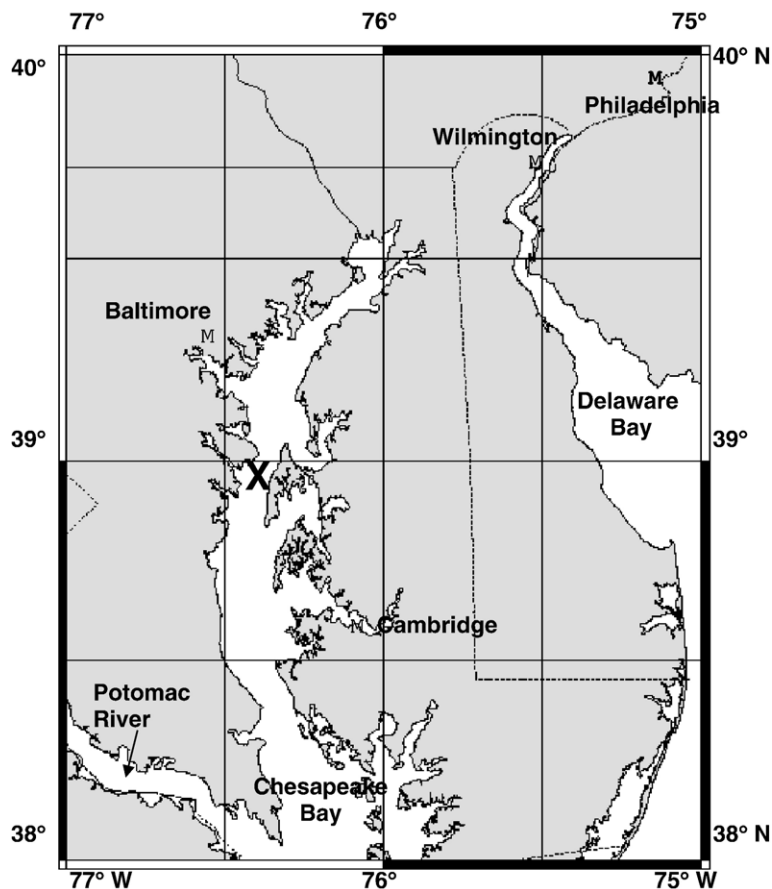
Fig. 1. Location of Station 858 on the Chesapeake Bay (X). The station is located just south of the Chesapeake Bay Bridge and east of the main channel, at 38°58.8′ N; 76°22′ E.

The first two years of this study (2002/2003) were a study in contrasts for the Bay. Whereas in 2002 the region was in the second year of drought conditions, 2003 was one of the wettest years on record. Drought conditions in 2001 and 2002 limited freshwater and nutrient inputs to the Bay, giving rise to some of the best water quality seen during the summer months for some time. Based on monitoring data from the Chesapeake Bay Program (http://www.chesapeakebay.net/wquality. htm), the spatial extent of hypoxia was not as great in 2002 as in 2003. Low oxygen conditions in 2002 continued to develop through July, before moderating in early August. In 2003, above average freshwater inputs in winter and spring combined with cooler than average bottom water temperatures to establish a particularly strong pycnocline. This condition persisted through June and early July. Together with high nutrient inputs, this in turn contributed to the development of an extensive body of low-oxygen water from north of the Chesapeake Bay Bridge to as far south as the York River.

These extreme low-oxygen conditions were partially alleviated in late July and August by a series of summer storms, disrupting the pycnocline and injecting oxygenated surface waters into the bottom layer of the Bay.

2. Methods

2.1. Sampling and ship-board analyses

In each year, the ship was anchored with stern and bow anchors to maintain positioning during sampling. This allowed the ship to serve as an observatory to document water column chemistry. Salinity and density were measured *in situ* using a rosette-mounted Seabird CTD. Samples for dissolved manganese and iron were collected using acid-cleaned 10-liter Go-Flo bottles (General Oceanics) or the ship's external-spring Niskin bottles (General Oceanics) on the ship's CTD-rosette system. Intercomparison of manganese and iron from simultaneously-collected samples showed no differences due to
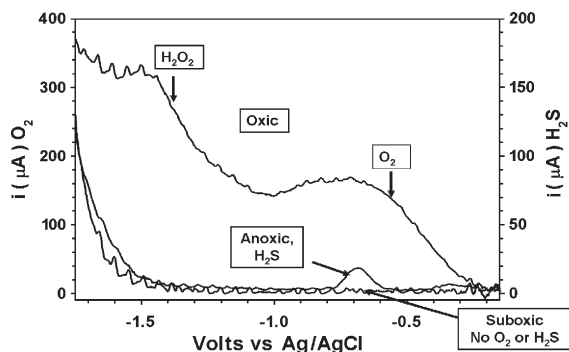
Fig. 2. Typical voltammograms obtained *in situ* using the DLK-Sub-III analyzer in oxygenated (surface), suboxic (mid-depth) and anoxic (bottom) waters.

bottle type (Lewis, unpublished data). To avoid oxidation artifacts, bottles were sub-sampled directly into acid-cleaned polyethylene syringes. Processing of subsamples was carried out in a shipboard clean van using trace-metal-clean protocol. Subsamples were immediately filtered through acid-cleaned 0.40 μm Nuclepore filters directly into 15 mL Falcon tubes. The latter were preloaded with the appropriate colorimetric reagents for each analyte. After the appropriate interval for color development, total dissolved manganese and iron(II) were determined colorimetrically using a Brinkmann dipping-probe colorimeter with a 5 cm pathlength. Total dissolved Mn was determined by the formaldoxime method (Brewer and Spencer, 1971) and dissolved Fe^{2+} by the ferrozine method (Stookey, 1970, as modified by Landing and Westerlund, 1988).

Dissolved oxygen concentrations were determined by (i) micro-Winkler titration on discrete bottle samples, (ii) a rosette-mounted amperometric sensor (ship's equipment), and (iii) *in situ* voltammetric measurements using Hg/Au microelectrodes (Brendel and Luther, 1995) interfaced to a DLK-SUB-III *in situ* electrochemical analyzer (Analytical Instrument Systems, Inc.; see Luther et al., 1999; Konovalov et al., 2003; Glazer et al., 2006a,b). The voltammetric system was also used for determination of sulfide in the water column.

2.2. Microelectrode/DLK system

The DLK-Sub-III system consisted of a pressure housing enclosing the voltammetry hardware linked to an internal IBM compatible computer. A Seabird Microcat CTD was included to allow deployment of the system as a stand-alone unit or mounted to the CTD-rosette unit of the R/V Cape Henlopen. The latter allowed for continuous comparisons to be made between the Microcat and the ship's CTD and for targeting of specific redox zones for

water sampling based on real-time voltammograms. Power was provided by an internal rechargeable 12 V D.C. battery. The internal computer communicated with a ship-board computer via a 300-m RS 232 cable and the system was controlled in real-time by a ship-board operator. A separate 1-meter cable was used to make connections between the pressure housing and the working, counter, and reference electrodes. This cable had four inputs for working electrodes, individually selectable by the operator via an internal multiplexer, one input for the counter electrode, one for the reference electrode, and one for grounding the reference electrode to insure signal integrity.

The working electrodes for *in situ* measurements were solid-state 100 μm diameter gold-mercury amalgam (Au/Hg) prepared in polyethyletherketone (PEEK™) tubing (Luther et al., 1999). The solid-state reference
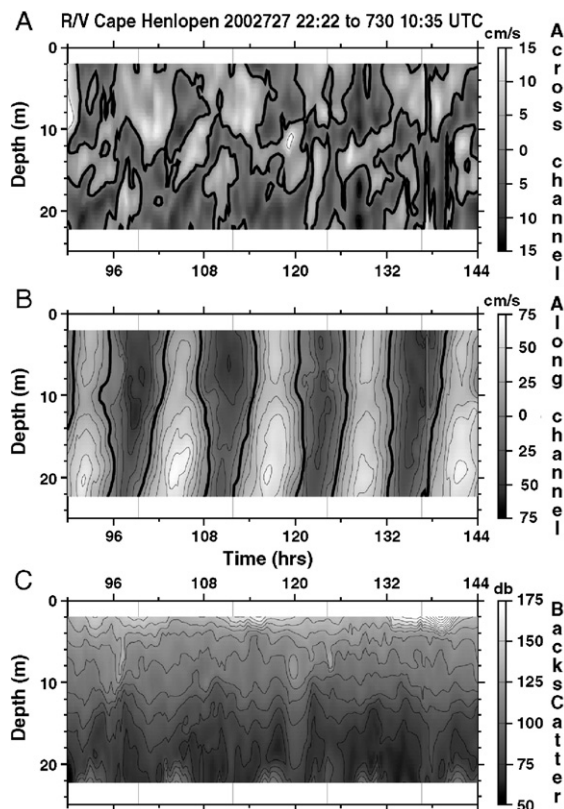

Fig. 3. Acoustic Doppler current profiler observations from July-27 22:22 UTC through July-30, 10:35 UTC 2002 for (A) across-channel velocity (−70 T; 70° counter-clockwise from true North), (B) along-channel velocity (+20 T), and (C) acoustic backscatter. Note the different (gray) scale for along-channel and across-channel velocities, the oscillatory nature of the along- but not the across-channel velocity, and the much enhanced near-bottom velocities coincident with peak flood tide velocities. The local bottom is at 25-m depth. Thick contours indicate zero velocities.

electrode was a 0.5 μm diameter Ag wire oxidized in 3 M KCl to make an AgCl coating. Typical voltammograms obtained with the *in situ* microelectrode/DLK system are given in Fig. 2 and document the oxic, suboxic and sulfidic zones of the water column. The voltage range was scanned from −0.1 V to −2.0 V at a scan rate of 1000 mVs^{-1}. Prior to field excursions, standard curves were produced for O_2, Mn, and sulfide, as described previously (Brendel and Luther, 1995; Rozan et al., 2000). Detection limits were ∼3 μM for O_2 and 30 nM for sulfide, with an analytical precision of 1–2%. Potentials for chemical species measured *in situ* and onboard ship with the same reference electrode were comparable, so no pressure effects were observed.

2.3. Current profiling

Vertical profiles of current vectors were measured using the 614-kHz vessel-mounted ADCP of the R/V Cape Henlopen (Joyce, 1989; Münchow, 2000). Velocity and backscattered acoustic energy (echo intensity) were estimated for each of four beams in vertical bins of 0.5-m from about 1-m below the surface to the bottom near 25-m depth at 0.5 Hz with four acoustic pings

averaged into ensembles. These measurements were rotated from relative ship- to absolute earth-referenced co-ordinates using Ashtech GPS for heading and a misalignment correction of 2.07°. The data were subsequently screened and averaged for 10 min averages using GPS data to remove the ship's motion vector.

3. Results

3.1. ADCP data

To assess the physical mixing in the sub-pycnocline layer, acoustic Doppler current profiler data have been analyzed for the period from 7/27–7/30, 2002. While this study was not directed toward a definitive evaluation of the current regime in this region of the Bay, the limited analysis presented here reveals features of the tidal mixing which aid in the interpretation of the water column chemistry. Fig. 3 shows observed currents at Station 858 as a function of time and depth in the across-channel (70° counter-clockwise from true North) and along-channel (20° clockwise from true North) directions. (Note that flood and ebb currents are indicated as positive and negative current velocities, respectively.
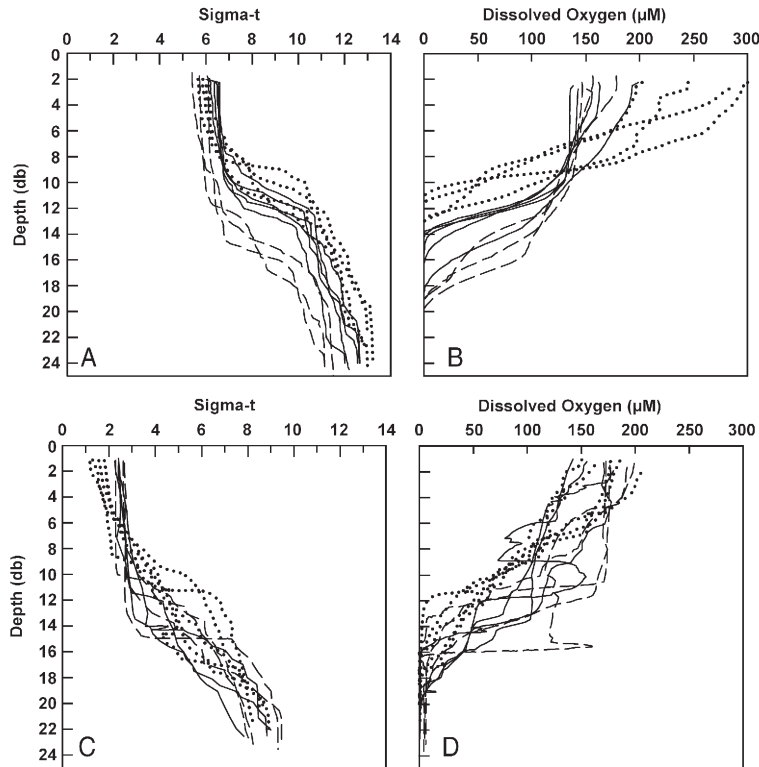

Fig. 4. Observed variability in the density and oxygen profiles (data from ship's CTD) over six day periods in late July 2002 (A,B) and early August 2003 (C,D). Data are shown for the first (dashed), third (solid) and sixth (dotted) days on station.

Note also the difference in the velocity scale for across-channel and along-channel flow components). Semi-diurnal current oscillations were most prominent in the along-channel direction and were most intense below the pycnocline (below ∼10–14 m; Fig. 3B). Maximum along-channel current velocities were on the order of 50–75 cm s^{-1}, while maximum across-channel velocities were less than 15 cm s^{-1}. Enhanced near-bottom currents coincide with backscatter signals of ∼100 db compared with a background of ∼60 db (Fig. 3C). The enhanced backscatter near the bottom during peak flood tide likely reflects increased turbidity caused by pulsed resuspension of surficial sediments by strong flood currents.

3.2. Stratification and water column chemistry

Fig. 4 shows the variability observed in the pycnocline depth and dissolved oxygen gradient over several days in late July, 2002 (7/24–29) and early August, 2003 (8/2–7). The pycnocline depth varied over several hours by as much as 2–5 m. This in turn caused rapid changes in the oxycline and in the thickness and depth of the suboxic layer (Fig. 5). At approximately mid-ebb tide (Fig. 5A), the profiles of oxygen and sulfide overlapped, with no suboxic zone present. Four hours later, at early flood tide
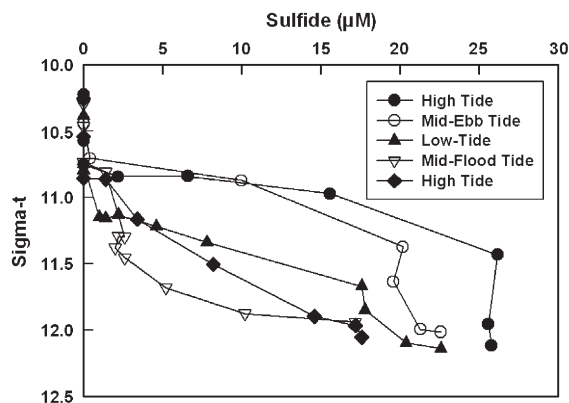
Fig. 6. Sulfide profiles measured *in situ* over a twelve hour period on July 28th, 2002. Data are plotted versus density (sigma-t) to factor out variations in the pycnocline depth.

(Fig. 5B), there was a clear separation of oxygen and sulfide, and a nearly 5 m thick suboxic layer.

Fig. 6 shows five vertical profiles of sulfide in the lower water column over a twelve hour period on July 28, 2002. (For direct comparison of the profiles, data are plotted versus density (sigma-t) rather than depth to factor out variations in the pycnocline depth). The highest bottom-water sulfide concentrations were observed at 0900, at
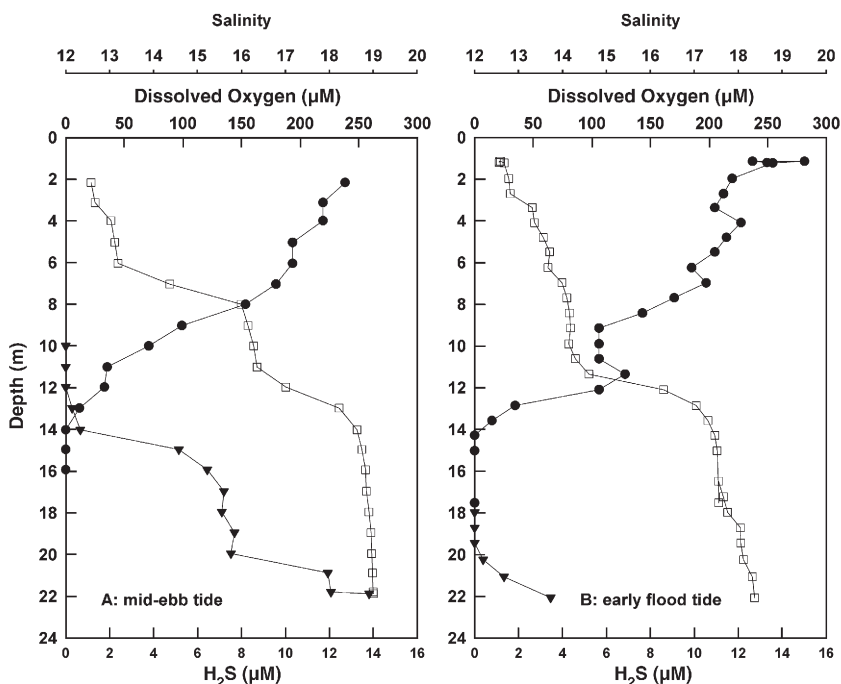
Fig. 5. Two vertical profiles collected approximately four hours apart on July 26th, 2002 using the DLK-Sub-III *in situ* system. Profile A, measured at 1500 UTC at approximately mid-ebb tide, shows very steep gradients for oxygen (circles) and sulfide (triangles), with no suboxic zone. Profile B, measured at early flood tide (1853 UTC), shows a clear separation between oxygen and sulfide, denoting the suboxic zone. Also shown is the salinity profile (open squares), approximating the structure of the pycnocline.

high tide. Over the next 10 h, sulfide levels dropped by over an order of magnitude, before beginning to increase again late in the day.

Fig. 7 shows the distributions with depth of total dissolved manganese and dissolved iron (II). Due to the limited number of depths sampled on each individual cast, the profiles shown are composites of all samples collected in each given year (2002–2005). Like sulfide, however, Mn^{2+} and Fe^{2+} concentrations regularly fluctuated by an order of magnitude on a time scale of hours. In July 2002, for example, subpycnocline concentrations of dissolved Mn^{2+} and Fe^{2+} in the deep waters

ranged from about 0.2 to nearly 7 µM for Mn^{2+} and from 0.2 to 1.4 µM for Fe over the tidal cycle.

Interannual differences in bottom water sulfide, Mn^{2+} and Fe^{2+} concentration were also observed. The more intense hypoxia/anoxia in early summer 2003 allowed the buildup of these species to higher levels than in 2002. Maximum dissolved manganese and iron concentrations in 2003 (Fig. 7B) were nearly double the 2002 values (Fig. 7A). Maximum sulfide concentrations in 2003 were >90 µM, more than three times the levels observed the previous year (data not shown). Dissolved Mn^{2+} and Fe^{2+} levels in 2004 and 2005 (Fig. 7C,D) were most similar to
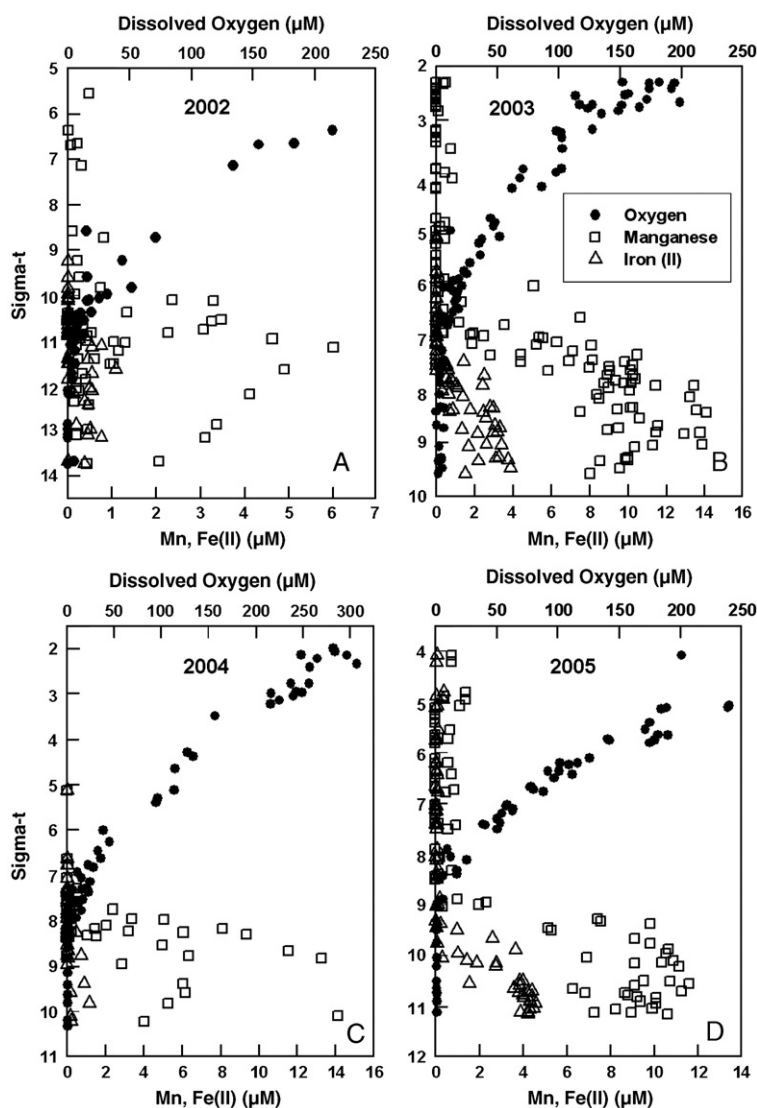

Fig. 7. Composite profiles of redox-sensitive chemical tracers (oxygen, total dissolved Mn and dissolved Fe(II)) for late July 2002, early August 2003 and mid-August 2004 and 2005. Data are plotted versus density to factor out variations in the pycnocline depth. (Note the difference in vertical scale between plots).

2002 and 2003, respectively (with the exception of one cast in 2004 when near-bottom Mn^{2+} concentrations reached 14 μM). Maximum bottom water sulfide concentrations were approximately 50 and >100 μM for 2004 and 2005, respectively, compared to about 30 and 90 μM in 2002 and 2003.

4. Discussion

4.1. Chesapeake Bay hypoxia

The general pattern of seasonal hypoxia in the bay begins with the spring influx of freshwater and nutrients to the upper and mid-Bay. The spring freshwater influx sets up salinity-driven density stratification of the water column, retarding vertical mixing rates and isolating the subpycnocline waters from physical reaeration processes and biological oxygen production. At the same time, the spring pulse of nutrients, in combination with increasing water temperatures and sunlight, fuels the spring phytoplankton bloom. Particulate organic matter produced in the bloom sinks below the pycnocline, where it is rapidly decomposed, consuming oxygen and decreasing subpycnocline DO concentrations to hypoxic/anoxic levels (Malone et al., 1986, 1988; Tuttle et al., 1987). As temperatures increase, sulfate reduction is also enhanced in the sediments, which reduces Fe(III) and Mn(III,IV) phases that release H_2S, Fe, Mn and phosphate to the overlying water column (Sholkovitz et al., 1992; Rozan et al., 2002). Oxygen depletion is most intense in the deep waters of the mainstem of the Bay, but may intrude into shallower waters along the flanks of the main channel and into the lower reaches of tributaries as well (Breitburg, 1990; Malone et al., 1986; Sanford et al., 1990). Hypoxic conditions generally continue into the mid- to late fall, when cooling temperatures and increased storm activity weaken the pycnocline and result in the injection of oxygen into the deep waters of the Bay. While this general model of seasonal change has been observed consistently for at least the past several decades, the details of finer-scale processes during the summer months are not as well understood. In this study, we focus predominantly on the effects of short-term tidal mixing on the depth and thickness of the suboxic zone and upon temporal variations in the vertical profiles of redox-sensitive chemical tracers (Mn^{2+}, Fe^{2+} and sulfide).

4.2. Tidal forcing

During this study, short-term variations in the pycnocline depth and water column chemistry at the sampling site were observed to be predominantly tidally-driven. Tidal forcing resulted in regular, semi-diurnal fluctuations in the pycnocline depth and in the depth and thickness of the suboxic layer (Figs. 4, 5). Despite strong vertical stratification, however, analysis of the ADCP data indicated significant horizontal transport due to tidal currents. The tidal currents were strongly polarized, with the principal axis of the currents aligned with the mainstem channel. ADCP data indicate that tidal currents constitute the major source of kinetic energy for both vertical mixing and horizontal advection in the study area.

The short-term variability in the oxygen and sulfide profiles (Fig. 5) illustrate the dynamic, tidally-driven variability of the water column chemistry at this location. At approximately mid-ebb tide, oxygen and sulfide gradients overlapped, with no suboxic zone present. Four hours later, at early flood tide, there was a clear separation of oxygen and sulfide, and a nearly 5 m thick suboxic layer.

During the 2002 sampling period, gradual warming of the surface layer by ~3 °C over several days resulted in a slow strengthening of water column stratification, superimposed upon the daily tidal fluctuations (Fig. 4). In response the pycnocline depth gradually shoaled over the six day sampling period (Fig. 4A), accompanied by a shoaling in the oxycline (Fig. 4B). The depth at which oxygen became undetectable shallowed by ~7 m, from 18–20 m on July 24th to 11–13 m on July 29th.

4.3. Horizontal mixing and sulfide

The ADCP data indicated strong along-channel horizontal advection of the subpycnocline water at Station 858 due to tidal currents. Tidally-driven horizontal advection is further evidenced by a regular temporal cycle in bottom-water sulfide concentrations (Fig. 6). The magnitude and cyclic nature of the sulfide variability and the evidence of strong tidal flushing indicate that physical mixing is the most likely dominant factor controlling the vertical distribution of sulfide (and of Mn^{2+} and Fe^{2+}) at this site. The highest bottom-water sulfide concentrations were observed at 0900, at high tide. Over the next 10 h, sulfide levels dropped by over an order of magnitude, before beginning to increase again late in the day. A similar pattern for sulfide was seen from the profiles presented in Fig. 5, collected on July 26, 2002. Bottom water dissolved Mn^{2+} and Fe^{2+} concentrations displayed comparable order of-magnitude changes over the tidal cycle (data not shown).

It appears from these data that the ebbing tide results in a partial flushing of the hole at Station 858 with

suboxic water. Given the strongly polarized tidal current flows, the probable source of low sulfide bottom water is horizontal advection from north of the site (where no holes are present), moving in the along-channel direction. Replenishment of bottom-water sulfide during the flood stage is also likely to be predominantly driven by horizontal advection, with smaller inputs from *in situ* microbial sulfate reduction in the water column and sediments. Some injection of porewater sulfide into the bottom waters may also occur as a result of sediment resuspension associated with the near-bottom peak flood tide current, as evidenced by the enhanced near-bottom backscatter recorded in the ADCP data.

An alternative hypothesis for the decrease in bottom water sulfide levels might be chemical oxidation of sulfide by reaction with oxygen and/or manganese or iron oxides. The magnitude and regularity of the changes in the sulfide concentration, coupled with the strong tidal flow indicated by the ADCP data, argue against this hypothesis. It is difficult to conceive of a cyclical chemical and/or biological mechanism that would operate on a timescale of 6–12 h, as previous work on samples held in the dark without added oxygen did not show sulfide oxidation (Luther et al., 1988). At the time these sulfide profiles were measured, no oxygen was observed below about 14 m depth, nor was the rate of oxygen diffusion from the overlying water column sufficient to explain the observed disappearance of sulfide. The latter can be demonstrated by a simple calculation based on the profiles shown in Fig. 5. Over an approximately 4 h period, the sulfide in the depth interval from 12–20 m dropped from nearly 8 μM to below the detection limit, equivalent to the removal of ~ 3.8 μmol-sulfide cm^{-2}. From the oxygen gradient in Fig. 5a, the estimated vertical diffusive flux of O_2 is approximately 5×10^{-7} μmol-O_2 cm^{-2} s^{-1}. Over four hours, vertical diffusion alone would thus supply only about 7.4×10^{-3} μmole/cm^{-2} of oxygen to the bottom layer, a factor of ~ 500 less than the observed sulfide depletion.

Another possibility could be the oxidation of sulfide by reaction with manganese and iron oxides. At this time of the year, however, Fe and Mn oxides will be at low concentrations, so oxidation by these oxidants is not expected (Anschutz et al., 1998). Furthermore, oxidation by the metal oxides would result in an inverse correlation between sulfide and Mn^{2+} and/or Fe^{2+}. Rather it was observed during this and previous studies (e.g. Luther et al., 1988) that maximum sulfide levels over a tidal cycle were coincident with high dissolved Mn^{2+} and Fe^{2+}.

The ADCP data indicated some bottom resuspension at the peak flood tidal current velocity. Because FeS and FeS_2 dominate in the sediments (Anschutz et al., 1998),

some near-bottom sulfide removal might thus be accounted for by FeS reacting with dissolved sulfide to produce FeS_2, but this is expected to be minimal compared to the role of physical forcing.

4.4. Comparison with other systems

As described in the previous sections, the Chesapeake Bay generally experiences summer long hypoxia/anoxia in the bottom waters. Strong tidal forcing, however, results in a regular oscillation of the pycnocline and the suboxic zone on a time scale of hours. In Narragansett Bay, on the other hand, Bergondo et al. (2005) observed monthly episodic sub-surface hypoxic events strongly influenced by tidal range. Summertime hypoxic events there coincided with periods of low tidal range (neap tides), while periods of high tidal range (spring tides) led to enhanced tidal mixing and the restoration of bottom water oxygen concentrations. Long Island Sound displays yet another pattern, in which the bottom waters oscillate in and out of hypoxia on an approximately weekly basis, with the timing and severity of an event strongly coupled to allochthonous input of ammonia after heavy rainfall (Anderson and Taylor, 2001). The Black Sea suboxic zone, which does not experience significant tidal forcing, changes on the order of days to months as a result of lateral (horizontal) intrusion of the Bosporus inflow (salty Mediterranean Sea waters) mixing with Cold Intermediate Layer (CIL) waters and/or seasonal changes in the rate of ventilation of CIL (Konovalov et al., 2003; Glazer et al., 2006b; Oguz et al., 2006).

In each case for these locations, while the general factors which combine to produce hypoxia are the same (e.g. elevated temperatures, water column stratification, nutrient supply and surface productivity), the specific causes, the timing and the duration of hypoxic events are unique. Thus the measures which may be taken to reduce the occurrence of seasonal hypoxia in coastal estuaries must be tailored to fit the system in question.

4.5. Redox-sensitive chemical parameter

Water column stratification and biological/chemical consumption of oxygen with depth in the Bay results in a vertical redox-cline inverse to the pycnocline. As dissolved oxygen levels decrease with depth, the redox potential decreases sharply from oxidizing conditions in the surface zone to reducing suboxic/anoxic conditions in near-bottom waters. In response, the microbial community composition shifts to take advantage of a characteristic sequence of reduction reactions coupled with organic matter oxidation: a) aerobic respiration in the

surface layer, b) denitrification and reduction of Mn- and Fe-oxyhydroxides in the suboxic zone, and c) sulfate reduction in the anoxic bottom waters and/or sediments. These processes can over time lead to a buildup of reduced chemical species (including dissolved Mn^{2+}, Fe^{2+} and sulfide) in the subpycnocline waters. Concentrations of these species are expected to vary in response to fluctuating oxygen concentrations and may thus provide a chemical signature of temporally and/or spatially varying oxygen conditions.

The range of Mn^{2+}, Fe^{2+}, and sulfide concentrations observed at this site are typical of those encountered in other seasonally or permanently anoxic basins, such as Saanich Inlet (Emerson et al., 1979), Framvaren Fjord (Jacobs and Emerson, 1982; Landing and Westerlund,

1988), the Black Sea (Lewis and Landing, 1991) and the Cariaco Trench (Scranton et al., 2001; Ho et al., 2004). While the concentration ranges are similar for each basin, the Chesapeake differs markedly from the others with respect to much greater horizontal advection and the rapidity of changes to water column chemistry demonstrated by the present study. The primary factors influencing the redox cycling of elements in these other basins are limited vertical advective–diffusive mixing, the rates of microbially-mediated redox reactions across relatively stable oxic/anoxic boundaries, upwelling events, and, for Saanich Inlet, a seasonal overturn of the water column. These processes generally operate on time scales of days to months to years (e.g. Ho et al., 2004; Glazer et al., 2006b). While these processes are also at
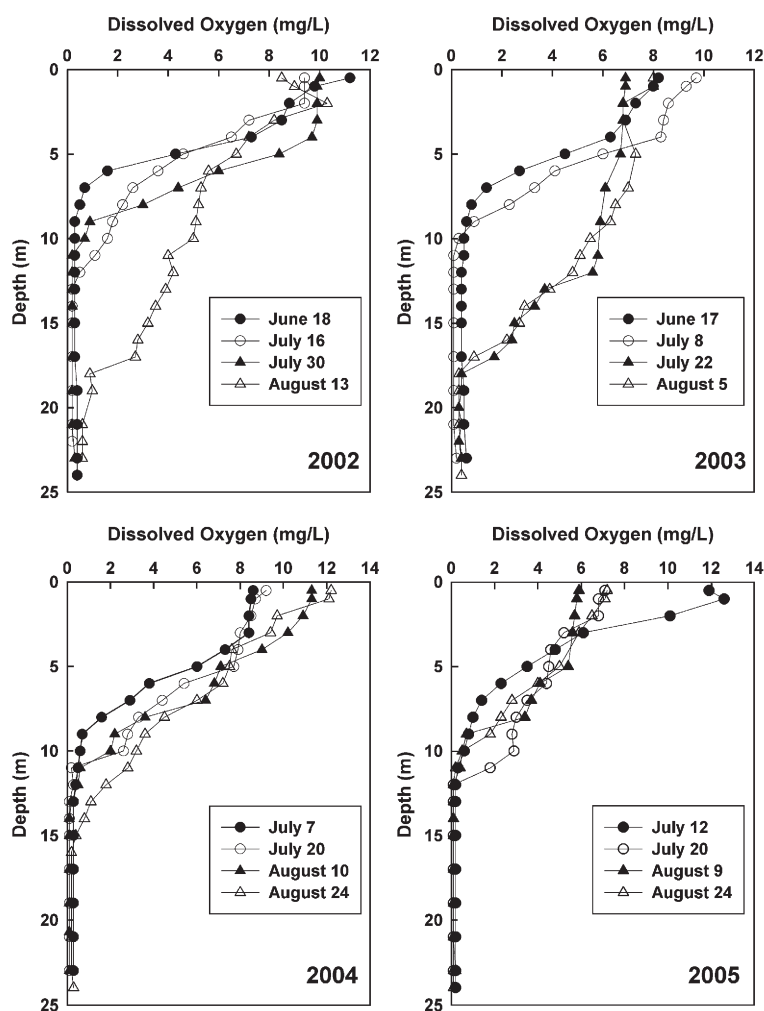

Fig. 8. Vertical distributions of dissolved oxygen at Chesapeake Bay Program mainstem monitoring station CB3.3C for several weeks during the summers of 2002–2005. (Chesapeake Bay Program. Chesapeake Bay Program Water Quality Database 1984–present. Accessed October 15th, 2005 from http://www.chesapeakebay.net/wquality.htm).

work in the Chesapeake, the addition of strong tidally-forced horizontal advection and vertical fluctuations of the depth and thickness of the suboxic zone resulted in the concentrations of dissolved constituents in the bottom waters regularly cycling from near zero to their maximum values on a time scale of hours.

The observed interannual changes indicate a linkage between ambient hypoxic/anoxic conditions and the concentrations of the redox-sensitive chemical parameters in the bottom waters. Although the details of this relationship cannot be ascertained from the present limited data set, comparison of the 2002 and 2003 data suggests that the Mn^{2+}, Fe^{2+}, and sulfide concentrations at any one time lag behind changes in ambient oxygen levels. In 2003, mid-summer storm-induced disruption of water column stratification caused a partial reoxygenation of the bottom waters prior to our arrival on station (Fig. 8B). In early August, however, the concentrations of redox-sensitive chemical tracers (dissolved Mn^{2+} and Fe^{2+}, sulfide) still reflected the intense low-oxygen conditions reported for June/early July 2003. This suggests that the response time for changes in the microbial processes involved in reduction and/or reoxidation of these elements lags behind that for storm-induced oxygen injection into the bottom waters. The chemical tracer data might thus be used to infer prior hypoxic/anoxic conditions not apparent from ambient oxygen levels at the time of sampling.

4.6. Episodic vertical mixing events

In addition to the strong tidal forcing just described, previous authors have reported that wind-forcing due to the passage of storms can also cause significant vertical mixing in the Bay, weakening stratification and injecting oxygenated surface water into the bottom waters (Goodrich et al., 1987; Sanford et al., 1990). Wind-induced destratification is most often seen during fall and winter, but partial destratification can and does occur during summer as well. Similarly, Luther et al. (2004) report vertical profiles of oxygen and sulfide in highly stratified dead-end canals of the Delaware Inland Bays, with anoxia below ~2 m to the bottom depth of about 6 m. On two occasions in 2001, storm events caused an overturn of the water column in the canals, mixing sulfide into the surface waters. Similar vertical disruption of the pycnocline is expected for the open Chesapeake Bay.

While no such storm events were observed during our times on station, the effects of storm-induced vertical mixing can be inferred from oxygen profiles shown in Fig. 8. (As shown in the present study (Fig. 4), the depth of the oxycline approximates that of the pycnocline).

Data for the figure were collected by the Chesapeake Bay Program (CBP) at mainstem Station CB3.3C, just north of the Bay Bridge and near our sampling site. Data are shown for several weeks each summer in 2002–2005, bracketing our sampling dates for each year at Station 858. With the exception of 2003, the water column appears to have been stable with respect to vertical mixing prior and during our time on station. In 2003, it appears that storm-induced mixing in late July and early August resulted in significant destratification of the water column and injection of oxygen to nearly 17 m (Fig. 8B). (A similar summer mixing event occurred in 2002, but not until after our sampling period (Fig. 8A)). In 2004 and 2005 (Fig. 8C,D), the water column remained stably stratified through July and August, with only small differences in the oxycline depth due to tidal variability.

5. Conclusions

The depth and thickness of the suboxic layer and vertical profiles of redox-sensitive chemical parameters (O_2, Mn^{2+}, Fe^{2+}, sulfide) were observed to vary on time scales ranging from hours to days, as predicted from the work of Sanford et al. (1990) and others. The dominant forcing factor was the tidally-driven semi-diurnal oscillation in the pycnocline depth, accompanied by a strong along-channel horizontal advective displacement of the bottom waters. Tidal flushing of the bottom waters was evidenced by order of magnitude changes in the concentrations of sulfide over the course of 2–4 h.

Although the present study was limited to one sampling site, it is expected that tidal forcing will exert a similar dominant influence on sub-pycnocline water column chemistry throughout the upper and mid-Bay. The bottom topography of these sections are similar, with numerous holes to as deep as 30+ m. There is no evidence in this or previous research to suggest that the station occupied in this study is unique. At the same time, we readily acknowledge the uncertainties involved in generalizing the present data to a discussion of spatial variability. The rapidly changing conditions observed in this study and the limitations of ship-board sampling argue strongly for the development of a comprehensive *in situ* monitoring system to adequately monitor Bay conditions. The monitoring program ideally should include instrumentation to measure as many redox species as possible.

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