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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.

Keywords: Hypoxia; Tidal mixing; Suboxic zone; Sulfide; Voltammetry; In situ measurements; Chesapeake Bay

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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. Narragansett 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.