The Roles of Anoxia, H_2S, and Storm Events in Fish Kills of Dead-end Canals of Delaware Inland Bays

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ABSTRACT: In 2001, the development of seasonal anoxia was studied in two waterways located at the head of Delaware's northern inland bay, Rehoboth Bay. Bald Eagle Creek is a northern tributary of the bay, which has tidal exchange with Torquay Canal (a dead-end canal) via a short channel with a 1.4 m sill. Mean low water depth in Torquay Canal is about 2 m, but dredging produced over a dozen depressions with a total water depth of 5.5 m. During the summer of 2000, four major fish kills were reported in Torquay Canal and Bald Eagle Creek with more than 2.5 million juvenile menhaden (*Brevoortia tyrannus*) killed. Low O_2 concentration was assumed to be the problem but production of toxic H_2S is more likely. From late spring 2001, we conducted in situ determination of temperature, salinity, pH, dissolved O_2, and H_2S in Torquay Canal and Bald Eagle Creek. During spring, water column stratification began in the depressions with warmer and less salty water observed in the upper layer, and cooler, saltier water below 2 m. O_2 was at saturation levels in the surface waters but was not detectable below 2 m by the end of May. The depressions were anoxic with H_2S accumulating to mM concentrations in June. A storm event prior to July 12 mixed these two layers with a subsequent loss of H_2S. The H_2S levels again increased in the deep water due to stratification and reached another maximum in late August. Another storm event occurred at this time resulting in no detectable O_2 and up to 400 μM H_2S in surface waters. H_2S appears to be the primary reason for fish kills in these tributaries. Aerators installed in Torquay Canal on June 21 had no significant effect on abating stratification and anoxic conditions beyond their immediate area.

Introduction

In nonrestricted shallow water areas, physical forcing (winds, storms, and tidal movement) allows O_2 to mix into deeper waters. In dead-end canals and creeks with restricted water movement and poor flushing rates, O_2 penetration is reduced (Maxted et al. 1997; Summers et al. 1997a,b; New York City Department of Environmental Protection [NYCDEP] 2001). Two other factors also enhance the depletion of O_2 content in deeper waters: nutrient overloading causes eutrophication with subsequent organic matter decomposition consuming O_2, and water column stratification inhibits deep water mixing with surface water particularly if the bottom topography is uneven with depressions deeper than the mean water depth. In coastal areas, excess nutrients enter shallow waters by many nonpoint and point sources. Fertilization of local farms and residential developments, sewage treatment plants as well as other sources of nutrients can result in eutrophication (Maxted et al. 1997; Price 1998). Once O_2 is fully consumed by the de-

composition of organic matter, sulfate is used as the terminal electron acceptor in sediments with the production of toxic H_2S, which can diffuse into overlying waters. Fish, shellfish, and benthic organisms cannot live in these waters, which have zero O_2 (anoxic) and high H_2S concentrations for any extended period of time (Theede 1973). Most studies concerning anoxia only document the loss or disappearance of O_2 and do not document the presence or extent of H_2S in the water column (Officer et al. 1984; Seliger et al. 1985; Maxted et al. 1997; Summers et al. 1997b) even though toxicity of H_2S to many organisms is well known (Theede 1973; Bagarinao and Lantin-Olgauer 1999). In fact, Summers et al. (1997b) noted that O_2 sensors can give false positives for unspecified reasons. In this study we document the significance of H_2S in dead-end canals.

The Black Sea (Konovalov and Murray 2001; Konovalov et al. 2003) and Framvaren Fjord (Skei 1988) are the most investigated permanent anoxic water basins (Dyrssen 1999). As the largest anoxic basin in the world, the Black Sea has a detectable H_2S concentration just below 100 m with high and almost constant concentration of H_2S between 500 and 2,000 m. The maximum concentration of H_2S approaches 425 μM (Luther et al. 1991; Konovalov

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and Murray 2001). In the Framvaren Fjord, the oxic-anoxic interface occurs from 18 to 20 m in a 183-m basin. The concentration of H_2S in the bottom waters is about 7 mM, the highest in an open anoxic basin because of its surface to volume ratio (Skei 1988; Dyrssen 1999).

In addition to permanent anoxic basins, seasonal anoxia areas have developed in coastal areas and have increased in extent with increased nutrient inputs. Seasonal anoxia in the Chesapeake Bay has been demonstrated since the 1930s (Officer et al. 1984). In recent years, O_2 has become depleted below 10 m in the central northern channel in the summer. The H_2S concentration reaches up to 60 μM (Luther et al. 1988). In some unusual years, the oxic-anoxic interface can rise to 5 m (Gavis and Grant 1986; Adelson et al. 2001). The large sulfidic water body found in the northern Chesapeake Bay transports H_2S via tidal motion to the bottom of tributaries and constitutes a threat to benthic organisms (Seliger et al. 1985) resulting in reduced commercial benefit to the fish and shellfish industries (Officer et al. 1984).

We report on the seasonal anoxia that develops in a tributary and a dead-end canal located in the shallow inland bay system of Delaware. Torquay Canal and Bald Eagle Creek are at the northern end of Rehoboth Bay, one of the three Delaware Inland Bays (Fig. 1). The normal water depth of this area is about 2 m at mean low tide. Torquay Canal is a man-made, dead-end canal that connects with Bald Eagle Creek, with a sill that has a water depth of only 1.4 m. Subaqueous sediments from these sites were dredged and used as fill material in the wetlands to create housing developments and a golf course in the 1960s (Hughes personal communication). This created over a dozen depressions at the bottom of Torquay Canal and Bald Eagle Creek with a maximum water depth of 5.5 m. The surface area and volume of these depressions are >55,000 m^2 and >170,000 m^3, respectively. These depressions become stratified, and seasonal anoxic conditions develop because of nutrient loadings that cause high primary productivity including harmful algal blooms. In summer of 2000, four major fish kills were reported in Torquay Canal and Bald Eagle Creek with the highest mortality occurring in Torquay Canal. More than 2.5 million juvenile menhaden (*Brevoortia tyrannus*) were killed, presumably due to low O_2 but more likely due to production of H_2S. One surface sample returned to the laboratory the day after the last fish kill, on September 5, 2000, measured 10 μM H_2S. Our main objective was to document the development of seasonal anoxia and H_2S formation in these waterways. From late spring through September 2001, in situ determinations of temperature, salin-
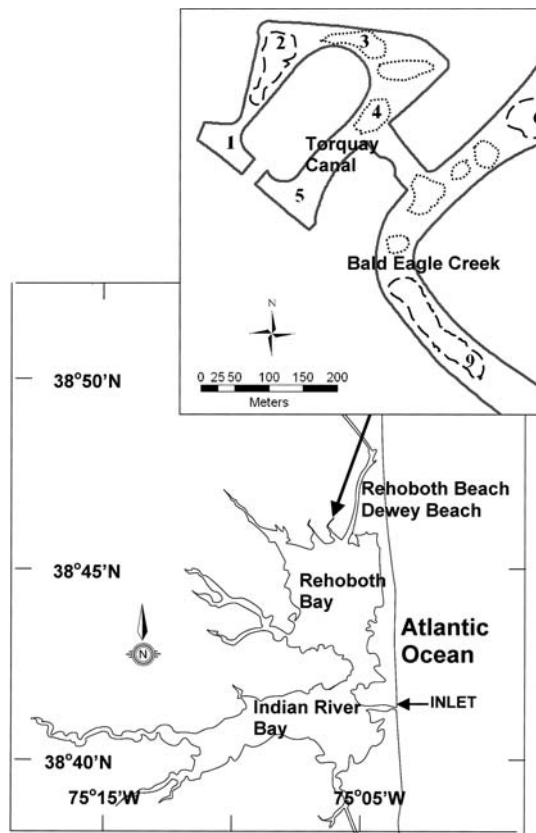

Fig. 1.   Map of Delaware's Inland Bays with an insert of the Bald Eagle Creek and Torquay Canal area at the top. The numbers indicate the sites studied, the dotted lines in the insert indicate water depths between 2–4 m, and the dashed lines indicate water depths between 4 and 5.5 m. The major land area is to the left and the Atlantic Ocean is on the right.

ity, pH, dissolved O_2, H_2S, and nutrient measurements were conducted in Torquay Canal and Bald Eagle Creek to follow the seasonal changes in water column chemistry and to document the development of seasonal anoxia. An aerator was also installed in an attempt to abate anoxic conditions.

Methods

REAL-TIME SAMPLING

Temperature, salinity, pH, dissolved O_2, and H_2S data were collected with in situ analyzers. Sampling times were biweekly and conducted between 0930 to 1230 on each field trip. Temperature and salinity were measured with a YSI-30 T-S meter with extended cable. pH was measured by a portable Digi-Sense pH meter using a Sensorex pH electrode with a 6 m cable. Dissolved O_2 and H_2S were measured using a solid-state gold-amalgam (Au/Hg) PEEK™, polyethyletherketone voltammetric microelectrode with a solid state Ag/AgCl reference and a counter (Pt) electrode that constituted a three-

electrode system (Brendel and Luther 1995; Luther et al. 1999, 2001). The waterproof wires for the T-S meter, pH meter, and voltammetric electrodes were tied together and weighted with a lead encased in plastic for lowering through the water column. Triplicate measurements were obtained in real time at each depth from the surface (0.2 m) of the water column to the bottom (approximately 5.5 m). In situ determination eliminated the possibility of artifacts or errors during sampling, sample storage, and transport back to the laboratory.

The solid state voltammetric electrodes were coupled with an Analytical Instrument Systems, Inc. model DLK-100 electrochemical analyzer and a laptop computer to perform real-time voltammetry. Both the electrochemical analyzer and the computer were powered with a 12 V D.C. marine deep cycle battery. The voltage scan range was from -0.1 to -1.8 V. The scan rate was 1,000 mV s^{-1}. Linear sweep voltammetry was used to determine O_2, and cyclic voltammetry was used to determine free H_2S and total sulfide (Luther et al. 2001). These electrodes do not foul as a potential of -0.9 V for 5 s was used as the conditioning (electrochemical cleaning) step to maintain reproducibility when H_2S existed (Brendel and Luther 1995). Standardizations of the Au/Hg PEEK™ electrode were performed as described in Brendel and Luther (1995) and Luther et al. (2002). Precision is typically better than 2% at the 95% confidence limit in laboratory solutions as well as in saline systems and freshwater lakes where no chemical changes are observed. We have performed in situ sediment calibrations with the Clark O_2 sensor (Luther et al. 1999) and there is excellent agreement (1–2% relative standard deviation [rsd]). Comparisons of in situ data with that obtained from standard conductivity-temperature-depth (CTD) rosette samples (samples where no mineral precipitation or oxidation occurs during traditional sampling and prior to measurement) is also excellent (1–2% rsd). Any change in field data over time as a result of chemical, biological, and physical processes greater than 2% is statistically significant. In most instances changes in concentration of O_2 and H_2S within a profile or over time at a given depth vary up to three orders of magnitude.

CONTINUOUS REAL-TIME SAMPLING

At site 2, the deepest and largest depression in Torquay Canal, three YSI 6000 datasondes were suspended from a buoy. These three units measured temperature, salinity, pH, and dissolved oxygen (DO) at approximately 0.75 and 2.25 m below the surface and 0.25 m above the bottom, approximately 5 m water depth. The datasondes were cleaned weekly and recalibrated every other week

as well as compared with the in situ voltammetry data. The DO sensor on the datasondes can give erroneous results when H_2S is present, this occasionally limited the available data from the DO sensor of the bottom datasonde, but other sensors of the unit contributed to the understanding to the dynamics of the system.

DISCRETE SAMPLING

Nutrient samples were collected at each sampling with a 2.2-l Van Dorn horizontal beta bottle sampler at the surface (0.2 m) and bottom waters (4.5 m), and kept in a cooler. After returning the samples to the laboratory, they were immediately filtered through 0.2 μm Nuclepore filters and kept frozen until nutrient determination. NO_3^- and NO_2^- were determined by the anion chromatography with ultraviolet detection method of Rozan and Luther (2002). NH_4^+ was determined by the flow injection analysis method of Hall and Aller (1992). PO_4^{3-} was determined by the molybdate blue complexation method (Koroleff 1983). Secchi depth was measured at each site.

SITES

Measurements were performed at 7 sites shown in Fig. 1 from April through September 2001. Sites 1 and 5 are control sites with a normal depth of 2 m and no depressions. Sites 2, 3, 4, 6, and 9 are sites with depressions ranging from 4.5 to 5.5 m deep. Sites 6 and 9 were added on June 13. On June 21, with approval from the State of Delaware Department of Natural Resources and Environmental Control (DNREC), installation began of a forced air flow system in the existing pipes under the roadway connecting site 1 with site 5. The pumps and aerators were expected to oxygenate the water and improve water circulation as water was pumped from site 1 to site 5. Due to deterioration of the existing pipes under the road, the designed system was not installed as planned. Instead two single point air diffusers fabricated by a local contractor were installed at site 5 powered by a 3.36 kw electric blower. These aerators were located within 100 m of control site 5.

Results

We report and compare results primarily from the control site (5) and from two other sites overlying depressions in Torquay Canal (site 2) and Bald Eagle Creek (site 9). Bald Eagle creek is not completely surrounded by a housing development as is Torquay Canal. The density and height of the housing and the density of trees around the canal restrict winds that can help mix surface with bottom waters. The total tidal range averages 0.5 m
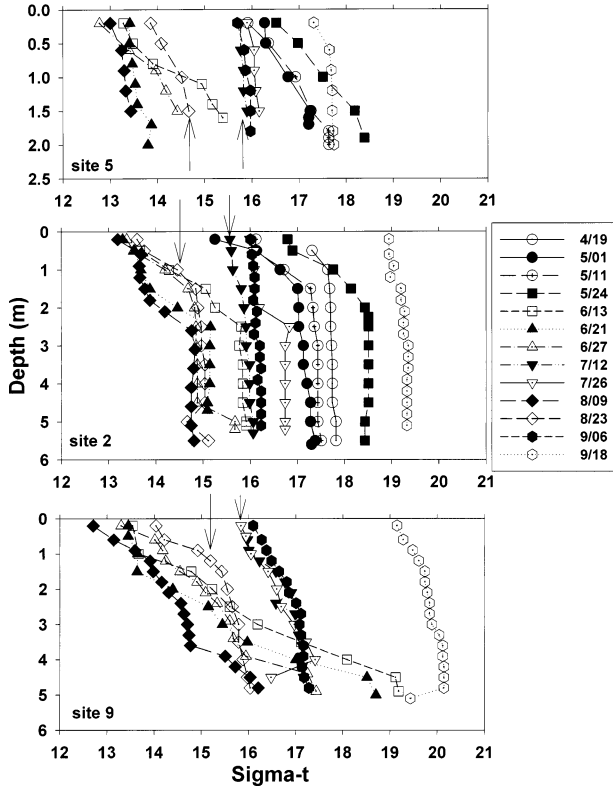
Fig. 2. Density (as σ-t) versus depth plots for Torquay Canal control site 5 for 2001, Torquay Canal site 2 for 2001, and Bald Eagle Creek site 9 for 2001. The arrows indicate when storm events occurred prior to July 12 and August 23.

(U.S. Geological Survey tide gauge at Dewey Beach), and the mean low water depth is 2 m.

DENSITY AND STRATIFICATION

Figure 2 shows density (as σ-t) plotted versus depth. At the shallow Torquay Canal control site 5, stratification was not extensive except for May 24 and June 13 and 27. These data indicate that the system was generally well mixed over the 2-m water depth.

Stratification increased at all the deep sites in Torquay Canal and Bald Eagle Creek from April to June when no major storm events occurred. Figure 2 shows data for sites 2 and 9. Only on July 12 and September 6 and 18 was there little or no stratification observed at site 2. The sampling on July 12 occurred after the first major storm event, which was sustained over 4 d. After this event, stratification developed again until another major sustained storm event occurred in late August. There was still some stratification after the second storm event on August 23, but this is related to lower surface (upper 2 m) salinity from freshwater input and not temperature, which varied little over depth (Fig.
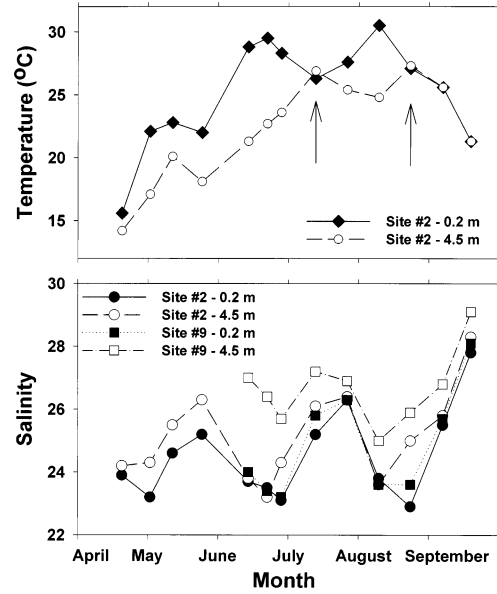

Fig. 3. Temperature data for 0.2 and 4.5 m water depths for Torquay Canal site 2. The arrows show when the storm events occurred and when temperature stratification was lost. Salinity data for 0.2 and 4.5 m water depths for Torquay Canal site 2 and Bald Eagle Creek site 9.

3). In September, stratification did not develop to any significant extent.

Site 9 showed stratification even after the storm events because the surface salinity (upper 2 m) was lower due to rainwater runoff. Site 2 showed that the mixed layer depth is about 2 m as the density is constant below the pycnocline. Site 9 showed a similar pattern; another deep layer below 4 m was observed on June 13 and 21 and August 9 and 23. Site 9 is not as enclosed as site 2, which is surrounded by trees and houses that can reduce wind velocity. O_2 also penetrates deeper at site 9 than site 2 as a result (see below).

TEMPERATURE AND SALINITY

To show what factors may control stratification at sites 2 and 9, Fig. 3 shows temperature and salinity versus time for water depths of 0.2 and 4.5 m to represent surface and bottom waters, respectively. Early in the year stratification appeared dominated by temperature decreases and salinity increases with depth (Fig. 3, sites 2 and 9 show similar trends but site 9 data are not plotted), but by mid July and into August stratification appeared to be driven more by salinity increases (Fig. 3) with depth. In fact, at sites 2 and 9, the salinity increased with depth by about 2 units on August 23 but the temperature was almost constant with depth. These data suggest that stratification of the water column is complex and driven by a combination of temperature and salinity changes related
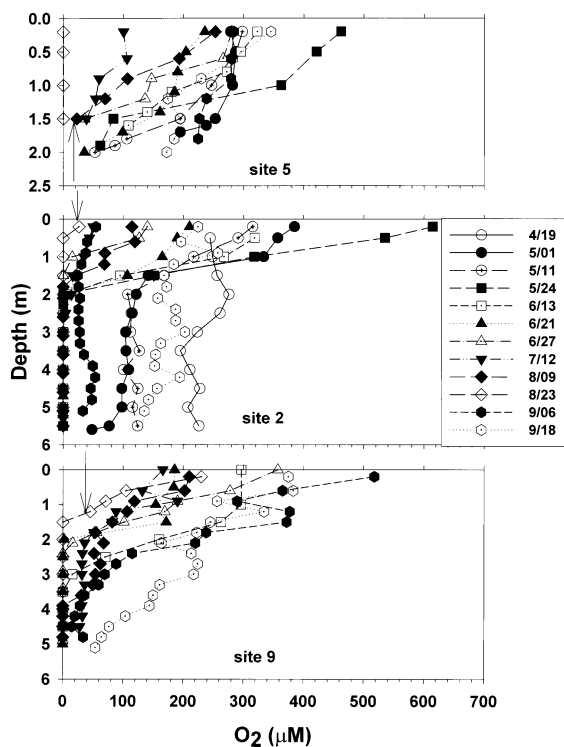
Fig. 4. O$_2$ profiles showing the extent of stratification for Torquay Canal control site 5, Torquay Canal site 2, and Bald Eagle Creek site 9. The arrow indicates data for the storm events prior to July 12 and August 23.
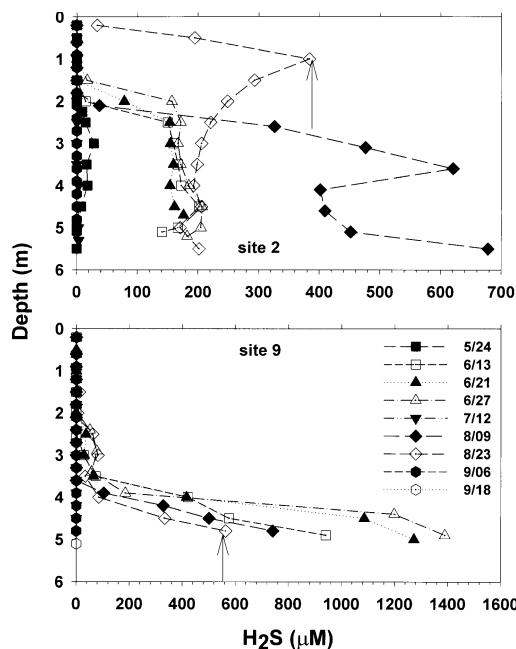

Fig. 5. H$_2$S profiles showing the extent of stratification for Torquay Canal control site 2 and Bald Eagle Creek site 9. The arrow indicates data for storm event two prior to August 23. Storm event one occurred prior to July 12.

to weather patterns. As will be shown below, both O$_2$ and H$_2$S indicate more significant stratification in the water column through the summer.

O$_2$ AND H$_2$S

In early May (Fig. 4), the surface waters (0.2 m depth) at all sites were well oxygenated with the percent saturation of O$_2$ frequently higher than 100% due to eutrophication. Stratification did not permit O$_2$ penetration into deeper waters. The Secchi depth at all sites was only 0.6 m, so light penetration declined and photosynthesis was lower. O$_2$ decreased to concentrations less than 100 μM in waters deeper than about 1.5 m. At the end of May and through June, O$_2$ could still be determined at the bottom of control site 5 (Fig. 4), but it was not detectable in the depressions below 2 m at sites 2 and 9 (Fig. 4). H$_2$S was present in the depressions and accumulated to millimolar concentrations in June (Fig. 5), but was not detectable at the control site 5.

A 4-d storm event before July 12 mixed the water column, and stratification decreased at the depressions. At site 9 in Bald Eagle Creek, O$_2$ penetrated into the deep water on July 12 (Fig. 4), and H$_2$S was not detected. In Torquay Canal, O$_2$ did not penetrate below 3 m at site 2 (Fig. 4) and H$_2$S was still detected at 3 μM in the bottom waters (Fig. 5). Figure 6 is a summary of the data for the O$_2$ in surface (0.2 m) and the H$_2$S in deep (4.5 m) waters with time. The weather was calm after this July storm event, and H$_2$S again accumulated to hundreds of micromolar in the bottom waters. Just prior to August 23, another storm event occurred, and signs of stratification decreased again. The mixing of surface waters with bottom waters resulted in no detectable O$_2$ at any depth for the control site 5 (Fig. 4) and only traces of O$_2$ in the surface water at site 2 of Torquay Canal on the sampling of August 23. At site 9 (and other sites) in Bald Eagle Creek, there was stratification with O$_2$ (Fig. 4) and H$_2$S (Fig. 5) detectable at 1.5 m, but below that depth on August 23 only hydrogen sulfide was detectable. Clearly control site 5 was affected by the mixing of surface and sulfide-rich bottom waters from the other areas with depressions in Torquay Canal. The Bald Eagle Creek sites such as 9 did not affect the Torquay Canal sites because of the sill and minimal tidal influx into the canal. The H$_2$S concentrations in these Delaware Inland Bays are among the highest reported in marine systems.

pH

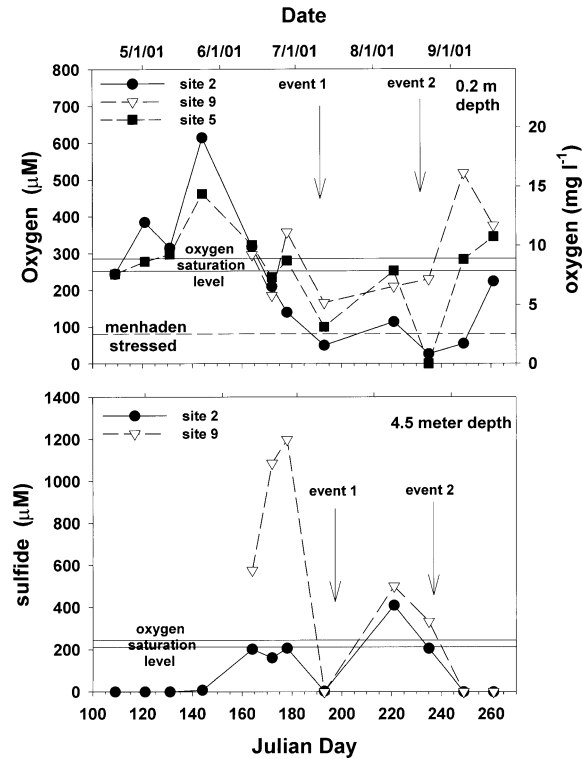pH is dependent on biogeochemical processes, such as photosynthesis, respiration, and organic

Fig. 6.   Surface (0.2 m) O$_2$ data for surface waters at sites 2, 5, and 9 in 2001. H$_2$S data at 4.5 m over the year shows the build-up and loss of H$_2$S based on weather patterns. Arrows indicate the storm events that mixed the water column.

Fig. 7.   Datasonde measurements at site 2 in Torquay Canal for O$_2$ from July 10–17, temperature from August 15–18, pH from August 15–18, and O$_2$ from September 5–8.

matter decomposition, and the pH reflected the changes in O$_2$ and H$_2$S concentrations. pH was higher (>7.5) in surface waters because of photosynthesis. In the H$_2$S rich depressions, pH was typically less than 7 and as low as 6.5, and appeared to be mainly controlled by the first acid dissociation constant of H$_2$S (pK of 6.7 in seawater; Millero 1986) because of the high H$_2$S concentrations.

NUTRIENTS

The concentrations of nutrients at these sites were high. In early August, surface waters had 85–105 μM NO$_3^-$ and 4–6 μM NH$_4^+$. NO$_2^-$ was not detectable. The concentration of PO$_4^{3-}$ in the bottom waters of depressions was 2.7 μM in August and decreased to about 0.3 μM in September after mixing and oxygenation of deep waters.

HYDRODYNAMICS

The three continuous recording datasondes gave a clear insight into the dynamics of Torquay Canal. While the DO sensors can give false readings in the presence of H$_2$S, which was often present at the middle and bottom depths, the other sensors revealed the movement of the water column and presumably the DO concentrations. Nu-
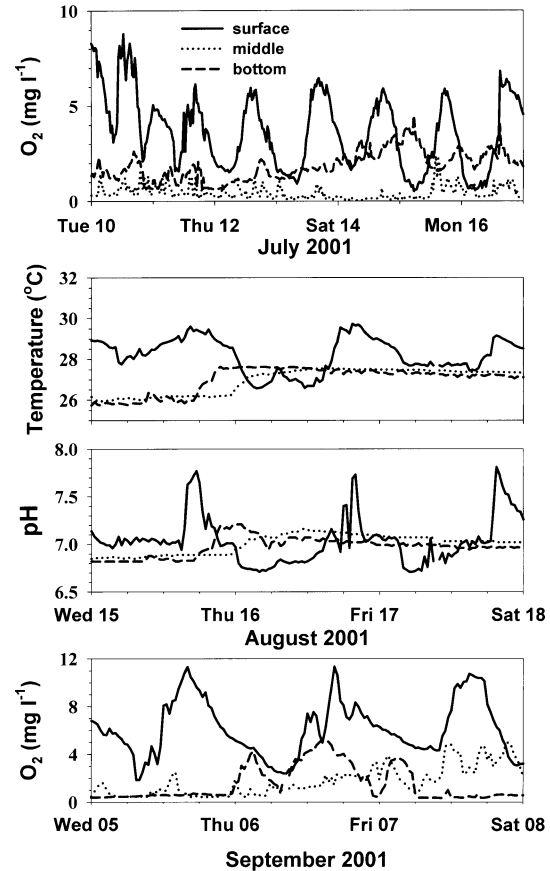
merous water column turnover events were captured by the data including the dates July 3, 15, and 20, August 15 and 22, and September 6. The July 15, August 15, and September 6 events were the most dramatic and are clearly shown in the data (Fig. 7).

The July 15 (Fig. 7) event is shown in the DO data with the surface showing typical diurnal fluctuation, the bottom and middle readings were extremely low until July 12 at 0600, at which point the bottom levels started a gradual rise up to 4 mg l^{-1}. The in situ voltammetry data for midday of July 12 showed that there was no detectable O$_2$ so the offset for the datasonde showed that a false but low reading resulted from the presence of H$_2$S. The middle datasonde indicated a minimum in DO at the pycnocline in agreement with in situ voltammetry data of July 12 until noon on July 15 with a sudden increase.

On August 10–14 there was a prolonged storm in the area and the surface water temperature (Fig. 7) decreased steadily from the rain. It was not until 1800 hours on August 15 that the bottom temper-

ature made a dramatic and sudden increase with a corresponding dramatic decrease in surface water temperature. These changes would indicate the cooler bottom water being exchanged with the warmer surface water. The middle water temperature did not fluctuate until around 2330 hours that night. This would indicate a circular flow pattern is responsible for the turnover and the circulation pattern did not affect the middle of the flow area until much later. Another type of turnover would be of a sudden and complete bubbling up of the bottom water to the surface, which would affect the middle data points immediately. The pH readings corroborate the temperature data (Fig. 7).

On September 4 a low pressure area passed through the area followed by a turnover event on September 6. The DO sensor was functioning on all three datasondes for this event and O_2 data were in agreement with in situ voltammetry data. The surface DO (Fig. 7) clearly shows the normal diurnal DO cycle due to respiration but also an overall decrease in surface DO concentration. After midnight on September 6 the bottom DO concentrations made a sudden rise from less than 1 mg l^{-1} to over 5 mg l^{-1}. This is the time of normal DO decrease from respiration. The middle DO concentrations make a more gradual rise starting approximately 6 h later. The bottom DO drops after 36 h followed 24 h later by the middle DO indicating a return to stratified conditions.

All of the 6 turnover events were preceded by rain events 1 to 3 d earlier and were usually followed by 1 to 3 d of sustained winds. Due to the limited meteorological data, it cannot be determined if the wind alone can induce the turnover flow pattern or if the addition of cooler rainwater and storm runoff are needed.

Discussion

We began this study to understand the possible roles of low O_2 and high H_2S concentrations as the cause of menhaden fish kills in Torquay Canal. Exposure to low O_2 concentrations can make aquatic species more susceptible to diseases and death (Theede 1973; Wannamaker and Rice 2000). Although each aquatic species has a specific O_2 concentration below which they become stressed, most begin to suffocate or show stress when the O_2 concentration is below 62.5 μM (2 mg l^{-1} O_2; Diaz 2001) or below 31 μM (1 mg l^{-1} O_2; Wannamaker and Rice 2000), especially during summer months when metabolic rates are high. Atlantic menhaden are the major species involved in the Delaware Inland Bays' fish kills and spend the early part of their lives in the shallow water of enclosed estuaries. They are surface dwellers and warm water migrants, which consume phytoplankton in their ear-
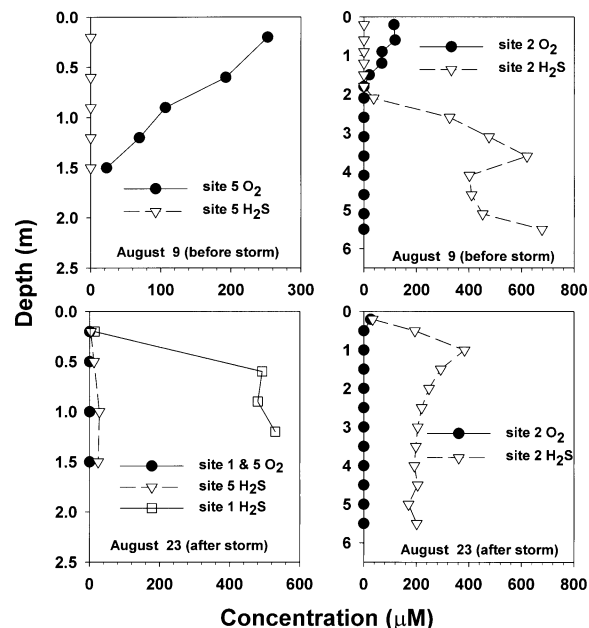

Fig. 8. O_2 and H_2S profiles for Torquay Canal control site 5 before and after the August storm event. Control site 1 data is also shown. O_2 and H_2S profiles for Torquay Canal site 2 before and after the August storm event.

ly life stages (Weston 1993). They are sensitive to low O_2 and have the highest sensitivity among the dominant fish species in the Delaware Inland Bays (Thornton 1975; Price 1998). Their lethal threshold of O_2 concentration is 34.4 μM (1.1 mg l^{-1} O_2; Burton et al. 1980; Wannamaker and Rice 2000) and they become stressed at about 80 μM (2.5 mg l^{-1} O_2). Although we do not know the level at which ammonia and sulfide are toxic to menhaden, Bagarinao and Lantin-Olgauer (1999) note that millimolar levels of ammonia are toxic to select marine fish in contrast to only micromolar levels of sulfide. Because ammonia levels were never higher than 6 μM and sulfide levels were as high as 2 mM, we focused on sulfide as the primary toxin to fish.

Besides pumping water through the gills to obtain O_2, menhaden and other marine fish ingest seawater to maintain osmotic balance. If H_2S is in the water, it will be taken in via both routes (Bagarinao and Vetter 1989). H_2S can damage the gill, which leads to diseases. H_2S is extremely toxic because it can combine with the iron in heme to replace O_2 and prohibit electron transport in aerobic respiration (Smith et al. 1977; Theede 1977; Bagarinao and Vetter 1989). Surface waters were typically well oxygenated at the time of our measurements (Figs. 6 and 8) except after storm events (Fig. 8). On July 12 and August 23, low or zero O_2 levels occurred, and these low levels of O_2 would

have stressed menhaden had they been present; they were not present and no fish kills occurred in Torquay Canal. The fish kills of 2000 occurred roughly the same time of year on July 6, August 29, and September 6 after storm events. On July 12, we observed that blue crabs (*Callinectes sapidus*) in Torquay Canal were on the pilings above the water-air interface to breathe O_2 from air since O_2 was not detectable and sulfide was detectable in the surface water at most locations in Torquay Canal (Fig. 8). Bald Eagle Creek surface waters always showed adequate O_2 levels.

Causes of Anoxia

Nutrients are highly enriched in coastal areas but especially in tidal creeks and sediments of the Delaware Inland Bays (Rozan et al. 2002). Excess eutrophication has long been identified (DNREC 2001) as a serious problem in Delaware's Inland Bays. For the 5-yr period of 1993–1997, total nitrogen and phosphorus concentrations exceeded the guidelines of 1.0 mg l^{-1} N (71.4 μM N) and 0.01 mg l^{-1} P (0.3 μM P) at most areas studied in the Delaware Inland Bays. Most of our nutrient data equaled or exceeded these guidelines as well. Excess nutrients accelerate unwanted algal blooms, which decrease light and O_2 penetration to deep waters. When algae die, they sink to the sediments where their organic matter is decomposed by sulfate reducing bacteria to produce H_2S in deep water. The H_2S reacts with iron(III) (oxy)hydroxides deposited in the sediment to form FeS and FeS_2 with release of the phosphate adsorbed to the Fe(III) phases to the overlying water (Rozan et al. 2002). In organic-rich environments, H_2S in excess to reactive iron(III) (oxy)hydroxides can then diffuse into the overlying water to cause fish kills (Nriagu and Hem 1978).

Stratification and Mixing via Storm Forcing

High temperatures and nutrient levels permit eutrophication via primary production and are the most common reasons for anoxia and water column stratification in Delaware's Inland Bays. In June, the temperature differences between surface waters and the deep waters in the depressions were largest (Fig. 3). The surface water temperatures were above 28°C but the deep waters were as low as 23°C (site 2) and 18°C (site 9). The large temperature difference makes stratification more stable and permits anoxic conditions to develop in the depressions. After each storm event, stratification decreased as shown by similar temperatures for bottom and surface waters on July 12 and August 23.

Figures 4 and 6 show that O_2 is present in the surface waters at all sites prior to August 23. Figure 8 shows the data for O_2 and H_2S before and after the August storm event for sites 1, 2, and 5. After the storm event, O_2 was not detected in the surface waters at control sites 1 and 5, and H_2S was detected in the water column at an average concentration of >200 μM at site 1 and 15 μM at site 5. At site 2 in Torquay Canal, the O_2 was 25 μM in the surface but not detectable elsewhere in the water column whereas the average H_2S concentration was about 200 μM throughout the water column. Clearly the control sites 1 and 5 were affected by the mixing of surface and sulfide-rich bottom waters from the other areas with depressions (such as sites 2, 3, and 4) in Torquay Canal. The Bald Eagle Creek sites such as 9 did not affect the Torquay Canal sites because tidal flushing is limited in these tributaries and the sill further restricts water exchange between Torquay Canal and Bald Eagle Creek. Consistent with the chemistry and poor tidal exchange, we could smell H_2S at the Torquay Canal sites on August 23 but not at the Bald Eagle Creek sites, which had well oxygenated surface waters (Fig. 6).

Aerators' Function

Our data indicate that the aerator systems did not improve water quality at any time during our study. The O_2 concentrations in surface waters at control site 5 were generally higher than site 2 (Figs. 4 and 6) after aerator installation except for storm events. Site 2 had higher O_2 concentrations than the control site 5 before aerator installation. As indicated above on August 23, O_2 was not detectable at virtually all water depths and sites in Torquay Canal, and the concentration of H_2S in surface waters was about 30 μM at sites 1 and 2 and 3 μM at site 5 (Fig. 8). Site 5 was located only 100 m from the aerator system so the aerators did not replenish O_2 to these waters. The site 2 (Fig. 8) profile also showed that the maximum H_2S concentration occurred at 1-m depth, which indicates the water column had mixed after the storm. Milky surface water (probably from S_8 formation) was observed at control sites 1 and 5 as well as site 2 on August 23. These data indicate that sulfide was oxidized to S_8 by any O_2 that was added to the waters by natural processes or by the aerators. At sites 2 and 9, the depressions are as large or larger than the surface area of a football field; these particular aerators did not have the capacity to eliminate seasonal anoxic conditions in Torquay Canal.

O_2-H_2S Interface

From May through August of 2001, high concentrations of H_2S accumulated in the bottom waters and diffused into the surface oxic layer in the absence of storms. The profiles of O_2 and H_2S (Fig.
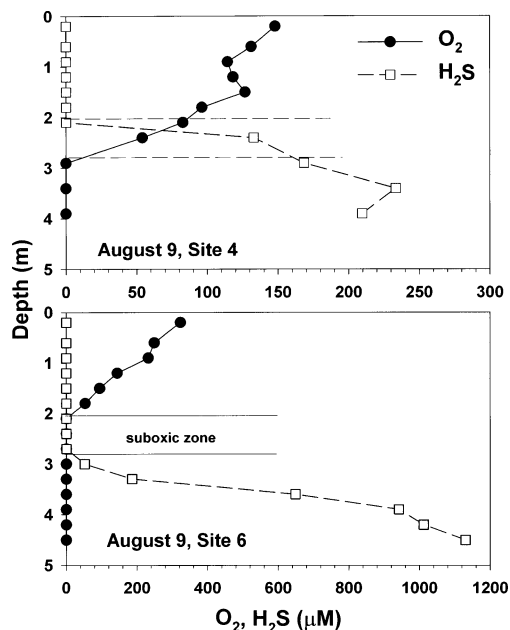
Fig. 9. O_2 and H_2S profiles for Torquay Canal site 4 show overlap, but a well-defined suboxic zone in Bald Eagle Creek site 6 on August 9.

9) showed different degrees of overlap. Figure 9 shows that the profiles overlap in the depressions whereas the second panel shows a suboxic zone where there is a clear separation between O_2 and H_2S profiles. The suboxic zone of these latter profiles is observed at many other oxic-anoxic interfaces such as the Black Sea and Chesapeake Bay (Luther et al. 1988, 1991). For the data in Fig. 9, the concentration gradient of H_2S (0.196 mol m^{-4}) is twice as large as the O_2 gradient (0.104 mol m^{-4}) in the interface layer. If the redox product of sulfide oxidation is presumed to be SO_4^{2-}, 1 mol of H_2S requires 2 mol of O_2 to oxidize it. This stoichiometry is not consistent with our stoichiometry of 2 mol of H_2S to 1 mol of O_2 from Fig. 9a. The actual concentration gradients are consistent with the production of S_8 as in Eq. 1.

$$2H_2S + O_2 \rightarrow 2H_2O + \tfrac{1}{4}S_8 \qquad (1)$$

Although we did not measure S_8 in discrete samples, we observed a milky substance in some surface waters as indicated above for August 23.

Conclusions

The extent of anoxic environments has increased in shallow coastal and estuarine areas because of nutrient loading from anthropogenic activities. Shallow water depths in estuaries lead to a tight coupling between benthic and pelagic processes (Flindt et al. 1999). Due to the bottom morphology (depressions) of Torquay Canal and Bald

Eagle Creek as well as poor tidal flushing and water circulation in Torquay Canal, the water masses in these depressions are isolated from reoxygenation with surface waters during calm periods. The depressions in this system have a great tendency to develop anoxic conditions. Seasonal stratification and nutrient overloading lead to low O_2 concentrations and the production of H_2S in deep waters. Eventual mixing of H_2S into surface water by storms with strong winds is the likely reason for past fish kills particularly since dead fish have no observable lesions from *Pfisteria* or other harmful algal species. In this system, when menhaden are killed, they are always found at control sites 1 and 5 at the end of the canal system. These sites are shallow, and when surface and bottom waters mix rapidly due to storm events, these surface-dwelling fish are trapped in the canal and cannot escape. Other tributaries in the Delaware Inland Bays as well as other dead-end canal systems in the United States (e.g., Shellbank basin, NYCDEP 2001) and elsewhere also have similar problems. A potential long-term solution to this problem is to remove the sill in this ecosystem, and fill the depressions so the waterway has a constant depth of about 2 m (the apparent mixed water depth in the absence of strong forcing). The fill sediment should be iron-rich to react with H_2S to form pyrite, which would precipitate the sulfide in the sediments during summer. Torquay Canal and Bald Eagle Creek should provide an ideal site to study restoration processes in dead-end canals found in many estuarine environments.

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