

Estuarine oxygen dynamics: What can we learn about hypoxia from long-time records in the Delaware Estuary?

Jonathan H. Sharp*

College of Earth, Ocean, and Environment, University of Delaware, Lewes, Delaware

Abstract

Hypoxia and anoxia occurred in the upper Delaware Estuary throughout much of the 20th century and diminished over the past several decades. I reviewed 30 yr of data from my laboratory's research efforts, 40 yr of consistent monitoring data from a multistate agency, results from inconsistent data collection from the past century, and anecdotal information to construct a long-time picture of the decline and increase of dissolved oxygen concentrations (DO) in the urban region of the estuary. The primary cause of the DO decline appeared to be inputs or allochthonous materials from urban sources (reduced nitrogen and carbon). In spite of extremely high nutrient concentrations, excess algal production did not influence DO anywhere along the tidal freshwater stretch or the saline portion of the well-mixed Delaware Estuary; and it does not have an influence today. The nutrient loading to the Delaware Estuary is very high, yet the typical signs of eutrophication are not obvious. Based on a model of apparent oxygen utilization, the Delaware Bay apparently had higher primary production 50 yr ago, a time when nutrient concentrations were as high or higher than today, shellfish and finfish production were apparently also higher, and DO was close to saturation. This analysis is offered as guidance in assessing and managing estuarine eutrophication, which is too often considered narrowly to be the result of inadvertent overfertilization by nutrients or a single nutrient element.

One of the major phenomena associated with estuarine and coastal eutrophication is hypoxia caused by excessive algal production due to nutrient enrichment (Bricker et al. 2007; Diaz and Rosenberg 2008). However, all hypoxia is not the result of nutrient enrichment; another major cause is from allochthonous inputs to the water of reduced materials that require oxygen for oxidation. While this difference is generally understood, there is a tendency to oversimplify and associate all aquatic hypoxia with algal response to nutrient enrichment, leading to proposals for simplistic remedial action. Oxygen depletion of urbanized estuarine waters probably has been observed for centuries. The reference to “two and seventy stenches” in Samuel Taylor Coleridge's poem “Cologne” (Keach 1997) is possibly an anecdotal reference to hypoxic waters in the Rhine River in the early 1800s. Many riverine estuaries with heavy urban biochemical oxygen demand (BOD) burdens had severe oxygen depletion in the past and many have had remarkable improvements in recent decades. However, hypoxia from allochthonous sources, both anthropogenic and natural, is still a major occurrence. While a few recent publications differentiate these causes (Nixon 1995; Mallin et al. 2006), and while some give excellent overviews of eutrophication-associated hypoxia (Diaz and Rosenberg 2008), there is an emphasis on nutrient-stimulated hypoxia as the only phenomenon from anthropogenic stress in aquatic systems. As an example, the U.S. Geological Survey (USGS) definition, along with a cited Ecological Society of America hypoxia fact sheet, makes no mention of hypoxia from allochthonous inputs (USGS 2006).

There is a continuing concern about nutrient eutrophication in estuarine and coastal ocean waters of the world,

which associate increases in nitrogen fluxes with aquatic consequences (Vitousek et al. 1997; Rabalais and Nixon 2002; Howarth and Marino 2006); this is justifiable. The ubiquitous nature of nutrient enrichment of estuarine and coastal waters has been linked with observations of eutrophication (Nixon and Pilson 1983; Nixon and Buckley 2002), including bottom-water hypoxia (Officer et al. 1984). Although a few recent publications have stressed the complexity of estuarine ecosystem response to nutrient enrichment (Cloern 2001; Caraco et al. 2006; Paerl 2009), the association of nutrient enrichment with eutrophication is often oversimplified.

The argument had been made that the loss of higher trophic levels, not nutrient enrichment, is the main cause of much of the deterioration of estuarine and coastal waters (Jackson et al. 2001; Heck and Valentine 2007). This argument has been criticized as inaccurate, emphasizing the need for nutrient removal (Boesch et al. 2001). While it would seem obvious that both influences contribute to degraded estuarine waters, disagreement on the main influence still leads to situations like the pro and con discussions on restoration of conditions in the Chesapeake Bay by top-down control, i.e., enhancement of higher trophic level consumers (Newell et al. 2007), as opposed to bottom-up nutrient controls (Pomeroy et al. 2007). These different characterizations of the problem can lead to quite different remedial action.

With an emphasis on nutrient loading causing eutrophication, there have been successful efforts to reduce nutrient inputs to some estuarine and coastal waters. The reduction of inputs, often referred to as oligotrophication, does not necessarily result in return to the expected pre-eutrophication conditions (Carstensen et al. 2006; Duarte et al. 2009).

In this paper, the long-time changes in the chemistry and primary production in Delaware Estuary are evaluated in

* Corresponding author: jsharp@udel.edu

relation to development, and alleviation of, hypoxia, with evaluation of the linkages between nutrients and estuarine response. This assessment is offered to provide an improved perspective on estuarine eutrophication.

Methods

The Delaware Estuary—The Delaware Estuary has been defined by resource managers as the 100-km-long tidal Delaware River plus the Delaware Bay (DELEP 1996). The Delaware River, with headwaters in the Catskill Mountains, provides drinking water to about 8% of the U.S. population. The tidal freshwater stretch passes through the sixth largest municipal region of the U.S. before grading into a saline bay surrounded by partially undeveloped salt marshes (Sharp et al. 1982). The Delaware Estuary has a long economic and ecological history. Philadelphia, Pennsylvania, which was settled by William Penn, was the most populous city in the colonial era (Stutz 1992). Philadelphia is currently one of the largest freshwater ports in the world (Sutton et al. 1996). The Delaware River carries one of the highest tonnages of shipping in the U.S. (Sutton et al. 1996). In the mid-18th century, Benjamin Franklin suggested regulations of street runoff and waste dumping in the river because of the degraded river condition (Stutz 1992). The urban region of this river was considered one of the most polluted in the U.S. by the early part of the 20th century (Sutton et al. 1996). While there are still significant water quality problems, the Delaware Estuary has experienced one of the most successful improvements in water quality of any estuary in the world (Albert 1988; Sharp 1988, 1994). While it is recognized that the Delaware Estuary water quality has experienced pronounced improvement, a more detailed estuary-wide evaluation of the causes and effects of the changes are offered here.

We have differentiated five zones along the Delaware Estuary for characterizing anthropogenic influences and primary production; these are discussed in detail elsewhere (Sharp et al. 2009). The 100-km stretch of the upper river and urban river regions are tidal freshwater; below 120 km, the salinity increases from zero to about 30 at the mouth of the bay (Fig. 1). The entire estuary is turbid, but the turbidity maximum region is extreme (surface-water concentrations to 100 mg L⁻¹ total suspended sediments) compared to the mid- and lower bay regions (Sharp et al. 2009). Dissolved nutrient concentrations in the river are high during the entire year and are regularly diluted down the salinity gradient to low values at the bay mouth, where they reach almost zero in the spring (Sharp et al. 2009). The maximum primary production in the estuary occurs in the mid-bay region around 30–50 km from the mouth of the bay in all seasons (Pennock and Sharp 1994; Yoshiyama and Sharp 2006).

Analyses of the database from our microbial biogeochemical research in the Delaware Estuary, combined with observations from routine monitoring data, provide a basis for assessing relationships among phytoplankton algae, bacteria, plant nutrients, and organic matter in this nutrient-rich urbanized estuary. The large changes demonstrated for dissolved oxygen and nitrogen and phosphorus

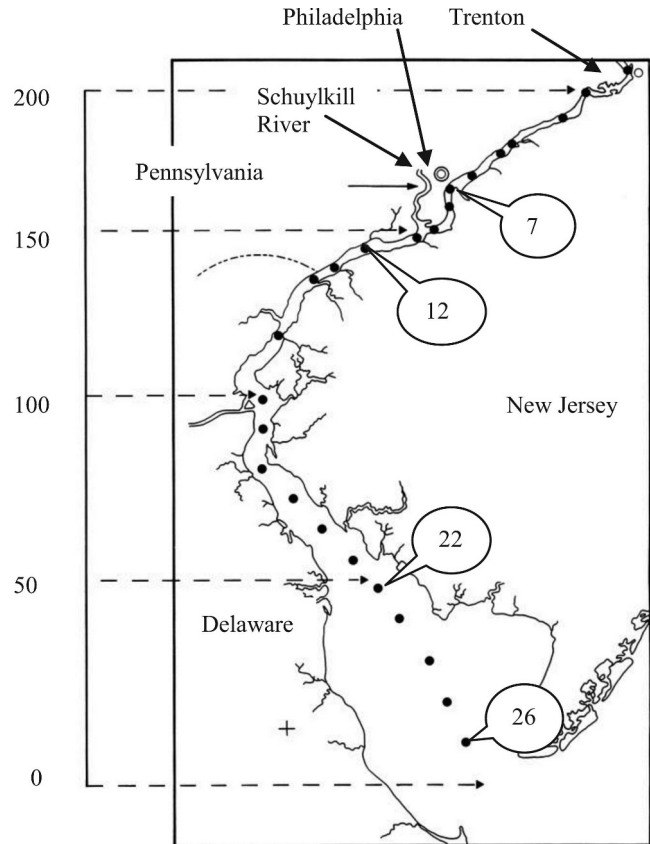


Fig. 1. The Delaware Estuary from the head of the tide of the Delaware River (river km 220) to the mouth of Delaware Bay (river km 0). Two tidal freshwater regions (upper river, urban river) run through the Philadelphia area to 120 km (Sta. 14). Three saline regions (turbidity maximum, mid-bay, lower bay) extend from there to the mouth of the bay. Four of the UD sampling stations are shown (numbered from head of tide to mouth of bay as 1 to 26).

nutrients in the water provide a unique information base to assist in understanding hypoxia and to undertake a generic evaluation of estuarine eutrophication.

General data and data analyses—My research group established routine sampling stations along the Delaware Estuary (Fig. 1). Many of the stations were at the same location as Delaware River Basin Commission (DRBC) stations used for their routine “Boat Run” monitoring. The DRBC monitoring consisted of 1-d sampling of surface waters along the length of the estuary, one to three times a month from March through November since 1967. The University of Delaware (UD) sampling was more sporadic, usually taking 2–3 d for cruises between one and four times in a year since 1978 (up to 13 times in the 1986–1988 period). The UD and DRBC sampling covered the same geographic area, but the UD effort had more emphasis on the bay and less on the river. Since the estuary is well mixed from surface to bottom most of the time (Sharp et al. 1984, 1986), only surface samples (~1 m below the surface) were routinely taken and all evaluations here are based on

surface samples. The UD database is available from <http://www.ocean.udel.edu/cms/jsharp/CruiseDatabase.htm>.

Selected station data from the DRBC program have been retrieved from the EPA storage and retrieval (STORET) systems for analysis in this paper. Efforts are underway to make this entire database (1967–present for all stations) more readily available. The sampling and chemical analyses for the UD data used well-described standard methods (Sharp et al. 1982) that have been shown to be consistent through our 30-yr period (a detailed description of sampling, methods, and analytical precisions is given in the Electronic Supplementary Material of Sharp et al. 2009). The DRBC sampling and routine water quality chemical analyses have been conducted consistently by the State of Delaware Department of Natural Resources and Environmental Control and were validated to conform to EPA quality assurance, quality control criteria.

Although some winter sampling was included several times in the sampling period, the DRBC core stations in the Delaware River were sampled consistently between March and November. The Paulsboro station, 135 km from the mouth of the Delaware Bay (our Sta. 12), was downstream of the confluence of the Schuylkill River with the mainstream of the Delaware River, and was also downstream of the effluents from the Philadelphia sewage treatment plants. Dissolved oxygen concentrations (DO) at the Paulsboro location have been equal to or lower than any other location in the estuary since the early 1970s, and evaluation of oxygen data from the 1950s and 1960s suggested that this location appears to have had the lowest DO throughout the last half century. An indirect comparison of the DRBC and UD data (Fig. 2) shows that there is no systematic difference for DO and dissolved inorganic nitrogen (DIN) for a 25-yr period. The DRBC data were monthly averages, based on one to four samplings per month while the UD data were from less frequent single samplings. A second location for 40-yr trend analyses was the DRBC Mahon River station, which was located near our Sta. 22 (Fig. 1). This station is in the lower bay, near the primary production maximum.

Consistent primary production measurements were made in my laboratory from 1980 to the present and, because there was only a slight trend in primary production over this time period, evaluations and comparisons can be made using the full time period. Chlorophyll concentration, depth-integrated areal production (APROD) estimates, and maximum production per volume normalized to chlorophyll biomass (P:B) were used as metrics (Yoshiyama and Sharp 2006). For evaluation in this paper, P:B and APROD were used.

An interesting database from 1913 through 2005 has been constructed with Philadelphia Water Department data for the Torresdale drinking water intake located close to our Sta. 7 (Fig. 1). Tabulation derived from handwritten records (N. Jaworski pers. comm.) was used for total alkalinity, chloride, nitrate, and ammonium concentration trend analyses.

Long-time DO trend—A 120-yr summer (July and August) DO time series analysis was performed using data

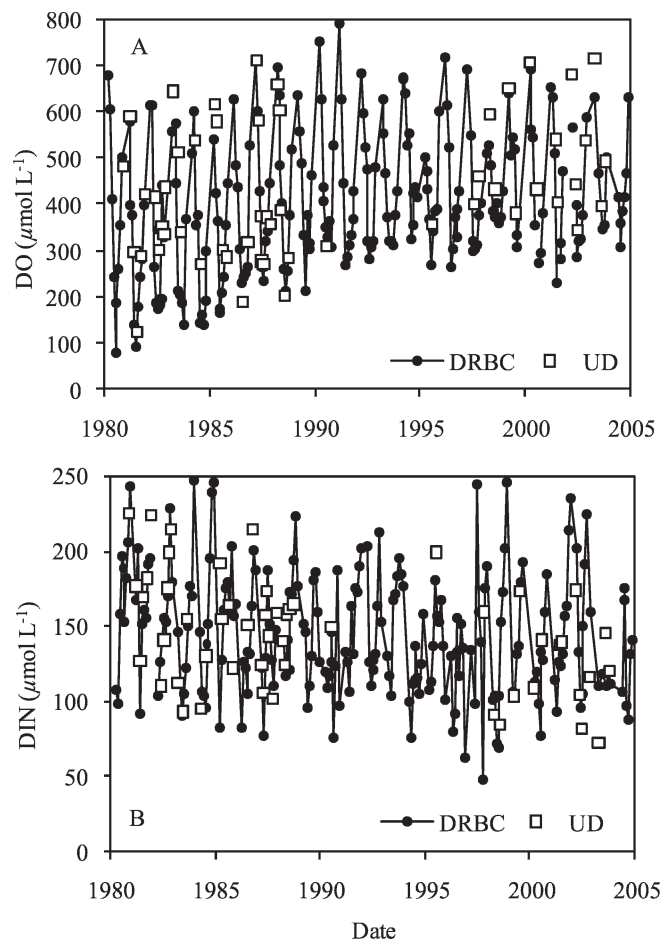


Fig. 2. An indirect comparison (separate sampling) of (A) dissolved oxygen (DO) and (B) total dissolved inorganic nitrogen (DIN; sum of nitrate, nitrite, and ammonium) concentrations from 1980 to 2005 for the DRBC monitoring data and UD research data; only sampling between March and November is included.

from a variety of sources that are discussed here. For that analysis, the July–August DRBC data (2–10 samplings each year) were averaged for the annual data points from 1967 to the present for our Sta. 12 location. Evaluation of older data from the 1950s and 1960s plus the more modern data showed that the months of July and August almost always had the lowest DO concentrations of the year. Thus, the intent is for analysis of annual minimal oxygen content. All data reported as mg L^{-1} were converted to molar units using $1 \text{ mg O}_2 \text{ L}^{-1} = 62.5 \text{ } \mu\text{mol O L}^{-1}$. Note, that throughout this paper, I use the molar units as $\mu\text{mol L}^{-1}$, so that for the diatomic DO, $1 \text{ } \mu\text{mol L}^{-1}$ indicates O, not O_2 ; consistent with molar units for other elements like N, P, and Si. Other data for this analysis were from data reports with limited availability. Data for 1957–1959 (INCODER 1960) were taken for the same location as Sta. 12. Data for 1949–1952 were from Durfor and Keighton (1954) from a station near Sta. 12. These two data sets, plus the DRBC data, provide annual data from 1967 to the present and less frequent data from 1949 to 1959. All of these data were

based on direct sampling for the relevant 2-month period at the selected location.

For the period of 1950–1964, data from a Philadelphia Water Department station (3 km downstream of our Sta. 12) were included in the 120-yr time series. This station is considered to be close enough to represent Sta. 12. These data were derived from the Baxter Report (1965). That report contained summer DO values for each year for several stations (based on 5-month averages). A figure in the report of annual 1964 DO for that station allowed an estimate of the ratio of the 5-month (June–October, equivalent to $106 \mu\text{mol L}^{-1}$) to a 2-month value (July–August, equivalent to $44 \mu\text{mol L}^{-1}$) period. This ratio of 2.4 was then used to convert the 1950–1964 data to the summer period.

Monthly summer DO data were available for the period of 1936–1965 from the Philadelphia Water Department Torresdale intake (near Sta. 7 in Fig. 1). These data were tabulated by manually copying data from individual and summary annual reports (Philadelphia Water Department 2005). The Sta. 7 location had considerably higher DO concentrations than downstream in the area of the Sta. 12 (see discussion of Fig. 3B in Results). By using the average data for Sta. 7 and a Philadelphia Water Department station, 8 km upstream from our Sta. 12 for the period of 1950–1964 (from Young et al. 1971), an adjustment factor was computed. The average July–August 1964 DO for the location near Sta. 12 (equivalent to $36 \mu\text{mol L}^{-1}$) was subtracted from the similar average for Sta. 7 (equivalent to $375 \mu\text{mol L}^{-1}$) to obtain a difference of $344 \mu\text{mol L}^{-1}$. The Sta. 7 data were transformed to represent downstream conditions by subtracting $344 \mu\text{mol L}^{-1}$ from the reported data. Five of the years had slightly negative results from this modeling (-6 to $-19 \mu\text{mol L}^{-1}$) and these five were assigned values of 0. Since the other adjusted data had calculated values of 0 to $172 \mu\text{mol L}^{-1}$, this modeling exercise was considered to be a reasonable approximation.

There is large day-to-day variability in the physical control of DO concentrations (Sharp et al. 2009), which results in a greater scatter when fewer samples are available for averaging. The four data sets mentioned above for the periods between 1936 and 1965 displayed more variability compared to the more regular and direct data of 1967–2002.

The successful migration of anadromous fish species requires ample DO in the water. The Delaware River was once the major route for spawning runs of American shad (*Alosa sapidissima*). An evaluation of shad fisheries landing data and population estimates showed very large landings in the late 1800s and a precipitous decline around 1920. This decline has been attributed to low DO in the Delaware River in the Philadelphia region (McHugh 1981; Killiam and Richkus 1992). It should be noted that this “oxygen block” was because the waters in this urban river region are always well mixed from surface to bottom (Sharp et al. 1986). Therefore, I assumed that the summer DO concentration in the river in the late 1800s must have been much higher than in the early and mid-1900s. I assigned a value of $450 \mu\text{mol L}^{-1}$ for the year 1890 (saturation equilibrium concentration at about 30°C). Because most fish can tolerate below-saturation oxygen concentrations, this assignment was arbitrary and could be higher than

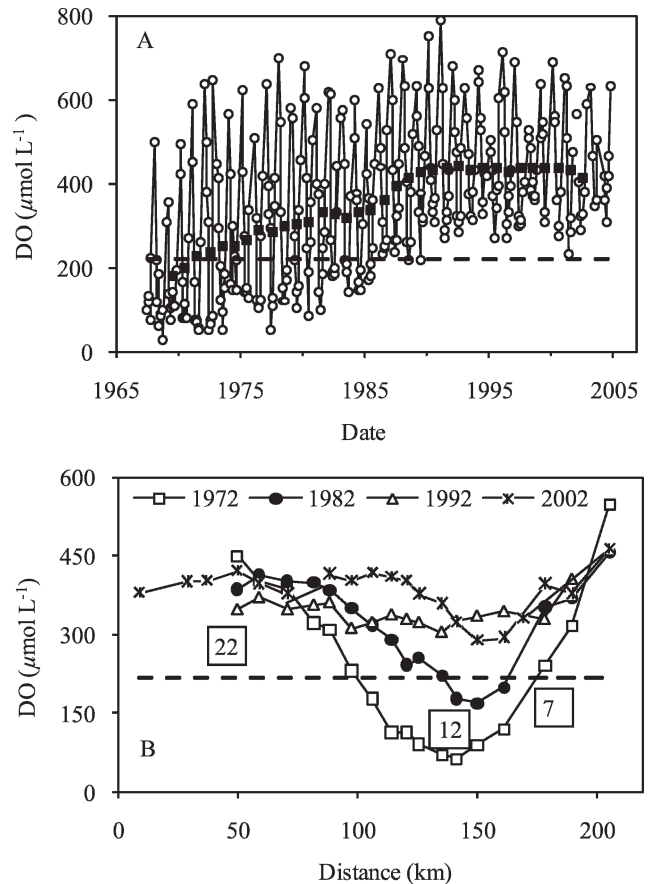


Fig. 3. Dissolved oxygen concentrations (DO) from DRBC Boat Run monitoring in Delaware Estuary; the dashed line shows the 3.5 mg L^{-1} standard (see text). The data were compiled by the author from EPA STORET files for 1967–2005. (A) Average monthly DO from Sta. 12 shown as open circles; running 5-yr average DO shown as filled squares. (B) Average summer (July–August) DO from all stations for four summers in decadal intervals; values for individual stations are averages of from 2 to 12 samples.

necessary; however, see Discussion for confirmation. From the Durfor and Keighton (1954) data discussed above, I averaged the 1949–1952 data to obtain a value of $60.9 \mu\text{mol L}^{-1}$ and used that for 1950. Census data of population in the Philadelphia area (U.S. Census 1998) were used to model oxygen demand. The assumption was that the BOD in sewage effluents should be directly proportional to the number of people being served by the sewage collection. A linear relationship was constructed of the effect of the population-pressure BOD using 1890 and 1950 as end-points for the recorded population, and estimated DO concentrations were 450 and $60.9 \mu\text{mol L}^{-1}$, respectively. Simulated DO concentrations were calculated from that regression for the 10-yr points between (1900, 1910, 1920, 1930, and 1940). It is somewhat arbitrary to assign all BOD to sewage inputs, ignoring industrial contributions. However, population may be an indicator of pressure from both municipal and industrial sources. Confirmation of the approximate shape of the resulting curve is given in the Results.

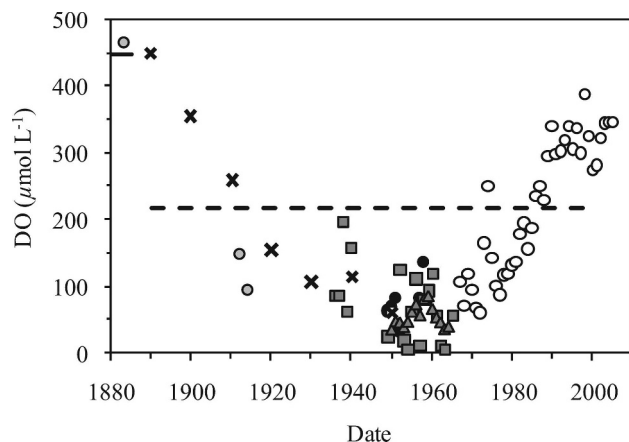


Fig. 4. Very long time record of dissolved oxygen concentrations (DO) in the Delaware River near Philadelphia (Sta. 12 in Fig. 1) from 1880 to present. The individual points represent average summer (July–August) values for individual years. Data for the period of 1967–present (open circles) and for 1949–1952 and 1957–1959 (solid circles) from active monitoring programs. For the period of 1950–1964, data are transformed from the 5-month to 2-month average (gray-filled triangles). Data from near Sta. 7 for 1936 through 1965 were transformed to approximate concentrations in the summer period for this location (gray-filled squares). The 1900–1940 values are from regression against population (x). The solid line across the left-hand y -axis represents summer (30°C) oxygen saturation. Values for 1912 and 1914 were computed from older measured values and an estimate of DO content from 1893 (gray-filled circles). The dashed line across the graph indicates the oxygen standard. See the General data and data analyses subsection in the Methods section for more detail.

Apparent oxygen utilization (AOU) modeling—The AOU concept comes from Redfield et al. (1963), see comments on application in Discussion. AOU modeling was performed for the Delaware Estuary in summer months using UD data for two 5-yr periods, 1978–1982 and 1999–2003. Data were averaged for different salinity intervals (< 3 , 3–9, 9–15, 15–21, 21–27, > 27 salinity) so that each AOU value was based on 5–17 points and the individual time period curve was based on a total of ~ 50 values. There was a consistent cooperative research survey program run between the marine laboratories of the UD and Rutgers University in the 1950s. Data from that program, which were available in a cruise data report (Kupferman 1971), were used to compare to our more modern data. About 75 individual samplings were used for the 1954–1957 AOU curve. With both those older data and those from our database, I calculated theoretical DO from the ambient temperature and salinity of the sample and subtracted the measured DO. A positive AOU value indicates that the waters were undersaturated, and a negative value indicates supersaturation.

Results

At Sta. 12 in the urban river region, the 40-yr record documented a large increase in dissolved oxygen from about 1970 to 1990 (Fig. 3A). A regression line of the 5-yr running averages from 1970 through 1990 showed a

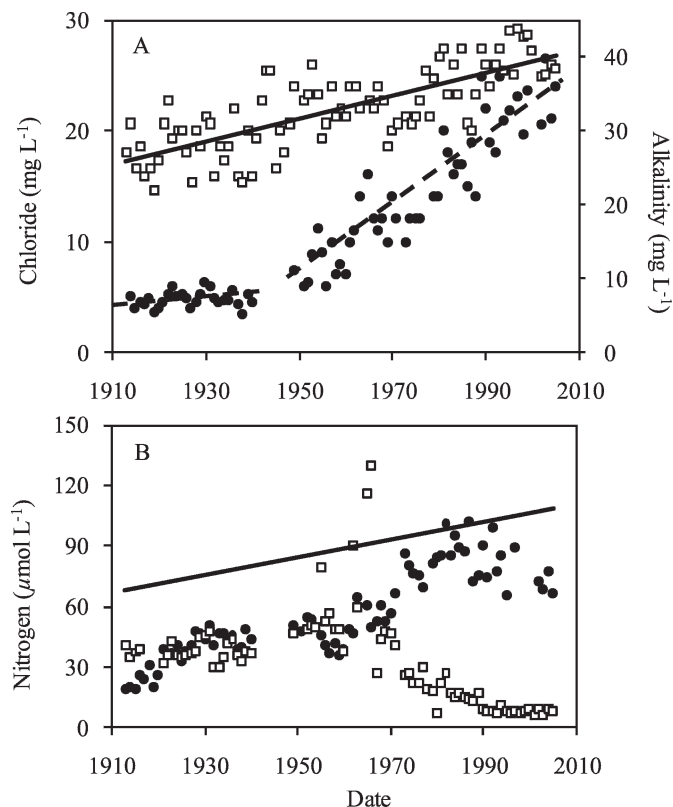


Fig. 5. Chemical concentrations in the Delaware River from City of Philadelphia Water Department monitoring from 1913 through 2005 (near Sta. 7 in Fig. 1). Data compiled into electronic file by N. Jaworski (pers. comm.) from records in the Philadelphia Water Department. (A) Chloride concentrations (solid circles) and total alkalinity concentrations (open squares). (B) Concentrations of nitrate (solid circles) and ammonium nitrogen (open squares); trend line for total dissolved inorganic nitrogen given as solid line.

significant annual increase of $10.4 \mu\text{mol L}^{-1}$ ($r^2 = 0.95$, $p < 0.001$). Low DO concentrations occurred over an appreciable length of the urban river, and can be characterized as a DO “sag.” The DO sag can be seen by plotting average summer DO concentrations on sample transects down the estuary (Fig. 3B). The DO sag, although large, did not extend into the lower bay. A consequence of this is that there appeared to be no systematic time trend in DO concentration in the mid- and lower bay (Fig. 3B). For Sta. 22 in the mid-bay, a regression similar to that in Fig. 3A, of DO against a 40-yr time period (not shown), had a slight annual decrease in average DO of $0.9 \mu\text{mol L}^{-1}$, which was not significant ($r^2 = 0.13$).

A 125-yr summertime DO composite picture for the urban Delaware River was developed to explore the time duration of the oxygen depression (Fig. 4). It started with close to saturation DO concentration in the late 19th century, showed close to zero DO in the mid-20th century, and is close to saturation again today. This combination of data and modeling analyses, described in the Methods, is further evaluated in the Discussion.

The total alkalinity (TA) and chloride (Cl^-) content in the urban river near our Sta. 7 (Fig. 1) show pronounced

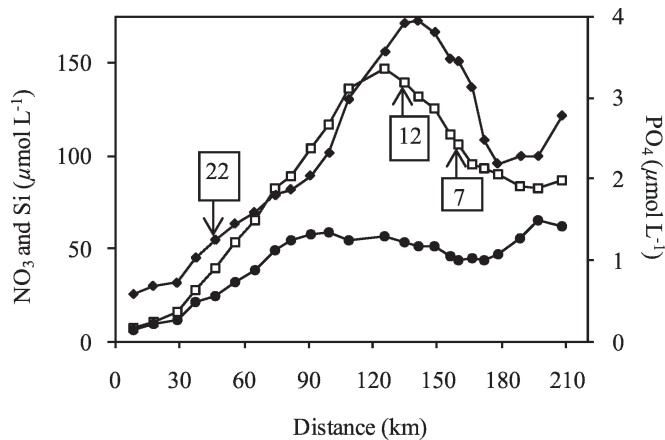


Fig. 6. Average present-day concentrations of nitrate, NO_3 (open square), phosphate, PO_4 (solid diamond), and silicate, Si (solid circles) along the length of the Delaware Estuary. The annual average is based on our data from monthly sampling in 1986–1987. Locations of Stas. 7, 12, and 22 shown.

increases in the past 90 yr (Fig. 5A). The more complex 90-yr trends of nitrate (NO_3) and ammonium (NH_4) nitrogen concentrations for the same period (Fig. 5B) are discussed below.

A transect with annual average concentrations of NO_3 , PO_4 , and silicate is shown in Fig. 6. These modern concentrations have been relatively constant over the past two decades (Sharp et al. 2009). Sta. 7, near the Torresdale intake for the Philadelphia Water Department, was the location of the 80-yr records shown in Fig. 5. Sta. 12 was the location of the data shown in Figs. 3A, 4. The Sta. 12 location was about 20 km farther downstream from Sta. 7 and, as can be seen in Fig. 3B, was in an area that had much greater DO demand in the past than did the Sta. 7 location. Trends in nutrients can be seen with the DRBC data set using the same river (Sta. 12) and bay (Sta. 22) locations discussed above for DO. The NH_4 concentration at Sta. 12 showed a large decrease after the late 1960s (Fig. 7A); a linear regression of 5-yr running average NH_4 values for 1970–1990 gave a decrease of $4.5 \mu\text{mol L}^{-1} \text{yr}^{-1}$ ($r^2 = 0.95$). The high NH_4 concentrations of the late 1960s occurred in the urban river and extended into the bay (Fig. 7B). Most of the DIN pool in the urban river consisted of NH_4 in the 1960s, 40–80% in the summer and up to 90% in the winter. In contrast, there was much less reduced nitrogen today as can be seen with the 1997 summer nitrogen pools (Fig. 7C); on the order of 90–99% of the DIN in the summer was found as NO_3 .

The trend for total phosphorus (Total P) for the same urban river station is shown in Fig. 8A. The decrease in Total P concentration was more abrupt and the present-day concentration appeared to have been achieved earlier than that for NH_4 (P in early 1980s and N in late 1980s). A linear regression analysis of the 5-yr average Total P values from 1970 to 1983 indicated a decrease of $2.21 \mu\text{mol L}^{-1} \text{yr}^{-1}$ (r^2 of 0.91). The large decrease in Total P gave rise to a large change in the molar ratio of N to P throughout the tidal river and partially down into the estuary (Fig. 8B). It can be seen that in the past, the N:P ratio was below the

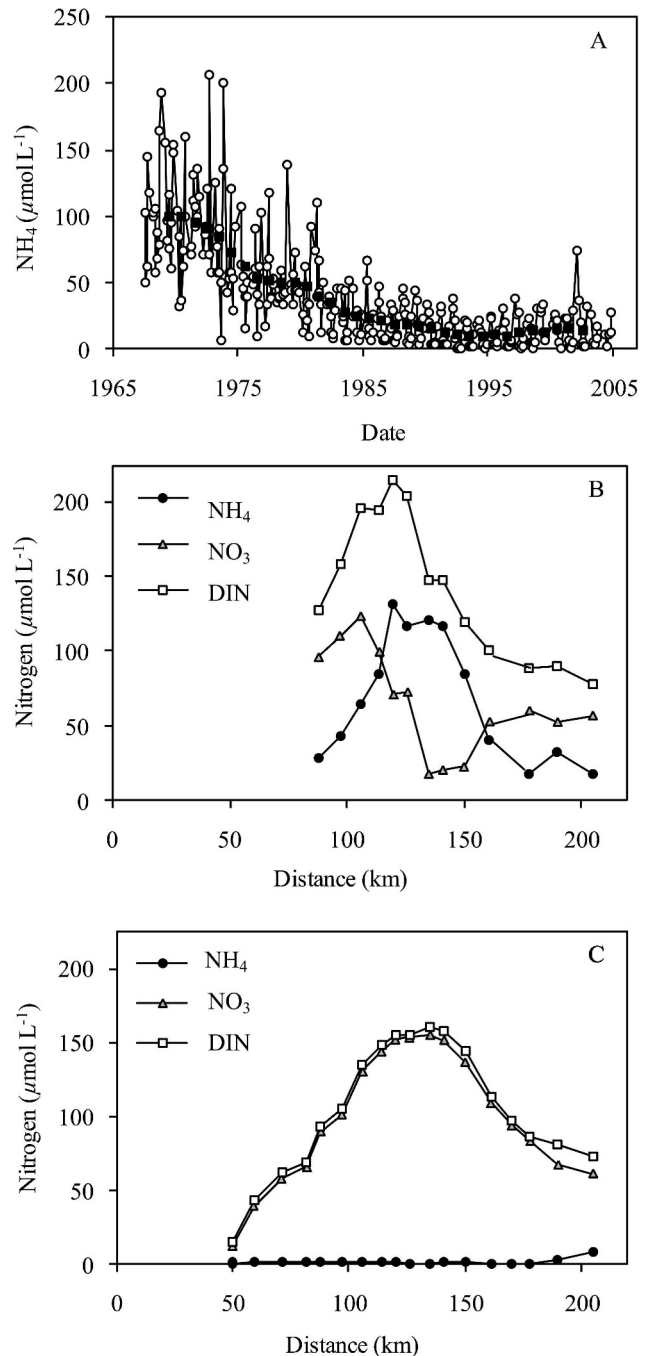


Fig. 7. Nitrogen concentrations in the Delaware Estuary from DRBC Boat Run sampling. (A) Ammonium (NH_4) concentrations shown for Sta. 12; average monthly values shown as open circles; running 5-yr average concentrations shown as solid squares. (B) Average July 1967 nitrogen concentrations along the length of the Delaware Estuary, NO_3 = nitrate, DIN = total dissolved inorganic nitrogen. (C) Similar average July values for 1997.

Redfield ratio for most of the urban river and down into the bay. Today, it is considerably above the Redfield ratio except in the mid-bay region.

Primary production was evaluated with seasonal plots of production normalized to biomass (P : B) in Fig. 9A. In the spring, the maximum biomass of the year was found in the

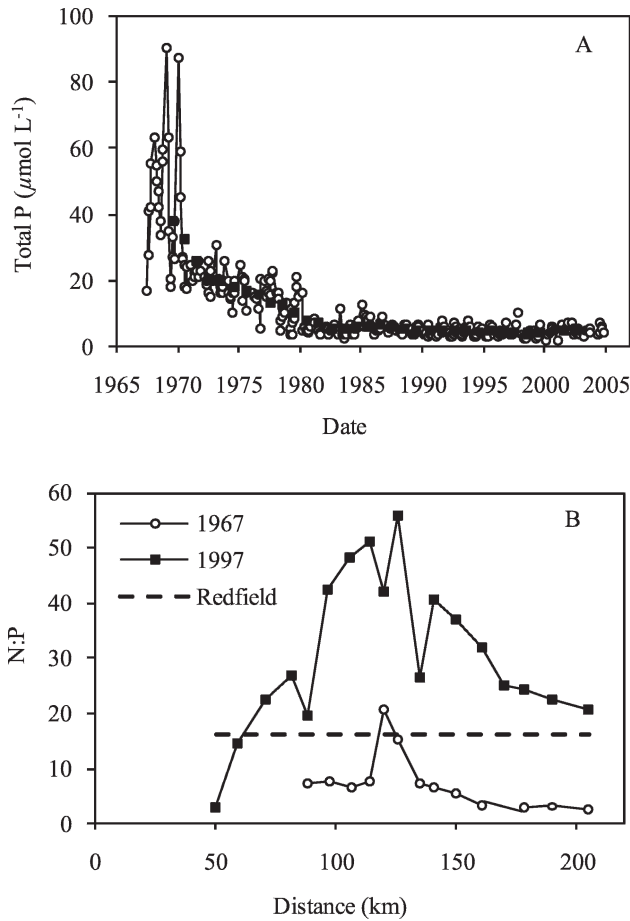


Fig. 8. Total phosphorus (Total P) concentrations in the Delaware Estuary from DRBC Boat Run sampling. (A) Total P concentrations shown for Sta. 12; same symbols and data source as Fig. 3A. (B) Ratio of DIN to Total P for summers of 1967 and 1997 along the length of the Delaware Estuary. The Redfield ratio is shown as a dashed line.

mid-estuary, so that individual chlorophyll concentrations were in the 40–70 $\mu\text{g L}^{-1}$ range in the area of 40–60 km from the bay mouth (not shown). The P:B ratio was elevated slightly compared to the rest of the estuary, but was not high compared to the summer ratio (Fig. 9A). In summer in the upper tidal river, the P:B ratio was high and chlorophyll concentrations were high, average value of $> 25 \mu\text{g L}^{-1}$. The highest P:B ratio overall occurred in the summer in the mid-bay with an average of about 10 μg chlorophyll L^{-1} . No clear trend was seen when the P:B ratio was plotted against the DIN concentration (Fig. 9B) and low production occurred at the highest DIN concentrations. Not only was there not a direct positive correlation when the P:B ratio was plotted against NH_4 concentration, there was an indication of low production at all NH_4 concentrations $> 10 \mu\text{mol L}^{-1}$ (Fig. 9C).

To test for a correlation between primary production and AOU, samples were used from the salinity gradient of the estuary in summer months in our 1980–2003 database (Fig. 10A). While there was considerable scatter, the correlation was significant ($r^2 = 0.59$, $p < 0.001$). There was sufficient short-term, day-to-day variability in chloro-

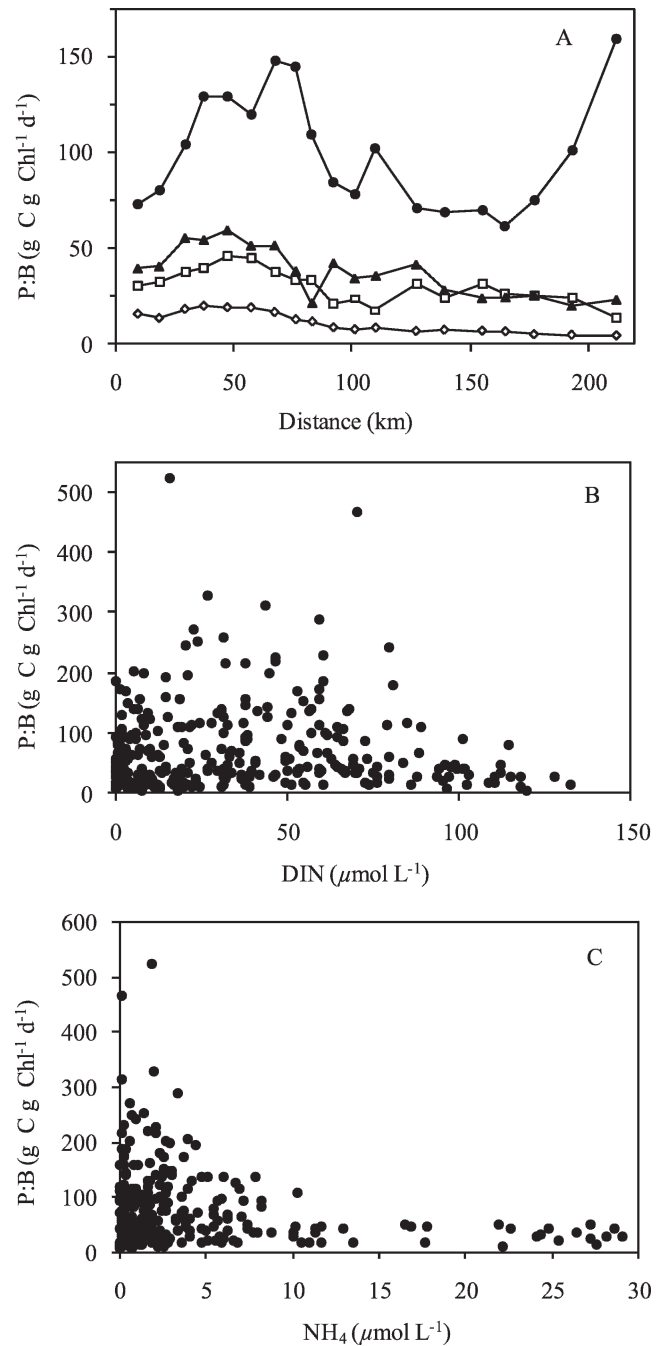


Fig. 9. Primary production normalized to chlorophyll biomass (P:B) for samples from the Delaware Estuary (1980–2003). (A) P:B along the length of the Delaware Estuary with average values separated by season: winter (open diamond), spring (open square), summer (solid circle), fall (solid triangle). (B) P:B vs. ambient total dissolved inorganic nitrogen (DIN) concentration for only mid- and lower bay for only spring and summer seasons. (C) P:B vs. ambient ammonium nitrogen (NH_4) concentration for mid- and lower bay for spring and summer seasons.

phyll concentration and primary production that it is difficult to discern trends with our limited irregular sampling. The time series summer data were plotted for two stations to look for trends over 25 yr. Sta. 14 is at the

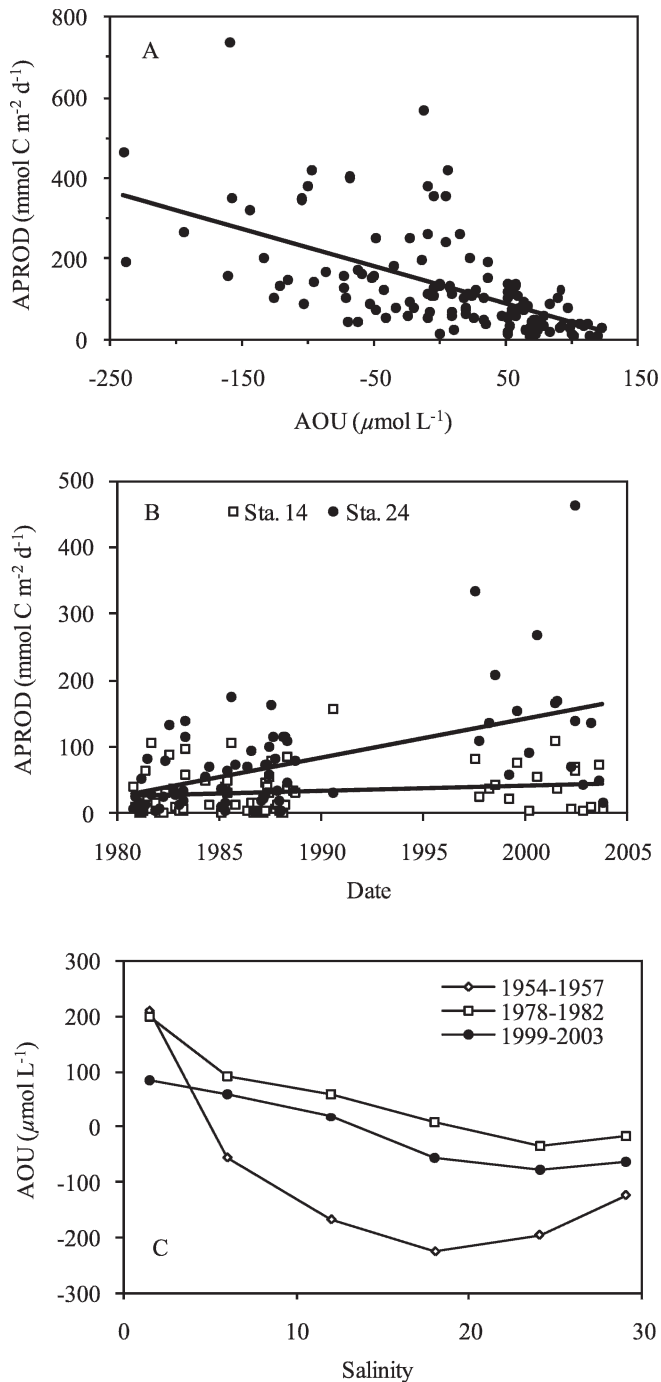


Fig. 10. Apparent oxygen utilization (AOU) and depth-integrated areal primary production (APROD) in the Delaware Estuary. AOU was calculated from theoretical saturation dissolved oxygen (DO) concentration, based on ambient temperature and salinity, from which the measured ambient DO concentration was subtracted. Areal primary production was calculated from depth-integrated 24-h incubations with H^{14}CO_3 . (A) APROD vs. AOU for summer months only along the full length of the salinity gradient of the Delaware Estuary from 1980 to 2003. (B) Summer APROD trends from 1980 to 2003 for a station at the head of the salinity gradient (Sta. 14) and one in the mid-bay (Sta. 24). (C) AOU calculated for dissolved oxygen (DO) samples from Delaware Estuary. Data from UD database used for the 1978–1982 and 1999–2003 curves; data from Jersey-Delaware cruises used for 1954–1957 curve (see the General data and data analyses subsection in the Methods section for more detail).

head of the salinity gradient (0 salinity); Sta. 24 is in the mid-bay, near the year-round primary production maximum (22–27 salinity). The regression analyses showed no change over the 25-yr period for chlorophyll concentration at either station (not shown) and no significant change in areal primary production for Sta. 14 (Fig. 10B), but a significant increase between primary production and time at Sta. 24 ($r^2 = 0.53$, $p < 0.001$).

Summer AOU curves were made by averaging AOU values for different salinity intervals for three 5-yr periods: the mid-1950s, the late 1970s to early 1980s, and the present period (Fig. 10C). At the lowest salinity interval (0–3 salinity), all three curves showed positive AOU values (oxygen undersaturation) and the 1950s and 1970s record showed similar values of 200–211 $\mu\text{mol L}^{-1}$, while the 1990s value dropped to 86 $\mu\text{mol L}^{-1}$. At the highest salinity interval (> 27 salinity), near the mouth of the bay, the AOU value was negative (–16 to –123 $\mu\text{mol L}^{-1}$ in all three periods), indicating slight net autotrophy. The largest difference over time was in the mid-estuary region (12–24 salinity range). The entire 1999–2003 curve showed a more negative AOU compared to the 1978–1982 period, and the 1950s AOU curve was considerably lower than either of the later curves. At the midpoint of 18 salinity, the 1950s value was –225 $\mu\text{mol L}^{-1}$, contrasted to 1970s value of +9 $\mu\text{mol L}^{-1}$.

Discussion

Dissolved oxygen in the Delaware River during the past century—The urban river Sta. 12, where the large DO increase was seen, was the location in the estuary where the lowest summer DO was usually found (Fig. 3B). This is a good location to look at improvements in water quality. Although the record was noisy, there were both large seasonal variations and a distinct long-time increase in DO concentration (Fig. 3A). It should be noted that these data were from surface-water samples and that the well-mixed water column at this location in the tidal river had, and continues to have, relatively uniform DO concentrations from surface to bottom. The cleanup effort for water quality of the Delaware River was based on the low summer DO (FWPCA 1966) and the Clean Water Act (CWA) standard of 3.5 mg L^{-1} ($\sim 219 \mu\text{mol L}^{-1}$) was the guide for improvements in effluent demand. Before 1990, the summer DO concentrations were consistently below this standard and, since then, they have almost always been above the standard (Fig. 3A). This result demonstrates a successful recovery from chronic hypoxia.

The DO sag in 1972 extended over 60 km along the estuary (Fig. 3B). The depth and breadth of the sag was partially alleviated by 1982 and since the early 1990s, the average summer DO concentrations have been above the CWA standard throughout the estuary. The DO sag was alleviated by improvements in water quality, especially upgrades of the large major sewage treatment plants in the greater Philadelphia area (Albert 1988). The waters near the head of tide (210 km) and in the mid- and lower bay (50–0 km) were close to saturation throughout this four-decade period; equilibrium saturation for summer temper-

ature around 30°C is about 450 $\mu\text{mol L}^{-1}$. The hypoxia has been attributed (Sharp 1994) to a primary BOD, resulting from reduced carbon and nitrogen in sewage effluents (allochthonous inputs). This demand is independent of algal production in the water due to nutrient enrichment. Thus, the phenomenon is not the excess algal biomass secondary BOD symptomatic of eutrophication. The heavy BOD followed by improvements in the Delaware Estuary was similar to that of a number of European riverine estuaries; an especially good example is the Thames River downstream of London, England (Tinsley 1998). The essentially zero summer DO observed in the Thames up until the 1960s had improved to about 50% saturation by 1980 (Andrews and Rickard 1980). Unlike the urban river, the mid-estuary station had no long-term change and the average summer values remained > 90% saturation throughout the period of record (1972–2005). Some subtle differences in the lower bay chemistry and primary production during this period, and very large differences in a longer, 60-yr, time frame are discussed below.

The DO time trend (Fig. 4) included the well-documented regular increase of the past 40 yr and low values in the period of 1920–1970, based on less regular direct data. Anecdotal information (Stutz 1992) indicated that the waters were close to anoxic in the warm summer months in mid-20th century. However, because of the very large shad landings in the late 19th century, these waters must have been well oxygenated at that earlier time. Therefore, the river must have contained high oxygen concentrations at the end of the 19th century, as it does today, and had severe hypoxia over a period of 50 yr in the middle of the 20th century. It can also be seen (Fig. 4) that summer average values were chronically below the water quality standard from about 1910 to 1980.

In some of the cited reports and in archived newspaper articles, there was discussion of stinking river waters and strong hydrogen sulfide odors arising from the river, a condition consistent with the very low average DO concentrations (Fig. 4). A number of anecdotal comments referred to concerns by the U.S. military about problems using the river as a port. A newspaper article during World War II is a good example with the quote: “The noxious fumes most Philadelphians accept philosophically as the ‘river smell’ are threatening the usefulness of Philadelphia as a port” (Anonymous 1944). In the article, it was stated that hydrogen sulfide was so strong as to discolor paint on the hulls and internal walls of navy ships (the classic phenomenon of lead-based paint discoloring from reaction of hydrogen sulfide to form lead sulfide) and tarnishing silverware and trophies aboard ships. Even if monthly average DO concentrations were above zero, there must have been many days in the summer when the waters were anoxic because only when the DO concentration is near zero will sulfide be present in the water (Millero 1996).

A survey was made early in the 20th century “to protect the public health by maintaining the rivers as fit sources of water supply, to provide for the comfort of the citizens by restoring the sewage laden streams to a clean condition, to improve the port by providing a clean, sanitary harbor” (Webster et al. 1914). The report included annual summer

DO measurements (July–August) for both 1912 and 1914 in the Delaware River at Arch Street (very near our Sta. 12). The average oxygen percent saturation values were used to calculate concentrations for these two times. These values fit relatively well with the population-modeled points (Fig. 4), possibly suggesting an even more rapid DO decrease in the early part of the 20th century or a slightly lower starting point for 1890 than the saturation value used.

All of the recent DO data came from analysis using the Winkler titration (Winkler 1888). Presumably, the Winkler titration was also used for the data as early as 1912, since the method was developed and widely used before the beginning of the 20th century. In the late 19th century, there was concern about the quality of the Philadelphia water supply and an 1884 report contained survey data including DO concentrations (Leeds 1884). This report included evaluation of DO content and concluded that the data presented resulting from several methods were consistent. Using July 1883 data (reported as cc per 1000 cc), an average value was calculated as 468 $\mu\text{mol L}^{-1}$. The DO content for the Delaware River in Philadelphia was similar to that from the supply streams in the upper drainage basin from the same time, so there is an expectation that the DO should be close to saturation. Discussion in the Leeds report indicated that the oxygen demand should not be large and that the waters were well oxygenated. “But a moment’s reflection will show that the total sewage of Philadelphia, if poured into the Delaware, would change the composition of so vast a volume of water by extremely minute amounts” (Leeds 1884). The calculated 1883 DO value is almost identical to the saturation value (Fig. 4). It is interesting to note that the river waters apparently did not have much oxygen depletion then in spite of the fact that there was a significant typhoid fever epidemic attributed to river water according to the Leeds report. The annual death rates from typhoid in the late 1880s of 60–70 per 100,000 residents is contrasted to fewer than 0.5 per 100,000 by the early 1940s (Jenne 1943), after routine water filtration was initiated. Ironically, the period when typhoid deaths were minimized is also the time when the effect of DO demand reached its maximum. The concerns about microbial pathology and chemical water quality appeared to be somewhat independent of each other.

Long-time chemistry record in the tidal river—The century-long chemical record showed that until about 1950, the Cl^- content was relatively low and constant (Fig. 5A), and since 1950, there was an increase. This increase appears to correlate with more use of road salts that accompany increased automobile traffic. It is possible that more extensive disinfection of sewage effluents and sewage treatment plant upgrades (Albert 1988) also contributes to increased Cl^- . The increase resulted in Cl^- content today that was 5 times that of a century ago. The TA showed an increase that is < 50% overall and was fairly linear (Fig. 5A). The increase in TA probably partially reflected the influence of increasing NO_3^- concentration over this time period. There was an increase in NO_3^- from a

value of $\sim 20 \mu\text{mol L}^{-1}$ to $> 60 \mu\text{mol L}^{-1}$ (Fig. 5B). The increase in NH_4 through the 1960s was followed by a decrease. The total DIN ($\text{DIN} = \text{NO}_3 + \text{NH}_4$) doubled from 1913 to the 1980s and then decreased slightly. The increase in DIN illustrated in the Delaware River was similar to trends found in many other estuaries in the U.S. during this period (Jaworski and Hetling 1996).

The trends shown in Fig. 5 were consistent with the increased effect resulting from population growth in the greater Philadelphia area in the early 20th century that caused the extensive DO depletion shown in Fig. 4. While the DO depletion had a major detrimental influence on the biology of the river and bay system (Stutz 1992; Albert 1988), the increases in Cl^- and TA probably had little or no direct effect on the estuarine biology. Since the changes in DO concentration were accompanied by increases in the nutrient concentrations, the relationship between nutrients and ecosystem response was explored.

Nutrients in the river and bay over the past 40 yr—Through examination of the present-day nutrient distribution (Fig. 6), it can be seen that both NO_3 and PO_4 concentrations were elevated at the head of the tide (Sta. 1) compared to what might be expected in a pristine river (Sharp et al. 1982). These nutrients showed peaks over the upper river concentrations in the area of our Stas. 11–14 in the urban river (120–150 km), largely due to the effects of sewage treatment plant effluents. All the nutrients showed decreases due to dilution going down the salinity gradient, from about 120 km to the mouth of the bay.

The trend analysis of NH_4 concentrations in the urban river (Fig. 7A) showed a large decrease from the late 1960s through the 1980s. Seasonal variations from microbial activity, higher in winter and lower in summer (Cifuentes et al. 1989), can also be seen along with the longer time trend. There was a long-time increase in NO_3 concentration (not shown) with the decrease in NH_4 concentration. The effect of these changes can be seen with the large difference in summer N speciation (Fig. 7B,C). In addition, there was an overall slight decrease in total DIN. By comparing these trends, it is possible to look at the correlation of DO, NH_4 , and DIN. For the period of 1969–1989, a linear regression of the 5-yr running average NH_4 concentrations gives a decrease of $4.5 \mu\text{mol L}^{-1} \text{yr}^{-1}$. This is the same time in which the increase in DO, discussed above, was seen. The result is a decrease in nitrogenous oxygen demand coincided with the DO increase. A 5-yr running average of DIN values for 1969–1989 (not shown) gave a decrease of $2.2 \mu\text{mol L}^{-1} \text{yr}^{-1}$. Subtracting the DIN decrease from the NH_4 decrease, I attribute the equivalent of $2.3 \mu\text{mol L}^{-1} \text{yr}^{-1}$ to oxidation of NH_4 to NO_3 . This nitrification process has a stoichiometric ratio of N:O of 1:–4 (Kaplan 1983). A simple interpretation is that the decreased NH_4 concentration from oxidation could account for an increase in DO concentration of $9.2 \mu\text{mol L}^{-1} \text{yr}^{-1}$, which was similar to the measured increase of $10.4 \mu\text{mol L}^{-1} \text{yr}^{-1}$. While the DO concentration was influenced by air–water exchange as well as microbial activity, it is probable from this calculation that a significant part of the oxygen demand in the past was due to nitrification. In addition,

it is possible that some of the DIN decrease was probably due to denitrification in the sediments. Delaware Estuary water quality management today recognizes “nitrogenous biochemical oxygen demand” as a primary target for water quality improvements (DELEP 1996).

The large change in N speciation between the late 1960s and 1990s (Fig. 7B,C) illustrated the success in sewage treatment plant upgrades where the residence time was longer (Albert 1988) and effluents apparently contain less reduced nitrogen than today. In addition, higher DO in the river probably also contributed to increased nitrification rate. The temporal trend at Sta. 22 in the Delaware Bay (not shown) had a decrease in NH_4 and DIN from the late 1970s through late 1980s even though there was no change in DO concentration at this location.

The effect of the improvements in sewage treatment during the 1970s through 1980s (Albert 1988) were illustrated in the concurrent decrease in NH_4 and increase in DO. A change also occurred with the phosphorus concentrations (Fig. 8A), but with a different pattern and for a different reason. The decrease of phosphorus in the Delaware Estuary and declines in other mid-Atlantic and New England estuaries (Jaworski and Hetling 1996; Roman et al. 2000), in European rivers (Billen et al. 1991), and in Tokyo Bay (Kawabe and Kawabe 1997) can be concluded to be partially due to the shift from phosphate-containing detergents (the phosphate detergent ban). Improvements in sewage treatment with increased removal of P in sludge probably also contributed to the decrease.

With the decrease in Total P, the molar ratio of N:P changed in much of the estuary (Fig. 8B). The well-known Redfield ratio of 16:1 for N:P (Redfield et al. 1963) has been used in aquatic systems as a guideline for evaluating the comparative growth limitation by N or P for phytoplankton (Hecky and Kilham 1988; Pennock and Sharp 1994). According to that guideline, the urban Delaware River waters would appear to have been N-limited in the past and to be P-limited today. However, with high nutrient concentrations, there was probably not strong nutrient limitation; but the shift in relative N and P controls may have had an influence on the overall microbial biogeochemistry. The high P in the river was also seen in the lower bay in the past. A plot of Total P at Sta. 22 is similar to that in Fig. 8A with values about half of those in the river (not shown). The N:P ratio in the bay remained fairly consistent over the past 40 yr with 5-yr running average values near or below Redfield ratio. It should be pointed out that Total P was used for the N:P ratio since only Total P data were available for the full time period. We have found that the majority of the particulate P was loosely sorbed PO_4 on particles which desorbed in seconds (Lebo 1991; Lebo and Sharp 1992). Thus, probably most of the Total P was readily available for biological use.

Primary production and nutrients—The large increase of nitrogen and phosphorus nutrients in nearshore waters of the world is the reason for concern about estuarine nutrient eutrophication (Howarth and Marino 2006). An underlying observation is that when phytoplankton biomass as

chlorophyll was plotted against nitrogen loading or concentration from multiple water bodies that there was a strong positive correlation (Nixon and Pilson 1983). This portrayal gave a good composite picture of global eutrophication, but it overemphasized the idea of a direct ecosystem response to nitrogen. In estuaries like the Delaware, where nutrient concentrations were elevated above natural levels and where strong light limitation, nutrient ratios, and other factors also influenced phytoplankton response, there was no linear relationship between a single nutrient and phytoplankton biomass or production (Sharp 1994; Yoshiyama and Sharp 2006).

The plot of maximum production per volume normalized to chlorophyll biomass (P:B) can be interpreted as a physiological response to environmental controls. Throughout the estuary, there was greater production in summer than in the other seasons (Fig. 9A). In the spring, summer, and fall, the relatively low P:B ratio near the mouth of the Delaware Bay appeared to be related to nutrient limitation (Pennock and Sharp 1994). There was a fairly pronounced minimum in production in the region of the turbidity maximum (~100 km) in spring, summer, and fall, which was due to light limitation (Pennock and Sharp 1986). A comparatively low P:B ratio in the urban river region was attributed to contaminant inhibition (Sharp 1994; Yoshiyama and Sharp 2006).

It is possible to evaluate the influence of nutrients on primary production by directly comparing ambient nutrient concentration measured at time of the sample collection to the production measured on the same sample. The phytoplankton biomass (chlorophyll) or areal primary production was not correlated to nitrogen nutrient concentration throughout the estuary (not shown). The mid- and lower bay regions have clearer waters with less light limitation and no indication of contaminant limitation of primary production. Production here in the spring and summer seasons was higher than in the fall and winter. However, the lack of increase in production with increasing N in this region (Fig. 9B) suggested that any influence of increased nutrients must be expressed on a time scale longer than ambient concentration and probably more through an ecosystem level, not as a direct response by primary producers. Smith (2007) has also recently suggested the need for using direct primary production measurements to understand eutrophication although he suggested that the P:B ratio was not the best metric. I have plotted chlorophyll, volume-based maximum production, depth-integrated areal production, and P:B against total DIN, individual nitrogen nutrients, phosphate, and silicate. In all cases, these plots show no simple systematic empirical relationship. I prefer using the P:B ratio rather than chlorophyll or production alone because normalizing for biomass appeared to give a better physiological indicator than primary production alone.

The lack of positive relationship between the P:B ratio and NH_4 concentration (Fig. 9C) also showed low production with elevated NH_4 concentration (Fig. 9C). This figure and figures based on data subsets for individual regions and seasons (not shown) were examined to discover that the maximum production was found at 2–5 $\mu\text{mol L}^{-1}$ NH_4 ,

with considerably lower production > 10 $\mu\text{mol L}^{-1}$. This somewhat surprising observation, discussed by Yoshiyama and Sharp (2006), was recently shown to also occur in the San Francisco Bay (Dugdale et al. 2007).

Simulated primary production over the past 50 yr—For the analyses of areal primary production and AOU, samples only from the salinity gradient were used (Fig. 10); on the distance axis, this represented the range from 120 to 0 km. At the upper end of this region, severe oxygen depletion was seen in the past. In the mid- and lower bay, oxygen concentrations have been near or above saturation in summer throughout the 40-yr period of analyses as was discussed above.

While our direct measurements of primary production cover only the last 25 yr, it was possible to evaluate the historical primary production with surrogate data. The AOU concept was developed to assess the integrated influence of oxygen demand in subsurface oceanic waters (Redfield et al. 1963). In the original AOU concept, the authors postulated that isolated oceanic subsurface waters would have no influence on DO concentrations other than in situ microbial processes; being removed from atmospheric mixing and below the photic zone, these waters would experience DO decreases from respiration.

The AOU concept has been extended to seasonally stratified coastal waters (Sharp and Church 1981). In that analysis, we postulated that the summer thermocline isolated the bottom waters and exchange with surface waters would only occur slowly by diffusion controlled by concentration gradients. Since air–water exchange can occur in surface waters, it might appear that to extend the concept to surface estuarine waters is unwarranted. However, in the presence of very high microbial metabolism, the air–water exchange becomes comparatively slow (Sharp et al. 1982; Culbertson 1988). As was seen in Figs. 3A and 4, the very high microbial oxygen demand caused chronic average low summer DO content in surface waters because microbial demand was in excess of what atmospheric exchange could resupply. Also, we have often measured 120–150% oxygen saturation in surface waters of the mid–Delaware Bay in the summer with high levels of primary production. In this case, photosynthetic production was in excess of what atmospheric exchange could remove.

Highly positive or negative AOU values probably indicated a cumulative multi-day influence in the absence of strong wind to increase air–water exchange. Each primary production value was the result of a 24-h incubation started at the time the ambient DO was measured. The measured DO value used to calculate AOU probably represented the influence of metabolic activity integrated over many hours prior to sample collection. Because individual primary production and DO values represented the varying influences of the immediate time period (multiple hours to a few days), AOU values gave an approximate representation of the oxygen exchange over several days. In the plot in Fig. 10A, positive AOU values (less than saturation DO) were found at low production and negative AOU values (DO supersaturation) at high production. This use of average

AOU analysis is suggested for large-scale evaluations to look at comparative net autotrophic or heterotrophic balance; in the present use, it does show a significant positive correlation to primary production.

The production increase in recent years in the lower bay (Fig. 10B) was consistent with other indications that there was a decrease in phosphate limitation for production. Because of changes in phosphate sorption and desorption from changing water chemistry, there was an increase in delivery of phosphorus from the tidal river region to the lower bay in the 1980s (Lebo 1991; Lebo and Sharp 1992, 1993). The increase in phosphate in the lower bay was different from and independent of the decrease in Total P in the river in the 1970s. An alternation has been shown between light limitation, N-limitation, and P-limitation (Pennock and Sharp 1994). The P-limitation occurred in the late spring and probably determined the amount of organic matter available for summer nutrient regeneration as the ultimate control of summer primary production (Cifuentes et al. 1988, 1989).

Examining the AOU curves (Fig. 10C), the recent decrease in AOU at the lowest salinity was consistent with changes between the low oxygen concentration shown in Fig. 4 for the tidal river in the 1950s and 1970s and the higher concentrations of today. This is mentioned to show that the indirect AOU model exercise with broad averaging gives information consistent with the more direct monitoring data. The more negative AOU curve in the modern vs. late 1970s (Fig. 10C) was consistent with the increased primary production shown in Fig. 10B. The even more negative AOU values for the mid-estuary region for 1954–1957 appeared to indicate that there was a considerably higher primary production in the 1950s compared to modern times. In fact, by comparing the 1950s AOU curve to the two modern ones, it appeared that the entire saline portion of the estuary had higher primary production in the past than it has today.

Although there were no data of direct measures of primary production from the 1950s, fisheries yields of shellfish and finfish were higher in that time period than today (Sutton et al. 1996; DELEP 1996). The high fisheries yields suggested that populations of higher trophic levels were not notably smaller than today. An inference is that there was higher primary production supporting higher secondary production at a time when nutrient concentrations were also very high.

I suggest that the Delaware Estuary is not an unusual environment, but that instead, there are generic lessons to be learned from the long-time perspective described herein. While increased nutrient loading from anthropogenic activities probably can cause more direct deterioration in some estuaries than others, there is need for a more thorough evaluation of microbial biogeochemistry in individual estuaries, rather than generic simple indirect correlations. As has been cautioned recently, nutrient removal will not necessarily result in return to estuarine water quality conditions similar to those before nutrient enrichment (Duarte et al. 2009). Here, I also provide caution on overinterpretation of expected influences from elevated nutrient concentrations. Anthropogenic nutrient

enrichment certainly causes problems, but it is necessary to recognize that other anthropogenic influences also are involved in the deterioration of estuarine and coastal ecosystems. We must recognize that all aquatic ecosystems are complex and that the combination of nutrient enrichment, habitat alteration and destruction, depletion of higher trophic levels, and inhibition by contaminants other than nutrients all contribute to deterioration of desired amenities. The overabundance of a single nutrient is not necessarily the cause of the estuarine deterioration. It is critical that we clearly understand the relationship between nutrients and phytoplankton response in waters where we have inadvertently enriched with nutrients. This reevaluation is all the more urgent because at the other end of the nutrient spectrum, the oligotrophic open ocean, there is continuing interest and concern about purposeful fertilization to increase algal response and draw down anthropogenic excess atmospheric CO₂ (Buesseler et al. 2008; Cullen and Boyd 2008).

Acknowledgments

Many individuals assisted in the collection and analyses of samples over about 30 yr. Seventeen former and current graduate students, 10 research assistants, 2 postdoctoral associates, and 5 faculty colleagues were heavily involved in assisting on research cruises. While not naming them individually, their contributions are acknowledged through citations of many of their Delaware Estuary publications in this overview paper. In addition, hundreds of high school students, undergraduate students, other graduate students, and local citizens have assisted as volunteers on research cruises. Norb Jaworski, retired from the U.S. Environmental Protection Agency (EPA), gathered the raw data on which Fig. 5 is based. Ed Santoro and Dick Albert of the Delaware River Basin Commission helped obtain data and provided advice and insight over a period of years. I thank Gary Burlingame, Adam Levine, and Chris Crockett of the Philadelphia Water Department for assistance in finding dissolved oxygen data from earlier years. Norb Jaworski, Ed Santoro, Dick Albert, Gary Burlingame, and Sue Kilham made valuable comments on an earlier version of this paper. The original data for this paper come from numerous research efforts over the past 30 yr. A major award from the Delaware Sea Grant program (National Oceanic and Atmospheric Administration grant NA83AA-D-00017) in the early 1980s, support from the Delaware River and Bay Authority in the early 1980s, and a major award from the National Science Foundation (NSF) Chemical Oceanography Program (OCE 86-01616) in the mid-1980s helped launch the effort. A number of smaller Sea Grant awards and auxiliary sampling from a number of NSF grants in the 1990s also helped support this activity. A Cooperative Agreement (CX82961601-4) with the EPA supported assembling a coherent database and helped in development of this paper. Also, recent grants from the Chemical Oceanography Program of the NSF (OCE 0082238, OCE 0352280) helped support sampling, analysis, and data compilation over the past several years.

References

- ALBERT, R. C. 1988. The historical context of water quality management for the Delaware Estuary. *Estuaries* **11**: 99–107.
- ANDREWS, M. J., AND D. G. RICKARD. 1980. Rehabilitation of the inner Thames estuary. *Mar. Pollut. Bull.* **11**: 327–332.
- ANONYMOUS. 1944 14 Jul. Usefulness of city as port threatened by river fumes. *Philadelphia Record*.

- BAXTER REPORT. 1965. Yearly variation in dissolved oxygen, Delaware River Estuary, 1950 through 1964. For Commissioner S. S. Baxter, Water Department, City of Philadelphia.
- BILLEN, G., C. LANCELOT, AND M. MEYBECK. 1991. N, P, and Si retention along the aquatic continuum from land to sea, p. 19–44. *In* R. F. C. Mantoura, J.-M. Martin, and R. Wollast [eds.], *Ocean margin processes in global change*. J. Wiley and Sons.
- BOESCH, D., AND OTHERS. 2001. Factors in the decline of coastal ecosystems. *Science* **293**: 1589–1591.
- BRICKER, S. B., B. LONGSTAFF, W. DENNISON, A. JONES, K. BOICOURT, C. WICKS, AND J. WOERNER. 2007. Effects of nutrient enrichment in the nation's estuaries: A decade of change [Internet]. NOAA Coastal Ocean Program Decision Analysis, Series 26. Silver Spring (MD): NOAA, National Centers for Coastal Ocean Science [accessed 2008 September 01]. Available from <http://ccma.nos.noaa.gov/publications/eutrouupdate/>
- BUESSELER, K. O., AND OTHERS. 2008. Ocean iron fertilization—moving forward in a sea of uncertainty. *Science* **319**: 162.
- CARACO, N. F., J. J. COLE, AND D. L. STRAYER. 2006. Top down control from the bottom: Regulation of eutrophication in a large river by benthic grazing. *Limnol. Oceanogr.* **51**: 664–670.
- CARSTENSEN, J., D. J. CONLEY, J. H. ANDERSEN, AND G. AERTEBERG. 2006. Coastal eutrophication and trend reversal: A Danish case study. *Limnol. Oceanogr.* **51**: 398–408.
- CIFUENTES, L. A., M. L. FOGEL, J. R. PENNOCK, AND J. H. SHARP. 1989. Biogeochemical factors that influence the stable nitrogen isotope ratio of dissolved ammonium in the Delaware Estuary. *Geochim. Cosmochim. Acta* **53**: 2713–2721.
- , J. H. SHARP, AND M. L. FOGEL. 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware Estuary. *Limnol. Oceanogr.* **33**: 1102–1115.
- CLOERN, J. E. 2001. Our evolving conceptual model of the coastal eutrophication problem. *Mar. Ecol. Prog. Ser.* **210**: 223–253.
- CULBERSON, C. H. 1988. Dissolved oxygen, inorganic carbon, and the acid–base system in the Delaware Estuary, p. 58–76. *In* S. K. Majumdar, E. W. Miller, and L. E. Sage [eds.], *Ecology and restoration of the Delaware River Basin*. Pennsylvania Academy of Sciences.
- CULLEN, J. J., AND P. W. BOYD. 2008. Predicting and verifying the intended and unintended consequences of large-scale ocean iron fertilization. *Mar. Ecol. Prog. Ser.* **364**: 295–301.
- DELEP. 1996. The Delaware Estuary, discover its secrets, A management plan for the Delaware Estuary [Internet]. The Delaware Estuary Program comprehensive conservation and management plan. Philadelphia, Pennsylvania: Delaware Estuary Program [accessed 2008 September 01]. Available from <http://www.delawareestuary.org/scienceandresearch/datasetsandreports/localandregional.asp/>
- DIAZ, R. J., AND R. ROSENBERG. 2008. Spreading dead zones and consequences for marine ecosystems. *Science* **321**: 926–929.
- DUARTE, C. M., D. J. CONLEY, J. CARSTENSEN, AND M. SANCHEZ-CAMACHO. 2009. Return to Neverland: Shifting baselines affect eutrophication restoration targets. *Estuar. Coast.* **32**: 29–36, doi: 10.1007/s12237-008-9111-2.
- DUGDALE, R. C., F. P. WILKERSON, V. E. HOGUE, AND A. MARCHI. 2007. The role of ammonium and nitrate in spring bloom development in San Francisco Bay. *Estuar. Coast. Shelf Sci.* **73**: 17–29.
- DURFOR, C. N., AND W. B. KEIGHTON. 1954. Chemical characteristics of Delaware River water Trenton, New Jersey, to Marcus Hook, Pennsylvania. Geological Survey Water-supply Paper 1262. U.S. Government Printing Office.
- FWPCA. 1966. Delaware estuary comprehensive study. U.S. Department of Interior, Federal Water Pollution Control Administration, Philadelphia, Pennsylvania.
- HECK, K. E., AND J. F. VALENTINE. 2007. The primacy of top-down effects in shallow benthic ecosystems. *Estuar. Coast.* **30**: 371–381.
- HECKY, R. E., AND P. KILHAM. 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on effects of enrichment. *Limnol. Oceanogr.* **33**: 796–822.
- HOWARTH, R. W., AND R. MARINO. 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over 3 decades. *Limnol. Oceanogr.* **51**: 364–376.
- INCODEL. 1960. Water quality survey—Delaware River Estuary. Interstate Commission on the Delaware River Basin, Philadelphia, Pennsylvania.
- JACKSON, J. B. C., AND OTHERS. 2001. Historical overfishing and the recent collapse of coastal ecosystems. *Science* **293**: 629–638.
- JAWORSKI, N. A., AND L. J. HETLING. 1996. Water quality trends of the Mid-Atlantic and northeast watersheds over the past 100 years, p. 980–983. *In* Conference Proceedings, Watersheds '96. American Society of Civil Engineers.
- JENNE, L. L. 1943. Philadelphia Water Department annual report, 1943. Bureau of Water, Philadelphia.
- KAPLAN, W. A. 1983. Nitrification, p. 139–190. *In* E. J. Carpenter and D. G. Capone [eds.], *Nitrogen in the marine environment*. Academic Press.
- KAWABE, M., AND M. KAWABE. 1997. Factors determining chemical oxygen demand in Tokyo Bay. *J. Oceanogr.* **53**: 443–453.
- KEACH, W. 1997. The complete poems by Samuel Taylor Coleridge. Penguin Classics.
- KILLIAM, K. A., AND W. A. RICHKUS. 1992. An assessment of fisheries landings records in the Delaware River Estuary [Internet]. Prepared for the Delaware Estuary Program, U.S. Environmental Protection Agency, Wilmington, Delaware: Partnership for the Delaware Estuary [accessed 2008 September 01]. Available from <http://www.delawareestuary.org/>
- KUPFERMAN, S. 1971. Compilation of raw data from JD Cruises I–XIV and XVI–XVII (1954–1959). Unpublished report from Graduate College of Marine Studies, University of Delaware, Newark, Delaware.
- LEBO, M. E., AND J. H. SHARP. 1992. Modeling phosphorus cycling in a well mixed coastal plain estuary. *Estuar. Coast. Shelf Sci.* **35**: 235–252.
- , AND ———. 1993. Phosphorus distributions along the Delaware. An urbanized coastal plain estuary. *Estuaries* **16**: 291–302.
- LEBO, M. L. 1991. Particle-bound phosphorus along an urbanized coastal plain estuary. *Mar. Chem.* **34**: 225–246.
- LEEDS, A. R. 1884. Preliminary report of a chemical investigation into the present and proposed future water supply of Philadelphia. Annual report of the Chief Engineer of the Philadelphia Water Department, Bureau of Water, Philadelphia, Pennsylvania.
- MALLIN, M. A., V. L. JOHNSON, S. H. ENSIGN, AND T. A. MACPHERSON. 2006. Factors contributing to hypoxia in rivers, lakes, and streams. *Limnol. Oceanogr.* **51**: 690–701.
- McHUGH, J. L. 1981. Marine fisheries of Delaware. *Fish. Bull.* **79**: 575.
- MILLERO, F. J. 1996. *Chemical oceanography*. CRC Press.
- NEWELL, R. I. E., W. M. KEMP, J. D. HAGY, C. F. CERCO, J. M. TESTA, AND W. F. BOYNTON. 2007. Top-down control of phytoplankton by oysters in Chesapeake Bay, USA: Comment on Pomeroy et al. *Mar. Ecol. Prog. Ser.* **341**: 293–298.

- NIXON, S. W. 1995. Coastal marine eutrophication—a definition, social causes, and future concerns. *Ophelia* **41**: 199–221.
- , AND B. A. BUCKLEY. 2002. A strikingly rich zone: Nutrient enrichment and secondary production in coastal marine ecosystems. *Estuaries* **25**: 782–796.
- , AND M. E. Q. PILSON. 1983. Nitrogen in estuarine and coastal marine ecosystems, p. 565–648. *In* E. J. Carpenter and D. G. Capone [eds.], *Nitrogen in the marine environment*. Academic Press.
- OFFICER, C. B., R. B. BIGGS, J. L. TAFT, M. A. TYLER, AND W. R. BOYNTON. 1984. Chesapeake Bay anoxia: Origin, development, and significance. *Science* **223**: 22–27.
- PAERL, H. W. 2009. Controlling eutrophication along the estuarine-marine continuum: Dual nutrient (N and P) reductions are essential. *Estuar. Coast.* **32**: 593–601.
- PENNOCK, J. R., AND J. H. SHARP. 1986. Phytoplankton production in the Delaware Estuary: Temporal and spatial variability. *Mar. Ecol. Prog. Ser.* **34**: 143–155.
- , AND ———. 1994. Temporal alternation between light- and nutrient-limitation of phytoplankton production in a coastal plain estuary. *Mar. Ecol. Prog. Ser.* **111**: 275–288.
- PHILADELPHIA WATER DEPARTMENT. 2005. Philadelphia Water Department, Bureau of Water annual reports—data taken from miscellaneous annual reports (1936–1940, 1949, 1952–1963, 1965). These limited-access reports were studied in the archives of the Philadelphia Water Department in December 2005.
- POMEROY, L. R., C. F. D'ELIA, AND L. C. SCHAFFNER. 2007. Top-down control of phytoplankton by oysters in Chesapeake Bay, USA: Reply to Newell et al. *Mar. Ecol. Prog. Ser.* **341**: 299–301.
- RABALAIS, N. N., AND S. W. NIXON. 2002. Preface: Nutrient over-enrichment of the coastal zone. *Estuaries* **25**: 639.
- REDFIELD, A. C., B. H. KETCHUM, AND F. A. RICHARDS. 1963. The influence of organisms on the composition of seawater, p. 26–77. *In* M. N. Hill [ed.], *The sea*, v. II. Interscience Publishers.
- ROMAN, C. T., N. JAWORSKI, F. T. SHORT, S. FINDLAY, AND R. S. WARREN. 2000. Estuaries of the northeastern United States: Habitat and land use signatures. *Estuaries* **23**: 743–764.
- SHARP, J. H. 1988. Trends in nutrient concentrations in the Delaware Estuary, p. 77–96. *In* S. K. Majumdar, E. W. Miller, and L. E. Sage [eds.], *Ecology and restoration of the Delaware River Basin*. Pennsylvania Academy of Sciences.
- . 1994. What not to do about nutrients in the Delaware Estuary, p. 423–428. *In* K. R. Dyer and R. J. Orth [eds.], *Changes in fluxes in estuaries: Implications from science to management*. Olsen and Olsen.
- , AND T. M. CHURCH. 1981. Biochemical modeling in Middle Atlantic coastal waters. *Limnol. Oceanogr.* **26**: 843–854.
- , L. A. CIFUENTES, R. B. COFFIN, J. R. PENNOCK, AND K. C. WONG. 1986. The influence of river variability on the circulation, chemistry, and microbiology of the Delaware Estuary. *Estuaries* **9**: 261–269.
- , C. H. CULBERSON, AND T. M. CHURCH. 1982. The chemistry of the Delaware Estuary: General considerations. *Limnol. Oceanogr.* **27**: 1015–1028.
- , J. R. PENNOCK, T. M. CHURCH, J. M. TRAMONTANO, AND L. A. CIFUENTES. 1984. The estuarine interactions of nutrients, organics and metals: A case study in the Delaware Estuary, p. 241–258. *In* V. S. Kennedy [ed.], *The estuary as a filter*. Academic Press.
- , K. YOSHIYAMA, A. E. PARKER, M. C. SCHWARTZ, S. CURLESS, A. Y. BEAUREGARD, J. E. OSSOLINSKI, AND A. R. DAVIS. 2009. A biogeochemical view of estuarine eutrophication: Lessons from seasonal and spatial trends and correlations in the Delaware Estuary. *Estuar. Coast.* **32**: 1023–1043, doi: 10.1007/s12237-009-9210-8.
- SMITH, V. H. 2007. Using primary productivity as an index of coastal eutrophication: The units of measurement matter. *J. Plankton Res.* **29**: 1–6.
- STUTZ, B. 1992. *Natural lives, modern times*. Crown Publishers.
- SUTTON, C. C., J. C. O'HERON, AND R. T. ZAPPALORTI. 1996. The scientific characterization of the Delaware Estuary [Internet]. Philadelphia, Pennsylvania: Delaware Estuary Program [accessed 2008 September 01]. Available from <http://www.delawareestuary.org/scienceandresearch/datasetsandreports/localandregional.asp/>
- TINSLEY, D. 1998. The Thames estuary: A history of the impact of humans on the environment and a description of the current approach to environmental management, p. 5–26. *In* M. J. Attrill [ed.], *A rehabilitated estuarine ecosystem: The environment and ecology of the Thames Estuary*. Kluwer Academic Publishers.
- U.S. CENSUS. 1998. Population of the 100 largest cities and other urban places in the United States: 1790–1990 [Internet]. Washington, DC: U.S. Census [accessed 2005 June 15]. Available from <http://www.census.gov/population/www/documentation/twps0027/twps0027.html>
- U.S. GEOLOGICAL SURVEY. 2006. Hypoxia [Internet]. Washington, DC: U.S. Geological Survey [accessed 2008 April 30]. Available from <http://toxics.usgs.gov/definitions/hypoxia.html/>
- VITOUSEK, P. M., J. D. ABER, R. W. HOWARTH, G. E. LIKENS, P. A. MATSON, D. W. SCHINDLER, W. H. SCHLESINGER, AND D. G. TILMAN. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecol. Appl.* **7**: 737–750.
- WEBSTER, G. S., G. E. DATESMAN, AND W. L. STEVENSON. 1914. Report on the collection and treatment of the sewage of the City of Philadelphia. Report of the Department of Public Works, Bureau of Surveys.
- WINKLER, L. W. 1888. The determination of the oxygen loosened in the water. *Ber. Dtsch. Chem. Ges.* **21**: 2843–2855. [In German.]
- YOSHIYAMA, K., AND J. H. SHARP. 2006. Phytoplankton response to nutrient enrichment in an urbanized estuary: Apparent inhibition of primary production by over-eutrophication. *Limnol. Oceanogr.* **51**: 424–434.
- YOUNG, G. K., L. S. COSTELLO, G. F. TIERNEY, R. S. TAYLOR, AND M. R. CHILDREY. 1971. An analysis of dissolved oxygen in the Delaware River. Final report to City of Philadelphia Water Department from Water Resources Engineers, Springfield, Virginia.

Associate editor: Samantha B. Joye

Received: 26 September 2008

Amended: 28 October 2009

Accepted: 01 November 2009