

## Paleo-indicators and water quality change in the Charlotte Harbor estuary (Florida)

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### *Abstract*

We reconstructed water quality changes for 1800 to 2000 in Charlotte Harbor (Florida), a shallow subtropical estuary, by using a suite of biological and geochemical proxies in dated sediments collected in the region of a present day, midsummer hypoxic zone. The declining freshwater loading into the estuary from 1931 to the 1980s is not the probable causal agent encouraging the appearance or expansion of a hypoxia zone (measuring up to 90 km<sup>2</sup> in summer). Rather, the reconstructed trends in nitrogen loading indicate increased phytoplankton production has likely caused a decline in bottom water oxygen concentrations. Sedimentary biogenic silica (BSi), carbon, nitrogen, and phosphorus concentrations increased concurrently with known or inferred changes in nutrient loadings. There were direct relationships between phytoplankton pigments and BSi, heavier  $\delta^{34}\text{S}$  with increased carbon loading, and sequestration of P, Al, and Fe as carbon loading increased. The results from the sediment analyses and the results from mixing models using C:N ratios and  $\delta^{13}\text{C}$  suggest an estuarine system that is responsive to increased carbon loading from the nitrogen-limited phytoplankton community and whose sediments are becoming increasingly anoxic as a result. The present nitrogen loading is about three times above that prior to the 1800s, suggesting that without management intervention the anticipated doubling of the watershed's population from 1990 to 2020 will greatly increase the nitrogen loading to this estuary and will lead to much higher amounts of phytoplankton biomass and accumulation and exacerbate hypoxic conditions.

Coastal eutrophication is a ubiquitous environmental problem accompanying population growth, agricultural

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expansion and intensification, and increased demands for food and energy products. Society has altered the global cycles of nitrogen and phosphorus and increased the mobility and availability of these nutrients to marine ecosystems (Howarth et al. 1996; Rabalais 2002) through wastewater discharge, application of fertilizers, nitrogen fixation by leguminous crops, and atmospheric deposition of oxidized nitrogen from fossil-fuel combustion. These changes in nutrient loads often compromise water quality as phytoplankton or filamentous algal growth increases, including that of some noxious and toxic algae. Changes

in the amounts or relative proportions of nitrogen, phosphorus, and silicate may favor harmful algal blooms, aggravate oxygen depletion, and alter marine food webs (Turner et al. 1998; Worm et al. 2000). Over the last half of the 20th century it became increasingly apparent that these symptoms of eutrophication were not minor and localized but had large-scale implications and were spreading rapidly (Diaz and Rosenberg 1995; National Research Council 2000).

Addressing the temporal and spatial significance of increased nutrient loading into a specific estuary can be a vexing problem for managers and scientists. Changes in estuarine nutrient loading from local urban or agricultural land use changes, for example, may or may not be as significant as the changes occurring from land use changes further up the watershed and be undetectable against a background that includes a substantial natural variability or inadequate monitoring. The rate of land use changes in most estuarine watersheds in the United States and Europe has increased, but their influence(s) may represent something between slight to large additions to an existing suite of other stressors. Without knowledge of these larger scale influences, we may remain uninformed, subject to overly simplistic arguments, and profoundly uncertain about remedial strategies, even though nutrient enrichment of coastal watersheds has many consequences for fish, humans, and habitat (Shumway 1990; Diaz and Rosenberg 1995; National Research Council 2000). Decisions will be made, however, regardless of the sufficiency of our knowledge.

The Charlotte Harbor watershed in southwest Florida has experienced many of the same land use changes observed in other estuaries, but has done so mostly in the last 50 yr, and these changes are continuing. This estuary (Fig. 1) has the second largest estuarine surface area in Florida (Turner 2001) and has a significant hypoxic zone (operationally defined as water with  $<2 \text{ mg L}^{-1}$ ) that approaches  $90 \text{ km}^2$  in September (Camp, Dresser, and McKee, Inc. 1998). The recreational and commercial fisheries and associated activities are valued at one billion dollars annually (SWFWMD 1999). Forty species of animals in the Charlotte Harbor area are listed by the state as endangered, threatened, or of special concern (SWFWMD 1999). The watershed population will double from 1990 to 2020 at current growth rates. Phytoplankton growth in the estuary is controlled by the availability of nitrogen (McPherson et al. 1990, 1996; Montgomery et al. 1991), but the baseline water quality measurements useful to estimate changes began only in the 1970s. Also, and unlike nearby Tampa, Sarasota, and Lemon Bays, variations in sea grass biomass and productivity in Charlotte Harbor do not seem to correlate with modeled nitrogen loads (Tomasko and Hall 1999). Previous efforts involving both empirical and mechanistic modeling approaches failed to produce a clear link between nitrogen loads and any quantifiable measure of eutrophication or trophic state (Pribble et al. 1997). The Charlotte Harbor estuary is thus an interesting place to test relationships between nutrient loading and estuarine water quality. We studied the Charlotte Harbor estuary to address certain water quality issues and to put into perspective how quickly and how much water quality

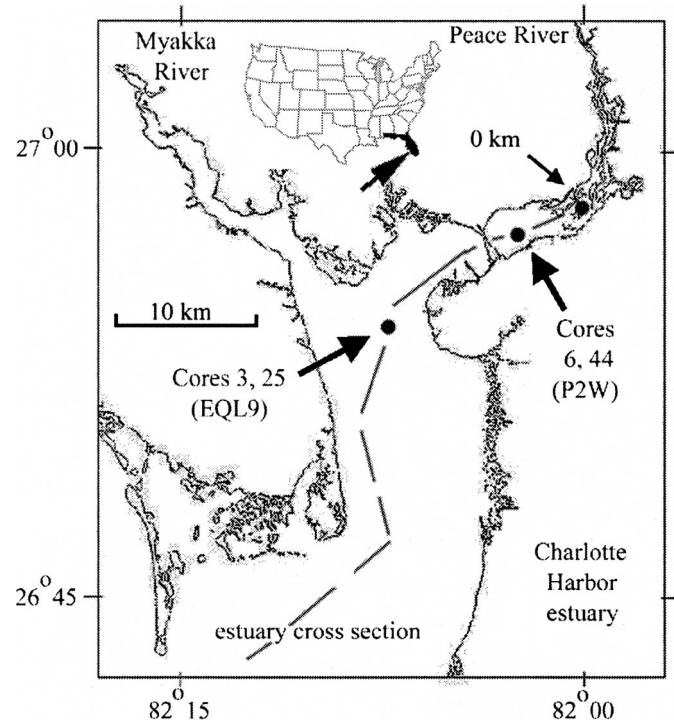


Fig. 1. Map of Charlotte Harbor area and location of sediment cores. The line running up the middle of the estuary is the transect mentioned in Fig. 2. EQL9 and P2W are collocated water quality monitoring stations established by the Southwest Florida Water Management District. The 0 km mark is the end of the transect line shown in Fig. 2.

changed in response to variations in nutrient loading over the past several decades.

We analyzed the constituent remains of biological and geochemical markers in sediments that are useful proxies of water quality at the time of deposition and used water quality data records to build a framework of regional influences and responses by the estuarine ecosystem. Particular attention was given to the occurrence of low oxygen conditions in bottom waters of the estuary—a significant indicator of water quality.

We used a suite of paleo-indicators because no single indicator provides adequate information concerning the multiple, interrelated components of the ecosystem. Shifts in biologically bound silica (BSi), a measure of remnant diatom frustules, have been used in a variety of aquatic systems to demonstrate water quality mediated changes in diatom productivity (e.g., Schelske et al. 1983; Turner and Rabalais 1994). Phytoplankton pigments are useful for understanding changes in water column and epibenthic algae and vascular plants in both extant communities and accumulated sediments in lakes, estuaries, and the ocean (e.g., Rabalais et al. 2004). Chl *a* (Chlorophyll *a*) provides an estimate of overall plant biomass, and carotenoid pigments provide taxonomic biomarkers (summarized in Jeffrey et al. 1997). Naturally occurring carbon, nitrogen, and sulfur isotopes are part of the deposited organic materials, their isotopic values may change under reducing conditions (e.g.,  $\delta^{34}\text{S}$ ), and they can be used as tracers of food web interactions (Peterson and

Fry 1987). Trace metal complexation is influenced by sediment redox potential; thus, the fate of trace metals (burial, sequestration, or diffusion rates) may be used to detect sedimentary responses to hypoxic conditions in the overlying water and the amount of organic carbon loading to the sediments. We use results from these analyses to discern the patterns of changes in the Charlotte Harbor estuary since 1800 and discuss how this suite of indicators may be useful tools for other estuaries.

*Description of the estuary*—The Charlotte Harbor estuary is a coastal plain estuary with an average depth of 2.4 m (Fig. 1). It receives water from a 12,950 km<sup>2</sup> watershed into its 805 km<sup>2</sup> surface area and has an average freshwater fill time (volume/[freshwater volume in 1 yr]) of 176 d. It has an estimated 2,525 km<sup>2</sup> of wetlands, including mangroves and submerged macrophytes. The human population density of the watershed was 64.5 people per km<sup>2</sup> in 1998, and the population will increase to 3 million in the 10 county area by 2020 at current growth rates. About three-fourths of the watershed is either agricultural land or rangeland. A general description of the watershed is given in McPherson et al. (1996).

The major rivers flowing into Charlotte Harbor estuary are the Peace (average 50 m<sup>3</sup> s<sup>-1</sup>) and Myakka (average 18 m<sup>3</sup> s<sup>-1</sup>) Rivers that enter from the north, and the Caloosahatchee River from the east and south. Stream flow decreased from 1931 to 1984 because of changes in the rainfall patterns during the wet season (Fraser 1991). A box model of physical transport within the system suggests that 50% of the river flow at high and average discharge would be flushed into the Gulf of Mexico within 10 and 20 d, respectively (McPherson et al. 1996). Most of this exchange is through the Boca Grande Pass at the southern end of the estuary. The Peace River is naturally enriched with dissolved phosphate from watershed phosphorites in the Bone Valley formation and from phosphate mining activities (originally in the river, and then on land after 1900s), including occasional catastrophic releases (Froelich et al. 1985).

Phytoplankton carbon production in the estuary is  $9.3 \pm 4$  mg C mg Chl *a*<sup>-1</sup> m<sup>-3</sup> h<sup>-1</sup> ( $\mu \pm 1$  SD,  $n = 6$  months or 1.2 g C m<sup>-2</sup> d<sup>-1</sup> at 1 d<sup>-1</sup> sunlight, 2.4-m water column and 11  $\mu$ g Chl *a* L<sup>-1</sup>; McPherson et al. 1996). Growth limitation of phytoplankton begins at a salinity of <10, which is within the river channel and upstream of where the estuary headwaters broaden significantly into the open water of the estuary (Froelich et al. 1985). The evidence that phytoplankton production is usually nitrogen limited for most of the estuary is based on the results of nutrient bioassay experiments, analyses of nutrient concentrations along the river-to-sea continuum, and the very low N:P atomic ratios, which are typically 1:1 or less (Fraser and Wilcox 1981; McPherson et al. 1990; Montgomery et al. 1991). High natural P loading makes water quality and phytoplankton production in this estuary particularly susceptible to changes in N loading.

## Materials and methods

*Water quality data sets*—Water quality data from 1957 to 1999 for nitrate and total nitrogen in the Peace River at

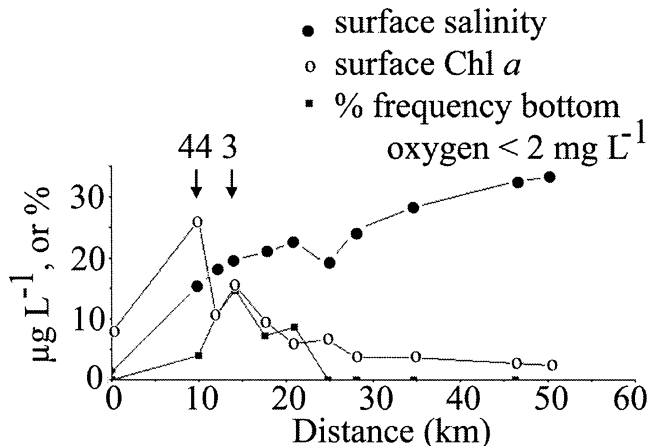


Fig. 2. Salinity and average annual chlorophyll *a* (Chl *a*) concentration in surface water and the frequency of oxygen concentrations in bottom water that are less than 2 mg L<sup>-1</sup> along the central axis of the estuary shown in Fig. 1. The percentage frequency is the occurrence of low oxygen concentrations determined from monthly sampling trips (Camp, Dresser, and McKee Inc. 1998), for annual averages for 1975 to 1990, inclusive. The surface Chl *a* data are for 1993 and 1994 and are the annual averages (Coastal Environmental, Inc. 1996). Arrows mark the locations of cores 44 and 3 (10 and 14 km, respectively).

Arcadia, Florida, are from a water quality network sampled by the U.S. Geological Survey and are reported in various annual water resources reports for the state of Florida. Coastal Environmental, Inc. (1996) analyzed trends in water quality data in upper Charlotte Harbor at their Stas. EQL9 and P2W, collocated where cores 3 and 44, respectively, were collected. These analyses include annual estimates of total Kjeldhal nitrogen (in their fig. 5.2d), which is the dominant form of nitrogen in the water column.

Data for oxygen concentration in surface and bottom water within Charlotte Harbor, including at the collection sites for cores 3 and 44, were provided by the Southwest Florida Water Management District, who conducted and/or supervised water collection and analyses. These include data from 1979 to 1990 and from 1993 to 1999.

*Sediment cores (collection, dating, archiving, and subsampling)*—Paired cores 3 and 25 and paired cores 6 and 44 were taken from open water stations in the hypoxic zone (Fig. 2). Each paired core was taken within 100 m of each other. Sediment samples were collected in 10-cm diameter  $\times$  50-cm long stainless steel core tubes by divers working in <2 m depth. The cores were kept upright and refrigerated until cutting into 1-cm sections. Triplicate subsamples for phytoplankton pigment analysis were taken from each section and stored in cryotubes, initially in liquid nitrogen and then in an ultracold freezer. A portion of wet sediment was retained for grain size analysis. The remaining portion of the sections was dried at 60°C, then ground to a 20- $\mu$ m mesh sieve size, weighed in sealed 26-cm<sup>3</sup> plastic Petri dishes, and held for 3 weeks before analysis to allow equilibrium to occur between <sup>222</sup>Rn and <sup>210</sup>Pb in the Petri dish. The remaining homogenized and ground sections were analyzed for indicators of diatom abundance and stable isotopes.

The sediments were dated by determining the downcore distribution of  $^{210}\text{Pb}$  activity (Nittrouer et al. 1979). The disequilibrium between  $^{225}\text{Ra}$  and its long-lived decay product  $^{210}\text{Pb}$  (half-life = 22.3 yr) is widely used to date aquatic and wetland sediments, but with different modeling approaches depending on sediment characteristics, radioisotopic analyses, and assumptions. We used an integrated gamma-spectroscopy system consisting of a Princeton Gamma-Tech 60-mm diameter intrinsic germanium "N" type coaxial detector (40% efficiency) interfaced to an EG&G Ortec 92X Spectrum Master multichannel spectrum analyzer. Ortec's GammaVision software was used to analyze the data. The system was calibrated using a multinuclide (60–1836 keV) standard solution (Isotope Products 7600) that was mixed with an estuarine soil and then packed in a 26-cm<sup>3</sup> plastic Petri dish. The calibration of the system was checked quarterly for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  with standard sediment from the International Atomic Energy Agency (IAEA-300). Samples were counted for at least 2. The background, with an empty Petri dish, was counted every 6 d for 24 h. The excess (unsupported)  $^{210}\text{Pb}$  was calculated by subtracting the supported  $^{210}\text{Pb}$  activity from the total  $^{210}\text{Pb}$  activity. Supported  $^{210}\text{Pb}$  was estimated from the activity of  $^{214}\text{Pb}$  (295 and 352 keV). Accretion rates were calculated using the constant initial concentration model (Robbins 1978). This model assumes there is negligible migration of  $^{210}\text{Pb}$  and associated radionuclides in sediments, a constant input of  $^{210}\text{Pb}$  from the atmosphere, and a constant proportion of  $^{210}\text{Pb}$  trapped from the water to the sediments by weight. This model is applied under the assumption that the excess  $^{210}\text{Pb}$  in sediments deposited at the surface will be the same regardless of sedimentation rate. This model uses the cumulative sedimentation rate downcore, a decay constant of  $^{210}\text{Pb}$ , and the change of excess  $^{210}\text{Pb}$  activities with depth to estimate sediment accretion rates. A linear regression of the excess  $^{210}\text{Pb}$  activity and the cumulative mass is used to estimate an annual sedimentation rate. The activity of  $^{210}\text{Pb}$  in the first few centimeters of the surface can aid in determining how much mixing has occurred. Counting errors were calculated using the counting uncertainties of  $^{210}\text{Pb}$  and  $^{214}\text{Pb}$  and the formula from Binford (1990). The counting uncertainty ranged from <10% for surface samples (<10 cm) to 15% for deeper samples. The sum of the excess  $^{210}\text{Pb}$  was estimated for the core using the interpolated values for core segments not counted and the measured dry weights.

*Chloropigments by high performance liquid chromatography (HPLC)*—Plant pigments were extracted and analyzed by high performance liquid chromatography (HPLC) according to the methods of Wright et al. (1991) on a Waters system equipped with a 600 controller, 600 pump, 996 photodiode array detector, and 474 fluorescence detector. The use of three columns (Waters Nova-Pak C<sub>18</sub> 3.9 × 150 mm, a Rainin Microsorb C<sub>18</sub>, and a Vydac Reverse-Phase C<sub>18</sub>) maximized peak separation. Pigment identification was determined by comparing retention times and visible absorption spectra of pigments with standards from Sigma Chemical Co. and the International Agency for C<sup>14</sup> determination, VKI Water Quality Institute, Denmark. Standards of pheophytin *a* and *b*, pheophorbides *a* and *b*, and chlorophyllide

*a* were obtained by the method detailed in Buffan-Dubau and Carman (2000). Pigment concentrations were expressed as micrograms of pigment per grams of dry weight sediment.

The pigment data were used to examine the phytoplankton community composition downcore and to investigate whether sediment mixing downcore might smudge or otherwise homogenize the chemical signature initially distinguishing recently accumulated material from that beneath it. Deep mixing of these sediments (>10 cm), under the right circumstances, could produce quasi-exponential  $^{210}\text{Pb}$  profiles. With this in mind we examined two cores for sharp changes in specific pigment concentrations, despite strong coherence in the pattern of downcore concentrations of other pigments.

*Diatom remains*—The amount of silica as diatom remnants was estimated using the methods described by DeMaster (1981). This method assumes that biologically bound silica digests within 1 h, but that nonbiologically bound silica continues to dissolve at a slower rate over the next several hours. The results are expressed as the weight of BSI as silica as SiO<sub>2</sub> per dry weight of sediment.

*Total carbon and nitrogen and percentage organic carbon*—Unacidified sediment samples for total carbon and nitrogen were analyzed with a Perkin Elmer 2400 CNS analyzer. Samples for percentage organic (loss on ignition) were weighed into porcelain crucibles and heated to 550°C for 1 h and then reweighed.

*Grain size*—Sediment grain size analysis was determined on sediments from which the organic matter was removed either by combustion of dried, ground sediments or by treatment of wet sediment with 3.5% H<sub>2</sub>O<sub>2</sub>. The subsequent sediments were dispersed in sodium hexametaphosphate (2.55 g L<sup>-1</sup> H<sub>2</sub>O) overnight then wet sieved through a 63- $\mu\text{m}$  sieve to collect the sand fraction. The mud fraction was divided into percentage silt and percentage clay by timed gravimetric extraction of dispersed sediments (Folk 1974).

*Stable isotope analyses*—Samples for carbon isotopes were acidified in 10% hydrochloric acid to remove carbonates, rinsed with deionized water, and dried at 60°C. Samples for sulfur isotopes were leached of sulfates by extracting the sample three times with deionized water and drying at 60°C. Dried but otherwise untreated samples were used for  $\delta^{15}\text{N}$  analyses. Samples were combusted in a Carlo Erba elemental analyzer coupled to a Thermoquest Delta Plus isotope ratio mass spectrometer, functioning as a continuous flow system for determining C, N, and S quantities and isotopic compositions. Isotopic results are reported relative to accepted international standards (VPDB [Vienna Pee Dee Belemnite] for carbon, atmospheric N<sub>2</sub> for nitrogen, and VCDT [Vienna Canyon Diablo Troilite] for sulfur). Precision is typically 0.2‰ or better for the C and N isotopic measurements, and 0.5‰ or better for the S isotopic determinations. Elemental compositions (percentage C, N, and S) are routinely precise at 5% coefficient of variation or better.

*Elemental analyses*—Samples for trace metal analyses were digested in nitric acid, hydrogen peroxide, and hydro-

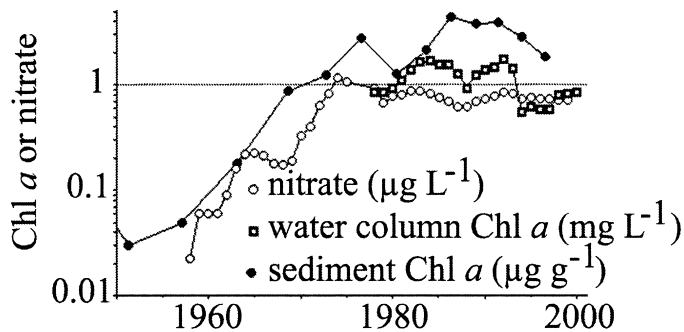


Fig. 3. The annual average concentration of nitrate ( $\mu\text{g N L}^{-1}$ ) at Arcadia, Florida; the average annual concentration of Chl *a* ( $\text{mg L}^{-1}$ ) in water collected at Sta. EQL 9 where core 3 was taken; and the Chl *a* in the dated sediment sections. The water column data are for 5-yr running averages.

chloric acid (U.S. EPA 1986). This method is not a total digestion but extracts environmentally available elements. Elements that are bound in silicate structures are not completely dissolved by this method, which was not a major concern since these elements are not usually mobile in the environment. The sample digest was analyzed for major and trace elements by inductively coupled atomic emission spectrometry and reported as a concentration (micrograms of element per gram of dry weight whole sediment).

## Results and discussion

*Phytoplankton, nutrients, river flow, and oxygen*—The concentration of nitrate in the Peace River at Arcadia increased since the 1960s (Fig. 3). Because of the strength of the nitrogen limitation on phytoplankton growth, it is not surprising that the variations in the annual nitrogen concentration in the Arcadia River and Chl *a* in Charlotte Harbor appear to change in concert with each other (Fig. 3). A linear regression of the relationship between Chl *a* and total nitrogen concentration yielded an  $R^2$  value of 0.24 ( $p < 0.05$ ;  $n = 20$ ). These data are for annual averages, and further analyses are certainly warranted to improve understanding of how the causal relationships change seasonally.

The oxygen concentrations in the estuary vary from >100% saturation in surface waters to 0% saturation in bottom waters at a station where hypoxia occurs frequently (Fig. 4, top panel). The average oxygen concentration at Sta. 9 (Fig. 4, bottom panel) declined from 1975 when monitoring was first established, until 1995, but had returned to 1975-era values by 1998. Low values typically occur in summer months, and there is considerable variability among years. Hypoxic water typically occurs when water temperatures are  $>27^\circ\text{C}$  and surface salinity is  $<25$ . Calculations on oxygen consumption dynamics (Camp, Dresser, and McKee, Inc. 1998) suggest that hypoxia could be initiated by either (1) the oxygen demand required to decompose a Chl *a* concentration of  $50 \mu\text{g L}^{-1}$  (an observed concentration during summer) or (2) the measured sediment oxygen demand in the estuary.

The long-term decline in river flow into the estuary has affected the oxygen dynamics in several important ways.

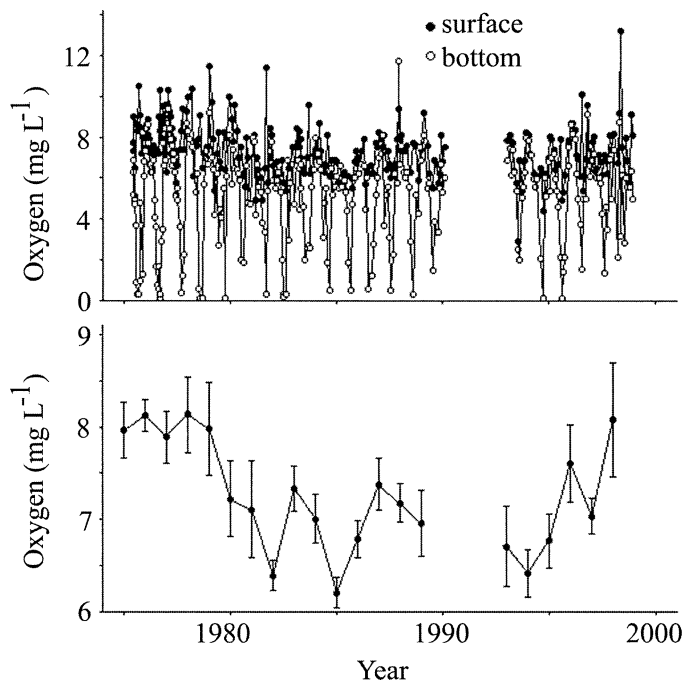


Fig. 4. Oxygen concentrations at Sta. EQL 9 where core 3 was taken (shown in Fig. 1). Upper panel, the monthly oxygen concentration ( $\text{mg L}^{-1}$ ) in surface water and bottom water. The low values in bottom water are in June–October. Lower panel, the variation in annual average oxygen concentration ( $\text{mg L}^{-1}$ ) in surface water. The mean  $\pm 1$  SE is shown.

First, decreased freshwater inputs will raise the average salinity of the estuary. The water column is more likely to be stratified when the surface water is low in salinity (Fig. 5, upper panel). Second, stratification reduces the exchange of oxygen between the bottom layer and the atmosphere. This is an important observation because stratification is necessary to form and maintain hypoxic conditions (Fig. 5, bottom panel). High, summer temperatures contribute to lower oxygen concentration in bottom layers because oxygen content is lower at higher temperatures, while potential respiratory rates in water column (from recent production) and sediments (stored organic carbon) are higher. In other words, a decline in river flow will reduce stratification and raise bottom water oxygen saturation. The higher salinities are, within the period of record, positively related to higher oxygen saturation in bottom waters (Fig. 6).

A polynomial regression of salinity and the surface oxygen concentration (or percentage saturation) at Sta. 9 yielded insignificant values of  $R^2$  ( $p = 0.22, 0.45$ , respectively;  $n = 69$ ; 1975 to 1998, summer months only). These results do not support the conclusion that a decreased flow led to greater light clarity, longer residence times, and more phytoplankton biomass accumulation. Decreased flow, therefore, is associated with less stratification and higher bottom water oxygen, but not increased phytoplankton production. However, a higher total nitrogen concentration leads to more Chl *a*, which tends to lower bottom water oxygen concentrations. Thus, reduced freshwater inflow has not caused hypoxia but

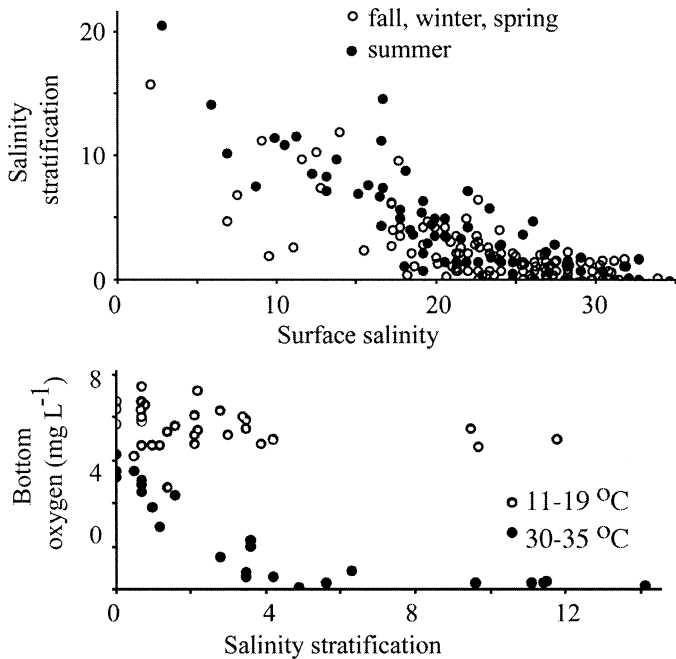


Fig. 5. Relationships between salinity, stratification, and oxygen in the estuary where core 3 was taken. The data are for June through October from sampling by the SWFWMD. Upper panel, salinity stratification (delta salinity) between surface and bottom water (Y axis) and surface salinity (X axis) where core 3 was taken. The data are from sampling by the SWFWMD for 1975 to 1990 (84 of the 198 data points shown are from June through September). Lower panel, the relationship between salinity stratification between surface and bottom water and bottom water oxygen concentration ( $\text{mg L}^{-1}$ ). Two portions of the data are included: where temperature in the surface water is  $30^{\circ}\text{C}$  or higher (closed circle) and between  $11^{\circ}\text{C}$  and  $19^{\circ}\text{C}$  (open circle).

may have had the effect of reducing the potential occurrence of hypoxia at these sites.

The effect of changing both river flow and nutrient load concentration is to cause an inverse relationship between phytoplankton biomass and bottom water oxygen concentration (Fig. 7). A linear regression of the two variables indicates that there is a 3.36% decline in oxygen saturation for each increase in  $\mu\text{g Chl } a \text{ L}^{-1}$ .

The general impressions of these relationships and observations are that (1) phytoplankton production is directly related to nitrogen loading to the estuary; (2) increased nitrogen loading over long periods of time should lead to increased oxygen demand in the water column and from in situ production accumulating in the sediments; and (3) the oxygen depletion caused by higher nitrogen loading is not sufficiently balanced by reaeration, so that a new and lower equilibrium oxygen concentration is reached as nitrogen loading increases.

*Dating and selecting cores for detailed analysis*—We compared the dry weight and organic content and then the decline of the excess  $^{210}\text{Pb}$  activities with depth to select one of the two replicate cores from each site that would be analyzed for the full suite of parameters. The absolute values and the variations from surface to 50 cm downcore in both

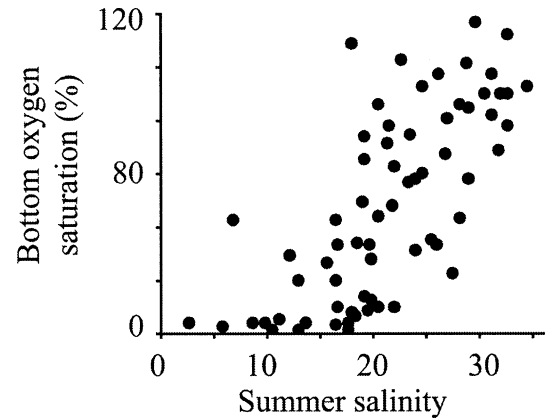


Fig. 6. The relationship between the salinity in the surface water and the bottom water oxygen saturation where core 3 was taken. The data are for June through August.

dry density and organic content of the replicate cores 3 and 25 and cores 6 and 44 and among all cores were similar (Fig. 8). Slight differences between core pairs are that the percentage organic content in the surface layer of cores 3, 25, and 44 rises at a smoother rate in the last 5 cm than in core 6, and that the average dry density in core 25 was 11% greater than in the paired core 3. The general absence of features distinguishing the dry density and organic content with depth among cores supports the conclusion that the cores were under the influence of similar depositional forces before they were collected.

The differences between the total  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  activities for the four cores decrease from the surface to halfway down the core, a point where the differences between  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  activities are less than the counting efficiency of this method (Fig. 9). The mean activity of  $^{226}\text{Ra}$  ranged between 1.6 to 2.2  $\text{pCi g dry weight sediment}^{-1}$ . The distribution of

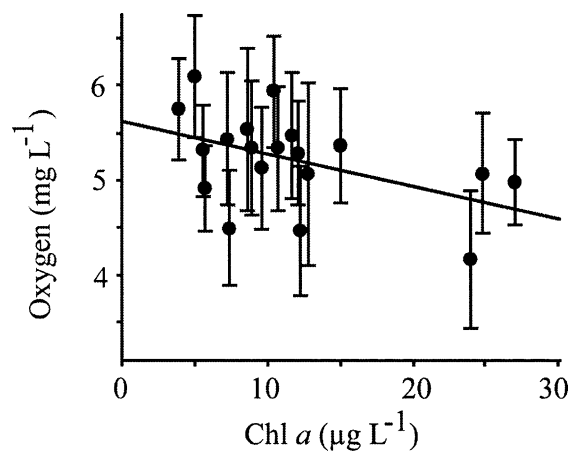


Fig. 7. The average Chl *a* in surface waters ( $\mu\text{g L}^{-1}$ ) and average oxygen concentration in bottom water ( $\text{mg L}^{-1}$ ) at the station where core 3 was collected. The data are from the SWFWMD for 1977 to 1998 and represent annual averages. A linear regression of the data is shown. The coefficient of determination ( $R^2$ ) is 0.22, and  $p = 0.04$ . The vertical bars are  $\pm 1$  standard error for the annual mean. The slope indicates a 3.36% decline for each increase in  $\mu\text{g Chl } a \text{ L}^{-1}$ .

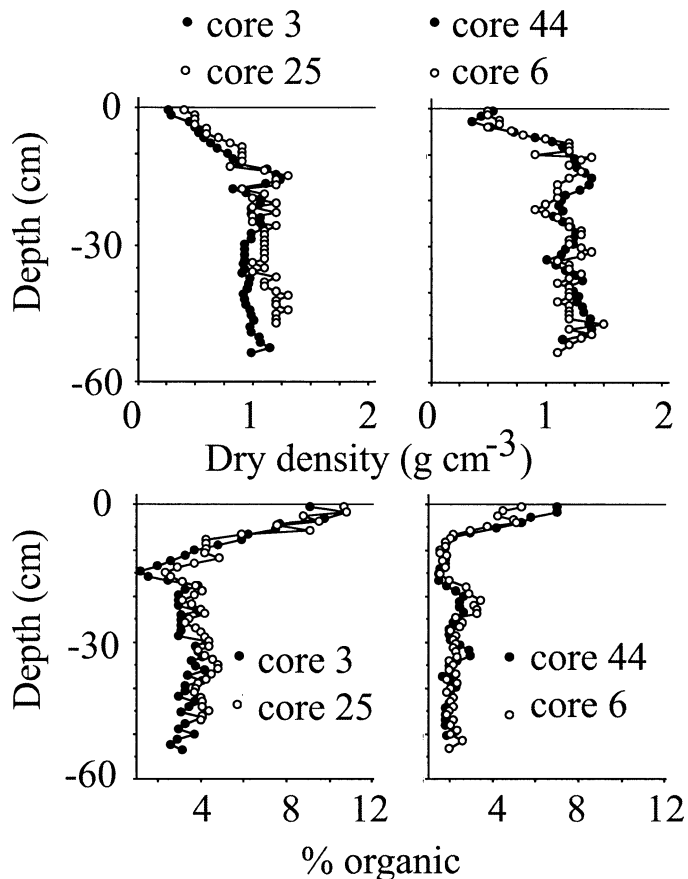


Fig. 8. Vertical profiles of density ( $\text{g cm}^{-3}$ ) and percentage organic matter (weight basis) for two sets of paired cores.

excess  $^{210}\text{Pb}$  downcore for the paired cores was similar (Fig. 9, upper panel). The regression model of excess  $^{210}\text{Pb}$  and sediment accumulation yielded a value for the coefficient of determination ( $R^2$ ) that is 0.90 or greater for at least one of the two paired cores (Fig. 9). Cores 3, 25, and 4 had similar sedimentation rates (0.24, 0.25, and  $0.17 \text{ g yr}^{-1}$ , respectively) and appeared equally useful for our purposes. Cores 6 and 4 had different sedimentation rates and linear regression statistics (Fig. 10). Compared with core 6, core 4 had a higher  $R^2$  value for the linear regression (0.89 vs. 0.59, respectively), a lower sedimentation rate ( $0.49$  vs.  $0.17 \text{ g yr}^{-1}$ , respectively), and a lower total inventory of excess  $^{210}\text{Pb}$ . The upper half of core had the same mass sedimentation rate as in core 6, but then increased downcore so much that the average mass sedimentation rate was 2.9 times greater than in core 3. The slopes for the regression lines shown in Fig. 10 for cores 3, 25, and 44 were not statistically different from each other but were different from that in core 6. The total inventories of  $^{210}\text{Pb}$  were similar in cores 3, 25, and 6, and lowest in core 44 (19.8, 23.4, 21.2, and  $9.2 \text{ pCi cm}^{-2}$ , respectively). The  $^{210}\text{Pb}$  inventories in these four cores are within the range found by Robbins et al. (2000) for four Florida Bay cores, which had about one half the  $^{226}\text{Ra}$  activity of the four Charlotte Harbor cores. The excess  $^{210}\text{Pb}$  in the surface layer ranged from 1.0 to  $1.9 \text{ pCi g dry weight sediment}^{-1}$ .

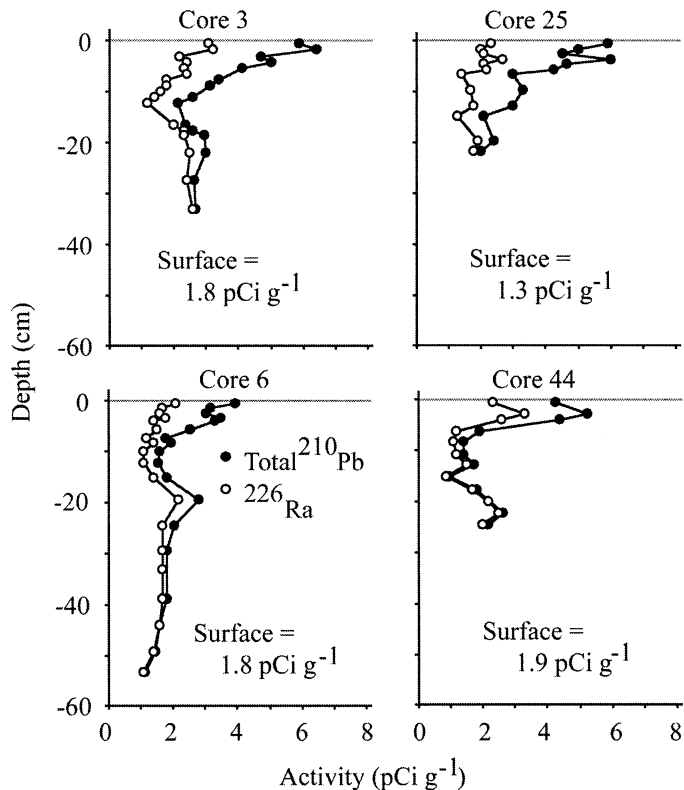


Fig. 9. Vertical profiles of total  $^{210}\text{Pb}$  and radon activity in the four cores. Also shown is the total activity in the surface layer for each core ( $\text{pCi g}^{-1}$ ).

We sought to confirm the  $^{210}\text{Pb}$ -based dating results by measuring the downcore distribution of  $^{137}\text{Cs}$ . We were unable to detect sufficient amounts of  $^{137}\text{Cs}$  in these cores, presumably because of the high sand content. Despite this complication, we concluded that the surface layer in cores 3 and 44 was recently deposited material and that sediments were not strongly mixed because of the previously mentioned among-core similarities in excess  $^{210}\text{Pb}$  activity throughout the core and their inventories. Further, the visual analysis of the pigment data (discussed later) indicates strong downcore coherence among cores for some pigments and sharp discontinuities for other pigments, which is not expected if sediments were well mixed.

We used these results to choose cores 3 and 44 for further analyses, whose oldest dated horizon extend to 32 cm (ca. 1879) and 20 cm (ca. 1935), respectively. We assumed that the accretion rate was homogeneous through the entire length of both cores and restricted the detailed chemical analyses to the post-1800 core sections.

**Sediment characterization**—The average percentage clay, bulk density, percentage C (acidified), percentage N, percentage P, percentage Fe, and percentage S for sediments dated from 1900 to 1998 are in Table 1. Sediments from cores 3 and 44 were 97% sand (Fig. 11). The finer fraction, consisting of mostly clays, was in the upper 5 cm. The silt fraction was  $<1\%$  and did not vary much with depth. Although the percentage clay-size particle content was less

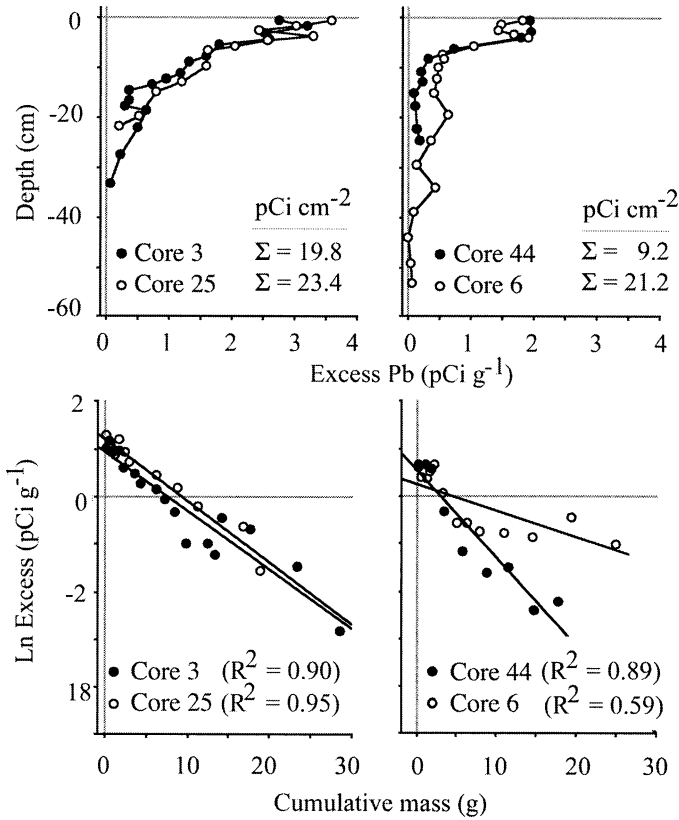


Fig. 10. Vertical profiles of excess  $^{210}\text{Pb}$  activity in four sediment cores. Upper panel, paired cores 3 and 25, and paired cores 4 and 6. The cumulative inventory ( $\text{pCi cm}^{-2}$ ) is also shown. Bottom panel, a plot of the relationship between  $\ln(\text{pCi cm}^{-2})$  and cumulative mass for each core. The coefficient of determination ( $R^2$ ) of a linear regression for each data set is given.

Table 1. The mean percentage clay, bulk density ( $\text{g cm}^{-3}$ ), and percentages of C, N, P, Fe, and S (dry weight basis) for sediments dated from 1900 to 1998 in cores 3 and 44.  $n=25$  and 15 for cores 3 and 44, respectively.

Constituent	Core	Mean	$\pm 1$ SD
Percentage clay-sized particles	3	0.49	0.29
	44	3.90	2.21
Bulk density	3	0.85	0.28
	44	0.98	0.37
Percentage C total	3	2.05	0.71
	44	1.53	1.08
acidified	3	1.09	0.82
	44	1.04	0.72
Percentage N	3	0.14	0.08
	44	0.11	0.11
Percentage P	3	0.16	0.03
	44	0.12	0.04
Percentage S	3	0.25	0.11
	44	0.22	0.14
Percentage Fe	3	0.54	0.21
	44	0.36	0.19

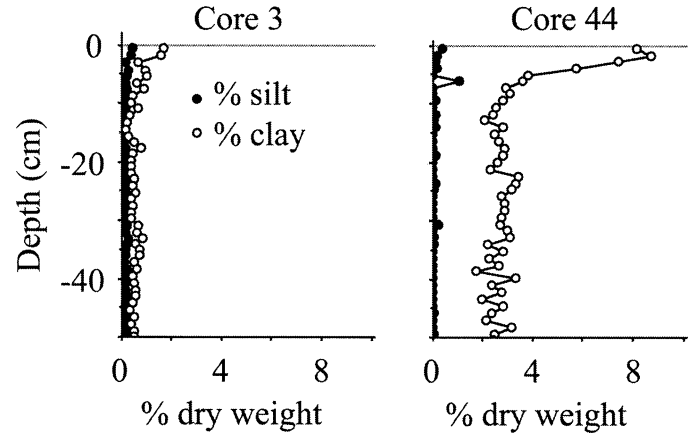


Fig. 11. The vertical distribution of silt and clay fraction for cores 3 and 44 (percentage dry weight). The remainder of the core is sand.

than 10% in both cores, it was nine times higher in core 44, compared with the downstream core 3, and increased in the top 5 cm (Fig. 11). The average content of C, N, P, S, and Fe (by weight) and of bulk density were the same in both cores. The carbonate C was an average 47% and 37% of the total C in sediments younger than 1990 in cores 44 and 3, respectively. The total amount of carbon increased upcore in both cores, primarily because of the increase in organic carbon, not inorganic carbon (Fig. 12).

The following were the same (within 10% of each other) for similarly dated horizons in cores 3 and 44: percentage BSi, percentage C, percentage N, percentage S, and the molar ratios for Fe:S, C:N, and S:C (Fig. 13). The concentrations of N, P, and S were proportional to the concentration of carbon (Fig. 14), implying a common biological origin of the parent material.

Sediment density, percentage organic C, and percentage organic C (acidified to remove inorganic C) increased circa 1950. Although there may be other explanations for these changes, they are consistent with the hypothesis that greater

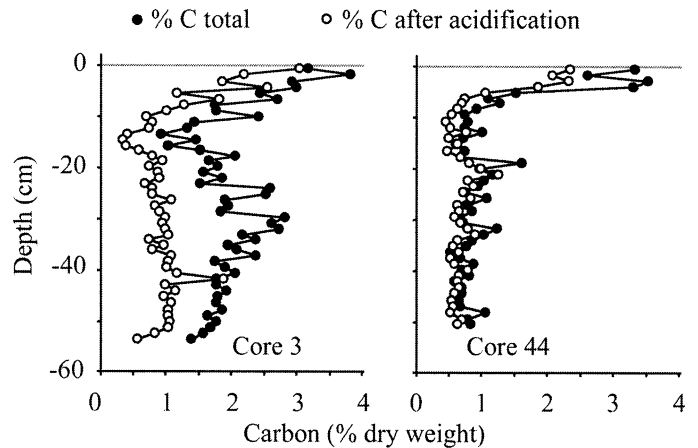


Fig. 12. The vertical distribution of the percentage total C and the percentage C in acidified samples from cores 3 and 44 (dry weight basis).

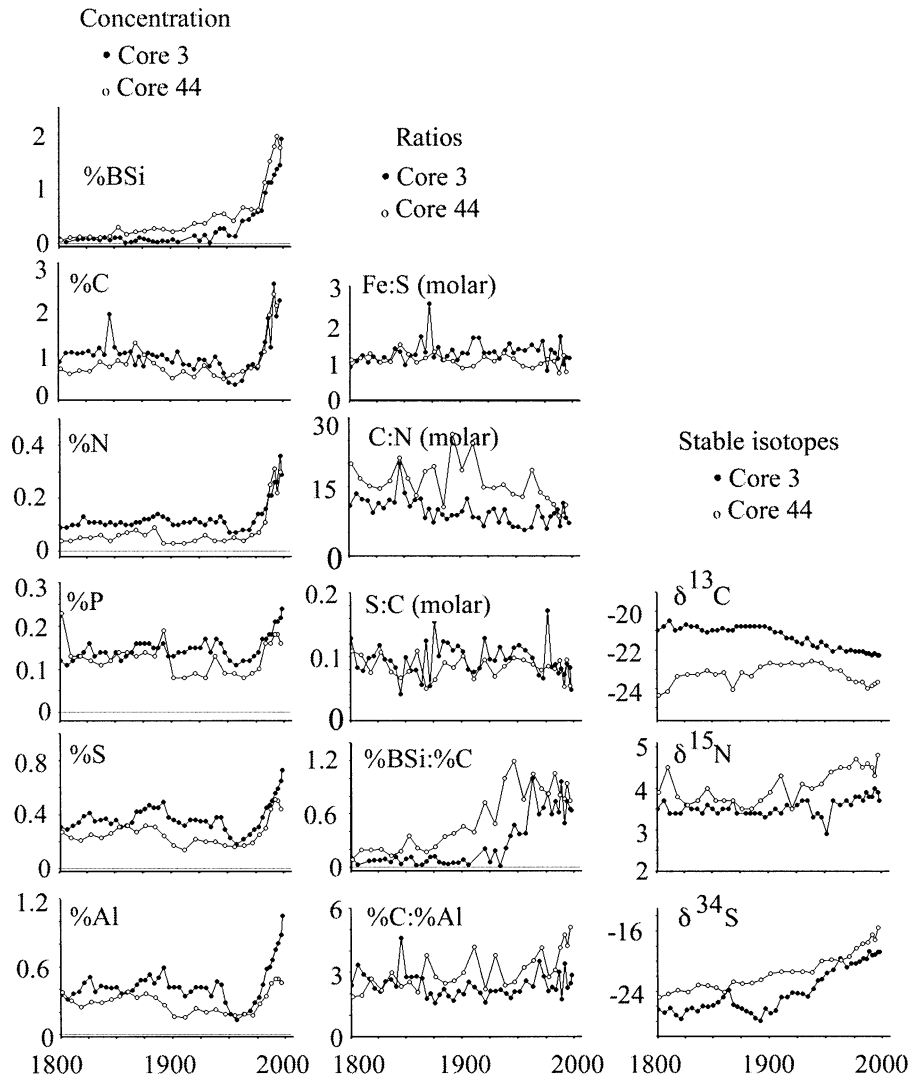


Fig. 13. The distribution of various components in dated core segments for cores 3 and 44, by concentration (percentage BSi, percentage organic C, percentage N, percentage P, percentage S, and percentage Al, dry weight basis), ratios (Fe:S, C:N, S:C, percentage BSi:percentage C, and percentage C:percentage Al), and stable isotopes ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$ ).

organic loading from phytoplankton production was being incorporated into the sediments.

We can make a rough estimate of whether there is enough organic carbon produced in the water column to influence the organic carbon loading to the sediments. Assume that the bulk density of sediments is  $0.5 \text{ g cm}^{-3}$ , that the carbon concentration is 2.75% of the dry weight, and that the sediment accumulation rate is  $0.27 \text{ cm yr}^{-1}$ . Under these assumptions the carbon accumulation rate was  $102 \text{ mg C m}^{-2} \text{ d}^{-1}$ , or  $10 \text{ mg C m}^{-2} \text{ h}^{-1}$  for a 10-h day. This accumulation rate compares with measured primary production rates averaging  $59 \text{ mg C m}^{-3} \text{ h}^{-1}$  for a 2.4-m water column (McPherson et al. 1990), which is 10 times the carbon accumulation rate in sediments. We conclude that the primary production by phytoplankton could be a source of the rise in organic matter in the recent sediments. Alternative explanations are that the increased organic loading is from changes in bulk terrestrial

loading as a result of land use, sewerage loading to the estuary, or dredging activity (*see discussion below*).

*Elemental analyses*—Trace metal accumulations varied in a similar manner in cores 3 and 44. All elements (Ba, Ca, Cd, Cu, Fe, Mn, Mo, P, S, Si, and V) varied linearly with changes in Al, with the exception of Mo and Si (Table 2, top). The strongest correlations with Al were with Fe, S, and V ( $R^2 > 0.75$ ). The relationship between Al and S was also robust ( $R^2 > 0.93$ ). Pyritization of trace metals in anoxic sediments is one mechanism to explain these results (Huerta-Diaz and Morse 1992). Hydrogen sulfide odors were detected in the sediment surface layer when the core's caps were repositioned aboard the sampling platform. The rise in N, P, S, and C was coincidental upcore (Fig. 13). A linear regression between percentage Fe (independent variable) and the percentage C, N, and P for sediment from cores 3 and

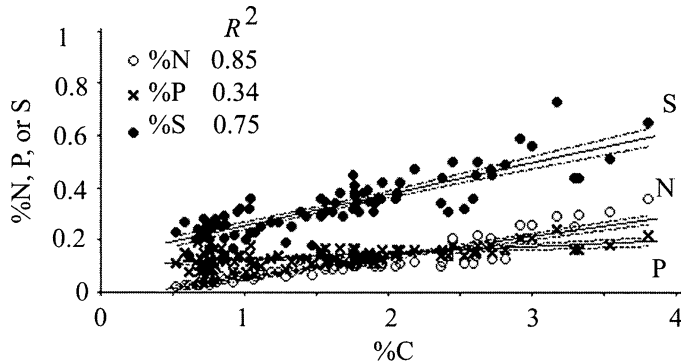


Fig. 14. The relationship between percentage carbon (unacidified) and percentage N, percentage P, and percentage S in cores 3 and 44 (combined). The values are on a percentage dry weight basis. There were 90 pairs for each regression ( $p = 0.001$ ). The coefficient of determination ( $R^2$ ) and 95% confidence interval for each regression are shown.

44 was statistically significant ( $R^2 > 0.6$ ;  $p = 0.001$ ), whereas the percentage Fe was not correlated to the amount of clay (Table 2, bottom).

**Stable isotopic values**—There are recent (upcore) increases in S isotopic composition (Fig. 13) that may be due to either terrestrial inputs or in situ processes, with in situ processes being more likely. If the terrestrial S inputs were significant, then the percentage S and  $\delta^{34}\text{S}$  would have risen in the 1800s and again in the 1900s, accompanying dredging in the river (beginning in the mid-1800s), surface mining for P fertilizer source material on land (beginning in the late 1800s), and population growth (beginning in the early 1900s). Because of this temporal mismatch of watershed inputs and S accumulation in cores, in situ processes such as sulfate reduction seem the more likely cause of S variation in the cores than does bulk loading of terrestrial sources. By the late 1900s,  $\delta^{34}\text{S}$  values became similar to average values for marine pyrite ( $\delta^{34}\text{S} = -20\text{‰}$ ; Payton et al. 1998) (Figs. 13, 15), which forms from sulfate reduction under strongly reducing conditions. Wijsman et al. (2001) found that the variability in  $\delta^{34}\text{S}$  value of pyrite ( $-6\text{‰}$  to  $-46\text{‰}$ ) in continental shelf sediments of the Black Sea could be explained by the reoxidation of  $\text{H}_2\text{S}$  under occasional oxic conditions.  $\delta^{34}\text{S}$  became heavier (higher) as waters became more anoxic (no oxygen). Thus, the observed recent increases in  $\delta^{34}\text{S}$  values in the Charlotte Harbor cores are consistent with the results expected from more intense reducing conditions due to increased organic loading in situ and lower oxygen concentrations in the overlying waters. Higher rates of sulfate reduction, a possible consequence of eutrophication, have also been associated with higher  $\delta^{34}\text{S}$  values (Goldhaber and Kaplan 1975).

The  $\delta^{15}\text{N}$  values were similar in the two cores, but  $\delta^{13}\text{C}$  was heavier in core 3 than in core 44 (Fig. 13). The changes in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values were more gradual and of smaller magnitude than changes in  $\delta^{34}\text{S}$  (Fig. 13), with the lower salinity station (core 44) having the more terrestrial signal (i.e., more negative  $\delta^{13}\text{C}$ ; see Hedges and Parker 1976). The  $\delta^{15}\text{N}$  values stayed the same or increased as the percentage

Table 2. Results of linear regression analyses. The coefficient of determination ( $R^2$ ) and  $p$  values are given for a sample size of (A) 90 or (B) 74 variables from cores 3 and 44. NS, not significant; ND, no data. All slopes between  $X$  and  $Y$  variables are positive. A: Al is the dependent variable and Ba, Ca, Fe, Mn, Mo, P, S, Si, and V as the independent variables. The original units were  $\mu\text{g}$  element per gram of dry weight. B: Fe as the independent variable and % C (acidified), % N (acidified), % P, and % S as the independent variables.

Independent variable	$R^2$	$p$
<b>A</b>		
Ba	0.27	0.001
Ca	0.33	0.0001
Fe	0.94	0.0001
Mn	0.56	0.0001
Mo	0.17	0.0001
P	0.65	0.0001
S	0.93	0.0001
Si	ND	ND
V	0.87	0.0001
<b>B</b>		
Percentage clay	NS	NS
Percentage C	0.62	0.0001
Percentage N	0.63	0.0001
Percentage P	0.76	0.0001
Percentage S	0.69	0.0001

C increased since 1950, whereas the  $\delta^{13}\text{C}$  value declined over the same period. Zimmerman and Canuel (2002) attributed the increase in  $\delta^{15}\text{N}$  values in Chesapeake Bay sediments to an enhanced recycling of organic matter that was subsidized by a rise in phytoplankton production that was driven by higher nutrient loading. However, their values for  $\delta^{13}\text{C}$  increased over the same period, which was different from our observations for Charlotte Harbor sediments. An anonymous reviewer reminded us that benthic algae have a heavier  $\delta^{13}\text{C}$  signal than phytoplankton, and that faster growing phytoplankton fractionate less than slower growing species. Eutrophication may have resulted in heavier  $\delta^{13}\text{C}$  in Chesapeake Bay because of the higher phytoplankton growth rates and limited flushing. Charlotte Harbor, with a relatively

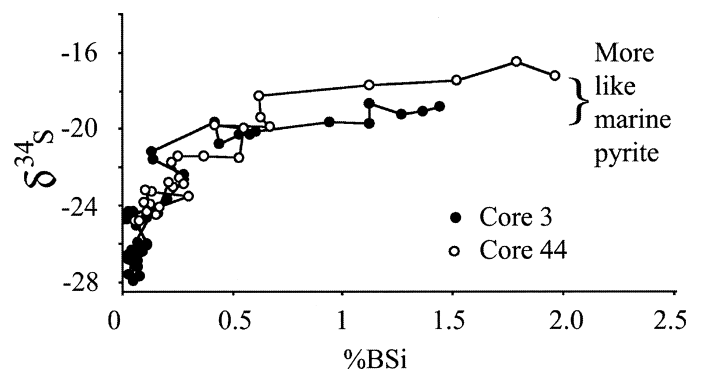


Fig. 15. The relationship between sulfur isotope values ( $\delta^{34}\text{S}$ ) and biogenic silica concentration (percentage dry weight) in sediments of cores 3 and 44.

Table 3. Results of linear regressions between percentage BSi and pigments for sediments dated from 1900 to 1997. Only correlation coefficients  $\geq 0.8$  are shown, with those  $\geq 0.9$  shown in bold. All values are significant at the 99% level of significance. Abbreviations: Chl *a* (Chlorophyll *a*), Totphea (pheophorbide *a* + pheophorbide *b* + pheophytin *a* like),  $\beta$ -caro ( $\beta$ -carotene), Allo (alloxanthin), Zea (zeaxanthin).

Pigment	Core 3	Core 44
Chl <i>a</i>	0.85	—
Totphea	0.81	—
$\beta$ -caro	0.80	—
Allo	0.84	0.98
Zea	0.82	<b>0.94</b>

faster water turnover time than in the Chesapeake Bay, might have a different  $\delta^{34}\text{S}$  response to eutrophication because of differential effects on the benthic and water column algae.

**BSi**—The concentration of biogenic silica (BSi; percentage dry weight) in both cores increased coincidentally, beginning around 1900 (Fig. 13). The ratio of percentage BSi: percentage C increased since 1900, which is consistent with a pelagic rather than land-based source of the increased organic carbon. The relationship between BSi and  $\delta^{34}\text{S}$  was robust and coincidental for both cores (Fig. 15). As the percentage BSi increased, the  $\delta^{34}\text{S}$  isotope values became heavier, possibly indicating a link between algal production and sulfate reduction dynamics in sediments.

The relationships between BSi and several pigments were significant (Table 3). If one accepts that, after the initial deposition in the mixed layer, BSi does not undergo significant diagenesis over 200 yr under reducing conditions (Parsons et al. 2002), then these results support the conclusion that the pigments are not undergoing rapid diagenesis under the in situ reducing conditions existing in these sediments, or that diagenesis declines rapidly. An alternative explanation is that all pigments and BSi are degrading at the same rate, which seems quite unlikely given their very different molecular structures. The degradation of several phytoplankton pigments, including carotenoids and chlorophylls, can be significant but varies considerably in oxic environments (Leavitt and Carpenter 1990) but not under anoxic conditions (Sun et al. 1993; McGowan et al. 1999). Furthermore, identification of BSi and various phytoplankton pigments in dated sediment layers has proved useful as proxies in reconstructing water quality in lakes, estuaries, and coastal waters, and the changes are in agreement with known nutrient loading scenarios (e.g., Schelske et al. 1983; Turner and Rabalais 1994; Poutanen and Nikklä 2001). The implied higher production in the water column and subsequent increased carbon loading to the sediments is, of course, expected to increase benthic oxygen metabolism (Hargrave 1973).

**Phytoplankton pigments**—Pigments extracted from sediments are used to identify taxa or taxonomic groups of phytoplankton, microphytobenthos, and higher plants and to differentiate the algal/plant community most closely associated with a particular location. The changing proportion of pig-

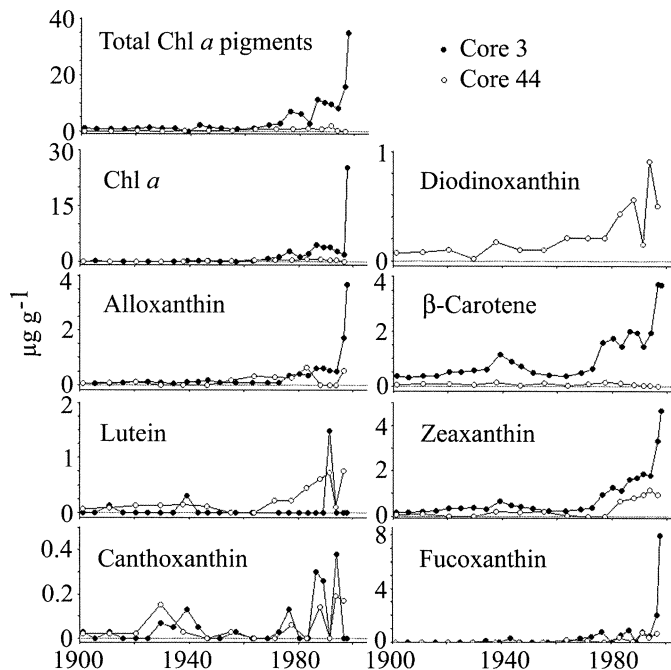


Fig. 16. Pigment concentrations in cores 3 and 44 (micrograms of pigment per gram of dry weight sediment). Total Chl *a* pigments includes Chl *a*, pheophorbide *a*, pheophorbide *b*, and pheophytin *a*-like pigments.

ments by time horizons does not represent the historical phytoplankton composition because of the potential for differential degradation of chloropigments (Leavitt 1993). The time course of any individual pigment, however, can be an indicator of the relative change in the productivity of a taxon.

The carotenoid concentrations within each core section were uniformly low from 1800 to 1925, with a period of transition from 1925 to 1950, and a general increase since 1950 (the upper 10 cm of each core) (Fig. 16). The surface layer concentration was sometimes much higher than the concentration in the layer immediately beneath, probably because it contains a flocculent layer that will not be permanently buried. Chl *a* decreased at a faster rate with depth than many of the carotenoid pigments (e.g., fucoxanthin, zeaxanthin, and  $\beta$ -carotene), which is consistent with the fact that the chlorophylls are more labile than the carotenoids (Hodgson et al. 1997). Overall, carotenoids increased through time, but some at a faster rate (which could indicate differences in degradation, productivity of specific taxa, or both). The concentrations of fucoxanthin (an indicator of diatoms) were higher in the upper sections of both cores, as was zeaxanthin (an indicator of cyanobacteria). Of the two pigments, zeaxanthin maintained trace levels through the depth of both cores with no peaks prior to the early 1950s, while fucoxanthin became negligible prior to the 1950s. Fucoxanthin is known to degrade more quickly than Chl *a* (Cariou-LeGall and Blanchard 1995), and its absence prior mostly to the 1950s is more likely due to its degradation rather than a lack of diatom production in Charlotte Harbor. However, both fucoxanthin and Chl *a* declined at similar rates (Fig. 16; Table 3), indicating an increase in production

of diatoms since the 1950s. Under anoxic conditions in lakes (Züllig 1981; Hodgson et al. 1997), fucoxanthin was preserved. Therefore, it is not unreasonable to also hypothesize that a reason for the increase in fucoxanthin in core 3 could be increasing anoxia in the overlying water with its relative change over time, indicating periods of eutrophication and anoxia (Züllig 1981).

The increase of the relatively stable zeaxanthin upcore (Züllig 1981; Bianchi et al. 2000) indicates an increase in cyanobacterial populations in more recent times. The lack of historic peaks, similar to those seen in paleostratigraphy from the Baltic (Bianchi et al. 2000), indicate that cyanobacterial blooms were not a feature in Charlotte Harbor from 1800 to 1925. Alloxanthin occurred in fairly high concentrations from the early 1950s to present in the open water cores, indicating the occurrence of aperiodic cryptophyte blooms since then.

The upcore increase in the percentage BSi concentration was accompanied by an increase in the concentration of six pigments in core 3 and two in core 44 (Table 3). Similar relationships were not evident for water column total nitrogen, nitrate, and Chl *a* measurements, likely because of the short period of measurement for water quality parameters. The concentration of Chl *a* in the dated sediments from core 3 varied temporally with the average annual concentration of Chl *a* ( $\mu\text{g L}^{-1}$ ) in water collected at Sta. EQL 9 where core 3 was taken (the water column data are for 5-yr running averages to match the approximate time period represented in each core section; Fig. 3).

The higher abundance of lutein as a proportion of the carotenoids versus  $\beta$ -carotene in core 44 indicates a higher relative influence of vascular plants (Bianchi et al. 1991) than water column phytoplankton as characterized by higher concentrations of  $\beta$ -carotene in core 3. This is consistent with the location of core 44 being closer to terrestrial plant communities. The high concentrations of diadinoxanthin in core 44, not observed in core 3, indicates the presence of freshwater algae, particularly euglenophytes, which is also consistent with the location of core 44 in fresher waters. Peridinin, found in dinoflagellates, was in trace concentrations in core 44 for the period 1900 to 1950 and in a fairly high concentration in core 3 for circa 1992. This observation supports the conclusion that there is a higher likelihood that dinoflagellate blooms originating in offshore waters affect the open bay system more than water at the terminus of the Peace River.

Three pigments illustrate the changes in pigments downcore after deposition and provide a means to evaluate the effect of mixing: fucoxanthin (indicative of diatoms, but also chrysophytes, prymnesiophytes, and raphidophytes), canthaxanthin (indicative of some cyanobacteria), and zeaxanthin (indicative of cyanobacteria) (Fig. 16). The downcore concentration of zeaxanthin in cores 3 and 44 is one of a gradual rise and fall before the most recent sedimentation layer sampled. In contrast, the concentrations of fucoxanthin and canthaxanthin rise and fall three times from 1960 to 1998. During this period, the peaks and valleys of canthoxanthin rise coincidentally in both cores but are offset in the first and second peak for fucoxanthin. The rise and fall in the concentration of zeaxanthin in both cores is more gradual.

These patterns are inconsistent with the hypotheses that vertical mixing exceeds the segment depth (1–2 cm) of the dated sediment segments. They support the conclusion that the chemistry in the dated horizons represents an average value for materials deposited over a few years and less than a decade.

*Diagenesis*—Diagenesis is not considered to be a consequential confounding interpretative influence on the above conclusion for several reasons. (1) The results in the scientific literature suggest that reduced sediments favor the retention of phytoplankton pigments and identifiable cells, and so diagenetic changes in anaerobic sediments like these will be less than in aerated sediments; (2) the changes in concentration of BSi downcore are coincidental with changes in several pigments known to be relatively stable in similar environments, which is an unlikely result if very different molecular structures in the pigments were undergoing diagenesis; (3) the pigment analyses suggest that the plankton community composition (as taxon) was not stable from decade to decade; and (4) the preservation of sharp peaks and troughs in specific pigments downcore (Fig. 16) are spaced downcore at intervals representing deposition over a few years, and not decades—significant diagenetic changes would have smeared this signature; and (5) both the C:N ratio and the C:Al ratio are nearly constant over the entire core length (Fig. 13), a pattern that is in contrast to what Cornwell et al. (1996) found in Chesapeake Bay, which had a rising organic C:Al ratio in sediments dated from 1900 to the 1990s. In fact, the contrasts between these two sediments are striking. Cornwell et al. (1996) report that sediments from the Chesapeake Bay have a varying C:N ratio and a rather noisy BSi profile that does match the C profile, and a rising C:Al profile. The Charlotte Harbor sediment profile has a relative steady C:N ratio, a rising BSi that parallels the C profile (and also P and N), and a relatively steady C:Al ratio. Cornwell et al. (1996) used the organic C:Al ratio to evaluate carbon diagenesis, assuming that Al behaves conservatively over time. We argue below that Al may become pyritized and may not behave conservatively.

*Carbon sources: terrestrial or in situ?*—Here we consider two explanations for the rise in organic matter in sediments more recent than 1950: (1) a “eutrophication hypothesis” that concludes that most materials in sediments reflect production in the local overlying water column, and (2) a contrasting “watershed hypothesis” that concludes that these materials are washed in from the watershed. The watershed hypothesis was initially attractive because many sediment constituents were closely correlated with aluminum concentrations and because aluminum is often considered a good indicator of watershed inputs (Cornwell et al. 1996).

However, the C:N ratios and  $\delta^{13}\text{C}$  values seemed more consistent with the first hypothesis (in situ production) because core 44, taken at the mouth of the river, had higher C:N ratios and lower  $\delta^{13}\text{C}$  values than would be expected of more terrestrial watershed inputs, while core 3 from mid-estuary had lower C:N ratios and higher  $\delta^{13}\text{C}$  values than would be expected of more marine inputs (Fig. 17). Thus, the organic-based parameters of C:N and  $\delta^{13}\text{C}$  together in-

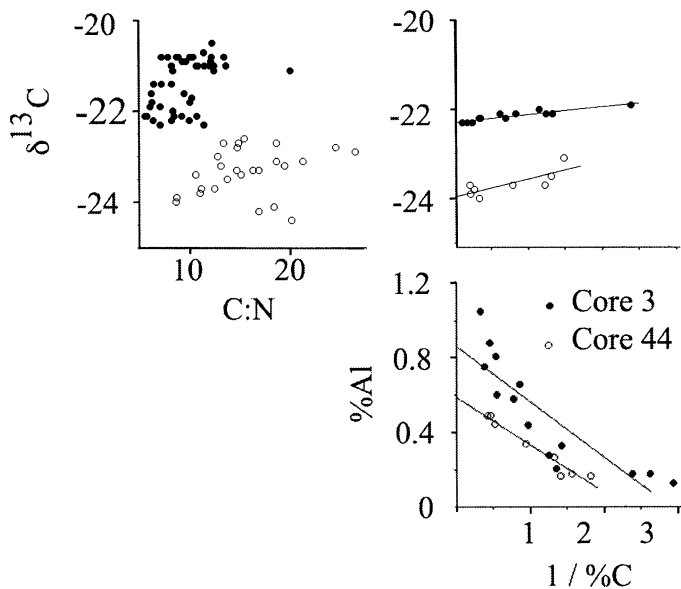


Fig. 17. Characterizations of organic material using the following. Upper right panel,  $\delta^{13}\text{C}$  versus  $1/\%C$  for sediments deposited since 1960; upper left panel,  $\delta^{13}\text{C}$  versus the C:N ratio (molar) for sediments deposited since 1800; and lower right panel, Al content versus  $1/\%C$  for sediments deposited since 1960. These graphs were used to determine the source materials found in the estuarine sediments (terrestrial or in situ algal production). See text for an interpretation of the results.

indicated a more local bias to the organic inputs rather than a simple watershed dominance for both cores.

We used an inverse graphing technique, which involves plotting  $\delta^{13}\text{C}$  versus the reciprocal of percentage C, to further characterize the organic material deposited since 1950 when sediment organic matter began sharply increasing (Fig. 13), (Fig. 17; upper right panel). In this plot, the intercept is the expected value of the material added when the amount of this material is extrapolated to an infinite addition, making the background contributions of other materials insignificant. The extrapolated  $\delta^{13}\text{C}$  values of  $-22.3\text{‰}$  for midestuarine core 3 and  $-24.0\text{‰}$  for riverine core 44 again supported a local origin of organic matter in each case, especially since  $-22\text{‰}$  values are characteristic of marine inputs and  $-27\text{‰}$  values are characteristic of terrestrial inputs (Hedges and Parker 1976).

We used the C:N ratios and  $\delta^{13}\text{C}$  values in mixing models to investigate the sources of organic carbon contributing to the strong increases in percentage C observed in the cores since 1950 (Fig. 18; Calder and Parker 1968; Fry and Sherr 1984). The two-source mixing models partitioned the carbon into algal versus terrestrial contributions by using algal and terrestrial end members, respectively, of  $-20.5$  and  $-27\text{‰}$  for the  $\delta^{13}\text{C}$  mixing model and 6.6 and 25 for the C:N mixing model. The overall results from both models indicate that most of the recent increase in organic C is due to algal inputs, not terrestrial materials (Fig. 18).

The mixing models of Fig. 18 can be criticized in several respects, especially that different selection of mixing end members can change the  $\delta^{13}\text{C}$  results (Gearing 1988), and that faster mineralization of N than C (Rosenfeld 1981) dur-

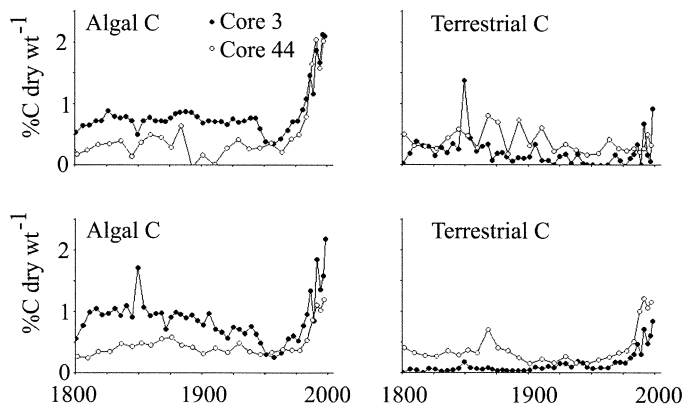


Fig. 18. The results of a mixing model used to quantify the source material found in the two sediment cores over time, partitioned into carbon from in situ algal production or from terrestrial sources. Upper panels, algal and terrestrial end members of 6.6 and 25, respectively, for a C:N mixing model. Lower panels, algal and terrestrial end members of  $-20.5$  and  $-27\text{‰}$ , respectively, for the  $\delta^{13}\text{C}$  mixing model. The Y axis is the percentage C per dry weight sediment.

ing sediment diagenesis will increase C:N ratios so that C:N ratios are not conservative indicators of source inputs. We investigated these possibilities by changing the end members in spreadsheet models that then updated graphs of Fig. 18 and found that the results shown in Fig. 18 are typical of a variety of end member selections. Also, the results of Fig. 18 were conservative with regard to the importance of algae because increasing the C:N ratio of algae to account for diagenetic shifts had the effect of increasing the importance of algae, and decreasing the  $\delta^{13}\text{C}$  of the algal end member to account for more negative algal  $\delta^{13}\text{C}$  typical of estuaries (Matson and Brinson 1990) also resulted in stronger algal inputs. Finally, recognizing that model results are always imperfect, it was also reassuring that the two independent models based on C:N ratios and on  $\delta^{13}\text{C}$  gave similar results (Fig. 18). Our overall conclusion from this modeling was that stronger algal inputs (Fig. 18) and local origin of those inputs (inferred from Fig. 17) reinforced the view that local production was the dominant input accounting for recent, post-1950 organic matter in these two cores from Charlotte Harbor.

With this perspective, we then considered the possibility that in these sandy sediments, other components such as aluminum, iron, and sulfur were accumulating and cycling in response to the increased algal inputs, rather than being deposited from the watershed. This idea is not commonly advocated by geochemists studying muddy and carbonate sediments but could explain otherwise counterintuitive results for these sandy soils, e.g., that there is a stronger accumulation of materials such as aluminum that are normally considered watershed markers occurring in the midestuarine core 3 sediments than in the riverine core 44 sediments (Fig. 13).

*Summary and synthesis of patterns*—A synthesis of results from these analyses and an analysis of the literature leads to the following conclusions. Phytoplankton in Charlotte Har-

bor estuary are nitrogen limited, and nitrogen loading has increased with land use changes over the last several decades. Indicators of phytoplankton production (BSi and pigments) found in dated sediments from the mixing zone of Charlotte Harbor change coincidentally with N loading from the watershed. Mixing models based on C:N ratios and  $\delta^{13}\text{C}$  suggest a marine, not terrestrial, source of the organic matter accumulating in recent decades. Further, there is a mismatch between the temporal inputs of S and the temporal changes in land use, suggesting that sulfate reduction is responsible for the changes in S downcore. Mass-normalized values of sedimentary trace metals are indicative of metal complexation with S, and their accumulation is directly related to increased organic loading. We conclude that (1) phytoplankton in the estuary increased in response to increased loadings of nitrogen and (2) the resulting increased in situ organic loading is causally related to an expanded hypoxic water mass formation in summer.

The results from our analyses create an interlocking set of conclusions for the Charlotte Harbor estuary that are summarized below.

A. 1800s to 1980: Nitrogen loading increased with population growth and intensified land use, as is commonly observed elsewhere (e.g., Howarth et al. 1996). Estimates of the total nitrogen loading for the area vary and include 678 (1957–1985) and 280 (1999–2000)  $\text{kg N km}^{-2} \text{ yr}^{-1}$  for the Peace River at Arcadia (Hammett 1990; Charlotte Harbor Environmental Center, Inc. 2001, respectively), and 269  $\text{kg N km}^{-2} \text{ yr}^{-1}$  for the Charlotte Harbor watershed (1992–1994; Coastal Environmental, Inc. 1995). These estimates are many times the background level (78  $\text{kg N km}^{-2} \text{ yr}^{-1}$ ; 1800 [Turner et al. 2000]) occurring before significant human changes after 1800. This period is when the accumulation of organic carbon, phytoplankton pigments, and diatom residues in sediments began, which was also coincidental with the appearance of heavier  $\delta^{34}\text{S}$  values. Freshwater flows into the estuary may have declined from the 1930s to the 1980s (Hammett 1990), with the result that average salinity stratification would have declined slightly, although there may have been additional (contradictory) seasonal changes. Lower river discharges that led to less stratification would have contributed to a lower likelihood of hypoxic conditions (and algal blooms). The relationships between nitrogen loading, algal growth, and hypoxia are implicit in these relationships.

B. 1980s to early 1990s: Improvements in water treatment facilities and land use management resulted in stable or slightly lower nitrogen loading from rivers, although regional population growth continued (together with local nonpoint runoff). There may have been a declining incidence of hypoxia in bottom waters, and there was a lower oxygen concentration in surface water during this period compared with 15 yr earlier. This result indicates that algal production had declined (thus the lower organic carbon loading to bottom waters). However, the organic carbon stored in sediments during previous periods remained a significant dissolved oxygen sink for many years. A modern example of the coupling between changing nitrogen loading and bottom water oxygen concentration is thus established.

C. After 1998 scenario: Further population growth will contribute to higher nitrogen loading to the estuary, which will increase the likelihood of additional incidences of hypoxia and anoxia, and perhaps harmful algal blooms. Decreased transparency and loss of the submerged aquatic vegetation could result, although light attenuation is currently dominated by the abundance of dissolved organic matter and suspended nonchlorophyllous material, not phytoplankton. These changes may be offset by reduced nutrient loading in the watershed, if appropriate land use changes and nutrient control strategies are implemented.

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