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Estuarine, Coastal and Shelf Science 62 (2005) 25–40
ESTUARINE COASTAL AND SHELF SCIENCE
www.elsevier.com/locate/ECSS

Modelling phytoplankton deposition to Chesapeake Bay sediments during winter–spring: interannual variability in relation to river flow

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Received 9 February 2004; accepted 11 August 2004

Abstract

The often-rapid deposition of phytoplankton to sediments at the end of the spring phytoplankton bloom is an important component of benthic–pelagic coupling in temperate and high latitude estuaries and other aquatic systems. However, quantifying the flux is difficult, particularly in spatially heterogeneous environments. Surficial sediment chlorophyll-*a*, which can be measured quickly at many locations, has been used effectively by previous studies as an indicator of phytoplankton deposition to estuarine sediments. In this study, surficial sediment chlorophyll-*a* was quantified in late spring at 20–50 locations throughout Chesapeake Bay for 8 years (1993–2000). A model was developed to estimate chlorophyll-*a* deposition to sediments using these measurements, while accounting for chlorophyll-*a* degradation during the time between deposition and sampling. Carbon flux was derived from these estimates via C:chl-*a* = 75.

Bay-wide, the accumulation of chlorophyll-*a* on sediments by late spring averaged 171 mg m^{-2}, from which the chlorophyll-*a* and carbon sinking fluxes, respectively, were estimated to be 353 mg m^{-2} and 26.5 gC m^{-2}. These deposition estimates were ~50% of estimates based on a sediment trap study in the mid-Bay. During 1993–2000, the highest average chlorophyll-*a* flux was in the mid-Bay (248 mg m^{-2}), while the lowest was in the lower Bay (191 mg m^{-2}). Winter–spring average river flow was positively correlated with phytoplankton biomass in the lower Bay water column, while phytoplankton biomass in that same region of the Bay was correlated with increased chlorophyll-*a* deposition to sediments. Responses in other regions of the Bay were less clear and suggested that the concept that nutrient enrichment in high flow years leads to greater phytoplankton deposition to sediments may be an oversimplification. A comparison of the carbon flux associated with the deposition of the spring bloom with annual benthic carbon budgets indicated that the spring bloom did not contribute a disproportionately large fraction of annual carbon inputs to Chesapeake Bay sediments. Regional patterns in chlorophyll-*a* deposition did not correspond with the strong regional patterns that have been found for plankton net community metabolism during spring.

Keywords: phytoplankton; chlorophylls; sinking; deposition; sediments; sediment traps; Chesapeake Bay

1. Introduction

The spring increase in phytoplankton production and biomass is a well-known feature of the phytoplankton dynamics of temperate and high latitude aquatic ecosystems. Significant ecological importance has been

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doi:10.1016/j.ecss.2004.08.004

ascribed to this annual event, particularly as it affects benthic processes. For example, both the quantity and high nutritional quality of the input have been shown to be important for macrobenthic production (Graf et al., 1982; Marsh and Tenore, 1990) and to enhance microbial processes and related nutrient regeneration (Jensen et al., 1990). Support of summer microbial activity by organic matter from the spring phytoplankton bloom has been identified as a critical connection between ecosystem processes in spring, particularly spring nutrient inputs associated with the winter–spring freshet, and summer conditions such as hypoxia and eutrophication (Malone, 1992; Hagy, 2002). The magnitude and timing of the spring phytoplankton bloom has even been related to recruitment success of juvenile demersal fishes (Townsend and Cammen, 1988). Thus, quantifying the magnitude and fate of the spring bloom is an important objective for understanding the behavior of these ecosystems.

Chesapeake Bay is a large, temperate estuary where the spring bloom is a well-known ecological feature. Although Chesapeake Bay is not unique in this regard, the long-term degradation of water quality in this well-studied system (eg. Harding and Perry, 1997; Officer et al., 1984; Hagy, 2002) makes it a case of special interest. In Chesapeake Bay, the spring increase in phytoplankton biomass typically begins in March. Biomass peaks begin to decline some time in April and the bloom stops by the end of May (Harding, 1994). Diatoms contribute a large fraction of the winter–spring phytoplankton assemblage (Marshall and Nesius, 1996). The often-rapid decline of spring phytoplankton blooms in Chesapeake Bay has been attributed to phosphorus and dissolved silica limitation (Conley and Malone, 1992; Malone et al., 1996). Nutrient limitation promotes a physiological response such as formation of large aggregates that leads to increased sedimentation of diatoms (Smetacek, 1985; Conley and Malone, 1992). Consequently, sinking is a quantitatively important fate of diatom blooms. In a mesocosm experiment simulating a spring bloom in Narragansett Bay, Keller and Riebesell (1989) estimated that sedimentation accounted for 14–65% of gross production.

Because of the potential importance of spring bloom deposition to ecosystem processes, quantifying the flux is of particular interest. Unfortunately, this is technically challenging, a fact reflected in the paucity of flux estimates. Sediment traps have been used to quantify vertical fluxes of particles in various aquatic systems (e.g., Smetacek et al., 1978), including in Chesapeake Bay (Wetzel and Neilson, 1989; Boynton et al., 1993). Although effective and useful, especially in open ocean environments, the design and use of sediment traps entails significant complications (Blomqvist and Håkanson, 1981; Knauer et al., 1984; Butman, 1986; Butman et al., 1986; Asper, 1987). In highly heterogeneous coastal waters, the effort required to maintain sediment traps may limit the number of traps to less than what is needed to adequately characterize the variability in space. If phytoplankton production is localized outside the vicinity of the trap, the measurement will underestimate the flux. In coastal waters, trapping of resuspended particles can lead to large errors (Wetzel and Neilson, 1989; Boynton et al., 1993). Therefore, research in coastal waters requires an approach that is not subject to resuspension artifacts and can estimate the flux at many locations.

Previous studies have demonstrated that chlorophyll-*a* and other phytoplankton pigments are effective indicators of fresh phytoplankton inputs to sediments (Sun et al., 1991; Josefson and Conley, 1997). Since sediment chlorophyll-*a* can be sampled and quantified rapidly and inexpensively at a large number of locations, such collections could form the basis of an effective approach for estimating the flux of winter–spring phytoplankton blooms to sediments at the ecosystem scale, provided that one can rule out microphytobenthos as a possible source of pigment. Given that a large fraction of mainstem Chesapeake Bay sediments is aphotic in spring (mean spring time secchi disk depth = 0.5–2.0 m, unpublished data, Chesapeake Bay Water Quality Monitoring Program) this approach can be implemented in this system. Thus, the objectives of this study were to (1) quantify the spatial distribution of chlorophyll-*a* in aphotic Chesapeake Bay surficial sediments at or near the conclusion of the spring bloom, (2) use this to estimate the total flux or phytoplankton-derived carbon to sediments during winter–spring, and (3) relate the fluxes measured over several years to large-scale differences in ecosystem function which are related to variations in spring freshwater inflow (e.g. Boynton and Kemp, 2000).

This study used surficial sediment chlorophyll-*a* measured in late spring as an indicator of deposition to sediments of phytoplankton originating from the spring bloom. The total flux of phytoplankton to sediments was estimated using a simple model describing deposition and chlorophyll-*a* decay. Interannual differences were assessed by repeating the chlorophyll-*a* measurements annually for a period of 8 years. Interpretation of results was supported by comparison with contemporaneous estimates of phytoplankton biomass in the water column, sedimentation estimates from a sediment trap study, estimated phytoplankton sinking rates, and by comparison with plankton community net production estimates (= gross production minus community respiration).

1.1. Study site

Chesapeake Bay is a large, partially stratified estuary that extends 300 km from the mouth of the Susquehanna River in Maryland to the Atlantic Ocean between Cape Henry and Cape Charles, VA (Fig. 1). The oligohaline

upper Bay has a mean depth of 4.5 m with a deeper (~10 m) channel near the eastern margin. During spring, the depth to which 1% of incident light penetrates ($z_{1\%}$) is approximately 2 m, making most of the sediments aphotic (Chesapeake Bay Monitoring Program, unpublished data). The mesohaline mid-Bay has a deep central channel, 20–50 m, flanked by shoal areas to the east and west, giving it a deeper mean depth of 10.3 m. The polyhaline lower Bay is broader with a wide central channel region averaging ~15 m depth and broad shoal areas on the flanks of the channel. The mean depth is 9.2 m. In the middle and lower Bay, $z_{1\%}$ is 5–6 m (Chesapeake Bay Monitoring Program, unpublished data). Thus, much of the sediments are also aphotic in this region of the Bay.

The physical transport regime throughout most of the estuary is best characterized by 2-layer gravitational circulation in which net up-estuary advection occurs below the pycnocline and net down-estuary advection occurs in the surface layer (Pritchard, 1952). In the upper Bay, the circulation is initially down-estuary at all depths and at some point down-estuary makes a transition to the 2-layer circulation.

Sediment types vary throughout the estuary. North of Patuxent River and in the western half of the Bay south of Patuxent River, sediments are >80% mud except in shallow waters (Fig. 1). In these shallow waters, and in deeper areas of the eastern half of the south Bay, more porous sandy sediments (>80% sand) predominate (Kerhin et al., 1983; Chesapeake Bay Benthic Monitoring Program, unpublished data).

2. Materials and methods

2.1. Field methods

Sediment cores were obtained at sites throughout the Bay during mid to late April in each year during 1993–2000 (Table 1, Fig. 3). Sampling cruises were conducted aboard the R/V Cape Henlopen and were part of a

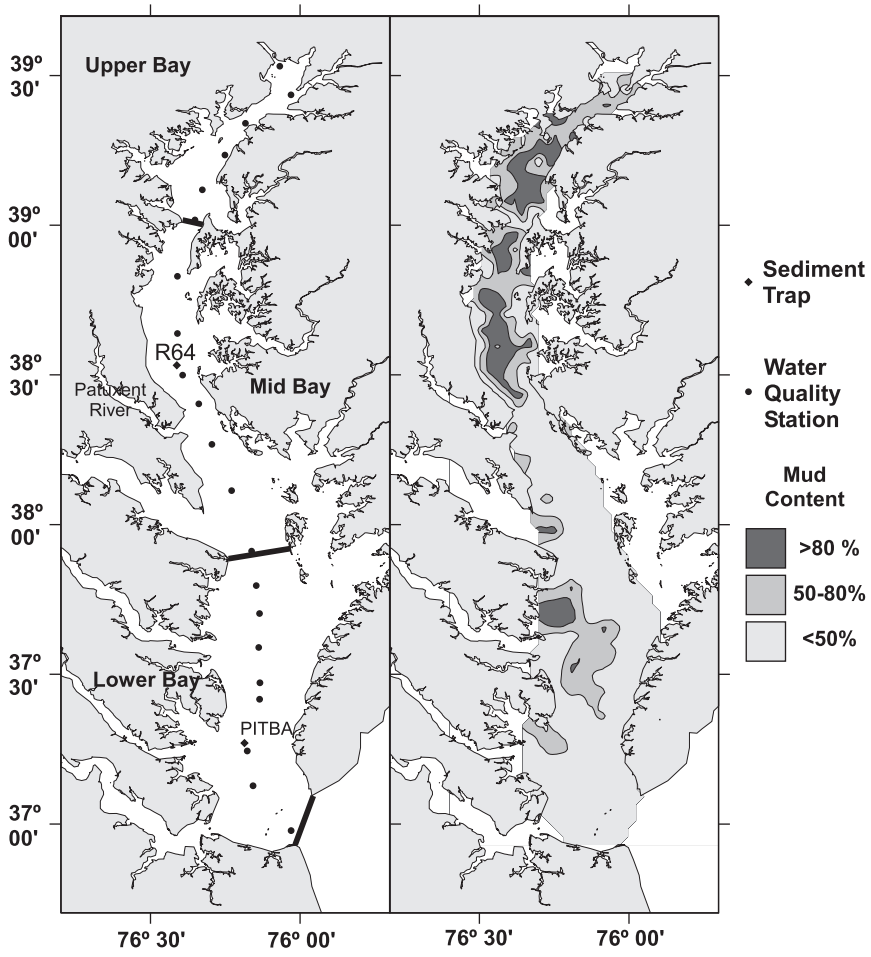

Fig. 1. Maps of Chesapeake Bay indicating (left panel) regional boundaries, the locations of Chesapeake Bay Water Quality Monitoring Stations used to compute water column chlorophyll-*a* concentrations and the locations of sediment traps in Virginia (PITBA, Wetzel and Neilson, 1989) and Maryland (R64, Boynton et al., 1993). The distribution of sediment types (right panel) was computed from the Chesapeake Bay Benthic Monitoring Program (unpublished data) and are comparable to that from Kerhin et al. (1983).

Table 1
Cruise dates for sediment chlorophyll-*a* surveys and the number of sediment cores collected in each region of the Bay

Year	Cruise dates		Number of cores		
	Begin	End	Upper Bay	Mid-Bay	Lower Bay
1993	5/8/93	5/12/93	8	25	23
1994	Mid May		9	21	33
1995	4/28/95	5/3/95	7	25	31
1996	4/27/96	5/7/96	8	13	10
1997	4/20/97	4/24/97	7	17	7
1998	4/11/98	4/15/98	6	13	15
1999	4/19/99	4/23/99	6	11	14
2000	4/29/00	5/2/00	6	8	6

multi-disciplinary research project (Chesapeake Bay Land Margin Ecosystem Research Program).

Cores with an intact and minimally disturbed sediment–water interface were obtained using a 0.25 m^2 Smith–Macintyre coring device at 20–50 locations usually located along east–west transects spaced ~20 km apart. Multiple attempts were needed in many instances to obtain a core of suitable quality. In 1993–1995, when the highest numbers of stations were sampled, additional stations were occupied between transects. Cores were obtained in waters from the deepest portions of the Bay to as shallow as 8 m. Shallower depths were not sampled due to draft limitations of the research vessel.

Once onboard, a sub-core was obtained using a 60 cc plastic syringe with the end removed. This provided a sample of precisely 5.7 cm^2 cross-sectional area and 1 cm depth, which was frozen immediately in a plastic centrifuge tube. Methods varied slightly over the course of the project. In 1993, the top 2 mm from two sub-cores was combined in a single centrifuge tube, rather than 1 cm from a single sub-core. In 1994–1995, two samples were obtained at each station. One sample included the top 1 cm from a single sub-core, while the other included the top 2 mm from two sub-cores, as in 1993. This provided a means for comparing the two types of samples. The reasons for these changes in field methods were unrelated to this study, but provided a limited means to examine the vertical distribution of chlorophyll-*a* in Chesapeake Bay sediments.

2.2. Pigment analysis

Frozen sediment samples were briefly thawed at room temperature, then 40 ml of 90% acetone was added. Samples were extracted for 12 h in a dark refrigerator, shaking 2–3 times during the course of the extraction, then centrifuged at ~1760 rpm for 5 min before decanting into a cuvette. Total chlorophyll-*a*, active chlorophyll-*a* and phaeopigment concentrations in the acetone extracts were determined fluorometrically using the acidification method described in Strickland and Parsons (1972) and Parsons et al. (1984). Only the total chlorophyll-*a* and phaeopigment data were examined in this study. The laboratory utilized a Turner Designs Model TD700 fluorometer calibrated against a spectrophotometer using pure chlorophyll-*a* from spinach (Sigma Chemical Company, C 5753), or liquid standards from Turner Designs, #10-850.

The extraction method that was used was later found to be different from that used by some published studies (e.g., Sun et al., 1991). Specifically, sediments were not sonicated prior to extraction, and only a single extraction was used. Therefore, a method comparison study was undertaken to determine whether the results would have differed significantly by use of sonication and/or an additional extraction. In this experiment, surficial sediments were obtained from box cores collected from the Patuxent River, an estuarine tributary of the Chesapeake Bay in which sediments are very similar to Chesapeake Bay sediments (Fig. 1). Sediments were processed in the field as described above. In the laboratory, the samples were thawed, and then homogenized. Fifteen equal size aliquots from the continuously stirred mud-slurry were extracted as described above after one of three sonication treatments. The treatments were: (1) no sonication (control); (2) microsonication for 3 min; and (3) sonication in a sonicator bath. The extracted pigments were decanted and analyzed as above. A second extraction of each sample was also analyzed as above, with the sum of the first and second extractions being recorded as the value for double extraction. No sonication was performed prior to the second extractions. Although this design resulted in 30 values describing each of six treatment combinations, there were only 15 independent observations. Therefore, statistical significance was evaluated using repeated-measures ANOVA. A comparison of single vs. double extraction (without any sonication) was also done on seven non-homogenized samples from different locations in Patuxent River.

2.3. Interpolation methods

Sediment chlorophyll-*a* data were interpolated to a regular grid for the purpose of contouring and computing regional means using the kriging procedure of Surfer software (Golden Software, Inc., Golden, CO). A quadrant-search algorithm was selected such that up to 4 observations were selected from each of 4 quadrants divided by north–south and east–west oriented axes.

2.4. Water column chlorophyll-a and phytoplankton species composition

Water column chlorophyll-*a* and phytoplankton species composition data were obtained from the Chesapeake Bay Water Quality and Phytoplankton

Monitoring Programs (CBMP). Richard Lacouture of the Philadelphia Academy of Natural Science Estuarine Research Center provided the carbon content of major taxonomic groups for stations in Maryland. Chlorophyll-*a* is measured by the CBMP spectrophotometrically from acetone extractions of ground filters (EPA, 1993). Seasonal and regional integrated chlorophyll-*a* distributions as well as regional mean integrated chlorophyll-*a* concentrations were computed from interpolated distributions based on data from a bi-weekly to monthly (Dec–Feb) sampling of approximately 20 stations located down the axis of the estuary (Fig. 1). Integrated chlorophyll-*a* was computed from vertical profiles of chlorophyll-*a* weighted by cross-sectional volumes per meter depth (Cronin and Pritchard, 1975; Hagy, 2002). Phytoplankton species composition was determined microscopically from samples collected monthly at three stations, one in each major region of the Bay.

3. Results and discussion

3.1. Pigment analysis method comparison

The results of a method comparison experiment, conducted after analysis of field samples was concluded, showed that sonication and multiple extraction of sediment samples (e.g., Sun et al., 1991) could be expected to give sediment chlorophyll-*a* measurements up to 16% higher than those obtained with the method used in this study (Table 2). The difference was found to be a nearly constant proportion of chlorophyll-*a* as measured using a single extraction with and without sonication, allowing a correction to be applied to the original value. Compared to the control (no sonication, single extraction), 3% more chlorophyll-*a* was extracted after use of a sonicator bath and 5% more chlorophyll-*a* was extracted after microsonication ($p < 0.01$, Table 2). The second extraction removed 10–11% more chlorophyll-*a* ($p < 0.01$), depending on the sonication treatment ($p < 0.01$). A larger amount was extracted on the second extraction if microsonication was used prior to the first extraction. Sediment chlorophyll-*a* measured in seven non-homogenized sediment samples from Patuxent River using a single extraction and no sonication varied between 77 and 148 mg chlorophyll-*a* m^{-2}. A second extraction obtained $11 \pm 0.5\%$ (mean $\pm$ std error) additional chlorophyll-*a*, a proportion comparable to that obtained for the corresponding treatments using homogenized samples (Table 2). This indicated that a proportional correction could be applied to the 1993–2000 Chesapeake Bay samples. We applied a proportion of 16%, which was the additional amount of chlorophyll-*a* extracted by microsonication and double extraction, as compared to no sonication and single extraction (Table 2). Although this correction is not large compared to other possible sources of uncertainty, we applied the correction because our analysis indicated that applying it was more likely to be correct than not doing so.

Table 2
Results of a method comparison experiment used to evaluate the effect of three sonication treatments and single vs. double extraction on the amount (mean $\pm$ se, % change from control) of chlorophyll-*a* (μg/g) extracted from 15 aliquots of homogenized Chesapeake Bay sediments

	Single extraction, μg/g	Double extraction, μg/g
No sonication	9.35 (0.02, 0%)[a]	10.32 (0.02, +10%)[a]
Microsonication	9.78 (0.05, +5%)	10.84 (0.06, +16%)
Sonicator bath	9.63 (0.03, +3%)	10.56 (0.04, +13%)

Each sonication treatment was replicated five times. All effects (sonication, extraction and interaction effect) were statistically significant (repeated-measures ANOVA, $p < 0.01$).

[a] These treatments were also compared using seven non-homogenized samples. The mean difference in those samples was $11.0 \pm 0.5\%$.

3.2. Computing sediment total chlorophyll-a inventories

Due to vertical mixing of sediments on short time scales (days to weeks), the total chlorophyll-*a* inventory (i.e., vertically integrated concentration) of recently deposited chlorophyll-*a* may not have been accurately represented by sampling the top 0–10 mm of sediments (see discussion below and Dellapenna et al., 1998). This leads to an underestimation of chlorophyll-*a* deposition, and, to the extent that sediment mixing could differ regionally, could affect comparisons among regions. The simultaneous collection of 0–2 mm and 0–10 mm sediment samples during 1994–1995 provided an opportunity to examine this issue and compute the sediment chlorophyll-*a* inventory.

Bay-wide, the ratio of the 0–10 mm to 0–2 mm chlorophyll-*a* inventories was estimated to be 2.75. If the chlorophyll-*a* concentration did not decrease with depth in the sediments, the ratio would be 5 (= 10 mm/2 mm). Therefore the observed ratio (2.75) indicates a decline in chlorophyll-*a* concentration with depth in the sediments. The ratio was found to differ significantly among regions of the Bay, with respective median ratios for the upper-, mid- and lower-Bay regions equal to 2.7, 2.3, and 3.1 (Kruskal–Wallis test; $p < 0.05$). Using more detailed vertical profiling of sediment chlorophyll-*a* in the top 10 cm of Long Island Sound sediments, Sun et al. (1994) observed an exponential decrease in chlorophyll-*a* with depth below the sediment–water interface. This model has been assumed to apply to Chesapeake Bay as well. Accordingly, the chlorophyll-*a* inventory (C_{int}) integrated to a depth h, is

$$C_{\text{int}} = C_{\max} \int_{z=0}^{z=h} e^{-kz} = C_{\max} \frac{1}{k}\left(1 - e^{-kh}\right) \quad (1)$$

where $C_{\max}$ is the maximum (surface) concentration and k is the rate of decrease with depth. Using this expression, the ratio, R, between the 0–10 mm concentration and the 0–2 mm concentration is $R = \left(1 - e^{-10k}\right)/\left(1 - e^{-2k}\right)$, which gives $k = 0.19$, 0.25, and 0.14 for the upper-, mid- and lower-Bay, respectively. Using these estimates of k, the top 10 mm was estimated to include (in same order) 85%, 92% and 76% of the total chlorophyll-*a* inventory ($\approx$ 0–10 cm integrated chlorophyll-*a*). These factors were used to compute the chlorophyll-*a* inventory from the measured concentrations.

The regional differences in vertical chlorophyll-*a* distribution (i.e., in k) may reflect differences in sediment properties and/or mixing processes. The mid-Bay is characterized by fine, silty sediments (Fig. 1), deep and seasonally anoxic water (Hagy, 2002), and lower physical energy (i.e. waves and currents) than other areas of the Bay. These characteristics would be expected to result in minimal physical and biological mixing of sediments. In contrast, the lower Bay is shallower and has an increased prevalence of sandy sediments. During winter–spring, the penetration depth of ^{7}Be (half-life = 53 d) in the lower Bay was 3–5 cm, with significant physical mixing due to tidal current and wave action (Dellapenna et al., 1998). This may explain the deeper mixing of deposited chlorophyll-*a* in the lower Bay, although no comparable data are available for the mid-Bay or upper Bay. An April minimum in sediment mixing in the lower Bay, prior to a summer increase associated with bioturbation (Dellapenna et al., 1998), suggests that macrobenthic activity was suppressed by water temperature (5–15 °C, low for Chesapeake Bay benthos) prior to the time that surficial sediment samples were collected. We also observed that macrobenthic biomass was either zero or appeared to be near zero in most cores, especially in the mid and upper Bay, and that there was no evidence of activity by macrobenthos. This is important to the overall approach of this study because losses of chlorophyll-*a* due to macrobenthic activity could be large and spatially variable, and therefore difficult to quantify. Where potentially important, effects of macrobenthos grazing cannot be ignored.

3.3. Phaeopigments

Phaeopigments are a product of the early breakdown of chlorophyll-*a*. Since they degrade more slowly than chlorophyll-*a* itself, the ratio of chlorophyll-*a* concentration to the concentration of phaeopigments can suggest the relative rate and timeframe of phytoplankton deposition. For the 84 measurements Bay-wide in 1996–2000 in which sediment phaeopigment concentration was measured, the ratio of chlorophyll-*a*/phaeopigments averaged 0.98 (range = 0.7–1.4). In a study in which this ratio was measured throughout one year in the Baltic Sea, the highest chlorophyll-*a*/phaeopigment ratio (0.67) co-occurred with peak sediment chlorophyll-*a* concentrations and occurred shortly after the end of the spring phytoplankton bloom (Bianchi et al., 2002). Similarly, Josefson and Conley (1997) examined the ratio chlorophyll-*a*/chlorophyll-*a* + phaeopigments, finding values between 0.15 and 0.60. Most values were less than 0.4. The highest values occurred in the vicinity of a high productivity frontal area, while lower values occurred at deeper depths. The corresponding ratio in this study averaged 0.47 (0.38–0.58). These results suggest that a high ratio of chlorophyll-*a* to phaeopigments indicates rapid and recent deposition of phytoplankton to sediments. The relatively higher values observed in Chesapeake Bay as compared to the other studies provide a qualitative indication that a large input of fresh phytoplankton was deposited to sediments during the period shortly prior to our sampling.

3.4. The spring phytoplankton bloom

Examination of water column chlorophyll-*a* (chlorophyll-*a*) data collected bi-weekly for >15 years revealed the average seasonal and spatial pattern of phytoplankton biomass in Chesapeake Bay (Fig. 2). The spring phytoplankton bloom occurred over the most seaward 230 km of the estuary, excluding approximately 60 km of turbid, mostly tidal fresh waters. The spring increase in phytoplankton biomass typically begins in March. Biomass peaks in early to mid April, and reaches values typical of summer by the end of May. Because blooms originate and terminate at varying times during spring, the average bloom distribution (Fig. 2) appears more protracted and achieves lower maximum biomass than is observed in most years.

Excluding abundant but small picoplankton (<8 μm), diatoms in winter–spring accounted for ~80% of phytoplankton cells in the lower Bay, 67% of cells in the mid-Bay (above pycnocline), and 56% of cells in the upper Bay (Chesapeake Bay Monitoring Program, unpublished data). Diatoms accounted for similar proportions of total phytoplankton carbon (R. Lacouture, personal communication, Table 3).

3.5. Distributions of sediment total chlorophyll-a

The computed sediment total chlorophyll-*a* inventory averaged 175 mg m^{-2} over 272 observations Bay-wide during 1993–2000. The median value was 164 mg m^{-2} (interquartile range = 88–234 mg m^{-2}). Regional and overall mean chlorophyll-*a* was calculated for each year from interpolated distributions to account for the non-random distribution of observations. Computed in this way, the long-term overall mean was 171 mg m^{-2}, very

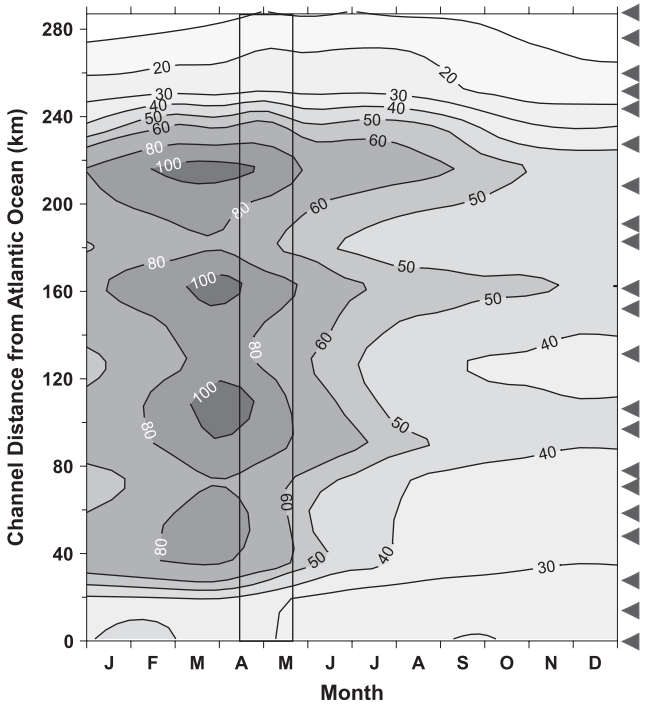

Fig. 2. Average seasonal distribution of water column integrated chlorophyll-*a* (mg m^{-2}) in Chesapeake Bay (1984–1999). Arrows on the right (◀) indicate the locations along the central axis of the Bay of the Chesapeake Bay Water Quality Monitoring Program stations used to generate the plot. The rectangle indicates the time period during which surficial sediment sampling was usually conducted. Exact dates are given in Table 1.

close to the unweighted average of all observations. However, regional means, particularly the upper Bay mean, were slightly more sensitive to the averaging procedure. Therefore, the interpolated fields were used to compute means rather than the raw data. The highest average chlorophyll-*a* inventory, 195 mg m^{-2}, was found in the mid-Bay. Lower chlorophyll-*a* was found in the lower Bay (148 mg m^{-2}) and the upper Bay (172 mg m^{-2}, Table 4). Interannually, the highest Bay-wide mean chlorophyll-*a* inventory was 244 mg m^{-2} in 1999, while the lowest was 117 mg m^{-2} in 1995, a >2-fold range (Table 4). The distribution of raw observations illustrates the patterns and magnitude of spatial and interannual variability in sediment chlorophyll-*a* (Fig. 3).

3.6. Responses to river flow

We expected that patterns of sediment chlorophyll-*a* might be related to large-scale external forcing, particularly river flow during winter–spring. Since nutrient loading to Chesapeake Bay is positively and strongly correlated with river flow (Boynton and Kemp, 2000), increased river flow can be expected to increase phytoplankton biomass and production when and where nutrient limitation is important. Direct inputs of chlorophyll-*a* derived from freshwater algae appear to be minimal. In the case of Chesapeake Bay, nutrient limitation, principally by phosphorus and silicate (for diatoms), is well known near the end of spring in the mid- and lower-Bay (Conley and Malone, 1992; Fisher et al., 1992; Fisher et al., 1999), but not in the upper Bay where increased flow could lead to decreased production by exacerbating light limitation and shortening the residence time (Hagy et al., 2000). Thus, one may hypothesize that river flow will be positively correlated with deposition of chlorophyll-*a* in the lower Bay, but negatively correlated in the upper Bay. Due to the larger area in the lower Bay, we expected that the overall average sediment chlorophyll-*a* would be higher in high flow years. We also expected that in high flow years, concentrations in the upper Bay would be lower relative to the lower Bay.

Six observations were consistent with an expected overall increase in sediment chlorophyll-*a* with river flow, but two years among those with low river flow had the highest sediment chlorophyll-*a*. Thus, no relationship could be demonstrated (Fig. 4). Similarly, a broad negative correlation suggested a down-Bay shift in chlorophyll-*a* deposition ($r^2 = 0.4$, $p = 0.10$), but the low statistical significance (i.e., $p > 0.05$) indicated that more data are needed to resolve the response (Fig. 4). A strong positive relationship was observed between water column chlorophyll-*a* in the lower Bay and winter–spring river flow (Fig. 5). In this relationship, the 1997 observation was a statistical outlier (absolute studentized residual >2) and was excluded from the calculation of the correlation coefficient. A likely explanation for this departure is provided below (see Section 3.7). This relationship indicates that under most conditions, high river flow was associated with high phytoplankton biomass in the lower Bay, while low river flow was associated with low biomass. No similar relationship was observed for the upper Bay or mid-Bay.

A correlation between chlorophyll-*a* deposited to lower Bay sediments and accumulated biomass in the water column illustrated responses for this portion of the Bay consistent with concepts of nutrient-driven eutrophication, namely that increased phytoplankton production and biomass in the water column led to more deposition of phytoplankton to sediments (e.g. Malone, 1992; Fig. 6). This type of relationship was not observed in other regions of the Bay, however (Fig. 6). Sediment chlorophyll-*a* in the upper Bay varied widely and was not correlated with water column chlorophyll-*a*, which remained within a narrower and lower range than in other regions of the Bay. Water column chlorophyll-*a* concentrations were higher in the mid-Bay than in the upper Bay, but were also uncorrelated with sediment chlorophyll-*a*. These uncorrelated observations may reflect alternate mechanisms that could affect the relationship between these two variables. For example, a high vertical flux of phytoplankton to sediments could deplete

Table 3
The most abundant phytoplankton taxa (excluding picoplankton) in three regions of Chesapeake Bay during spring and the average fraction of total phytoplankton carbon contributed by diatoms

Region	Most abundant phytoplankton taxa (excluding picoplankton) during Jan–Apr. (% of cells)	% of total phytoplankton counts	% of total phytoplankton carbon
Upper Bay	Unclassified centric diatoms[a] (23%), *Katodinium rotundatum*[b] (12%), *Skeletonema costatum*[a] (12%), *Cryptomonas* spp.[c] (12%), *Cyclotella* spp.[a] (8%), *Skeletonema potamos*[a] (7%).	56	59
Mid-Bay	Unclassified centric diatoms[a] (17%), *Katodinium rotundatum*[b] (15%), *Cryptomonas* spp.[c] (15%), *Cyclotella* spp.[a] (12%), *Cerataulina pelagica*[a] (9%), *Skeletonema costatum*[a] (9%), *Chaetoceros* spp.[a] (5%)	67 (above pycnocline)	69 (above pycnocline)
Lower Bay	*Skeletonema costatum*[a] (20%), unclassified centric diatoms[a] (18%), *Cerataulina pelagica*[a] (9%), *Cryptomonas* spp.[c] (9%), unclassified pennate diatoms[d] (9%), *Nitzschia pungens*[d] (8%), *Rhizosolenia fragilissima*[d] (4%), *Rhizosolenia delicatula*[d] (3%)	83 (above pycnocline), 84 (below pycnocline)	n/a

Phytoplankton species counts from unpublished Chesapeake Bay Water Quality Monitoring Program data (available from USEPA Chesapeake Bay Program web site). Unpublished carbon composition data provided by R. Lacouture (personal communication).
[a] Centric diatoms.
[b] Dinoflagellates.
[c] Cryptomonads.
[d] Pennate diatoms.

the water column standing stock, while a low flux could help maintain the phytoplankton community in the water column. This may be especially likely in the upper Bay, where rates of net production in the plankton are known to be low (Smith and Kemp, 1995). Factors unrelated to nutrient enrichment could also be important. An estuary or region of an estuary flushed rapidly by high river flow could exhibit low primary production, low biomass in the water column, and low deposition of phytoplankton to sediments. If the relative importance of competing processes that affect an ecosystem change from year to year with changing environmental conditions, one may expect a lack of any correlations in long-term data sets. Conversely, the fact that some correlations hold for observations spanning nearly a decade and a range of environmental conditions (e.g. Fig. 5, Fig. 6, lower panel) suggests that even if these simple relations do not address all the relevant complexity of the ecosystem, they characterize the most important responses to changes in external forcing and are therefore useful models of the system.

Table 4
Regional/annual mean sediment total chlorophyll-*a* inventories

Year	Upper Bay	Mid-Bay	Lower Bay	Overall	Jan–Apr flow ($m^3 s^{-1}$)
1993	84	182	161	155	2989
1994	147	217	187	191	2624
1995	139	130	98	117	1206
1996	107	132	146	134	2383
1997	223	243	231	235	1403
1998	195	169	122	153	2471
1999	315	323	150	244	1392
2000	162	162	92	137	1739
Average	172	195	148	171	2026

These were computed from 0 to 1 cm chlorophyll-*a* inventories by adjusting for mixing to below 1 cm on short time scales (i.e. days–weeks). Calculation of the overall mean accounts for differences in the area of the respective regions and is therefore not the mean of the regional means.

3.7. Departures from general trends

Even when strong correlations are observed over time, dramatic departures from the general trends sometimes occur. Examining these observations closely may illustrate limitations of the model, or possibilities for improving the model as more data become available. In some cases, obvious outliers indicate that an important assumption underlying the simple model is not met. For example, Figs. 4 and 5 suggest that a Jan–Apr time domain for river flow forcing and ecosystem response is

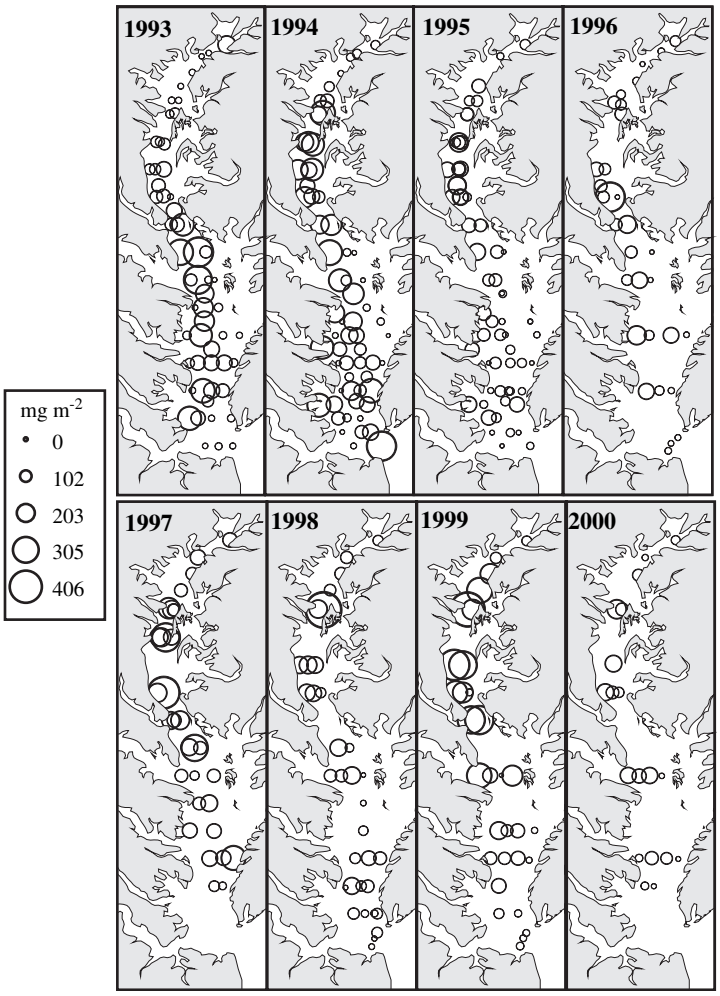

Fig. 3. The distribution of total chlorophyll-*a* in the top 1 cm of Chesapeake Bay sediments during late spring in 1993–2000. The center of each circle indicates the location at which the core was collected, while the size of the circle indicates total chlorophyll-*a* values. The values for 1993 are estimated from total chlorophyll-*a* in the top 2 mm.

appropriate for Chesapeake Bay, an observation that can generally be supported (Hagy, 2002). However, water quality in the spring of 1997 was affected by unseasonably high river flow and nutrient loading that occurred in December 1996. Thus, despite low flow in spring 1997, nutrient concentrations (N, P, Si) in surface waters at a lower Bay station were much higher than the long-term (1984–1999) average. Total N was 51 μM in January 1997 compared to the long-term January average of 27 μM. Similarly, total P and dissolved Si were 1.16 and 11.6 μM, respectively, in January 1997 compared to the long-term January averages of 0.88 and 5.5 μM (Chesapeake Bay Monitoring Program, unpublished data). These higher January nutrient concentrations were able to support larger biomass accumulations in 1997 without a substantial spring freshet (Fig. 5). In other cases, the cause of apparently unusual values is not readily apparent. In this study, sediment chlorophyll-*a* was highest Bay-wide in 1999, with the highest concentrations in the upper Bay (Fig. 4). Although the up-bay distribution was expected from the lower river flow, the higher concentrations were neither expected nor readily explainable.

A possible source of variability in the correlations involving sediment chlorophyll-*a* (Figs. 4 and 6) is the timing of phytoplankton dynamics relative to the sediment surveys (Fig. 7). In this study, the dates of sediment chlorophyll-*a* surveys were fixed in advance, while the dates of maximum phytoplankton biomass accumulation and bloom collapse varied (Fig. 7). This can be expected to introduce random noise to obscure any real correlation between average water column biomass and deposition to sediments. For example, peak water column chlorophyll-*a* in 1996 occurred on 5/14/96 in both the mid- and lower-Bay, one week after sediment sampling was concluded. In contrast, peak water column biomass occurred just prior to sampling in 1997, 1998 and 2000 and variously earlier dates in other years (Fig. 7). Ideally, to the extent that real-time observations could provide evidence that the spring phytoplankton

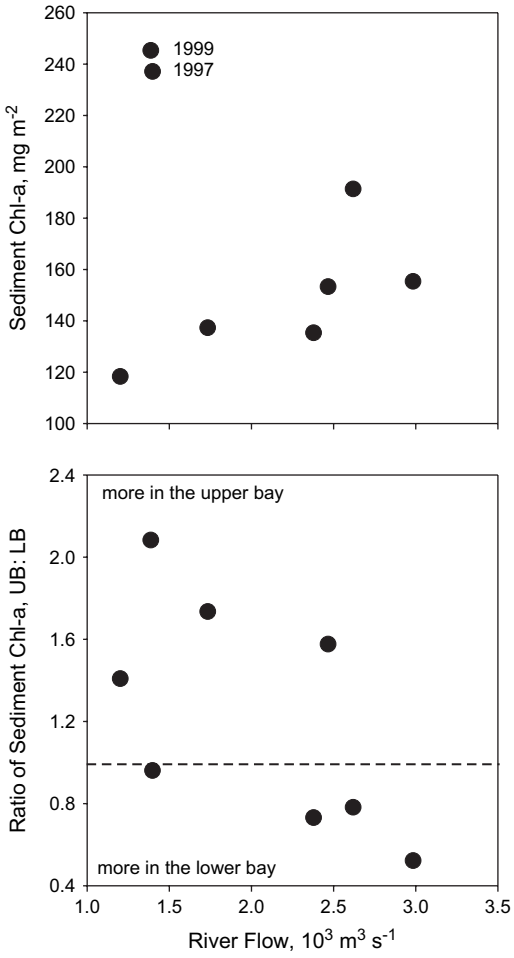

Fig. 4. Bay-wide average sediment total chlorophyll-*a* inventories in late spring related to winter–spring (Jan–Apr) average Susquehanna River flow (upper panel), and the ratio of average sediment chlorophyll-*a* in the upper Bay to that of the lower Bay (lower panel), also related to winter–spring river flow. Sediment chl-*a* inventories were computed from the top 0–1 cm of sediments.

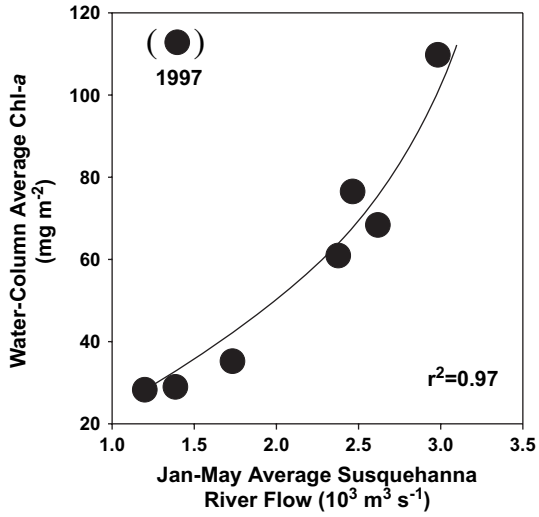

Fig. 5. January–April average water column integrated chlorophyll-*a* in the lower Chesapeake Bay during 1993–2000 related to Jan–Apr average Susquehanna River flow. A second-order polynomial explains 97% of the variation, excluding the 1997 observation.

bloom has concluded, scheduling sediment surveys flexibly around this date would be useful. Alternatively, repeated surveys through the probable period of maximum deposition would provide very useful data, but at the expense of much more sampling effort.

3.8. Phytoplankton species composition

The species composition of the winter–spring phytoplankton assemblage in 1993–2000 was examined in an effort to explain more of the variability that was observed in sediment chlorophyll-*a* deposition (Chesapeake Bay Phytoplankton Monitoring Program, unpublished data). It was hypothesized that higher sedimentation in some years was due in part to a greater relative abundance of diatoms, whose tendency toward sinking has been noted (Smetacek, 1985). Some suggestive results were obtained. In the lower Bay, diatom counts largely paralleled average chlorophyll-*a* in the water column due to the dominance of diatoms in the winter–spring phytoplankton community. However, diatom counts did not predict sediment chlorophyll-*a* as well as water column chlorophyll-*a*, probably due to larger random variability in diatom counts and less temporal resolution (monthly vs. bi-weekly) in the cell count data. For example, the cell count data was very likely to entirely miss the peak of the diatom bloom. Sediment chlorophyll-*a* in the upper Bay appeared to be higher in years when average diatom counts for the water column were higher (data not shown), apparently contradicting the negative correlation with phytoplankton suggested by water column chlorophyll-*a* (Fig. 6). However, both relationships were weak, suggesting that the appearance of any relationship could have occurred by random chance. Thus, the analysis of phytoplankton species data was not conclusive, in significant part because the temporal (monthly) and spatial resolution of these labor-intensive data collections was too low to adequately characterize the highly variable phytoplankton community during winter–spring.

3.9. Estimates of chlorophyll-a deposition

A simple model of chlorophyll-*a* deposition and decay was used to estimate the deposition of phytoplankton to sediments during spring in each year using the observed accumulation of sediment chlorophyll-*a* as an indicator of deposition. A few simplifying assumptions were needed due to data limitations. It was assumed that the input to sediments occurred at a constant rate, I (mg m^{-2} d^{-1}) over a period of t days, during which time deposited chlorophyll-*a* decayed at

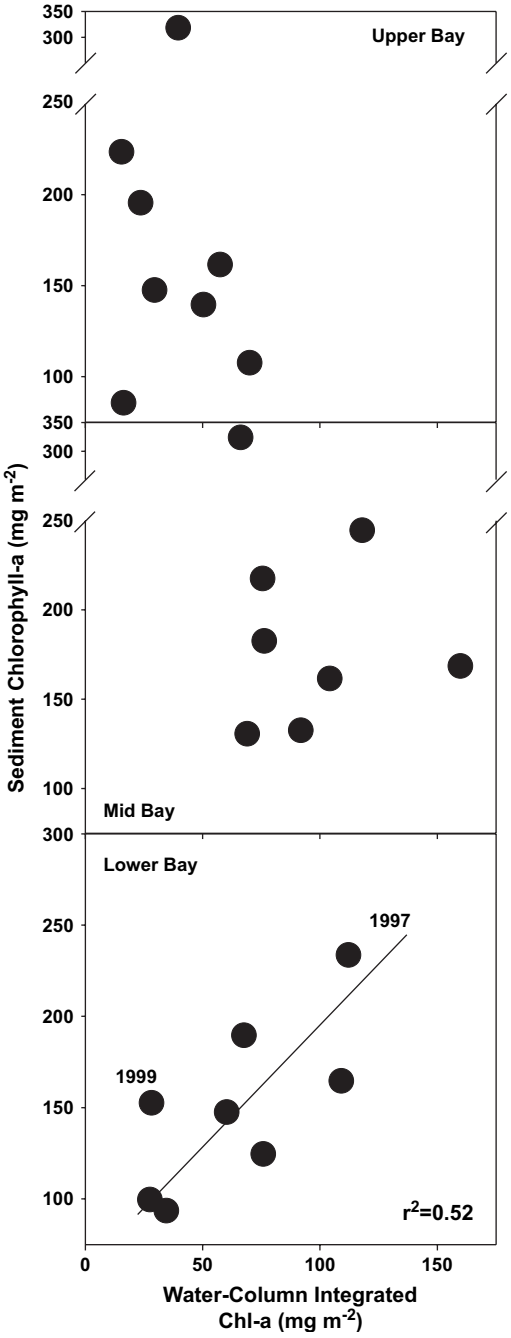

Fig. 6. The relationship between January–April average water column integrated chlorophyll-*a* and sediment chlorophyll-*a* in each of three regions of Chesapeake Bay. There is a significant correlation in the lower Bay; the indicated line is the model II regression line.

a first-order decay rate, k (d^{-1}). The net accumulation rate of chlorophyll-*a* on the sediment surface can be described by $dC/dt = I - kC$. Solving under the boundary condition that when $t = 0$, $C = C_0$ yields

$$C_t = \frac{I}{k} + \left(C_0 - \frac{I}{k}\right)e^{-kt} \tag{2}$$

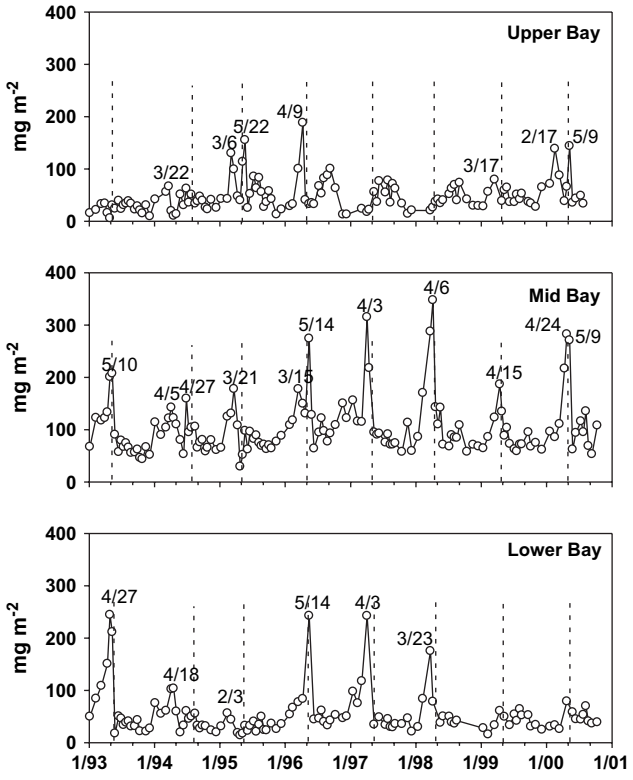

Fig. 7. Water column integrated chlorophyll-*a* concentrations in Chesapeake Bay averaged by region. Vertical dotted lines indicate the dates of sediment chlorophyll-*a* mapping studies. Dates indicate the date of the adjacent water column chlorophyll-*a* observation, which can be compared to the sediment chlorophyll-*a* mapping dates indicated in Table 2.

Solving for I gives

$$I = \frac{k\left(C_t - C_0\ e^{-kt}\right)}{1 - e^{-kt}} \tag{3}$$

Although not immediately obvious, it can be shown using L' Hôpital's rule that $\lim_{k\to 0} I = (C_t - C_0)/t$. Thus, if the degradation rate is very small, and minimal chlorophyll-*a* was present prior to the period of interest ($C_0 \approx 0$), total deposition ($I \times t$) equals the observed accumulation (C_t) and does not depend on t. In contrast, the deposition rate depends inversely on t. As the degradation rate (k) increases relative to the deposition rate (I), a steady state model as suggested by Sun et al. (1991) may be more appropriate. In Chesapeake Bay, the time period, t, during which most spring bloom phytoplankton deposition occurs probably varies from year to year (Fig. 7), but it was assumed that most deposition occurred between mid to late February and the time of the sediment surveys, a period of ~60 days. Based on Figs. 2 and 7, a range of 30–75 days was considered possible. A few measurements of sediment chlorophyll-*a* in Chesapeake Bay in early January–February were available for a number of years during

the 1980s (Garber et al., 1989). These values varied between 37 and 83 mg m^{-2} and averaged 58 mg m^{-2}, providing a base case and range of variability for C_0. Estimates for the first-order chlorophyll-*a* decay rate (k) were obtained by considering the work of Sun et al. (1993a) and other studies by Sun and colleagues (Sun et al., 1991; Sun et al., 1993b; Sun et al., 1994). These studies provide a good assessment of chlorophyll-*a* degradation under a variety of conditions. The rates most applicable for this study appear to be those obtained for unfrozen, oxic sediments (Sun et al., 1993a), since surficial sediments in Chesapeake Bay were observed to be well oxidized at this time of the year and are not subject to freezing. Oxic degradation of chlorophyll-*a* is highly temperature-dependent, with the first-order decay constant for free chlorophyll-*a* (k_d) increasing 4-fold between 5 °C and 25 °C (Sun et al., 1993a). The first-order rate for release of chlorophyll-*a* from a particle-bound state to a free state (k_r), which was required for most chlorophyll-*a* degradation, also increases more than 6-fold over the same temperature range (Sun et al., 1993a). Over 5–25 °C, k_r was 30–50 times greater than k_d; therefore, only the smaller rate is relevant here. During the period from mid-March through May 1, bottom water temperature increased from 4 to 15 °C in the upper and lower Bay and from 4 to 13 °C in the mid-Bay. The average in all regions during March–May was ~7–9 °C. In this temperature range, k_d was 0.028 d^{-1}. Thus, 0.028 d^{-1} was used as a base case estimate for k in Eq. (1) and Eq. (2), with values between 0.02 and 0.04 considered as a reasonable range of variability.

Estimates of chlorophyll-*a* deposition (±standard deviation) were computed for each region and year using Monte-Carlo simulations (Tables 5 and 6). In these simulations, the parameters C_0, t and k were chosen randomly from triangular distributions specified using the estimated min, max and mode, which is equal to the base case estimate for each parameter (Table 5). For each value of C_t (i.e. each region, year), many (10^4) estimates of the average daily deposition rate (I) and total deposition (It) were computed using Eq. (3). Means and standard deviations were then computed (Table 6). The 1993–2000 average chlorophyll-*a* deposition rate was estimated to range from 5.08 mg m^{-2} d^{-1} in the lower Bay to 6.81 mg m^{-2} d^{-1} in the mid-Bay. Average cumulative winter–spring chlorophyll-*a* deposition varied from 277 mg m^{-2} in the lower Bay to 371 mg m^{-2} in the mid-Bay. Estimated coefficients of variation for chlorophyll-*a* deposition rate and cumulative deposition estimates averaged 12% and 16%, respectively. Chlorophyll-*a* deposition rate and cumulative deposition were not directly proportional to the late-spring chlorophyll-*a* inventory (C_t) because C_0 was not equal to zero (see Eq. (3)). However, because C_t was typically much greater than C_0, the ratios I/C_t and It/C_t were much less variable than C_t. For example, I/C_t ranged from 0.032 to 0.036 d^{-1}. The ratio It/C_t ranged from 1.76 to 1.95. In other words, the cumulative winter–spring deposition of chlorophyll-*a* was slightly less than two times the observed sediment chlorophyll-*a* inventory near the end of April. Therefore, regional and interannual patterns of chlorophyll-*a* deposition rates were comparable to corresponding patterns in late spring chlorophyll-*a* inventories (Table 4).

3.10. Sediment trap comparisons

Two studies have investigated the vertical sinking flux of chlorophyll-*a* in Chesapeake Bay using sediment traps. One study estimated deposition for 8 years (1985–1992) in the mid Chesapeake Bay (Fig. 8, Boynton et al., 1993), while the other estimated deposition at a lower Bay site during 1988 (Wetzel and Neilson, 1989). Wetzel and Neilson (1989) intentionally duplicated the methods of Boynton et al. (1993) to ensure comparability. Both studies used consecutive short-term (~1 week) deployments of sediment traps located near the surface, just below the pycnocline, and within the bottom mixed layer. Both investigators noted trapping of resuspended sediments, especially in the bottom traps. Therefore, mid-depth traps were believed to be the best estimates of the vertical flux to the bottom. In most years, chlorophyll-*a* deposition in the mid-Bay was ~5–10 mg m^{-2} d^{-1} in late February, then increased to 10–20 mg m^{-2} d^{-1} in April (Fig. 8). From the earliest trap deployments in early February until early May, integrated chlorophyll-*a* deposition as measured by the traps was 600–1200 mg m^{-2} with an average of 789 mg m^{-2}. The comparable mid-Bay estimate from this study is 371 mg m^{-2}, or about 50% of the sediment trap estimate. This study estimated the average chlorophyll-*a* deposition rate in the mid-Bay to be 6.81 mg m^{-2} d^{-1}, 71% of the 9.6 mg m^{-2} d^{-1} computed from the sediment trap data (Fig. 8). Because Wetzel and Neilson (1989) did not report values for late winter, only two observations in their data set are relevant to this study. They reported chlorophyll-*a* deposition rates to the mid-depth trap of 8.5 mg m^{-2} d^{-1} on April 28, 1988 and 5.2 mg m^{-2} d^{-1} on May 2, 1989. The comparable lower Bay estimate from this study is 5.08 mg m^{-2} d^{-1}, similar to their lower value.

Even though sediment traps are a direct method for estimating the flux, one should not assume that sediment traps provide a more accurate estimate. Sediment traps have many known deficiencies (Blomqvist and Håkanson, 1981; Knauer et al., 1984; Asper, 1987). The most important deficiency may be their tendency in coastal waters to overestimate the vertical flux by collecting resuspended particles. Resuspension clearly affected the fluxes to the deeper sediment traps, and to a lesser extent the mid-depth traps (Wetzel and Neilson, 1989; Boynton et al., 1993). Chlorophyll-*a* fluxes are likely less affected

Table 5
Minimum, maximum and modal values used to specify triangular distributions for parameters in Eq. (3)

Parameter	Min	Mode	Max
Initial chl-*a* concentration, C_0, mg m^{-2}	30	58	80
First-order decay coefficient, k, d^{-1}	0.02	0.028	0.04
Period of bloom deposition, t, days	30	60	75

Parameter values were randomly drawn from these distributions and used in Monte-Carlo simulations to estimate the mean and standard deviation of chlorophyll-*a* deposition in each region and year.

than particulate carbon fluxes, since "old" resuspended particles are much more likely to contain organic carbon than intact chlorophyll-*a*.

3.11. Phytoplankton sinking rates

Another check on the chlorophyll-*a* deposition estimates can be made by using the estimated chlorophyll-*a* deposition rate and estimates of water column chlorophyll-*a* concentrations to estimate an effective sinking velocity for phytoplankton cells. This velocity can then be compared with measurements from the published literature. This approach requires that one assume a uniform vertical chlorophyll-*a* distribution in the water column, which may be appropriate in late winter and early spring in Chesapeake Bay, but not in summer. The effective sinking rate (v_z) can be estimated from the integrated water column chlorophyll-*a* concentration (C_{int}), the mean depth ($\bar{z}$) and the rate of chlorophyll-*a* deposition to sediments (F) using

Table 6
Estimated average (±standard deviation) chlorophyll-*a* deposition rates (mg m^{-2} d^{-1}) and total winter–spring chlorophyll-*a* deposition (mg m^{-2}) for winter–spring in the upper, mid and lower Chesapeake Bay during 1993–2000

Year	Upper Bay	Mid-Bay	Lower Bay
(a) Average deposition rate during winter–spring (mg m^{-2} d^{-1})			
1993	2.69 ± 0.34	6.34 ± 0.73	5.56 ± 0.64
1994	5.04 ± 0.58	7.64 ± 0.88	6.52 ± 0.74
1995	4.74 ± 0.55	4.40 ± 0.52	3.21 ± 0.39
1996	3.55 ± 0.43	4.48 ± 0.52	4.99 ± 0.59
1997	7.86 ± 0.90	8.61 ± 0.98	8.16 ± 0.94
1998	6.81 ± 0.79	5.85 ± 0.67	4.10 ± 0.49
1999	11.29 ± 1.28	11.57 ± 1.33	5.14 ± 0.59
2000	5.59 ± 0.65	5.59 ± 0.64	2.99 ± 0.37
Average	5.95	6.81	5.08
(b) Winter–spring chlorophyll-*a* deposition (mg m^{-2})			
1993	148 ± 28	345 ± 54	304 ± 49
1994	275 ± 45	415 ± 63	355 ± 55
1995	258 ± 42	241 ± 41	175 ± 32
1996	193 ± 34	244 ± 41	272 ± 44
1997	429 ± 65	470 ± 70	444 ± 67
1998	371 ± 57	319 ± 51	224 ± 38
1999	613 ± 90	631 ± 92	280 ± 45
2000	305 ± 49	305 ± 48	163 ± 30
Average	324	371	277

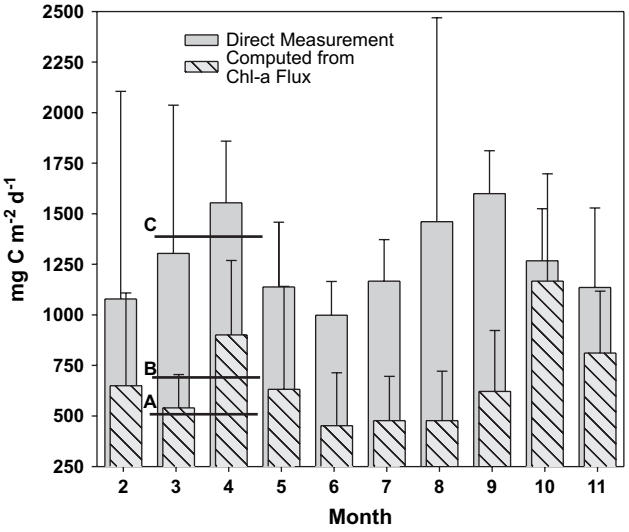

Fig. 8. Monthly means and standard errors of particulate carbon (PC) sinking fluxes measured using sediment traps just below the pycnocline in the mid Chesapeake Bay during 1984–1992. Sediment trap data from Boynton et al. (1993) and related unpublished data. Stippled bars indicate vertical PC fluxes computed from chlorophyll-*a* fluxes. Reference lines indicate: A = spring average PC deposition (510 mgC m^{-2} d^{-1}, this study); B = March–April average PC deposition computed from chlorophyll-*a* flux to sediment traps (720 mgC m^{-2} d^{-1}); C = March–April average deposition computed directly from PC flux to sediment traps (C:chl-*a* = 75 in all cases).

$$v_z = \frac{F}{C_{wc}} \text{ where } C_{wc} = \frac{C_{\text{int}}}{\bar{z}} \tag{4}$$

Given C_{int} = 50–100 mg m^{-2} (Fig. 7), $\bar{z} \approx 8$ m, and F = 6.0 mg m^{-2} d^{-1}, this gives v_z = 0.5–1.0 m d^{-1}. Mean upwelling velocities in the range of 0.5 m d^{-1} would affect cells sinking through the water column (Hagy, 2002). Thus, the actual sinking rate may be 1.0–1.5 m d^{-1}, approximately the same as the 1.1–1.5 m d^{-1} estimated for larger cells (8–53 μm) within a whole phytoplankton assemblage in an experimental enclosure (Bienfang, 1981). This estimate exceeds the minimum sinking rates estimated for *Skeletonema costatum*, the most abundant species in lower Chesapeake Bay in winter–spring (Table 1), but approximates the maximal sinking rates for the same species (Smayda, 1970). Thus, the observed deposition probably represents sinking of senescent and/or nutrient limited cells, consistent with observations of Smetacek (1985).

The cursory analysis of average sinking rate noted above is intended to show only that the estimated chlorophyll-*a* deposition is consistent with reported sinking rates and observed chlorophyll-*a* concentrations in the water column. It is not known, however, if the deposition actually occurred at this average sinking velocity. Formation of large "flocs" can lead to settling rates of 10–100 m d^{-1} (Smetacek, 1985), sufficient to

deposit an entire senescent phytoplankton bloom to Chesapeake Bay sediments within one day.

3.12. Carbon flux to sediments

Given an estimate of C:chl-*a*, the estimated spring chlorophyll-*a* flux to sediments described above can be used to estimate the carbon flux associated with spring bloom phytoplankton deposition. An often cited ratio is ~50; however, literature values for this ratio have been found to vary quite widely. For example, estimates compiled by Jørgensen et al. (1991) for a single abundant species in our study area, *Skeletonema costatum*, varied from 61 to 178. Depending on growing conditions, values much lower than 50 have been reported for some other species. We addressed this uncertainty by estimating empirically a ratio for our study site and time of year. We computed the long-term January–April average C:chl-*a* ratio in each region of the Bay using bi-weekly suspended particulate organic carbon and chlorophyll-*a* data from one station in each region (Chesapeake Bay Monitoring Program Data). For the lower- and mid-Bay, this value was ~100, while for the upper Bay, the ratio was as high as >250. These values are higher than expected values, suggesting that a non-phytoplankton (i.e. detritus) component was present within the suspended particulate organic carbon. Within this record, when chlorophyll-*a* increased quickly and substantially (e.g. Fig. 7), C:chl-*a* decreased to an asymptotic value of ~50, with values between 50 and 100 when chl-*a* was high ($>20\ \mu g\ l^{-1}$). As chlorophyll-*a* concentration decreased following a bloom, C:chl-*a* increased quickly. This suggests that the particulates that accumulated during the bloom and were lost, partially due to sinking, at the end of the bloom had C:chl-*a* ≈ 50–100. This conclusion was supported by sediment trap data (Boynton et al., 1993), which showed that the ratio of carbon to chlorophyll-*a* sinking flux in March–April was ~75 when the chlorophyll-*a* flux was at the highest values ($>8\ mg\ m^{-2}\ d^{-1}$).

Using an intermediate value of C:chl-*a* = 75 and an average total chlorophyll-*a* deposition of 277–371 $mg\ m^{-2}$ (Table 6) the carbon flux to sediments associated with spring bloom phytoplankton deposition is estimated to have been 21–28 $gC\ m^{-2}$. The effect of the assumed C:chl-*a* ratio on this estimate is a simple proportion; therefore, the choice of a higher or lower value within the range of reasonable values would introduce a proportionate change in the estimates. Converting chlorophyll-*a* deposition rates to C deposition rates using the same proportion have an estimate of 0.51 $gC\ m^{-2}\ d^{-1}$, 71% of the C flux computed from chlorophyll-*a* fluxes to mid-Bay sediment traps (also assuming C:chl-*a* = 75), but only 36% of the directly measured PC fluxes to the same sediment traps (Fig. 7, Boynton et al., 1993). The same pattern was observed for the lower Bay sediment traps. The larger disparity observed between directly measured PC fluxes and estimates from this study reflects periods in which the sediment traps received particles with high C:chl-*a*. This is likely an artifact, reflecting resuspension of sediments.

3.13. Comparative analysis and relative importance of spring bloom

These carbon flux estimates for the spring bloom in Chesapeake Bay are substantially higher than reported carbon fluxes associated with spring phytoplankton blooms in some other systems. For example, a 34-day bloom in the Baltic Sea deposited 6.2 $gC\ m^{-2}$ to sediments (Smetacek et al., 1978, cited in Keller and Riebesell, 1989). A 25-day bloom in the Kiel Bight deposited 11.5 $gC\ m^{-2}$ (Peinert et al., 1982, cited in Keller and Riebesell, 1989). The estimated C flux rate for Chesapeake Bay is similar to that of the Kiel Bight bloom, but persisted for a longer period of time, leading to a larger cumulative C flux (Table 6). This seems reasonable given the eutrophic condition of Chesapeake Bay.

The estimated carbon flux associated with the spring bloom (21–28 $gC\ m^{-2}$) sediments accounts for 10–14% of annual benthic respiration (163 $gC\ m^{-2}\ y^{-1}$) plus carbon burial (39 $gC\ m^{-2}\ y^{-1}$, Kemp et al., 1997), slightly less than proportional to the fraction of the year encompassed (60/365 days = 16%). That the spring bloom deposition did not support a larger fraction of annual metabolic C demand was surprising considering the clear seasonality of phytoplankton biomass (Fig. 2) and net plankton metabolism (i.e., gross plankton production minus plankton respiration, Kemp et al., 1997), and the importance generally ascribed to this annual ecosystem event. Assuming that the spring bloom deposition was not larger than estimated, but that it was important to the macrobenthic community as has been suggested, one may conclude that the importance arises from food quality rather than quantity (e.g. Marsh and Tenore, 1990).

Another surprising result is that the spring phytoplankton deposition differed only slightly by Bay region and that the regional variation did not parallel the large regional differences in net plankton metabolism (NPM) reported by Smith and Kemp (1995). For the mid-Bay, the estimated carbon flux (0.51 $gC\ m^{-2}\ d^{-1}$) is slightly greater than NPM (= 0.41 $gC\ m^{-2}\ d^{-1}$) estimated by Smith and Kemp (1995; converted from O_2 flux using $gC = 0.375\ g\ O_2$). In contrast, the estimated winter–spring carbon deposition to sediments in the lower Bay (0.38 $gC\ m^{-2}\ d^{-1}$) was only 24% of the much higher estimate of NPM for the lower Bay (1.6 $gC\ m^{-2}\ d^{-1}$, Smith and Kemp, 1995). The fate of the apparent surplus production in the lower Bay is unknown, but may include export to the mid-Bay via the landward advection in the lower water column, or possibly export to the coastal ocean. The presence of significant chlorophyll-*a* fluxes to sediments in the upper Bay,

despite negative NPM may indicate that allochthonous C inputs supported plankton respiration and reduced NPM, while autochthonous phytoplankton production supported vertical C fluxes to sediments.

4. Conclusions

Surficial sediment chlorophyll-*a* can be used effectively as a biomarker for spring bloom phytoplankton deposition to sediments, provided that benthic primary production can be ruled out as a source of pigment to sediments. These deposition estimates obtained are the only known Bay-wide estimates for Chesapeake Bay. Deposition was 2–4 times greater than estimated spring bloom deposition from some other estuarine and coastal systems, illustrating the intense primary production associated with spring phytoplankton blooms in Chesapeake Bay. Increased river flow was correlated with increased algal biomass in the lower Bay, which in turn predicted greater deposition of phytoplankton to sediments in the same region of the Bay. Similar responses were not identified in other regions of the Bay, suggesting that models describing nutrient enrichment, algal biomass, deposition responses may be an oversimplification. Physical transport effects may affect the location within the estuary of maximum algal production and deposition to sediments, although results in this area were inconclusive. The estimated springtime deposition, although large, did not account for a larger than proportional fraction of annual benthic metabolic requirements. A lack of regional correspondence between plankton net community production and deposition to sediments leaves key questions unanswered about this important benthic–pelagic coupling mechanism.

Acknowledgements

We thank N. Burger and J. Fetcho for conducting fieldwork in 1995 and 2000, respectively. We thank P. Moylan for his careful attention to the maintenance of the Smith–Macityre corer and the rest of the crew of the R/V Cape Henlopen for their patient pursuit of high quality cores. We thank B. Stankelis and J. Frank for collecting benthic cores in Patuxent River for use in the method comparison and N. Kaumeyer for her skillful laboratory work on the method comparison. We thank R. Lacouture for sharing his unpublished estimates of the carbon composition of major phytoplankton taxonomic groups. We are grateful for the detailed review of W. M. Kemp as well as reviews by T. Miller, E. Russek-Cohen, and R. Ulanowicz. We also thank E. Canuel, R. Dickhut and J. Cornwell for helpful discussions. This study is a product of the Chesapeake Bay Land Margin Ecosystem Research Programs (PROTEUS and TIES) funded by the National Science Foundation (Grant Nos: BSR-8814272 and DEB-9412113). This is contribution no. 3802 from the University of Maryland Center for Environmental Science and contribution no. 1151 from the US Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division.

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