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Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll *a* for the Chesapeake Bay and Its Tidal Tributaries

2007 Chlorophyll Criteria Addendum

November 2007



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U.S. Environmental Protection Agency
Region III
Chesapeake Bay Program Office
Annapolis, Maryland

and

Region III
Water Protection Division
Philadelphia, Pennsylvania

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Office of Water
Office of Science and Technology
Washington, D.C.

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the states of
Delaware, Maryland, New York,
Pennsylvania, Virginia, and
West Virginia and the District of Columbia

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chapter i

Introduction

In April 2003, the U.S. Environmental Protection Agency (EPA) published the *Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll* a *for the Chesapeake Bay and Its Tidal Tributaries* (*Regional Criteria Guidance*) in cooperation with and on behalf of the six watershed states—New York, Pennsylvania, Maryland, Delaware, Virginia, and West Virginia—and the District of Columbia. The culmination of three years of work, the criteria document resulted directly from the collective contributions of hundreds of regional scientists, technical staff, and agency managers as well as the independent review by recognized scientific experts across the country (U.S. EPA 2003).

In October 2004, EPA published the first addendum to the 2003 *Regional Criteria Guidance* (U.S. EPA 2004). The addendum provided additional guidance on: applying the temperature-based open-water dissolved oxygen criteria required to protect the endangered shortnose sturgeon; assessing attainment of the instantaneous minimum and 7-day mean dissolved oxygen criteria using monthly mean water quality monitoring data; deriving site-specific dissolved oxygen criteria for tidal systems where the extensive adjacent tidal wetlands cause naturally low dissolved oxygen levels; delineating the upper and lower boundaries of the pycnocline; defining attainment of the shallow-water bay grass designated use; and determining where numerical chlorophyll *a* criteria should apply to local Chesapeake Bay and tidal tributary waters.

From 2004 through early 2006, Delaware, Maryland, Virginia, and the District of Columbia adopted: the EPA-published Chesapeake Bay water quality criteria for dissolved oxygen, water clarity, and chlorophyll *a*; the EPA-recommended tidal water designated uses; and the EPA-established criteria assessment procedures into their respective state water quality standards regulations. All four jurisdictions[1] promulgated narrative chlorophyll *a* criteria in their standards regulations. Virginia promulgated numerical segment- and season-specific chlorophyll *a* criteria for the tidal James River. The District of Columbia promulgated numerical chlorophyll *a* criteria for its reach of the tidal Potomac River and its remaining tidal waters, hav-

[1]References throughout the text to "states" or "jurisdictions" means a collective reference to the states of Delaware and Maryland, the Commonwealth of Virginia, and the District of Columbia. All four have Chesapeake Bay tidal waters within their jurisdictional boundaries.

ing previously adopted numerical chlorophyll *a* criteria for protection of the tidal Anacostia River.

In July 2007, EPA published a second addendum to the 2003 Regional Criteria Guidance (U.S. EPA 2007). This second addendum documented the revised, refined, and new criteria assessment methods for the published Chesapeake Bay dissolved oxygen, water clarity, and chlorophyll *a* criteria.

This third addendum documents numerical Chesapeake Bay chlorophyll *a* criteria and reference concentrations.

- **Chapter 2** documents the scientific basis for numerical chlorophyll *a* criteria.
- **Chapter 3** documents historical chlorophyll *a* reference concentrations.
- **Chapter 4** documents the chlorophyll *a* relationship to dissolved oxygen impairments.
- **Chapter 5** documents the chlorophyll *a* contribution to water clarity impairments.
- **Chapter 6** documents chlorophyll *a* concentrations characteristic of addressing impairments by harmful algal blooms.
- **Chapter 7** documents the recommended Chesapeake Bay chlorophyll *a* criteria.
- **Chapter 8** documents the recommended procedures for assessing attainment of numerical chlorophyll *a* criteria.

This document represents the third formal addendum to the 2003 Chesapeake Bay water quality criteria document. As such, readers should regard the sections in this document as new or replacement chapters and appendices to the original published report and two prior published addendums. The criteria attainment assessment procedures published in this addendum replace and otherwise supercede similar criteria assessment procedures originally published in the *2003 Regional Criteria Guidance* and the 2004 and 2007 addendums (U.S. EPA 2003, 2004, 2007). Publication of future addendums by EPA in coordination with and on behalf of the Chesapeake Bay Program watershed jurisdictional partners is likely. Continued scientific research and management applications reveal new insights and knowledge that should be incorporated into revisions of state water quality standards regulations in upcoming triennial reviews.

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U.S. Environmental Protection Agency. 2007. *Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for Chesapeake Bay and Its Tidal Tributaries – 2007 Addendum*. EPA 903-R-07-003. CBP/TRS 285/07. Region III Chesapeake Bay Program Office, Annapolis, MD.

chapter ii

Chlorophyll *a* Criteria

STATE WATER QUALITY STANDARDS

With publication of the April 2003 *Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and Its Tidal Tributaries*, the U.S. Environmental Protection Agency (EPA) provided the states with recommended narrative chlorophyll *a* criteria applicable to all Chesapeake Bay and tidal tributary waters (Table II-1) (U.S. EPA 2003a). The four jurisdictions that include Chesapeake Bay tidal waters within their boundaries—Delaware, Maryland, Virginia, and the District of Columbia—all have narrative water quality standards in their existing regulations that require achievement and maintenance of a balanced, non-nuisance phytoplankton community (Appendix A). Individually and collectively, these four jurisdictions' existing water quality standards regulations contain clear narrative requirements that address the adverse human health and aquatic life impairments caused by overabundant, nuisance algal production measured as chlorophyll *a*. The absence of numerical chlorophyll *a* criteria, however, prevents the jurisdictions from assessing whether their tidal waters are meeting their designated uses. Beyond the tidal James River and the District's tidal waters, however, the absence of a numerical interpretation of the narrative desired ecological condition prevents the states from fully and properly applying the narrative sections of their water quality standards regulations (as described in Appendix A).

From 2004 through early 2006, Virginia and the District of Columbia adopted numerical chlorophyll *a* criteria for the tidal James River (Virginia) and across all the District's jurisdictional tidal waters. Both jurisdictions determined that algal-related

Table II-1. Chesapeake Bay narrative chlorophyll *a* criteria.

Concentrations of chlorophyll *a* in free-floating microscopic aquatic plants (algae) shall not exceed levels that result in ecologically undesirable consequences—such as reduced water clarity, low dissolved oxygen, food supply imbalances, proliferation of species deemed potentially harmful to aquatic life or humans or aesthetically objectionable conditions—or otherwise render tidal waters unsuitable for designated uses.

Source: U.S. EPA 2003a.

designated use impairments were likely to persist in these waters even after attainment of the applicable dissolved oxygen and water clarity criteria. The water quality standards regulations in Virginia and the District of Columbia now contain numerical chlorophyll *a* criteria for the protection of aquatic life. The technical information supporting both jurisdictions' adoption of numerical chlorophyll *a* criteria was published in the 2003 Chesapeake Bay water quality criteria document (U.S. EPA 2003a). Delaware, Maryland, Virginia and the District of Columbia all adopted narrative chlorophyll *a* criteria into their states' water quality standards regulations (Table II-1).

DERIVING SCIENTIFICALLY SOUND NUMERICAL CHLOROPHYLL *a* CRITERIA

The EPA's published narrative criteria states that chlorophyll *a* "*. . . not exceed levels that result in ecologically undesirable consequences—such as reduced water clarity, low dissolved oxygen, food supply imbalances, proliferation of species deemed potentially harmful to aquatic life or humans or aesthetically objectionable conditions—or otherwise render tidal waters unsuitable for designated uses for balanced aquatic plant life populations and against the overgrowth of nuisance, potentially harmful algal species*" (U.S. EPA 2003a). Quantifying undesirable chlorophyll *a* levels in the water remains a challenge, however, because concentrations that cause "ecologically undesirable consequences" in one tidal tributary or in one region of the Bay do not necessarily cause problems in other tidal tributaries or regions.

This duality comes about for two primary reasons. First, as a measure of phytoplankton biomass, chlorophyll *a* also becomes a measure of the amount of food available for animals in the Bay. Second, while chlorophyll *a* functions as an indicator of phytoplankton biomass as a whole, phytoplankton are a highly diverse group of microscopic algal (plant) species. Many constitute important sources of food for planktonic animals (zooplankton), fish, and shellfish while others are poor quality food sources. Some phytoplankton produce chemicals toxic to humans and other organisms. Thus, the Bay's "carrying capacity" or its ability to support productive and diverse populations of flora and fauna, including highly valued species, depends largely on how well the quantity and quality of phytoplankton meet the nutritional needs of animal consumers. However, chlorophyll *a* is solely an index of quantity, not quality.

PHYTOPLANKTON, WATER QUALITY, AND CHLOROPHYLL *a*

Excessive accumulation of phytoplankton biomass due to nutrient over-enrichment is one of the primary causes of declining water quality in the nation's estuaries (Howarth et al. 2000), including the Chesapeake Bay (Neilson and Cronin 1981; Boynton et al. 1982; Harding et al. 1986; Seliger et al. 1985; Fisher et al. 1988; Malone 1992; Malone et al. 1996; Harding and Perry 1997; Kemp et al. 2005). High and variable nutrient inputs coming from freshwater runoff can destabilize coastal

ecosystems when nutrient loading exceeds the ecosystem's rate compensating capacity[1] (Malone et al.1996). This situation has occurred in Chesapeake Bay, marked by increases in phytoplankton biomass, decreases in water clarity, and a shift from demersal to pelagic food webs which began about 100 years ago (Cooper 1995; Cooper and Brush 1993; Kemp et al. 2001; Kemp et al. 2005).

Variations in phytoplankton biomass and water clarity are the primary links between nutrient loading and changes in water quality (e.g., water clarity and bottom water dissolved oxygen levels), submerged aquatic vegetation (SAV) abundance, and trophic dynamics in coastal marine and estuarine ecosystems (Kemp et al. 2005 and references therein). Thus, nutrient over-enrichment[2] causes ecological symptoms in Chesapeake Bay of impaired designated uses as defined by the Clean Water Act.

Chlorophyll *a* concentration serves as an especially useful indicator of water quality for two important reasons. First, as concluded by Harding and Perry (1997), "Chlorophyll *a* is a useful expression of phytoplankton biomass and is arguably the single most responsive indicator of N [nitrogen] and P [phosphorus] enrichment in this system [Chesapeake Bay]." Second, measurements are routine and techniques are now available to obtain them in near-real time. Relatively rapid methods evolved over the years to measure the concentration of chlorophyll *a* in discrete water samples and *in vivo* (Flemer 1969). Methods have also been developed to measure chlorophyll *a* using aerial surveillance techniques (remote sensing) based on passive multispectral signals associated with phytoplankton (Harding et al. 1992).

Improvement in water clarity is a major issue for the recovery of the Bay's shallow-water underwater grasses. Correcting the low dissolved oxygen problem that occurs in the deeper waters of the mesohaline mainstem Chesapeake Bay, lower tidal tributaries and episodic events in shallow water has remained a challenge to Bay restoration for decades. Increases in water clarity and dissolved oxygen occur when excess phytoplankton biomass—measured as chlorophyll *a*—is substantially reduced (National Research Council 2000). Water clarity improves throughout the water column when light attenuation by phytoplankton decreases. The extent of oxygen depletion in bottom waters (leading to hypoxia and anoxia) decreases when the sedimentation of organic matter produced by phytoplankton into bottom waters decreases. Thus, attaining the Chesapeake Bay dissolved oxygen and water clarity criteria requires reductions in chlorophyll *a* concentrations by lessening nutrients to limit the production of phytoplankton biomass (in addition to reducing sediment loading which also contributes to lower water clarity). For these reasons, the EPA believes developing and adopting numerical chlorophyll *a* criteria (in addition to water clarity and dissolved oxygen criteria) is necessary to protect Chesapeake Bay tidal waters.

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[1]Rate compensating capacity is the capacity of a system to respond to nutrient inputs by increasing biomass-specific rates of nutrient assimilation into biomass (Caperon et al. 1971). This capacity is exceeded when increases in the rate of nutrient assimilation can only be achieved through increases in biomass. An important assumption is that all of the nutrient input to the system from external sources is taken up within the system.

[2] Nutrient over-enrichment in the case of Chesapeake Bay refers to both nitrogen and phosphorus since both must be controlled to manage nutrient impacts (D'Elia et al. 1986; Fisher et al. 1992, 1999).

While excessive chlorophyll *a* levels are often associated with low bottom-water dissolved oxygen and the loss of SAV, such negative outcomes are not always the result. Some regions of the Bay and its tidal tributaries experience excessive accumulations of chlorophyll *a* without such impairments—especially shallow well-mixed systems. Conversely, harmful algal blooms may occur in the absence of other water quality impairments. Consequently, the EPA recommends adoption of numerical chlorophyll *a* criteria for protection of open-water designated uses for tidal waters where algal-related impairments will likely persist even after attainment of the Chesapeake Bay dissolved oxygen and water clarity criteria.

CHLOROPHYLL *a* DYNAMICS IN THE MAINSTEM CHESAPEAKE BAY

Plots of the seasonal variation in chlorophyll *a* concentrations capture both episodic (e.g., storm-induced) and month-to-month variations in nutrient loading. Chlorophyll *a* levels over time, therefore, offer a good indication of phytoplankton biomass response to nutrient loading and the effects of phytoplankton on water quality and benthic habitats. The seasonal asynchrony of the annual cycles of phytoplankton chlorophyll *a* in the Chesapeake as well as phytoplankton productivity also indicate that the rate compensating capacity of the Bay has been exceeded (Caperon et al. 1971). The chlorophyll *a* content of the water column (chlorophyll *a* concentration integrated from surface to bottom) rises in the Bay to a spring maximum (usually from March to May) when grazing rates are low and nutrient loads are high. During this period, chlorophyll *a* concentrations are elevated throughout the water column. As the Bay transitions from the spring biomass maximum to the summer phytoplankton productivity maximum (May to June), bottom-water chlorophyll *a* concentrations decline rapidly with high concentrations restricted to the surface layer throughout the summer. In contrast to the annual cycle of phytoplankton biomass, phytoplankton productivity (which is generally limited to the surface layer) increases rapidly from a winter minimum to a summer maximum (usually from July to August) as incident solar radiation increases (Malone et al. 1988; Malone 1991, 1992; Miller and Harding 2006).

The magnitudes of both the spring water-column-integrated chlorophyll *a* maximum and the summer phytoplankton productivity maximum vary widely from year to year, but no evidence exists for a secular trend over the last two to three decades (Harding and Perry 1997; Harding et al. 2002; Miller and Harding 2006). Under current conditions (1980–present), seasonal and interannual variations in phytoplankton productivity are primarily related to the annual cycles of incident solar radiation and temperature (Malone 1991, 1992; Harding et al. 2002). In contrast, seasonal and interannual variations in chlorophyll *a* levels in the salt-intruded reach of the mainstem Bay are caused primarily by variations in nitrate loading (using flow of the Susquehanna River as a proxy) (Malone 1991; Malone et al. 1996).

In summary, the rate of nutrient assimilation by phytoplankton (per unit biomass) is nutrient saturated during spring; therefore, increases in nutrient assimilation can only occur when biomass increases (Malone et al. 1996). The rate compensating capacity of the Chesapeake Bay ecosystem is exceeded and phytoplankton biomass accumulates (i.e., the consumption of phytoplankton biomass by benthic and pelagic consumers cannot keep pace with phytoplankton production on a baywide scale).

This effect may have been exacerbated by the Bay's oyster population decline during the 20th century (Newell 1988). In summer, nutrient assimilation and phytoplankton growth rates are nutrient limited and the rate compensating capacity of the Bay is not exceeded.

CHLOROPHYLL *a* DYNAMICS IN THE TIDAL TRIBUTARIES AND EMBAYMENTS

Chlorophyll *a* concentrations that impair tidal-water designated uses, as defined by the Clean Water Act, will differ among Chesapeake Bay's "subsystems" (the mainstem Bay along with its tidal tributaries and embayments) depending on salinity, depth, flushing rate, and the degree of vertical stratification. For example, massive blue-green algae blooms occur primarily in the upper tidal-fresh Potomac River (Jaworski 1990) while many small shallow-water (vertically mixed) embayments have inordinately high chlorophyll *a* concentrations associated with supersaturated dissolved oxygen levels in the afternoon and hypoxic to anoxic conditions during the hours before sunrise (D'Avanzo and Kremer 1994). In some parts of the Bay and its tidal tributaries, reductions of nutrient and sediment loading to levels that meet the deep-water and deep-channel dissolved oxygen and shallow-water water clarity criteria may not prevent development of harmful algal blooms nor ensure the return of high-quality food to open-water habitats. Such areas include, but are not limited to, waters that do not experience oxygen depletion for hydrodynamic reasons (e.g., high mixing rates) and those in which reduced water clarity results primarily from suspended sediment rather than algae (e.g., tidal James River).

SCIENTIFIC BASIS FOR NUMERICAL CHLOROPHYLL *a* CRITERIA

HISTORICAL CHLOROPHYLL *a* REFERENCE CONCENTRATIONS

Seasonal accumulations of chlorophyll *a* in the Chesapeake Bay remain excessive. Using changes in chlorophyll *a* to assess shifts in the Bay's condition due to human activities requires: long-term time series measurements of chlorophyll *a* with seasonal resolution along the salinity gradients of the mainstem Bay and its tributaries; and a "baseline" annual cycle of water column-integrated chlorophyll *a* with seasonal resolution to assess changes in terms of positive and negative deviations from the baseline.

Ideally, this baseline would be the mean annual cycle based on monthly means and standard errors for a range of climate conditions prior to European settlement of the Chesapeake Bay watershed. However, data to calculate means and standard errors are available only from about 1960 to the present. Even so, establishing secular trends based on numerical deviations necessitates a quantitative reference. Given the strong seasonality of chlorophyll *a* concentrations, a mean annual cycle with seasonal resolution is needed. Chapter 3, "Historical Chlorophyll *a* Reference Concentrations", documents this approach for deriving numerical chlorophyll *a* concentrations protective against ecological impairments.

DISSOLVED OXYGEN IMPAIRMENTS

Although bottom-water hypoxia has probably occurred in Chesapeake Bay for over 100 years (Cooper and Brush 1991), analysis of available data suggests that the time-space extent of hypoxia began to increase with nutrient loading in the 1950s (Hagy et al. 2004; Kemp et al. 2005) and continues to increase in some areas (e.g., Fisher et al. 2006). A statistically significant relationship between nutrient loading and the severity of oxygen depletion from 1950 to 2001, however, has not been established.

Seasonal accumulations of water column-integrated chlorophyll *a* during winter and spring provide the fuel for oxygen depletion and summer hypoxia in the Chesapeake mainstem and its tidal tributaries. The rate of decline of bottom-water oxygen shows little interannual variability and is primarily a function of temperature (Malone 1992; Hagy et al. 2004). In contrast, the time-space extent of bottom-water hypoxia varies considerably from year to year due primarily to interannual variations in vertical stratification during the summer and secondarily to variations in the spring freshet's magnitude (Malone 1991, 1992; Hagy 2002). These observations suggest that the aerobic capacity of the Bay to assimilate the winter-spring accumulation of phytoplankton biomass has been exceeded for the last 20 to 30 years, explaining the lack of correlation between nutrient loading and the severity of oxygen depletion. Given the Bay's current eutrophic state, therefore, relationships between chlorophyll *a* concentrations and oxygen depletion may not necessarily yield useful numerical chlorophyll *a* criteria. This hypothesis is tested in Chapter 4, "Chlorophyll *a* Relationship to Dissolved Oxygen Impairments."

WATER CLARITY IMPAIRMENTS

Clear water with sufficient penetration of solar radiation is essential for SAV growth (Dennison et al. 1993; Kemp et al. 2004). Chlorophyll *a* creates a major source of light attenuation in the water column, along with suspended inorganic sediments and colored dissolved organic material (CDOM). In the 1700s and 1800s, much of the turbidity in the Chesapeake Bay resulted from anthropogenic sediment inputs. Land-based inputs of sediments have declined over the last 50 to 60 years (Brush 1989), however, and declines in water clarity during spring and summer are related primarily to accumulations of chlorophyll *a* (Gallegos and Jordan 2002). Increases in chlorophyll *a* were already affecting underwater bay grass distributions throughout much of the Chesapeake Bay by the early 1960s (Orth and Moore 1983). If the effects of sediments and CDOM can be accounted for, then the quantitative relationships between chlorophyll *a* concentration and diffuse light attenuation should provide the basis for numerical chlorophyll *a* criteria. Chapter 5, "Chlorophyll *a* Contribution to Water Clarity Impairments", pursues this approach for deriving numerical chlorophyll *a* concentrations protective against water clarity impairments.

HARMFUL ALGAL BLOOM IMPAIRMENTS

As defined in *Harmful Algal Research and Response: A National Environmental Science Strategy 2005–2015*, harmful algae are those algae that "cause harm to the environment through the production of toxins . . . or through the accumulation of

biomass that, in turn, affects co-occurring organisms and alters food webs in negative ways" (HARRNESS 2005). The latter impairments are addressed in chapters 3 through 5. The focus of Chapter 6 is on algae that produce toxins harmful to humans and/or living resources.

Not all toxic algae are pigmented and many toxic algae can cause human pathologies at low cell densities. In addition, most variability in the time-space distributions of chlorophyll *a* is not caused by pigmented toxic algae, especially in the high-salinity lower reaches of the Chesapeake Bay mainstem and its higher salinity tidal tributaries. Thus, chlorophyll *a* can be used as an indicator of toxic harmful algal blooms (HABs) under three special conditions:

1. the toxic algal species must contain chlorophyll *a*;
2. the health risk to humans or aquatic life must be relatable to chlorophyll *a* concentration; and
2. the toxic algal species must have known periods during the year as well as specific places (hot spots) where it dominates increases in chlorophyll *a* concentrations.

Under these conditions, increases in chlorophyll *a* concentrations can also be used to trigger an adaptive sampling program to identify and enumerate the toxic species. This approach is pursued in Chapter 6, "Chlorophyll *a* Concentrations Characteristic of Impairments by Harmful Algal Blooms."

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chapter iii

Historical Chlorophyll *a* Reference Concentrations

Chlorophyll *a* constitutes an important indicator of water quality in estuaries such as the Chesapeake Bay where chlorophyll *a* has increased significantly since World War II (Figure III-1). Chlorophyll *a* increases have coincided with a doubling or more of nitrogen loadings (Boynton et al. 1995), particularly in the Bay's lower polyhaline regions. Long-term data on chlorophyll *a* for the Chesapeake Bay extend back more than 50 years to provide a historical context for the more recent observations from the extensive ongoing Chesapeake Bay water quality monitoring program (Chesapeake Bay Program 1989). The focus on historical reference concentrations to set concentrations protective against ecological impairments is based on the conclusion that chlorophyll *a* levels in the 1950s and 1960s were lower than contemporary levels documented by Harding 1994 and Harding and Perry 1997. While not characteristic of "pristine" conditions, data from these earlier decades provide "baseline" concentrations for a less-stressed ecosystem prior to severe eutrophication with widespread hypoxia, loss of submerged aquatic vegetation, and declines in productive fisheries (Kemp et al. 2005).

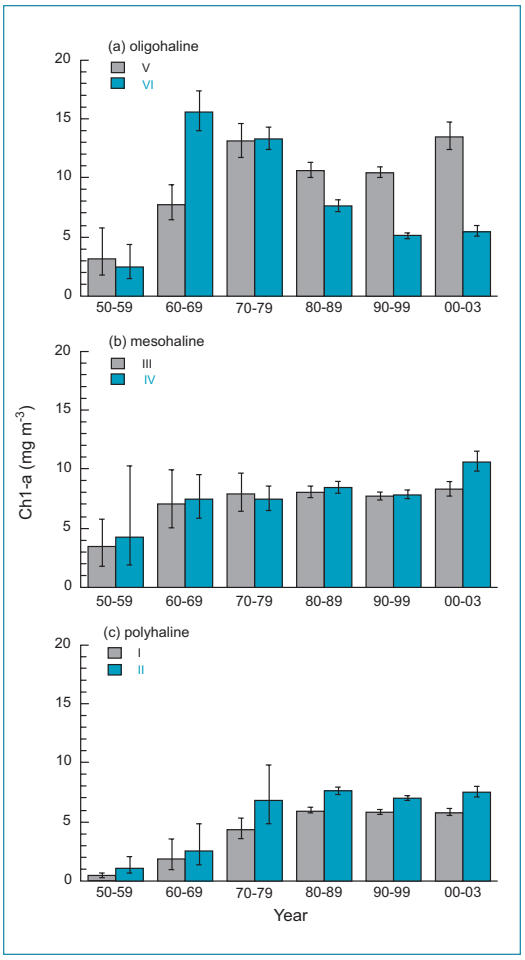


Figure III-1. Historical changes in surface chlorophyll *a* concentrations from 1950 to 2003.

Sources: Harding 1994; Harding and Perry 1997, updated in Kemp et al. 2005.

RATIONALE FOR THE 1950S TO 1960S REFERENCE PERIOD

The extensive review paper, "Eutrophication of Chesapeake Bay: historical trends and ecological interactions" by Kemp et al. (2005), chronicles significant changes in the Chesapeake Bay ecosystem over the past five decades, noting degradation of water quality that accelerated from the 1950s through the 1960s. The 18 estuarine scientists who contributed to this paper provide a systematic account of the eutrophication record in Chesapeake Bay and its ecological implications. Evidence from dated sediment cores revealed organic enrichment in ~200-year-old strata, while signs of increased phytoplankton biomass and decreased water clarity first appeared about 100 years ago. Kemp et al. (2005) summarize changes from the most recent 50 years against a backdrop of long-term changes spanning the period since colonization. Two manifestations of water quality degradation evident since the 1950s and 1960s are recurring deep-water hypoxia (Officer et al. 1984) and the loss of submerged aquatic vegetation (Kemp et al. 1983; Orth and Moore 1983). This degradation coincides with a significant increase in the use of commercial fertilizers after the 1950s along with a ~2.5-fold increase in total nitrogen loadings from the Susquehanna River from 1945 to 1990 (Boynton et al. 1995).

The sediment record also reveals a major shift in phytoplankton community composition within the same 50-year period, exemplified by a shift in the ratio of planktonic to benthic diatoms. This shift indicates decreased water clarity, which led to the suppression of benthic algal production (Cooper and Brush 1991, 1993). Consistent with this shift was a sharp increase of bacterial carbon burial beginning in the mid-20th century (Zimmerman and Canuel 2000), paralleled by increases in the ratio of bacterial carbon to biogenic silica that suggests a decline in the efficiency at which diatom production transfers to upper trophic levels (e.g., Kemp et al. 2001).

Direct measurements of the macroinvertebrate benthic community were not available prior to 1950. However, shifts in dominant macrofaunal species occurred in the early 1960s in the York River (Boesch and Rosenberg 1981) and in the early 1970s in the mainstem Chesapeake Bay (Holland et al. 1987). Finally, the authors suggest that eutrophication also affects higher trophic levels, noting that the shifts in primary producers (that accompanied fundamental changes of ecological structure) have altered fisheries production (Kemp et al. 2005).

REFERENCE CONCENTRATION DERIVATION APPROACH

The reference concentration derivation approach began with the acquisition of historical through present-day (1950–2004) chlorophyll *a* data from archival holdings (1950–1983) and the Chesapeake Bay Water Quality Monitoring Program (1984–2004). All data used comes from the Chesapeake Bay Program website's data hub (www.chesapeakebay.net/data). These data holdings consisted of surface chlorophyll *a* and vertical chlorophyll *a* profiles from various sources (Table III-1).

These data were analyzed and modeled to develop reference chlorophyll *a* concentrations for the Chesapeake Bay. Models of surface chlorophyll *a* and depth-weighted average chlorophyll *a* from profiles were devised for the complete historical time series to generate predictions for specific periods and flow conditions. This process allowed selection of a time period (e.g., a decade) to function as a reference restoration target. The approach follows the logic that chlorophyll *a* concentrations have increased significantly between the 1950s and 1980s (Harding and Perry 1997) (Figure III-1). It also accounted for strong climate forcing of chlorophyll *a* concentrations (past and present) by establishing regional seasonal reference chlorophyll *a* concentrations (based on mean chlorophyll *a* concentrations) and factoring in spatial and temporal variances for wet, dry, and average conditions.

HISTORICAL DATA SOURCES AND TEMPORAL COVERAGE

The analysis presented here extends the earlier published analyses of Harding (1994) and Harding and Perry (1997) which only used data from the Chesapeake Bay Institute (1950–1982) and the first 8 years of data from the Chesapeake Bay Water Quality Monitoring Program (1985–1992) to quantify trends in surface chlorophyll *a* during the post-World War II period. To derive chlorophyll *a* reference concentrations, additional data were identified in the archived data holdings (Table III-1).

Table III-1. Sources of historical 1950–1983 Chesapeake Bay chlorophyll *a* concentration data used in the derivation of historical chlorophyll reference concentrations.

Source	Period
AFO-MAINBAY	1979
AFOLIGHT	1979
CBI-AESOP	1969–1971
CBI-PROCON	1975–1976
CBIBAY	1950–1980
CBITRIB	1950–1980
FLEMER-BIGGS	1965–1967
HEINLE-WILSON	1966–1971
MARYLAND106	1969–1981
NUTRIENT	1977–1978
STORET	1978–1980
TAFT	1980
VIMS	1975–1979
WHALEY-CARPENTER	1964–1966

The field collection and laboratory analytical methods used in the 1950s, 1960s, and 1970s were carefully evaluated to ascertain comparability with current field and analytical methods in terms of: (a) filter type used to collect suspended material; (b) solvent used to extract phytoplankton pigments; (c) spectrophotometric approach (monochromatic, trichromatic); and (d) calibration approach (use of pure chlorophyll *a* to develop standards for spectrophotometric and fluorometric measurements). The historical data archives were also queried for vertical chlorophyll *a* profile data to determine if the spatial and temporal coverage remained adequate to compute integrated-water column chlorophyll *a* prior to 1984. The geo-locations of all stations were examined to assure that they were located within the mainstem Chesapeake Bay and not in the tidal tributaries. A parallel set of queries was conducted using chlorophyll *a* data from the Chesapeake Bay Water

Quality Monitoring Program (1984–2004) for mainstem stations, including both surface and water column measurements.

MODELING APPROACH

The surface chlorophyll *a* (chla) model for historical data consists of a General Linear Model (GLM) in SAS with $\log_{10}$ (chlorophyll *a*) as the dependent variable and a set of eight independent categorical variables: decade, salinity zone, season, month (season), decade*salinity zone, decade*season, decade*month (season), and salinity zone*season. In addition, four continuous variables—salinity, salinity*month (season), water temperature, and total depth—were used. The model used three salinity zones (oligohaline (OH), mesohaline (MH), and polyhaline (PH)) as well as five complete decades (1950s through 1990s) along with 2000 to 2004 data. Each year was divided into five seasons: winter (January, February, March), spring (April, May), transition (June), summer (July, August, September), and fall (October, November, December).

ACCOUNTING FOR FLOW

Climate forcing of phytoplankton dynamics in Chesapeake Bay is strongly expressed by the seasonal to interannual variability of chlorophyll *a* in aircraft remote sensing data (aggregated for "wet," "long-term average," and "dry" conditions) from 1989 to 2004 (Figure III-2). Statistical methods to incorporate flow as an independent variable in historical chlorophyll *a* models have met with mixed success. The unequal experimental designs in the temporal dimension limit specification of the correct flow-lag and flow-averaging window since the historical dataset compiles many different tidal-water data collection and field research projects with distinct goals and designs. In contrast, salinity nested within a salinity zone was a very successful independent variable. Nesting salinity within a salinity zone is important so that the salinity term models the effect of high or low flow, rather than the along-axis spatial distribution of chlorophyll *a* in the Chesapeake Bay.

To equate salinity to flow, the model assumed a direct correspondence between these two variables. For spring and summer seasons of each decade, the 10^{th} percentile, median, and 90th percentile of the monthly mean salinity were computed. A synthetic prediction data set with $\log_{10}$ (chlorophyll *a*) set to "missing" was created with one observation for each decade, month, salinity zone, and salinity value. Water temperature was computed as the seasonal average with station depth set to the salinity zone average. Using GLM, the predicted value of $\log_{10}$ (chlorophyll *a*) was obtained for each of these synthetic observations. In plots and output, these predictions are labeled as:

GLM (10th salinity percentile) = high-flow prediction;

GLM (median salinity) = mid-flow prediction; and

GLM (90th salinity percentile) = low-flow prediction.

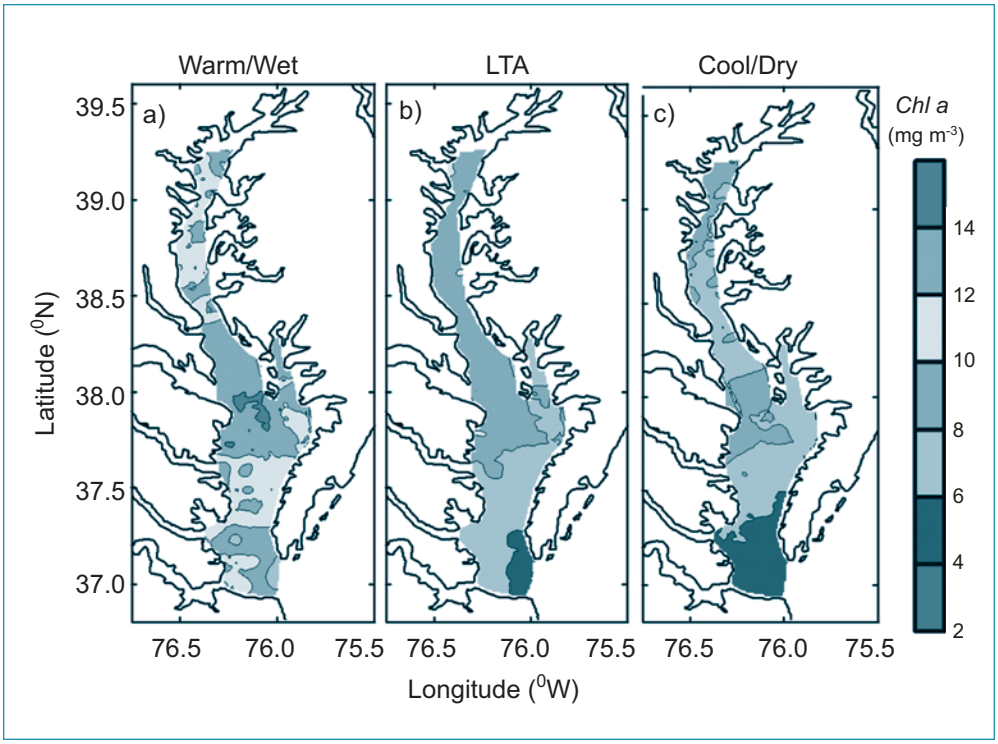


Figure III-2. Climate forcing of phytoplankton biomass as chlorophyll *a* from aircraft remote sensing data. Warm/wet, LTA, and cool/dry are predominant climatic conditions for which LTA represents the long-term average (1989–2005).

Source: Miller and Harding 2006.

DERIVATION OF REFERENCE THRESHOLDS BASED ON SPATIAL AND TEMPORAL VARIANCES

To complete the definition of chlorophyll *a* concentrations of the 1960s and 1970s as reference concentrations, establishing a criteria threshold for each season/salinity zone combination to use for criteria attainment assessment proved necessary (U.S. EPA 2003a). The criteria threshold for chlorophyll *a* is a concentration that should rarely be exceeded by a "population" of chlorophyll *a* concentrations characterizing healthy levels. When the population is unidimensional (e.g., the nutrient concentration in a wastewater treatment facility effluent), then one can obtain an upper threshold based on the simple distribution of values in a "healthy population" (Figure III-3).

The 90th percentile of this distribution might be chosen as the "criterion threshold" to allow 10 percent noncompliance due to the expectation of a low level of naturally occurring exceedances even in a healthy population (U.S. EPA 2003). A standard technique to estimate distribution percentiles is assuming a mathematical form for the distribution (e.g., a normal distribution for logarithm-transformed chlorophyll *a*) and estimating the percentile as some number of standard deviations above the mean.

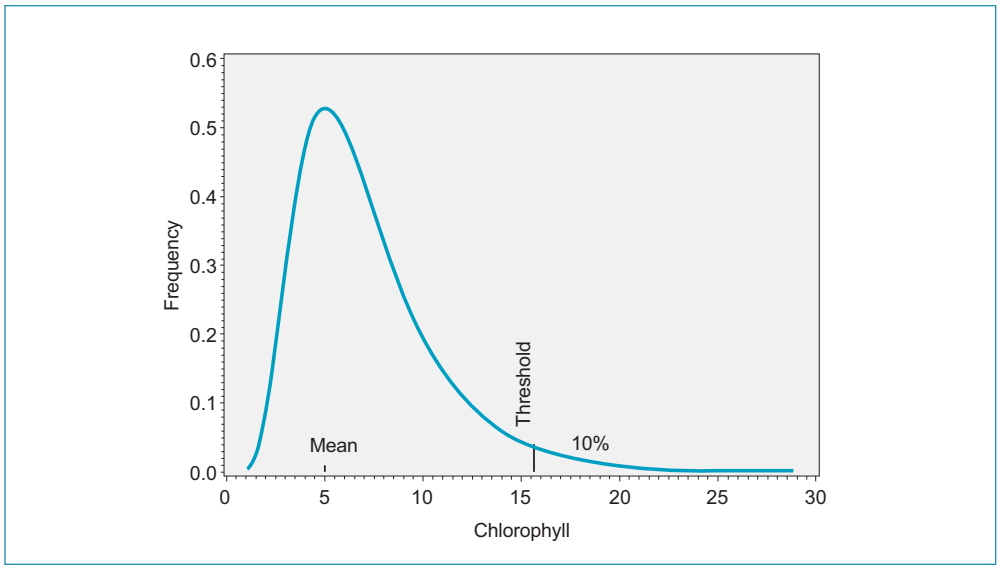


Figure III-3. Hypothetical log-normal distribution typical of chlorophyll *a* concentrations, illustrating the relationship of the geometric mean and the criterion threshold set at the 90th percentile.

The 90th percentile of the normal distribution is 1.2815 standard deviations above the mean.

When regulating "populations" distributed in both space and time, this simple concept for assessing non-attainment must be extended to account for variability in each dimension. This extension adds some complexity to the mathematics, but the fundamental concept remains the same: to set the criterion threshold a certain distance above the mean concentration such that exceedance of that threshold remains rare in a healthy population. In this case, the distance by which the threshold must exceed the mean is a function of both the spatial and temporal variance components, as described below.

To establish these criteria thresholds, one could assume the simple model:

$$x_{ij} = u + a_i + b_{ij} \qquad \text{Equation 1}$$

where:

u is the desired mean level of chlorophyll *a* (in log space);
a_i is a random term for variation over time with variance Φ^2_a;
b_{ij} is a random term for variation over space with variance Φ^2_b; and
x_{ij} is a $\log_{10}$ chlorophyll *a* at time i and location j.

The variance of x_{ij} is $\Phi^2_a + \Phi^2_b = \Phi^2$ (Equation 2). The standard deviation of x_{ij} is $\text{sqrt}(\Phi^2) = \Phi$ (Equation 3). It is common to allow an overall 10 percent exceedance rate without declaring an assessment unit out of compliance (U.S. EPA 2003). Ten percent of the x_{ij} is expected to fall above $u + 1.2815*\Phi$, for which 1.2815 is the 10th percentile of the standard normal distribution. Assuming normality, a population with spatial and temporal variances characterized by Φ^2_a and Φ^2_b with a mean

1.2815*Φ below the threshold criterion will have an exceedance rate of 10 percent over space and time. To illustrate this process, thresholds were computed for spring and summer for three salinity zones using 1960s and 1970s mid-flow surface chlorophyll *a* concentrations as the "desirable" levels to attain (Tables III-2 and III-3).

The spatial and temporal variances from the ongoing Chesapeake Bay Water Quality Monitoring Program data (1985–2004) were used to determine thresholds to apply to the historical means. The 1960s and 1970s historical data were too limited in spatial and temporal coverage to support these variance computations. The 1985 to 2004 monitoring program data, on the other hand, are more synoptic in design; each field sampling cruise is completed in just a few days. Moreover, they are the principal data that will be used to assess attainment of the chlorophyll *a* criteria.

The temporal and spatial variance terms in Tables III-2 and III-3 were completed from mean square terms of the decadal model fitted to 1985–2004 chlorophyll *a* concentration data from the Chesapeake Bay Water Quality Monitoring Program. In

Table III-2. Surface chlorophyll *a* (chla) reference concentrations ($\mu g \cdot liter^{-1}$) derived by computing an upper threshold based on predicted surface mean log_{10} (chlorophyll *a*) for the 1960s at mid-flow conditions.

Season	Salinity zone	Mean log chla	Geometric mean chla	Temporal variance	Spatial variance	Standard deviation log chla	Threshold criterion log chla	Threshold criterion chla
Spring	OH	0.768	5.87	0.0233	0.0658	0.2985	1.26	18.2
Summer	OH	1.17	14.8	0.0233	0.0658	0.2985	1.66	45.7
Spring	MH	0.414	2.59	0.0233	0.0658	0.2985	0.905	8.03
Summer	MH	0.863	7.29	0.0233	0.0658	0.2985	1.35	22.6
Spring	PH	0.139	1.38	0.0233	0.0658	0.2985	0.630	4.26
Summer	PH	0.218	1.65	0.0233	0.0658	0.2985	0.709	5.12

Table III-3. Surface chlorophyll *a* (chla) reference concentrations ($\mu g \cdot liter^{-1}$) derived by computing an upper threshold based on predicted surface mean log_{10} (chlorophyll *a*) for the 1970s at mid-flow conditions.

Season	Salinity zone	Mean log chla	Geometric mean chla	Temporal variance	Spatial variance	Standard deviation log chla	Threshold criterion log chla	Threshold criterion chla
Spring	OH	1.06	11.4	0.0233	0.0658	0.2985	1.55	35.3
Summer	OH	1.24	17.4	0.0233	0.0658	0.2985	1.73	53.8
Spring	MH	0.948	8.87	0.0233	0.0658	0.2985	1.44	27.5
Summer	MH	0.955	9.01	0.0233	0.0658	0.2985	1.45	27.9
Spring	PH	0.658	4.55	0.0233	0.0658	0.2985	1.15	14.1
Summer	PH	0.734	5.42	0.0233	0.0658	0.2985	1.23	16.8

this model, the Chesapeake Bay Program segment (U.S. EPA 2004, 2005) replaced salinity zone while cruise replaced month relative to the model for the historical data. The spatial variance term was taken directly from the mean square error (MS(error)) term and the temporal variance term computed from the cruise(season) mean square term. The expected mean square obtained using the RANDOM statement of the GLM program is:

$$EMS[CRUISE(season)] = Var(Error) + 38.505\ Var[CRUISE(season)] \quad \text{Equation 4}$$

The estimate of temporal variance is:

$$\Phi^2_a = MS[month(season)] - MS(error)/38.505 \quad \text{Equation 5}$$

DEPTH-WEIGHTED INTEGRATED WATER COLUMN CHLOROPHYLL *a*

The analysis of historical chlorophyll *a* data included vertical chlorophyll *a* profiles, supporting the use of integrated water column chlorophyll *a* as a measure of phytoplankton biomass. The rationale for this approach is the strong link of nutrient loading to phytoplankton biomass that develops during the spring bloom of diatoms (Malone 1992; Malone et al. 1996). The prevailing view is that the winter-spring diatom bloom sequesters nutrients from freshwater rivers and other sources, and that the timing, position, and magnitude of the bloom are sensitive to the variability of freshwater flow that relates closely to climate (Adolf et al. 2006; Miller and Harding 2006). Surface chlorophyll *a* data, collected using aircraft remote sensing and aggregated by climatic conditions, illustrate the strong role of climate (see Figure III-2). The vertical chlorophyll *a* concentration profiles reveal strong seasonality, reflecting the accumulation of diatom biomass in spring and subsequent sedimentation below the pycnocline. The resultant below pycnocline phytoplankton biomass ultimately brings about hypoxia (Malone 1992).

Sufficient historical data containing vertical chlorophyll *a* profiles were available to conduct an analysis similar to the study of surface chlorophyll *a* above. As the Bay's bathymetry strongly affects integral-water column chlorophyll *a* computed from these profiles within a major salinity region, the integrated-water column chlorophyll *a* were normalized to water column depth for each sampling site to take account of the effect on the integral. This approach generated depth-weighted average chlorophyll *a* values for the same seasons and regions used to develop the criteria in Tables III-2 and III-3 for surface chlorophyll *a*. Spatial and temporal variances for depth-weighted average chlorophyll *a* were computed using Chesapeake Bay Water Quality Monitoring Program data from 1985 to 2004. Tables III-4 and III-5 give depth-weighted chlorophyll *a* means in logarithmic space, back-transformed geometric means, variances, and threshold concentrations for the 1960s and 1970s for mid-flow conditions. Separate solutions for low- and high-flow conditions were also calculated, as for surface chlorophyll *a*. Thresholds computed from depth-weighted average chlorophyll *a* were typically lower than those in Tables III-2 and III-3. The polyhaline Chesapeake Bay proved the exception, partly due to the lower

Table III-4. Depth-weighted average chlorophyll *a* (dwachl) reference concentrations ($\mu g \cdot liter^{-1}$) derived by computing an upper threshold based on predicted means for mid-flow 1960s data.

Season	Salinity zone	Mean log dwachl	Geometric mean dwachl	Temporal variance	Spatial variance	Standard deviation log dwachl	Threshold criterion log dwachl	Threshold criterion dwachl
Spring	OH	0.551	3.56	0.0251	0.0404	0.2559	0.9723	9.38
Summer	OH	0.906	8.05	0.0251	0.0404	0.2559	1.3270	21.2
Spring	MH	0.299	1.99	0.0251	0.0404	0.2559	0.7202	5.25
Summer	MH	0.617	4.14	0.0251	0.0404	0.2559	1.0384	10.9
Spring	PH	0.222	1.67	0.0251	0.0404	0.2559	0.6430	4.40
Summer	PH	0.492	3.10	0.0251	0.0404	0.2559	0.9124	8.17

Table III-5. Depth-weighted average chlorophyll *a* (dwachl) reference concentrations ($\mu g \cdot liter^{-1}$) derived by computing an upper threshold based on predicted means for mid-flow 1970s data.

Season	Salinity zone	Mean log dwachl	Geometric mean dwachl	Temporal variance	Spatial variance	Standard deviation log dwachl	Threshold criterion log dwachl	Threshold criterion dwachl
Spring	OH	0.980	9.54	0.0251	0.0404	0.2559	1.40	25.2
Summer	OH	1.043	11.0	0.0251	0.0404	0.2559	1.46	29.1
Spring	MH	1.081	12.1	0.0251	0.0404	0.2559	1.50	31.8
Summer	MH	0.689	4.89	0.0251	0.0404	0.2559	1.11	12.9
Spring	PH	0.873	7.46	0.0251	0.0404	0.2559	1.29	19.7
Summer	PH	0.650	4.47	0.0251	0.0404	0.2559	1.07	11.8

spatial variance of the depth-weighted average compared to the spatial variance for surface chlorophyll *a*.

Figure II-4 provides a graphical summary and comparison of model outputs for surface chlorophyll *a* and depth-weighted average chlorophyll *a* from the historical analysis for the three major salinity regions. The plots indicate that the 1960s and 1970s had lower surface chlorophyll *a* and depth-weighted average chlorophyll *a* in the polyhaline Bay—the region most sensitive to nutrient loading variability (Harding et al. 2005). The 1960s showed the strong effect of prolonged low-flow conditions as a lessening of light limitation in the upper oligohaline Bay and as heightened nutrient limitation in the lower polyhaline Chesapeake Bay. The 1970s highlighted the strong effects of prolonged high-flow conditions (superimposed on historical increases of chlorophyll *a*) as higher surface chlorophyll *a* and depth-weighted average chlorophyll *a* in all salinity regions. The strong seasonality of both chlorophyll *a* measures supports separate spring and summer chlorophyll *a* reference concentrations.

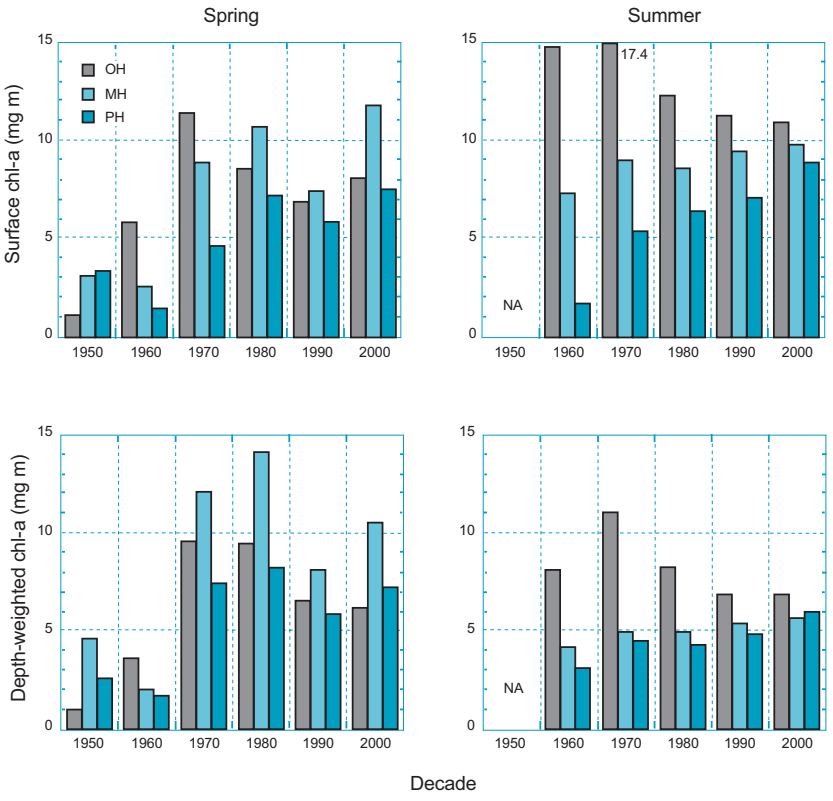


Figure III-4. Geometric means of surface and depth-weighted chlorophyll *a* by the oligohaline (OH), mesohaline (MH) and polyhaline (PH) salinity zones and decade (1950s–2000s) for mid-flow conditions.

HISTORICAL CHLOROPHYLL *a* REFERENCE CONCENTRATIONS

These historical analyses were undertaken to offer a spatial and temporal context for developing numerical chlorophyll *a* criteria for Chesapeake Bay. The described analyses drew upon extensive data spanning nearly six decades to quantify seasonal regionally based chlorophyll *a* reference concentrations. Few coastal ecosystems in the world, if any, have the data to support such analyses. The trajectory over time of chlorophyll *a* concentrations in Chesapeake Bay signifies increased nutrient loading, making chlorophyll *a* an invaluable indicator. This indicator, however, is strongly affected by climate. The challenge is to separate climatically induced variability from long-term trends related to increased nutrient loading. This challenge was met here using nearly six decades of data along with statistical modeling. The resultant surface chlorophyll *a* and depth-weighted average chlorophyll *a* concentrations based on 1960s thresholds represent chlorophyll *a* reference concentrations characteristic of a more balanced Chesapeake Bay ecosystem.

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chapter IV

Chlorophyll *a* Relationship to Dissolved Oxygen Impairments

Scientists have long recognized the ecological relationships between various water quality parameters, such as chlorophyll *a* in surface waters and dissolved oxygen in bottom waters. These relationships were initially recognized in freshwater lakes where eutrophication problems developed because of the lakes' proximity to anthropogenic nutrient sources. Taken from a textbook on water quality (Novotny and Olem 1994), Table IV-1 summarizes water quality studies in fresh waters, including their classification in terms of trophic status. Shallower Secchi readings, along with higher total phosphorous (TP), chlorophyll *a*, and primary production, are all associated with increasing eutrophication and lower dissolved oxygen in bottom (hypolimnetic) waters. In terms of the water quality parameters documented in Table IV-1, the current conditions in Chesapeake Bay are equivalent to those of eutrophic lakes.

Analyses focused on several key systems to determine whether significant quantitative relationships between chlorophyll *a* and dissolved oxygen concentrations in Chesapeake Bay could prove useful in developing chlorophyll *a* criteria. For instance, data from the tidal Choptank River were analyzed to determine if such

Table IV-1. Trophic status of lakes and characteristic water quality parameter values.

Water quality parameter	Oligotrophic	Mesotrophic	Eutrophic
TP, $\mu g \cdot liter^{-1}$	<10	10 – 20	>20
chlorophyll *a*, $\mu g \cdot liter^{-1}$	<4	4 – 10	>10
Secchi depth, m	>4	2 – 4	<2
hypolimnetic O_2, % sat.	>80	10 – 80	<10
phytoplankton productivity $g \cdot C \cdot m^{-2} \cdot d^{-1}$	7 – 25	75 – 250	350 – 700

Source: Novotny and Olem 1994, p. 784.

relationships exist since this well-studied system is representative of many rural tidal tributaries on the Eastern Shore Coastal Plain with low human population density and significant agriculture. Similarly, the tidal Patuxent River was included because this tidal tributary, although smaller than many of the other major tidal tributaries on the western shore, represents the more urbanized western shore tributaries that rest on Piedmont and Coastal Plain lands with high population densities and large sewage inputs. These analyses also included fixed-station water quality monitoring data from all major tidal tributaries and the mainstem Chesapeake Bay to identify overarching relationship patterns between chlorophyll *a* and dissolved oxygen concentrations.

Chlorophyll *a*—the universal algal pigment indicative of phytoplankton biomass—varies on interannual, seasonal, and shorter time scales based on phytoplankton dynamics. Interannually, chlorophyll *a* varies least with no consistent trends in annual average chlorophyll *a* concentrations baywide or in the tidal fresh, oligohaline, mesohaline, and polyhaline zones of the Bay (Figure IV-1). Seasonally, larger variations in chlorophyll *a* occur, typically with a cool-season minimum and warm-season maximum in biomass (Figure IV-2). Chlorophyll *a* production in tidal fresh regions is typically light-limited during times other than summer due to high turbidities and short residence times. Large increases in chlorophyll *a* occur in July and August (Fisher et al. 1999) under conditions of low freshwater flow and high light intensity. In contrast, mesohaline and polyhaline regions have damped seasonal cycles driven primarily by river-borne nutrient inputs.

The long-term means for early and late growing season in the Patuxent River estuary show these interacting influences on the time and space distributions of chlorophyll *a* (Figures IV-3 and IV-4). The normal spatial pattern in the tidal Patuxent River is a

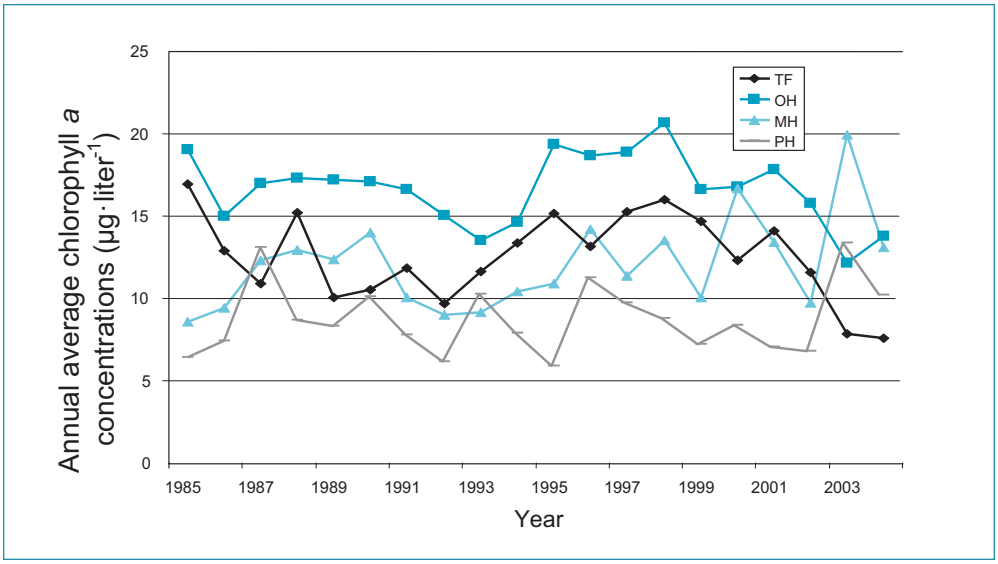


Figure IV-1. Interannual variations in average surface chlorophyll *a* concentrations for the tidal fresh (TF), oligohaline (OH), mesohaline (MH), and polyhaline (PH) zones of the Chesapeake Bay and its tidal tributaries (1985–2004).

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

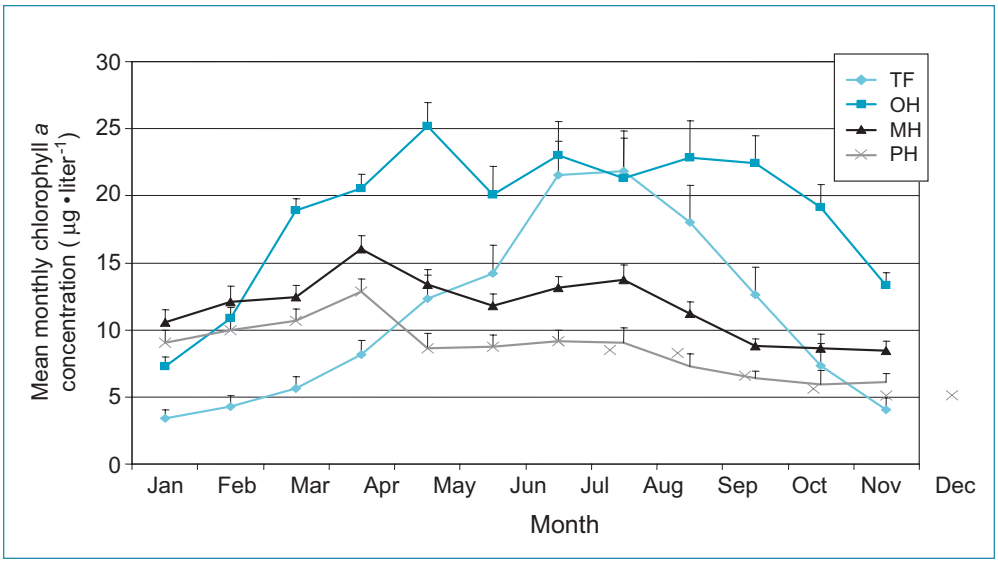


Figure IV-2. Mean monthly surface chlorophyll *a* concentrations for the tidal fresh (TF), oligohaline (OH), mesohaline (MH) and polyhaline (PH) salinity zones of the Chesapeake Bay (1985–2004) with standard error bars.

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

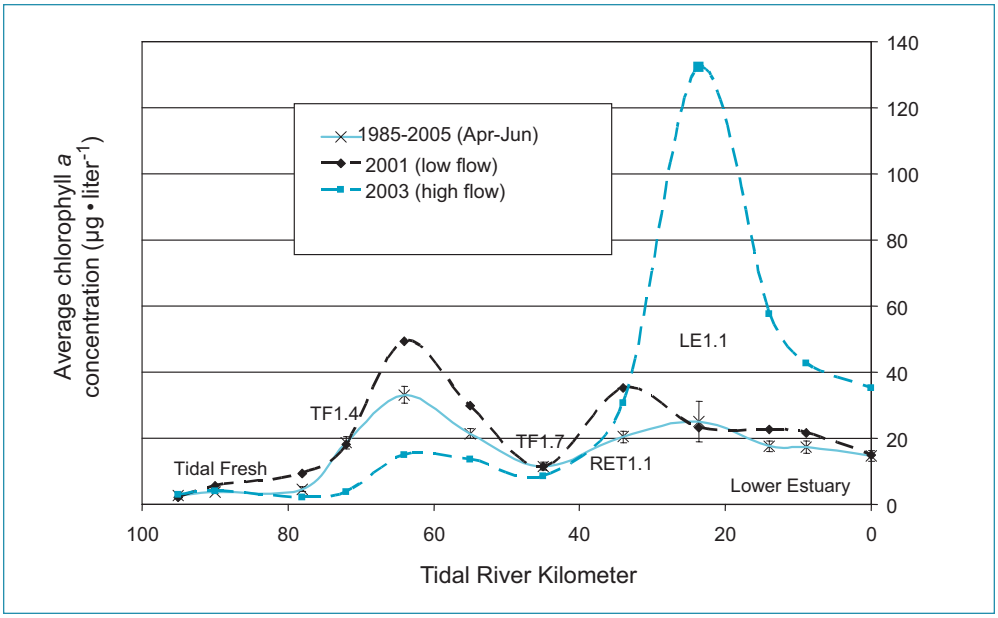


Figure IV-3. Average surface chlorophyll *a* in the tidal Patuxent River during the early growing season (April–June, 1985–2005) by Chesapeake Bay Water Quality Monitoring Program station with high- and low-flow years. Standard error bars are shown for the long-term average.

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

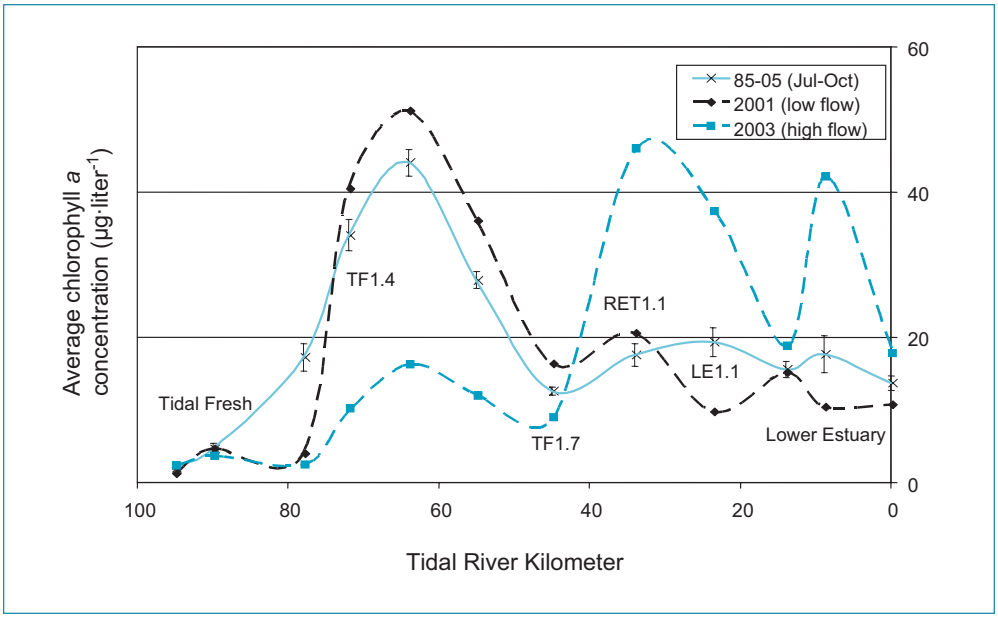


Figure IV-4. Average surface chlorophyll *a* concentrations in the tidal Patuxent River during the late growing season (July–October from 1985–2005) by Chesapeake Bay Water Quality Monitoring Program station with high- and low-flow years. Standard error bars are shown for the long-term average.

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

chlorophyll *a* maximum in tidal fresh waters at ~60 km from the river mouth, with lower concentrations downstream. The chlorophyll *a* maximum represents initial consumption of the local terrestrial nutrient supply, with recycling and processing of this material downstream (Fisher et al. 1988). This spatial pattern is accentuated at low flows, whereas higher flows push the chlorophyll *a* maximum downstream into the lower estuary. This pattern also occurs in the mainstem Chesapeake Bay in near-synoptic data, with higher temperatures focusing the chlorophyll *a* maximum in the upper Bay (Figure IV-5).

At issue is whether surface chlorophyll *a* represents total integrated water column chlorophyll *a*—especially important in the spring when chlorophyll *a* accumulates both above and below the pycnocline until the hypoxia onset (Malone et al. 1988). At mainstem water quality monitoring stations in the Bay, the annual average surface chlorophyll *a* (µg chla·liter $^{-1}$) correlated strongly with the annual, average, integrated water column chlorophyll *a* (mg chla·m^{-2}) (Figure IV-6). The spring accumulations of chlorophyll *a* in bottom waters, therefore, do not significantly influence annual averages of surface chlorophyll *a*, which can be used to estimate annual average phytoplankton accumulation in the water.

In most tidal tributaries, chlorophyll *a* is usually related to nutrient loading on an annual time scale. For instance, at the tidal Choptank River water quality monitoring station ET5.2, stream discharge from the Greensboro, Maryland stream gauging station is a proxy for nutrient loading. Annual average chlorophyll *a* increases to >20 µg·liter^{-1} with increasing annual discharge (Figure IV-7). The year 2003 had

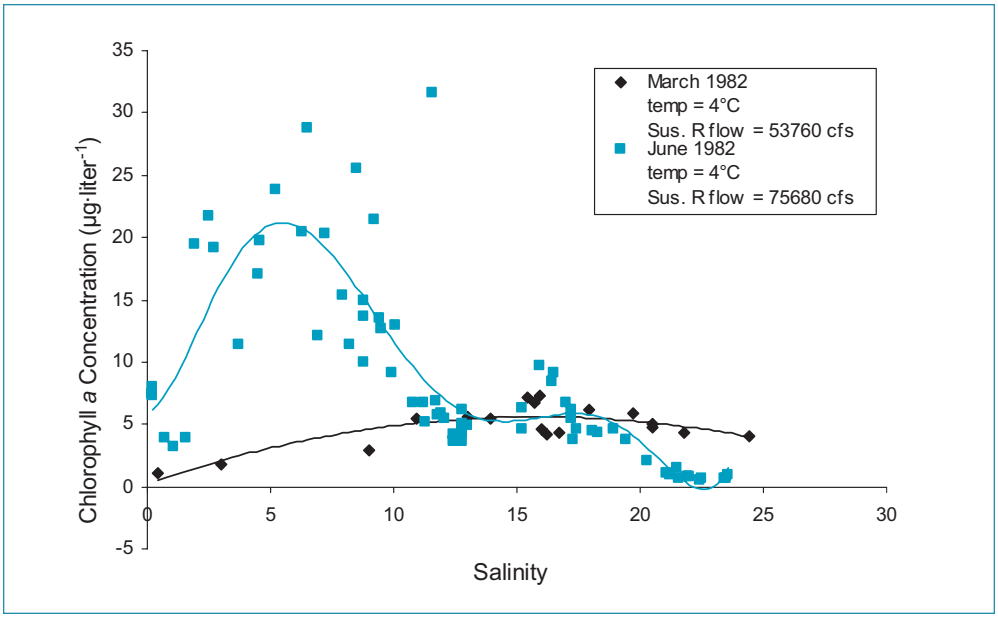


Figure IV-5. The distribution of surface chlorophyll *a* concentrations in the Chesapeake Bay mainstem in March and June 1982 showing the distinct chlorophyll *a* maximum in the upper Bay (lower salinities) during warmer months and the more diffuse chlorophyll maximum in the mid to lower Bay (higher salinities) during cooler months.

Source: Fisher et al. 1988.

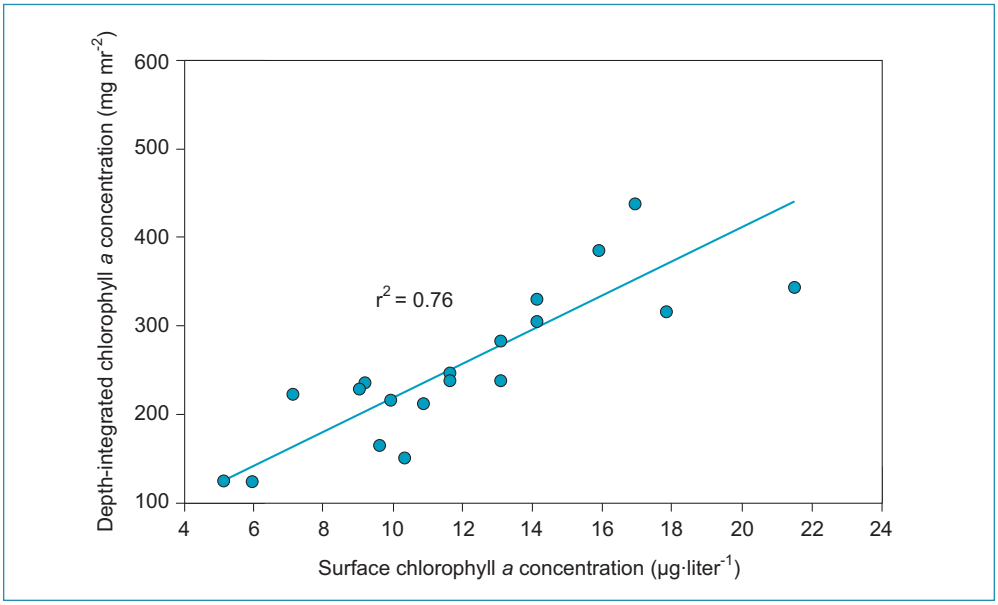


Figure IV-6. Relationship between surface chlorophyll *a* and depth-integrated chlorophyll *a* concentrations for select water quality monitoring stations in the mainstem Chesapeake Bay (March–June, 1985–2004).

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

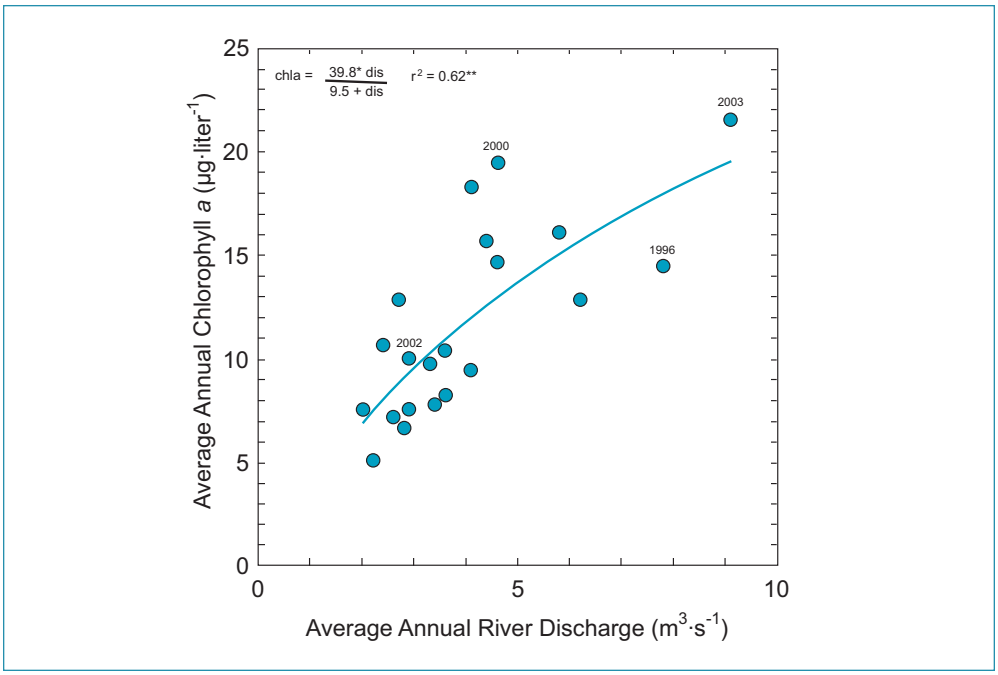


Figure IV-7. Average annual river discharge versus average annual surface chlorophyll *a* concentration for the tidal Choptank River water quality monitoring station ET5.2 (1985– 2003).

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data); U.S. Geological Survey Stream Gage Network (www.usgs.gov)

record rainfall and was also one of the highest discharge years in the U.S. Geological Survey's 50-year record. The relationship is hyperbolic, much like a saturation function. Under high loading (high river flows), the chlorophyll *a* maximum is likely displaced downstream from station ET5.2 or is suppressed by the high turbidity accompanying the high freshwater flows.

Higher chlorophyll *a* concentrations at the tidal Choptank River station ET5.2 are linked to lower bottom dissolved oxygen (Figure IV-8, top panel). Both the annual average and the January-to-August average chlorophyll *a* concentrations at station ET5.2 are inversely correlated with the summer (June, July, August) bottom dissolved oxygen concentrations in the tidal Choptank River at the same station (r^2 = 0.40 and 0.33, respectively). Figure IV-8 shows the somewhat weaker relationship between summer bottom dissolved oxygen and January-to-August chlorophyll *a* because it is more logically consistent with, although statistically weaker than, annual average chlorophyll *a* concentration. These relationships are caused by sedimentation of organic matter from the water column to the river bottom, where microbial and metazoan benthos consume the matter and deplete oxygen in the near-bottom waters. Annual and January-to-August average chlorophyll *a* concentrations over 10 to 15 µg·liter^{-1} are consistently associated with summer bottom dissolved oxygen concentrations under 5 mg·liter^{-1}.

Summer average bottom dissolved oxygen is also inversely correlated with stratification in the water column (Figure IV-8, bottom panel). Here stratification is characterized as the difference in salinity from top to bottom (DS) during summer (June–August). This relationship is stronger than the one between chlorophyll *a* concentration and summer average bottom dissolved oxygen concentration ($r^2 = 0.67$

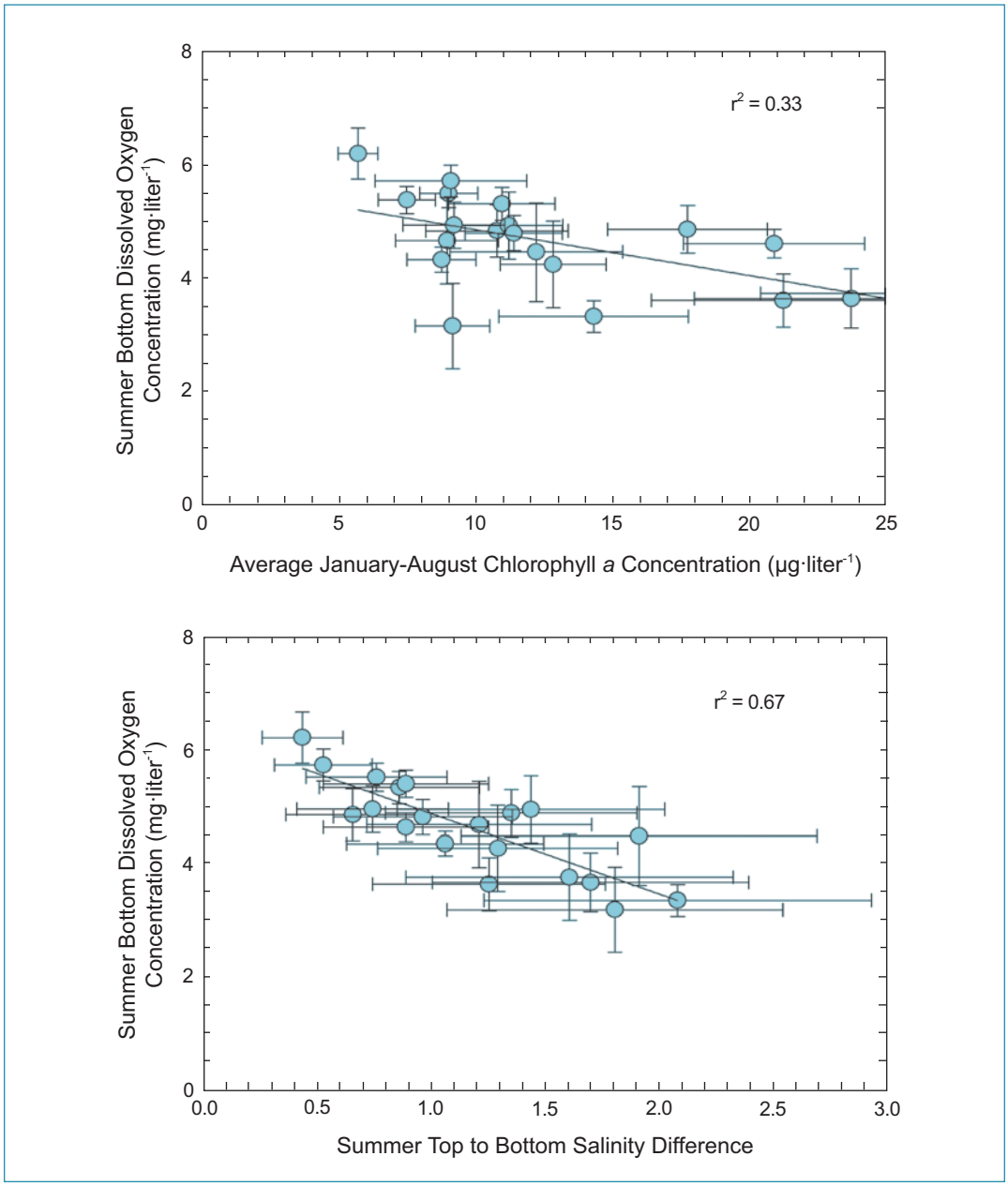


Figure IV-8. *Top panel:* Summer bottom dissolved oxygen concentration vs. average January-to-August surface chlorophyll *a* concentration for the Choptank River water quality monitoring station ET5.2 (1985–2004). *Bottom panel:* Summer bottom dissolved oxygen concentration vs. summer top-to-bottom salinity difference (ΔS) (1984–2004).

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

and 0.33, respectively). A multiple linear regression between summer bottom dissolved oxygen and summer DS with January-through-August chlorophyll *a* (Jan Aug Chla) is dominated by DS. Substituting annual average chlorophyll *a* gives a similar result with a nearly identical r^2. All terms in both equations are significant, with an r^2 of 0.73:

Summer average bottom dissolved oxygen =
6.51 – 1.22*DS – 0.0361*JanAugChla Equation 6

This statistical relationship may be viewed as an initial value of dissolved oxygen slightly below saturation, which is weakly diminished by increasing chlorophyll *a* (the organic matter source) and strongly diminished by increasing stratification (the isolating mechanism). Indeed, Malone (1992) found a strong inverse relationship between stratification and summer average bottom dissolved oxygen concentration in the Chesapeake Bay mainstem between stations CB4.2 and 4.3, indicating that the relationship of dissolved oxygen concentration to stratification strength is a ubiquitous phenomenon in the Chesapeake Bay.

The tidal Patuxent River has a somewhat similar relationship between annual average chlorophyll *a* and summer average bottom dissolved oxygen concentrations (Figure IV-9). The tidal Patuxent River consistently experiences low summer bottom dissolved oxygen concentrations and somewhat higher annual average chlorophyll *a* concentrations. However, the morphological features of the tidal Patuxent River—a small deep estuary with a large basin/estuary ratio—increases the sensitivity of the relationship between these parameters in the tidal Patuxent River compared to the tidal Choptank River—a broad shallow estuary with a small basin/estuary ratio (Fisher et al. 2006).

Combining data for the tidal Patuxent and Choptank rivers, an envelope of concentrations indicate a tendency for summer average dissolved oxygen to decline by 0.15 – 1.1 mg·O_2 per µg chlorophyll *a*. This amount of variation in summer bottom dissolved oxygen sensitivity to increasing annual average chlorophyll *a* concentration is caused by differences in physical properties (morphology, stratification) and by differences in nutrient inputs (agriculture, sewage, rainfall).

Despite the variability, the relationship is still useful. Chlorophyll *a* concentrations of 7 to 28 µg·liter^{-1} are associated with violations of the 30-day, open-water dissolved oxygen criterion; annual average chlorophyll *a* values greater than 20 µg·liter^{-1} are consistently associated with summer average bottom dissolved oxygen concentrations under 4 mg·liter^{-1} in two important tidal tributaries of the Bay.

To broaden the basis of the chlorophyll *a*/dissolved oxygen relationship, data were examined from additional portions of the Chesapeake Bay and its tidal tributaries. Four time domains (calendar year, water year, January–August, and May–August) were examined (Table IV-2). Although some of the r^2 values reported below are small (indicating only small fractions of the variance explained), the large sample size (number of stations x 20-year time periods) enables detection of significant relationships. Figure IV-10 shows an example of one of these relationships.

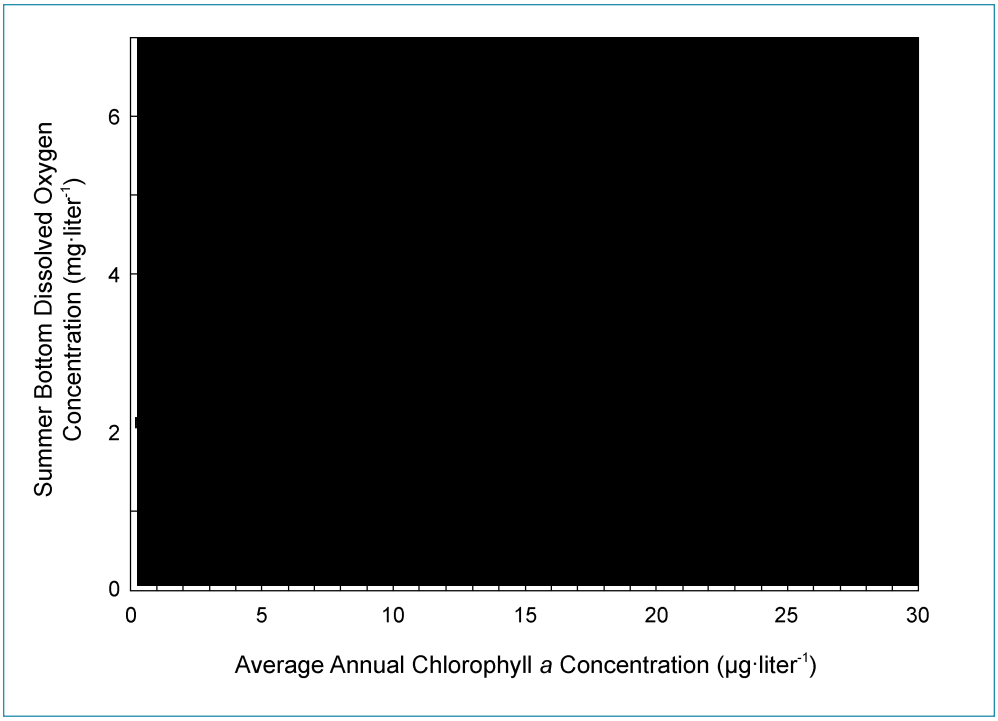


Figure IV-9. Comparison of the annual average surface chlorophyll *a* (chla) concentration versus summer average bottom dissolved oxygen (DO) concentration relationships for the tidal Choptank and Patuxent rivers.

Choptank River relationship:	DO = 5.9 – 0.11 * chla	r^2 = 0.37 **
Patuxent River relationship:	DO = 2.4 – 0.057 * chla	r^2 = 0.26 *
All data relationship:	DO = 5.6 – 1.9 * chla	r^2 = 0.36 **

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

Table IV-2. Summary of statistical relationships between summer average bottom dissolved oxygen (mg·liter^{-1}) and average surface chlorophyll *a* (µg·liter^{-1}) at several time scales. The r^2 is the percent of the variance in summer average bottom dissolved oxygen explained by average surface chlorophyll *a* at each time scale, and the symbols represent the significance level.

	Time scale	Calendar Year	Water Year	January–August	May—August
Chesapeake Bay Mainstem	r^2	0.23 **	0.23 **	0.23 **	0.27 **
	Slope	-0.123 ± 0.020	-0.127 ± 0.021	-0.098 ± 0.016	-0.076± 0.011
Tidal Tributaries	r^2	0.12 **	0.11 **	0.11 **	0.07 *
	Slope	-0.105 ± 0.025	-0.082 ± 0.021	-0.076 ± 0.020	-0.046 ± 0.015

r^2 = percent of the variance in summer average bottom dissolved oxygen explained by average surface chlorophyll *a* at each time scale
* = $p < 0.05$
** = $p < 0.01$
Slope = change in summer average bottom dissolved oxygen per unit chlorophyll a (mg·O_2 [µg·chla]$^{-1}$ ± standard error).

Figure IV-10 illustrates the relationship between summer (with a one-month delay of May to August) average chlorophyll *a* concentrations and summer (June–August) average bottom dissolved oxygen concentrations. The relationship is similar to the others in Table IV-2, but with a more pronounced shift to low bottom dissolved oxygen when May-to-August chlorophyll *a* averages >15 µg·liter^{-1}. No paired observation at any Chesapeake Bay Water Quality Monitoring Program station within the Chesapeake Bay has a May-to-August chlorophyll *a* that exceeds 15 µg·liter^{-1} with a summer average bottom dissolved oxygen value (June–August) that exceeds 3 mg·liter^{-1}. Variations in physical morphology, nutrient loading, and stratification among stations result in the scatter shown in Figure IV-10. Clearly, however, May-to-August average surface chlorophyll *a* concentrations >15 µg·liter^{-1} are associated with summer average dissolved oxygen values <3 mg·liter^{-1} in the bottom waters.

An inverse relationship between chlorophyll *a* and dissolved oxygen is also apparent in the high-frequency monitoring data collected by the Maryland Department of Natural Resources. In Figure IV-11, inverse relationships occur between long-term average dissolved oxygen, chlorophyll *a*, dissolved inorganic phosphorous, and dissolved inorganic nitrogen concentrations at the high-frequency water quality monitoring stations in the tidal Magothy and Severn rivers. In this shallow-water

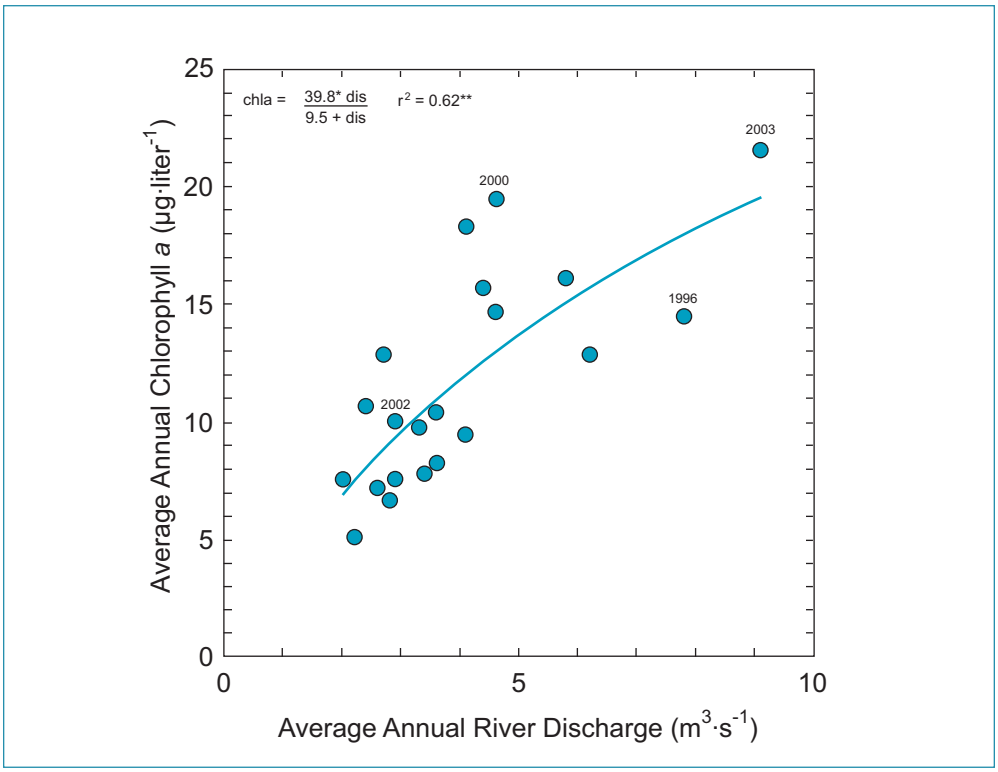


Figure IV-10. Average chlorophyll *a* (May–August) concentration versus summer average (June–August) bottom dissolved oxygen concentration for various Chesapeake Bay mainstem water quality monitoring program stations identified by their respective Chesapeake Bay Program segment (CB3 MH, CB4 MH, CB5 MH, and CB6 PH).

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

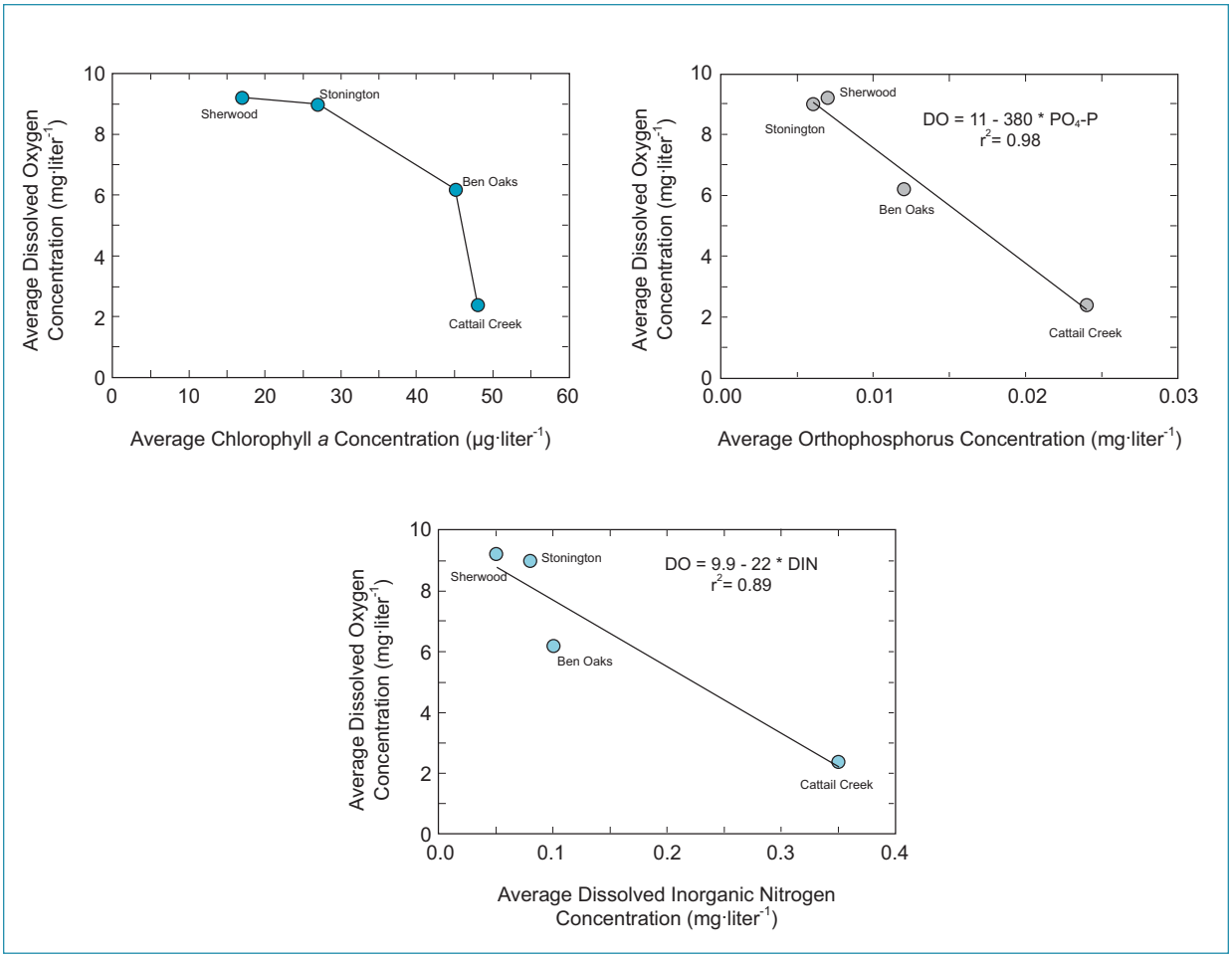


Figure IV-11. Significant relationships among average concentrations of the continuous monitoring surface chlorophyll *a*, orthophosphorous, and dissolved inorganic nitrogen data versus dissolved oxygen concentrations for the tidal Magothy and Severn rivers.

Source: Fisher and Gustafson 2005.

case, average surface concentrations of chlorophyll *a* less than 30 µg·liter^{-1} are associated with depressed dissolved oxygen concentrations in surface waters, further strengthening the link between nutrient loading, phytoplankton abundance, and low dissolved oxygen.

A simple conceptual model can be derived from these observations. The sequence of events leading to low dissolved oxygen conditions in the Chesapeake and its tidal tributaries can be viewed as follows: high nutrient inputs lead to high chlorophyll *a* in excess of the needs of local phytoplankton-consuming organisms. Excess organic matter settles to the bottom, where it is microbially degraded and results in low bottom dissolved oxygen. This conceptual model applies to deep waters separated from the upper mixed layer by a pycnocline via sedimentation at lower concentrations of average surface chlorophyll *a* (10–15 µg·liter^{-1}, Figures IV-8 through IV-10) or directly in the surface layer of shallow waters at higher concentrations of average chlorophyll *a* (>30 µg·liter^{-1}, Figure IV-11) due to the greater access to atmospheric

O_2 in the upper mixed layer. These relationships provide quantitative linkages between the amount of chlorophyll *a* in surface waters and dissolved oxygen impairment of bottom waters.

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chapter V

Chlorophyll *a* Contributions to Water Clarity Impairments

Deterioration of water clarity is widely believed to be the principal cause of the catastrophic decline in submerged aquatic vegetation (SAV) that occurred throughout most of the Chesapeake Bay during the 1960s to 1980s (Orth and Moore 1983). Compared to other plants, SAV requires strong light—about 22 percent of surface light for polyhaline and mesohaline communities and about 13 percent for oligohaline and tidal-fresh communities (Dennison et al. 1993). The light requirement for SAV, together with the depth to which the plants can potentially grow, places an upper limit on the diffuse attenuation coefficient (K_d) for photosynthetically active radiation (PAR) that permits maintenance or restoration of SAV (Kemp et al. 2004). Phytoplankton chlorophyll is one of three constituents that increase the light attenuation above that due to water alone. On average, the contribution of chlorophyll to diffuse attenuation can be calculated from a bio-optical model incorporating the effects of phytoplankton chlorophyll on the absorption and scattering of light (Gallegos 2001). The upper limit of chlorophyll that will permit SAV growth in a particular location can also be calculated, but the precise value depends on the concentrations and optical properties of other attenuating substances.

The two constituents in addition to chlorophyll *a* that contribute to light attenuation are colored dissolved organic matter (CDOM) and suspended particulate matter (quantified by the concentration of total suspended solids, TSS). The general approach to establishing chlorophyll *a* concentrations which will not impair water clarity, therefore, requires determination of the characteristic concentrations of CDOM and TSS and their effect on light attenuation for a particular system. The approach then determines the allowable chlorophyll *a* concentration that permits (when combined with the characteristic CDOM and TSS concentrations) the required level of light to penetrate to the appropriate application depth as established on a segment-specific basis in the 2003 EPA *Regional Criteria Guidance* and *Designated Uses Technical Support Document* (U.S. EPA 2003a, 2003b).

Figure V-1 illustrates this concept. Bio-optical modeling can be used to determine the threshold concentrations of light-attenuating water quality parameters that allow some surface light (13 or 22 percent, depending on salinity zone) to penetrate to a

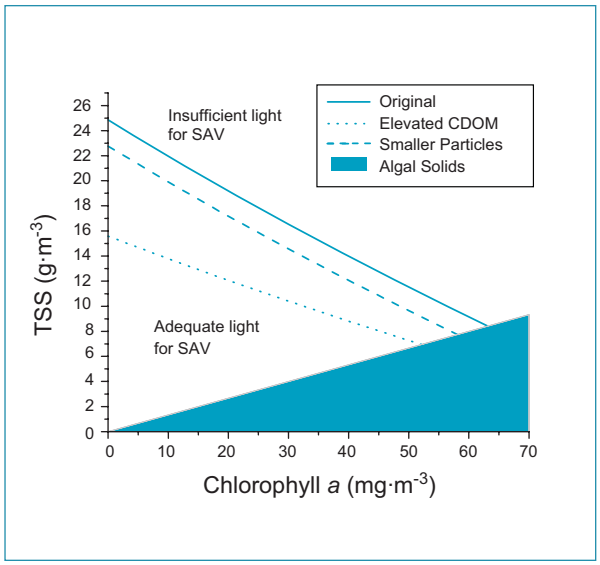


Figure V-1. Chlorophyll thresholds and TSS for SAV survival depend on other parameters. Increases in CDOM (dashed line) or in the absorption and scattering per unit mass of TSS (dotted line) move thresholds toward the origin (i.e., make the system more sensitive to the deterioration of water quality).

given application depth. The figure uses two-dimensional plots for clarity of illustration with chlorophyll *a* and TSS concentrations as x-axis and y-axis, respectively (Figure V-1). Changes in the concentration of CDOM (solid line), or optical properties of the particulate matter (largely determined by particle-size distribution, dotted line), and application depth determine the thresholds. Chlorophyll *a* adds to the particulate matter concentration of any sample; the gray shaded region denotes the approximate contribution of chlorophyll *a* to TSS. Systems with median concentrations of chlorophyll *a* and TSS that fall closer to the origin than the threshold line have water quality conditions that will provide sufficient light for SAV, while systems with concentrations that fall beyond the threshold line will not (Figure V-1).

The chlorophyll *a* concentration that will support SAV light requirements (e.g., water clarity criteria) clearly depends on the concentration of other attenuators (CDOM and TSS). Colored dissolved organic matter comes from decaying plants, which includes phytoplankton but mostly emanates from terrestrial sources in estuarine waters. It absorbs light strongly in the blue portion of the spectrum. Concentrations of CDOM can be very high in some systems, such as the tidal Pocomoke River on the Eastern Shore of Chesapeake Bay, which drains low-lying coastal wetlands. While some slight reduction in CDOM may accompany reductions in chlorophyll *a* concentrations, CDOM is considered a fixed characteristic of a particular tidal tributary or Bay region in deriving chlorophyll *a* criteria.

Due to the unique hydrodynamics, morphology, and basin characteristics of each tributary, Sanford (personal communication 25 October 2005) has suggested that each tidal tributary may have some natural or "background" concentration of TSS that represents a dynamic balance between settling and resuspension, and persists in the absence of immediate riverine inputs. Management may be able to lower TSS concentrations only to "background" concentrations; therefore, identifying the background level for each tributary will prove critical (see below).

Figure V-2 illustrates the determination of light-based chlorophyll *a* concentration thresholds. The concentration of CDOM and optical properties, along with the designated application depth for a segment, determines the threshold concentrations of chlorophyll *a* and TSS that will support SAV (Figure V-2, outer dark blue edge). The medium blue region denotes an adjusted threshold obtained by subtracting the background TSS concentration characteristic of that waterbody. The point at which this adjusted threshold intersects the algal contribution to TSS represents the maximum allowable chlorophyll *a* that will meet the SAV requirements at the application depth (for the given CDOM and background TSS concentrations for that Chesapeake Bay Program segment (Figure V-2).

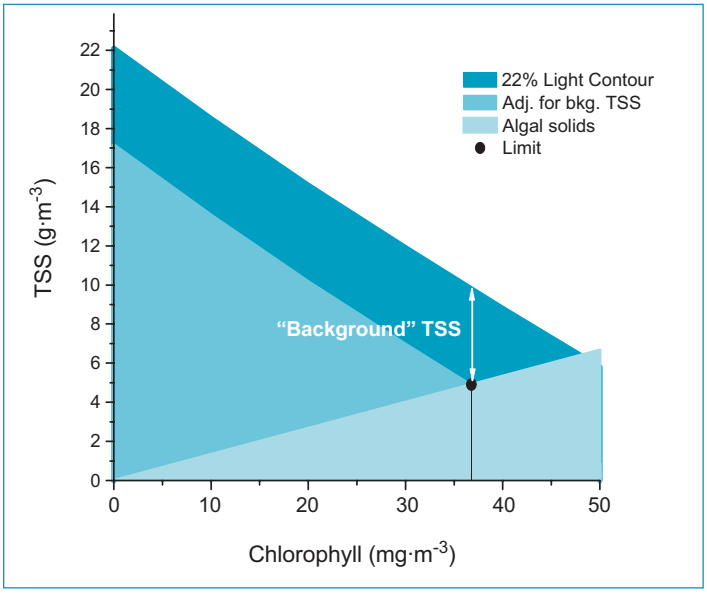


Figure V-2. Determination of maximum allowable CHLA that will meet light requirements of SAV, adjusting for "background" concentration of TSS.

DETERMINING BACKGROUND TSS CONCENTRATIONS

This analysis made several general assumptions: a background TSS concentration could be determined for each Chesapeake Bay Program segment; this concentration would vary from month to month; and the median value of the TSS concentration distribution for each month would represent this concentration after removing outlier concentration values (Sanford, personal communication). Identifying and removing outlier TSS values is important because high-flow or wind events can elevate concentrations above the background range. Based on these assumptions, a SAS program was developed to estimate the monthly background TSS concentration for each monitoring segment using surface TSS concentration data from 1985 through 2004 from the Chesapeake Bay water quality monitoring program.

The monitored TSS concentrations were first converted to non-algal suspended solids (NASS). The formula for this conversion is:

$$NASS = TSS - 0.1333[CHLA] \qquad \text{Equation 7}$$

The 0.1333 coefficient is based on a carbon to chlorophyll ratio of 40 mg C per mg chlorophyll *a* and the Redfield algal composition (Gallegos 2001). The resultant NASS concentration data were grouped by segment, year, and month. Mean NASS concentration was then determined.

Figure V-3 shows an example of the output from this step for Chesapeake Bay Program segment CB2OH. This graph is generally representative of the distribution of monthly NASS levels for the majority of segments. Mean NASS concentrations tended to cluster at lower levels with the means for some years well above these clusters. These outliers, as discussed, most likely represent NASS concentrations during high-flow or wind events. The next step identifies these outliers for each month in the 78 Chesapeake Bay Program segments, removing them before calculating background TSS concentrations.

Mean NASS concentrations for each month and segment were sorted in descending order and the difference between each mean concentration and the mean concentration just above it was determined. The mean difference for each month and segment was then calculated and the individual differences expressed as a percentage of this mean. Since the objective was to identify high-concentration outliers, individual means below the monthly median were not included in the outlier search. From the remaining numbers, if the individual difference was greater than 250 percent of the mean difference, the data point was also identified as an outlier.

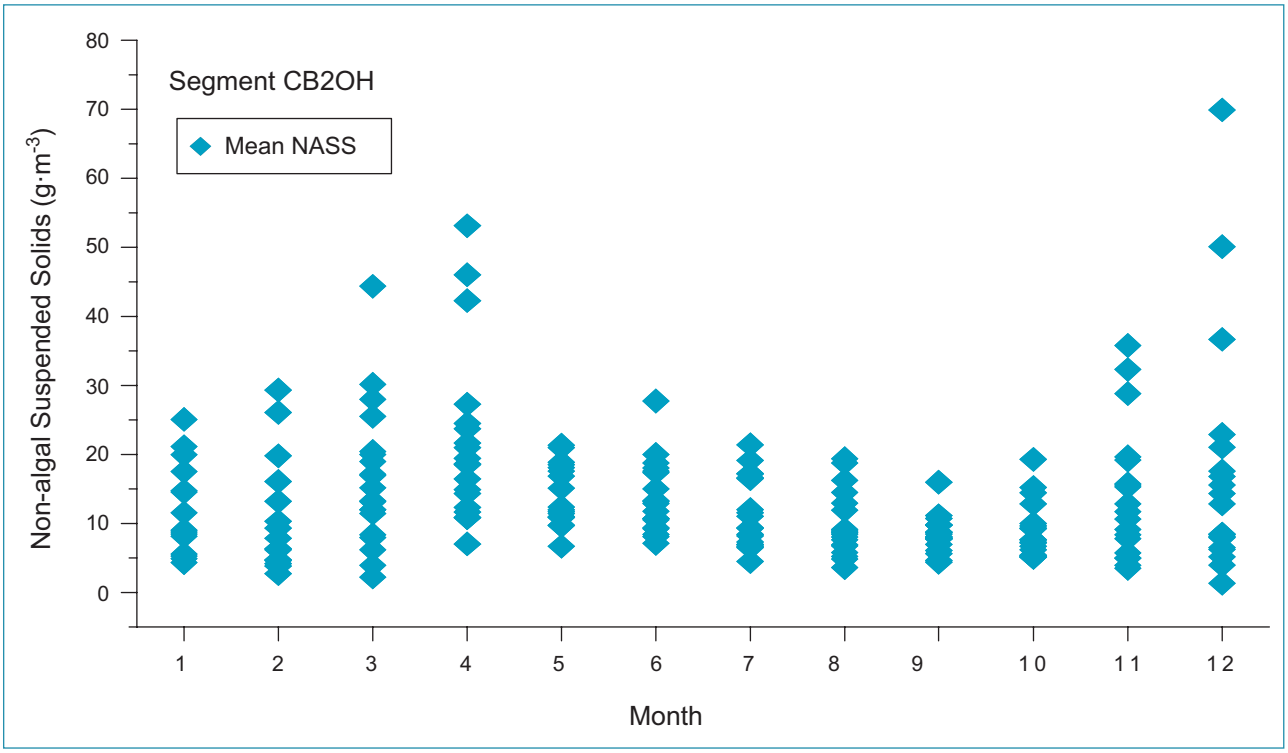


Figure V-3. Segment mean non-algal suspended solids (NASS) levels calculated for each month of each year (1985–2003) for monitoring segment CB2OH. NASS was calculated from TSS as NASS = TSS-0.13*CHLA.

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

The outliers for each month and segment were then grouped with the minimum value tagged as the breakpoint for values outside the typical distribution of monthly means. For each month, the mean NASS concentrations that matched this breakpoint were identified (more than one concentration was possible for each month). The next lowest mean NASS concentration was identified as the upper end of background distribution NASS levels (since more than one concentration for each month is possible, the mean is used). Figure V-4 provides an example of these upper end thresholds for segment CB2OH.

The median of all monthly mean NASS concentrations less than or equal to these upper end values is then selected as the background TSS concentration (Figure V-5). In cases with no outlier concentration values, the median became the background TSS concentration for that segment.

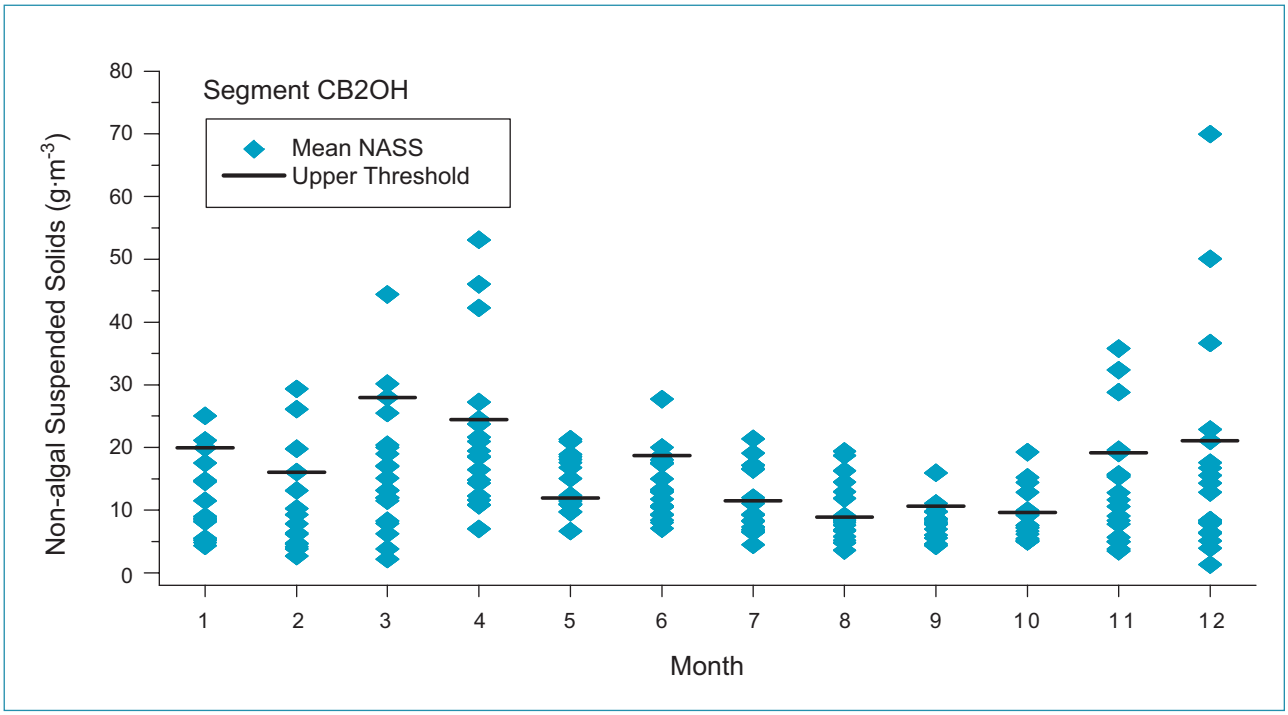


Figure V-4. Segment mean TSS levels calculated for each month of each year (1985–2003) for monitoring segment CB2OH. Black bars represent the upper level of the "background" distribution of means for each month.

Source: Chesapeake Bay Water Quality Monitoring Program (www.chesapeakebay.net/data)

ECOLOGICAL RELATIONSHIP BETWEEN CHLOROPHYLL *a* AND WATER CLARITY IMPAIRMENTS

Phytoplankton are pigment-bearing photoautotrophs; they require light and absorb light. This basic fact drives the ecological connection between chlorophyll *a* and water clarity impairments. The relatively simple exponential decrease of PAR with depth, along with the contribution of phytoplankton chlorophyll to light attenuation,

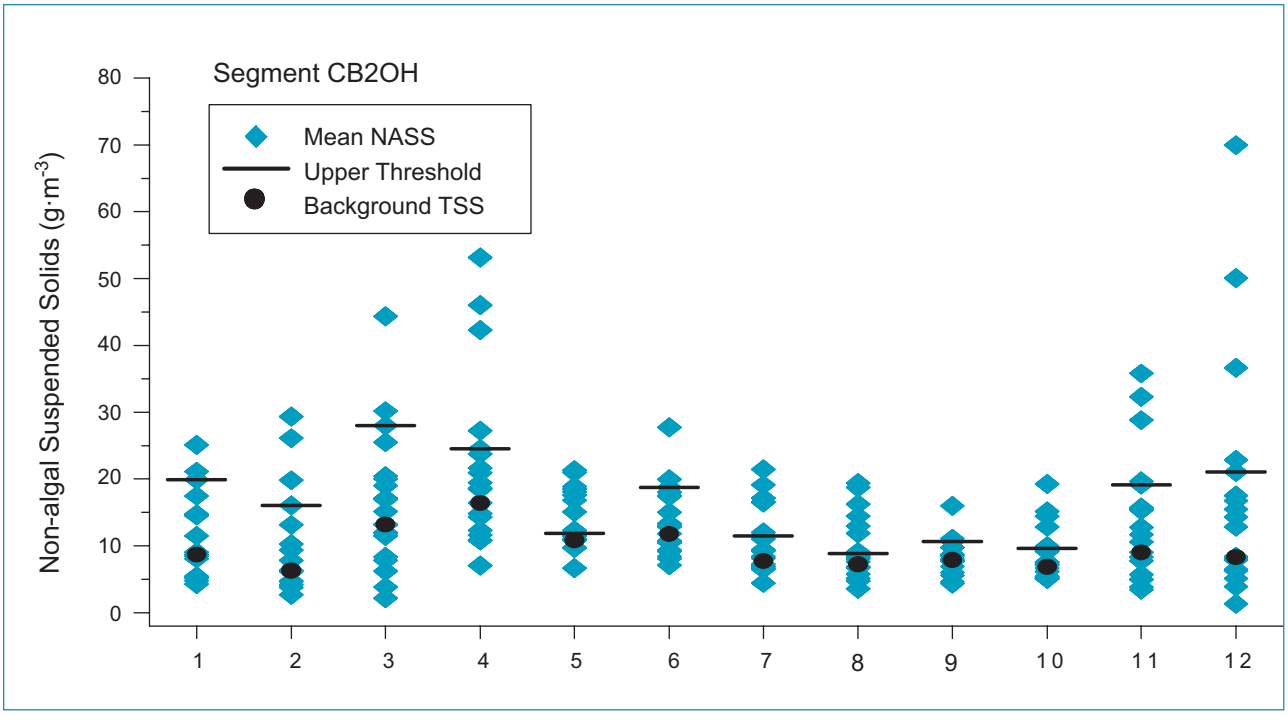


Figure V-5. Segment mean NASS levels calculated for each month and each year for segment CB2OH (blue diamonds), along with upper thresholds for "normal" conditions (horizontal black lines) and "background TSS" calculated as the median of values less than or equal to the threshold.

provided the basis for previous models of environmental controls on phytoplankton production (Talling 1957; Ryther and Yentsch 1957). Wofsy (1983) derived equations for the maximum phytoplankton standing crop that can be supported in a nutrient-saturated mixed layer based on self shading. His treatment explicitly accounted for the attenuation of light by water and other substances (notably suspended sediments). Figure 5a in his publication bears strong resemblance to Figure V-2 here, except that his treatment offers concentration limits for phytoplankton growth rather than SAV.

The direct connection between chlorophyll *a* concentration and water clarity-based impairments was inherent in Carlson's (1977) Trophic State Index. Each increase of ten units for the index represented a doubling in algal biomass. Carlson showed that values calculated from Secchi depth readings were roughly equivalent to those estimated from chlorophyll *a* measurements for temperate lakes. He recognized, however, that Secchi depth measurements in lakes with large amounts of non-algal particulate matter might prove erroneous.

The practice of partitioning the diffuse attenuation coefficient into components due to water, dissolved color, phytoplankton, and other particulates has had both proponents (Lorenzen 1972; Smith 1982, Verduin 1982; Xu et al. 2005) and critics (Morel and Bricaud 1981; Stavn 1988; Kirk 1994; Gallegos 2001). The approach is appealing because it ostensibly permits calculation of each component's relative attenuation (as a percent of the total) (Xu et al. 2005). One problem with using partial

attenuation coefficients, however, is that the linearity of the diffuse attenuation coefficient with water quality concentrations only pertains to small variations in concentration (Kirk 1994). The partial attenuation coefficient of a component estimated from field data will be smaller at higher concentrations of the component. For chlorophyll *a*, this means that the percentage of attenuation attributed to chlorophyll *a* will be underestimated in eutrophic systems, when the partial attenuation of chlorophyll *a* is estimated from a regression of field data on K_d against water quality measurements.

An alternative approach partitions the inherent optical properties—namely absorption and scattering coefficients—into contributions due to water, dissolved color, chlorophyll, and other particulates. Inherent optical properties, unlike K_d, are truly additive and proportional to the concentration of the causal component (Kirk 1994). Radiative transfer modeling provides the link between the inherent optical properties, and apparent optical properties such as K_d (Kirk 1994; Mobley et al. 1993). Gallegos (1994, 2001) used this approach to calculate the threshold concentrations of optically active water quality constituents that would permit SAV growth in the Rhode River, a mesohaline tidal tributary of Chesapeake Bay. Figure V-2 is based on that approach, modified to allow for a background concentration of TSS.

REGIONALIZING THE FACTORS CONTRIBUTING TO WATER COLUMN LIGHT ATTENUATION

Although linearity between K_d and water quality is not assumed when determining the threshold boundaries that determine the water clarity-based chlorophyll *a* threshold concentrations, the boundaries are very nearly linear and can be represented as such for algebraic convenience. Figure V-1 indicates that the threshold boundaries depend on CDOM concentrations and the optical properties of the particulate matter. Hence, the slopes and intercepts of the threshold lines vary regionally, as for "background" TSS concentration, and this variability needs to be incorporated into the procedure for determining water clarity-based chlorophyll *a* concentration thresholds.

The bio-optical modeling approach represents the absorption and scattering spectra as functions of water quality concentrations (Gallegos and Bergstrom 2005). Several coefficients are required to relate light absorption and scattering to water quality concentrations. The absorption at wavelength λ [$a(\lambda)$] can be expressed as the sum due to water, [$a_w(\lambda)$], CDOM, chlorophyll *a*, and TSS (Gallegos and Bergstrom 2005)

$$a(\lambda) = a_w(\lambda) + a_g(440)g(\lambda) + a_\phi^*(675)[CHLA]\phi(\lambda) + a_{p-\phi}^*(440)[TSS]p(\lambda) \qquad \text{Equation 8}$$

in which $g(\lambda)$, $\phi(\lambda)$, and $p(\lambda)$ are spectral shapes of absorption due to CDOM, chlorophyll *a*, and TSS, respectively, $a_g(440)$ is the absorption by CDOM at 440 nm, and $a_f^*(675)$ and $a_{p\text{-}\phi}^*(440)$ are specific-absorption coefficients for chlorophyll and TSS at reference wavelengths 675 and 440 nm, respectively.

Scattering is due to particulate matter, therefore:

$$b_p(\lambda) = b_p^*(555)[TSS]b_n(\lambda) \qquad \text{Equation 9}$$

in which $b_p(\lambda)$ = particulate scattering spectrum, $b_p^*(555)$ is the specific-scattering coefficient at 555 nm, and $b_n(\lambda)$ is the spectral shape of scattering.

In their effect on K_d, variations in the spectral-shape functions are of third-order importance behind variations in water quality concentrations and specific-absorption and specific-scattering coefficients. The literature offers information on spectral shape functions (Gallegos 1994, Magnuson et al. 2004). Absorption by CDOM has been measured in Chesapeake Bay segments for about one-and-a-half years. Magnuson et al. (2004) characterized seasonal variations in $a_\phi^*(675)$ for mainstem Chesapeake Bay. A few studies (Gallegos 2001) have measured specific-absorption and specific-scattering coefficients for TSS, but for most segments estimates for $a_{p\text{-}\phi}^*(440)$ and $b_p^*(555)$ relied on an inverse procedure described by Gallegos and Bergstrom (2005).

WATER CLARITY IMPAIRMENT-BASED CHLOROPHYLL *a* CONCENTRATION THRESHOLDS

Segment-specific chlorophyll *a* concentration thresholds—the maximum allowable concentration protective of SAV minimum light requirements (state-adopted water clarity criteria) assuming achievement of background TSS concentrations—vary widely among the segments. The concentration thresholds range from "no chlorophyll *a* concentration could be determined" (due to high background TSS preventing achievement of the SAV minimum light requirement at the selected application depth) to "greater than 150 µg·liter^{-1}" (Table V-1).

Several reasons exist for some of the inordinately high (e.g., greater than 80 µg·liter^{-1} chlorophyll *a*) concentrations. In several cases, the EPA-published water clarity criteria application depths (U.S. EPA 2003b) seem too low for the given water quality conditions, especially in some mainstem Chesapeake Bay segments (e.g., CB2OH (0.5 m), CB3MH (0.5 m), CB6PH (1 m) and CB8PH (0.5 m)). The low application depths may be appropriate given that the SAV restoration goals for these segments were set based on factors other than water clarity (e.g., historical distributions or limitations by physical factors) (U.S. EPA 2003b). In other segments (ANATF, JMSTF, and CHOTF), the background TSS concentrations appear too low for the salinity zone represented. In another segment (BSHOH), the specific-absorption and specific-scattering coefficients may be too low. Finally, segments designated entirely as SAV no-grow zones (WBEMH, SBEMH, EBEMH, LAFMH, ELIPH, CHOTF, NANTF, and POCTF) were omitted from Table V-1 and from the analyses used to generate Table V-2 (U.S. EPA 2007).

Aggregation of segment-specific results (listed in Table V-2 by the EPA-published water clarity criteria application depths (U.S. EPA 2003b) and the four salinity regimes) provides water clarity-based chlorophyll *a* concentration thresholds that are intuitively more reasonable than those for individual segments. These aggregates should meet SAV minimum light requirements (Table V-2). Summarized in this way, the chlorophyll *a* concentration thresholds range from 2.7 µg·liter^{-1} for mesohaline and polyhaline zones with 2-meter application depths to 43 µg·liter^{-1} for tidal fresh and oligohaline zones with 0.5-meter application depths (Table V-2).

Table V-1. Segment-specific chlorophyll *a* (CHLA) ($\mu g \cdot liter^{-1}$) concentration thresholds determined by inversion of a bio-optical model for the given colored dissolved organic matter (CDOM) ($\mu g \cdot liter^{-1}$) and non-algal suspended solids (NASS) ($\mu g \cdot liter^{-1}$) concentrations. Concentration thresholds were calculated for all three water clarity criteria application depths (0.5, 1, and 2 meters). Bold values represent assigned application depths. The text describes the methods for determining CDOM. Segments designated entirely as SAV no-grow zones were omitted from the analysis based on U.S. EPA 2007.

Chesapeake Bay Program Segment	Water Clarity Criteria Application Depth	Salinity Zone	CDOM	NASS	CHLA-0.5 m	CHLA-1.0 m	CHLA-2.0 m	Notes
ANATF	0.5	TF	0.94	7.87	**85.6**	17.9	U	2
APPTF	0.5	TF	1.50	22.74	**61.5**	U	U	
BACOH	0.5	OH	3.79	16.31	**50.5**	U	U	
BOHOH	0.5	OH	0.78	22.62	**21.7**	U	U	
BSHOH	0.5	OH	0.91	22.56	**81.5**	U	U	3
C&DOH	0.5	OH	0.84	18.70	**78.8**	U	U	
CB2OH	0.5	OH	0.47	7.88	**124.8**	39.5	U	1
CB3MH	0.5	MH	0.39	5.88	**91.6**	27.9	U	1
CB8PH	0.5	PH	0.23	5.80	**141.4**	55.3	13.4	1
CHKOH	0.5	OH	0.79	17.15	**52.9**	U	U	
CHOOH	0.5	OH	1.22	22.08	**20.6**	U	U	
CHSOH	0.5	OH	1.56	42.04	**38.6**	U	U	
CHSTF	0.5	TF	1.36	41.94	**U**	U	U	
ELIPH	0.5	PH	1.17	8.95	**53.9**	U	U	
FSBMH	0.5	MH	4.50	21.05	**17.4**	U	U	
JMSMH	0.5	MH	0.54	12.30	**56.8**	U	U	
JMSOH	0.5	OH	0.73	21.27	**57.5**	U	U	
JMSTF	0.5	TF	1.44	13.94	**89.2**	8.3	U	2
LYNPH	0.5	PH	0.80	7.36	**N/A**	N/A	N/A	
MPNOH	0.5	OH	2.75	27.81	**24.1**	U	U	
MPNTF	0.5	TF	3.12	6.21	**37.6**	U	U	
NANMH	0.5	MH	1.62	30.20	**U**	U	U	
NANOH	0.5	OH	4.85	30.20	**N/A**	N/A	N/A	
NANTF	0.5	TF	1.98	17.94	**35.2**	U	U	
NORTF	0.5	TF	1.06	11.43	**60.5**	U	U	
PAXOH	0.5	OH	0.81	26.45	**9.6**	U	U	
PAXTF	0.5	TF	1.07	18.44	**48.9**	U	U	
PMKOH	0.5	OH	1.55	41.83	**12.5**	U	U	
PMKTF	0.5	TF	1.92	12.01	**42.8**	U	U	
RPPTF	0.5	TF	1.41	19.59	**69.0**	U	U	
WBRTF	0.5	TF	1.10	9.85	**55.2**	U	U	
WICMH	0.5	MH	1.46	21.31	**11.4**	U	U	
POCOH	0.5	OH	6.34	17.22	**68.6**	U	U	
RHDMH	0.5	MH	0.51	8.57	**65.1**	8.4	U	
RPPOH	0.5	OH	0.78	21.15	**14.8**	U	U	
WSTMH	0.5	MH	0.41	10.05	**59.7**	3.0	U	
YRKMH	0.5	MH	0.77	25.28	**10.0**	U	U	
CB6PH	1	PH	0.27	6.68	131.9	**48.8**	8.4	1

Table V-1. (continued)

Chesapeake Bay Program Segment	Water Clarity Criteria Application Depth	Salinity Zone	CDOM	NASS	CHLA-0.5 m	CHLA-1.0 m	CHLA-2.0 m	Notes
CHOMH2	1	MH	0.39	11.74	47.1	**U**	U	
CHSMH	1	MH	1.56	6.71	59.6	**6.4**	U	
CRRMH	1	MH	0.48	4.50	53.2	**10.4**	U	
JMSPH	1	PH	0.37	9.17	89.2	**21.1**	U	
MAGMH	1	MH	0.68	3.89	52.5	**11.2**	U	
MATTF	1	TF	1.22	12.27	91.8	**12.8**	U	
PATMH	1	MH	0.82	7.45	30.5	**U**	U	
PAXMH	1	MH	0.54	8.28	35.1	**U**	U	
POCMH	1	MH	0.55	16.27	82.7	**8.7**	U	
POTMH	1	MH	0.85	6.61	100.4	**29.8**	U	
RPPMH	1	MH	0.49	13.37	77.3	**8.7**	U	
SASOH	1	OH	0.64	12.53	38.1	**U**	U	
SEVMH	1	MH	0.55	4.59	76.9	**22.1**	U	
SOUMH	1	MH	0.50	4.62	66.6	**16.9**	U	
YRKPH	1	PH	0.58	7.08	91.4	**24.9**	U	
BIGMH	2	MH	0.82	14.73	88.9	13.2	**U**	
CB1TF	2	TF	0.63	8.85	73.0	9.7	**U**	
CB4MH	2	MH	0.32	4.02	97.5	34.5	**3.7**	
CB5MH	2	MH	0.32	5.35	99.1	33.0	**0.8**	
CB7PH	2	PH	0.28	7.05	122.3	43.0	**4.4**	
CHOMH1	2	MH	0.55	6.87	107.2	34.2	**U**	
EASMH	2	MH	0.67	4.24	100.2	34.3	**1.8**	
ELKOH	2	OH	0.85	13.56	90.7	10.4	**U**	
GUNOH	2	OH	0.84	14.68	108.8	19.3	**U**	
HNGMH	2	MH	0.60	14.68	N/A	N/A	**N/A**	
LCHMH	2	MH	0.39	7.36	108.5	34.8	**U**	
MANMH	2	MH	2.58	19.34	52.2	U	**U**	
MIDOH	2	OH	0.54	10.07	89.0	16.1	**U**	
MOBPH	2	PH	0.47	8.56	109.4	33.1	**U**	
PIAMH	2	MH	0.46	6.64	97.7	29.7	**U**	
PISTF	2	TF	1.36	11.11	59.5	U	**U**	
POTOH	2	OH	0.64	14.32	73.7	0.1	**U**	
POTTF	2	TF	1.13	13.31	85.5	7.8	**U**	
TANMH	2	MH	0.60	10.27	107.7	30.0	**U**	

TF = tidal fresh (0 – <0.5 ppt)
OH = oligohaline (0.5 – < 5ppt)
MH = mesohaline (5 – 18 ppt)
PH = polyhaline (>18 ppt)
CDOM = soluble absorption at 440 nm
NASS = Non-algal suspended solids or "background TSS" - 0.133*CHLA
U = "Unattainable" (for reasons described in text)
N/A = insufficient data

Notes:
1. Application depth too low or SAV distribution limited by factors other than water clarity.
2. Suspect "background" TSS.
3. Suspect particulate optical properties.

Sources: U.S. EPA 2004, 2005 (Chesapeake Bay Program segments); U.S. EPA 2003b (water clarity criteria application depths)

Table V-2. Surface chlorophyll *a* concentration thresholds determined by inversion of bio-optical model as protective of SAV minimum light requirements, averaged by salinity zone and water clarity criteria application depth. Averages were calculated over all segments with sufficient data (see Table V-1). Segments flagged with concentration thresholds too high due to one of three identifiable reasons (see Table V-1, notes) were excluded from the below salinity/application depth-based averages.

Salinity zone	Water clarity criteria application depth (m)	Number of segments included in average	Chlorophyll *a* concentration threshold ($\mu g \cdot liter^{-1}$)	Standard error ($\mu g \cdot liter^{-1}$)
TF/OH	0.5	20	43	4.6
TF/OH*	1.0	7	10.9	2.3
MH/PH	0.5	7	39.2	9.4
MH/PH	1	10	16.0	2.6
MH/PH	2	4	2.7	0.8

TF = tidal fresh (0 – <0.5 ppt)
OH = oligohaline (0.5 – <5 ppt)
MH = mesohaline (5 – 18 ppt)
PH = polyhaline (>18 ppt)

*Includes six segments with assigned water clarity criteria application depths of 2 meters.

Interestingly, the water clarity-based chlorophyll *a* concentration thresholds for tidal-fresh/oligohaline segments with 0.5-meter application depths falls close to that for mesohaline/polyhaline segments with 0.5-meter application depths despite the different minimum light requirements (Table V-2). Also noteworthy, the water clarity-based chlorophyll *a* concentration thresholds for mesohaline/polyhaline segments with 1-meter application depths fell close to the 15 $\mu g \cdot liter^{-1}$ chlorophyll *a* habitat requirement listed in the first Chesapeake Bay SAV technical synthesis (Table V-2) (Batiuk et al. 1992; Dennison et al. 1993). The water clarity-based chlorophyll *a* concentration thresholds for mesohaline/polyhaline segments with a 2-meter application depth came close to the 1960s average surface chlorophyll *a* concentration for the lower Chesapeake Bay (see Table III-2) (Harding and Perry 1997).

Given the variability in segment-specific chlorophyll *a* concentration thresholds within fixed application depths and salinity zones, this procedure should not presently be used for determining and applying water clarity-based chlorophyll *a* criteria on a segment-specific basis. The variability is due largely to the fluctuation in calculated background TSS concentrations and to the considerable uncertainty in segment-specific CDOM concentrations and particulate optical properties (due to the lack of local CDOM and optical properties data in all tidal waters). At this time, the segment-specific chlorophyll *a* concentration thresholds in Table V-1 should be used only to derive the numerical chlorophyll *a* criteria averaged by salinity zone and water clarity criteria application depth (Table V-2).

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chapter VI

Chlorophyll *a* Concentrations Characteristic of Impairments by Harmful Algal Blooms

Harmful algal blooms (HABs) appear to be increasing in coastal waters around the world due to cultural eutrophication (CENR 2000, HARRNESS 2005). Since the 1910s, there is a growing recognition and appreciation for HAB-producing taxa occurring in Chesapeake Bay (Marshall and Alden 1997, Marshall 1996, Marshall et al. 2005). While diatoms dominate production in the Chesapeake Bay mainstem, dinoflagellate blooms are frequent in higher salinity waters and cyanobacteria blooms are increasingly common in the tidal-fresh and low-salinity habitats of the Chesapeake Bay as well as its tidal tributaries and embayments. Because many (but not all) HABs are frequently associated with high chlorophyll *a* concentrations in the environment, a logical and relevant goal of numerical chlorophyll *a* criteria (applied as a state water quality standard) is prevention of harmful algal bloom outbreaks.

Harmful effects of HABs include dissolved oxygen impairments, shading of submerged aquatic vegetation, adverse ecosystem trophic and biogeochemical effects caused by shifts in community structure, and the release of toxins (HARRNESS 2005). Globally, over 50 countries have reported toxic algal blooms with increased frequency in recent decades (Graham et al. 2006). Long-term Chesapeake Bay phytoplankton monitoring programs have identified over 1,450 phytoplankton species; 43 of these species are toxigenic (Marshall et al. 2005) (Appendix B). Toxigenic taxa include raphidophytes, diatoms, and dinoflagellates in more saline waters along with cyanobacteria in tidal fresh and low-salinity waters. The production of microcystins by a marine picoplankton, *Synechococcus*, is a recent finding (Carmichael and Li 2006) that may extend the range of habitats.

Such toxins and their effects can be found in Chesapeake Bay. Animal mortality and human illness related to cyanobacterial toxin exposure have been well documented in the United States (Yoo et al. 1995). Researchers have noted socioeconomic and living resource effects for dinoflagellate taxa in Chesapeake Bay (e.g., Luckenbach et al. 1993, Lipton 1999, Glibert and Magnien 2004, Tango et. al. 2005). Table VI-1 lists living resource effects and human health risk events documented within the Chesapeake Bay basin and linked with cyanobacteria.

Table VI-1. Timeline of toxic cyanobacteria events in the Chesapeake Bay basin.

Year	Events	Source
1930 to 1931	Tisdale and Veldee describe a regional epidemic of waterborne gastroenteritis in 1930 to 1931, related to "a chemical irritant" in the water and associated with algae blooms, including the Potomac River drainage near Washington, D.C. The authors refer to the musty taste and odors of the river waters, characteristics of cyanobacteria bloom effects on water quality. Tisdale noted heavy blooms were made up of "algae." In Tisdale's second paper (1931b), algae referred to as blue-greens.	Tisdale (1931a, b) and Veldee (1931)
1975	Endotoxic shock of 23 dialysis patients in Washington, D.C. attributed to a cyanobacterial bloom in a drinking water reservoir in the Potomac River basin.	World Health Organization (2003)
2000	In the Sassafras River, four samples from a cyanobacteria bloom dominated by *Microcystis* show high concentrations of the hepatoxin microcystin. Betterton Beach is closed for the rest of the year.	Carmichael (2000)
2001	Waterbird deaths linked with accumulation of microcystins.	Driscoll et al. (2002)
2003	Summer cyanobacteria blooms in the Potomac River and other Bay tributaries show diverse toxic activity with positive results for microcystin, anatoxin-a, and cyano-saxitoxin.	Maryland Department of Natural Resources (2003): www.dnr.state.md.us/bay/hab/index.html; Carmichael (2003)
2004	Beach closures on the tidal Potomac and Sassafras rivers due to toxic cyanobacteria blooms.	Maryland Department of Natural Resources (2004): www.dnr.state.md.us/bay/hab/index.html; Carmichael (2004); Boyer (2004)
2005	Cautions issued for recreation on upper tidal Transquaking and tidal Sassafras rivers when diverse cyanobacteria blooms are encountered. Since 2000, 100 percent of cyanobacteria bloom samples submitted by Maryland Department of Natural Resources from Chesapeake Bay for toxin testing came back positive for microcystins.	Maryland Department of Natural Resources (2005): www.dnr.state.md.us/bay/hab/index.html; Carmichael (2005); Boyer (2005)

The challenges in deriving water quality criteria for chlorophyll *a* based on HABs include:

1) blooms of non-harmful species can also result in high chlorophyll *a* concentrations;

2) chlorophyll *a* does not necessarily correlate with blooms of every HAB species due to various factors including migratory behavior or the mixotrophic life history of some species affecting potential spatial and temporal relationships of the parameters;

3) expression of toxic activity in HABs may not correlate to chlorophyll *a* measures;

4) spatial and temporal aspects of monitoring programs may not capture characteristics of HAB phenomena accurately (e.g., magnitude, duration, frequency, coverage, toxicity, etc.); and

5) natural variability of chlorophyll *a* in the environment.

One or more of these five listed issues has limited attempts to derive HAB-based chlorophyll *a* criteria for much of the Chesapeake Bay's higher salinity waters. However, the record of cyanobacteria blooms in tidal fresh and oligohaline Chesapeake Bay habitats—their impacts, toxicity, and subsequent risk levels related to human health guidance values in the global literature—provided the basis to derive habitat-specific chlorophyll *a* criteria for Chesapeake Bay.

Since chlorophyll *a* is commonly considered one of the most direct (and perhaps best) indices of trophic status in water bodies (Auer et al. 1996), the relationship between toxin levels and chlorophyll *a* provides a sound basis for deriving HAB-based water quality criteria. Microcystin, produced by multiple cyanobacteria species including genera of *Microcystis*, *Anabaena,* and *Oscillatoria*, is one of the most common cyanotoxins found in various freshwater environments, ranging from oligotrophic alpine lakes to tropical reservoirs (Graham et al. 2006). Microcystin has been detected in 100 percent of cyanobacteria bloom samples collected between 2003 and 2005 in Chesapeake Bay tidal-fresh and oligohaline waters (Maryland Department of Natural Resources, unpublished data). No federal guidelines for cyanobacteria or their toxins exist at this time in the United States, but state and local guidelines have been implemented (Burns 2005).

While toxin expression in HABs is notably variable in space and time, Giani et al. (2005) and Kotak and Zurawell (2006) note a possible link between microcystin-LR and nutrients (total nitrogen and phosphorus). They also suggest a strong relationship with toxin-producing cyanobacteria and the trophic status of a water body leading to higher incidence of toxic species and toxin concentrations as the trophic status degrades. In developing these HAB-based chlorophyll *a* criteria, therefore, the data analyses focused on tidal-fresh and low-salinity habitats where human health risks have been most prevalent and the likelihood of success in reducing the impacts of HABs is high.

DERIVING NUMERICAL CHLOROPHYLL CRITERIA

A literature review was used to develop a gradient of management action thresholds that focused on human health risks, but also included living resource impacts and coincident chlorophyll *a* concentrations associated with the condition (Table VI-2). Cyanobacteria toxins, principally the hepatotoxin microcystin, formed the basis of human health thresholds. Conversions were developed between toxin concentration, cell counts related to toxin levels, and chlorophyll *a* as a function of cell counts.

These values were then available for use in:

1) Assessing the chlorophyll *a* levels expected based on literature-derived human health risks associated with cyanobacteria blooms;

Table VI-2. Literature-derived management action levels relative to human health and living resource risk levels and their relationship to cyanobacteria cell counts and chlorophyll *a* concentrations.

Chlorophyll *a* concentrations (µg·liter^{-1})	Cells per milliliter cyano-bacteria	Risk level	Background and Source
0–2.5	<5,000	No effects.	NHMRC 2005 "Green level" for recreational health protection. Based on cell count threshold converted to chlorophyll *a* based on Chorus and Bartram's (1999) proposed relationship—100,000 cells per milliliter give ~50 µg·liter^{-1} of chlorophyll *a* (p. 167). Also by conversion, this level should meet the World Health Organization drinking water standard of 1 µg·liter^{-1} microcystin.
2.5–25	5,000–50,000	Guidance protective of children in recreational setting.	NHMRC (2005) "Amber alert," protects against levels of microcystin >10 µg·liter^{-1}, the level of concern for human health. Computations are based on the lowest observable effects level for microcystin-LR for 100 µg per kg body weight derived from a 44-day study of pigs. Cell number is derived from NHMRC/NRMMC (2004) assumption of 2×10^{-7} µg total microcystins/cell. Pilotto et al. (1997) showed participants exposed to cells densities >5,000 cells per milliliter for >1 hour had significantly higher levels of health symptoms than those unexposed.
10	20,000	Protects against irritative or allergenic effects from cyanobacterial compounds.	World Health Organization guidance published in Chorus and Bartram (1999). Still used by some states (e.g., California).
25	Estimated at equivalent to 50,000	Australia revision to World Health Organization criteria. Red Alert = ≥25 µg·liter^{-1} with cyanobacteria dominance.	Requires the local government authorities and health departments to warn the public that the waters are unsuitable for recreational use (NHMRC 2005).
25		Risk of cyanobacteria dominance >50 percent.	Estimated point from graphic in Downing et al. (2001) in which risk of cyanobacteria dominance relative to chlorophyll *a* in study lakes transitions to >50 percent (n = 99 lakes).
33	10,000	10,000 cells/ml was a level cited as negatively impacting zooplankton populations.	The 33 µg·liter^{-1} chlorophyll *a* derived from Maryland Department of Natural Resources data on *Microcystis* cell concentration versus chlorophyll *a* levels (U.S. EPA 2003).
40	Cyanobacteria dominant (qualitatively)	Germany lakes: promotes microcystin analyses of water samples.	If microcystin >10 µg·liter^{-1}, publish warnings and recommend temporary closures of waters for bathing. Chorus (2005), p. 62.
50	100,000	Moderate health risks expected (e.g., fever, nausea, vomiting, gastroenteritis).	World Health Organization guidance published in Chorus and Bartram (1999). Moderate health alert, but considers a child could be exposed to ten times the Tolerable Daily Intake under this condition. Risk of scum formation (high-risk condition) is high. Potential for long-term illness effects and short-term adverse effects. A management threshold still used in some states (e.g., California).

2) Assigning risk categories based on cell counts to determine whether previously described management action thresholds in the literature made sense with Chesapeake Bay data; and

3) Evaluating Chesapeake Bay cyanobacteria toxins data to gauge if the published risk levels are applicable to Chesapeake Bay were being exceeded and, if so, how frequently and in accordance with what observed ambient chlorophyll *a* concentrations.

Data in the following analyses come from Chesapeake Bay water quality and phytoplankton monitoring programs from 1984 to 2006. The source data sets and related data documentation files can be accessed through the Chesapeake Bay Program's website at www.chesapeakebay.net. The Maryland Department of Natural Resources houses additional data from phytoplankton and toxin surveys.

Summer data (July, August, and September) from tidal-fresh and oligohaline stations (salinity 0–5 ppt) were compiled for the above-pycnocline layer of the water column for the classification and regression tree (CART) analyses. Time series of *Microcystis* concentrations were developed from Maryland Department of Natural Resources annual data; habitat conditions associated with blooms generally occurred when water temperatures were greater than or equal to 15°C.

Specific HAB sampling of the mainstem Chesapeake Bay and tidal tributaries from 2000 to 2006 illustrated the distribution and abundance of cyanobacteria HAB species and their toxins. Cell abundance and level-of-toxin data from these algal bloom investigations were compared with literature recommendations regarding recreational and living resource thresholds of human health and aquatic life concern. These comparisons illustrated the applicability of such thresholds to Chesapeake Bay tidal waters.

Graphical analyses illustrate the behavior of chlorophyll *a* concentration in relation to cyanobacteria and toxin monitoring. Linear regression, correlations, and CART analyses complement the literature-derived thresholds for living resource (>10,000 cells·ml^{-1} *Microcystis*) and human health (50,000 cells·ml^{-1} related to 10 µg·liter^{-1} microcystin as the concentration threshold that protects children exposed to recreational waters) to support and further validate applicable chlorophyll *a* concentration thresholds.

The current world literature does not provide adequate guidance values specific to the cyanobacteria-derived neurotoxins. In sufficiently high doses, cyanotoxins are lethal. In recreational settings, however, there are reports of illness but no confirmed deaths. Detection of the neurotoxin anatoxin-a has been common in Maryland surveys (Carmichael 2000, 2003, 2004, 2005; Boyer 2004, 2005); one detection of saxitoxin in blooms containing microcystins also occurred.

Fitzgeorge et al. (1994) demonstrated that microcystin toxicity is cumulative and gave evidence for disruption of nasal tissues by microcystin-LR. The membrane damage by microcystin enhanced the toxicity of anatoxin-a in this animal study (Fitzgeorge et al. 1994). Considering the relative lack of predictive capability for toxin levels and the dearth of information on cyanotoxin interaction effects, the synergy of multiple toxins could enhance risks associated with aquatic sports recreation and

cyanoblooms (NHMRC 2005). The possibility of synergistic effects (given the multiple toxins detected in Chesapeake Bay waters) stresses the need for supporting, at a minimum, either the criterion recommended below or one that is more conservative.

MICROCYSITIS CELL DENSITIES/CHLOROPHYLL A RELATIONSHIP

The Maryland Department of Natural Resources has a data set independent from the Chesapeake Bay Phytoplankton Monitoring Program that encompasses additional monitoring stations, but also includes the traditional long-term stations with surface-water sampling (Figure VI-1). The data show that *Microcystis* blooms greater than 10,000 cells·ml^{-1} (considered the threshold that impacts the food web) and 50,000 cells·ml^{-1} (a recommended threshold of risk for recreational waters and children) are a nearly annual feature of Maryland's Chesapeake Bay tidal-fresh and low-salinity waters.

Tests for log normality of the tributary data showed six of eight tidal tributaries were significant for log normally distributed chlorophyll *a* measures (Table VI-3).

A significant and increasing linear regression was found in the baywide assessment between log chlorophyll *a* concentrations and log *Microcystis* cell counts using the Chesapeake Bay long-term water quality and phytoplankton monitoring programs' data ($P < 0.001$; Figure VI-2). Subestuary level analyses illustrated significant positive relationships for Maryland waters except for the small data set for the Patapsco River (n = 7). The tidal Virginia Rivers—Rappahannock and York—tended not to demonstrate the relationship except for the tidal James River (Table VI-3).

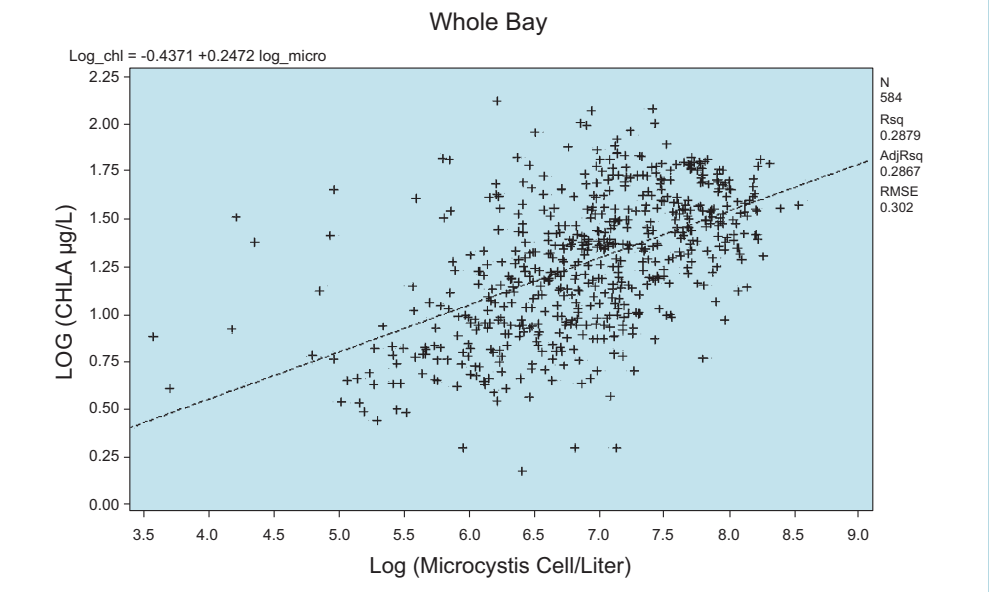


Figure VI-1. Log-log regression of *Microcystis* concentrations against chlorophyll *a* concentrations illustrating the positive relationship found in the water quality and phytoplankton monitoring data for Chesapeake Bay tidal-fresh and oligohaline habitats from 1984 to 2004.

Source: Chesapeake Bay Water Quality and Phytoplankton Monitoring Programs http://www.chesapeakebay.net/data; Maryland Department of Natural Resources, unpublished data.

Table VI-3. Chesapeake Bay mainstem and tidal tributary regressions of log *Microcystis* cells·L^{-1} (X) against log chlorophyll *a* mg·L^{-1} (Y) from 1984 to 2004.

Subestuary	N	Regression	r^2	Pr > F
Upper Bay	102	Y = 0.186X – 0.285	0.20	<0.0001*
Choptank River	95	Y = 0.138X + 0.192	0.24	<0.0001*
Patapsco River	7	Y = 0.211X – 1.133	0.27	0.2353
Patuxent River	107	Y = 0.230X – 0.044	0.19	<0.0001*
Potomac River	148	Y = 0.304X – 0.913	0.54	<0.0001*
James River	85	Y = 0.125X + 0.520	0.09	0.0143*
Rappahannock River	44	Y = 0.072X + 0.731	0.04	0.231
York River	27	Y = 0.080X + 0.362	0.06	0.280

*= significant at P < 0.05.

Source: Chesapeake Bay Water Quality and Phytoplankton Monitoring Programs http://www.chesapeakebay.net/data.

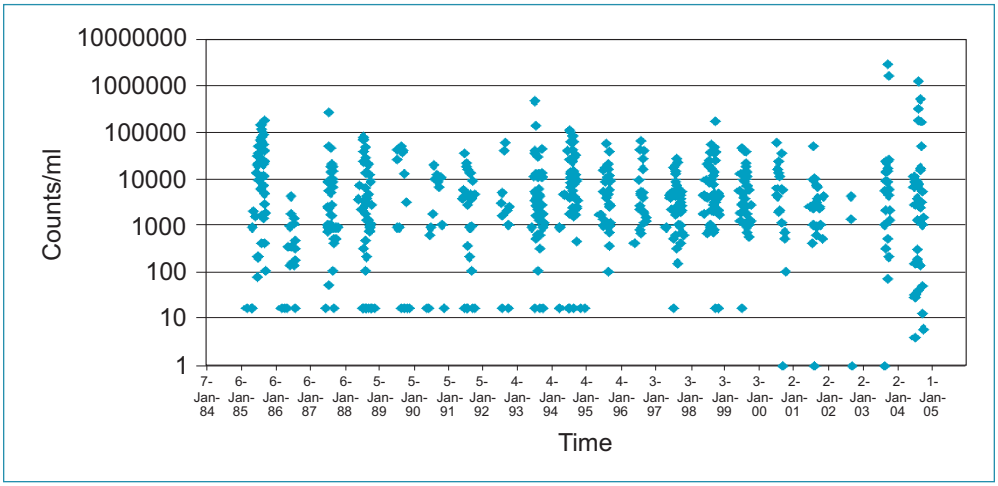


Figure VI-2. Maryland Department of Natural Resources independent *Microcystis* data set with cell densities (cells·ml^{-1}) measured for surface water only from 1984 to 2004.

Source: Maryland Department of Natural Resources Phytoplankton Monitoring Program, unpublished data.

LITERATURE-BASED TOXIN LEVELS, CELL COUNTS AND CHLOROPHYLL CONVERSIONS

Originally, water quality management guidance values for chlorophyll *a* in the presence of cyanobacteria were published during the late 1990s through the World Health Organization. The World Health Organization then provided two thresholds of interest for risks associated with cyanotoxins:

- 10 µg·liter^{-1} chlorophyll *a* and 20,000 cells·ml^{-1} cyanobacteria protects against irritative or allergenic effects from cyanobacterial compounds; and

- 50 µg·liter^{-1} chlorophyll *a* and 100,000 cells·ml^{-1} cyanobacteria**,** resulting in moderate health risks.

In the most recent reassessment of world literature (NHMRC 2005), Australian authorities suggested guideline values for cyanobacterial exposure in recreational waters based on the Lowest Observable Effects Level (LOAEL) for microcystin-LR of 100 µg·kg^{-1} body weight per day derived from a 44-day study in pigs. These values are 10 µg·liter^{-1} total microcystins for children and 44 µg·liter^{-1} total microcystins for adults (NHMRC 2005).

To derive a cell count that is equivalent to this toxin hazard, a toxin cell quota of 2×10^{-7} µg total microcystins per cell is assumed (NHMRC/NRMMC 2004). Tolerable concentration limits for child and adult during recreational activities, therefore, are suggested by the following conversions. A LOAEL of 10 µg·liter^{-1} of toxin for children converts to 50,000 cells·ml^{-1} *Microcystis* based on:

10 µg toxin·liter^{-1} * 0.001 (Liter·ml^{-1})/ 2×10^{-7} mg microcystins per cell Equation 10

Protection at this level would likewise safeguard adults in a recreational setting.

Chorus and Bartram (1999, p. 167) defined a conversion between cell concentration and chlorophyll *a* when cyanobacteria are in abundance. A density of 100,000 cells·ml^{-1} is equivalent to ~50 µg·liter^{-1} chlorophyll *a* if cyanobacteria dominate or 2,000 cells·ml^{-1} ~1 µg·liter^{-1} chlorophyll *a*. Therefore, 50,000 cells·ml^{-1} is estimated at 25 µg·liter^{-1} chlorophyll *a*—a concentration comparable to the above-cited recreational risk threshold protective of children at 10 µg·liter^{-1} total microcystins.

The Australian revision to the World Health Organization criteria (NHMRC 2005) uses three levels and is more protective than the original two-tiered World Health Organization approach:

Green Level: No effects level at less than 5,000 cells·ml^{-1} or less than 2.5 µg·liter^{-1} chlorophyll *a* based on a cell:chlorophyll *a* translation.

Amber Alert: Increased monitoring intensity to assess risk at a chlorophyll *a* concentration range of 2.5–25 µg·liter^{-1}.

Red Alert: Requires local government authorities and health departments to warn the public that the waters are unsuitable for recreational use at chlorophyll *a* concentrations greater than or equal to 25 µg·liter^{-1} with cyanobacteria dominance.

Based on the extensive literature review, Table VI-2 summarizes a gradient of risk thresholds for chlorophyll *a* concentrations associated with the presence of cyanobacteria blooms. The chlorophyll *a* concentrations in Table VI-2 were based on the toxin concentration to cell count conversion as well as the cell count to chlorophyll *a* conversion described and cited above.

CHESAPEAKE BAY *MICROCYSTIS* TOXINS COMPARISON WITH THRESHOLDS

In September 2000, a cyanobacteria bloom dominated by *Microcystis aeruginosa* was identified on the tidal Sassafras River with four samples collected and analyzed

for microcystin toxin. Analyses showed levels approaching acute toxicity for consumption (Carmichael 2000).

Toxins data collected during cyanobacteria bloom investigations in tidal waters of Chesapeake Bay from 2002 to 2006 show significant exceedances of suggested human health risk thresholds for microcystins (Tango and Butler 2007). Among samples tested (n=70), 71% and 31% of results exceeded WHO drinking water guidance (1 µg·liter^{-1} in Chorus and Bartram 1999) and NHMRC (2005) recreational safety thresholds for children (10 µg·liter^{-1}) respectively (Figure VI-3). All areas where cyanobacteria blooms have been identified have demonstrated microcystin toxin production in excess of 10 µg·liter^{-1} (Tango and Butler 2007) and such events were documented each year.

Coincident activity of additional cyanotoxins—neurotoxins anatoxin-a and PSP-toxin—were also noted. Fitzgeorge et al. (1994) noted synergistic interactions between microcystin and anatoxin-a exposures in mice that could lower the guidance thresholds for the two toxins when found together in the environment. Extensive work with toxin interactions is in its infancy and no firm guidance taking account of the simultaneous presence of multiple toxins is available at this time.

Microcystin toxin relationship to chlorophyll *a*

Falconer et al. (1999) indicate a cyanobacterial density of 100,000 cells·ml^{-1} is expected to be equivalent to 50 µg·liter^{-1} chlorophyll *a*. Coincidently these conditions are expected to have at least 20 µg·liter^{-1} microcystin. This relationship gives us an expected ratio of 1 µg·liter^{-1} microcystin: 2.5 µg·liter^{-1} chlorophyll *a*: 5,000 cells·ml^{-1} cyanobacteria.

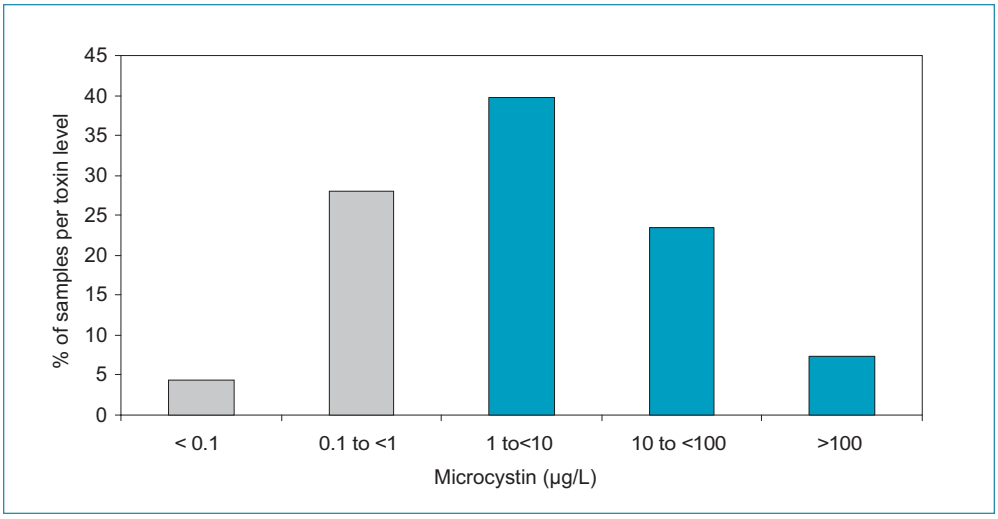


Figure VI-3. Frequency distribution of microcystin results from bloom sample investigations in Maryland (n=70, 2003–2006). 71% of results exceed 1 μg·liter^{-1} while 31% of results exceed 10 μg·liter^{-1}.

Source: Adapted from Tango and Butler 2007.

For Chesapeake Bay monitoring data, *Microcystis aeruginosa* concentrations showed a significant increasing relationship with chlorophyll *a* concentration on Bay-wide scale as well as for tributary specific relationships. Chlorophyll *a* concentrations represent one indicator level to the potential for cyanotoxin blooms. Species taxonomy and abundance, however, will be required to understand if there is a heightened risk situation that may involve elevated levels of toxins.

Microcystin concentrations have been shown to increase with increasing levels of *Microcystis aeruginosa* (Figure VI-4, adapted from Tango and Butler 2007). With species identification and abundance data available, an initial risk level can be provided. Chlorophyll *a* concentrations, species identification and cell counts alone cannot define the impairment. Toxin results will be needed to confirm any exceedance of human health risk thresholds since there are 2–3 orders of magnitude of variation in toxin concentration surrounding the regression relationship.

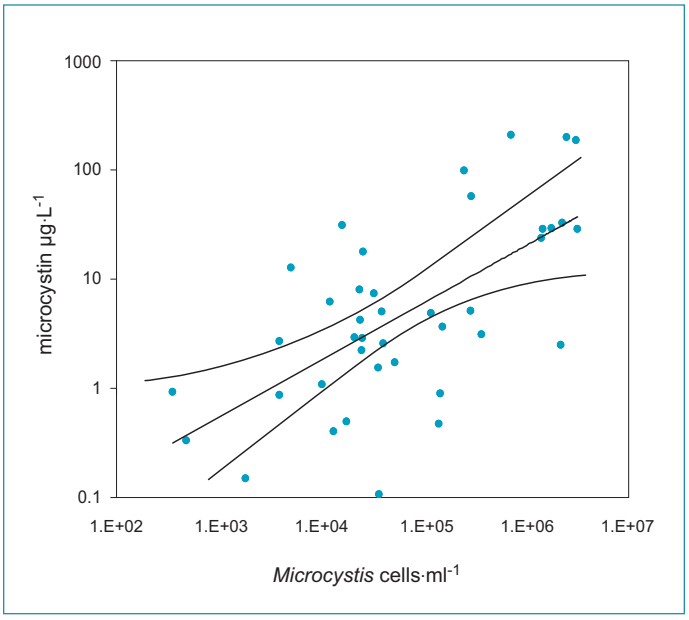


Figure VI-4. Microcystin toxin relationship with *Microcystis aeruginosa* concentrations for Chesapeake Bay monitoring data.

Source: Adapted from Tango and Butler 2007.

CART ANALYSES ASSESSMENT OF RISK LEVELS

Recently, classification and regression tree (CART) has proven useful in environmental data analysis (Verbyla 1987). The water quality parameters for this analysis included salinity, Secchi depth, orthophosphate, dissolved inorganic nitrogen (i.e., NH_4, NO_2, and NO_3), chlorophyll *a*, pheophytin, dissolved organic carbon, particulate carbon, and water temperature as they relate to human- and ecosystem-health risk categories developed for zooplankton effects and *Microcystis* concentrations. Buchanan et al. (2005) offers additional details on the protocol for compilation of data.

In CART analysis, values of a dependent parameter are being predicted from one or more independent predictor parameters. One of CART's strengths is that it is a non-parametric technique. There are no underlying assumptions about the distributions of either the dependent or independent variables are normal or even known. This

technique also does not require a linear relationship between dependent and independent variables.

Exploratory CART analyses were conducted to determine those chlorophyll *a* concentration thresholds that would prevent toxic *Microcystis* bloom events. The CART analysis for this application used the tree algorithms in the Insightful SPLUS 7.0.6 software (SPLUS 2005). *Microcystis* abundance was the response variable, with three categories of risk based on cell count. Individual CART analyses were run for each of the major tidal tributaries and the upper Chesapeake Bay as well as for all data combined.

Most results show that average above-pycnocline chlorophyll *a* or surface chlorophyll *a* concentrations were the most significant factors related to *Microcystis* risk (seven of eight analyses). In the one exception—the above-pycnocline Choptank River analysis—chlorophyll *a* concentration was the second-most significant factor after dissolved inorganic nitrogen concentration. The average chlorophyll *a* concentration thresholds separating high-risk water quality condition from middle- and low-risk water quality conditions for the surface and above-pycnocline water samplings were 28.96 and 29.17 $\mu g \cdot liter^{-1}$, respectively.

HAB IMPAIRMENT BASED CHLOROPHYLL *a* CRITERIA

The analyses presented here illustrate the positive relationship between cyanobacteria levels (which have inherent human health risks seen in Chesapeake Bay tidal-fresh and oligohaline waters based on cyanobacteria toxin surveys), cyanotoxin levels and measured chlorophyll *a* concentrations. The management action threshold gradient illustrated in Table VI-2 shows 25 $\mu g \cdot liter^{-1}$ chlorophyll *a* as the first level that generates water closures protective of human health. The World Health Organization previously considered 50 $\mu g \cdot liter^{-1}$ a level for moderate health effects; however, concentrations at which scum formation and significant human health risks are possible (particularly for children) have been documented at lower chlorophyll *a* concentrations. CART analyses of Chesapeake Bay data that provide an average of subestuary surface water chlorophyll *a* values separating high human health risk ($\geq$25 $\mu g \cdot liter^{-1}$ chlorophyll *a*) from lower risk levels was nearly the same (28.96 and 29.17 $\mu g \cdot liter^{-1}$ chlorophyll *a* for surface and above pycnocline water's respectively).

As the CART assessment thresholds analysis derived a slightly higher threshold chlorophyll *a* concentration after factoring in data and conditions specific to the Chesapeake ecosystem, the most recent child-protective toxin threshold converted to chlorophyll *a* (25 $\mu g \cdot liter^{-1}$) and the CART-derived threshold (29 $\mu g \cdot liter^{-1}$) were averaged to reach a criterion threshold value of 27.5 $\mu g \cdot liter^{-1}$ chlorophyll *a*. This value is characteristic of the expected cell counts and toxin concentrations for toxigenic cyanobacteria protective against human health impairments, as demonstrated in the above analyses, respecting the variability in those related measures. Tidal tributaries throughout the northern Chesapeake Bay (e.g., Transquaking, Chester, Sassafras, Elk, Bush, Middle, Magothy, and Potomac rivers), the open waters of the northern Chesapeake Bay, and the upper tidal James River (Virginia Department of Environmental Quality 2005) have demonstrated the capacity to support blooms,

making the criteria broadly applicable to tidal fresh and oligohaline waters. Regression analyses showed local variation in relationships with chlorophyll *a* and *Microcystis* suggesting local tailoring of trigger values for analyses could be implemented. Protecting against criteria exceedances also safeguards against associated risks of harmful cyanobacteria blooms and their potential impacts.

Chlorophyll *a* concentration data across the Chesapeake Bay and its tidal tributaries and embayments demonstrate log normally distributed behavior. To attain the HAB-based chlorophyll *a* criterion, there should be a limited number, e.g. less than 10 percent, of ambient concentrations observed above 27.5μg·liter^{-1} with rare observations of large values that would be indicative of high human and living resource health risk. Measures of central tendency for log normally distributed populations of chlorophyll *a* exceeding the criterion concentration by less than 10 percent are similar to historical chlorophyll *a* concentrations (i.e., 1960s) documented in Table III-2 for low-salinity habitats.

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chapter VII

Chesapeake Bay Chlorophyll *a* Criteria and Reference Concentrations

These Chesapeake Bay numerical chlorophyll *a* criteria and reference concentrations were derived to address specific water quality, human, and aquatic life impairments when applied in specific seasons and to specific salinity-based tidal habitats (Tables VII-1 and VII-2). These criteria and reference concentrations protect the open-water fish and shellfish designated use to "support the survival, growth and propagation of balanced, indigenous population of ecologically, recreationally and commercially important fish and shellfish species inhabiting open-water habitats" (U.S. EPA 2003b).

At a minimum, the EPA strongly encourages the states to adopt the harmful algal bloom-based numerical chlorophyll *a* criteria for tidal fresh and oligohaline tidal waters where algal-related impairments are expected to persist even after attainment of the Chesapeake Bay dissolved oxygen and water clarity criteria. The states may adopt the published Chesapeake Bay chlorophyll *a* reference concentrations as a numeric criteria for the applicable salinity regimes and seasons. In addition, the states can use the scientific findings and data published here to derive tidal river, embayment, and/or segment-specific numeric chlorophyll *a* criteria to account more precisely for localized impairments and conditions.

HARMFUL ALGAL BLOOM IMPAIRMENT-BASED CHLOROPHYLL *a* CRITERION

The numeric chlorophyll *a* criterion that protects against human and aquatic life impairments from harmful algal blooms should only be applied to tidal-fresh and oligohaline reaches of the Chesapeake Bay and its tidal tributaries and embayments (Table VII-1). This criterion applies only to surface waters during the summer season (June 1 through September 30). See Chapter VIII for the detailed criteria assessment procedures. As documented previously, the scientific basis for establishing Chesapeake Bay numerical chlorophyll *a* criteria that address impairments for higher salinity harmful algal bloom species and communities remains insufficient at this time.

Table VII-1. Chesapeake Bay harmful algal bloom impairment-based chlorophyll *a* criterion.

Salinity Regime[1]	Season[2]	Chlorophyll *a* Criterion Concentration[3] (µg·liter^{-1})
Tidal Fresh-Oligohaline	Summer	27.5

[1]Tidal fresh = 0 - <0.5 ppt salinity; oligohaline = 0.5 - <5 ppt salinity.
[2]Summer = June 1–September 30.
[3]The 27.5 µg·liter^{-1} concentration is applied as a 90th percentile for log normal distribution of data coincident with a mean chlorophyll *a* concentration of 14.7 µg·L for minimizing the risk of *Microcystis* concentrations >50,000 cells·ml^{-1} and microcystin concentrations exceeding 10 µg·liter^{-1}.

HISTORICAL CHLOROPHYLL *a* REFERENCE CONCENTRATIONS

The historic chlorophyll *a* reference concentrations based on 1960s Chesapeake Bay mainstem concentrations under medium-flow conditions should only be used for the applicable salinity regime within mainstem Bay tidal waters (Table VII-2). These reference concentrations specifically address the States' existing water quality standards' narrative requirements that: "concentrations of chlorophyll *a* in free-floating microscopic aquatic plants (algae) shall not exceed levels that result in ecologically undesirable consequences." These reference concentrations should only be applied to mainstem Chesapeake Bay surface, open-water habitats only during the spring (March 1 through May 31) and summer (July 1 through September 30) seasons, the most critical seasons for addressing algal-related impairments.

DISSOLVED OXYGEN IMPAIRMENT-BASED REFERENCE CONCENTRATIONS

A set of chlorophyll *a* reference concentrations were determined to characterize water column conditions having suitable open-water, summer averaged bottom-water dissolved oxygen conditions. These annual averaged chlorophyll *a* reference concentrations—10–15 µg·liter^{-1} over deeper waters which routinely stratify and 30 µg·liter^{-1} in the surface layer of shallow waters—complement and support the HAB-based chlorophyll *a* criteria and the chlorophyll *a* reference concentrations that address other water quality, human, and aquatic life impairments (Table VII-2). Evidence from the multi-decadal record of Chesapeake Bay water quality monitoring supports the conclusion that meeting these chlorophyll *a* reference concentrations will contribute to the achievement of desired dissolved oxygen concentrations. However, these low dissolved oxygen impairment-based chlorophyll *a* reference concentrations should not be adopted and applied as water quality criteria to protect against the adverse impacts of low dissolved oxygen. As described previously, many other factors must be considered in quantifying the relationship between excess phytoplankton biomass and the onset and continuance of low dissolved oxygen conditions. In the Chesapeake Bay's current eutrophic state ("supersaturated" with phytoplankton biomass), relationships between the accumulation of chlorophyll *a* and oxygen depletion are not likely to yield useful numeric chlorophyll *a* criteria.

Table VII-2. Chesapeake Bay chlorophyll *a* reference concentrations.[1]

Salinity Regime[2]/ Water Column Location	Season[3]	Water Clarity Criteria Application Depth[4] (m)	Chlorophyll *a* Reference Concentration (µg·liter^{-1})
Historical Chlorophyll *a* Reference Concentrations[5]			
Oligohaline	Spring	–[6]	18
Mesohaline	Spring	–	8
Polyhaline	Spring	–	4
Oligohaline	Summer	–	46
Mesohaline	Summer	–	23
Polyhaline	Summer	–	5
Dissolved Oxygen Impairment-Based Chlorophyll *a* Reference Concentrations			
Deeper Waters Which Stratify	Annual	–	10–15
Shallow Waters	Annual	–	30
Water Clarity Impairment-Based Chlorophyll *a* Reference Concentrations			
Tidal Fresh/Oligohaline	SAV	0.5	43
Tidal Fresh/Oligohaline	SAV	1.0	11
Mesohaline/Polyhaline	SAV	0.5	39
Mesohaline/Polyhaline	SAV	1	16
Mesohaline/Polyhaline	SAV	2	3

[1]All chlorophyll *a* reference concentrations apply as µg·liter^{-1} across the surface waters of open-water designated-use segments for the applicable salinity regime and season.

[2]Tidal Fresh = 0 – <0.5 ppt salinity; oligohaline = 0.5– <5 ppt salinity; mesohaline = 5–18 ppt salinity; polyhaline = >18 ppt salinity.

[3]Spring = March 1–May 31; Summer = June 1–September 30; SAV or SAV growing season: for tidal-fresh, oligohaline, and mesohaline habitats = April 1–October 31; for polyhaline habitats = March 1–November 30 (U.S. EPA 2003a).

[4]Water clarity criteria application depth for each Chesapeake Bay Program segment as published in U.S. EPA 2003b and as adopted into Delaware, Maryland, Virginia and the District of Columbia's water quality standards regulations.

[5]Reference concentrations only apply to mainstem Chesapeake Bay segments.

[6]Not applicable.

WATER CLARITY IMPAIRMENT-BASED CHLOROPHYLL *a* REFERENCE CONCENTRATIONS

The water clarity impairment-based chlorophyll *a* reference concentrations should be applied as threshold concentrations to surface waters across open-water designated-use habitats by the applicable salinity regime. These reference concentrations

are for the applicable water clarity criteria application depth over the applicable SAV growing season in those Chesapeake Bay Program segments with the shallow-water bay grass designated use (Table VII-2). Given the degree of variability in segment-specific chlorophyll *a* reference concentrations within specific application depths and salinity zones (see Table V-1), the procedure described previously should not be used to determine and apply numeric water clarity-based chlorophyll *a* criteria on a Chesapeake Bay Program segment-specific basis but only on a salinity regime basis.

These chlorophyll *a* reference concentrations complement and support (but do not replace) the EPA published water clarity criteria and SAV restoration acreage criteria already adopted by Delaware, Maryland, Virginia, and the District of Columbia into their respective water quality standards regulations (U.S. EPA 2003a, 2003b). These reference concentrations quantify the chlorophyll *a* water column concentrations required to allow sufficient penetration of surface light to attain the applicable water clarity criteria at the established application depth given achievement of background concentrations of total suspended solids (TSS). The *a priori* assumption of background TSS concentration achievement is critical. At ambient TSS concentrations higher than the segment-specific background TSS concentration, chlorophyll *a* concentrations lower than the salinity-regime/application-depth reference concentrations in Table VII-2 are required to meet the applicable water clarity criteria.

OTHER CHLOROPHYLL *a* CONCENTRATION THRESHOLDS, CRITERIA, AND STANDARDS

In their comprehensive synthesis of the global scientific literature entitled *A Literature Review for Use in Nutrient Criteria Development for Freshwater Streams and Rivers in Virginia*, Walker et al. (2006) provided a concise summary of chlorophyll *a* concentrations as thresholds, criteria, and standards in freshwater, estuarine, and marine ecosystems around the world. Dodds et al. (1998) recommended a series of concentration ranges using benthic chlorophyll *a*, sestonic chlorophyll *a*, total nitrogen, and total phosphorus for the trophic classification of streams based on cumulative frequency distributions. The oligotrophic-mesotrophic boundary rested at 10 $mg \cdot liter^{-1}$ chlorophyll *a* with the mesotrophic-eutrophic boundary at 30 $mg \cdot liter^{-1}$ chlorophyll *a*.

As reported by Walker et al (2006), Reckhow et al. (2005) used structural equation modeling to identify the relationships between nutrient-related parameters and the predictive use attainment for four water bodies in the United States: Neuse River estuary, San Francisco Bay, Lake Washington, and Lake Mendota. The authors found that the existing North Carolina chlorophyll *a* water quality standard for the Neuse River estuary had a 60 percent probability of attaining the designated uses supported by a 5 $mg \cdot liter^{-1}$ dissolved oxygen standard. The authors reported that their model predicted that chlorophyll *a* concentrations under 10 $mg \cdot liter^{-1}$ were necessary to achieve dissolved oxygen concentrations of at least 5 $mg \cdot liter^{-1}$.

In the April 2003 publication *Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and Its Tidal Tributaries*, U.S. EPA (2003a) documented the results of worldwide literature on aquatic system trophic status as characterized by mean chlorophyll *a* concentrations (see Table V-6

on page 112 in U.S. EPA 2003a). In freshwater aquatic systems, oligotrophic waters were characterized by chlorophyll *a* concentrations ranging from 0.3 to 4 mg liter^{-1}, mesotrophic systems a range of 2 to 15 mg·liter^{-1}, and eutrophic systems a range of greater than 10 to 31 mg·liter^{-1} (Novotny and Olem 1994; Ryding and Rast 1989; Smith 1998; Wetzel 2001). In marine ecosystems, oligotrophic systems were characterized by chlorophyll *a* concentrations less than 2 mg·liter^{-1}, mesotrophic systems a range of 1 to 7 mg·liter^{-1}, and eutrophic systems a range of 3 to greater than 7 mg·liter^{-1} (Smith et al. 1999; Novotny and Olem 1994). U.S. EPA (2003a) provided detailed narrative descriptions of the trophic status, water quality, phytoplankton community, and ecological function along a trophic continuum, defining oligotrophic, mesotrophic, eutrophic, and highly eutrophic status as these terms apply to the Chesapeake Bay ecosystem, both past and present (see Table V-2 on page 106 in U.S. EPA 2003a).

In their paper on Chesapeake Bay phytoplankton reference communities and development of an index of biotic integrity, Buchanan et al. (2005) quantified the habitat conditions supporting these communities. They reported maximum spring and summer chlorophyll *a* concentrations (in μg·liter^{-1}), respectively, for tidal fresh (13.5, 15.9), oligohaline (24.6, 24.4), mesohaline (23.8, 13.5), and polyhaline (6.4, 9.2).

In its report to the Virginia Department of Environmental Quality, the Academic Advisory Committee (2005a) recommend April to October median chlorophyll *a* concentrations of 4 µg·liter^{-1} for cold-water habitats designated for trout, 10 µg·liter^{-1} for other cold-water habitats, and 25 µg·liter^{-1} for warm-water aquatic habitats to "accommodate fishery recreation and protect aquatic life." In an addendum to their original report, the Academic Advisory Committee (2005b) recommended chlorophyll *a* criteria derivation using a regression approach and application of 90th percentile chlorophyll *a* concentrations to protect fishery recreation and aquatic life. The recommended April to October, 90th percentile chlorophyll *a* concentrations were: 8 µg·liter^{-1} for cold-water habitats designated for trout, 20 µg·liter^{-1} for other cold-water habitats, and 50 µg·liter^{-1} for warm-water aquatic habitats. The authors recommended "the regression approach uses the mathematical relationship between chl-a median (chl-$a_{\ med}$) and the 90th percentile (chl-$a_{\ 90}$) to translate candidate criteria expressed as medians to a 90th percentile basis" (Academic Advisory Committee 2005b).

Although the EPA has not published national chlorophyll *a* water quality criteria, efforts are underway to derive and publish eco-region-based chlorophyll *a* criteria. At least eight states across the country, along with Virginia and the District of Columbia, have adopted numerical chlorophyll *a* criteria into their water quality standards regulations (U.S. EPA 2003c; Walker et al. 2006). Although the exact concentrations range widely given the variable needs in protecting Hawaii's coastal oceans to Alabama's reservoirs, most of these state's chlorophyll *a* water quality standards, stated as seasonal averages, tend to fall within 15 to 27 µg·liter^{-1} (Appendix C), closely matching the concentration range of the Chesapeake Bay chlorophyll *a* criteria and reference concentrations (Tables VII-1 and VII-2). Many of these states' adopted chlorophyll *a* criteria are water body- and/or habitat-specific water quality standards or are used as part of an overall trophic index.

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chapter viii

Chesapeake Bay Chlorophyll *a* Criteria Recommended Attainment Assessment Procedures

There are two sets of procedures recommended for assessing attainment of the numeric chlorophyll *a* criteria. The first set of procedures, described below, are for assessing the harmful algal bloom impairment-based chlorophyll *a* criterion published within this document. The second set of procedures, also described below and originally published in the July 2007 addendum to the original 2003 Chesapeake Bay water quality criteria document (see pages 61-62 in U.S. EPA 2007), apply to the state adopted numerical chlorophyll *a* concentration-based criteria.

HARMFUL ALGAL BLOOM IMPAIRMENT-BASED CHLOROPHYLL *a* CRITERIA ASSESSMENT PROCEDURES

A structured tiered sample collection, analysis and assessment procedure is recommended for determining exceedance of the harmful-algal bloom based chlorophyll *a* criterion. Note that while the criterion has its foundation in human health risk-related science, the sampling and assessment program is not specifically intended for use as a short-term recreational health risk evaluation procedure. This criterion and assessment procedure considers a seasonal time scale and focuses on Chesapeake Bay Program segment assessments. Risk evaluation and management may be triggered by information gleaned in these assessments but require other time (daily to within weekly) and space (beach focus or other significant recreational unit) assessments without regard for the segment boundaries.

SAMPLING REGIME

The previously described chlorophyll *a* concentration threshold of 27.5 $\mu g \cdot liter^{-1}$ is used as the generalized trigger value for initiating sampling and enumeration of cyanobacteria species composition-related samples. The value was based on a significant regression relationship using a composite of tidal tributary and mainstem Chesapeake Bay data. Tributary-specific chlorophyll *a*-*Microcystis* relationships,

such as those expressed in Chapter VI, could, however, be used to justify an adjustment of the 27.5 µg·liter^{-1} sampling trigger threshold concentration. Significant area-specific regressions relating chlorophyll *a* measures to 50,000 cells·ml^{-1} *Microcystis* should be thoroughly documented to support such a decision. Alternatively, the presence of visible surficial algal scum can also be used as sampling trigger to evaluate for toxin without chlorophyll *a* data. For water quality conditions represented by chlorophyll *a* concentrations below 27.5 µg·liter^{-1}, sampling for cyanobacteria determination would not be required.

Water quality monitoring in Chesapeake Bay segments presently involves multiple approaches for chlorophyll *a* assessments: vertical fluorescence profiles, horizontal fluorescence, dataflow mapping and calibration sites, in-situ continuous monitoring, and emergency rapid response sampling due to anomalous water quality conditions, fish or human health related events. Triggered by the above 27.5 µg·liter^{-1} chlorophyll *a* concentration threshold, an extra water sample would be collected at 5-6 sites separated by 1-2 miles within the appropriate season, defined by temperatures greater than 15 ^{o}C and a segment characterized by less than 5 ppt salinity. The population of *Microcystis* should be enumerated in each of these extra samples. If *Microcystis* bloom conditions ($\geq$ 50,000 cells per milliliter) are observed in any single sample, all the collected extra samples (n = 5 to 6) from the segment being assessed would be processed for microcystin toxin analysis. If no *Microcystis* bloom conditions were evident in the collected samples, the samples would be discarded.

TIME AND SPACE DIMENSIONS

In the most recent evaluation conducted by the Australian Government National Health and Medical Research Council (2006), the basis for the 10 µg·liter^{-1}microcystin toxin threshold is conventional toxicological calculations used to derive a short term (14 day) exposure, in this case to children. The guideline is derived from a study based on lowest observable adverse effect levels considered the most suitable for deriving the short-term exposure threshold. Dataflow assessments during the critical bloom season are conducted at monthly intervals, therefore, the time dimension for determining criteria exceedance is defined by encountering *Microcystis* blooms conditions and observing toxin concentrations exceeding 10 µg·liter^{-1} microcystin in two successive sampling events bracketing a minimum of a two week period. Violations need to be captured in at least two successive sampling events providing evidence of continuity in bloom persistence representative of extended risk conditions in the Chesapeake Bay segment.

The recommended spatial dimension for defining criterion exceedance is based on the fact that surface blooms shift with tides and winds. Tidal currents are highly variable on the Bay. The Potomac River at Point Lookout for early June 2007 shows a typical maximum flood or ebb tide average approximately 0.3 knots with time between slack water periods approximately 7 hours (http://tidesandcurrents.noaa.gov/ for Point Lookout June 2007). A single bloom point could move linearly in one direction approximately 1 nautical mile (1.15 miles or 1.8 km) at this current speed. However, current speed up near the Chesapeake and Delaware Canal can have a maximum current of over 2 knots, and a parcel of water could travel over 7 nautical miles (approximately 8 miles or 12.8 km) in half a tidal cycle.

A single data point is not necessarily suggestive of a large bloom. Two or more data points from water quality monitoring sites, generally spaced 1-2 miles (1.6-3.2 km) apart in small to medium sized segments, achieving ≥ 50,000 cells per milliliter *Microcystis* and subsequently measuring ≥ 10 ug/L microcystin toxin would suggest an extensive bloom and significant impairment status due to human health risks. There is a significant risk due to tides and winds that can shift the bloom throughout a large area of the segment over a relatively short period of time. Therefore, combining space and time parameters, it is recommended that the exceedance of the harmful algal bloom-based chlorophyll *a* criterion is defined by two or more samples from separate fixed water quality monitoring and/or Dataflow calibration stations within a Chesapeake Bay Program segment collected during each of two or more consecutive sampling events (timed two weeks or more apart) with ≥ 10 $\mu g \cdot liter^{-1}$ microcystin toxin concentrations observed.

Please note, from a human health risk management perspective, identifying tidal waters in a single sampling event with ≥ 27.5 $\mu g \cdot liter^{-1}$ chlorophyll *a*, ≥ 50,000 cells per milliliter *Microcystis* and microcystin toxin levels ≥ 10 ug/L would be suitable grounds for issuing a caution for recreational activity on affected waters, specifically swimming and other water contact sports. Samples with fewer than 50,000 cells per milliliter *Microcystis* in a cyanobacteria-dominated community can still pose a human health risk though the probability of exceeding the microcystin toxin threshold tends to decline with decreasing *Microcystis* abundance in Chesapeake Bay tidal waters (Tango and Butler 2007). However, it is up to the individual jurisdictions and their respective state and local environmental health departments to make such decisions regarding issuing advisories dependent on taxonomic assessments, cell counts and toxin results. These assessments should recognize that other cyanobacteria species may be present and producing different toxins independently and coincidently. Phytoplankton community composition and toxin assessments beyond those for microcystin should be considered in making their advisory assessments.

CHLOROPHYLL *a* CONCENTRATION-BASED CRITERIA ASSESSMENT PROCEDURES

To assess attainment of the State adopted numerical chlorophyll *a* concentration-based criteria, it was necessary to establish a reference curve for use in the CFD criteria attainment assessment process (U.S. EPA 2003, 2007). In the case of chlorophyll *a* criteria where a biologically-based reference curve is not available, EPA recommends the states use of the default reference curve originally described in Chapter 2, Figure II-4 and Equation 1 in U.S. EPA 2007.

A criterion threshold is a concentration that should rarely be exceeded by a "population" of concentration data exhibiting healthy levels. The state-adopted concentration-based chlorophyll *a* criteria values are threshold concentrations that should only be exceeded infrequently (e.g., <10%) since a low number of naturally occurring exceedances occur even in a healthy phytoplankton population. The assessment of chlorophyll *a* criteria attainment, therefore, should use the CFD-based assessment method described in U.S. EPA 2007 (Chapter 2) that applies the default

reference curve. These concentration-based Chesapeake Bay chlorophyll *a* criteria apply only to those seasons and salinity-based habitats for which they were defined to protect against applicable human health and aquatic life impairments. Each season—spring (March 1-May 31) and summer (July 1–September 30)—should be assessed separately to evaluate chlorophyll *a* criteria attainment.

Assessments of seasonal mean chlorophyll *a* criteria should be based on seasonal averages of interpolated data sets. To calculate the seasonal averages, each interpolated cruise within a season should be averaged on a point-by-point basis in matching interpolator grid cells. Spatial violation rates should be calculated for each seasonally aggregated interpolation in an assessment period. For example, for a summer open-water seasonal chlorophyll *a* criteria assessment of a three-year assessment period, three seasonal average interpolations representing each season (Year 1 Summer, Year 2 summer, Year 3 summer) should be used.

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Acronyms

^{o}C	degrees Celsius
CART	classification and regression tree
CBP	Chesapeake Bay Program
CDOM	colored dissolved organic matter
CFD	cumulative frequency diagram
cfs	cubic feet per second
cells·ml^{-1}	cells per milliliter
Chla	chlorophyll *a*
Chla (mg·m^{-3})	milligrams of chlorophyll *a* per meter cubed
dwachl	depth-weighted average chlorophyll *a*
DIN	dissolved inorganic nitrogen
DO	dissolved oxygen
g·C·m^{-2} ·d^{-1}	grams of carbon per meter squared per day
GLM	general linear model
g·m^{-3}	grams per meter cubed
HAB	harmful algal bloom
LOAEL	Lowest Observable Effects Level
km	kilometers
LOAEL	lowest observable acute effects level
m	meter
m	milligram
µg·kg^{-1}	micrograms per kilogram
µg·liter^{-1}	micrograms per liter
mg·chla·m^{2}	milligrams of chlorophyll *a* per meter squared
mg·liter^{-1}	milligrams per liter
MH	mesohaline
NASS	non-algal suspended solids
NH_4	ammonium
NO_2	nitrite
NO_3	nitrate
O_2	oxygen
OH	oligohaline
PAR	photosynthetically active radiation
PO_4	dissolved inorganic phosphorous/ orthophosphorous
ppt	parts per thousand
PSU	practical salinity unit
% sat	percent saturation
SAV	submerged aquatic vegetation
TP	total phosphorous
TF	tidal fresh
TSS	total suspended solids
U.S. EPA	United States Environmental Protection Agency

appendix a

Delaware, Maryland, Virginia and the District of Columbia's Narrative Water Quality Standards Regulations Relevant to Algal-Related Impairments

DELAWARE

In the definitions section of Delaware's water quality standards regulation, nuisance species are defined as "any species of fish, other animal, or plant living in or near the water, the presence of which causes unreasonable interference with the designated uses of the waters or the uses of adjoining land areas. Nuisance species include but are not limited to filamentous and blue green-algae".

Within the criteria to protect designated uses section of the regulation, Delaware states that "all surface waters of the state…shall meet the following minimum criteria: 4.1.1.3. Any pollutants, including those of a thermal, toxic, corrosive, bacteriological, radiological, or other nature, that may interfere with attainment and maintenance of designated uses of the water, may impart undesirable odors, tastes, or colors to waters or to aquatic life found therein, may endanger public health, or may result in dominance of nuisance species.

MARYLAND

Upfront in Maryland's water quality standards regulation, the term 'balanced indigenous community' is defined as "a biotic community typically characterized by diversity, the capacity to sustain itself through cyclic seasonal changes, presence of necessary food chain species, and by a lack of domination by pollutant tolerant species" (26.08.01.01).

Within the surface water quality protection section of Maryland water quality standards regulations, it is stated that "water quality standards shall provide water quality for the designated uses of (a) water contact recreation, (b) fishing, (c) propagation of fish, other aquatic life and wildlife, and (d) agricultural and industrial water supply."

Within the designated use section of the regulation, Maryland defines open-water fish and shellfish designated use as including "waters of the Chesapeake Bay and its tidal tributaries that have the potential for or are supporting the survival, growth and propagation of balanced, indigenous populations of ecologically, recreationally and commercially important fish and shellfish species inhabiting open-water habitats" (26.08.02.02).

Within Maryland's General Water Quality Criteria: The waters of this State may not be polluted by: (1) Substances attributable to sewage, industrial waste, or other waste that will settle to form sludge deposits that: (a) Are unsightly, putrescent, or odorous, and create a nuisance, or (b) Interfere directly or indirectly with designated uses; and (2) Any material, including floating debris, oil, grease, scum, sludge, and other floating materials attributable to sewage, industrial waste, or other waste in amounts sufficient to: (a) Be unsightly; (b) Produce taste or odor; (c) Change the existing color to produce objectionable color for aesthetic purposes; (d) Create a nuisance; or (e) Interfere directly or indirectly with designated uses. (26.08.02.03)

VIRGINIA

Virginia's surface water quality standards contain the following text for ecological conditions for the state's waters and protection of human health and aquatic life that directly relate to ensuring balanced, non-nuisance phytoplankton communities.

Within the state's designation of uses section of the regulation, "all State waters, including wetlands, are designated for the following uses: recreational uses, e.g., swimming and boating; the propagation and growth of a balanced, indigenous population of aquatic life, including game fish, which might reasonably be expected to inhabit them; wildlife; and the production of edible and marketable natural resources, e.g., fish and shellfish. (9 VAC 25-260-10).

Under the general criteria section of Virginia's water quality standards regulation, "all State waters, including wetlands, shall be free from substances attributable to sewage, industrial waste, or other waste in concentrations, amounts, or combinations which contravene established standards or interfere directly or indirectly with designated uses of such water or which are inimical or harmful to human, animal, plant, or aquatic life" (9 VAC 25-260-20).

Further, this section states that "specific substances to be controlled include, but are not limited to: floating debris, oil, scum, and other floating materials; toxic substances (including those which bioaccumulate); substances that produce color, tastes, turbidity, odors, or settle to form sludge deposits; and substances which nourish undesirable or nuisance aquatic plant life (9 VAC 25-260-20).

Virginia's Water Quality Standards regulation (9 VAC 25-260-10) has been around since the late 1960s. It designates all waters for "*the propagation and growth of a balanced, indigenous population of aquatic life, including game fish, which might reasonably be expected to inhabit them.*" The intent of the use designation is to maintain balanced populations of all aquatic life from the base of the food chain (algae) up to commercial and recreational fishes. This existing narrative criteria in

the Water Quality Standards further require that substances "*which nourish undesirable or nuisance aquatic plant life*" will be controlled (9 VAC 25-260-20).

To meet that requirement, Virginia adopted the Nutrient Enriched Waters (9 VAC 25-260-330-350) and Policy for Nutrient Enriched Waters (9 VAC 25-40) in 1988. These adopted regulations recognized that nutrients were contributing to undesirable growths of aquatic plant life, classified waters as nutrient enriched and imposed phosphorus limits on discharges to waters classified as such. The Chesapeake Bay and its tidal tributaries were all classified as nutrient enriched under these same regulations. Chlorophyll *a* was also recognized in the Nutrient Enriched Waters sections of the regulation as an indicator of nutrient enrichment.

Despite these narrative criteria having been in place for years, the tidal James River was listed as impaired in May 1999 under the Clean Water Act required 303(d) list. It was based on violations of the general narrative criteria and nutrients. The tidal James River was later characterized by the most 'unbalanced' phytoplankton community compared to Virginia's other tidal waters with numerous observations of over-abundances of 'undesirable' plant life.

Criteria for dissolved oxygen and water clarity were adopted in 2005 to address water quality impairments in Virginia's two northerly tributaries, namely York and Rappahannock river and Virginia's portion of the Chesapeake Bay mainstem. However, this was not the case in the tidal James River. Nutrients loads from this southern watershed did not significantly impact dissolved oxygen concentrations or water clarity conditions in James River or other Bay waters. Unlike the other major tributary systems, the tidal James River itself is relatively shallow and well mixed. These physical characteristics allow enhanced diffusion of atmospheric oxygen into the water column. The proximity of the James to the Atlantic Ocean and its input of relatively well oxygenated waters tends to keep the dissolved oxygen in the tidal James comparatively good compared to the other systems exposed to excessive nutrients and high chlorophyll a concentrations.

Therefore, it was determined that continuing with a narrative criteria approach to the tidal James River ecosystem would not provide the technical basis for the implementing the necessary nutrient loading reduction actions needed to restore balance to that ecosystem. Virginia's State Water Control Board adopted numerical chlorophyll *a* water quality standards for the tidal James River.

DISTRICT OF COLUMBIA

The District of Columbia's water quality standards regulations sets forth five designated uses applicable to its tidal waters: (A) primary contact recreation, (b) secondary contract recreation, (C) protection and propagation of fish, shellfish and wildlife, (D) protection of human health related to consumption of fish and shellfish, and (E) navigation.

Within the standards section of the regulation, the District of Columbia states that "within tidally influenced Class C waters, concentrations of chlorophyll a in free-floating microscopic aquatic plants (algae) shall not exceed levels that result in ecologically undesirable consequences such as reduced water clarity, low dissolved

oxygen, food supply imbalances, proliferation of species deemed potentially harmful to aquatic life or humans or aesthetically objectionable conditions or otherwise render tidal water unsuitable for designated uses."

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Maryland COMAR Title 26, Subtitle 08 Water Pollution Chapter 02 Water Quality.

Virginia Water Quality Standards regulations: 9 VAC 25-260-10 and 9 VAC 25-260-20.

appendix b

Listing of Harmful Algae Species in Chesapeake Bay

Latin Name	Taxa Group	Toxic Effect	Notes	Synonyms	References
Akashiwo sanguinea	dinoflagellate	PSP,BF	Has been implicated in some fish kills, echanism of action appears to be physical congestion of gills during dense bloom conditions.		30, 12
Amphidinium operculatum	dinoflagellate	NSP	Compounds with haemolytic and antifungal properties (amphidinols) known.	*Pouchetia polyphemus*	52
Amphora coffaeiformis	diatoms	ASP	A strain from Canada was found to produce domoic acid.		3, 32, 40
Anabaena affinis	cyanobacteria	HP,PSP	Produces Microcystin, Saxitoxins, and Anatoxin		55
Anabaena circinalis	cyanobacteria	HP,PSP	Produces Microcystin, Saxitoxins, and Anatoxin		55
Anabaena flosaquae	cyanobacteria	HP,PSP	Produces Microcystin, Saxitoxins, and Anatoxin		54, 55
Anabaena recta	cyanobacteria	HP,PSP	Produces Microcystin, Saxitoxins, and Anatoxin		55

Key to Toxic Effects:

ASP — Amnesic Shellfish Poison
BF — Fish killing and bloom forming
CFP — Ciguateric Fish Poison
DSP — Diarrheic Shellfish Poison
NSP — Neurotoxic Shellfish Poison
NTX — Neurotoxic, fish killing and bloom forming
PSP — Paralytic Shellfish Poison
HP — Known Hepatotoxin Producer

Latin Name	Taxa Group	Toxic Effect	Notes	Synonyms	References
Anabaena spiroides	cyanobacteria	HP,PSP	Produces Microcystin, Saxitoxins, and Anatoxin		55
Aphanizomenon flosaquae	cyanobacteria	PSP	Produces Saxitoxins and Anatoxin		55
Aphanizomenon issatschenkoi	cyanobacteria	PSP	Produces Saxitoxins and Anatoxin		55
Chattonella subsalsa	dinoflagellate	NSP	Produces brevitoxins which has been linked to numerous fish kills.		5, 30, 35, 36
Chattonella verruculosa	dinoflagellate	NSP	Produces brevitoxins which has been linked to numerous fish kills.		2, 30, 35, 36, 50
Cylindrospermopsis raciborskii	cyanobacteria	HP	Produces cylindrospermopsin, associated with fish kills, considered the likely organism in alligator kills in Florida	*Anabaena raciborskii*	57
Cochlodinium polykrikoides	dinoflagellate	NSP	Associated with mortality of fish. Physical contact with taxa and not a released toxin, was the cause of oyster larvae (Crassostrea virginica) deformation and mortality during a red tide in the York River.	*Cochlodinium heterolobatum*	26, 53
Dinophysis acuminata	dinoflagellate	DSP	Producer of okadaic acid	*Dinophysis borealis, Dinophysis lachmanni, Dinophysis boehmii*	1, 23, 27
Dinophysis acuta	dinoflagellate	DSP	Producer of okadaic acid and dinophysistoxin-1 (DTX1) or dinophysistoxin-2 (DTX2)		23, 27

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Latin Name	Taxa Group	Toxic Effect	Notes	Synonyms	References
Dinophysis caudata	dinoflagellate	DSP	Producer of okadaic acid, toxin implicated in DSP.		16, 24
Dinophysis fortii	dinoflagellate	DSP	Producer of dinophysistoxin – 1 (DTX1) and pectenotoxin-2 (PTX2)	*Dinophysis laevis*	27, 47, 51
Dinophysis norvegica	dinoflagellate	DSP	Producer of dinophysistoxin-1 and okadaic acid.		27
Dinophysis rotundata	dinoflagellate	DSP	Production of DTX-1 demonstrated in Japan. North American strains apparently non-toxic.	*Phalacroma rotundatum*	10, 27
Dinophysis sacculus	dinoflagellate	DSP	Producer of okadaic acid, toxin implicated in DSP.	*Dinophysis pavillardi, Dinophysis reniformis, Dinophysis ventrecta, Dinophysis phaseolus*	13, 17
Dinophysis tripos	dinoflagellate	DSP	Producer of dinophysistoxin-1 (DTX1), a toxin implicated in DSP	*Dinophysis caudata tripos*	27
Heterosigma akashiwo	dinoflagellate	BF	Linked to mortality of fish	*Heterosigma carterae, Olisthodiscus carterae*	11, 21, 30, 41
Karlodinium micrum/ Karlodinium veneficum	dinoflagellate	BF	Linked to mortality of fish	*Gymnodinium galatheanum , Gymnodinium micrum, Gyrodinium galatheanum*	6, 12, 25, 29, 30
Lingulodinium polyedra	dinoflagellate	PSP	Producer of saxitoxin		7
Microcystis aeruginosa	cyanobacteria	HP,PSP	Produces Microcystin and saxitoxins,	*Micraloa aeruginosa, Poly-cystis aeruginosa*	15, 22, 30

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Latin Name	Taxa Group	Toxic Effect	Notes	Synonyms	References
Microcystis firma	cyanobacteria	HP,PSP	Produces Microcystin and saxitoxins,		15,22,30
Microcystis viridis	cyanobacteria	HP,PSP	Produces Microcystin and saxitoxins,		15,22,30
Pfiesteria piscicida	dinoflagellate	NTX, BF	Known to cause lesioning and ulcers on fish resulting in sometimes massive fish kills. There are cases of human respiritory distress, and memory loss associated with Pfiesteria	*Nitzschia delicatissima, Nitzschia actydrophila*	8, 9, 45
Pfiesteria shumwayae	dinoflagellate	NTX, BF	Fish are killed by Pfiesteria feeding on them. Cells attach to the skin of fish and denude the fish of the epidermis.		8, 9, 18, 45
Planktothrix agardhii	cyanobacteria	NSP,PSP	Produces Microcystin and anatoxin	*Oscillatoria Agardhii*	55, 56
Planktothrix limnetica	cyanobacteria	NSP,PSP	Produces Microcystin and anatoxins,	*Oscillatoria limnetica*	55, 56
Planktothrix limnetica acicularis	cyanobacteria	NSP,PSP	Produces Microcystin and anatoxins,		55, 56
Prorocentrum lima	dinoflagellate	DSP,BF	Has been found to produce the Diarrhetic Shellfish Poisoning (DSP) toxins: okadaic acid (Murakami et al. 1982), DTX-1 (Lee et al. 1989), DTX-2 (Hu et al. 1993), in Addition to a proro-centrolide (Torigoe et al. 1988) and a Fast Acting Toxin (FAT) (Tindall et al. 1984).	*Exuviella lima, Exuviella marina*	27, 34, 48, 49

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Prorocentrum minimum	dinoflagellate	NSP, BF	Intra-peritoneal injections of methanol extracts are toxic to mice. Ingested cells can cause detrimental effects in molluscs. Some strains excrete substances toxic to Artemia-nauplii. Producer of venerupin (heap-totoxin) which caused shellfish poisoning.	*Exuviaella marina lima*	19, 30, 44
Pseudo-nitzschia delicatissima	diatoms	ASP	A strain from Canada and one from New Zealand found to produce domoic acid	*Prorocentrum mariae-lebouriae, Prorocentrum triangulatum*	37, 42, 43
Pseudo-nitzschia multiseries	diatoms	ASP	Domoic acid producer	*Nitzschia pungens multiseries, Pseudo-nitzschia pungens multiseries*	4, 14, 46
Pseudo-nitzschia Pseudodelicatissima	diatoms	ASP	Domoic acid producer	*Pseudo-nitzschia calliantha*	31, 33
Pseudo-nitzschia pungens	diatoms	ASP	This species is usually non-toxic. Toxic clones have been reported from New Zealand and the West Coast of the U.S.A.	*Nitzschia pungens*	4, 38
Pseudo-nitzschia seriata	diatoms	ASP	Several clones of this species have been found to produce domoic acid	*Nitzschia seriata*	31
Pyrodinium bahamense	dinoflagellate	PSP	Producer of paralytic shellfish poisoning toxins	*Gonyaulax schilleri, Pyrodinium schilleri*	20, 39
Snowella lacustris	cyanobacteria	HP,PSP	Produces Microcystin and saxitoxins,		55

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PSP — Paralytic Shellfish Poison
HP — Known Hepatotoxin Producer

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appendix C

States Chlorophyll *a* Criteria and Water Quality Standards

Alabama	Lake and reservoir specific chlorophyll *a* criteria ranging from 5–27 µg·liter^{-1}.
Colorado	Single reservoir with a 15 µg·liter^{-1} chlorophyll *a* criteria.
Connecticut	Lake Trophic Classification System (also includes TP, TN, Secchi) Chlorophyll *a* Concentrations (µg·liter^{-1}) by Trophic Class: Oligotrophic = 0–2 Mesotropic = 2–15 Eutrophic = 15-30 Highly Eutrophic = >30
District of Columbia	Seasonal July 1–September 30 segment average chlorophyll *a* concentration of 25 µg·liter^{-1} applied to tidally influenced waters only.
Georgia	Lake and reservoir specific chlorophyll *a* criteria ranging from 15–27 µg·liter^{-1}.
Hawaii	Chlorophyll *a* criteria applying to different locations within Lake Mead ranging from 5–45 µg·liter^{-1}.
Nevada	"Chlorophyll *a* (corrected): not greater than 40 µg·liter^{-1} for lakes, reservoirs and other waters subject to growths of macroscopic or microscopic vegetation not designated as trout waters, and not greater than 15 µg·liter^{-1} for waters subject to growths of macroscopic or microscopic vegetation designated as trout waters" (15ANCAC 02B.0211)
North Carolina	Freshwater class C waters and tidal saltwaters: For lakes and reservoirs and other waters subject to growths of macroscopic and microscopic vegetation not designated as trout waters: <40 µg·liter^{-1}. For lakes and reservoirs and other waters subject to growths of macroscopic and microscopic vegetation designated as trout waters: <15 µg·liter^{-1}.

Oregon

Chlorophyll *a* criteria for:

- Natural lakes which don't thermally stratify: <10 mg·liter^{-1}
- Natural lake which doesn't thermally stratify, reservoirs, rivers and estuaries: <15 µg·liter^{-1} (OAR340-041-0019)

Virginia

Site specific seasonal numerical chlorophyll *a* criteria applicable March 1–May 31 and July 1–September 30 for the tidal James River segments JMSTF2, JMSTF1, JMSOH, JMSMH, JMSPH (9 VAC 25-260-310)

Designated Use	Chlorophyll *a*	Chesapeake Bay Program	Temporal Application
Open-Water	10	JMSTF2	March 1–May 31
	15	JMSTF1	
	15	JMSOH	
	12	JMSMH	
	12	JMSPH	
	15	JMSTF2	July 1–September 30
	23	JMSTF1	
	22	JMSOH	
	10	JMSMH	
	10	JMSPH	

Source: U.S. Environmental Protection Agency. 2003. Survey of States, Tribes and Territories Nutrients Standards. Washington, D.C.



U.S. Environmental Protection Agency
Region III
Chesapeake Bay Program Office
Annapolis, Maryland
1-800-YOUR-BAY

and

Region III
Water Protection Division
Philadelphia, Pennsylvania

in coordination with

Office of Water
Office of Science and Technology
Washington, D.C.

and

the states of
Delaware, Maryland, New York,
Pennsylvania, Virginia and
West Virginia and the District of Columbia