An Analysis of Continuous Monitoring Data Collected in Tidal Potomac Embayments and River Flanks

FINAL

Prepared by

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Correlation is not causation, but it sure is a hint. Edward Tufte

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Contents

Acknowledgments Back of Front Cove	er
Contents	i
Executive Summary i	iii
Introduction	1
Data Sources	3
Data Analysis	7 7 9
Results 1 Chlorophyll a 1 Dissolved Oxygen 1 pH 1 Turbidity 1	10 10 11 12 13
Discussion and Conclusions 2 Metric Correspondence and Protectiveness 2 Plant Groups 3 Some Management Implications 3 Are pH values that exceed 9.0 an interim sign of recovery? 3 What are the most likely causes of minimum DO criteria failures? 3 Which of the nine CMON-based metrics analyzed are most useful? 3 Will watershed TMDLs for listed causes of impairment be effective? 3	29 29 32 33 34 34 35 36
References	17

Executive Summary

High frequency "continuous monitoring" (CMON) data collected between 2004 and 2008 in shallow tidal waters of the Potomac River were analyzed using Maryland and/or Virginia short-interval water quality criteria and other metric thresholds indicative of eutrophication. High frequency data provide a more robust evaluation of criteria/threshold attainment in shallow waters than daytime sampling done once or twice a month, especially if the criteria and thresholds involve instantaneous minima or maxima. Seasonal failure rates of the Maryland and Virginia instantaneous minimum criteria for dissolved oxygen (%DO<Min) ranged from 0% to 31.5%. Seasonal failure rates of the Virginia pH criterion of 9.0 (%pH>9) ranged from 0% to 61.7%. Failure rates of the Maryland turbidity criterion of 150 NTU (%Turb≥150) ranged from 0% to 4.2%.

The CMON data analysis suggests several metric thresholds protective of human and ecosystem health. Seasonal median chlorophyll *a* concentrations less than 16 µg/liter are protective of concentrations that have been associated with algal bloom toxicity and human health impacts while medians less than 10 µg/liter are protective of desirable phytoplankton communities and, by inference, desirable water quality conditions. A seasonal frequency of supersaturated dissolved oxygen (DO%Sat) less than 40% is protective of Virginia's pH 9.0 criterion in the Potomac's poorly buffered waters while DO%Sat greater than 40% is protective of %DO<Min. A DO%Sat between 30% and 50% is thus semi-protective of both the DO and pH criteria. A 7-day mean dissolved oxygen concentration of ~8 mg/liter is also protective of %DO<Min. Maryland's instantaneous maximum turbidity criterion of 150 NTU is protected if turbidity measurements greater than 50 NTU occur in less than 2.8% of the CMON shallow water records.

High frequencies of supersaturated DO and pH greater than 9.0 occur at several shallow water sites and demonstrate that plant photosynthesis can be relatively strong in both spring and summer/autumn. Phytoplankton, expressed as water column chlorophyll *a*, are often abundant in spring and seem most responsible for the high pH values and saturated DO in that season. Chlorophyll *a* concentrations in summer/autumn are lower and approaching levels deemed desirable for Chesapeake Bay restoration. SAV beds and possibly benthic algae appear most responsible for high pH values and saturated DO in summer and autumn. Primary production is shifting from the water column in spring to the bottom in summer and autumn.

Failure of the instantaneous minimum DO criteria and exposure to lethal concentrations occurs more often in tidal Potomac shallow waters than failure of the 7-day mean DO criteria and exposure to chronic, sublethal concentrations. Failure rates of the minimum criteria, or %DO<Min, were particularly high in Piscataway Cr. (2004), Breton Bay (2006-2008), and St. Mary's R. (2008). In spring, the highest failure rates of the minimum criteria are associated with large magnitudes of diel (24-hour) change in DO saturation (DM%Sat). In summer and autumn, the highest failure rates occur at sites with low frequencies of supersaturated DO *and* relatively large DM%Sat.

Abundant SAV beds to the tidal Potomac River–one of the desired signals of ecosystem recovery–are associated with higher frequencies of pH exceeding 9.0 and DO failing the instantaneous minimum criteria in summer/autumn. The results suggest state water quality

criteria may not be achieved immediately or completely as shallow tidal waters recover from historic nutrient and sediment impacts. Sufficient time could be needed before turbidity levels no longer impede photosynthesis, bottom-oriented plant communities become well established, sediment nutrient releases to the water column are further reduced, and the competing processes of oxygen production and consumption produce moderate frequencies of saturated DO and smaller magnitudes of diel change in DO. The CMON results suggest restoration efforts *in* tidal Potomac shallow waters rather than upstream of them may expedite recovery.

Introduction

Water quality conditions indicative of eutrophication are found throughout the tidal Potomac River, Chesapeake Bay's largest sub-estuary. Most estuarine waters of the Potomac are currently listed as impaired by eutrophication factors in 303(d)/305(b) reports to the US EPA (VADEQ 2008, MDE 2008, DDOE 2008). Eutrophication is evident in estuarine waters as algal blooms expressed as high chlorophyll *a*, dissolved oxygen levels that fall below aquatic life requirements, suspended sediment levels that block sunlight and suppress plant growth, and high pH that enhances ammonia toxicity. Maryland, Virginia, and the District of Columbia have established water quality standards with numeric criteria to protect designated uses in their estuarine waters, namely non-degraded aquatic life and safe consumption of fish and shellfish (VADEQ 2008, MDE 2008, DDOE 2008). Some criteria can be assessed with data collected once or twice monthly at mid-channel sites. Other criteria are designed to capture short-duration variability in conditions affecting aquatic life (e.g., instantaneous minima) and are difficult to assess with once or twice monthly monitoring data.

Virginia, Maryland, and the District, in collaboration with multiple partners, placed "continuous monitoring" (CMON) sondes at 21 embayment and river flank sites in the tidal Potomac River (**Figure 1**) between 2004 and 2008. The sondes measured water quality parameters every fifteen minutes from March or April through October or November. These high frequency data can be used to evaluate short-duration criteria in shallow water environments. Shallow water environments link Coastal Plain watersheds with tidal river mainstems and estuaries. They are more likely than the open or deep water environments in the tidal rivers and estuaries to show strong 24-hour (diel) variability, and can potentially fail short-interval criteria more often. Shallow waters are important to monitor because they serve as refuge and nursery areas for many fish and invertebrate species, provide physical habitat for underwater grass beds, and are the first tidal waters exposed to watershed nutrient and sediment loads from the Coastal Plain.

This data analysis evaluates the failure rates of 5 short-interval numeric criteria and the exceedance rates of 6 screening thresholds for chlorophyll *a*, pH, dissolved oxygen, and turbidity measured at the 20 Maryland and Virginia CMON sites. (Data for the two District sites have not been QA/QC'ed as of this writing, and so were not included in the analysis.) Virginia Department of Environmental Quality (VADEQ) and/or Maryland Department of the Environment (MDE) apply the 5 water quality criteria to their respective Potomac waters for 303(d)/305(b) reporting purposes (**Table 1**).

One objective of the analysis was to determine if achievement of certain short-interval criteria and thresholds is protective of other ones, so relationships between the different criteria and thresholds were examined. Another objective was to determine which plants are responsible for criteria and threshold exceedances. Three types of plants common to the Potomac estuary have the potential to directly or indirectly influence pH, turbidity, and dissolved oxygen: algae that inhabit the water column (phytoplankton); nearshore vascular plants or submerged aquatic vegetation (SAV); and algae attached to sediments or hard surfaces in shallow, well-lit waters (benthic algae). Phytoplankton, expressed as water column chlorophyll *a*, and SAV are presently monitored in Potomac embayments; benthic algae are not monitored but their presence can sometimes be inferred.

ontinuous mo AH, mesohali	onitoring data in this analysis. Sali ne.	inity zone (Salzone) is the long-ter	m mean salinity at the station: TF	⁻ , tidal fresh; OH, oligohaline,
Parameter	Maryland (MDE 2008)	Virginia (VADEQ 2008)	District of Columbia (DDOE 2008)	Criteria Used in This Analysis
Chlorophyll <i>a</i>	"may not exceed levels that result in ecologically undesirable consequences that would render tidal waters unsuitable for designated uses"	"shall not exceed levels that result in undesirable or nuisance aquatic plant life, or render tidal waters unsuitable for the propagation and growth of a balanced, indigenous population of aquatic life or otherwise result in ecologically undesirable water quality conditions 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."	"Concentrations of chlorophyll <i>a</i> 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." (EPA 2003)	none
Dissolved Oxygen	7-day mean, <u>></u> 6.0 mg/liter, Feb 1 - May 31, migratory spawning	7-day mean, <u>></u> 6.0 mg/liter, Feb 1 - May 31, migratory spawning	7-day mean, ≥ 6.0 mg/liter, Feb 1 - May 31, migratory spawning	7-day mean, <u>></u> 6.0 mg/liter, Feb 1 - May 31 TF & OH
	7-day mean, \geq 4.0 mg/l, year-round, open water, all salinities	7-day mean, \geq 4.0 mg/l, year-round, open water, all salinities	7-day mean, \geq 4.0 mg/l, year-round, open water, all salinities	7-day mean, <u>></u> 4.0 mg/l, Jun 1 - Jan 31 all salzones and Feb 1 - May 31 MH
	Instantaneous, <u>></u> 5 mg/l, Feb 1 - May 31 migratory spawning	Instantaneous, <a>> 5 mg/l, Feb 1 - May 31 migratory spawning	Instantaneous, <u>></u> 5 mg/l, Feb 1 - May 31 migratory spawning	Instantaneous, 25 mg/l, Feb 1 - May 31 TF & OH
	Instantaneous, $\geq 3.2 \text{ mg/l}$ at $\leq 29^{\circ}\text{C}$ and $\geq 4.3 \text{ at} > 29^{\circ}\text{C}$, year-round, open water, all salinities	Instantaneous, \geq 3.2 mg/l at < 29°C and \geq 4.3 at \geq 29°C, year-round, open water, all salinities	Instantaneous, $\geq 3.2 \text{ mg/l}$ at $< 29^{\circ}\text{C}$ and $\geq 4.3 \text{ at} \geq 29^{\circ}\text{C}$, year-round, open water, all salinities	Instantaneous \geq 3.2 mg/l at $<$ 29°C and \geq 4.3 at \geq 29°C Jun 1 - Jan 31 all salzones and Feb 1 - May 31 MH
pH	Instantaneous, 6.5 - 8.5	Instantaneous, 6.0 - 9.0	Instantaneous, > 6 and < 8.5	Instantaneous, 6.0 - 9.0
Turbidity	Instantaneous, <150 NTU	none	Instantaneous, ≤ 20 NTU increase above ambient	Instantaneous, ≤150 NTU

Table 1. Short-interval water quality criteria for Maryland Use II waters in support of estuarine and marine aquatic life (MDE 2008), Virginia Class II waters in the Chesapeake Bay and its tidal tributaries (VADEQ 2008), and the District of Columbia Use C tidal waters for protection and propagation of fish, shellfish, and wildlife (DDOE 2008), and the numeric criteria applied to the 2004 - 2008 tidal Potomac River shallow water

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Data Sources

Continuous monitoring (CMON) data were obtained from Maryland Department of Natural Resources (MDDNR), from Virginia Institute for Marine Sciences (VIMS) on behalf of Virginia Department of Environmental Quality (VADEQ), from VADEQ directly, and from the District of Columbia Department of the Environment (DDOE) contractor supported webpage. A total of 22 Maryland, Virginia, and District sites (**Figure 1**) were monitored for 1 - 5 years between 2004 and 2008.

In Maryland and Virginia, measurements were made with a YSI 6600 sonde (sensors and data logger) equipped with the Clean Sweep Extended Deployment System which wipes the sensors at 15-minute intervals. Water temperature, salinity, dissolved oxygen (DO) concentration, % DO saturation, pH, turbidity, and chlorophyll *a* readings were made at 15-minute intervals. The sondes were housed in perforated 4" PVC pipes for protection, and attached to a pier, dock, or free-standing post where boat traffic was not likely to cause turbidity. Most sondes were anchored 0.3 m - 0.5 m above bottom and experience tidal changes in depth. Median depths over the course of the sampling period ranged between 0.20 and 2.99 m. The Occoquan sonde was attached to a marker buoy and therefore suspended at a constant depth of 1.0 m below the surface of the water. The sondes were deployed between late March and early November, when plant productivity rates are highest. Sondes were deployed for 1-2 weeks, and then switched out for cleaning and recalibration. Sampling periods and location attributes are listed in **Table 2**. Data flagged as problematic by the data collectors were excluded from the analysis. The data and data documentation are available online at <u>http://www2.vims.edu/vecos/</u> and <u>http://mddnr.chesapeakebay.net/eyesonthebay/index.cfm</u>.

The two District sondes were attached to bridges crossing the Anacostia River. They were operated from March 24 to the end of the year in 2008, and the data fed directly to <u>http://www.ysieconet.com/public/WebUI/Default.aspx?hidCustomerID=167</u>, a web site supported by Yellow Springs Inc. (YSI). Biofouling was quite extreme in the summer (J. Zahn, pers. comm.) and initial examination of the data indicated potential problems with some of the readings. The District CMON data were not included in this analysis at this time. However, they would add significantly to the results and conclusions if they were QA/QC'ed and incorporated at a later time.



Figure 1. Map of the shallow water continuous monitoring (CMON) sites in the District of Columbia, Maryland, and Virginia, 2004 - 2008.

Table 2. Maryland and Virginia 2004 - 2008 continuous monitoring sites in the tidal Potomac River. Sonde median depth is calculated from all available depth measurements. Salinity zone (Salzone) is the long-term mean salinity at the station: TF, tidal fresh; OH, oligohaline, MH, mesohaline. Site type (Type): E, embayment; PR, river flank. a, attached to floating channel marker (most sondes are anchored 0.3 -0.5 m above bottom, and often attached to a pier).

System	Sal-	Туре	Station	Latitudo	Longitudo	Voar	Start	End	Median
Discataway Cr MD	TE	F	VER2184	28 7016°	_77 0250°	2004	1/21	11/1	0.76
FISCalaway Or MD		L	AI 02104	30.7010	-11.0200	2004	4/∠i 3/31	10/24	0.70
						2000	3/21	10/21	0.88
						2000	3/21	10/31	0.00
						2007	3/31	11/3	0.00
Fenwick MD	TF	PR	XFB0231	38 6699°	-77 1151°	2000	4/21	10/27	0.30
			A DOLC .	00.0000		2005	3/31	10/24	0.39
						2006	3/21	10/31	0.44
						2007	3/21	10/31	0.38
						2008	3/26	10/21	0.45
Pohick/Gunston VA	TF	Е	POH002.10	38.6761°	-77.1640°	2007	4/9	10/31	1.35
						2008	4/7	10/28	1.47
Occoquan Bay VA	TF	Е	OCC002.47	38.6405°	-77.2194°	2005	4/5	9/29	1.00 a
, -						2007	4/3	10/30	1.00 a
						2008	4/1	10/14	1.00 a
Neabsco Cr. VA	TF	PR	NEA000.57	38.6000°	-77.2569°	2006	5/18	10/31	1.00
Mattawoman Cr. MD	TF	Е	XEA3687	38.5593°	-77.1887°	2004	4/21	11/1	1.12
						2005	3/31	10/24	1.15
						2006	3/21	10/31	0.94
						2007	3/21	10/31	1.03
						2008	3/26	11/3	0.99
Potomac Creek VA	OH	Е	POM000.97	38.3438°	-77.3049°	2007	3/20	10/31	1.01
						2008	3/21	11/4	1.06
Blossom Point MD	OH	PR	XDB4544	38.4084°	-77.1102°	2006	4/5	8/23	0.30
(Nanjemoy Cr)						2007	5/16	11/5	0.20
						2008	3/26	11/3	0.46
Port Tobacco R. MD	OH	Е	PRT	38.4796°	-77.0275°	2007	4/4	3/31	0.71
						2008	3/26	11/3	0.72
Popes Creek MD	MH	PR	XDC3807	38.3960°	-76.9891°	2006	4/19	11/1	1.71
						2007	3/22	10/31	1.75
						2008	3/26	11/3	1.68
Swan Point MD	MH	PR	XCC8346	38.3054°	-76.9239°	2006	4/5	10/18	0.85
						2007	3/22	10/31	0.52
		_				2008	3/26	11/3	0.60
Monroe Bay VA	MH	E	MON000.18	38.2322°	-76.9640°	2007	3/20	11/2	1.86
		-		00 00 7 50		2008	3/26	11/4	1.81
Wicomico R. MD	MH	E	XCC9680	38.3275°	-76.8660°	2006	4/5	11/1	0.29
						2007	3/22	10/31	0.28
		-		00 40400	70 74700	2008	3/26	10/21	0.32
Nomini Bay VA	MH	E	NUMUU2.30	38.1318	-/0./1/0	2007	3/20	10/31	0.00
Broton Boy MD	м	5		20 2500°	76 67130	2000	5/20	11/4	0.49 1.53
Breton bay wid		E	XCD0099	30.2090	-10.0113	2000	0/20 1/5	0/20	1.55
						2007	4/3 2/2/	9120 10/22	1.02
Vaccomico R VA	мц	_	MES000 18	38 0300°	76 5510°	2000	3/24 2/28	10/21	0.44
Teoconnico R. VA		L	VVL3000.10	30.0290	-70.5519	2007	3/20	11/4	0.44
						2000	5/20	11/4	0.54

System	Sal- zone	Туре	Station Designation	Latitude	Longitude	Year	Start Date	End Date	Median Depth (m)
Piney Point MD	MH	PR	XBE8396	38.1377°	-76.5058°	2004	4/23	10/29	0.90
						2005	3/24	11/30	0.89
						2006	4/10	10/31	0.88
						2007	4/3	10/30	0.88
						2008	3/27	10/21	0.92
St Georges Cr. MD	MH	Е	SGC	38.1311°	-76.4934°	2006	4/25	10/31	nd
						2007	4/5	10/30	nd
						2008	3/27	10/21	0.54
Sage Point MD	MH	PR	XBF6843	38.1893°	-76.4339°	2004	4/23	10/29	0.79
(St. Mary's R.)						2005	3/24	11/30	0.97
St Mary's R. MD	MH	Е	SMC	38.1894°	-76.4338°	2008	4/16	12/12	2.99

Data Analysis

Continuous monitoring data collected for four water quality parameters were evaluated against 5 numeric criteria encoded in Maryland and Virginia Water Quality Standards to protect aquatic life uses and 6 thresholds considered indicative of eutrophication. Sample collection was not synchronized, and start dates ranged from 3/21 to 5/18 and end dates ranged from 9/29 to 11/30. Furthermore, some blocks of records in individual data sets were censored for QA/QC reasons. The criteria and thresholds were applied to all available uncensored CMON data prior to June 1 to obtain the "Spring" values at each site and to all available uncensored CMON data after May 31 to obtain the "Summer/Autumn" values.

Metrics

Chlorophyll *a* is a green pigment involved in photosynthesis in all plants, including algae. Water column concentrations of chlorophyll *a* are a rough indicator of phytoplankton (water column algae) biomass.¹ High phytoplankton biomass is a common result of excess inputs of nutrients such as nitrogen and phosphorus, and is considered an indicator of eutrophication. Neither Virginia nor Maryland has a numeric chlorophyll *a* criteria for Potomac estuarine waters (Table 1). The seasonal metrics used in this analysis to evaluate chlorophyll *a* were the median of all CMON observations, the frequency of all CMON observations greater than or equal to 50 μ g/liter (%Chla \geq 50), and the frequency of all CMON observations exceeding the maximal, or 95th percentile, of the Chesapeake Bay phytoplankton reference communities (%Chla>Ref). The median (or the mean) chlorophyll *a* concentration is often used to assess trophic status of fresh and marine waters (see summaries in US EPA 2003a, US EPA 2007) or to rate observations (e.g., OSPAR Commission 2005). The %Chla>50 metric was suggested as a "point of reference" for the tidal Potomac by participants of a 1987 Nutrient Control Standards workshop at the University of Virginia, although it was never formally adopted by the Commonwealth (University of Virginia 1987). VADEQ currently uses 50 µg/liter as a chlorophyll a screening value to identify nutrient enriched tidal fresh waters, estuaries and lakes (VADEO 2007). Chlorophyll *a* concentrations greater than 50 µg/liter are also linked by the World Health Organization (WHO) to a moderate probability of short-term adverse health effects including fever, nausea, vomiting, and gastroenteritis, and the potential for long-term illness related to cyanobacteria toxins (Chorus and Bertram 1999). The %Chla>Ref metric is based on seasonand salinity-specific percentiles identified from reference communities, or phytoplankton growing in water quality conditions deemed desirable for Chesapeake Bay restoration. These are waters with adequate light for plant photosynthesis and (algae) bloom-limiting nitrogen and phosphorus concentrations. The spring (March - May) and summer (July - September) maximal chlorophyll *a* thresholds, in µg/liter, are 13.5 and 15.9 in tidal fresh waters, 24.6 and 24.4 in oligohaline waters, and 23.8 and 13.5 in mesohaline waters, respectively (from Buchanan et al. 2005).

¹ Algal cells increase their cellular chlorophyll *a* concentrations and maintain a high ratio of chlorophyll a to biomass when underwater light conditions are poor. Chlorophyll *a* concentration can thus overestimate phytoplankton biomass in poor water clarity. In open water environments of the Chesapeake system, this occurs when Secchi depth is less than about 0.8 meters in tidal fresh and oligohaline salinity zones and less than 1.8 m (spring) and 1.5 m (summer) in the mesohaline salinity zone (Buchanan et al. 2005). Secchi depth thresholds for shallow water have not been determined.

Plants release oxygen during photosynthesis, and plants, animals, and aerobic bacteria consume oxygen (respire) in order to extract energy from food. Oxygen is also consumed by estuarine geochemical processes. When underwater photosynthesis is limited by low light levels and/or biological demand for oxygen is high, consumption outweighs production and dissolved oxygen concentrations decline over time. Very low dissolved oxygen concentrations stress and kill aquatic plants and animals and can alter sediment-water chemical exchanges. Four seasonal metrics were used to evaluate dissolved oxygen: the percent of observations with super-saturated concentrations (%SatDO), the median magnitude of diel change in percent saturation (DM%Sat), the frequency of observations failing instantaneous minimum DO criteria (%DO<Min), and the frequency of 7-day means failing the 7-day mean DO criteria (%DO<7Day). The first two metrics indicate how much photosynthetic production is occurring in a season relative to total community respiration. When daytime plant production is very high relative to oxygen consumption, water becomes super-saturated with dissolved oxygen and holds more than the maximum equilibrium amount.² Very high plant production coupled with very high nighttime community oxygen consumption leads to large 24-hour (diel) swings in percent saturation. DM%Sat is the seasonal median of the daily differences between the daytime maximum and nighttime minimum in dissolved oxygen percent saturation. The instantaneous minimum DO criteria and 7-day mean DO criteria have been adopted by Maryland and Virginia, and are designed to be protective of key biological groups in specific habitats, or "designated uses" (US EPA 2003a). The two criteria vary by season and salinity zone (Table 1). The instantaneous minimum criteria is based on evidence that short-term exposure to very low oxygen concentrations leads to rapid mortality. The 7-day mean criteria was established to protect fish reproduction and early life stages against chronic, sublethal impacts of low dissolved oxygen. %DO<7Day is calculated as the mean of all DO observations from day, at 00:00 h to day_{i+6} at 23:45 h. Means are calculated for running 7-day periods.

Rapid photosynthesis by abundant plant populations can quickly reduce dissolved carbon dioxide (CO_2) concentrations in poorly buffered, nutrient rich waters. This causes a shift in the CO_2 -water equilibrium and results in high pH levels. High pH levels favor another equilibrium shift from the relatively non-toxic ionized ammonium (NH_4^+) to the more toxic un-ionized ammonia (NH_3) . Accumulating NH_3 can cause fish kills. In tidal fresh systems, high pH values also allow sediment bound phosphorus to be released to the water column where it can spur more phytoplankton growth and algal blooms. The metrics used in this analysis to evaluate pH were the frequencies of observations greater than the value of 9.0 (%pH>9) and less than the value of 6.0 (%pH<6). These reflect the Virginia pH criteria (**Table 1**). The Maryland pH criteria are slightly stricter (6.0 - 8.5).

Turbidity measured in "nephelometric turbidity units," or "NTUs.," is the amount of light scattered in a 90° angle by particles suspended in the water column. Particles that scatter light typically range in size from 0.00025 mm (very fine clay) to 1.0 mm (coarse sand). Light scattering can significantly reduce the depth to which incident light penetrates the water column (water clarity) and can suppress underwater photosynthesis and plant growth. High turbidity

 $^{^2}$ In the absence of biological production or consumption of oxygen, dissolved oxygen reaches an equilibrium maximum amount that depends on temperature, pressure, and salinity. Percent saturation is calculated relative to this amount.

levels impair the reproduction, respiration, and filter-feeding of aquatic animals. It can provide "shelter" for pathogens and other microbes by reducing their exposure to disinfectants (US EPA 1999). The metrics used in this analysis to evaluate excessive turbidity were the frequency of observations greater than or equal to 150 NTU (%Turb≥150) and the frequency of observations greater than 50 NTU (%Turb>50). An instantaneous maximum threshold of 150 NTU is Maryland's criteria for estuarine and marine aquatic life and shellfish harvesting (**Table 1**), and is among the most relaxed turbidity criteria in United States WQS (US EPA 2003b). The stricter maximum criterion of 50 NTU in combination with various allowable exceedance rates is used for estuarine waters by British Columbia (Singleton 2001, British Columbia Water Management Branch 1997) and for marine waters by Washington state (Washington Administrative Code 173-201A-210, 2006).

Approach

Seasonal failure rates, exceedance rates, and medians of the criteria and thresholds were calculated in Microsoft Excel 2003 for all available spring (March 1 - May 31) and summer/autumn (June 1 - November 30) CMON observations. In some cases, equipment malfunctions in the field prevented data collection for long periods, and the remaining observations were not analyzed. CMON sites located in small tributaries and afforded some protection by geographic features from mainstem tidal influences were identified as "embayment." Sites located at tributary mouths or in shallow waters adjacent to the mainstem were identified as "river flank." Sites were grouped by salinity zone, representing the long-term mean salinity experienced in the area of the site. Tidal fresh waters are 0 - 0.5 ppt salinity; oligohaline, >0.5 - 5.0 ppt salinity; mesohaline, >5.0 - 18.0 ppt salinity.

Results

The total number of records per CMON site in the 2004-2008 data sets averaged 5,626 in spring and 14,042 in summer/autumn. Collected every 15 minutes, day and night, the records capture both diel and episodic variability. Threshold exceedance and criteria failure rates calculated from these data are thus robust measurements of shallow water conditions near the site. This is especially important for dissolved oxygen and pH which show strong diel cycles and tend to fail criteria outside of normal daylight sampling times.

Results for the spring and summer/autumn seasons are given in **Tables 3a** and **3b** (tidal fresh), **Tables 4a** and **4b** (oligohaline), and **Tables 5a** and **5b** (mesohaline). Sites are ordered from upstream (top) to downstream (bottom) in each table. The results are also depicted in **Figures 2a** through **2k** as longitudinal series along the tidal Potomac River. Note that values in the tables are rounded to the first decimal place, so failures or exceedances in less than about 0.05% of the total n are not recognized, i.e., approximately 3 of 5,626 records in spring and 7 of 14,042 records in summer/autumn.

Chlorophyll a

Median concentrations were higher and more variable in spring than in summer/autumn at both embayment and river flank sites (**Figure 2a**). Spring concentrations increased downstream, with the highest medians clustered in the mesohaline embayments Nomini Bay, Breton Bay, St. George's Cr., and Yeocomico R. and the flank sites Swan Pt. and Piney Pt. Spring medians at flank sites were typically lower than those in neighboring embayments. Summer medians were highest in embayments located near the oligohaline-mesohaline interface (**Figure 1**). Monroe Bay near Colonial Beach, VA had the highest summer medians. Summer medians at flank sites were again lower than those in neighboring embayments. Tidal fresh sites with 5 years of CMON data–Piscataway Cr., Fenwick, and Mattawoman Cr.– are showing stable or declining (improving) median concentrations in both spring and summer/autumn. An increasing (degrading) 5 year trend is occurring at the mesohaline flank site Piney Pt. in spring.

Chlorophyll *a* concentrations in shallow waters sometimes exceed the 50 µg/liter WHO screening threshold in spring but rarely exceeded that threshold in summer/autumn (**Figure 2b**). Sites exceeding the threshold more than 5% of the time in spring for one or more years were the tidal fresh embayment Piscataway Cr. (2004, 2005), the oligohaline embayment Port Tobacco R. (2007), the mesohaline embayments Monroe Bay (2007), Nomini Bay (2008), and Breton Bay (2007, 2008), and the mesohaline flank sites Swan Pt. (2006) and Piney Pt. (2008). In summer/autumn, only Monroe Bay near Colonial Beach, VA had %Chl≥50 greater than 5% (2007).

Exceedance rates of the stricter reference community maximum thresholds for chlorophyll *a* ranged as high as 93.6% (embayments) and 48.8% (flanks) in spring, and as high as 88.3% (embayments) and 33.1% (flanks) in summer/autumn (**Figure 2c**). Six embayment sites repeatedly had high seasonal exceedance rates (>50%) indicating these shallow water sites support undesirable phytoplankton communities, and by inference have poorer water column conditions. These embayments were the tidal fresh Piscataway Cr. (2004-2006), Pohick Bay

(2007-2008) and Occoquan Bay (2005, 2007, 2008), the oligohaline Potomac Cr. (2007-2008), and the mesohaline Breton Bay in spring (2007-2008), and the mesohaline Monroe Bay (2007-2008) in summer/autumn. The three tidal fresh sites with 5 years of CMON data are showing steeply declining (improving) or low/stable exceedance rates. The 5 year data set at the mesohaline Piney Pt. site is showing steeply increasing (degrading) exceedance rates in spring but possibly a declining (improving) trend in summer.

Dissolved Oxygen

The frequency of super-saturated dissolved oxygen concentrations, %SatDO, was highly variable in shallow waters, ranging from 12.6% to 93.7% in spring and 5.8% to 82.5% in summer (**Figure 2d**). %SatDO is expected to be higher in spring due to that season's cooler temperatures, which keep biological demand for oxygen low relative to photosynthesis production. This was usually the case in the tidal Potomac shallow waters. The exceptions were the embayments Pohick Bay (2008) and Port Tobacco R. (2007) and the flank sites Fenwick (2005, 2007, 2008) and Blossom Pt. (2008) which had substantially lower %SatDO in spring relative to summer. Overall, the oligohaline flank sites Blossom Pt. and Popes Cr. had the lowest %SatDO in spring; the mesohaline embayment sites Breton Bay, St. George's Cr. and St. Mary's R. and flank site Popes Cr. had the lowest % DOSat in summer/autumn.

The diel magnitude of change in percent DO saturation, or DM%Sat, reflects the alternating effects of daytime photosynthesis and nighttime community respiration over a 24-hour period. Seasonal medians of DM%Sat in shallow waters ranged from 19.2% to 71.2% in spring. They ranged from 37.1% to 78.5% in summer, with three exceptions. The exceptions were the Piscataway Cr. embayment site, the Fenwick flank site, and the Neabsco Cr. flank site, all in the tidal fresh zone (**Figure 2e**). Summer median DM%Sat values were 89.3% -131.4% at Piscataway Cr., 91.9% -121.7% at Fenwick, and 99.5% at Neabsco Cr. (**Table 3b**). On individual dates in summer, DM%Sat reached as high as 232.7% in Piscataway Cr. and as high as 228.6% at Fenwick (**Figure 3**). These are unusually large diel swings in dissolved oxygen percent saturation for any aquatic system. DM%Sat for individual dates at tidal fresh sites just a few miles downstream of Piscataway Cr. and Fenwick only reached as high as 152.9% in summer (e.g., **Figure 4**). DM%Sat correlates strongly with daily average temperature (**Figures 3, 4**), but the regression lines differ for each site and year.

Sixty-five of 110 site-season-year combinations in the tidal Potomac failed the instantaneous minimum DO criteria (%DO<Min) to some degree. Observations failed the criteria more often in summer/autumn than in spring (**Figure 2f**). In spring, only Piscataway Cr. (2004), Blossom Pt. (2006), Wicomico R. (2008), Breton Bay (2008), Piney Pt. (2006), and St. Mary's R. (2008) failed the minimum criterion more than 1% of the time. In summer/autumn, most of the 20 sites failed the minimum criterion more than 1% of the time in one or more years. Sites with *less than* 1% of observations failing in *all* season-years of monitoring were the tidal fresh sites at Fenwick (5 yrs), Pohick Bay (2 yrs), and Occoquan Bay (3 yrs), the oligohaline sites at Potomac Cr. (2 yrs), and the mesohaline sites at Nomini Bay (2 yrs) and Yeocomico R. (2 yrs).

Ten of 110 site-season-year combinations failed the 7-day mean DO criteria (%DO<7Day), 3 in spring and 7 in summer/autumn (**Figure 2g**). They were the embayments Piscataway Cr. (2004,

2005) and St. Mary's R. (2008) in spring and the embayments Piscataway Cr. (2004), Breton Bay (2006, 2007, 2008), St. George's Cr. (2008), and St. Mary's R. (2008), and the flank site Piney Pt. (2006) in summer/autumn. When criteria failures occurred, they ranged from 0.7% (St. George's Cr. 2008) to 47.9% (St. Mary's R. 2008).

Values reported for %DO<7Day in **Tables 3, 4,** and **5** are the percent of all 7-day means over an entire season that fail the CBP 7-day mean dissolved oxygen criteria for migratory fish spawning and nursery (6.0 mg/liter in spring, 4.0 mg/liter in other seasons) or open water (4.0 mg/liter in all seasons) designated uses. To more closely examine the data for relationships between the 7-day mean DO criteria and the instantaneous minimum DO criteria, the means of all CMON observations for each 7-day periods (day 1-7, day 2-8, etc.) were compared to the corresponding frequencies of instantaneous minimum DO criteria failure for those same periods.

Results for spring and summer/autumn show that the frequency of instantaneous minimum DO criteria failures observed in the CMON data during 7-day periods begins to exceed 0% at a 7-day mean of about 8 mg/liter in all salinities, well above the 7-day mean DO criteria for Maryland and Virginia water quality standards (**Figures 5, 6**). Failure frequencies of the instantaneous minimum criteria are roughly 10%-40% per 7-day period when the 7-day mean is 6.0 or 4.0 mg/liter in spring and >30% when the 7-day mean is 4.0 mg/liter in summer and autumn.

Although most Potomac CMON sites failed the instantaneous minimum criteria to some extent in one or more of the sampled 7-day periods, individual sites show different statuses. In the tidal fresh, 20% and 35% of the sampled 7-day periods for the Mattawoman and Piscataway embayments, respectively, had DO minimum criteria failures while less than 6% of the sampled 7-day periods in the Occoquan and Pohick Bay embayments and flank site Fenwick had failures. The frequency of 7-day periods with DO minimum criteria failures is much higher in Potomac oligohaline and mesohaline salinities, reaching as high as 73.5% at the Breton Bay site. Eleven of the 14 oligohaline and mesohaline sites had many (>10%) 7-day periods with minimum criteria failures. The flank site Blossom Pt. and the Potomac Cr. and Yeocomico R. embayments had the fewest 7-day periods with minimum criteria failures.

<u>pH</u>

Observations rarely fell below the instantaneous minimum criterion of pH 6.0 at the 20 CMON sites (**Figure 2h**), but frequently exceeded the instantaneous maximum criterion of pH 9.0 in oligohaline and mesohaline shallow waters during spring and in tidal fresh shallow waters during summer/autumn. (**Figure 2i**). When they occurred, failures of pH 9.0 criterion ranged from 0.1% to 61.7% (average 12.5%) in spring observations and from 0.1% to 46.9% (average 9.7%) in summer observations. Spring failure rates of the pH 9.0 criterion were highest in the mesohaline embayments Breton Bay (2007, 2008) and Yeocomico R. (2007, 2008) and at the mesohaline flank site Piney Pt. (2008). Summer/autumn failure rates were highest in the tidal fresh embayments Occoquan Bay (2005) and Mattawoman Cr. (2007) and at the flank site Fenwick (2006-2008). Failure rates of the pH 6.0 criterion only occurred in Mattawoman (spring & summer 2008) and Port Tobacco R. (spring 2008), and only in 0.3% or less of the observations. At the sites with 5 years of CMON data, %pH>9 failure rates are increasing sharply at the tidal

fresh flank site Fenwick in summer and at the mesohaline flank site Piney Pt. in spring. Otherwise, no seasonal trends are occurring.

Turbidity

Forty-one of the 110 site-season-year combinations (37%) failed the 150 NTU turbidity instantaneous maximum criterion to some degree. Failure rates were highest in spring in the tidal fresh and oligohaline salinity zones (**Figure 2j**). When they occurred, failure rates averaged 1.3% in spring and 0.3% in summer. They reached as high as 4.2% in spring (Blossom Pt. 2008) but only as high as 1.5% in summer (Piscataway Cr. 2006).

Eighty-seven of the 110 site-season-year combinations (79%) exceeded the stricter 50 NTU turbidity threshold to some degree. Frequency of exceedance was highest in spring in the oligohaline salinity zone (**Figure 2k**), reaching 30.5% in Port Tobacco R. (2008) and 28.7% at Blossom Pt. (2008). Summer exceedances of 50 NTU were generally less than 3% except for embayment and flank sites near the oligohaline-mesohaline interface. Of the 4 sites with 5 years of CMON data, the two most upstream sites, Piscataway Cr. and Fenwick, are showing increasing (degrading) trends in spring in both turbidity metrics. The mesohaline site Piney Pt. typically achieves both turbidity thresholds.

concentration in µg/liter; "%Chla > 50," % of chlorophyll a records failing the WHO screening threshold of 50 µg/liter; "%Chla > Ref," % of chlorophyll a records "%DO<Min," % of dissolved oxygen records failing the CBP instantaneous minimum dissolved oxygen criteria for migratory fish spawning and nursery use in failing a value 1/3 the MDE instantaneous maximum screening threshold. Site: E, embayment; PR, flank of tidal Potomac River. ALL VALUES ROUNDED criteria for tidal pH; "%Turb>150," % of turbidity records failing the MDE instantaneous maximum screening threshold, "%Turb>50," % of turbidity records spring, or 5 mg/liter; "%DO<7Day," % of 7-day means of dissolved oxygen records failing the CBP 7-day mean dissolved oxygen criteria for migratory fish spawning and nursery use, or 6 mg/liter for running 7-day periods; "%pH<6" and "%pH>9," % of pH records below and above, respectively, the Virginia exceed the maximal concentrations of the season- and salinity-specific phytoplankton reference communities (Buchanan et al. 2005); "% SatDO," % of records with saturated dissolved oxygen (> 100%); "DM%Sat" the median magnitude of diel (24-hr) change in dissolved oxygen percent saturation; Table 3a. Spring (March/April - May 31) continuous monitoring results for shallow tidal fresh Potomac sites. "Median Chla," median chlorophyll a

0 L	1 DECIMAL PLACE. S	See text	for further (details.									
	Potomac		Median	%Chla	%Chla			%DO	%DO	Hq%	Hq%	%Turb	%Turb
Site	Tidal Fresh (TF) Sites	Year	Chla	<u>></u> 50	>Ref	%SatDO	DM%Sat	<min< th=""><th><7Day</th><th>9≥</th><th>-9</th><th>≥ 150</th><th>>50</th></min<>	<7Day	9≥	-9	≥ 150	>50
Щ	Piscataway Cr MD	2004	21.2	7.7	88.0	43.9	71.2	7.9	10.4	0.0	5.8	0.7	11.8
		2005	18.7	6.5	58.7	51.7	35.4	0.0	3.5	0.0	11.5	0.0	19.4
		2006	21.4	4.4	72.7	69.1	48.8	0.0	0.0	0.0	13.0	0.2	7.0
		2007	11.3	3.9	41.0	55.5	40.4	0.0	0.0	0.0	2.3	2.6	21.3
		2008	6.2	0.0	12.8	31.3	25.9	0.0	0.0	0.0	0.8	3.6	18.9
PR	Fenwick MD	2004	8.3	0.1	22.5	57.2	58.4	0.0	0.0	0.0	0.7	0.2	8.6
		2005	2.0	0.0	0.1	20.3	19.2	0.0	0.0	0.0	0.0	0.0	9.9
		2006	2.1	0.0	0.4	62.6	38.2	0.0	0.0	0.0	1.9	0.0	2.0
		2007	2.3	0.0	5.5	48.0	23.7	0.0	0.0	0.0	0.0	0.1	6.0
		2008	3.0	0.0	0.0	35.5	26.4	0.0	0.0	0.0	0.0	1.9	12.0
Щ	Pohick/Gunston VA	2007	13.8	0.0	51.6	69.4	62.0	0.0	0.0	0.0	12.0	0.1	0.3
		2008	15.4	0.0	56.6	53.9	40.5	0.5	0.0	0.0	1.2	0.1	6.6
Щ	Occoquan Bay VA	2005	14.4	0.0	53.5	79.0	25.4	0.0	0.0	0.0	2.0	0.0	8.1
		2007	15.5	0.0	59.9	60.8	21.1	0.1	0.0	0.0	2.7	0.0	3.4
		2008	14.0	0.0	53.8	72.4	21.1	0.0	0.0	0.0	0.7	1.1	7.5
PR	Neabsco Cr VA	2006	1	1	ł	1	1	1	1	1	1	1	1
Щ	Mattawoman Cr. MD	2004	15.4	0.7	62.0	87.9	43.8	0.0	0.0	0.0	0.7	0.0	0.6
		2005	8.1	0.0	18.9	47.9	19.7	0.0	0.0	0.0	0.0	0.0	0.4
		2006	12.1	0.0	39.0	81.2	26.0	0.0	0.0	0.0	0.0	0.0	0.2
		2007	11.9	0.0	39.1	62.3	24.6	0.0	0.0	0.0	9.1	2.8	4.8
		2008	5.9	0.0	5.6	39.4	24.9	0.7	0.0	0.3	0.0	0.4	3.1

dissolved oxygen records failing the CBP instantaneous minimum dissolved oxygen criteria for open water fish and shellfish use, or less than 3.2 mg DO per liter at temperatures 29°C or lower and less than 4.3 mg DO per liter at temperatures greater than 29°C; "%DO<7Day," % of 7-day means of dissolved oxygen criteria for open waters fish and shellfish use, or 4 mg/liter. "DM%Sat" is separated into summer (June 1 - September 30) and autumn (after 30 September). SAV: - , no SAV in vicinity, +, SAV sparse or in vicinity, ++, SAV beds adjacent to or Table 3b. Summer and autumn (June 1 - October/November) continuous monitoring results for shallow tidal fresh Potomac sites. "%DO<Min," % of

surrounding sonde. See	Table 3a	heading ¿	and text fc	or further	details.									
Potomac		Median	%Chla	%Chla		DM%Sat	DM%Sat	%DO	%DO	Hq%	Hq%	%Turb	%Turb	
Site Tidal Fresh (TF) Sites	Year	Chla	<u>></u> 50	>Ref	%SatDO	summer	autumn	<min< td=""><td><7Day</td><td>9></td><td>->9</td><td>≥ 150</td><td>>50</td><td>SAV</td></min<>	<7Day	9>	->9	≥ 150	>50	SAV
E Piscataway Cr MD	2004	5.4	0.0	7.5	22.9	89.3	50.2	8.5	10.3	0.0	2.1	0.1	3.0	+++++++++++++++++++++++++++++++++++++++
	2005	3.2	0.0	10.2	35.9	91.5	60.6	8.4	0.0	0.0	4.5	0.0	0.2	+++++++++++++++++++++++++++++++++++++++
	2006	5.0	0.2	17.9	41.9	98.5	70.4	1.0	0.0	0.0	6.4	1.5	5.0	+++++++++++++++++++++++++++++++++++++++
	2007	2.6	0.1	7.9	53.6	131.4	63.4	0.8	0.0	0.0	8.9	0.0	0.5	+++++++++++++++++++++++++++++++++++++++
	2008	3.3	0.0	5.7	40.1	106.5	56.1	0.7	0.0	0.0	3.8	0.1	1.4	++++
PR Fenwick MD	2004	3.5	0.0	0.0	53.4	91.9	49.6	0.0	0.0	0.0	10.5	0.6	4.9	+ +
	2005	2.3	0.0	0.3	57.1	101.4	66.5	0.4	0.0	0.0	12.6	0.0	1.5	+++++++++++++++++++++++++++++++++++++++
	2006	2.3	0.0	0.1	58.6	104.6	54.7	0.3	0.0	0.0	23.5	0.1	1.8	+++++++++++++++++++++++++++++++++++++++
	2007	1.9	0.0	0.2	77.5	115.6	79.5	0.0	0.0	0.0	46.9	0.0	0.1	+++++++++++++++++++++++++++++++++++++++
	2008	2.3	0.0	0.3	80.3	121.7	79.6	0.0	0.0	0.0	30.5	0.0	1.0	+++++++++++++++++++++++++++++++++++++++
E Pohick/Gunston VA	2007	6.5	0.0	7.9	78.1	69.7	45.7	0.0	0.0	0.0	12.5	0.0	0.2	+ +
	2008	10.3	0.0	9.2	72.9	56.2	29.9	0.0	0.0	0.0	7.2	0.0	0.5	+++++++++++++++++++++++++++++++++++++++
E Occoquan Bay VA	2005	21.0	0.6	88.3	82.5	59.3		0.5	0.0	0.0	39.6	0.0	0.8	1
	2007	7.3	0.0	1.4	47.3	37.9	27.8	0.0	0.0	0.0	1.3	0.5	1.0	+
	2008	11.5	0.0	9.8	58.8	37.1	32.6	0.0	0.0	0.0	3.3	0.0	0.1	+
PR Neabsco Cr VA	2006	16.0	0.0	50.3	62.7	99.5	ł	0.2	ł	0.0	2.5	0.0	4.4	+
E Mattawoman Cr MD	2004	11.6	0.0	21.1	65.1	54.5	18.6	0.3	0.0	0.0	6.2	0.0	0.6	+++++++++++++++++++++++++++++++++++++++
	2005	6.2	0.1	6.9	44.0	50.9	35.5	5.0	0.0	0.0	0.4	0.0	0.1	‡
	2006	3.2	0.0	0.0	48.5	73.5	33.3	1.1	0.0	0.0	3.6	0.0	0.0	‡
	2007	2.7	0.0	0.0	52.9	78.5	50.3	0.5	0.0	0.0	19.5	0.0	0.0	‡
	2008	2.5	0.0	0.0	39.7	63.1	39.5	0.0	0.0	0.2	1.2	0.0	0.0	‡

and nursery use (instantaneous minimum 5 mg/liter, 7-day mean 6 mg/liter) were used because most records have tidal fresh salinities in these embayments Table 4a. Spring (March/April - May 31) continuous monitoring results for shallow oligohaline Potomac sites. The DO criteria for migratory fish spawning

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	ng. See Table 3a h∈	eading ar	nd text for fi	urther deta	ılı.								
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Potomac												
SitesYearChla ≥ 50 >Ref $\sqrt[6]{6}$ SatDODM%Sat $\langle Min$ $\langle 7Day$ $\langle 6$ ≥ 9 ≥ 150 Potomac Creek VA 2007 25.7 2.4 93.6 85.5 38.7 0.0 0.0 0.0 25.9 1.1 2008 23.2 0.8 83.7 74.5 34.8 0.0 0.0 0.0 14.0 0.3 Blossom Point MD 2006 7.8 1.5 7.3 30.3 50.6 1.6 0.0 0.0 0.6 0.7 2007 2.2 2.2 $1.7.0$ 21.1 0.0 0.0 0.0 0.0 0.6 0.7 2008 5.3 0.2 2.5 17.0 21.1 0.0 0.0 0.0 0.1 4.2 Port Tobacco R. MD 2007 30.7 7.2 37.4 -1 -1 -1 -1 -1 -1 -1 -1 -1 2008 16.3 0.1 20.0 31.2 38.1 2.7 0.0 0.0 0.0 0.0 0.0 0.0 0.0 2008 16.3 0.1 20.0 31.2 38.1 2.7 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	Oligohaline (OH)		Median	%Chla	%Chla			% DO	%DO	Hq%	Hq%	%Turb	%Turb
Potomac Creek VA 207 25.7 2.4 93.6 85.5 38.7 0.0 0.0 25.9 1.1 2008 23.2 0.8 83.7 74.5 34.8 0.0 0.0 25.9 1.1 Blossom Point MD 2006 7.8 1.5 7.3 30.3 50.6 1.6 0.0 0.0 0.6 0.3 Blossom Point MD 2006 7.8 1.5 7.3 30.3 50.6 1.6 0.0 0.0 0.6 0.7 2007 -	Sites	Year	Chla	<u>></u> 50	>Ref	%SatDO	DM%Sat	<min< td=""><td><7Day</td><td>9></td><td>-9</td><td>≥ 150</td><td>>50</td></min<>	<7Day	9>	-9	≥ 150	>50
2008 23.2 0.8 83.7 74.5 34.8 0.0 0.0 14.0 0.3 Blossom Point MD 2006 7.8 1.5 7.3 30.3 50.6 1.6 0.0 0.0 0.6 0.3 2007 - <	Potomac Creek VA	2007	25.7	2.4	93.6	85.5	38.7	0.0	0.0	0.0	25.9	1.1	9.6
Blossom Point MD 2006 7.8 1.5 7.3 30.3 50.6 1.6 0.0 0.0 0.6 0.7 2007 - </td <td></td> <td>2008</td> <td>23.2</td> <td>0.8</td> <td>83.7</td> <td>74.5</td> <td>34.8</td> <td>0.0</td> <td>0.0</td> <td>0.0</td> <td>14.0</td> <td>0.3</td> <td>3.6</td>		2008	23.2	0.8	83.7	74.5	34.8	0.0	0.0	0.0	14.0	0.3	3.6
2007 - 4.2 Port Tobacco R. MD 2007 30.7 7.2 37.4 - - - 0.0 0.0 0.0 0.1 4.2 2008 16.3 0.1 20.0 31.2 38.1 2.7 0.0 0.1 0.0 2.9	Blossom Point MD	2006	7.8	1.5	7.3	30.3	50.6	1.6	0.0	0.0	0.6	0.7	7.7
2008 5.3 0.2 2.5 17.0 21.1 0.0 0.0 0.1 4.2 Port Tobacco R. MD 2007 30.7 7.2 37.4 0.0 29.3 1.6 2008 16.3 0.1 20.0 31.2 38.1 2.7 0.0 0.1 0.0 29.3 1.6		2007	1	ł	ł	:	:	1	ł	ł	1	ł	ł
Port Tobacco R. MD 2007 30.7 7.2 37.4 0.0 29.3 1.6 2008 16.3 0.1 20.0 31.2 38.1 2.7 0.0 0.1 0.0 2.9		2008	5.3	0.2	2.5	17.0	21.1	0.0	0.0	0.0	0.1	4.2	28.7
2008 16.3 0.1 20.0 31.2 38.1 2.7 0.0 0.1 0.0 2.9	Port Tobacco R. MD	2007	30.7	7.2	37.4	1	1	1	ł	0.0	29.3	1.6	6.9
		2008	16.3	0.1	20.0	31.2	38.1	2.7	0.0	0.1	0.0	2.9	30.5

 Table 4b.
 Summer and autumn (June 1 - October/November) continuous monitoring results for shallow oligohaline Potomac sites. "DM%Sat" is separated

		SAV	ı	I	+	+	I	+	+
	%Turb	>50	1.2	0.7	7.8	6.3	11.5	3.9	4.2
	%Turb	<u>></u> 150	0.0	0.0	0.2	0.1	0.3	0.0	0.3
	Hq%	-6<	0.4	3.7	0.0	0.0	0.0	0.0	0.0
detail.	Hd%	90	0.0	0.0	0.0	0.0	0.0	0.0	0.0
or turther	%DO	<7Day	0.0	0.0	0.0	0.0	0.0	0.0	0.0
g and text i	%DO	<min< td=""><td>0.1</td><td>0.0</td><td>0.1</td><td>0.0</td><td>0.0</td><td>3.1</td><td>2.1</td></min<>	0.1	0.0	0.1	0.0	0.0	3.1	2.1
3b heading	DM%Sat	autumn	34.8	42.7	1	29.1	25.7	43.2	40.1
See lable	DM%Sat	summer	61.5	64.8	71.6	55.4	58.2	64.8	65.5
ember 30).		%SatDO	47.7	54.9	25.5	34.9	27.1	21.2	28.6
atter Septe	%Chla	>Ref	1.8	14.9	14.9	9.4	1.1	31.1	27.0
autumn (%Chla	<u>></u> 50	0.0	0.0	1.1	0.7	0.0	1.9	0.2
ir 30) and	Median	Chla	10.3	12.0	8.0	7.4	7.6	12.9	11.1
ptembe		Year	2007	2008	2006	2007	2008	2007	2008
nto summer (June 1 - Se	Potomac Oligohaline (OH)	Site Sites	3 Potomac Creek VA		R Blossom Point MD			Port Tobacco R. MD	
⊆		\mathbf{v}	I		H			Ш	

failing the CBP instantaneous minimum dissolved oxygen criteria for open water fish and shellfish use, or < 3.2 mg DO per liter at temperatures 29°C or lower and < 4.3 mg DO per liter at temperatures greater than 29°C; "%DO<7Day" % of dissolved oxygen records over a 7 day period failing the CBP 7-day mean Table 5a. Spring (March/April - May 31) continuous monitoring results for shallow mesohaline Potomac sites. "%DO<Min" % of dissolved oxygen records dissolved oxygen criteria for open waters fish and shellfish use, or 4.0 mg/liter. See Table 3a heading and text for further details.

Table 5b. Summer and autumn (June 1 - October/November) continuous monitoring results for shallow mesohaline Potomac sites. "DM%Sat" is separated into summer (June 1 - September 30) and autumn (after September 30). See Table 3b heading and text for further details.

Tabl€	e 5a. Spring.												
1.0	Potomac Mesohaline	T. S.	Median	%Chla	%Chla			%DO	%DO	Hd%	₩d%	%Turb	%Turb
Site	(MH) SITES	Y ear	Chia	0C <u><</u>	>ker	%SatDO	DM%Sat	<th><!-- Uay</th--><th>0~</th><th>6<</th><th><u>-150</u></th><th>00<</th></th>	Uay</th <th>0~</th> <th>6<</th> <th><u>-150</u></th> <th>00<</th>	0~	6<	<u>-150</u>	00<
PR	Popes Creek MD	2006	8.1	0.2	40.6	12.6	40.6	0.0	0.0	0.0	0.0	0.0	0.6
		2007	6.9	0.0	0.9	22.9	24.5	0.0	0.0	0.0	0.0	2.7	6.1
		2008	5.3	0.8	4.4	13.4	21.3	0.0	0.0	0.0	0.0	0.6	4.8
PR	Swan Point MD	2006	23.1	22.7	48.8	66.1	55.5	0.0	0.0	0.0	4.2	0.0	0.7
		2007	13.8	1.1	13.9	57.5	30.2	0.0	0.0	0.0	1.6	0.0	3.4
		2008	12.2	2.1	25.1	63.8	32.7	0.0	0.0	0.0	0.2	0.0	2.5
Щ	Monroe Bay VA	2007	22.9	9.1	48.1	43.3	37.4	0.5	0.0	0.0	1.1	0.0	15.7
		2008	17.4	2.6	33.4	55.2	36.5	0.2	0.0	0.0	0.0	0.0	7.2
Щ	Wicomico R. MD	2006	11.3	3.5	33.0	29.4	39.9	0.2	0.0	0.0	0.0	0.0	2.3
		2007	17.1	2.0	18.1	38.6	33.0	0.2	0.0	0.0	0.9	0.3	5.1
		2008	12.9	2.6	47.5	45.0	34.4	1.5	0.0	0.0	2.4	0.3	6.6
Щ	Nomini Bay VA	2007	22.4	1.0	42.7	84.4	34.5	0.0	0.0	0.0	13.3	0.0	1.7
		2008	24.0	19.8	50.0	75.6	40.0	0.8	0.0	0.0	2.9	0.0	0.0
Щ	Breton Bay MD	2006	1	1	ł	ł	1	1	1	1	ł	1	1
		2007	35.4	38.5	76.5	65.0	42.5	0.0	0.0	0.0	43.8	0.0	0.0
		2008	25.1	10.2	52.1	59.1	43.6	9.3	0.0	0.0	61.7	0.0	0.0
PR	Piney Point MD	2004	8.4	0.0	0.2	57.5	30.1	0.5	0.0	0.0	0.0	0.0	0.3
		2005	13.5	0.0	2.5	66.3	19.7	0.0	0.0	0.0	8.9	0.0	0.0
		2006	12.1	0.7	15.4	34.8	49.3	1.2	0.0	0.0	1.0	0.0	0.1
		2007	16.8	0.2	27.4	80.9	26.4	0.0	0.0	0.0	23.6	0.0	0.0
		2008	16.6	13.8	41.6	64.4	33.8	0.2	0.0	0.0	42.9	0.0	0.0
Е	St Georges Cr. MD	2006	19.6	0.8	34.2	31.6	33.3	0.3	0.0	0.0	0.0	0.0	0.0
		2007	21.1	0.5	35.3	61.0	24.8	0.0	0.0	0.0	12.4	0.0	0.0
		2008	19.3	1.6	42.2	64.2	29.4	0.2	0.0	0.0	28.3	0.0	0.1
Щ	Yeocomico R. VA	2007	20.8	1.7	40.0	91.9	30.2	0.0	0.0	0.0	30.4	0.0	0.0
		2008	26.1	3.5	55.0	85.1	30.5	0.0	0.0	0.0	37.7	0.0	0.1
PR	Sage Point MD	2004	7.9	0.0	0.1	81.8	29.5	0.0	0.0	0.0	0.0	0.0	0.0
		2005	13.2	0.0	6.3	93.7	21.3	0.0	0.0	0.0	0.0	0.0	0.0
Щ	St Mary's R MD	2008	15.9	0.6	27.3	44.0	46.0	16.0	21.7	0.0	24.5	0.0	0.0

Table	e 5b. Summer and a	autumn.													
	Potomac Mesohaline (MH)		Median	%Chla	%Chla		DM%Sat	DM%Sat	%DO	%DO	Ha%	Ha%	%Turb	%Turb	
Site	Sites	Year	Chla	<u>></u> 50	>Ref	%SatDO	summer	autumn	≤Min	<7Day	€ 99		<u>>150</u>	>50	SAV
PR	Popes Creek MD	2006	4.0	0.0	33.1	7.7	45.6	16.7	3.6	0.0	0.0	0.0	0.1	1.9	I
		2007	4.4	0.0	5.1	7.7	51.6	32.9	4.1	0.0	0.0	0.0	0.1	7.7	ı
		2008	4.6	0.2	4.1	5.8	56.7	25.0	3.2	0.0	0.0	0.0	0.5	1.9	'
PR	Swan Point MD	2006	8.3	0.5	22.9	34.5	70.1	1	1.6	0.0	0.0	0.0	0.1	5.4	ı
		2007	7.7	0.7	24.1	30.6	56.5	36.2	0.8	0.0	0.0	0.0	0.1	4.1	ı
		2008	9.9	0.4	9.3	36.4	65.3	34.0	0.3	0.0	0.0	0.0	0.0	2.7	'
Щ	Monroe Bay VA	2007	17.3	15.8	60.4	9.7	49.0	29.3	1.5	0.0	0.0	0.0	0.0	12.4	ı
		2008	18.5	3.5	77.1	21.4	58.4	27.3	1.4	0.0	0.0	0.0	0.0	6.5	ŀ
Щ	Wicomico R. MD	2006	12.8	3.0	43.6	29.6	59.5	24.5	2.4	0.0	0.0	0.0	0.9	6.0	
		2007	12.5	1.7	43.3	33.1	58.4	33.6	0.1	0.0	0.0	0.0	0.7	6.9	ı
		2008	11.0	0.2	12.0	28.8	59.4	29.4	0.1	0.0	0.0	0.1	0.1	3.8	ı
Щ	Nomini Bay VA	2007	13.2	3.3	45.5	32.0	59.8	33.5	0.7	0.0	0.0	0.0	0.0	0.0	•
		2008	12.1	0.1	34.4	38.6	59.4	36.1	0.4	0.0	0.0	0.0	0.0	0.2	1
Е	Breton Bay MD	2006	8.0	2.3	15.4	18.6	73.2	33.3	11.6	4.2	0.0	0.0	0.0	0.0	+
		2007	4.8	0.9	10.3	8.1	70.3	39.7	11.7	5.3	0.0	0.0	0.1	0.9	ı
		2008	5.2	0.1	36.9	9.5	71.7	49.2	21.2	13.4	0.0	0.0	0.0	0.0	ı
PR	Piney Point MD	2004	8.2	0.0	17.4	44.2	40.5	35.0	0.5	0.0	0.0	0.0	0.0	0.3	+
		2005	6.2	0.0	2.2	20.6	47.9	18.9	2.4	0.0	0.0	0.2	0.0	0.0	+
		2006	5.9	0.0	1.7	20.3	45.8	28.9	6.7	3.7	0.0	0.0	0.0	0.0	+
		2007	5.0	0.0	4.9	20.2	42.2	28.6	1.7	0.0	0.0	0.0	0.0	0.0	+
		2008	5.6	0.0	2.4	26.3	45.5	33.5	2.1	0.0	0.0	0.0	0.0	0.8	
Щ	St Georges Cr. MD	2006	6.2	0.0	3.6	12.1	47.6	32.2	2.5	0.0	0.0	0.0	0.0	1.7	+
		2007	4.4	0.1	0.9	9.1	48.2	25.4	2.4	0.0	0.0	0.0	0.0	0.1	+
		2008	4.0	0.0	2.0	11.7	62.9	36.9	7.4	0.7	0.0	0.0	0.0	0.1	+
Щ	Yeocomico R. VA	2007	7.5	0.0	8.9	40.4	47.6	24.3	0.1	0.0	0.0	0.0	0.0	0.0	ı
		2008	6.9	0.0	2.4	47.9	49.2	22.3	0.1	0.0	0.0	0.0	0.0	0.0	'
PR	Sage Point MD	2004	6.5	0.0	10.9	48.9	45.4	34.9	0.4	0.0	0.0	0.0	0.0	0.1	ī
		2005	6.4	0.0	14.5	36.5	52.0	22.5	1.5	0.0	0.0	0.2	0.0	0.0	'
Щ	St Mary's R. MD	2008	5.5	1.2	9.6	6.9	69.4	22.8	31.5	47.9	0.0	0.0	0.0	3.2	+

Figure 2. Longitudinal series of tidal Potomac River embayments and river flanks for 11 metrics calculated from continuous monitoring data (2004 - 2008)

a)

- a) seasonal median chlorophyll a (ug/liter)
 - b) % chlorophyll a > 50 ug/liter
 - c) % chlorophyll a > Reference
- d) % saturated dissolved oxygen
- e) magnitude of diel change in DO % saturation
- f) % of DO failing instantaneous minimum criteria
 - g) % of DO failing 7-day mean criteria h) % of pH < 6.0
- i) % of pH > 9.0
- j) % turbidity <u>></u> 150 NTU
 - k) % turbidity > 50 NTU

flank groups. See Figure 1 for site locations and relative distances from selow Fenwick in the flank group. The mesohaline salinity zone begins above Monroe Bay in the embayment group and at Popes Creek in the upstream (left) to downstream (right) in both the embayment and river each other. See Table 3, 4, and 5 headings for metric definitions and salinity zone occurs below Mattawoman in the embayment group and Open circles (o) indicate years prior to 2008, gray circles (•) indicate applications. The approximate downstream extent of the tidal fresh 2008, dashed line (- - -) is min-max line. Sites are arranged from flank group.





Embayment Stations

Flank Stations







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saturation. Summer begins on June 1 or day 152 (day 153 in leap year). Autumn begins on October 1 or day 274 (day 275 in leap year). Summer solstice, with the highest solar angle of incidence and longest daytime in the northern hemisphere, is usually on June 22 or day 173 correlations between DM%Sat and average daily temperature. DM%Sat is the difference between a date's maximum and minimum DO % Figure 3. Diel magnitude of change in dissolved oxygen % saturation (DM%Sat) at the Piscataway Creek and Fenwick sites, and yearly (day 174 in leap year).









Tidal Fresh





Figure 6. Dissolved oxygen instantaneous minimum criteria failure rates for successive 7-day periods versus the mean dissolved oxygen for the same 7day periods at 11 Potomac River nearshore sites in brackish waters (i.e., mesohaline salinities). Data are divided into embayment sites located in tidal tributaries and river flank sites located along the Potomac mainstem. Triangle: 7-day mean criteria.

Discussion and Conclusions

Metric Correspondence and Protectiveness

A metric is protective of another metric when its exceedance or failure rates are more likely to occur than those of the other metric. Significant regressions between the values of two metrics and thresholds apparent in metric-versus-metric scatter plots can indicate one metric's protectiveness of another.

Seasonal values of the three chlorophyll *a* metrics correlate significantly with each other in tidal Potomac shallow waters (**Table 6**). The spring and summer/autumn regression slopes are similar to each other, suggesting that seasonal phytoplankton community differences do not strongly influence the relationships (**Figure 7**). The frequency of chlorophyll *a* records exceeding 50 μ g/liter (%Chla \geq 50) is low until median Chla increases above 16 μ g/liter, regardless of salinity zone (**Figure 7a**). Thus, seasonal median chlorophyll *a* concentrations less than 16 μ g/liter appear to be protective of probable algal bloom toxicity and human health impacts. Exceedance rates of the phytoplankton reference community thresholds (%Chl>Ref) are clearly protective of %Chla \geq 50. **Figure 7c** shows that all the data points fall below the 1:1 line. %Chl>Ref as high as 37% are protective of %Chl \geq 50.

Wetzel (2001), Molvaer et al. (1997), and others analyzed chlorophyll *a* measured at a variety of locations and concluded that median or mean concentrations $<10 \mu g/liter$ in freshwater and <7µg/liter in marine waters generally represent desirable (mesotrophic) water quality conditions. These values are in-line with chlorophyll *a* criteria used by EPA to evaluate coastal waters in the National Coastal Condition Report III (USEPA 2008b) where "Good" is <5 µg/liter and "Fair" is 5-20 µg/liter. Several studies specific to Chesapeake Bay open water environments, including the study that quantified chlorophyll *a* concentrations of phytoplankton reference communities (Buchanan et al. 2005), have determined that median or mean chlorophyll *a* concentrations between 1.1 and 9.7 µg/liter represent desirable levels for the Bay (Table 7). The CMON data suggest these same chlorophyll *a* concentrations may also be desirable in tidal Potomac shallow waters. The average %Chla>Ref exceedance frequencies-as indicated by the linear regression lines in Figure 7b-are less than 23% when seasonal median Chla is less than 10 µg/liter. A seasonal median Chla of 5 µg/liter has average %Chla>Ref exceedance frequencies of roughly 5% to 10%. Thus, where a median Chla less than 16 μ g/liter is protective of algal bloom toxicity and human health impacts, a median Chla less than 10 µg/liter may be protective of desirable phytoplankton communities and, by inference, desirable water quality conditions.

Of the four dissolved oxygen metrics, only seasonal failure rates of the instantaneous minimum (%DO<Min) and the 7-day mean (%DO<7Day) correlate strongly and consistently with each other in both spring and summer/autumn (**Table 6**). Five of the 10 site-season-year combinations failing %DO<7Day had higher failure rates of %DO<Min; the other five failing %DO<7Day had either lower failure rates of %DO<Min or did not fail it. Based on these seasonal statistics, it is difficult to say if one DO criteria is protective of the other. When %DO<Min is calculated for 7-day periods and compared to the corresponding 7-day mean DO values, it becomes clear that the 7-day mean DO criteria of 4 and 6 mg/liter are not protective of the instantaneous minimum DO criteria (**Figures 5, 6**). The results suggest a 7-day mean DO criteria of 8 mg/liter will be

protective of the minimum criteria in most shallow waters, regardless of season, salinity, differences in plant community composition and abundance, and site-specific variations in biogeochemical oxygen consumption.

This conclusion doesn't necessarily contradict the 7-day mean DO criteria of 4 and 6 mg/liter currently in the Maryland and Virginia water quality standards. The 4 and 6 mg/liter criteria are intended to protect against chronic, sublethal impacts of low dissolved oxygen (EPA 2003). They may be more appropriate for open and deep water environments where the magnitudes of diel change in dissolved oxygen are likely to be smaller. Of the 110 site-season-year combinations in tidal Potomac CMON data, 65 failed the minimum criteria while only 10 failed the 7-day mean criteria. The results suggest the risk of mortality due to short-term exposure to very low oxygen concentrations is more common in shallow waters than the risk of chronic, sublethal impacts of low dissolved oxygen.

DM%Sat and %SatDO are not consistently protective of either %DO<Min or %DO<7Day. DM%Sat, or the seasonal median of the diel magnitude of change in dissolved oxygen percent saturation, does not correlate with %DO<Min or %DO<7Day in either season. %SatDO, the percent of super-saturated dissolved oxygen records and an indicator of the balance between plant oxygen production and community oxygen consumption, correlates negatively with both %DO<Min and %DO<7Day in summer/autumn (more supersaturated DO = less criteria failure) but with neither in spring (**Table 6**).

The frequency of pH less than 6.0, or %pH<6, does not correlate significantly with the frequency of pH greater than 9.0, or %pH>9 (**Table 6**). Only two embayments—the tidal fresh Mattawoman Cr. (2008) and oligohaline Port Tobacco (2008)—failed (fell below) the pH 6.0 criteria, and levels only dipped infrequently and slightly below 6.0. %pH>9 on the other hand is a recurring problem (**Tables 3a, 4a, 5a, Figure 2i**). Thirty-eight of 54 site-year combinations (70%) in spring experienced some level of failure of the pH 9.0 criteria, and 26 of 57 site-year combinations (45.6%) in summer/autumn failed the criteria. Daytime %pH>9 are significantly higher than nighttime values (p<0.01)

The frequency of turbidity records greater than 50 NTU (%Turb>50) correlates positively and significantly with the frequency of turbidity records greater than or equal to 150 NTU (%Turb>150) in both seasons (p<0.05). Not surprisingly,%Turb>50 is always protective of %Turb>150. The relationship between the two metrics in spring is fairly strong ($r^2=0.53$). Lower turbidity levels in summer/autumn make that season's relationship between the two metrics more difficult to discern ($r^2=0.08$). The regressions suggest that an average %Turb>50 value of ~2.5% (approximate y-axis intercept) is protective of %Turb>150. Turbidity is somewhat affected by daily precipitation at each site (**Figure 8**). It is also influenced by other factors including the presence of submerged aquatic vegetation (**Figure 9**) in summer which slows water flow and allow particles to settle, and by sediment resuspension and watershed runoff which increases turbidity.

In the Potomac shallow water CMON results, there are several instances where a metric based on one water quality parameter is protective of a metric based on another parameter. This is possible because all of the parameters are related to each other through plant production. Median Chla and %Chla>Ref correlate positively with %SatDO, DM%Sat, and %pH>9 in spring when chlorophyll *a* levels are relatively high, but not in summer/autumn when chlorophyll *a* levels are low. For spring only, higher median chlorophyll a levels and greater exceedances of the reference community thresholds are associated with higher frequencies of saturated dissolved oxgyen levels and pH 9.0 criteria failures and greater diel magnitudes of change in DO percent saturation. Overall, median Chla less than 10 µg/liter and %Chl>Ref less than 25% (with one exception) are associated with %pH>9 less than 2%, and are thus protective of the pH 9.0 criterion.

%SatDO and %pH>9 are positively correlated in both spring and summer/autumn (**Table 6**, **Figure 10a**). Diel changes in pH and dissolved oxygen saturation are also positively correlated at individual sites, indicating that as photosynthesis-driven production of oxygen increases dissolved oxygen percent saturation in daytime, photosynthesis-driven consumption of carbon dioxide and H⁺ is driving up pH. When the spring and summer/autumn %SatDO are less than 40% in tidal Potomac shallow waters, %pH>9 are less than 4.5% in all salinities. %SatDO less than 40% is thus somewhat protective of the pH 9.0 criteria.

%SatDO less than 40% may protect against high pH, but some embayments sites with particularly low %SatDO in summer/autumn–less than 20%–can fail the dissolved oxygen criteria. Very low %SatDO indicates overall oxygen consumption is outweighing oxygen production in shallow waters. Ten of the 11 summer/autumn site-year combinations with %SatDO <20% fail the summer/autumn dissolved oxygen minimum criteria by more than 2%. All are mesohaline embayments or flank sites: Monroe Bay (2007), Breton Bay (all years), St. George's Cr. (all years), St. Mary's R. (2008), and Popes Cr. (all years). Two of these–Breton Bay (2007, 2008) and St. Mary's R. (2008)–also fail the summer/autumn dissolved oxygen 7-day mean criteria. Popes Cr is somewhat turbid, but the other sites are not unusually turbid. Five of the ten site-season-year combinations had sparse SAV beds in the vicinity of the sondes, indicating some photosynthesis is occurring. DM%Sat was generally on the high side at these sites (**Table 5b**), indicating oxygen consumption is probably high.

%SatDO is negatively correlated with %Turb>50 in both spring and summer/autumn (**Figure 10c**). The seasonal relationships have similar slopes but are displaced, with the summer/autumn slope lower than the spring slope. Increasing turbidity in spring is likely suppressing photosynthesis by phytoplankton, given that %SatDO correlates positively with the chlorophyll *a* metrics in that season (above). The absence of summer/autumn relationships between %SatDO and the chlorophyll *a* metrics, and the persistence of a relationship between %Turb>50 and %Sat DO, suggests turbidity is depressing photosynthesis by another plant group(s).

The magnitude of diel change in dissolved oxygen is an important management consideration if pre-dawn oxygen levels fail the minimum criteria. The usefulness of the metric DM%Sat is complicated by the influence of temperature (**Figures 4, 5**), gas transfer across the air-water interface, and the site-specific and competing influences of oxygen production by plant and oxygen consumption by plants, animals, bacteria, and sediments. It thus does not exhibit straightforward relationships with %DO<Min in spring or summer/autumn. DM%Sat relationships with plant parameters indicates the relative influence of plant oxygen production on the metric. For example, a positive albeit weak relationship between DM%Sat and the

chlorophyll *a* metrics occurs in spring (**Table 6**, **Figure 10b** upper panel); it does not occur in summer/autumn (see below). DM%Sat in summer/autumn is significantly higher at embayment and flank sites with either sparse or abundant SAV (p<0.01). Summer/autumn DM%Sat also correlates significantly with %SatDO and %pH>9 (p<0.01) (**Table 6**).

The summer/autumn DM%Sat-chlorophyll *a* relationship is complicated by the Piscataway Cr. embayment and Fenwick river flank site (**Figure 10b** lower panel). When data for these two sites are included, the DM%Sat-median Chla relationship appears *negative*; when the data are removed, the relationship is not significant (p<0.05). Piscataway Cr. and Fenwick are closest to metropolitan Washington DC. They have low median Chla ($\leq 5 \mu g$ /liter) and abundant SAV in summer/autumn. When compared to similar tidal fresh embayments further downstream, the two sites have higher %Turb>50 and unusually large DM%Sat. These results suggest the potentially high oxygen production rates from the abundant SAV in Piscataway Cr. and Fenwick may be somewhat suppressed by turbidity and significantly countered by high chemical and/or biological oxygen demand in the embayment. The two sites exemplify the importance of considering multiple parameters when assessing shallow water systems.

Phytoplankton are a constituent of turbidity and one of the factors that attenuate underwater light. Conventional wisdom says phytoplankton blooms block sunlight from reaching underwater grasses, or SAV (<u>www.chesapeakebay.net</u>). Seasonal correlations between %Chla \geq 50 or %Chla>Ref and %Turb \geq 150 test whether the frequency of phytoplankton *blooms* correlates with the frequency of the larger turbidity spikes. They do not in spring and summer/autumn (**Table 6**). Similarly, %Chla \geq 50 and %Chla>Ref do not correlate with the lower turbidity threshold %Turb \geq 50 in spring. However, the summer correlations with %Turb \geq 50 are inconclusive. The %Chla \geq 50 - %Turb \geq 50 relationship is driven by a single data point and is not significant if this point is removed. The %Chla \geq Ref - %Turb \geq 50 relationship is significant but weak (p<0.01, r² = 0.12) and the plot shows a lot of scatter.

These results suggest phytoplankton *blooms* are not a major constituent of the turbidity spikes in tidal Potomac shallow waters. Seasonal *medians* of chlorophyll *a* and turbidity represent the central tendencies or the non-bloom, non-spike periods of the two parameters. The seasonal medians do not correlate in spring (n=54, p<0.05). They are significantly, strongly, and positively correlated in summer/autumn (n=57, p<0.01, r²=0.49) (**Figure 11**). The summer/autumn relationship suggests that, in this season, reducing chlorophyll *a* concentrations in shallow waters can lower background turbidity in a fairly predictable manner.

Plant Groups

Seasonal changes in the chlorophyll *a* relationships with %SatDO,%pH>9, and DM%Sat indicate phytoplankton are important primary producers (i.e., consumers of carbon dioxide and producers of dissolved oxygen) in spring when their abundances are relatively high, but not in summer and autumn when their abundances are typically lower. Photosynthesis by abundant phytoplankton, or water column algae, appears responsible for many of the spring pH 9.0 criterion failures in Potomac shallow waters between 2004 and 2008. The fact that a) the seasonal %SatDO and %pH>9 values remain correlated in summer/autumn, even as their relationships with chlorophyll *a* disappear, and b) the summer diel magnitude of change in dissolved oxygen saturation–as well

as the diel magnitude of change in pH– remain large, suggests that plant group(s) other than phytoplankton are important summer and autumn primary producers.

Examination of the summer/autumn data support this idea. Of the 25 site-year combinations failing the pH 9.0 criteria to some degree in summer/autumn, 17 have abundant SAV beds adjacent to or surrounding the sonde and 3 have sparse SAV beds or beds in the vicinity. Of the 23 site-year combinations with %SatDO greater than 40%, the threshold protective of the pH 9.0 criteria (see above), 14 are associated with SAV beds adjacent to or surrounding the sonde and 3 have SAV beds or beds in the vicinity. The 27 summer/autumn site-year combinations with no pH 9.0 criteria failures *and* %SatDO less than 40% have either sparse SAV beds or no SAV.

SAV are monitored in a yearly CBP aerial survey during the April 1 - October 31 SAV growing season (http://web.vims.edu/bio/sav/). SAV emerge from the sediments each spring, grow during summer, and die off in late autumn. Populations have become reestablished in the tidal fresh Potomac (Figure 12a through 12e). Piscataway Cr. and Mattawoman Cr. met or exceed their CBP SAV goals. Pohick Bay in Gunston Cove is approaching its goal. The river flank site Fenwick has dense SAV beds and SAV are returning to Occoquan Bay and Neabsco Cr. SAV status in Potomac oligohaline and mesohaline salinity zones is not as robust (Tables 4b, 5b). Sparse SAV beds are found at Blossom Pt., Port Tobacco R., Breton Bay, Piney Pt., St. George's Cr., and St. Mary's R. The beds at Blossom Pt., Breton Bay, and Piney Pt. have recently declined.

Not much is known about benthic algal populations in the tidal Potomac because they are not routinely monitored. The term "benthic algae" is used generically here and includes seaweeds, epiphytic algae, and algae living in or on sediments or attached to hard surfaces. Their presence in summer/autumn can be inferred at CMON sites with relatively low median Chla ($<8 \mu g$ /liter) *and* little or no SAV (+, –) *and* dissolved oxygen or pH values associated elsewhere with high photosynthesis rates. The presence of abundant benthic algae in spring can be similar inferred if we assume the sparse SAV beds identified in the summer survey reflect sparse SAV emerging in spring. For this analysis, %SatDO >40% or pH 9.0 criteria failing more than 0% or DM%Sat >51% (summer only) were thresholds used to identify potential site-season-years with abundant benthic algae populations (**Table 8**). Their populations, according to these criteria, seem to be most prevalent in higher salinity waters, on the river flanks. Benthic algae in shallow well lit waters are thought to be capable of significantly slowing the nutrient transfer between sediments and the water column (Cerco and Seitzinger 1997).

Some Management Implications

Tidal waters of the Potomac River are weakly buffered by carbonate alkalinity and thus will be subject to daytime pH increases when photosynthetic CO_2 consumption is heavy. In the 1960s-1980s, massive algal blooms in the tidal fresh Potomac mainstem and embayments regularly drove summer pH values to very high levels, causing the release of sediment phosphorus to the water column where it further fueled the algal blooms (MWCOG 1984, Thomann et al. 1985). Dissolved oxygen levels "sagged" in the upper Potomac mainstem as these blooms peaked and died (Jaworski and Romano 1999).

Summer phytoplankton populations in Potomac shallow waters are not as abundant as they once were. Spring and especially summer chlorophyll *a* concentrations at embayment and flank sites along the length of the Potomac are approaching Chesapeake Bay historical (1950s) levels, benchmark levels (Olson 2002, EPA 2003 Table V-5), and phytoplankton reference community levels (**Table 7**). These levels are deemed desirable for rehabilitating tidal ecosystems. The 1960s-1980s phenomenon of huge summer phytoplankton blooms and extremely high pH in shallow, tidal fresh Potomac waters are no longer indicated in the 2004-2008 CMON results. However, pH still rises above 9.0, albeit more frequently in spring than summer (**Figure 2i**), and summer dissolved oxygen drops below minimum criteria (**Figure 2f**) at most of the shallow water CMON sites.

Are pH values that exceed 9.0 an interim sign of recovery?

The high frequencies of pH>9 and supersaturated DO found at some Potomac shallow water sites demonstrate that plant photosynthesis is still relatively strong in both spring and summer/autumn regardless of the plant type responsible. This is true for both high (mesohaline) and low (oligohaline and tidal fresh) salinities. Low summer/autumn chlorophyll *a* concentrations in concert with abundant SAV or high pH-high %SatDO at many sites indicate primary production is shifting out of the water column to the bottom in summer and autumn.

High primary production in tidal shallow waters is not necessarily linked to high nutrient loads from the watershed. Jones et al. (2008), Jones (2009), and others hypothesize that phosphorus stored in sediments is released to the tidal water column when pH is high and has, until recently, maintained water column phosphorus at concentrations higher than those in the non-tidal tributaries. The apparent summer/autumn shift of primary production to the bottom suggests that sediment phosphorus concentrations have declined to a point where they can no longer support high water column concentrations, and benthic algae and SAV are gaining a competitive advantage over phytoplankton due to their closer proximity to the diminishing sediment phosphorus supply. High primary production, indicated by high %pH>9 and %SatDO, *and* low chlorophyll *a* may thus represent an intermediate stage of recovery in shallow waters.

What are the most likely causes of minimum DO criteria failures?

Spring %DO<Min occurred at approximately 1/3 of the site-season-year combinations but failure rates were typically low, less than 3%. The exceptions are Piscataway (2004), Breton Bay (2008), and St Mary's R (2008). Summer/autumn %DO<Min were more frequent, occurring at slightly more than ½ of the tidal fresh and oligohaline and all of the mesohaline site-season-year combinations. Piscataway (2004), Breton Bay (2006-2008), and St Mary's R (2008) had the highest failure rates.

Conventional wisdom says that phytoplankton blooms deplete oxygen both with night-time respiration and when they die, sink, and decay (<u>www.chesapeakebay.net</u>). The three chlorophyll *a* metrics representing phytoplankton did not correlate with %DO<Min in spring or in summer/autumn at the Potomac shallow water CMON sites (**Table 6**). Phytoplankton are thus not immediately and directly associated with the DO criteria failures. A cross-season comparison between spring median Chla and summer/autumn %DO<Min in Potomac embayments is also

non-significant (p<0.05). Dying spring blooms may wash out of embayments before too much of their organic matter is incorporated into the sediments. Phytoplankton respiration and decomposition are no doubt factors in overall oxygen consumption in shallow waters, but other factors appear to have more of an impact on %DO<Min in Potomac shallow waters–even in spring when chlorophyll *a* concentrations are highest.

If we consider %DO<Min as the cumulative, site-specific result of all oxygen production and consumption factors and look at plant relationships with the DO metrics that reflect these competing influences, some of the underlying plant relationships to %DO<Min can be discerned. In spring, phytoplankton are strongly related to both %SatDO and DM%Sat. Cooler temperatures in spring tend to favor higher %SatDO, so failures of the minimum DO criteria-when they occur-often correspond to large DM%Sat. In summer/autumn, SAV and the inferred benthic algae populations are correlated with %SatDO or DM%Sat; phytoplankton are not. Sites with very low %SatDO and relatively large DM%Sat have, on average, the highest failure rates of the DO minimum criteria (Figure 13a). The large DM%Sat at these sites indicate high primary production rates paired with high oxygen consumption rates. The low %SatDO indicate the balance between these competing processes is periodically upset by environmental factors that temporarily reduce oxygen production (e.g., storm-related spike in turbidity), making the site prone to DO criteria failure. This pattern occurs at sites with little or no SAV (Figure 13b) and with abundant SAV (Figure 13c). Areas with abundant SAV may in fact be more prone to %DO<Min than areas with little or no SAV because higher %DO<Min occur at equivalent %SatDO and DM%Sat ranges. Based on Figure 10c, one can hypothesize that this phenomenon occurs because periods of high turbidity and poor water clarity impact SAV and benthic algae photosynthesis more than they impact phytoplankton photosynthesis.

Which of the nine CMON-based metrics analyzed are most useful?

Of the nine metrics used in this analysis, %pH<6 was the least useful for integrating information and interpreting shallow water ecological condition. Low (acid) pH is very rarely a problem in the tidal Potomac. %Chla≥50, %DO<7Day, and %Turb≥150 were frequently 0.0%, making them difficult to use in correlative analyses, but their failure rates are associated with specific human health issues or ecosystem stresses and are thus useful as "red flags." The metrics most useful in interpreting the CMON data and demonstrating achievement of desirable water quality conditions were median Chla, %Chla>Ref, %SatDO, DM%Sat, %DO<Min, %pH>9, and %Turb>50.

Integrative analyses of CMON shallow water data using these metrics yielded insights into the stages of recovery from eutrophication impacts. Just as some failure of the pH 9.0 criterion in the presence of low chlorophyll *a* concentrations may be an interim sign of recovery, some failure of the DO minimum criteria may be associated with returning SAV–one of the desired signs of ecosystem recovery. State water quality criteria may not be achieved immediately or completely as tidal shallow waters recover from eutrophication impacts. Sufficient time could be needed before turbidity levels no longer impede photosynthesis, bottom-oriented plant communities become well established, sediment nutrient releases to the water column are further reduced, and the competing processes of oxygen production and consumption produce smaller DM%Sat and %SatDO ranging between 30% and 50%. Future analysis of the CMON

conductivity and salinity data will help delineate the extent of the Potomac mainstem's tidallydriven incursions as well as the influence of watershed nutrient and sediment loads on embayment and flank conditions.

Will watershed TMDLs for listed causes of impairment be effective?

Most of the tidal Potomac embayments are listed as impaired by one or more eutrophication parameters. Virginia's tidal fresh Neabsco Bay and Occoquan Bay have been listed as impaired for high pH in multiple TMDL reporting cycles. Virginia has listed all of its mesohaline embayments between Mathias Pt. neck and the Potomac River mouth as impaired by low dissolved oxygen and by poor water clarity (as evidenced by the absence of abundant SAV). Maryland has listed MD-POTTF, MD-POTOH, and MD-POTMH, its 3 Chesapeake Bay Program segments for the tidal Potomac mainstem, as impaired by total nitrogen, total phosphorus, and/or total suspended sediments. The mainstem segments include all Maryland tidal embayments except Mattawoman Cr. (MATTF), Piscataway Cr. (PISTF), Port Tobacco (POTOH2), and Nanjemoy Cr. (POTOH3). These four embayments are listed separately as impaired by total nitrogen and total phosphorus, and Piscataway Cr. is listed for total suspended solids (MDE 2008).

303(d)/305(b) listings of Potomac estuarine water bodies often implicate watershed nutrient and sediment loads as the ultimate source(s) of impairment. Rigorous comparisons of nutrient and sediment concentrations in the watershed, the shallow waters, and the mainstem waters are a future analysis that can inform the Potomac TMDL process. Currently, the ambient water quality data collected bi-weekly or monthly in Potomac Coastal Plain watersheds are showing long-term declines in total phosphorus (TP) and total suspended sediment (TSS) in many tributaries. TSS concentrations upstream of, for example, Piscataway Cr., Pohick Bay, Occoquan Bay, and Mattawoman Cr. are typically lower now than in the embayments. TP concentrations upstream of Pohick Bay and Mattawoman Cr. are also lower than in the embayments. Phosphorus in tidal shallow waters sometimes drops to concentrations that forestall estuarine algal bloom formation (Buchanan 2008, unpublished analyses), and chlorophyll *a* levels are substantially lower than a decade ago and are approaching desirable levels. The CMON results presented in this report suggest that the passage of adequate time to draw down sediment-bound phosphorus may now be more effective in restoring Potomac tidal shallow waters than additional watershed reductions. Restoration efforts in the shallow waters rather than upstream of them, such as boat wake restrictions, shoreline stabilization, and re-vegetation to reduce sediment resuspension, could expedite recovery (e.g. Reel 2009).

Table 6. Linear regressions for spring (lower left) and summer/autumn (upper right) CMON results for tidal Potomac shallow waters. See Tables 3, 4, and 5 headings for metric definitions. Significance: **, p<0.01; *, p<0.05; ns, not significant. Blue highlight, seasonal regressions are both significant (p<0.01); yellow highlight, seasonal regressions are different; a, regression is misleading (see text for details) or removal of 1 data point makes regression non-significant (p<0.05).

SUMMER/ AUTUMN	%Chla>50	%Chla>Ref	Median Chla	%SatDO	DM%Sat	%DO <min< th=""><th>%DO<7Day</th><th>%PH<6</th><th>%pH>9</th><th>%Turb<u>></u>150</th><th>%Turb>50</th><th></th></min<>	%DO<7Day	%PH<6	%pH>9	%Turb <u>></u> 150	%Turb>50	
02 <d1ut%< td=""><td>** a</td><td>*</td><td>*</td><td>*</td><td>su</td><td>su</td><td>su</td><td>su</td><td>su</td><td>**</td><td></td><td>02<d1ut%< td=""></d1ut%<></td></d1ut%<>	** a	*	*	*	su	su	su	su	su	**		02 <d1ut%< td=""></d1ut%<>
021 <u>≤</u> d1uT%	SU	SU	Su	SU	SU	us	SU	su	IJS		**	021 <u>≤</u> d1uT%
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9>Hq%	su	su	su	su	su	su	su		ns	su	su	9>Hq%
%DO<7Day	su	su	su	*	su	* *		su	su	su	su	%DO<7Day
niM>OU%	su	su	su	* *	su		* *	su	su	su	su	niM>OG%
DM%Sat	su	su	** a	* *		* *	su	su	su	SU	su	DM%Sat
%SatDO	su	su	su		su	su	su	su	* *	* *	* *	%SatDO
Median Chla	* *	* *		* *	*	su	su	su	* *	su	su	Median Chla
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Table 7. Range of spring and summer/autumn chlorophyll *a* (µg/liter) mean or median concentrations observed in the tidal Potomac River shallow water CMON data as compared to various indicators of desirable chlorophyll *a* concentrations for Chesapeake Bay phytoplankton communities: spring and summer (June-September) historical (1950s) means in the Bay mainstem, benchmark medians for open waters derived with the Relative Status Method (from Olson 2002 and USEPA 2003 Table V-5), and phytoplankton reference community medians (Buchanan et al. 2005). See text for details.

Salinity zone	Historic mean	Benchmark Mean	Ref. Com. Median	CMON Embayments Medians	CMON Flanks Medians
			Spring		
Tidal Fresh	1.1	3.1	4.3	5.9 - 21.4	2.0 - 8.3
Oligohaline	2.3	5.1	9.7	16.3 - 30.7	5.3 - 7.8
Mesohaline	3.7	6.9	5.6	11.3 - 35.4	5.3 - 23.1
			Summer/Autu	ımn	
Tidal Fresh	1.1	7.3	8.6	2.5 - 21.0	1.9 - 16.0
Oligohaline	2.0	8.0	6.0	10.3 - 12.9	4.0 - 8.0
Mesohaline	4.4	8.4	7.3	4.0 - 18.5	5.0 - 8.3

Table 8. Site-season-year combinationsindicated in the results as potentially havingsignificant summer benthic algaepopulations (see text for details).

Salzone	Name	Year
Embayments		
TF	Occoquan Bay VA	2007
MH	Breton Bay MD	2007
MH	Breton Bay MD	2008
MH	St Georges Cr. MD	2008
MH	Yeocomico R. VA	2007
MH	Yeocomico R. VA	2008
MH	St Mary's River MD	2008
River Flanks		
OH	Blossom Point MD	2007
OH	Blossom Point MD	2008
MH	Popes Creek MD	2007
MH	Popes Creek MD	2008
MH	Swan Point MD	2007
MH	Swan Point MD	2008
MH	Piney Point MD	2005
MH	Sage Point MD	2004
MH	Sage Point MD	2005







Figure 8. Relationships of daily maximum turbidity (NTU) from CMON data and daily total precipitation (mm) for four tidal fresh embayments, 2008. Precipitation is the averaged daily amounts measured at National (Reagan)Airport VA, College Park MD, Laurel MD, and Frederick MD.



Figure 9. Frequency of summer/autumn exceedances of the 50 NTU turbidity threshold versus relative abundance of submerged aquatic vegetation (SAV). Key: -, no SAV in vicinity; +, SAV sparse or in vicinity; ++, SAV beds adjacent to or surrounding sonde.



regressions through spring and summer/autumn results; dashed line, spring regression line inserted for comparison purposes; symbols circled in blue, Piscataway (•) and Fenwick (◊) results; *, DM%Sat in lower panel is only for summer, not summer/autumn. Figure 10. Correlations between a) %pH>9 and %SatDO, b) DM%Sat and median Chla, and c) %SatDO and %Turb>50. Solid black line, linear



Figure 11. Median chlorophyll a (Chla) versus median turbidity for tidal Potomac River embayments (solid symbols) and river flanks (open symbols). Phytoplankton, expressed here as chlorophyll a, are a constituent of turbidity.



Figure 12a. Annual SAV coverage in the embayment Piscataway Cr.MD and river flank site Fenwick MD. CMON site indicated with red *. Data downloaded from http://web.vims.edu/bio/sav/.



Figure 12b. Annual SAV coverage in the embayment Pohick Cr. / Gunston Cove VA.





10-405

0-10%

1,000 2,00 Hectares of SAV: 535.73 Date Flown: 10/03, 10/31, 11/06

1,000





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