Elevated pH Levels in Potomac Tidal Fresh Embayments as a Possible Indicator of Recovery

Claire Buchanan
Interstate Commission on the Potomac River Basin
51 Monroe St PE-08
Rockville, MD 20850
cbuchan@icprb.org

October 31, 2008

ICPRB Report 08-3

This report was prepared by the Interstate Commission on the Potomac River Basin. Funds were provided by the U.S. EPA (I-98339408, I-98339409) and the signatory bodies to the Commission: The District of Columbia, Maryland, Pennsylvania, Virginia, and West Virginia.

Elevated pH Levels in Potomac Tidal Fresh Embayments as a Possible Indicator of Recovery

Claire Buchanan
Interstate Commission on the Potomac River Basin
51 Monroe St PE-08
Rockville, MD 20850
cbuchan@icprb.org

October 31, 2008

Introduction

This analysis begins to explore relationships between water quality and living resources in the Potomac River's tidal freshwater embayments. The analysis focuses primarily on continuous monitoring data for total chlorophyll (chl), dissolved oxygen (DO), DO percent saturation (%DOsat), and pH, with the purpose of determining if phytoplankton (free-floating algae), benthic algae, and/or submerged aquatic vegetation were possible causes of elevated pH levels in these systems. pH values greater than 9.0 are considered an indication of nutrient enrichment because they are often the result of rapid photosynthesis by aquatic plants in poorly buffered, nutrient rich environments. Rapid photosynthesis by abundant plant populations quickly reduces dissolved carbon dioxide (CO_2), causing a shift in the CO_2-water equilibrium and resulting in high pH levels. The high pH levels then allow sediments to release the nutrient phosphorus more quickly to the water column, where it can spur more phytoplankton growth and algal blooms.

Several Potomac tidal fresh embayments frequently have pH values of 9.0 and above. Virginia's Neabsco Bay and Occoquan Bay have been specifically listed as impaired for high pH in one or more TMDL reporting cycles. The source of the pH impairment is listed as unknown, although excess nutrient loads from the watershed are suspected because water column concentrations of chlorophyll *a* in these waters have sometimes been high (greater than 50 µg/liter). Maryland has listed Piscataway Creek and Mattawoman Creek as impaired for high loads of nitrogen, phosphorus, and/or total suspended solids. High pH values and chlorophyll concentrations have been documented in these and other Maryland tidal fresh embayments of the Potomac. TMDLs intended to correct pH impairments are essentially the same as TMDLs intended to correct nutrient and sediment impairments – both focused on reducing controllable nutrient and sediment loads to the estuary from non-tidal streams and watershed runoff.

TMDL-related reductions in watershed nutrient and sediment loads will probably not elicit immediately responses (reductions) in pH. Legacy sediments in Potomac tidal fresh embayments are rich in phosphorus. Sediment phosphorus releases are likely to counteract watershed phosphorus load reductions and sustain high phytoplankton productivity rates and high pH levels in the years immediately following TMDL load reductions. Eventually, water column phosphorus concentrations decline, resulting in lower phytoplankton abundance. Primary production rates, however, can still remain high if benthic algae and/or submerged aquatic vegetation (SAV) successfully replace phytoplankton as the dominant primary producers of the system. Such a shift would be evident as a decrease in water column chlorophyll coupled with continued high (supersaturated) dissolved oxygen and high pH. Large benthic algae or SAV populations have the potential to further limit the phytoplankton growth. Benthic algae in or on the sediment surface intercept dissolved phosphorus diffusing from the sediments, and SAV roots and rhizomes absorb phosphorus directly from sediment interstitial waters before it reaches the water column.

Low water column concentrations of chlorophyll juxtaposed with high pH and DO saturation levels can thus indicate a stage of recovery in tidal fresh embayments of the Potomac River. In this report, continuous monitoring data collected in four tidal fresh embayments (Piscataway Creek MD, Pohick Bay in Gunston Cove VA, Occoquan Bay VA, Mattawoman Creek MD) were explored to determine if they support this conceptual model. The results were compared to a nearshore continuous monitoring site on the flank of the Potomac mainstem (Fenwick MD) and to biomonthly data collected at fixed stations in the Potomac mainstem (TF2.1, TF2.2, TF2.3, TF2.4). Although continuous monitoring data were obtained for all Potomac salinity zones, the analysis presented here is restricted to tidal fresh embayments because a) higher salinities tend to buffer pH in the 7-8 range, and b) there were inconsistencies in the low salinity (oligohaline) data that made them difficult to interpret with confidence at this time.

Data

Continuous monitoring data were obtained from the Maryland Department of Natural Resources (MDDNR) and the Virginia Institute for Marine Sciences (VIMS). The data can also be downloaded from http://mddnr.chesapeakebay.net/eyesonthebay/index.cfm and http://www2.vims.edu/vecos/. Water temperature, salinity, dissolved oxygen (DO) saturation, DO concentration, pH, turbidity, and fluorescence (a measure of chlorophyll-a present in the water column) measurements are recorded at 15 minute intervals with a YSI 6600 sonde (sensors and data logger) that is anchored 0.3 m - 0.5 m above bottom or suspended at a constant depth below the surface of the water. The sondes are usually deployed between late March and early November, when plant productivity rates are highest. Station locations and sampling periods are listed in **Table 1**.

Data from the Potomac fixed station bimonthly monitoring program located outside of these embayments (TF2.1, TF2.2, TF2.3, and TF2.4) were downloaded from www.chesapeakebay.net. These data are collected in mid-channel in the Potomac mainstem by MDDNR.

Analysis Results

Values of pH $\geq$ 9.0 in the continuous monitoring (CMON) data sets of four tidal fresh Potomac River embayments (Piscataway, Pohick, Occoquan, Mattawoman) ranged from 0.31% to 27.4% over the April - October period (**Table 1**). pH $\geq$ 9.0 on the flank of the Potomac mainstem (Fenwick) were slightly higher, ranging from 8.7% to 33.1%. In contrast, values of pH $\geq$ 9.0 were not observed after 2001 in the bimonthly Potomac River mainstem data collected in the Maryland tidal fresh zone (**Table 2**).

All the CMON measurements show a diel (daily) cycle of pH and dissolved oxygen percent saturation, with rising values during the daytime and falling values at night time. The frequency of pH ≥ 9.0 is on average 1.2% higher when only daytime pH values, when photosynthesis occurs, are considered (**Table 1**). These pattern strongly implicate the influence of plant photosynthesis on water chemistry in these shallow environments.

Three types of plants common to the Potomac estuary have the potential to influence pH and dissolved oxygen percent saturation to this degree: algae that inhabit the surface layer of sediments in shallow, well-lit waters (benthic algae); algae that inhabit the water column (phytoplankton); and vascular plants which include submerged aquatic vegetation (SAV). Benthic algae are presently not monitored in the tidal fresh Potomac.

Water column chlorophyll, a rough indicator of phytoplankton biomass, is routinely measured. Concentrations at the mainstem, flank, and embayment stations did not exceed the Virginia screening threshold of 50 µg/liter very often between 2004 and 2007. The continuous monitoring data indicates median concentrations are higher and screening threshold exceedances are more frequent in Spring (**Table 3**). Piscataway Creek generally has the highest median concentrations and exceedance frequencies. Fenwick, along the flank of the mainstem, had the lowest median concentrations and exceedance frequencies. The mainstem stations TF2.1, TF2.2, TF2.3 and TF2.4 had no March - November chlorophyll *a* records greater than 50 µg/liter after 2002, and median concentrations were lower than Fenwick and trending downward (**Table 2**).

SAV became reestablished in many Potomac tidal fresh embayments in the mid- to late 1980s. SAV coverage during the years that continuous monitors were deployed is shown in Figures 2-5. The coverage extent ranged from nearly 100% (Piscataway 2007) to sparse (Occoquan 2005).

In the tidal fresh embayments, high chlorophyll *a* concentrations are associated with high pH values and high percentages of dissolved oxygen saturation during Spring, but not Summer and Autumn (**Figures 6 - 9**). Clear and significant relationships between daily maximum chlorophyll concentration and daily maximum pH value occur in all years in Piscataway, Pohick, and Occoquan and in two of four years in Mattawoman during Spring. [The same relationships appear for daily mean chlorophyll and mean pH because the mean and maximum are correlated (not shown)]. Similar, significant relationships are found during Spring between daily maximum chlorophyll and daily maximum percent saturation of dissolved oxygen. As phytoplankton biomass increases in Spring, pH and % DO saturation in the water column increase. Both relationships disappear in Summer and Fall, even though chlorophyll concentrations exceed the screening threshold at times and could be expected to influence pH and % DO saturation (e.g. Mattawoman Creek and Occoquan Bay in 2005, Piscataway Creek in 2006 and 2007). Summer pH levels and % DO saturation are generally greater than Spring levels (**Figures 6 - 9**), indicating the combined primary production of all plant types in these shallow tidal fresh waters is at the annual peak. The highest pH value recorded was 9.89 (Piscataway 2006); the highest % DO saturation was 259%.

The Spring relationships between chlorophyll-pH and chlorophyll-% DO saturation are not as strong at Fenwick on the tidal fresh river flank. The Spring relationship is evident in only one (2004) of four years (**Figure 10**). Like the embayments, no relationships are evident during

Summer and Autumn in any of the four years. Overall productivity of the area seems to be increasing, however, with daily maximum pH reaching as high as 10.0 and daily maximum % DO saturation exceeding 250% in 2007. While this environment is shallow like the four embayments, it is more exposed to the influence of the river mainstem.

At the four stations in the river mainstem, positive Spring *and* Summer relationships to chlorophyll a concentration are evident in pH (**Figure 11)** and % DO saturation (**Figure 12**). Unlike the embayments, values of pH and % DO saturation tend to be higher in Spring rather than Summer. Phytoplankton would be the dominant primary producer in the mainstem. SAV and benthic algae are not likely to influence pH and % DO saturation here except through horizontal transport from the river flanks and embayments. The relatively low, narrow ranges of values for pH (7.1 - 9.1) and % DO saturation (52% - 164%) indicate overall primary production may presently be lower in the mainstem than in either the river flanks or embayments.

Discussion

Significant, positive relationships of pH and % DO saturation with water column chlorophyll concentration during Spring indicate that phytoplankton are primarily responsible for the observed variability in pH and % DO saturation at this time in the tidal fresh Potomac embayments and mainstem. These relationships continue in the Potomac mainstem during Summer and Autumn but disappear in the embayments, where pH and % DO saturation climb to high daily maxima and chlorophyll concentrations generally decline or remain the same as in Spring. The results suggest that shallow water plants–specifically SAV and/or benthic algae–may assume an influential role in the embayments during Summer and Autumn.

Continuous monitoring sondes in Piscataway Creek, Mattawoman Creek, and Pohick Bay were initially located at the edges of the SAV beds but over time have become surrounded by SAV beds (**Figures 2, 3, and 4**). The influence of SAV photosynthesis cannot be differentiated from that of benthic algae in these systems. The continuous monitoring sonde in Occoquan Bay is located offshore, relatively distant from SAV beds (>1000 m). The SAV beds were very small in 2005 (**Figure 5**). Occoquan Bay thus offers an opportunity to indirectly examine the influence of benthic algae on pH and % DO saturation when phytoplankton (chlorophyll *a*) levels are apparently too low to influence pH and %DO saturation (**Figure 9**) and SAV are absent. Continuous monitoring data collected in the Summer of 2005 shows a median pH value of 8.91 in Occoquan Bay as compared to 7.82 in Mattawoman Creek and 7.91 in Piscataway.Creek. The median % DO saturation was 118.3% in Occoquan Bay as compared to 96.0% in Mattawoman Creek and 81.1% in Piscataway Creek. The results suggest that photosynthesis by benthic algae in unvegetated embayments is capable of raising pH and % DO saturation to levels higher than those in embayments with SAV communities.

Chlorophyll *a* concentrations in Occoquan Bay have declining from median values of roughly 50 - 350 μg/liter in the 1990s (Buchanan 2008). The median value for Summer 2005 was 20.7 μg/liter (**Table 3**). Occoquan Bay pH levels declined slightly in the early 1990s but are still high, exceeding 9.0 frequently in Summer (**Figures 9, 13**). The lack of correspondence between Summer chlorophyll and pH in Occoquan Bay's long-term monitoring data and the 2005 and 2007 continuous monitoring data points to the presence of a benthic algae community that has replaced the phytoplankton to a large extent and may potentially be replaced by SAV. SAV was very sparse in 2005 but is rapidly expanding across the bay.

The results suggest that high pH levels in tidal fresh waters are not necessarily related directly to high phosphorus loads. Reductions in sediment phosphorus concentrations usually lag behind watershed load reductions, and load reductions have been going on since the early 1980s. High pH in the presence of high % DO saturation and declining chlorophyll concentrations likely indicates that sediment phosphorus concentrations have declined to a point where benthic algae are beginning to gain a competitive advantage over phytoplankton in the water column due to their closer proximity to the diminishing phosphorus supply. Low water column chlorophyll concentrations juxtaposed with high pH and DO saturation levels may thus indicate an intermediate stage of recovery in Potomac tidal fresh embayments.

It is not clear if an embayment or river flank that achieves 100% of its SAV goal will have pH levels consistently below 9.0 since the tidal fresh Potomac River is poorly buffered and susceptible to photosynthesis-induced pH swings. However, both Piscataway and Mattawoman are at or approaching their SAV restoration goals and experience very few pH values greater than 9.0 during summer.

Literature Cited

Buchanan, C. 2008. Exploratory analysis of Occoquan Bay station 1AOOC002.47 continuous monitoring data, September 30, 2008. Prepared by ICPRB for Virginia Department of Environmental Quality, Northern Regional Office.

Table 1. Continuous monitoring data for pH collected at locations in the tidal fresh Potomac estuary. All %, frequency of pH ≥ 9.0 in all records; Day %, frequency of pH ≥ 9.0 in daytime records (8 am - 8 pm). Fenwick is located on the flank of the tidal fresh Potomac mainstem; the remaining sites are located about midway in each embayment.

System	Station	Lat	Long	Year	Start-End Dates	All % pH≥9	Day % pH≥9
Tidal Fresh (TF)							
Piscataway Cr MD	XFB2184	38.7016°	-77.0259°	2004	4/21-11/1	2.72%	3.96%
				2005	3/31-10/24	5.87%	6.04%
				2006	3/21-10/31	8.90%	12.54%
				2007	3/21-10/31	6.37%	8.60%
Fenwick MD	XFB0231	38.6699°	-77.1151°	2004	8/18-10/27	8.83%	12.16%
				2005	3/31-10/24	8.73%	11.28%
				2006	3/21-10/31	18.61%	21.09%
				2007	3/21-10/31	33.06%	34.14%
Pohick/Gunston VA	POH002.10	38.6761°	-77.1640°	2007	4/9-10/31	13.14%	15.65%
Occoquan Bay VA	OCC002.47	38.6405°	-77.2194°	2005	4/5-9/29	27.01%	27.42%
				2007	4/3-10/30	1.79%	2.11%
Mattawoman Cr. MD	XEA3687	38.5593°	-77.1887°	2004	4/21-11/1	5.29%	6.35%
				2005	3/31-10/24	0.31%	0.37%
				2006	3/21-10/31	2.67%	3.64%
				2007	3/21-10/31	15.41%	16.26%

Table 2. Exceedance of pH ≥ 9.0 for March through October tidal fresh Potomac mainstem stations in Maryland: TF2.1, TF2.2, TF2.3, and TF2.4. Measurements are made during daytime. *, partial year (August - October data not available).

Year	% pH ≥ 9.0	% Chl *a* ≥ 50 μg/liter	Median Chl *a* μg/liter	% DO Saturation > 100%
2000	1.6%	3.3%	11.5	34.4%
2001	1.5%	1.5%	10.9	17.6%
2002	0.0%	0.0%	6.3	17.6%
2003	0.0%	2.8%	7.3	12.5%
2004	0.0%	0.0%	6.2	13.2%
2005	0.0%	0.0%	4.5	12.5%
2006	0.0%	0.0%	4.8	5.9%
2007*	0.0%	0.0%	2.7	18.8%

Table 3. Continuous monitoring data for pH collected at locations in the tidal fresh Potomac estuary. Fenwick is located on the flank of the tidal fresh Potomac mainstem; the remaining sites are located about midway in each embayment.

		Spring (April - May)			Summer&Fall (June - October)		
Tidal Fresh (TF)	Year	% Chl *a* ≥ 50 µg/liter	Median Chl *a* µg/liter	% DO Saturation ≥ 100%	% Chl *a* ≥ 50 µg/liter	Median Chl *a* µg/liter	% DO Saturation ≥ 100%
Piscataway Cr MD	2004	5.7%	20.7	42.6%	0.0%	5.4	22.9%
	2005	6.4%	15.9	42.8%	0.0%	2.9	29.8%
	2006	4.4%	21.4	69.1%	0.2%	5.0	41.9%
	2007	3.9%	11.3	55.5%	0.1%	2.6	53.6%
Fenwick MD	2004	0.1%	7.2	57.6%	0.0%	3.5	53.0%
	2005	0.0%	2.0	20.3%	0.0%	2.3	57.1%
	2006	0.0%	2.1	62.6%	0.0%	2.3	58.6%
	2007	0.0%	2.3	48.0%	0.0%	1.9	77.5%
Pohick/Gunston VA	2007	0.0%	13.7	68.3%	0.0%	6.5	78.1%
Occoquan Bay VA	2005	0.0%	14.5	80.9%	0.5%	20.7	81.1%
	2007	0.0%	15.5	60.8%	0.0%	7.3	47.3%
Mattawoman Cr. MD	2004	0.7%	15.4	87.9%	0.0%	11.6	65.1%
	2005	0.0%	8.1	47.9%	0.1%	6.2	44.0%
	2006	0.0%	12.1	81.2%	0.0%	3.2	48.5%
	2007	0.0%	11.9	62.3%	0.0%	2.7	52.9%

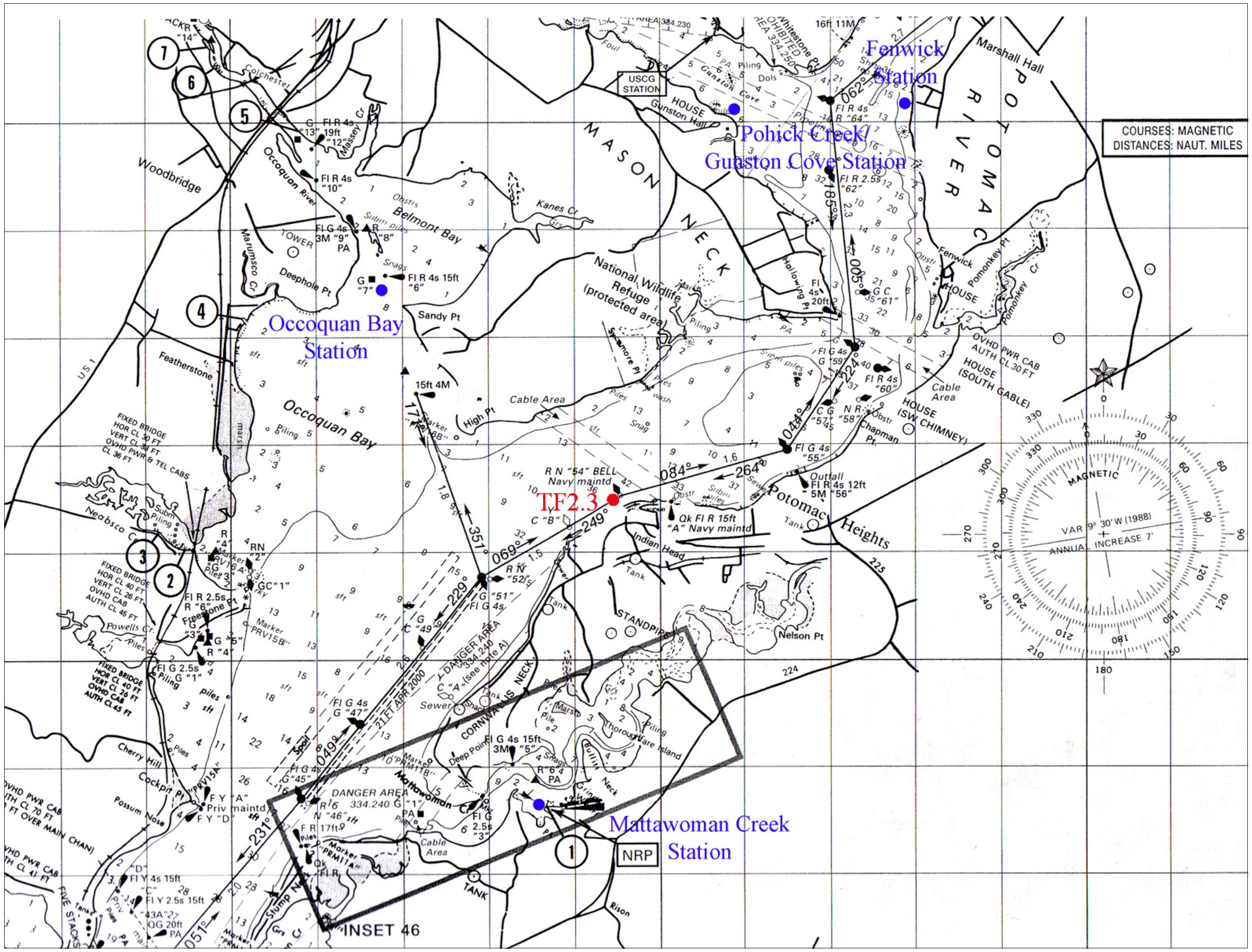

Figure 1. Nautical map of the lower tidal fresh Potomac River and embayments showing depth in feet below mean low tide (from Maryland Cruising Guide 2002-2003, Williams & Heintz Map Corporation, Capitol Heights, MD 20743). Locations of continuous monitoring sondes are indicated by blue dots; Chesapeake Bay Program bimonthly shipboard monitoring station indicated by red dot. The Piscataway continuous monitoring sonde and an adjacent CBP station are located upstream of this area.

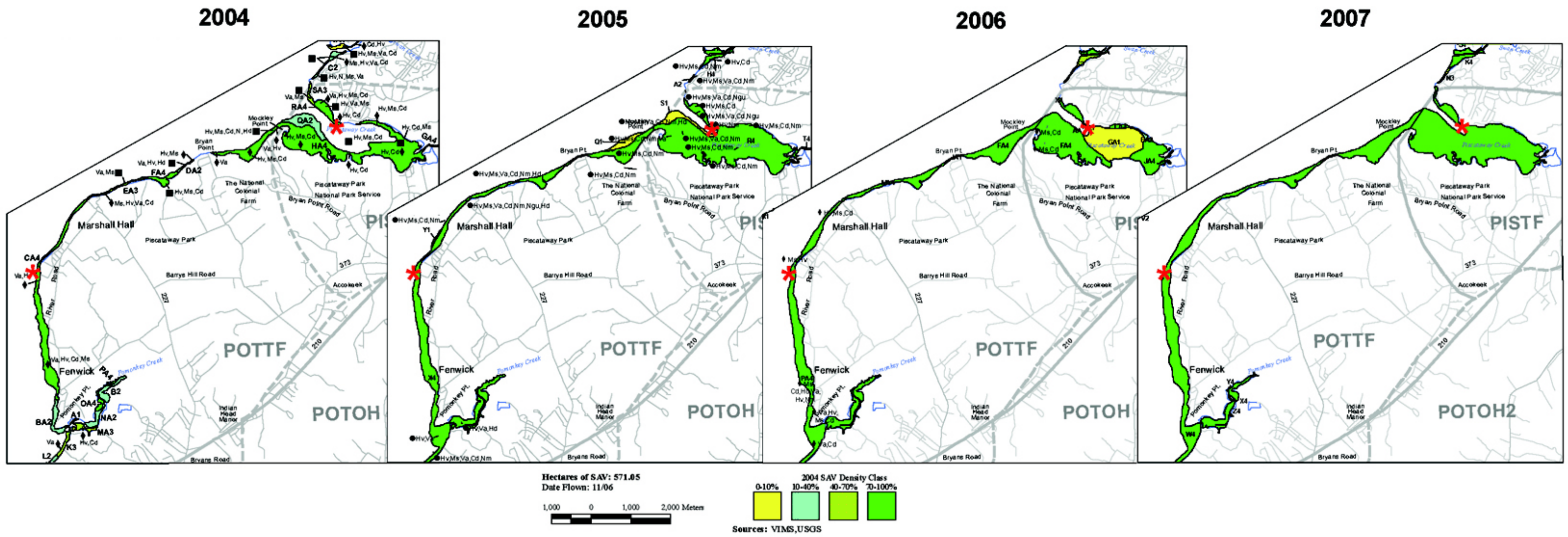

Figure 2. Annual SAV coverage in Piscataway Creek MD and Fenwick MD. Continuous monitoring station indicated with red *. Data downloaded from http://web.vims.edu/bio/sav/. The CBP station TF2.1 is located off the mouth of Piscataway Cr.

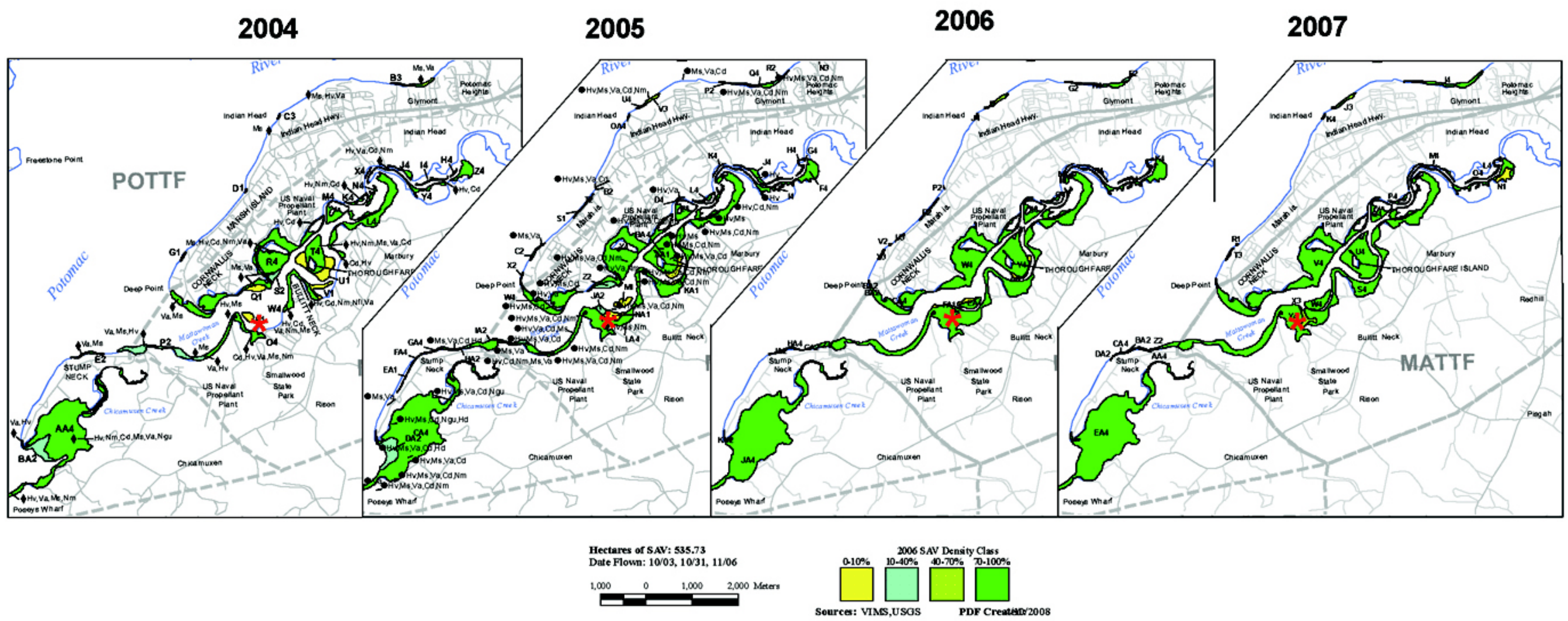

Figure 3. Annual SAV coverage in Mattawoman Creek MD. Continuous monitoring station indicated with red *. Data downloaded from http://web.vims.edu/bio/sav/.

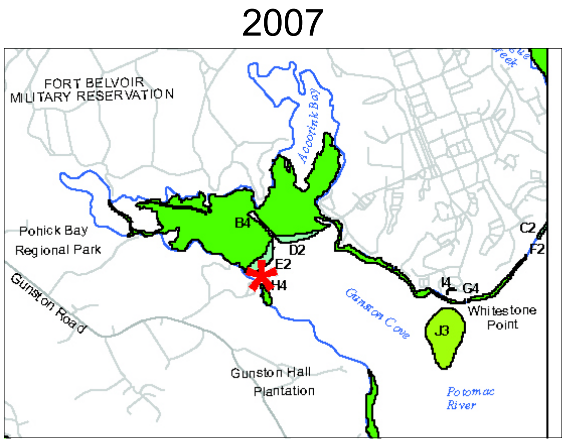

Figure 4. Annual SAV coverage in Pohick Bay VA, 2007. Data downloaded from http://web.vims.edu/bio/sav/.

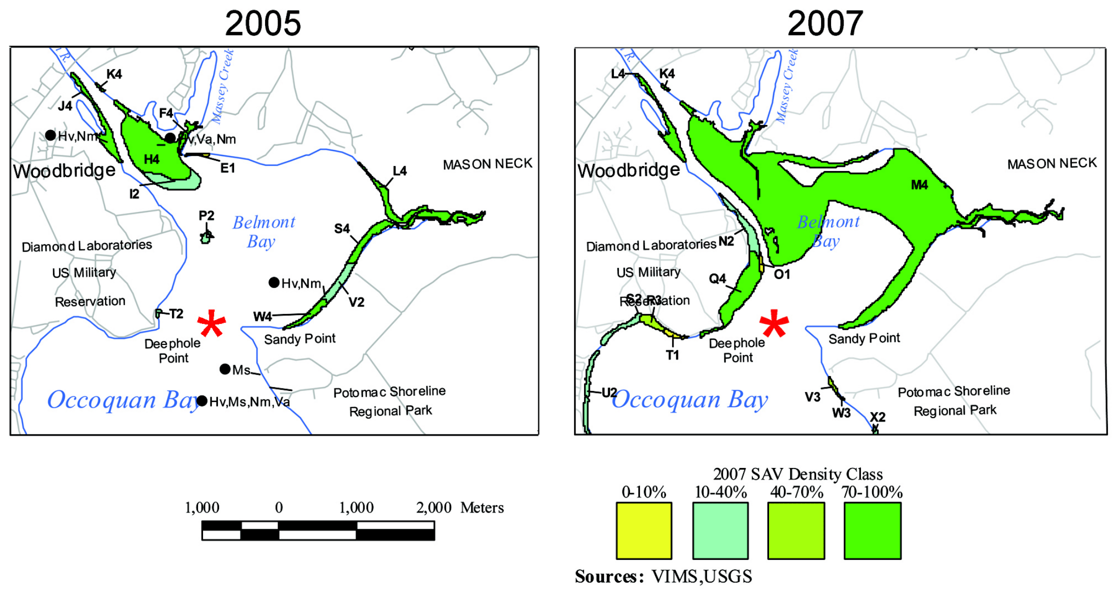

Figure 5. Annual SAV coverage in Occoquan Bay VA, 2005 and 2007. Data downloaded from [http://web.vims.edu/bio/sav/.](http://web.vims.edu/bio/sav/)

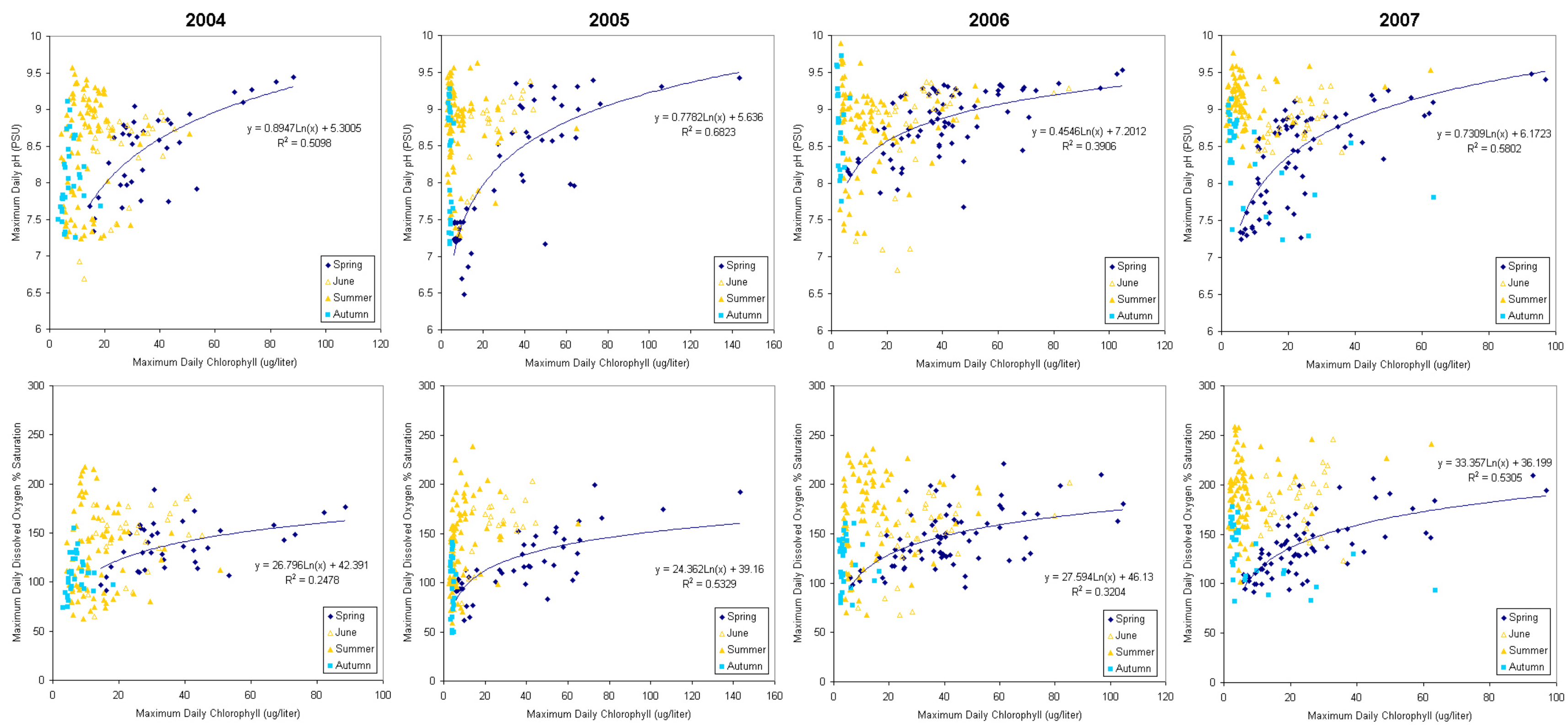

Figure 6. Piscataway Creek MD, 2004 - 2007. Maximum daily chlorophyll vs maximum daily pH (top panel) and vs maximum daily percent saturation of dissolved oxygen (bottom panel) in the water column. Significant regression shown with line. Notice the slight increase in summer maximum pH and percent saturation of dissolved oxygen from 2004 to 2007.

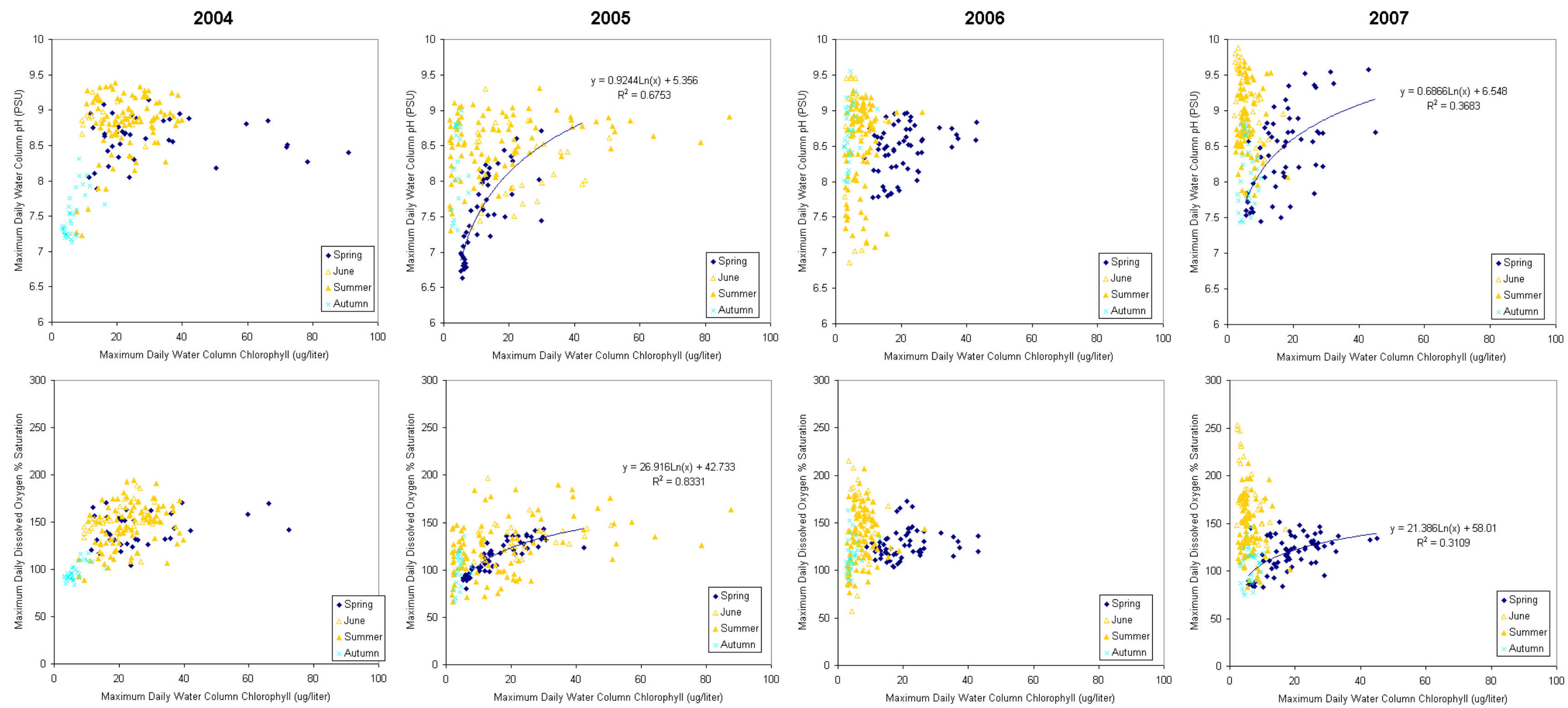

Figure 7. Mattawoman Creek MD, 2004 - 2007. Maximum daily chlorophyll versus maximum daily pH (top panel) and versus maximum daily percent saturation of dissolved oxygen (bottom panel) in the water column. Significant regression shown with line. Notice the slight increase in summer maximum pH and percent saturation of dissolved oxygen from 2004 to 2007.

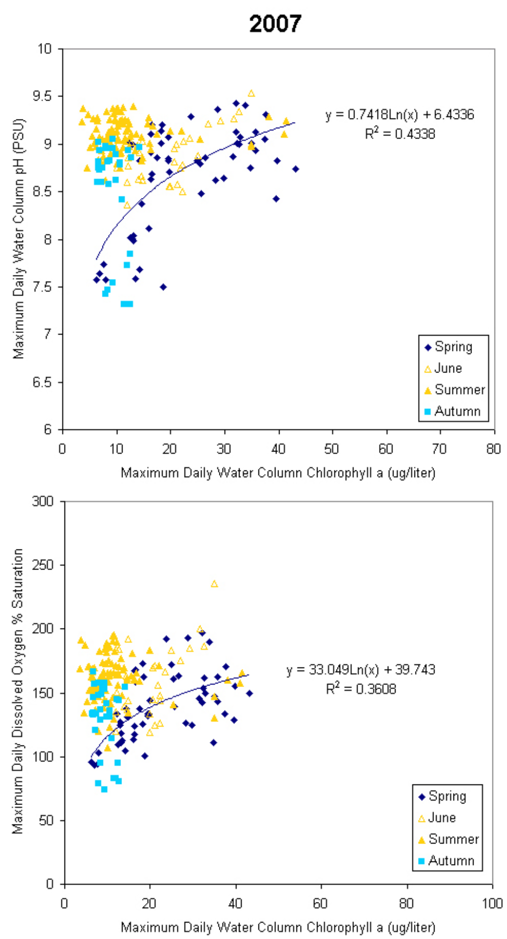

Figure 8. Pohick Bay VA, 2007.

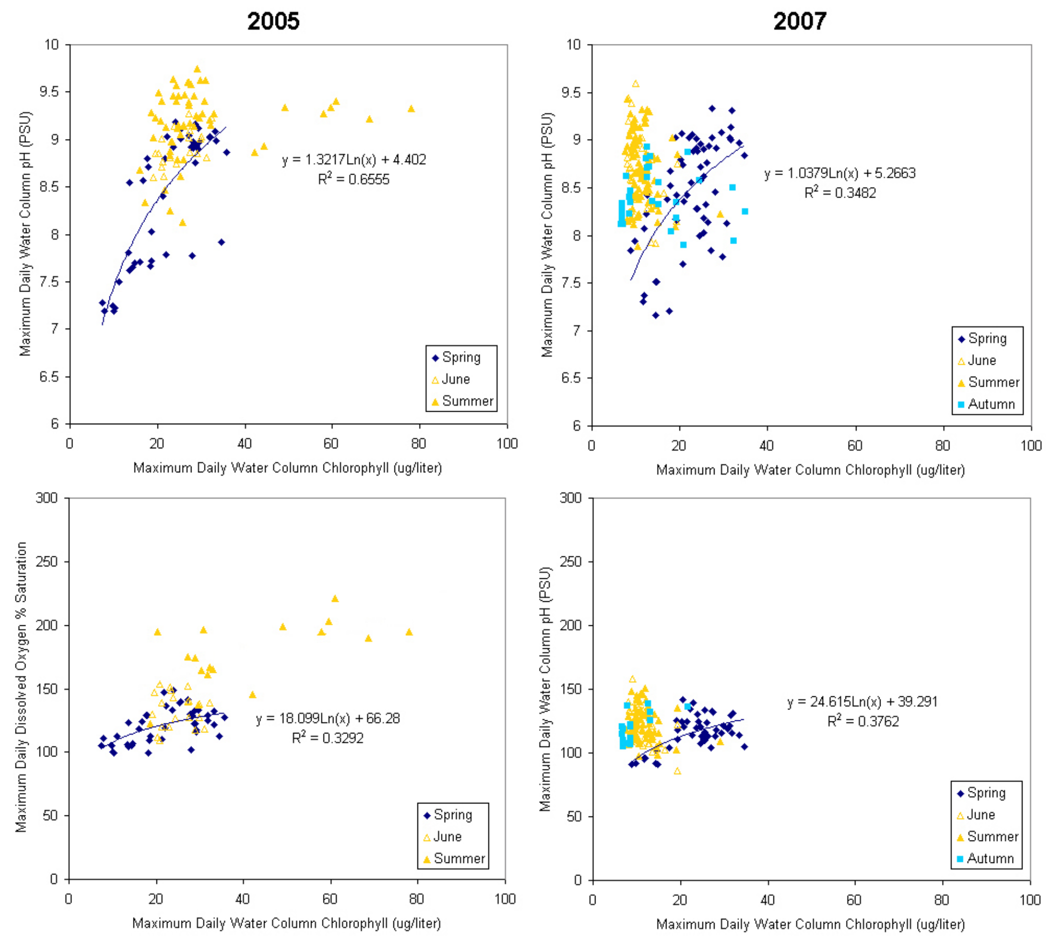

Figure 9. Occoquan Bay VA, 2005, 2007.

Maximum daily chlorophyll versus maximum daily pH (top panel) and versus maximum daily percent saturation of dissolved oxygen (bottom panel) in the water column. Significant regression shown with line.

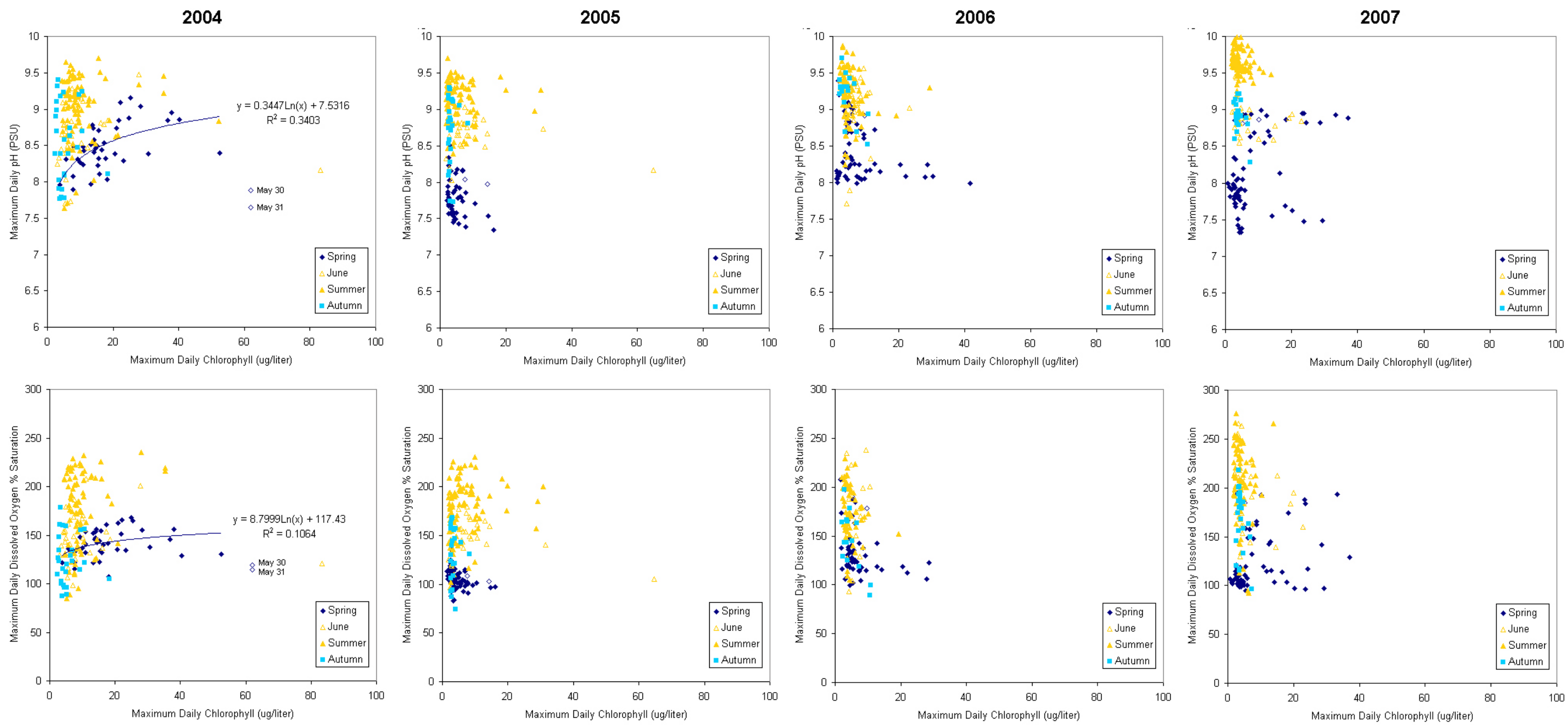

Figure 10. Fenwick MD, 2004 - 2007. Maximum daily chlorophyll vs maximum daily pH (top panel) and vs maximum daily percent saturation of dissolved oxygen (bottom panel) in the water column. Significant regression shown with line. Notice the slight increase in summer maximum pH and percent saturation of dissolved oxygen from 2004 to 2007.

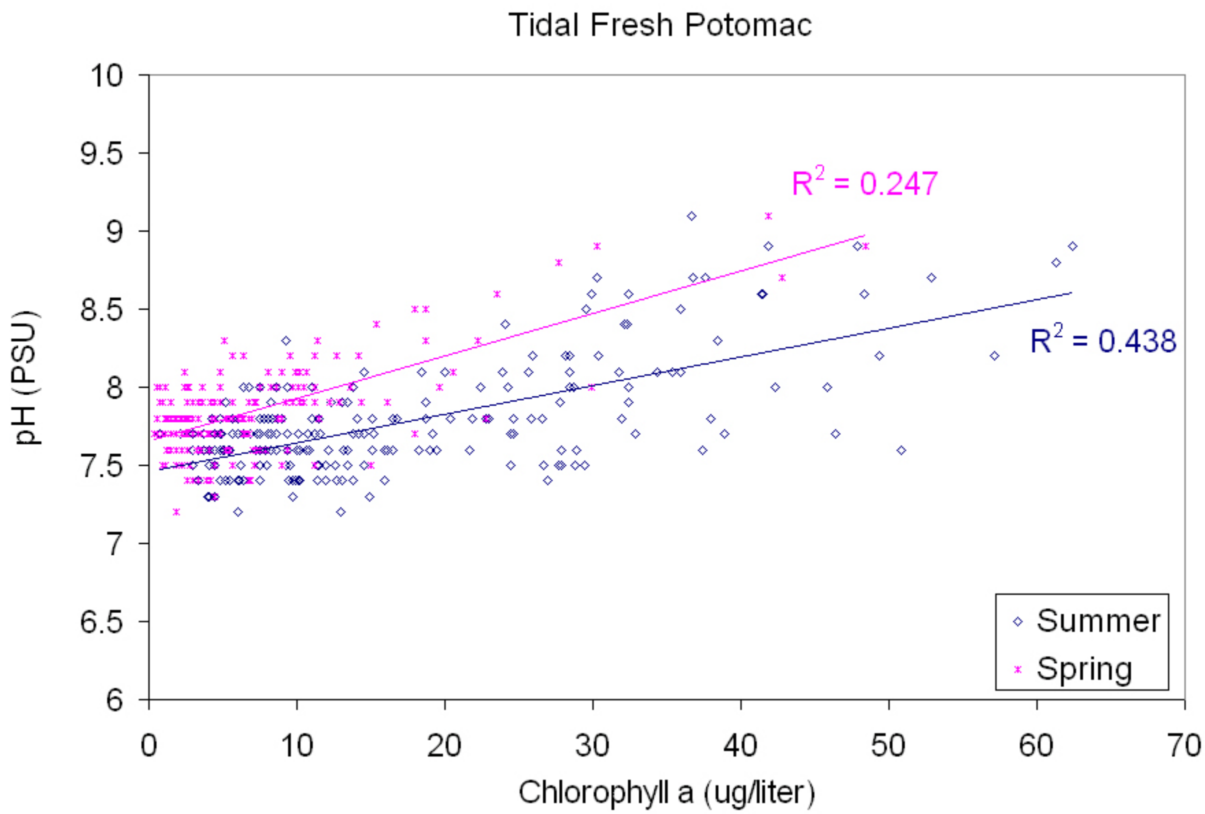

Figure 11. pH versus chlorophyll *a* for individual station-date events at the tidal fresh Potomac mainstem mid-channel stations (TF2.1, TF2.2, TF2.3, and TF2.4), 2000 - 2007.

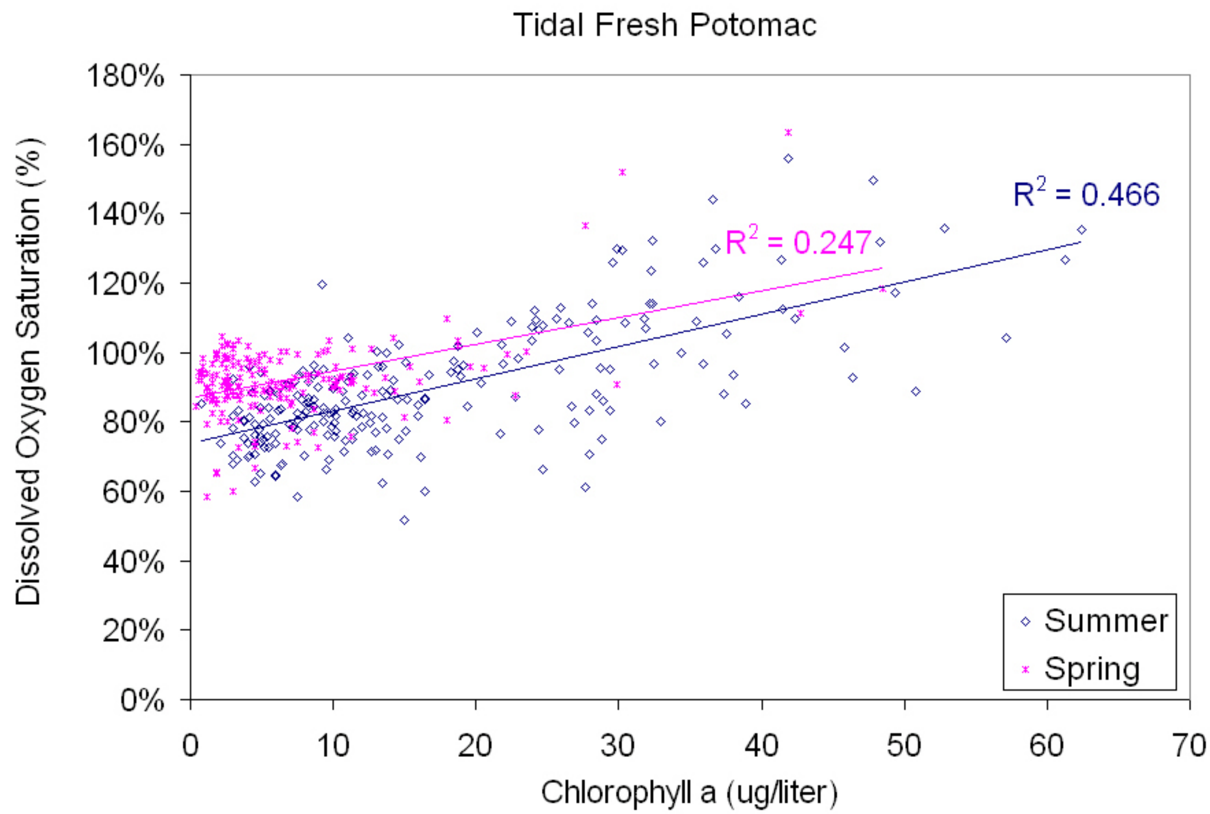

Figure 12. Dissolved oxygen saturation versus chlorophyll *a* for individual station-date events at the tidal fresh Potomac mainstem mid-channel stations (TF2.1, TF2.2, TF2.3, and TF2.4), 2000 - 2007.

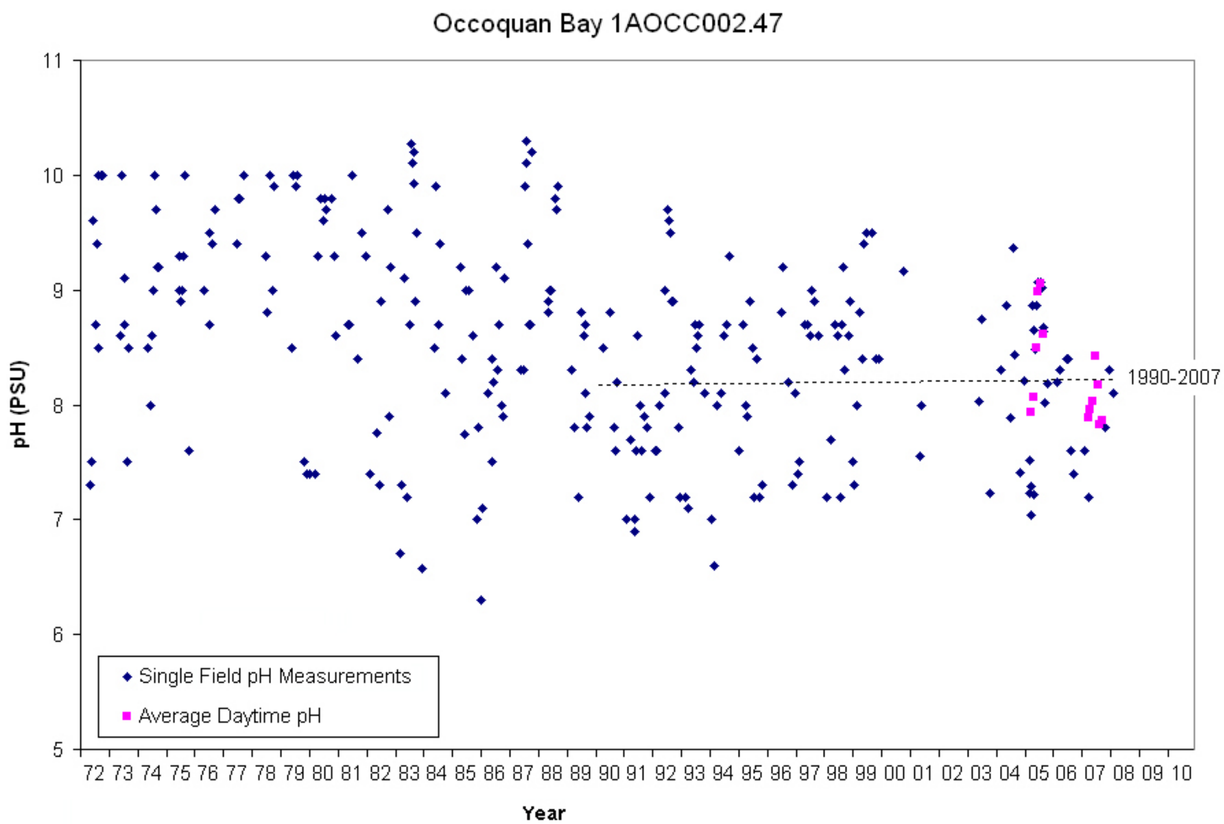

Figure 13. Observed pH field measurements from ambient monitoring program (◆) and monthly averages of all daytime (7am - 6pm) pH values from the continuous monitoring program (■).