Exploratory analysis of Occoquan Bay station 1AOCC002.47 continuous monitoring data

FINAL REPORT

October 2009

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ICPRB Report 09-1

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. The opinions expressed are those of the authors and should not be construed as representing the opinions or policies of the United States or any of its agencies, the several states, or the Commissioners of the Interstate Commission on the Potomac River Basin.

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Introduction

The Virginia Department of Environmental Quality (VADEQ) monitors ambient water quality at station 1AOCC002.47 located on the boundary line of Occoquan Bay and Belmont Bay northeast of Sandy Point, VA at 38.6404ºN -77.2194ºW (Figure 1). Values of pH greater than 9.0 have occurred frequently enough at the station that they exceeded the Virginia water standard for pH (§ 9 VAC 25-260-50). In 2002, the Commonwealth of Virginia declared a half-mile radius around station 1AOCC002.47 (0.59 square miles) as impaired for pH and not meeting its Aquatic Life designated use (VADEQ 2006). The source of the impairment is listed as unknown, although excess nutrient loads are suspected. Excess nutrients can stimulate explosive algal growth in the presence of adequate light, and rapid algal photosynthesis is known to raise pH levels. The photosynthesis hypothesis is supported by the fact that water column concentrations of chlorophyll *a* (Chl *a*), an indicator of algal biomass, have sometimes exceeded the Virginia screening level of 50 $\mu g\ l^{-1}$ at the station in the past.

High pH values negatively impact aquatic life uses because, in the presence of warm temperatures, non-toxic ionized forms of certain compounds dissociate more rapidly into toxic, un-ionized forms. Of particular concern is the dissociation of ammonium ions (NH_4^+) into toxic, free ammonia (NH_3) as pH and temperature rise. In aqueous solutions at equilibrium when pH and temperature are both low, total ammonia exists primarily as ammonium ions. The proportion of free ammonia increases as pH and temperature rise, and comprises more than 35% of total ammonia when pH > 9 and temperature > 25 ºC (from USEPA 1999 Equation 4). Free ammonia is toxic to aquatic organisms because it is a neutral molecule and thus is able to diffuse across membranes more readily than the charged ammonium ion. High concentrations of ammonia in the external environment reduce or reverse the diffusion of ammonia waste from aquatic organisms (excretion) and cause the buildup of ammonia in gill tissue and blood (USEPA 1999).

A “continuous monitoring” (CMON) data sonde was placed in Occoquan Bay at station 1AOCC002.47 in 2005, 2007, and 2008 to document short-term and daily changes in pH and associated water quality parameters. As part of a larger study, ICPRB conducted an exploratory analysis of the Occoquan Bay data with the objective of characterizing the bay’s pH levels and identifying possible causes of the high pH levels. This report presents the results and conclusions of that exploratory analysis.

Data Sources

A YSI 6600 data sonde with the Clean Sweep Extended Deployment System located at station 1AOCC002.47 collected measurements at 15 minute intervals between April 5 and September 29 in 2005, April 3 and October 30 in 2007, and April 1 and October 14 in 2008. The data sonde recorded measurements of pH, water temperature, salinity, total chlorophyll, turbidity, and dissolved oxygen. The total chlorophyll value is generated by the YSI data logger from raw fluorescence readings, and is considered equivalent to Chl *a* concentration (Joy Austin, VIMS, pers. comm.). See http://www2.vims.edu/vecos/ for further details. All data flagged with codes indicating errors or questionable data quality were excluded from the data analysis.

The continuous monitoring data were compared to ambient monitoring data collected at 1AOCC002.47 from 1972 to 2008. The ambient monitoring data and related data documentation were obtained from staff at VADEQ's Northern Regional Office or downloaded from the VADEQ website http://gisweb.deq.virginia.gov/monapp/mon_query_form.cfm.

Occoquan Bay pH

Values of pH ranged from 7.00 to 9.75 in 2005 (Figure 2a), from 6.62[1] to 9.59 in 2007 (Figure 3a), and from 6.80 to 9.48 in 2008 (Figure 4a). pH exceeded the Virginia state water standard criteria of 9.0 in 3,931 of 15,055 (26.11%) records for 2005, in 329 of 19,659 (1.67%) records for 2007, and in 471 of 18,761 (2.51%) records for 2008. Exceedences of 9.0 occurred in all months between April and October but were most common in July and August of 2005, in April and July of 2007, and in July of 2008. Daily exceedences of 9.0 were most frequent in the afternoon and evening, between 3 pm and 9 pm, and least frequent in the morning (Figure 5).

Possible causes of elevated pH in Occoquan Bay

Background

pH is a measure of the free hydrogen ions (H^+) concentration in water. The pH of an aquatic environment is largely controlled by 1) the dissolved carbon dioxide (CO_2)-bicarbonate (HCO_3^-)-carbonate (CO_3^{-2}) equilibrium system, and 2) the concentrations various salts, acids, and bases. The CO_2-HCO_3^--CO_3^{-2} equilibrium system occurs in aquatic environments because some of the carbon dioxide (CO_2) dissolved in water (H_2O) chemically bonds with water to form carbonic acid (H_2CO_3), a weak acid. Carbonic acid rapidly transforms into a mixture of bicarbonate (HCO_3^-), carbonate (CO_3^{-2}), H_2O, hydroxyl (OH^-), and H^+ through a series of hydration and dissociation reactions. If this mixture's equilibrium is disrupted by the loss or gain of CO_2, HCO_3^-, or CO_3^{-2}, reaction rates change until equilibrium is restored. H^+ and OH^- produced in the reactions tend to form H_2O and neutralize each other if both concentrations exceed 10^{-7} g ion liter^{-1}, so pH is slow to change. The pH at equilibrium in pure water is 7 (neutral) and the most abundant carbon component of the equilibrium mixture is HCO_3^-. Large quantities of acids in the water (e.g., "acid rain," dissolved organic acids) increase H^+ concentrations (lower pH) and change the CO_2-HCO_3^--CO_3^{-2} equilibrium reaction rates so that dissolved CO_2 becomes the most abundant inorganic carbon form. Large quantities of certain bases like ammonia (NH_3) can decrease H+ concentrations (raise pH), and make CO_3^{-2} the most abundant inorganic carbon form.

Respiration and photosynthesis are biological processes in aquatic environments that directly alter the CO_2-HCO_3^--CO_3^{-2} equilibrium system. Respiration adds CO_2, and photosynthesis removes CO_2 and HCO_3^-. The magnitude of their influence on the CO_2-HCO_3^--CO_3^{-2} equilibrium system depends on the alkalinity of the water. Alkalinity, which is sometimes used

[1] The isolated pH reading of 5.31 at 10:15 am on 9/18/2007 is considered an outlier since it is more than 1 PSU unit lower than the readings before and after 10:15 am that day.

interchangeably with the term acid neutralizing capacity (ANC), is the water's ability to take up H^+ ions without changing its pH. Alkalinity in natural aquatic environments depends largely on carbonate and bicarbonate salts, and to a much lesser extent on borates, silicates, phosphates, ammonium, sulfides, and organic ligands. The mineral calcium carbonate ($CaCO_3$) reacts to respiration-related increases in dissolved CO_2 by combining with it and H_2O and dissolving into calcium bicarbonate ($Ca(HCO_3)_2$). This removes the CO_2 from the CO_2-HCO_3^--CO_3^{-2} equilibrium system. Calcium bicarbonate reacts to heavy, prolonged CO_2 losses to photosynthesis by precipitating $CaCO_3$ and releasing H_2O and CO_2 to the system.

Alkalinity

An extremely weak alkalinity buffering system is not the cause of the elevated pH values in Occoquan Bay. The Bay has alkalinity concentrations and a buffering capacity typical of other tidal waters in the region, including the Potomac estuary mainstem. Samples collected at 1AOCC002.47 between 1990 and 2007 had values ranging from 17.6-109 mg $CaCO_3$ liter^{-1}, with a median of 52.1 mg $CaCO_3$ liter^{-1} (n = 133). Alkalinity measured over the same period in the Potomac estuary adjacent to Occoquan Bay (station TF2.3) ranged from 26-113 mg $CaCO_3$ liter^{-1}, with a median of 69 mg $CaCO_3$ liter^{-1} (n = 970). Alkalinity in neighboring Pohick Bay/Gunston Cove to the north ranged from 5.53 - 133 mg $CaCO_3$ liter^{-1}, with a median of 63.2 mg $CaCO_3$ liter^{-1} (n = 216). No trends are apparent in any of the tidal data over the 1990 - 2007 time period. Concentrations of 20-200 mg $CaCO_3$ liter^{-1} are common in freshwater systems and are generally thought to provide modest buffering capacity (Wetzel 2001). Concentrations below 20 mg $CaCO_3$ are thought to have weak buffering capacity. The fact that pH > 9 is experienced for prolonged periods in Occoquan Bay and other nearby shallow water sites suggests that alkalinity levels are generally modest, and can occasionally be weak.

An analysis of the non-tidal streams and the Occoquan Reservoir above Occoquan Bay found significant upward trends in alkalinity over the longer period of 1973 - 2002 (Van Den Bos 2003). A similar upward trend was found in Potomac River, above the Piedmont fall-line, with alkalinity changing from ~55 to ~85 mg $CaCO_3$ liter^{-1} between 1905 and 2003 (Jaworski 2007). The upward trends suggest the buffering capacity of the region's rivers is increasing slightly, although the causes are not clear.

Watershed sources of elevated pH

Watershed sources of base compounds that can raise pH, such as OH^- and ammonia, do not appear to be directly responsible for the elevated Occoquan Bay pH values. In fact, Occoquan Bay pH values at station 1AOCC002.47 decreased sharply after relatively large rain events, indicating watershed runoff of precipitation is more acidic than tidal water in the Bay (Figure 2, 3, 4). Flow from the Occoquan Reservoir into the Bay ceased for most of the dry summer of 2007, and the scattered, small rainfall events during this summer had little effect on Occoquan Bay pH (Figure 3). On average, the Occoquan River supplies an estimated 95% of the annual freshwater surface flow from the Occoquan watershed to the Potomac estuary (derived from the CBP Watershed Model). The remaining 5% comes from lands directly adjacent to the Bay and the Potomac called direct drainage. These proportions vary depending on the amount of rainfall and reservoir releases.

Base flow from the watershed subsurface also does not appear to be a source of elevated pH values. Between 1973 and 2002, medians of the seasonal pH values ranged from 7.0 (winter) to 7.5 (autumn) at river stations above Occoquan Reservoir and from 6.9 (winter) to 7.4 (summer) below the reservoir, near the head of the Bay (Van Den Bos 2003). These values are slightly lower than the seasonal medians of pH values collected by the ambient water quality monitoring program in Occoquan Bay between 1990 and 2007, which ranged from 7.1 (spring) to 8.14 (summer). Van Den Bos (2003) identified downward trends in NH_3 and TKN at river stations above and below the reservoir. Downward trends would tend to reduce river pH values, not raise them. The pH levels of direct drainage flows are not known.

Internal sources of elevated pH

Fluxes of ammonia and other bases from sediments in Occoquan Bay are a possible, although not probable, cause of the elevated pH values in Occoquan Bay. *In situ* flux measurements made at depths of 2.9 - 8.6 m (9.4 - 29 ft) in the neighboring tidal fresh and oligohaline Potomac River in 2004 documented fluxes of NH_4^+ (~500 µmoles m^{-2} h^{-1}) out of the sediments and NO_{23}^- (~150 µmoles m^{-2} h^{-1}) into the sediments (Bailey et al. 2006). The study did not measure sediment-water fluxes in shallow areas like Occoquan Bay. High concentrations of total ammonia in the water column could be expected if large sediment fluxes of NH_4^+ were occurring in the Bay. However, about 70% of the water column measurements of total ammonia were below the method detection limit of 0.04 mg $liter^{-1}$ between 1990 and 2007 and the maximum value observed was 0.24 mg $liter^{-1}$. If a large amount of NH_4^+ is in fact moving from the sediment to the water column, it is being rapidly consumed by plants or nitrified by bacteria to NO_{23}^-.

Rapid photosynthesis is a possible, and the probable, cause of elevated pH values in Occoquan Bay. As mentioned above, photosynthesis removes CO_2 and HCO_3^- from the CO_2-HCO_3^--CO_3^{-2} equilibrium system. Water will resist change in the pH as long as the equilibria are operational and alkalinity is sufficient, but pH begins to rise when the supply of carbonates and bicarbonates is exhausted. The available dissolved oxygen and water clarity data support the photosynthesis hypothesis. Dissolved oxygen super-saturation exhibits a diel cycle in all seasons with minimum in the early morning and a maximum around 6 pm - 7 pm, or a few hours before sunset (Figure 6). This pattern reflects the dependence of plant photosynthesis on the daily light cycle. Recently, Jones and Buchanan (2009) found strong correlations between photosynthetically active radiation (PAR) and both DO saturation and pH measured in Belmont Bay upstream of Occoquan Bay. Their results support the hypothesis that photosynthesis is the primary factor raising daytime pH levels.

Dissolved oxygen concentrations in the water column are supersaturated for much of the spring and summer growing season (Figures 2a, 3a, 4a), reaching as high as 221.2% in 2005, 158.3% in 2007, and 166.9% in 2008. Levels this high could only be reached if daytime photosynthesis rates were high. Secchi depths were small, ranging from 0.2 - 1.2 m with a grand median of only 0.5 m in 2003-2007. Despite the small Secchi depths, the photic zone (estimated as twice the Secchi depth) usually reaches the bottom in the upper Bay and adjacent Belmont Bay and encompasses most of the water column in the lower Bay because of the shallowness of Occoquan Bay (Figure 1).

The question is: what plant type is responsible for the rapid photosynthesis rates? Three types are common in the Potomac estuary: vascular plants which include submerged aquatic vegetation (SAV); algae that inhabit the water column (phytoplankton); and algae that inhabit the surface layer of sediments in shallow, well-lit waters (benthic algae). Several anaerobic bacteria can photosynthesize, but dissolved oxygen concentrations appear to be too high in Occoquan Bay for these bacteria to be a significant factor.

SAV were not established in Occoquan or Belmont bays prior to 2002 (Chesapeake Bay Program annual aerial surveys, www.vims.edu/bio/sav). In 2005, SAV were still confined to a small area at the mouth of the Occoquan River and a narrow strip on the east side of Belmont Bay. By 2007 and 2008, the SAV had expanded to cover much of the upper portion of Belmont Bay (Figure 7). A small cattail dominated marsh occurs just below Sandy Point. Neither the SAV beds nor the cattail marsh appear to be close enough to affect the pH value at station 1AOCC002.47. Mean field pH values from the ambient monitoring program collected at 1AOCC002.47 prior to 2002, when the Bay was unvegetated, and after 2002 are comparable: 8.20 ($\pm$0.15, n=93) and 8.00 ($\pm$0.14, n=69), respectively.

The continuous monitoring data suggest that phytoplankton populations in the water column could be a cause of elevated pH in the Bay in spring of all three study years. Median (and maximum) concentrations of water column Chl *a* in spring were 14.4 (35.7) µg liter^{-1} in 2005, 15.5 (34.6) µg liter^{-1} in 2007, and 14.0 (40.9) µg liter^{-1} in 2008. Daytime (7 am - 6 pm) maximum values of pH, Chl *a*, and percent saturation of dissolved oxygen all correlated significantly and positively with each other in the spring months of April and May (Table 1). Average daily (24 hr) values were similarly correlated. Springtime DO concentrations were super-saturated ($\geq$100%) in 78.6% of the 2005 records, 60.6% of 2007 records, and 72.4% of 2008 records. These results meet the expectations of the hypothesis that rapid photosynthesis rates by abundant plant biomass (expressed as supersaturated DO) causes pH to rise.

The June-September results for all three years also support the photosynthesis hypothesis, but indicate that phytoplankton may not be primarily responsible for elevating pH in summer. pH and %DO saturation remain strongly correlated to each other. However, their respective correlations with water column Chl *a* are in many cases weaker or non-significant (Table 1). Maximum daytime values of pH increased to peak levels in late July and August in all years, with occasional interruptions by rain events, whereas Chl *a* values fluctuated with no seasonal pattern in 2005, dropped to low summer levels in 2007, and dropped to moderate summer levels in 2008 (Figures 2a, 3a, 4a).

Benthic algae, the third type of plant, have not been monitored in Occoquan Bay. Their populations can be estimated with Chl *a* samples collected in surficial sediments or with taxonomic counts made from settling plates or other substrates. Studies in other shallow estuarine systems indicate benthic algae can play a substantial role as primary producers and can significantly influence burial and export rates of nitrogen, phosphorus, and carbon. For example, a study in the shallow (1.6 m mean depth) Indian River-Rehoboth Bay estuary in Delaware concluded that annualized benthic algae primary production, or consumption of carbon, was 1.8X greater than the water column phytoplankton production (Cerco and Seitzinger 1997).

Discussion

The monitoring results indicate that strong plant photosynthesis coupled with a modest-to-low alkalinity buffering capacity in Occoquan Bay are responsible for prolonged periods of elevated pH values between April and October. Phytoplankton populations in the water column appear to be the primary cause of elevated pH levels in spring, as evidenced by significant correlations between Chl *a* and pH metrics (Table 1, Figure 8). During this season, pH exceeded 9.0 in 2.0% (2005), 2.6% (2007), and 0.7% (2008) of the continuous monitoring records (Table 2). The occurrence of weak, non-significant, or negative correlations between Chl *a* and pH metrics beginning in June indicate other plants were factors contributing to diel pH swings between June and October (Table 1, Figure 8). pH exceeded 9.0 in 39.6% (2005), 1.6% (2007), and 3.7% (2008) of the summer/autumn continuous monitoring records (Table 2). The relative scarcity of SAV and emergent shoreline plants Occoquan Bay and the absence of summer phytoplankton algal blooms in 2007 and 2008 suggest benthic algae may becoming primarily responsible for the diel photosynthetic consumption of CO_2 in summer, although there are no monitoring data to confirm the benthic algae role.

The Occoquan Bay light environment expressed as Secchi depth is slowly improving (Figure 9) and can now support benthic algae and SAV as well as phytoplankton. SAV did not begin to return to Occoquan Bay until roughly 2003 and did not become locally abundant until 2007. The 1AOCC002.47 monitoring station is still distant from the recovering SAV beds and does not appear to be affected by them yet. In contrast, phytoplankton blooms expressed as Chl *a* concentrations greater than 50 µg liter^{-1} were common in the early-to-mid 1990s at the monitoring station but have become rare since 2000 despite a wide range of environmental conditions. Summer Chl *a* concentrations in 2005 are atypically high compared to summer concentrations across the 2003-2008 period, but still low relative to pre-2000 levels (Figure 10). Despite the drop in the Occoquan Bay phytoplankton abundance after 2000, pH at the 1AOCC002.47 station has yet to show a significant difference between 1990 - 2000 and post-2001 values ($p<0.05$) (Figure 11).

If abundant benthic algae are in fact the cause of the supersaturated dissolved oxygen concentrations and elevated pH values in recent summers, the phosphorus that fuels their growth appears to be coming from Occoquan Bay sediments rather than the water column. Dissolved orthophosphate (PO_4) concentrations in the water column have declined significantly in Occoquan Bay since the early 1990s ($p<0.01$), and by 2007 they averaged 0.005 mg liter^{-1}. This level is approximately equal to the PO_4 growth limitation threshold experimentally determined for Chesapeake Bay phytoplankton (Fisher and Gustafson 2003). Below this threshold, phytoplankton in an adequate light environment maintain relatively constant densities and do not form blooms.

Sediment phosphorus concentrations reflect a dynamic balance between input loads from the watershed and river mainstem and losses in the bay due to export and biological uptake rates. Concentrations of total phosphorus (TP) upstream of Occoquan Bay appear to be substantially lower than those in the bay; those in the Potomac River mainstem are slightly lower. Input loads from Occoquan River, the major watershed source of phosphorus, have declined in the last three decades. A 1973-2002 analysis of total phosphorus (TP) concentrations at the mouth of Occoquan River show a significant declining trend in winter ($p<0.01$) and weak declining trends in spring ($p<0.05$) and autumn ($p<0.10$) (Van Den Bos 2003). No trend was apparent in summer, however Van Den Bos noted that the dry summers of 1999-2002 affected the 1973-2002 summer trend and a 1973 - 1997 summer trend was negative. Tidally driven inputs from the Potomac River mainstem, as reflected in TP concentrations at CBP monitoring station TF2.3 (Figure 1), have also declined significantly in the last three decades. TP concentrations for March through October, 2000 - 2007, in Occoquan Bay and the river mainstem were 0.079 and 0.075 mg liter^{-1}, respectively. (PO_4 in the river mainstem was slightly higher than in the bay, averaging 0.0187 mg liter^{-1} between 2000 and 2007).

The long-term negative trends in phosphorus inputs and the low levels of PO_4 currently found in the shallow Occoquan Bay water column suggest the phosphorus available in the water column is being rapidly utilized. Expanding SAV beds can be expected to take up increasing amounts of phosphorus even as the declining phytoplankton populations (as measured by water column Chl *a*) are sequestering less phosphorus. No monitoring data is available about phosphorus fluxes to and from the sediment in Occoquan Bay, but benthic algal uptake of phosphorus has the potential to be significant.

The high frequency of % DO saturation shows that shallow Occoquan Bay is still a very productive environment. Chl *a* declines indicate primary production is shifting from phytoplankton to SAV and probably benthic algae. As water clarity continues to improve in the bay, the importance of benthic algae in open areas will increase and modified sediment nutrient fluxes to the water column, which in turn will limit and further reduce the role of phytoplankton. The resurgent SAV will compete with benthic algae populations as their coverage expands into available open areas.

Comparison with other Potomac tidal fresh shallow water sites

The continuous monitoring results show that Occoquan Bay had notably higher chlorophyll *a* and pH in the summer of 2005 compared to other tidal fresh shallow water sites in the Potomac. Spring 2005 and spring and summer 2007 and 2008 were not particularly different from the other sites except for the modifying influence of Occoquan Reservoir on freshwater inflows and the bay's slow progress in rebuilding SAV populations. Table 2 (from Buchanan 2009) compares the continuous monitoring results for five embayment sites and one river flank site in the tidal fresh Potomac. Occoquan Bay's Chl *a* exceedances of 50 ug/liter, Virginia screening threshold for algal blooms, were 0% except for the summer of 2005 which had an exceedance rate of 0.6%. Spring exceedances of the maximal (95th percentile) chlorophyll *a* concentration for phytoplankton tidal fresh reference communities (Buchanan et al. 2005) were relatively high, ranging from 53.5% to 59.9%; summer/autumn exceedances were 88.3% in 2005 but only 1.4% in 2007 and 9.2% in 2008. Occoquan Bay's seasonal failure rates for the pH 9.0 criterion were comparable to those of other tidal fresh sites, with the exception of the high failure rate (39.6%) in summer 2005. The bay's frequency of dissolved oxygen records failing the Chesapeake Bay Program (CBP) instantaneous minimum criteria ranged from 0% to 0.5%. The bay never failed the CBP 7-day mean criteria.

Mattawoman and Piscataway creeks can be used as reference conditions against which other embayments are evaluated. These two systems recently attained their CBP SAV goals (320 ha Mattawoman, 319 ha Piscataway), and by default their water clarity goals, and both appear to be attaining their CBP dissolved oxygen goals. Specifically, DO criteria failure rates in both embayments are showing downward trends and were <1% in 2007-2008. Mattawoman and Piscataway are references in the sense that they are currently the least degraded tidal fresh Potomac embayments. They do not meet all reference condition thresholds. For example, water column Chl *a* concentrations in the two embayments exceeded the spring tidal fresh reference community threshold of 13.5 ug/liter by as much as 88% and the summer threshold of 15.9 ug/liter by as much as 21.1% (Table 2). Water column nutrient concentrations in Mattawoman are close to the ortho-phosphate (PO_4) algal bloom-limiting threshold of ~0.007 mg/liter, but frequently exceed the dissolved inorganic nitrogen (DIN) algal bloom-limiting threshold of ~ 0.07 mg/liter (thresholds from Fisher and Gustafson 2003). Piscataway concentrations frequently exceed both the PO_4 and DIN bloom-limitation thresholds.

With one exception (summer 2005), the cumulative distribution frequency (CDF) of seasonal pH values in Occoquan Bay are indistinguishable from the Mattawoman-Piscataway reference curves (Figure 12). At the two reference sites, pH exceeded the Virginia 9.0 criterion by as much as 13% in spring and 19.5% in summer/autumn (Table 2).

Conclusions

High frequencies of super-saturated dissolved oxygen demonstrate that Occoquan Bay is still a productive system despite its precipitous post-2000 drop in water column chlorophyll *a* concentrations. Strong plant photosynthesis coupled with a modest-to-low alkalinity buffering capacity appears to be responsible for the elevated pH values observed between March and October in the 2005, 2007, and 2008 continuous monitoring data. Positive, significant correlations in spring between water column chlorophyll *a* and pH implicate phytoplankton as the plant group primarily responsible for elevated pH values in that season. Beginning in June, correlations between chlorophyll *a* and pH are at times negative, weak, or non-significant and another plant group or groups contributes to elevated summer pH values. Recolonization of Occoquan Bay by submerged aquatic vegetation (SAV) has lagged behind other Potomac tidal fresh embayments and SAV are still relatively sparse in the bay. This leaves benthic algae, a plant group that is not monitored, as the current likely cause of elevated summer pH values. If SAV beds expand in the bay, they will exert a greater influence on pH. Analysis of continuous monitoring data from Piscataway Cr. and Mattawoman Cr., two Potomac tidal fresh embayments that recently met their SAV goals, suggests pH levels will continue to exceed the Virginia 9.0 criterion to some extent in Occoquan Bay if the bay attains its SAV goal. A continuous monitoring sonde located near abundant SAV beds upstream of Occoquan Bay in Belmont Bay had a summer pH criterion failure rate of 0.8% in 2009 (Jones and Buchanan 2009).

Occoquan Bay is an example of a shallow water system recovering from eutrophication impacts. It is in the process of slowly transitioning from a plankton dominated to an SAV/benthic algae dominated community. Recent physical changes in the bay give competitive advantages to benthic algae and SAV over phytoplankton: a) water clarity has improved so that the photic zone often reaches the shallow bay's bottom sediments, and b) PO_4 concentrations in the water column have declined to levels that can limit phytoplankton bloom formation. Total phosphorus concentrations in Occoquan watershed streams, Occoquan Bay's water column, and the tidal Potomac River mainstem all show long-term declines. The primary source of phosphorus supporting the bay's continued high productivity appears to be phosphorus stored in the bay's sediments, although large storm events and high tides still probably contribute substantial amounts. Increases in pH to levels above 9.0 can continue to enhance phosphorus releases from the bay's sediments, but the frequency of high pH values has declined since the 1970s and 1980s (Figure 11). Benthic algae and SAV will further limit sediment phosphorus fluxes to the water column as they become more established. The declining frequency of high pH values and the low concentrations of ammonium (NH_4^+) observed in Occoquan Bay makes the risk of ecologically significant ammonia (NH_3) toxicity unlikely at the present time.

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Table 1. Coefficients of determination (r^2) for linear regressions between pH, Chl *a* (ug/liter), and DO % saturation, by season, with significance indicated: ***, p<0.001; **, p<0.01; *, p<0.05; ns, not significant. Daytime: 7 am - 6 pm. Daily: 24 hours. All measurements made at depth of 1 meter; water column mean depth is 1.8 meters. Data gaps (see Figures 2, 3, 4) may bias results.

Parameter	Parameter	Year	Spring (Apr-May)	June	Summer (Jul-Sep)	Autumn (Oct)	All Seasons
max daytime pH	max daytime chl *a*	2005	+ 0.608 ***	+ 0.268 *	ns		+ 0.290 ***
		2007	+ 0.265 ***	— 0.141 *	ns	ns	ns
		2008	+ 0.373 ***	ns	+ 0.228 ***		+ 0.171 ***
max daytime pH	max daytime DO % saturation	2005	+ 0.633 ***	+ 0.494 ***	+ 0.214 **		+ 0.502 ***
		2007	+ 0.561 ***	+ 0.477 ***	+ 0.688 ***	+ 0.718 ***	+ 0.568 ***
		2008	+ 0.582 ***	+ 0.530 ***	+ 0.648 ***		+ 0.578 ***
max daytime DO % saturation	max daytime chl *a*	2005	+ 0.284 ***	ns	+ 0.361 *		+ 0.522 ***
		2007	+ 0.296 ***	— 0.349 **	ns	+ 0.386 *	ns
		2008	+ 0.103 *	ns	+ 0.092 **		+ 0.041 **
avg daily pH	avg daily chl *a*	2005	+ 0.743 ***	+ 0.639 ***	+ 0.085 *		+ 0.506 ***
		2007	+ 0.368 ***	— 0.433 ***	ns	+ 0.741 ***	+ 0.024 *
		2008	+ 0.407 ***	ns	+ 0.443 ***		+ 0.421 ***
avg daily pH	avg daily DO % saturation	2005	+ 0.702 ***	+ 0.136 *	ns		+ 0.416 ***
		2007	+ 0.501 ***	+ 0.392 ***	+ 0.608 ***	+ 0.839 ***	+ 0.431 ***
		2008	+ 0.422 ***	+ 0.465 ***	+ 0.442 ***		+ 0.421 ***
avg daily DO % saturation	avg daily chl *a*	2005	+ 0.446 ***	ns	ns		+ 0.471 ***
		2007	+ 0.323 ***	— 0.731 ***	ns	+ 0.719 ***	+ 0.085 ***
		2008	+ 0.197 ***	ns	+ 0.047 *		+ 0.151 ***

Table 2a. Spring (March/April - May 31) continuous monitoring results for shallow tidal fresh Potomac sites. "Median Chla," median chlorophyll *a* 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 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, with the magnitude of diel change being the difference between a day's maximum and minimum; "%DO<Min," % of dissolved oxygen records failing the CBP instantaneous minimum dissolved oxygen criteria for migratory fish spawning and nursery use in 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 criteria for tidal pH; "%Turb≥150," % of turbidity records failing the MDE instantaneous maximum screening threshold, "%Turb>50," % of turbidity records failing a value 1/3 the MDE instantaneous maximum screening threshold. Site: E, embayment; PR, flank of tidal Potomac River. ALL VALUES ROUNDED TO 1 DECIMAL PLACE. See Buchanan 2009 for further details.

Site	Potomac Tidal Fresh (TF) Sites	Year	Median Chla	%Chla ≥50	%Chla >Ref	%SatDO	DM%Sat	%DO <Min	%DO <7Day	%pH <6	%pH >9	%Turb ≥150	%Turb >50
E	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
E	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
E	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	--	--	--	--	--	--	--	--	--	--	--
E	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

Table 2b. Summer and autumn (June 1 - October/November) continuous monitoring results for shallow tidal fresh Potomac sites. "%DO<Min," % of 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 29ºC or lower and less than 4.3 mg DO per liter at temperatures greater than 29ºC; "%DO<7Day," % of 7-day means of dissolved oxygen records failing the CBP 7-day mean 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 surrounding sonde. See Table 2a heading and Buchanan 2009 for further details.

Site	Potomac Tidal Fresh (TF) Sites	Year	Median Chla	%Chla ≥50	%Chla >Ref	%SatDO	DM%Sat summer	DM%Sat autumn	%DO <Min	%DO <7Day	%pH <6	%pH >9	%Turb ≥150	%Turb >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	-
		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	--	0.2	--	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	++

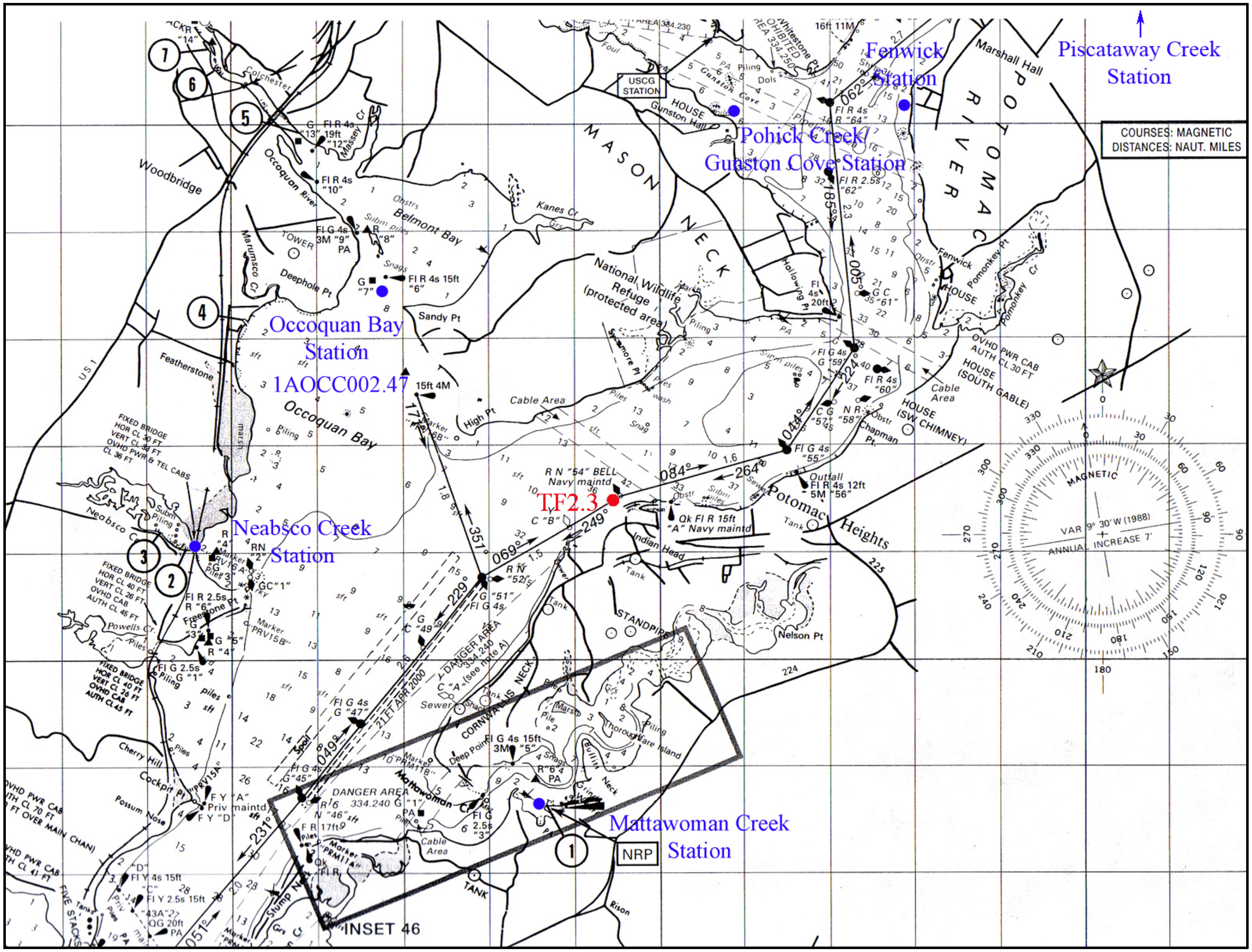


Figure 1. Nautical map of Occoquan Bay and adjacent tidal Potomac River showing depth in feet below mean low tide (from Maryland Cruising Guide 2002-2003, Williams & Heintz Map Corporation, Capitol Heights, MD 20743). Locations of continuous monitoring sondes at 1AOCC002.47 and nearby continuous monitoring stations are indicated by blue dots; Chesapeake Bay Program bimonthly shipboard monitoring station indicated by red dot.

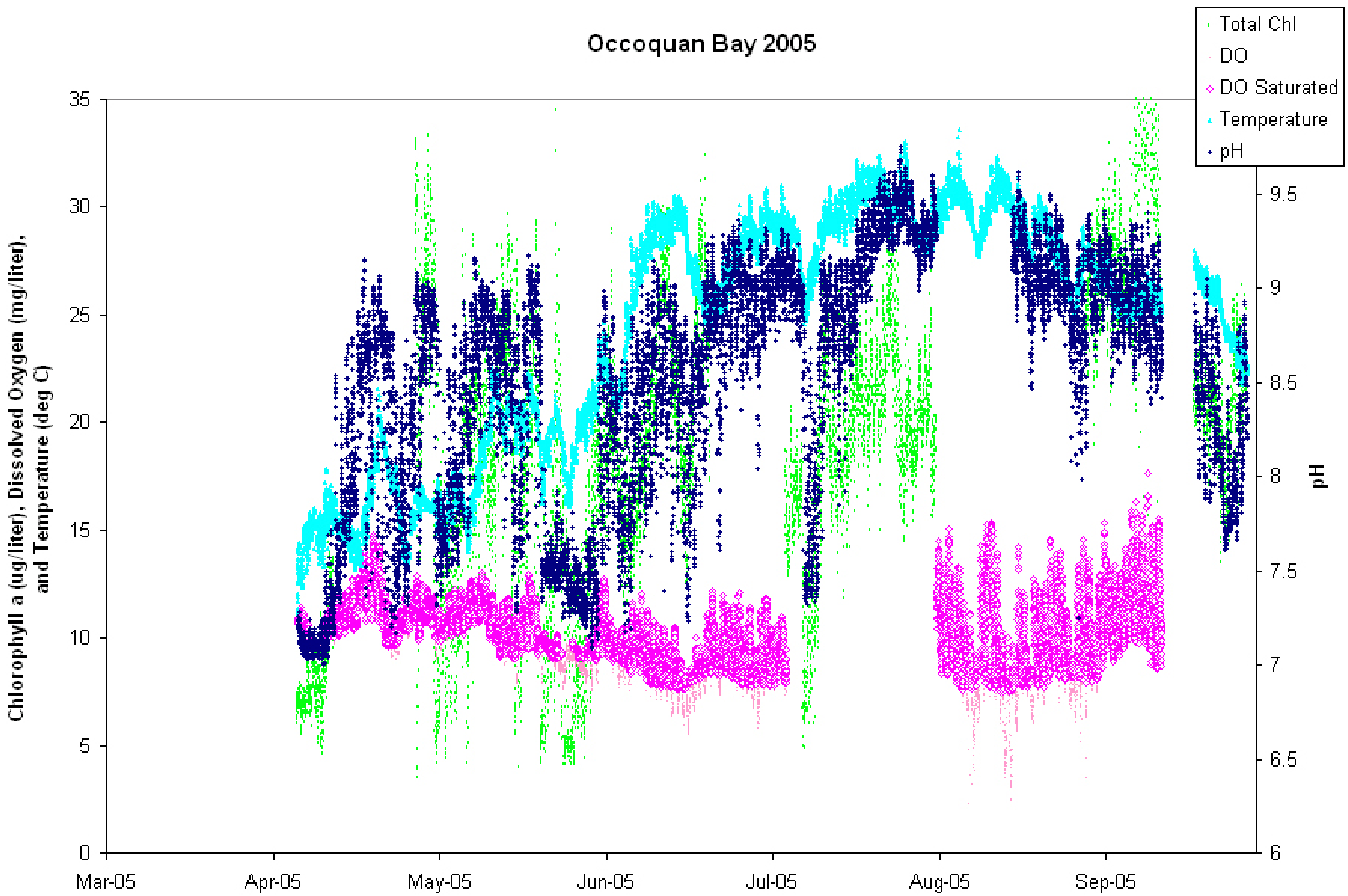


Figure 2a. Chlorophyll *a* (ug/liter), pH, temperature (deg C), and dissolved oxygen (mg/liter) collected every 15 minutes between April 5 and September 29, 2005, with a continuous monitoring sonde located at Occoquan Bay station 1AOOC002.47. Saturated and unsaturated dissolved oxygen (DO) values are differentiated.

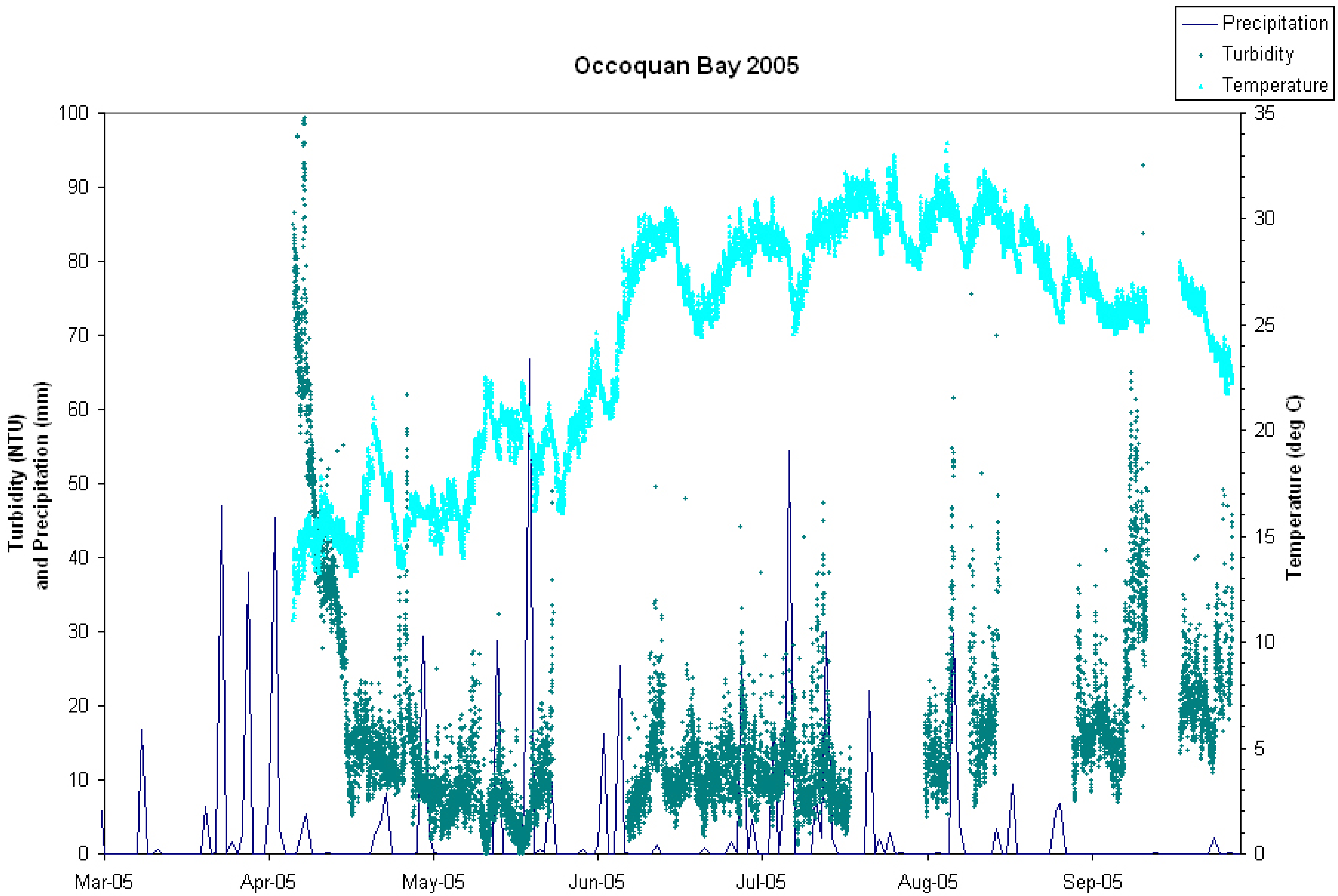


Figure 2b. Turbidity (NTU) and temperature (deg C) collected every 15 minutes between April 5 and September 29, 2005, with a continuous monitoring sonde located at Occoquan Bay station 1AOOC002.47. Daily precipitation (mm) data were collected at National Airport. Total precipitation for April-September was 516 mm (20.3").

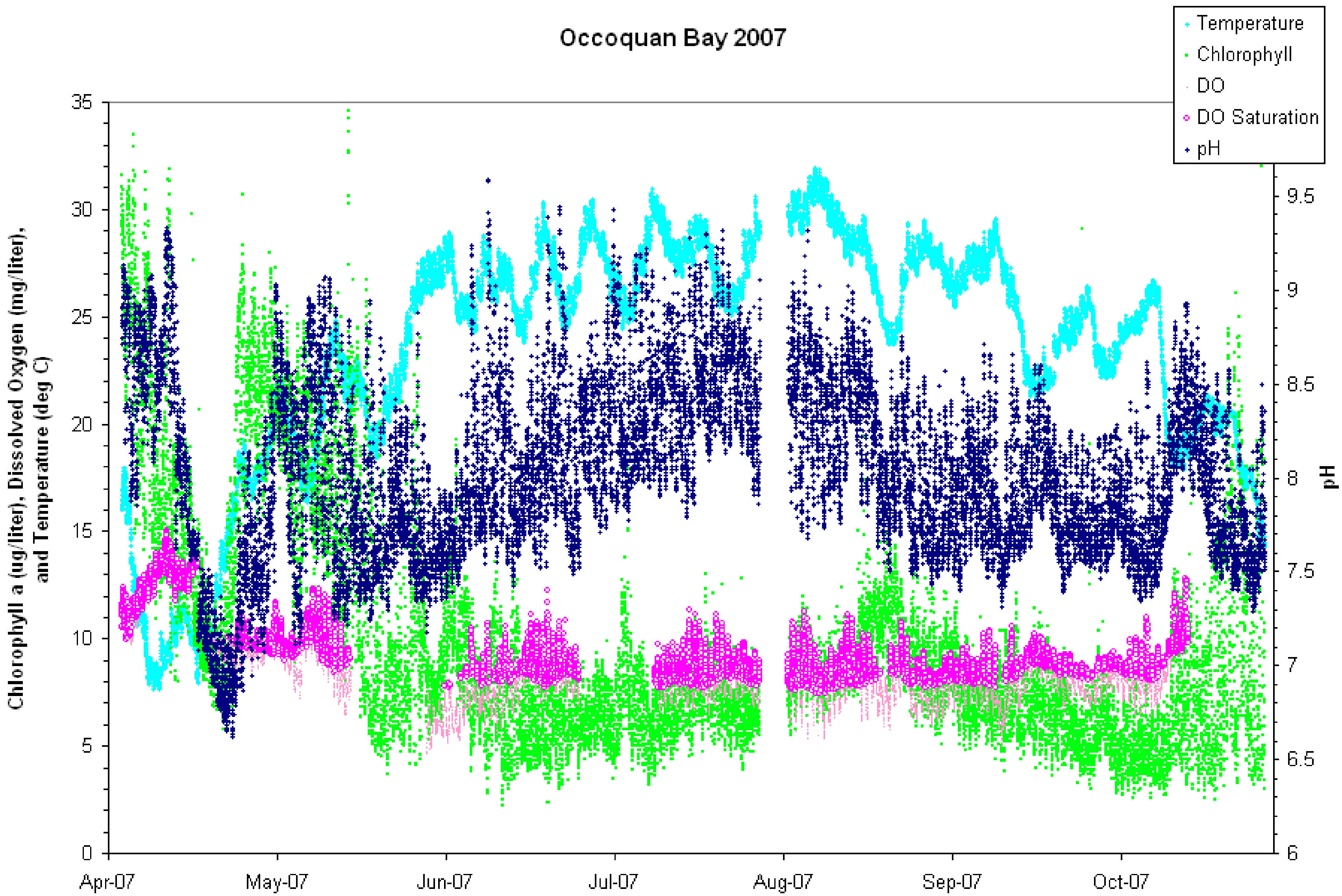


Figure 3a. Chlorophyll *a* (ug/liter), pH, temperature (deg C), and dissolved oxygen (mg/liter) collected every 15 minutes between April 3 and October 30, 2007, with a continuous monitoring sonde located at Occoquan Bay station 1AOOC002.47. Saturated and unsaturated dissolved oxygen (DO) values are differentiated.

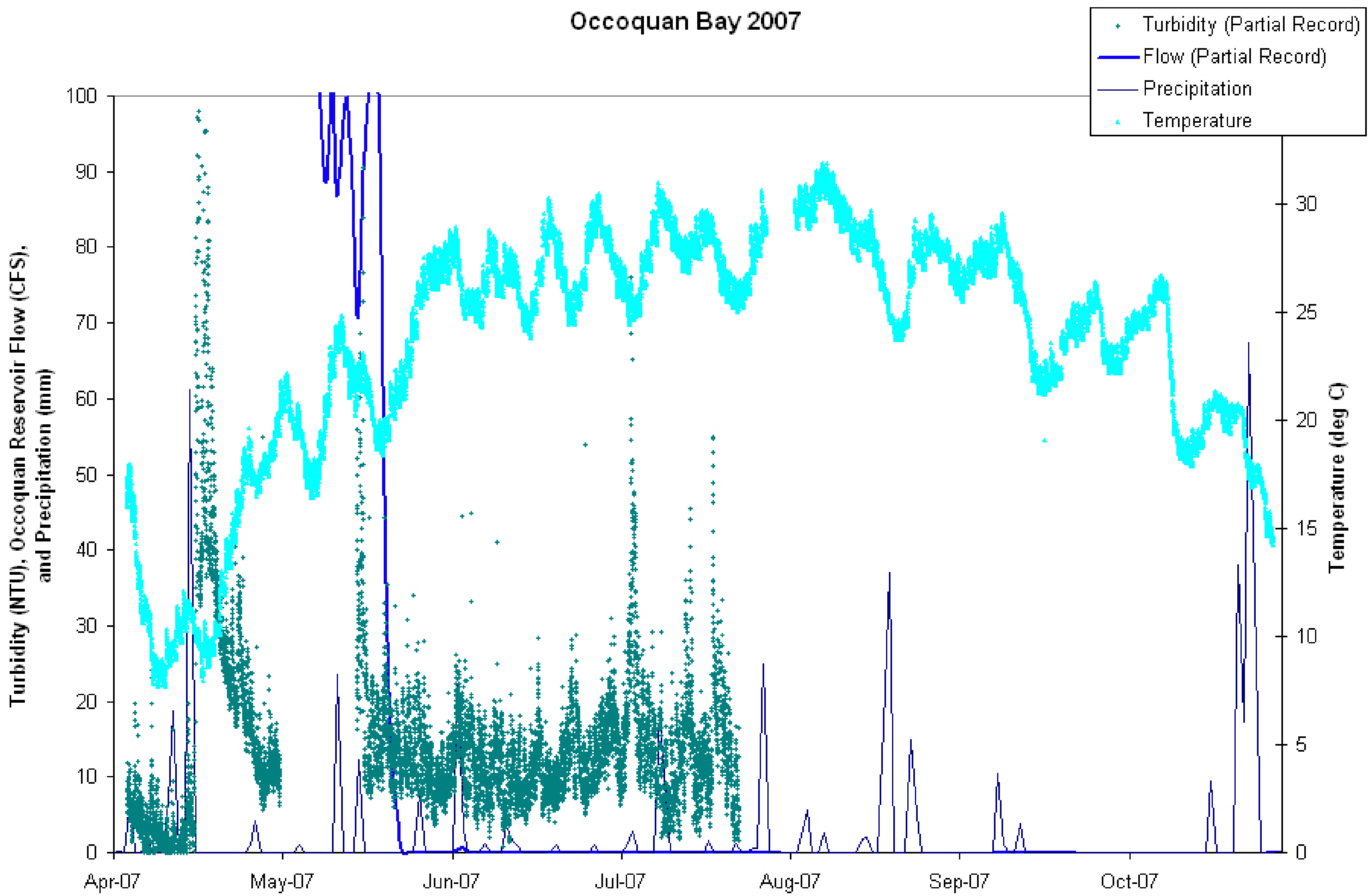


Figure 3b. Turbidity (NTU) and temperature (deg C) collected in 2007 from a continuous monitoring sonde located at Occoquan Bay station 1AOOC002.47. Daily precipitation (mm) data collected at National Airport. Total precipitation for April-September was 350 mm (13.8"). Daily average flow (cfs) from the Occoquan Reservoir ranged between 100 and 879 cfs from April 5th to May 8th, fell to 0 cfs by May 24th, and appears to have remained at 0 cfs until at least October 31st (although there are some gaps in the data).

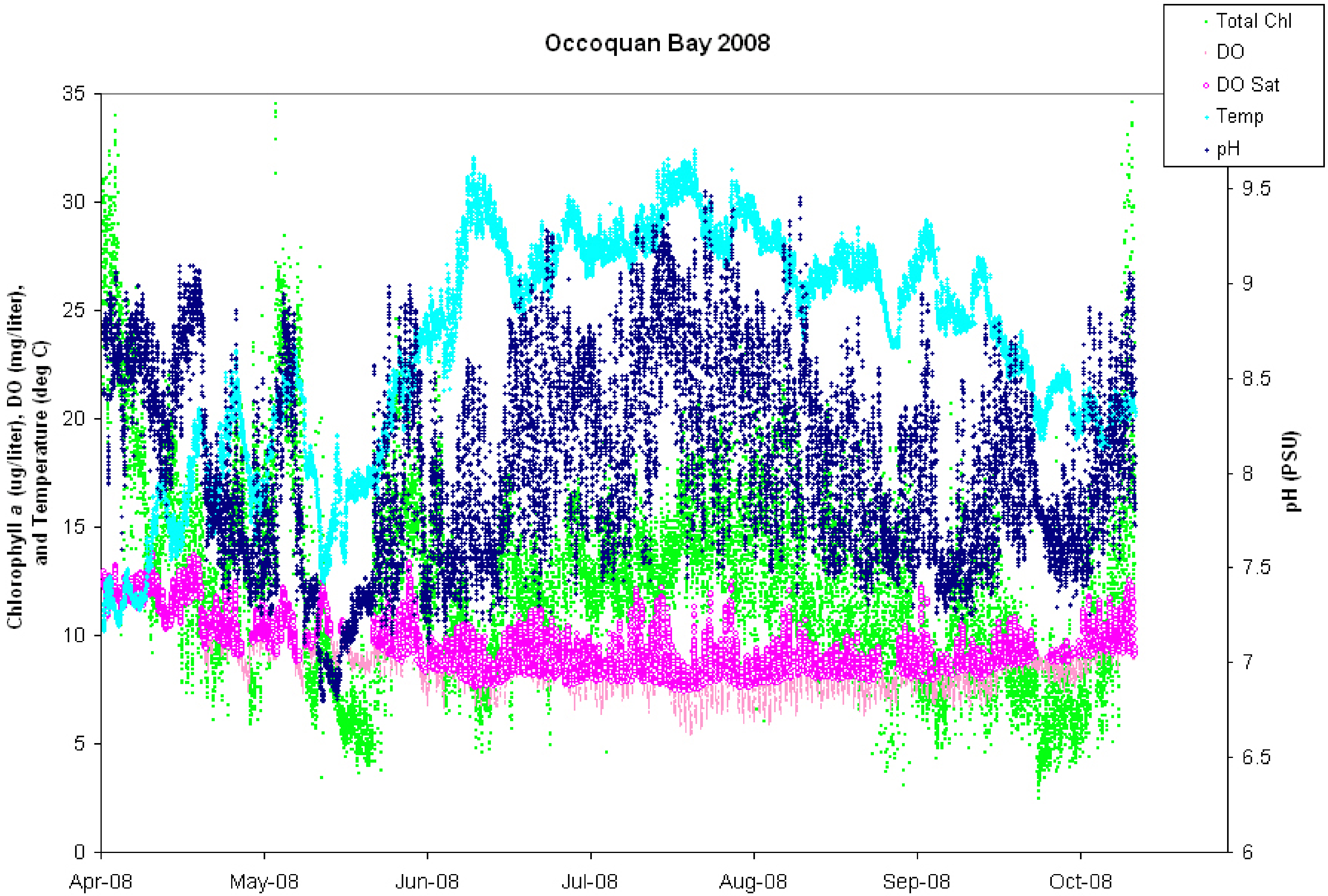


Figure 4a. Chlorophyll *a* (ug/liter), pH, temperature (deg C), and dissolved oxygen (mg/liter) collected every 15 minutes between April 1 and October 14, 2008, with a continuous monitoring sonde located at Occoquan Bay station 1AOOC002.47. Saturated and unsaturated dissolved oxygen (DO) values are differentiated.

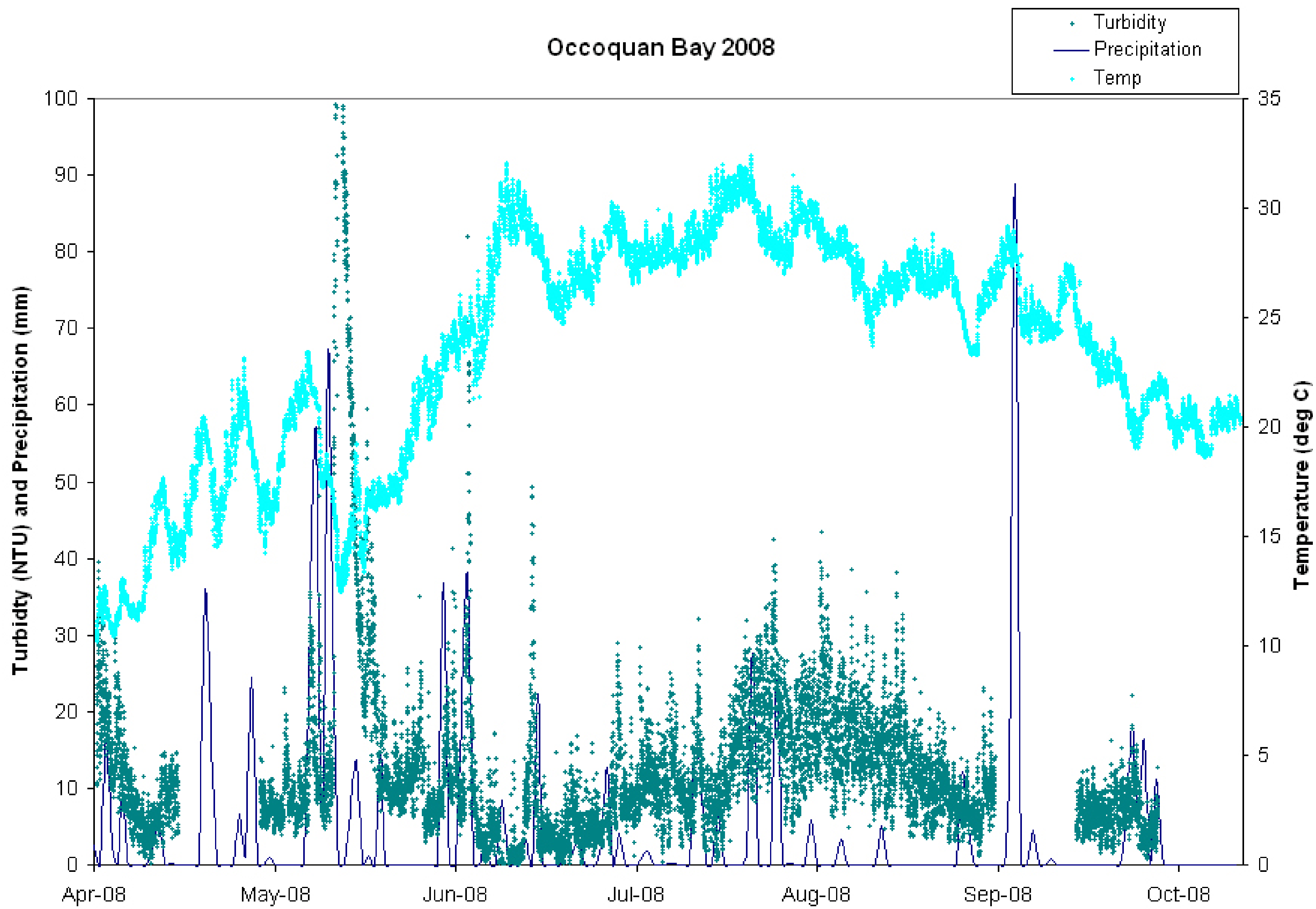


Figure 4b. Turbidity (NTU) and temperature (deg C) collected every 15 minutes between April 1 and October 14, 2008, with a continuous monitoring sonde located at Occoquan Bay station 1AOOC002.47. Daily precipitation (mm) data were collected at National Airport and other Washington, DC region sites and averaged. Total precipitation for April-September was 803 mm (31.6").

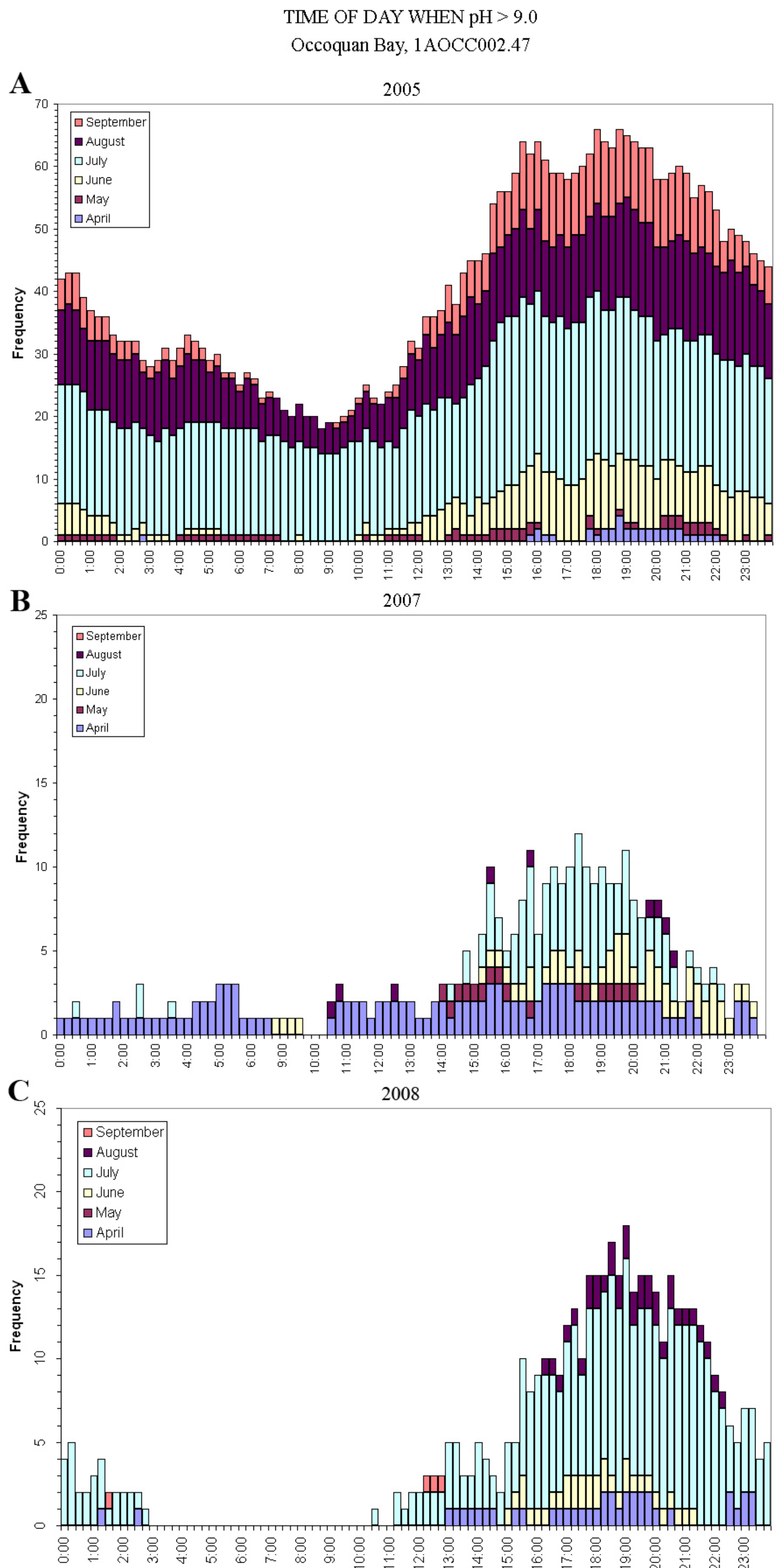


Figure 5A-C. Frequency of pH > 9.0 (by the quarter hour) at Occoquan Bay station 1AOCC002.47 in 2005 (A), 2007 (B), and 2008 (C).

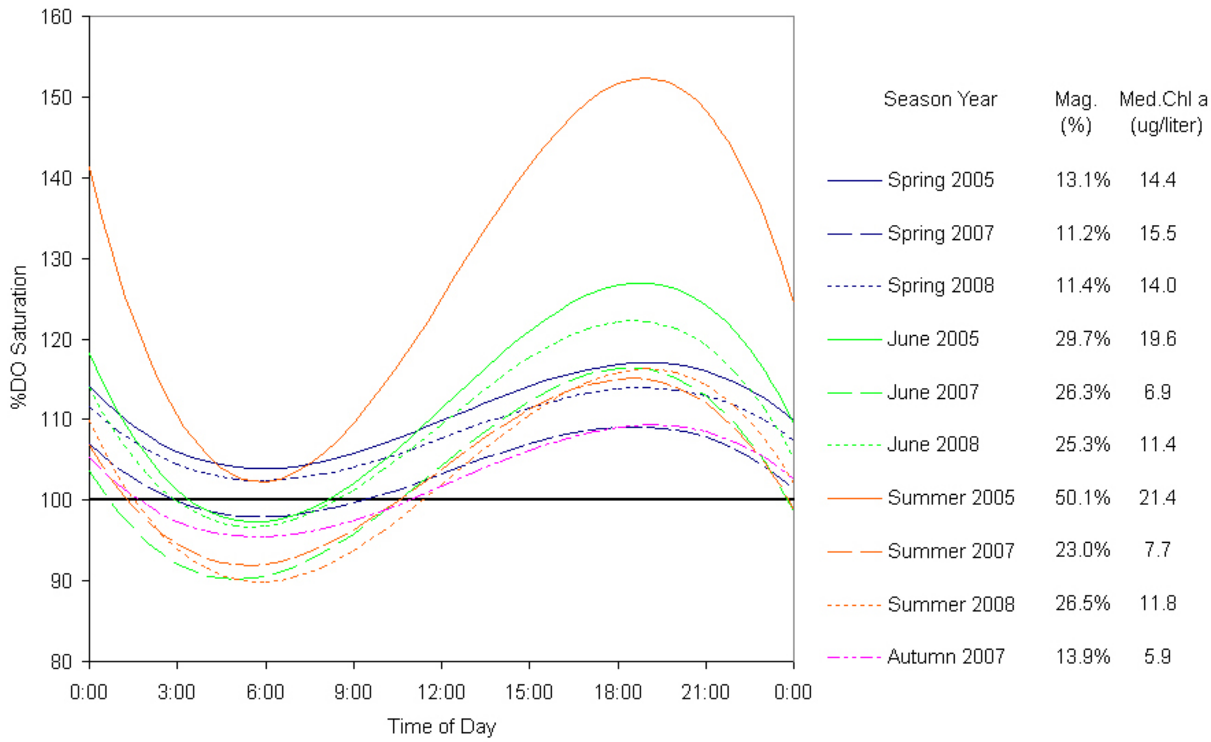


Figure 6. Diel cycle in % dissolved oxygen saturation in Occoquan Bay. Lines are 3° polynomial regressions through the raw data grouped by season and year. They represent the approximate average %DO saturation at that time of day for a given season-year. Mag, magnitude of daily change in polynomial regression; med. Chl a, median chlorophyll *a* concentration in ug/liter.

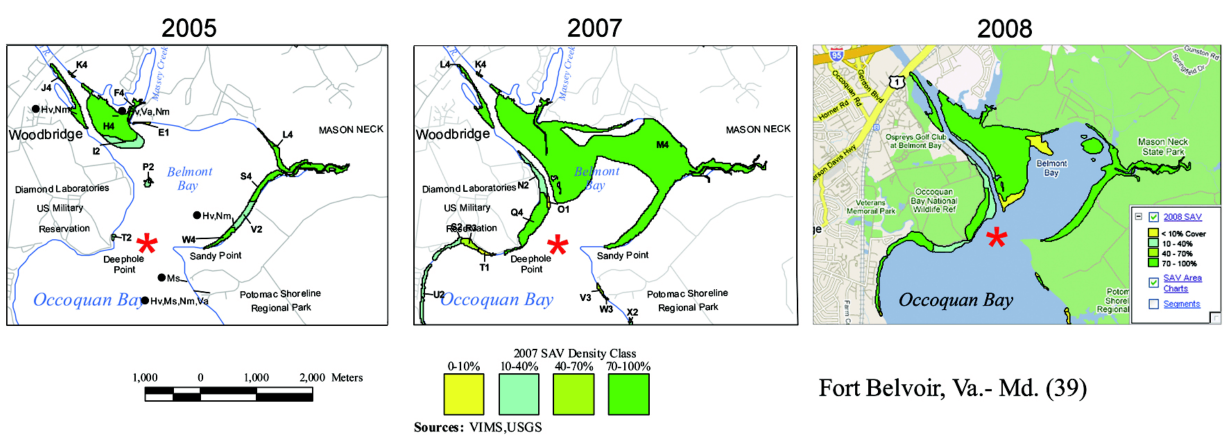


Figure 7. Station 1AOCC002.47 (*) location relative to submerged aquatic vegetation (SAV) beds, as documented in 2005, 2007, and 2008 with aerial survey and ground truthing. Maps extracted from SAV quad map 39 available at www.vims.edu/bio/sav/.

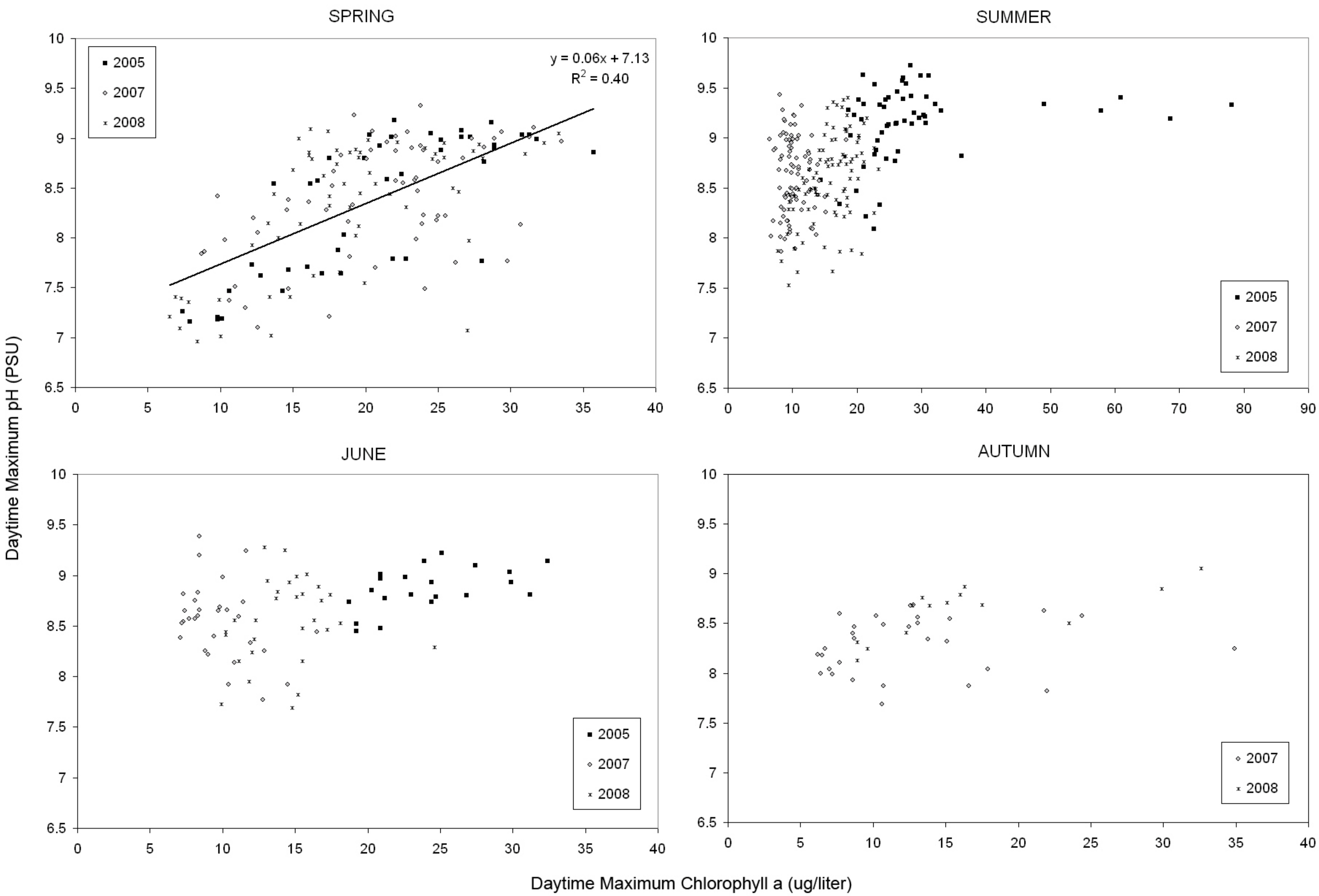


Figure 8. Seasonal linear relationships between daytime (7 am - 6 pm) maximum chlorophyll *a* concentration and daytime maximum pH for each day. The spring (April - May) relationship is significant; the June, summer (July-September), and autumn (October) relationships are not significant ($p<0.01$).

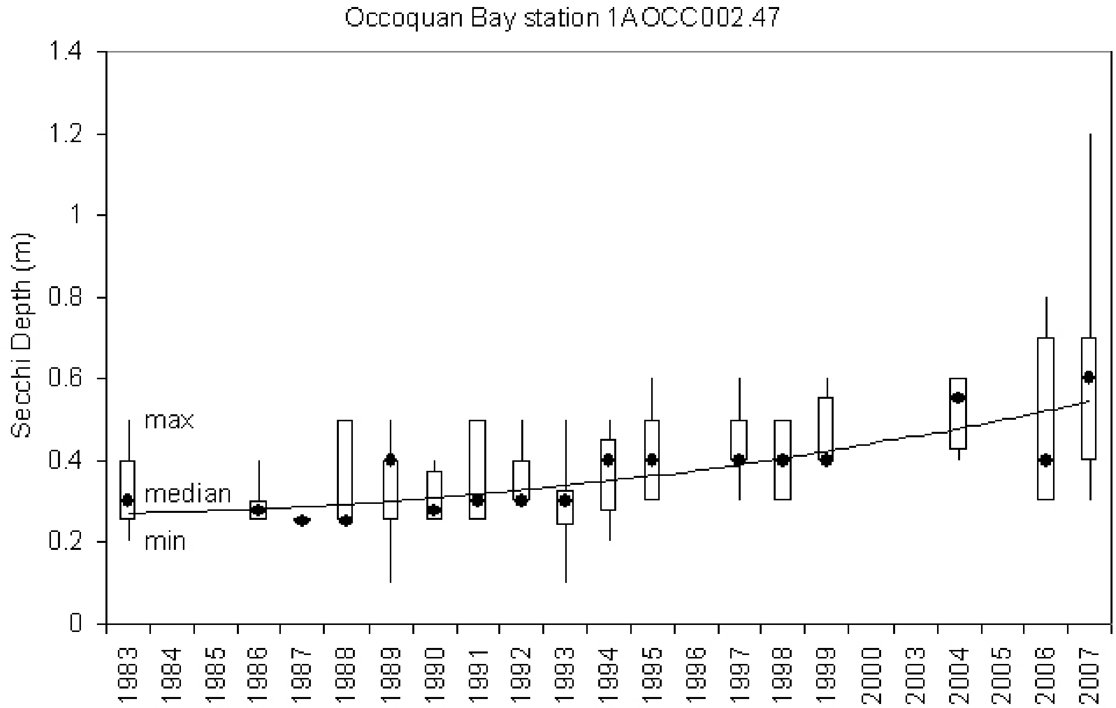


Figure 9. Observed annual variation and increasing trend in Secchi depth (meters). Years with n≤4 not shown.

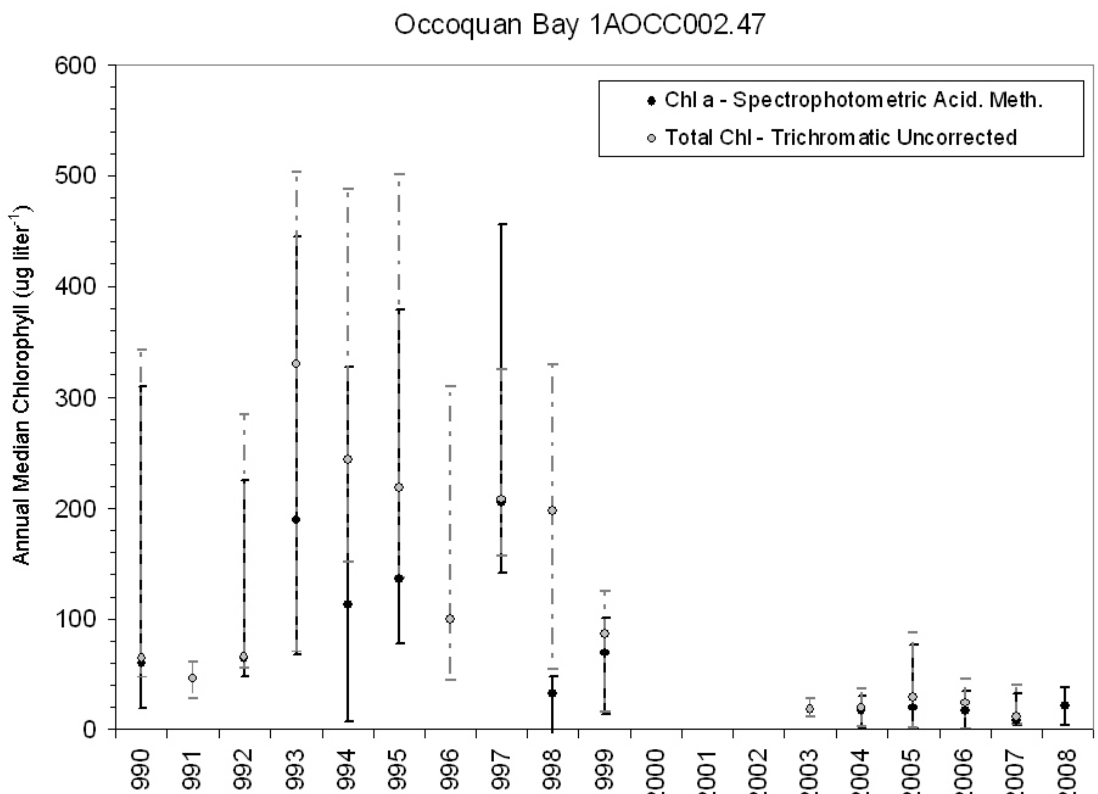


Figure 10. Annual median chlorophyll *a* (●) and total uncorrected chlorophyll (o) concentrations (µg liter^{-1}) for 1990 - 2007, with observed minimum and maximum values indicated. Years with n≤4 not shown.

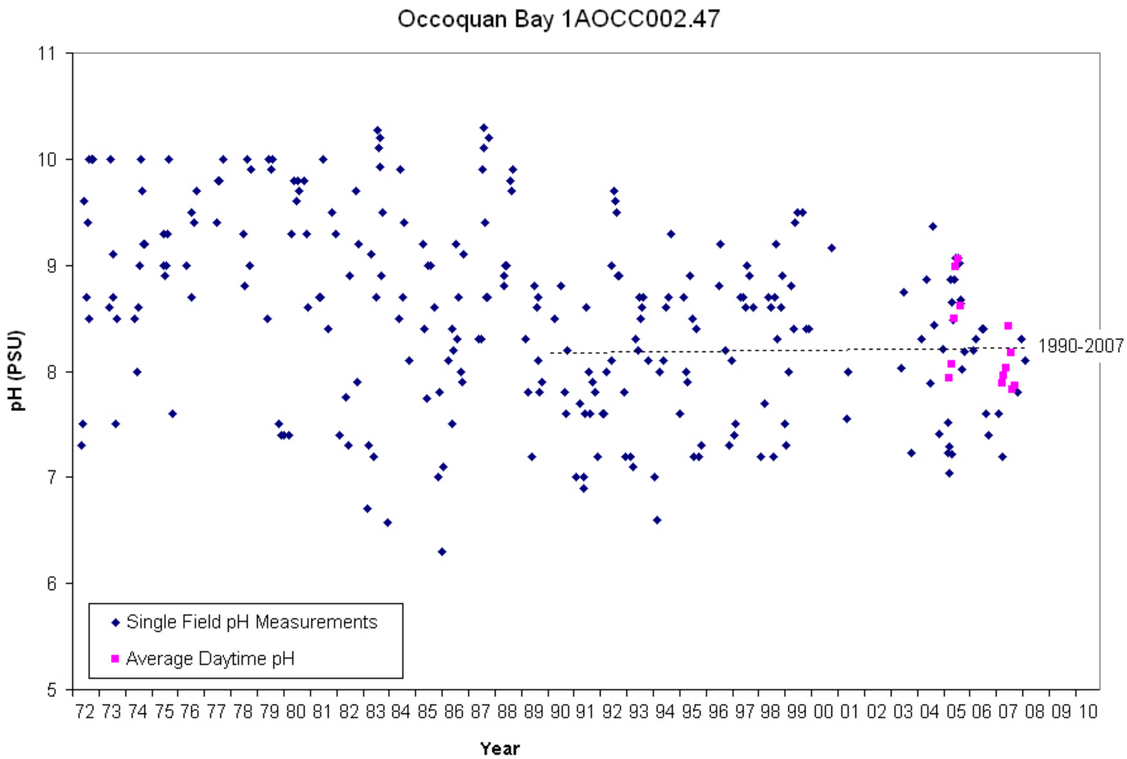
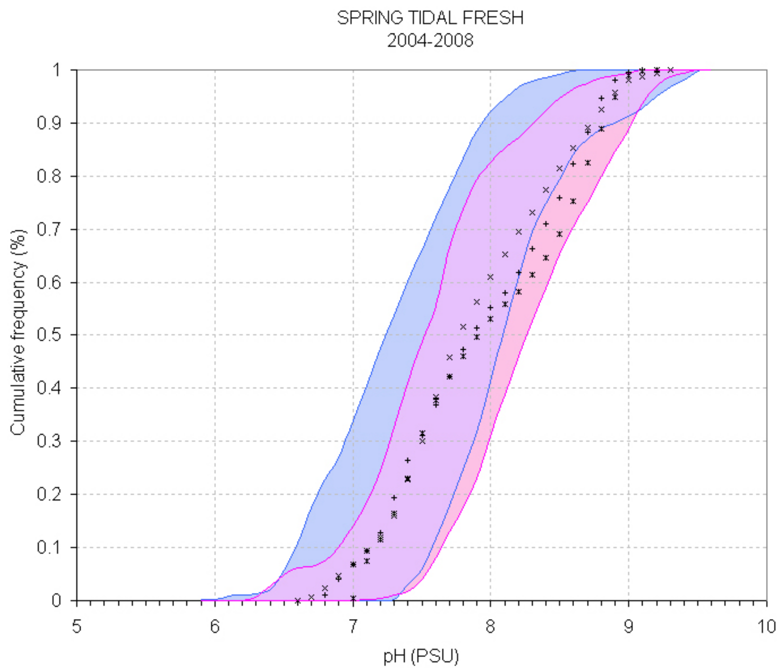


Figure 11. Observed pH field measurements from ambient monitoring program (◆) and monthly averages of all daytime (7am - 6pm) pH values from the continuous monitoring program (■).



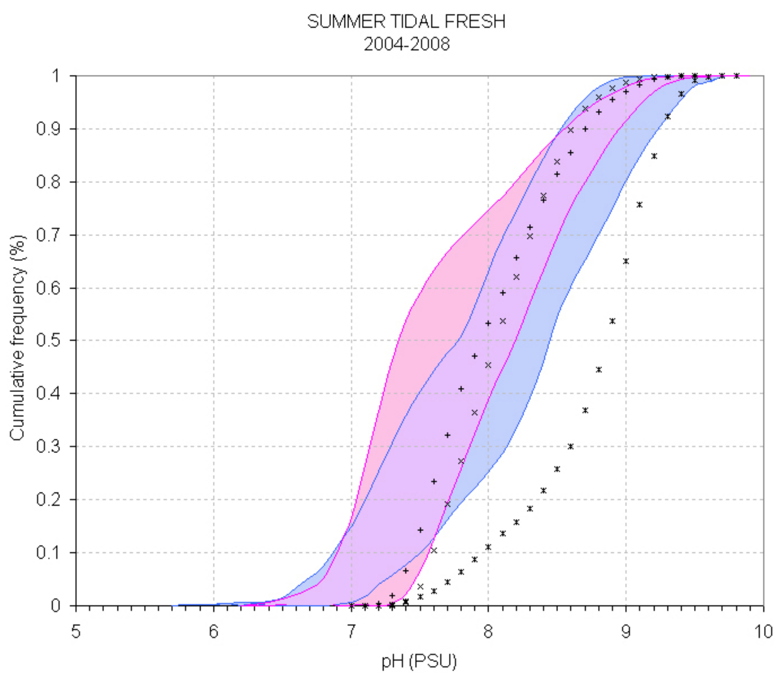


Figure 12. Occoquan Bay's spring and summer distributions of pH values compared to reference distributions. All distributions are derived from continuous monitoring data collected every 15 minutes during spring (March/April - May 31) and summer (June 1 - September 30) between 2004 and 2008. The envelopes enclosing the seasonal 2004 - 2008 CDF curves for the Mattawoman Cr and Piscataway Cr embayments are used to represent reference conditions. Key: Mattawoman Creek envelope (blue); Piscataway Creek envelope (red); Mattawoman and Piscataway overlap (purple); Occoquan Bay pH CDF for 2005 (*), 2007 (x), and 2008 (+).