Salinity, dissolved oxygen, and nutrient concentrations

in Oyster Pond, Falmouth, Massachusetts

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ABSTRACT

Anthropogenic impacts have considerable effects on coastal waters, and distributions of salinity, dissolved oxygen, and nutrients may be used to assess water quality and the extent of eutrophication in water bodies. Oyster Pond (OP), a regulatedtidal pond in Falmouth, MA, is a valuable model, and ongoing testament to how human manipulation *will* distort the natural composition of flora and fauna in delicately balanced estuarine waters. By implementation of a weir, to minimize regular tidal flushing, in hopes of aiding choice fish species, the salinity of OP has leveled out after several years at concentrations significantly lower than a nearby free-flowing tidal pond, Salt Pond (SP). Dissolved O2 is only slightly higher in the fresher waters of OP, and has remained somewhat constant between 2001 and 2004. Similarly, although slightly more eutrophic waters are seen in SP, with NO3 and NH4 concentrations measured throughout the majority of both ponds being higher SP—PO4 being practically absent from both ponds-little change has occurred in the concentrations of these nutrients within OP between 2001 and 2004. The exceptions to these trends are the notably higher NH4 and PO4 and lower O2 concentrations in the deep basins of OP, in 2004, than found either in SP or in OP in 2001. This suggests that unlike SP, which remains well mixed throughout the water column by daily tidal flushing; due to regulation, deeper waters in OP receive minimal mixing, because of greatly reduced tidal exchange, and are, therefore, becoming continually more stratified than SP.

INTRODUCTION

Evidence of eutrophication includes increases in nutrient concentrations, and decreases in dissolved oxygen concentration with depth (Valiela, 1997). Nitrate and ammonium are the most common sources usable nitrogen; nitrate being the most plentiful source in freshwater (Newton et al., 2003). Ammonium is produced by the decay of organic nitrogen (Rosenfeld, 1979). Phosphate (usually in the form of orthophosphate) is generally present in low concentrations in surface waters as it is consumed quickly by aerobic organisms, and is often the limiting nutrient in freshwater (Valiela, 1997). In deep waters, ammonium and phosphate concentrations increase due to specific chemical reactions in anoxic waters (Krom and Berner, 1980).

Nutrient and dissolved oxygen concentrations may differ in waters with different salinity (Valiela, 1997). These relationships are apparent in estuaries, salt marshes, and other coastal water bodies with outlets to the ocean (Newton et al., 2003). The tidal flow of salt water into and out of a coastal freshwater system has a significant effect on salinity, dissolved oxygen, and nutrient concentrations (NRC, 2000). Dissolved oxygen concentrations decrease in areas where water flow is slow (Gillibrand, 1996). Aerobic life can no longer live in these areas and is replaced by anaerobic bacteria that utilize other compounds, namely, nitrate and sulfate, the latter accounting for the sulfurous odor of these regions (Valiela, 1997).

Shallow waters of coastal areas are being exposed to increasing nutrient loads. One such example is Oyster Pond (OP), on Cape Cod. In this area, nutrient input from its watershed has changed and led to changes in water quality. Similarly, Salt Pond (SP), located near OP, has been exposed to greater nutrient loads and is generally saltier. These contrasts allow for comparison of the effects of salinity and nutrient load on water quality. In addition, data on water quality of OP collected in 2001 allow interannual comparison (Burdick, 2001). Knowledge of the distribution and concentrations of nutrients is important to evaluate their potential consequences at high levels, such as increased primary producer growth. One approximate way to assess whether N or P may limit growth of primary producers is to evaluate the ratio of N to P in the water, and compare that ratio to the Redfield Ratio of 16 N to 1 P, which is the ratio needed by producers (Caraco, 1998).

This study had three primary objectives. 1) To measure the vertical and horizontal distributions of salinity, dissolved oxygen, nitrate, ammonium, and phosphate in OP and SP in 2004, and compare these distributions to better understand the exchange of salt and nutrients in both systems, and to evaluate the their effects on water quality. 2) To assess whether growth of primary producers in OP and SP is limited by N or P. 3) To Define inter-annual changes in water quality within OP between 2001 and 2004.

METHODS

We sampled water to measure nitrate $[NO_3]$, ammonium $[NH_4]$, phosphate $[PO_4]$, dissolved oxygen $[O_2]$, salinity, and temperature throughout OP and SP. At OP, sample sites were chosen along the long axis of the pond, from the Treetops area to the outlet

4

into Vineyard Sound (Fig. 1A). In OP, sixty-five samples were collected from twenty stations. At SP, twenty samples were collected from eleven stations (Fig. 1B). Stations corresponded to those used in the 2001 study (Burdick et al., 2001). For consistency and comparability to 2001 data, all collections were done in the afternoons, at mid- to high-tide, October 8 through 15, at OP and on October 18 at SP. Measurements of all six variables were taken every meter from the surface to within 0.25m of the bottom sediment, to create depth profiles (Fig.s 2-7). The only exception to this procedure was at site 9 of OP, the deepest point in the pond's southern basin, where measurements were taken at half-meter depths from 4m to the bottom, at 6.75m, to examine stratification in more detail.

Measurements for temperature and O_2 were taken using an YSI meter. For salinity, a refractometer was used. A water sampler was used to collect two replicate water samples to be used for nutrient analysis of NO₃, NH₄, and PO₄. In the lab, samples were filtered with GF/F ashed glass microfiber filters using vacuum suction to remove any particulate matter, which might have been capable of harming the nutrient analysis apparatus (especially important for deeper samples and those closest to the bottom). All filtered samples were frozen until analyzed for nutrient content.

Concentrations of NO₃, NH₄, and PO₄ were measured with the Lachat 8000 autoanalyzer, using QuickChem Methods 31-107-04-1-E, 31-107-06-1-B, and 31-115-01-1-H, respectively.

RESULTS

1. COMPARISON OF OYSTER POND TO SALT POND

1.A. VARIABLE DISTRIBUTIONS

Temperature ranged from 15-20°C in OP with lower temperatures at the Vineyard end (lowest in the Southern Basin (station 9) at 6.5m and 15°C), and higher temperatures at the northern end, near Treetops (Fig. 2A). In SP (Fig. 2B), temperatures varied less (14-15°C). Points not located on our north-to-south transects (stations 13, 14, 15, Fig. 1A; stations 1,2, Figure 1B) had similar concentrations to the transects points for all variables, and were not included in our depth profiles.

Salinity in OP was about 1-2ppt in most of the upper regions (Fig. 3A), and increased in the deepest part of the Southern Basin (station 9, Fig. 3A) and in the Lagoon (stations L3, VS1, Fig. 3A). In SP (Fig. 3B), salinity was uniformly 25ppt, except in the deepest region (station 4), where salinity increased to 27 ppt (Fig. 3B).

Dissolved oxygen in OP ranged from 9-11mg L⁻¹ down to depths of 4.5 m (Fig. 4A). Below this depth (station 9), dissolved oxygen decreased rapidly, dropping to 1.4mg L⁻¹ at 6.5m. In SP (Fig. 4B), dissolved oxygen ranged from 8-9mg L⁻¹ down to 2.5m. Below this level, O_2 concentration decreased to $3mg L^{-1}$ (station 4, Fig. 4B).

Concentrations of NO₃ in OP were variable (Fig. 5A). Lowest levels of NO₃ were in the Southern Basin, with trace amounts in the open water. The highest concentrations were 1.5-3 μ M and were seen at the north end, near Treetops where the most likely source is wastewater treatment, and at VS1, where high concentrations may be caused by the release of nutrients (from piles of decomposing seaweed on the shore), in the form of ammonium that can be nitrified by bacteria, in this highly aerobic location (Valiela, 1997). Although low concentrations of NO₃ were present in surface waters throughout OP, it was completely absent at greater depths, presumably due to consumption by organisms. NO₃ concentrations were variable, but higher in SP, the up to approximately 5μ M (station 7; Fig. 1B). These concentrations were found at the northern end of the pond (station 3), and at stations 6-8 where the transect begins to curve (Fig. 1B) Higher NO₃ concentrations suggest that SP may be slightly more eutrophic than OP.

Concentrations of NH₄ were between 1-3 μ M throughout most of the open water at OP (Fig. 6A). The concentrations after 3m increased quickly with depth, reaching values of 51-107 μ M in the Southern Basin (station 9). The Lagoon also had higher NH₄ concentrations, ranging from 4-15 μ M. After an initial high level of NH₄ (17uM), the concentration swiftly drops again in Vineyard Sound to 1-2 μ M. Concentrations in the open water of SP (Fig. 6B) were higher on average than those seen in Oyster Pond (Fig. 6A). This may be due to the greater amount of vertical mixing which mixes up NH₄ produced by decaying nutrients at the bottom of SP, since it is shallower than OP. The highest concentration was 55 μ M, at the pond's lowest depth (station 3).

Concentrations of PO₄ were practically zero for the majority of points in both OP and SP (Fig.s 7A and 7B). Increased concentrations of PO₄ were only seen in Oyster Pond in the depths of the Southern Basin (up to 21 μ M) and at the VS1 surface station (4.2 μ M).

Phosphate and nitrogen both limit growth of primary producers in OP and SP (PO₄ limiting at the surface and NO₃ limiting near the bottom) since plants, algae and bacteria all consume dissolved phosphate and nitrogen to aid in their methods of obtaining energy through ATP (Valiela 1997).

1B. SALINITY RELATIONSHIP COMPARISONS

Comparing salinity versus each of our other variables was useful in uncovering how dissolved oxygen and nutrient concentration distribution varied in relation to salinity. To compare the affect of salinity on O₂, OP data was split into Vineyard Sound (VS), the Lagoon (OL), and OP (Fig. 8).

In OP, measurements from the surface at stations with low salinity had the highest O_2 concentrations, averaging 10ppt (Fig. 8). Surface measurements from stations with high salinity (Vineyard Sound and SP) had somewhat high O_2 ; however deep measurements from stations with low surface salinity (Southern Basin), had increased Sali9nity and much lower concentrations of O_2 (1.4-5.5ppt). The points for the Lagoon (OL), VS, and SP, all of which had higher salinity, showed similarly high concentrations of O_2 (10ppt, 8ppt, and 9ppt on average). This suggests that although O_2 concentrations are generally lower at higher salinities across a small, stratified area, on wider spatial scales between water-bodies, these concentrations may be more affected by depth, or proximity to bottom sediments, than by salinity levels alone.

1.C. IMPACT OF NUTRIENT LIMITATION ON PRIMARY PRODUCER GROWTH

To interpret the possible consequences of the concentrations of nutrients in the pond, we used the Redfield Ratio, which suggests PO₄ limitations on plant and algal growth in waters with values over 16, and usable nitrogen limitation at values below 16 (Caraco et al, 1998). The Redfield Ratio of N/P (nitrate plus ammonium then divided by phosphate concentration) was plotted versus salinity to assess the trends of variation from

16 in waters of differing salinity (Fig. 12). Most of the N/P ratios for OP and SP fell above 16. Areas of low dissolved oxygen in the Southern Basin in OP, as well as Vineyard Sound, were NO₃ limiting, with N/P ratios less than 16. To display how many points had a phosphate concentration of zero, the total number was written at the arbitrary value of 120. These points were phosphate limited according to the N/P ratio. It seems that N/P ratios are correlated much more closely to changes in conditions related to depth, such as mineral composition of water, anoxia and stratification, rather than on salinity or O_2 concentrations.

2. INTERANNUAL COMPARISON OF OYSTER POND: 2004-2001

Ratios of concentrations for each of the nutrients, as well as salinity and O_2 , between data collected in 2001 and those from 2004 allowed interannual comparisons of Oyster Pond, which were very useful for determining long-term trends in water quality in OP (Valiela 2001). Slope ratios of 1:1 between the years express no difference in the concentrations of a variable at matched conditions in 2001 and 2004; whereas, deviations from 1:1 express a change from 2001 to 2004. Salinity concentrations at matched depths across OP were similar between 2004 and 2001 (Fig. 10). The concentrations of dissolved oxygen are also similar between the two years (Fig. 11), and slight increases in the Southern Basin at depth in 2004 may be explained by recent salt water influxes from tidal flow (Gillibrand 1996).

Concentrations of NO₃ were lower in 2004 than in 2001 (Fig. 12). Overall, NH₄ concentrations were similar in 2004 and 2001, with the exception of notably greater NH₄ concentration in the Southern Basin of OP in 2004 (Fig. 13). No PO₄ was present

9

throughout most of OP both years; however, concentrations were notably greater in the Southern Basin of OP in 2004 (Fig . 14). Increased levels of NH_4 and PO_4 suggest that there may be more decomposition of organic matter occurring in OP in 2004 than in 2001, possibly due to decreased tidal flushing of stratified, anoxic water (Emery 1997).

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Figure Legends

- Figure 1. Surface transects with numbered sample site locations at Oyster Pond (A) and Salt Pond (B).
- Figure 2. Temperature distribution (°C), with depth (m) on y-axis, and site locations on xaxis, for Oyster Pond 2004 (A) and Salt Pond (B).
- Figure 3. Salinity distribution (ppt), with depth (m) on y-axis, and site locations on xaxis, for Oyster Pond 2004 (A) and Salt Pond (B).
- Figure 4. Dissolved oxygen distribution (mg L⁻¹), with depth (m) on y-axis, and site locations on x-axis, for Oyster Pond 2004 (A) and Salt Pond (B).
- Figure 5. Nitrate concentration distribution (μM), with depth (m) on y-axis, and site locations on x-axis, for Oyster Pond 2004 (A) and Salt Pond (B).
- Figure 6. Ammonium concentration distribution (µM), with depth (m) on y-axis, and site locations on x-axis, for Oyster Pond 2004 (A) and Salt Pond (B).
- Figure 7. Phosphate concentration distribution (μM) with depth (m) on y-axis, and site locations on x-axis, for Oyster Pond 2004 (A) and Salt Pond (B).
- Figure 8. Scatter plot of salinity (ppt) on the x-axis versus O₂ (mg L⁻¹) on the y-axis, comparing Oyster Pond 2004 (OP), the Lagoon (OL), Vineyard Sound (VS), and Salt Pond (SP).

Figure 9. Scatter plot of salinity (ppt) on the x-axis versus total nitrogen (NO₃ (μ M) + NH₄ (μ M)) / PO₄ (μ M) on the y-axis. With dark red line at 16 on the y-axis to indicate the Redfield Ratio.

Figure 10. Scatter-plot of salinity averages by depth comparing Oyster Pond 2004 (x-axis) to Oyster Pond 2001 (y-axis).

- Figure 11. Scatter-plot of dissolved oxygen (mg L₋₁) averages across depth layers of the pond between Oyster Pond 2004 (x-axis) and Oyster Pond 2001 (y-axis).
- Figure 12. Scatter-plot of nitrate, NO₃ (μM), averages across depth layers of the pond between Oyster Pond 2004 (x-axis) and Oyster Pond 2001 (y-axis).
- Figure 13. Scatter-plot of ammonium, NH₄ (µM), averages across depth layers of the pond between Oyster Pond 2004 (x-axis) and Oyster Pond 2001 (y-axis).
- Figure 14. Scatter-plot of phosphate PO₄ (μM) averages across depth layers of the pond between Oyster Pond 2004 (x-axis) and Oyster Pond 2001 (y-axis).

