



Phosphate oxygen isotope ratios as a tracer for sources and cycling of phosphate in North San Francisco Bay, California

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[1] A seasonal analysis assessing variations in the oxygen isotopic composition of dissolved inorganic phosphate (DIP) was conducted in the San Francisco Bay estuarine system, California. Isotopic fractionation of oxygen in DIP (exchange of oxygen between phosphate and environmental water) at surface water temperatures occurs only as a result of enzyme-mediated, biological reactions. Accordingly, if phosphate demand is low relative to input and phosphate is not heavily cycled in the ecosystem, the oxygen isotopic composition of DIP ($\delta^{18}\text{O}_p$) will reflect the isotopic composition of the source of phosphate to the system. Such is the case for the North San Francisco Bay, an anthropogenically impacted estuary with high surface water phosphate concentrations. Variability in the $\delta^{18}\text{O}_p$ in the bay is primarily controlled by mixing of water masses with different $\delta^{18}\text{O}_p$ signatures. The $\delta^{18}\text{O}_p$ values range from 11.4‰ at the Sacramento River to 20.1‰ at the Golden Gate. Deviations from the two-component mixing model for the North Bay reflect additional, local sources of phosphate to the estuary that vary seasonally. Most notably, deviations from the mixing model occur at the confluence of a major river into the bay during periods of high river discharge and near wastewater treatment outlets. These data suggest that $\delta^{18}\text{O}_p$ can be an effective tool for identifying P point sources and understanding phosphate dynamics in estuarine systems.

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1. Introduction

[2] Urban and agricultural runoff are major sources of phosphate to aquatic systems. Estuaries in particular receive more nutrients per unit area compared to any other type of ecosystem, in some cases more than 1000-fold that of heavily fertilized agricultural land [Nixon *et al.*, 1986]. However, the majority of nutrient inputs to these systems are nonpoint phosphate sources and consequently are difficult to quantify and regulate because they are derived from activities spread out over large areas and are variable in time [Carpenter *et al.*, 1998]. As a result of anthropogenic activity, fluxes into coastal areas and the ratios of these nutrients (N:P:Si) have been perturbed and there is growing evidence that these perturbations are impacting coastal ecosystems [Jickells, 1998; Beman *et al.*, 2005]. Nutrient enrichment in aquatic systems can cause diverse problems such as toxic algal blooms, anoxia, fish kills, loss of biodiversity, and other problems [Carpenter *et al.*, 1998].

Thus identifying and understanding nutrient inputs and their impact on estuarine systems are of critical importance for management and restoration of these ecosystems.

[3] Phosphorus (P) is a required element for life and consequently, its availability may impact primary production rates as well as species distribution and ecosystem structure [Smith, 1984; Sharp, 1991; Benitez-Nelson, 2000; Karl *et al.*, 2001]. Because P has only one stable isotope, P stable isotope ratios cannot be used for studies of nutrient sources, cycling and utilization (as is the case for nitrogen and carbon). However, most of the P found in nature is strongly bound to oxygen (O), which has three stable isotopes; hence phosphate (PO_4) can be analyzed for its oxygen isotopic composition. Oxygen isotopic composition is reported in standard delta notation ($\delta^{18}\text{O}$), which is calculated using the following equation:

$$\delta^{18}\text{O} = \left[\frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right] * 1000, \quad (1)$$

where R_{sample} is the ratio of $^{18}\text{O}/^{16}\text{O}$ in our sample and R_{VSMOW} is the ratio of $^{18}\text{O}/^{16}\text{O}$ in the isotopic standard for oxygen, Vienna Standard Mean Ocean Water (VSMOW).

[4] The P-O bond in phosphate is resistant to inorganic hydrolysis and, at the temperature and pH of most natural

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systems, phosphate does not exchange oxygen with water without biological mediation [Longinelli *et al.*, 1976; Blake *et al.*, 1997; O'Neil *et al.*, 2003]. Thus any observed variability in the oxygen isotopic composition of phosphate will either reflect mixing of isotopically distinct sources of phosphate or the alteration of the phosphate $\delta^{18}\text{O}$ as the result of the exchange of oxygen during the cycling of phosphate through living cells. In the latter case, each time a phosphate molecule is cycled (taken up by organisms and processed by enzymes), phosphate oxygen will be exchanged with cellular water, resulting in isotopic equilibrium with the surrounding water at the temperature of reaction.

[5] The expected equilibrium $\delta^{18}\text{O}_p$ can be calculated from the temperature and the oxygen isotopic composition of the environmental water using the empirically derived fractionation equation between phosphate and water developed by Longinelli and Nuti [1973],

$$T(^{\circ}\text{C}) = 111.4 - 4.3(\delta^{18}\text{O}_p - \delta^{18}\text{O}_w), \quad (2)$$

where T is the environmental temperature, $\delta^{18}\text{O}_p$ is the isotopic composition of the phosphate, and $\delta^{18}\text{O}_w$ is the isotopic composition of the environmental water. A similar equation was derived by Blake *et al.* [1997] for phosphate extracted from microbial cultures,

$$T(^{\circ}\text{C}) = 155.8 - 6.4(\delta^{18}\text{O}_p - \delta^{18}\text{O}_w). \quad (3)$$

Thus, if isotopic equilibrium is achieved between phosphate and water (owing to extensive P utilization and cycling by organisms), the oxygen isotopic composition of phosphate in natural samples may provide information about temperature and the $\delta^{18}\text{O}$ of water [Longinelli and Nuti, 1973; Kolodny *et al.*, 1983]. However, if isotopic equilibrium has not been achieved, the $\delta^{18}\text{O}_p$ can be used to identify isotopically distinct phosphate sources and/or the extent of phosphate cycling in aquatic systems (i.e., the deviation from the isotopic composition of the source toward the expected equilibrium value).

[6] Results of several laboratory studies characterizing the exchange and fractionation of phosphate oxygen isotopes suggest that the $\delta^{18}\text{O}_p$ of DIP could be used to evaluate the degree of recycling of the DIP pool [Blake *et al.*, 1997, 1998; Paytan *et al.*, 2002; Blake *et al.*, 2005]. Experiments assessing the isotope effects of enzyme-mediated turnover of phosphate and microbially mediated degradation of organic matter demonstrated that significant exchange of oxygen isotopes between phosphate and water accompanies the hydrolytic cleavage and metabolism of both organically bound phosphate and inorganic orthophosphate [Blake *et al.*, 1997]. Bacterial metabolic processes have also been found to significantly alter the $\delta^{18}\text{O}_p$ of DIP in laboratory culture experiments, even when phosphate concentrations were high [Blake *et al.*, 1998]. Furthermore, results of an algae culture experiment indicate that intracellular oxygen isotope exchange between phosphorus compounds and water is very rapid (hours to days) [Paytan *et al.*, 2002].

[7] Phosphate oxygen isotope effects have been observed in microbial culture experiments and in cell-free systems

where specific enzymes were used [Blake *et al.*, 2005]. Intracellular phosphate cycling by inorganic pyrophosphatase results in the temperature-dependent equilibrium oxygen isotope fractionation (equation (2)), which imparts the equilibrium $\delta^{18}\text{O}_p$ on phosphate recycled within cells. In contrast, extracellular phosphate regeneration by alkaline phosphatase is accompanied by disequilibrium isotope effects (both kinetic effects and inheritance of phosphate oxygen from hydrolyzed phosphomonoesters) in the inorganic phosphate released into the system [Blake *et al.*, 2005]. However, the equilibrium isotope effects associated with intracellular phosphate cycling are expected to dominate in natural systems [Blake *et al.*, 2005].

[8] To date, there are relatively few studies assessing the oxygen isotopic composition of DIP in natural systems. Pioneering work by Longinelli *et al.* [1976] found no variation in the $\delta^{18}\text{O}_p$ of DIP in seawater or of marine organism soft tissue with either depth or latitude in the Atlantic and Pacific oceans, although there was a significant difference between the two ocean basins. The $\delta^{18}\text{O}_p$ values were thought to reflect kinetic-biological isotopic fractionation. However, Longinelli *et al.* [1976] extracted P from seawater without prefiltration and used iron-coated fibers which absorb both inorganic and organic P and such complications may confound interpretation of their results. More recently, Colman [2002] concluded that the large deviations in $\delta^{18}\text{O}_p$ between riverine and coastal waters in the Long Island Sound reflected equilibration with local water and indicated that rapid microbial cycling overprints source $\delta^{18}\text{O}_p$ values on a timescale of weeks. Finally, Colman *et al.* [2005] found that $\delta^{18}\text{O}_p$ in open ocean waters is a function of DIP transport and biological turnover in both the Atlantic and the Pacific oceans and highlighted the importance of cell lysis in the regeneration of DIP in the euphotic zone. They also found that depth profiles of $\delta^{18}\text{O}_p$ are near the temperature-dependent equilibrium (equation (2)), suggestive of turnover of DIP in seawater [Colman *et al.*, 2005].

[9] In this study, we utilize $\delta^{18}\text{O}_p$ as a tracer for phosphate sources and cycling within the North San Francisco Bay. The $\delta^{18}\text{O}_p$ measured along surface water transects from the Sacramento/San Joaquin Delta to the Pacific Ocean may reflect either (1) two-component mixing between DIP in the Sacramento/San Joaquin Delta and Oceanic DIP and possibly other point source inputs or (2) equilibrium $\delta^{18}\text{O}_p$ as organisms cycle phosphate along a flow path from freshwater to marine conditions. Differentiating between these two possibilities is difficult using isotope data alone; however, the two end-member mixing between oceanic and river water masses within the North Bay can be used to distinguish these mechanisms and estimate the extent that each process contributes to the overall isotopic signature of DIP. Because phosphate does not limit primary productivity in the North Bay and phosphate concentrations are high throughout the bay [Peterson *et al.*, 1985], we hypothesize that the contribution of new sources of phosphate to the bay may overwhelm the in situ cycling of phosphate. When phosphate turnover is small compared to the reservoir (e.g., low utilization), $\delta^{18}\text{O}_p$ of DIP should be a useful tracer for phosphate sources (assuming source signatures are distinct). However, some degree of phosphate cycling undoubtedly takes place along the mixing path as expected in any

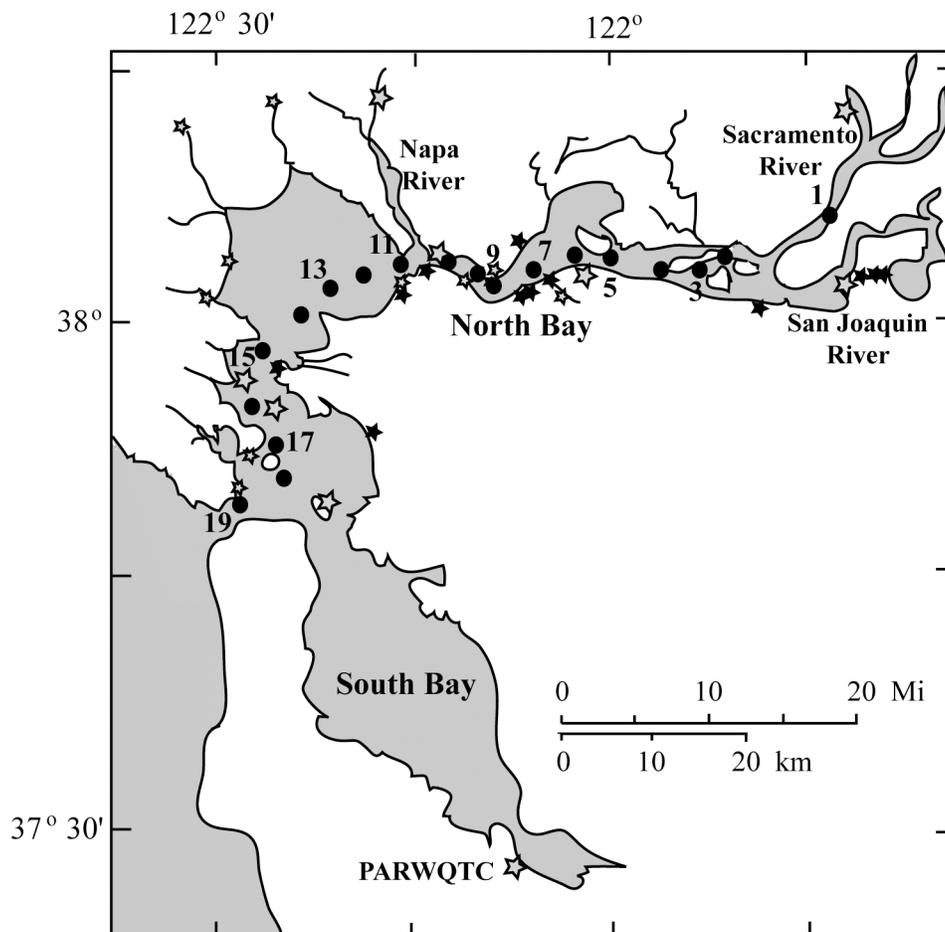


Figure 1. Station Map of North San Francisco Bay. Sampling stations are the solid black circles, and odd stations are numbered. Major creeks into North Bay are drawn. Municipal wastewater discharge sites are the open stars (larger stars have discharge rates greater than $0.4 \text{ m}^3/\text{s}$ or $35,000 \text{ m}^3/\text{d}$), and industrial wastewater discharge sites are solid black stars [Hetzel, 2001].

biologically active system and also evidenced by the presence of alkaline phosphatase activity within the San Francisco Bay [Nicholson *et al.*, 2006].

2. Site Description

[10] San Francisco Bay (Figure 1) is the largest coastal embayment on the Pacific coast of the United States [Conomos *et al.*, 1985]. The primary source of freshwater to this estuary comes from the Sacramento–San Joaquin River drainage basin which encompasses about 40% of the state of California [Conomos *et al.*, 1985]. The San Francisco Bay comprises of two distinct subestuaries, North Bay and South Bay, each with its own unique circulation, water chemistry, and biological communities [Conomos *et al.*, 1985]. The focus of this paper is on the North Bay, which has characteristics of a partially mixed estuary, exhibiting large horizontal gradients of salinity, suspended sediments, nutrients, and biological communities [Cloern, 1996]. The North Bay is dominated by seasonal river inflow, resulting in variable quantities of freshwater input from the Sacramento–San Joaquin River

Delta (henceforth referred to as the Delta) mixing with salt water of the Pacific Ocean [Conomos *et al.*, 1985; Ingram *et al.*, 1996]. Most of the freshwater ($\sim 90\%$) enters the bay via the Delta; the remaining 10% of the water is from small stream runoff, small rivers (such as the Petaluma and Napa Rivers), and wastewater outlets [Conomos, 1979]. Variations in the water properties (salinity, temperature, nutrient concentrations, etc.) in the bay are controlled by changes in the coastal ocean due to seasonal upwelling and by variations in the amount of riverine freshwater inflow [Conomos *et al.*, 1985; Hager and Schemel, 1992]. While the North Bay largely receives its high nutrient inputs via agricultural drains and wastewater treatment plants [Hager and Schemel, 1992; Sigleo and Macko, 2002], it does not exhibit obvious symptoms of nutrient enrichment [Cloern, 1996]. This is most likely due to the strong coupling between primary production and benthic consumption, and the short retention time and strong tidal mixing of the North Bay [Cloern, 1996]. Water residence times within the northern reaches of the North Bay are seasonally variable, ranging from ~ 2 months during low riverine outflow in the summer to approximately 5 days

during high riverine outflow in the winter and spring [Smith, 1987].

3. Materials and Methods

[11] We collected surface water samples along a transect from the Golden Gate into the Sacramento River ending at Rio Vista, California (Figure 1) in October 2002, January 2004, June 2004, and August 2004. Eight liters of surface water were pumped into acid-washed high-density polyethylene bottles and filtered through 0.4- μm pore size Millipore HTP polycarbonate filters to remove particulates. For low-salinity samples, magnesium chloride (Fisher ACS grade) was added as needed to raise the magnesium content to that of seawater and samples were then processed according to *McLaughlin et al.* [2004] for $\delta^{18}\text{O}$ phosphate analysis of DIP. Isotopic analyses were conducted on a Eurovector Elemental Analyzer coupled to a Micromass (now GVI) IsoPrime mass spectrometer at the U.S. Geological Survey in Menlo Park, California. Results were calibrated and precision monitored using two internal silver phosphate standards, STDH ($\delta^{18}\text{O}_p = 20.0\text{‰}$) and STDL ($\delta^{18}\text{O}_p = 11.3\text{‰}$) that were run in duplicate after every 10 samples. The isotopic values of these standards were determined previously by comparison to other standards which had also been analyzed by the traditional fluorination method [McLaughlin et al., 2004]. Water $\delta^{18}\text{O}$ was determined using a Finnigan MAT 251 mass spectrometer also at the U.S. Geological Survey in Menlo Park. All oxygen isotopic measurements are reported in the standard delta notation in per mil units (‰) with respect to Vienna Standard Mean Ocean Water (VSMOW); the precision of $\delta^{18}\text{O}_p$ is approximately $\pm 0.3\text{‰}$ and the precision of $\delta^{18}\text{O}_w$ is $\pm 0.1\text{‰}$.

[12] The *McLaughlin et al.* [2004] procedure involves coprecipitation of phosphate with magnesium hydroxide. A small amount of dissolved organic phosphate is also coprecipitated during this step [Karl and Tien, 1992]. To determine if the subsequent acid dissolution of the magnesium hydroxide involved any hydrolysis of organic phosphorus compounds and incorporation of reagent oxygen, we split 20 L of coastal water in quarters and precipitated magnesium hydroxide in each quarter sample. Two of the quarters were then dissolved in nitric acid that was spiked with H_2^{18}O (90.0‰) and the other two were dissolved in unamended nitric acid (−13.8‰). The samples were then processed identically according to *McLaughlin et al.* [2004] and analyzed for $\delta^{18}\text{O}_p$. The measured $\delta^{18}\text{O}_p$ for each of the samples were identical within analytical error showing there is no acid hydrolysis of dissolved organic P compounds and incorporation of reagent ^{18}O during the phosphate purification procedure. However, we do recognize that the nature and presence/absence of organic phosphate sorbed onto the magnesium hydroxide pellets may be sample specific and this test was only conducted on replicates of a single sample.

[13] Phosphate concentrations of duplicate samples were determined colorimetrically using HACH phosver 3 reagent powder pillows on a HACH portable spectrophotometer and are reported in micro moles per liter ($\mu\text{mol L}^{-1}$) with an analytical precision of $\pm 0.2 \mu\text{mol L}^{-1}$. Temperature and salinity were determined for each station using a Seabird

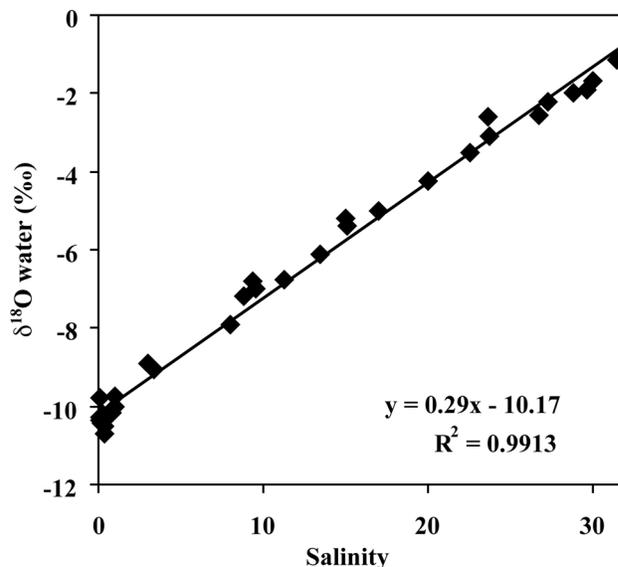


Figure 2. Linear correlation between water oxygen isotope ratios and salinity for each of the months sampled.

CTD package. Temperature is reported as degrees Celsius ($^{\circ}\text{C}$) and salinity reported using the Practical Salinity Scale. Chlorophyll was measured by a fluorometer and was calibrated with discrete water samples where chlorophyll was extracted in acetone solvent overnight and the light absorption of the solution measured (<http://sfbay.wr.usgs.gov/access/wqdata/overview/measure/>). Chlorophyll is reported in micrograms per liter ($\mu\text{g L}^{-1}$). These data are available to the public via the USGS website at: <http://sfbay.wr.usgs.gov/access/wqdata>.

4. Results

[14] The waters of the North San Francisco Bay are best represented by a two end-member mixing system between the Pacific Ocean waters and waters of the San Joaquin and Sacramento River Delta. This was evident from the linear correlation between water oxygen isotope ratios and salinity along the transect (Figure 2) such that mixing between freshwater from the Delta and water from the Pacific Ocean can be represented by the following equation:

$$\delta^{18}\text{O}_w = 0.29 \times \text{Salinity} - 10.17. \quad (4)$$

In contrast, phosphate concentrations were nonlinear with respect to salinity and showed no trend as a function of station number (Figure 3).

[15] In order to determine how closely the observed $\delta^{18}\text{O}_p$ approached isotopic equilibrium with environmental water we calculated the expected equilibrium $\delta^{18}\text{O}_p$ using equations (2) and (3) and the temperature and $\delta^{18}\text{O}_w$ measured at each station. We then compared this value to the observed $\delta^{18}\text{O}_p$ data (Figure 4). The difference between $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_w$ (i.e., $\delta^{18}\text{O}_p - \delta^{18}\text{O}_w$) was plotted on the y axis and temperature on the x axis, such that the two equilibrium expressions, equations (2) and (3), could be represented by

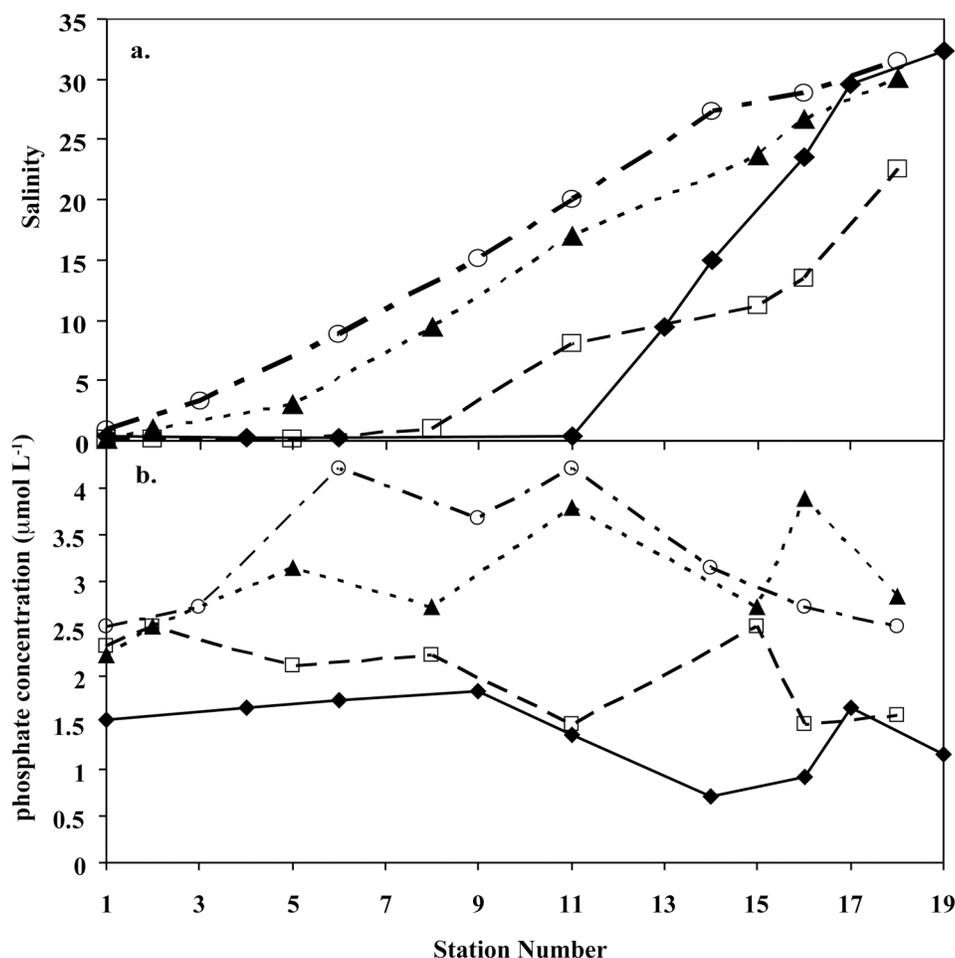


Figure 3. (a) Salinity and (b) phosphate concentrations measured at each station for each of the months sampled: October 2002 (diamonds, solid line), January 2004 (squares, dashed line), June 2004 (triangles, dotted line); and August 2004 (circles, dash-dotted line).

linear relationships. Comparison between the observed $\delta^{18}\text{O}_p - \delta^{18}\text{O}_w$ values relative to the expected $\delta^{18}\text{O}_p - \delta^{18}\text{O}_w$ from the linear equilibrium expressions indicates that phosphate is largely out of equilibrium with the temperature and $\delta^{18}\text{O}_w$ at each station in all seasons (Figure 4). Typically, $\delta^{18}\text{O}_p$ values are lower than the expected equilibrium value at the head of the estuary and higher than expected from equilibrium near the mouth of the estuary (Table 1a).

[16] The $\delta^{18}\text{O}_p$ steadily increased from the Delta region toward the Pacific as a function of salinity (Figure 5). The highest $\delta^{18}\text{O}_p$ values at the mouth of the estuary are similar to those reported for coastal California waters in nearby Monterey Bay [McLaughlin *et al.*, 2006], ranging from 17.1‰ in January 2004 (during the rainy season) to 20.1‰ in October 2002 (during the dry season). The $\delta^{18}\text{O}_p$ values within the Sacramento River, the primary contributor of freshwater to the North Bay [Conomos *et al.*, 1985], ranged from 11.4‰ in October 2002 to 14.8‰ in January 2004. The lowest observed $\delta^{18}\text{O}_p$ value (7.8‰) occurred during the rainy season month of January at Station 11, which lies near the confluence of the Napa River with the North Bay. We measured the $\delta^{18}\text{O}_p$ of effluent from a wastewater treatment plant (Palo Alto

Regional Water Quality Control Plant, PARWQCP), which receives a mixture of residential and industrial wastewater from several communities in South San Francisco Bay. During high sewage outflow the $\delta^{18}\text{O}_p$ of the sewage water was $8.4 \pm 0.2\text{‰}$, and during low outflow it was $11.1 \pm 1.3\text{‰}$.

[17] The increase in $\delta^{18}\text{O}_p$ from the Delta to the Pacific could either be attributed to mixing of two isotopically distinct sources of phosphate or could result from the cycling of phosphate within the bay, which would result in the equilibration of phosphate with waters of steadily increasing $\delta^{18}\text{O}_w$. In order to explore the former case, we constructed a two end-member mixing model to characterize $\delta^{18}\text{O}_p$ in the North Bay. To construct these mixing models for $\delta^{18}\text{O}_p$, we could have used phosphate concentration, salinity or $\delta^{18}\text{O}_w$. Phosphate concentrations were nonlinear with respect to salinity and showed no trend as a function of station number (Figure 3). Therefore we used salinity, which has previously been used as a conservative tracer for water mass mixing in the bay [Ingram *et al.*, 1996], to determine the relative contribution of each end-member. Using a freshwater salinity of 0 and a seawater salinity of 32, the fraction of water from the delta can be

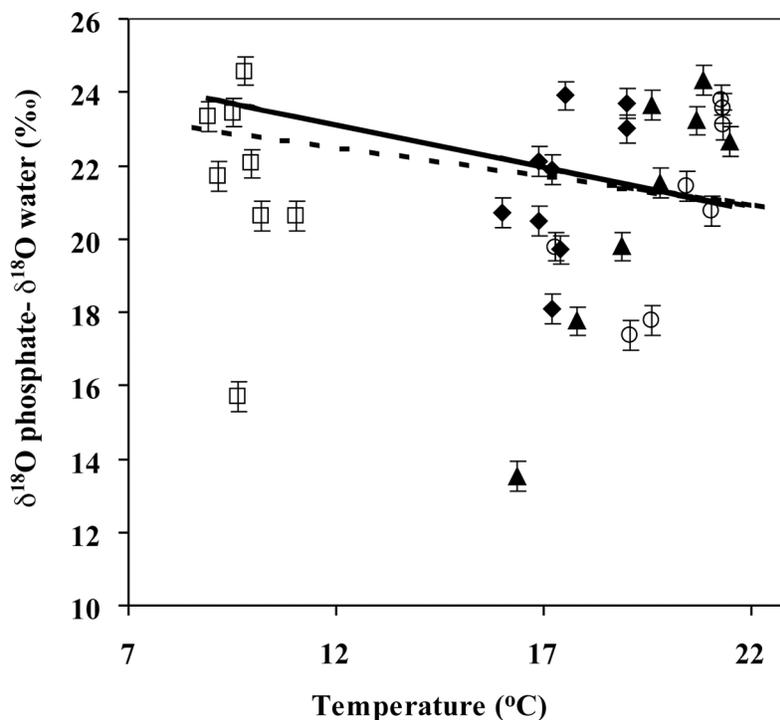


Figure 4. The $\delta^{18}\text{O}_p - \delta^{18}\text{O}_w$ as a function of temperature for each month: October 2002 (diamonds), January 2004 (squares), June 2004 (triangles), and August 2004 (circles) and expected equilibrium values according to the *Longinelli and Nuti* [1973] equation (equation (2), solid line) or for the *Blake et al.* [1997] equation (equation (3), stippled line). The y axis is written as $\delta^{18}\text{O}_p - \delta^{18}\text{O}_w$ so that the equilibrium values can be represented in a linear relationship with temperature.

calculated for any salinity in the North Bay using the following equation:

$$f_w = -0.03s + 1, \quad (5)$$

where f_w is the fraction of water from the delta (freshwater) and s is the salinity at each station. Using the end-member phosphate concentrations and $\delta^{18}\text{O}_p$ values and the relative contribution of each water mass determined from the salinity values at each station, we were able to calculate by mass balance the expected $\delta^{18}\text{O}_p$ for the salinity measurement at each station using the following equation:

$$\delta_s = (f_w \times p_d \times \delta_d) + ((1 - f_w) \times p_o \times \delta_o), \quad (6)$$

where δ_s is the expected $\delta^{18}\text{O}_p$ due to linear mixing between Pacific Ocean water and freshwater from the delta, f_w is the fraction of water from delta, $(1 - f_w)$ is the fraction of water from the Pacific, p_d is the phosphate concentration of the delta end-member, p_o is the phosphate concentration of the Pacific end-member, δ_d is the $\delta^{18}\text{O}_p$ of the delta end-member, and δ_o is the $\delta^{18}\text{O}_p$ of the Pacific end-member. Values for the mass balance equation are listed in Table 1a. Using equation (6), δ_s values were calculated for the f_w calculated for each station sampled. A polynomial best-fit trend line was fit through each of the δ_s values to generate a two end-member mixing model for $\delta^{18}\text{O}_p$ in the North Bay for each month sampled (Figure 5, solid lines).

[18] The characteristics of the riverine end-member: $\delta^{18}\text{O}_p$, phosphate concentration, $\delta^{18}\text{O}$ of water, and salinity,

changed seasonally. Therefore we used specific end-member values relevant to each month sampled and developed four distinct mixing models, one for each sampling season (Table 1a and Figure 5). There were several values that could have represented the “freshwater end-member” for each of the transects (e.g., stations 1 through 3 all have freshwater salinities during all months sampled). Therefore we chose to use the value within the Sacramento River to represent the freshwater end-member for all seasons. This choice is based on the premise that the Sacramento River is the primary source of freshwater to the North Bay [Smith, 1987], having a significantly higher discharge rate than the San Joaquin River but similar phosphate concentrations.

[19] We used the October 2002 Station 19 value as the oceanic end-member value because the January, June, and August 2004 transects did not extend to Station 19 and the salinity values measured at Station 18 are suggestive of some degree of freshwater influence during these periods. The values for salinity, $\delta^{18}\text{O}_p$, and phosphate concentration observed in October 2002 at Station 19 are similar to values observed in January, June, and August 2004 in the coastal waters of Monterey Bay, 100 miles south of the San Francisco Bay, suggesting that this end-member is indeed representative and is relevant for all of the transects (all seasons) [McLaughlin et al., 2006].

[20] In order to explore the contribution of phosphate cycling, we constructed a mixing model for $\delta^{18}\text{O}_p$ assuming that phosphate had reached the temperature-dependent equilibrium (equation (2)) with water along the $\delta^{18}\text{O}_w$ /Salinity mixing-line (equation (4)). Combining equations

Table 1a. Summary Data for Cruise Transects

Date	Station Number	Salinity	[PO ₄], $\mu\text{mol/L}$	Temperature, °C	$\delta^{18}\text{O}_{\text{w}}$, ‰	$\delta^{18}\text{O}_{\text{p}}$, ‰	Equilibrium $\delta^{18}\text{O}_{\text{p}}$, ‰	Equilibrium – Measured $\delta^{18}\text{O}_{\text{p}}$, ‰
Oct 2002	1 ^a	0.4	1.5	16.9	−10.7	11.4	11.3	−0.1
	4	0.3	1.7	19.0	−10.2	12.8	11.3	−1.5
	6	0.3	1.7	19.0	−10.4	13.3	11.1	−2.2
	11	0.4	1.8	17.5	−10.5	13.4	11.3	−2.1
	13	9.5	1.4	17.2	−7.0	14.9	14.9	0.0
	14	15.0	0.7	17.4	−5.2	14.5	16.7	2.2
	16	23.6	0.9	17.2	−2.6	15.5	19.3	3.8
	17	29.6	1.7	16.9	−1.9	18.6	20.1	1.5
	19 ^b	32.3	1.2	16.0	−0.6	20.1	21.6	1.5
	Jan 2004	1 ^a	0.1	2.3	9.8	−9.8	14.8	13.8
2		0.1	2.5	9.5	−10.3	13.2	13.4	0.3
5		0.1	2.1	9.1	−10.4	11.3	13.4	2.1
8		1.0	2.2	8.9	−10.0	13.3	13.8	0.5
11		8.0	1.5	9.6	−7.9	7.8	15.8	8.0
15		11.2	2.5	10.0	−6.8	15.3	16.8	1.5
16		13.5	1.5	10.2	−6.1	14.5	17.4	2.9
18		22.5	1.6	11.0	−3.5	17.1	19.8	2.7
Jun 2004		1 ^a	0.2	2.2	20.9	−10.4	13.9	10.6
	2	1.0	2.5	21.5	−9.7	12.9	11.2	−1.7
	5	3.0	3.2	20.7	−8.9	14.3	12.2	−2.1
	8	9.4	2.7	19.8	−6.8	14.7	14.5	−0.2
	11	17.0	3.8	19.6	−5.0	11.9	16.4	4.5
	15	23.7	2.7	18.9	−3.1	16.7	18.4	1.7
	16	26.7	3.9	17.8	−2.6	15.2	19.2	4.0
	18	30.0	2.8	16.4	−1.7	18.6	20.4	1.8
	Aug 2004	1 ^a	0.8	2.5	21.3	−10.2	13.4	10.8
3		3.3	2.7	21.3	−9.1	14.7	11.9	−2.8
6		8.8	4.2	21.3	−7.2	15.9	13.8	−2.2
9		15.1	3.7	21.0	−5.4	15.3	15.6	0.3
11		20.0	4.2	20.4	−4.3	17.2	16.9	−0.3
14		27.3	3.2	19.6	−2.2	15.6	19.1	3.6
16		28.8	2.7	19.1	−2.0	15.4	19.5	4.1
18		31.4	2.5	17.3	−1.1	18.7	20.8	2.1

^aRiverine end-member value.^bOceanic end-member value.

(2) and (4) yields the following equilibrium mixing equation for $\delta^{18}\text{O}_{\text{p}}$ in the North San Francisco Bay:

$$\delta^{18}\text{O}_{\text{p}} = (0.29 \times \text{Salinity} - 10.17) - ([\text{Temperature} - 111.4]/4.3). \quad (7)$$

If phosphate was rapidly and/or extensively cycled through the biomass, we would expect the measured $\delta^{18}\text{O}_{\text{p}}$ to fall along this mixing line. However, while some stations do approach the mixing line, there are considerable deviations, most notably near the head and mouth of the estuary for all months sampled and at Station 11 near the center of the transect (Figure 5, dotted line).

5. Discussion

[21] The linear correlation between the $\delta^{18}\text{O}_{\text{w}}$ and salinity along the transect (Figure 2) indicates that the North San Francisco Bay is best represented by a two end-member mixing model between Pacific Ocean water and San Joaquin–Sacramento River water. These results confirm those reported for the North San Francisco Bay by *Ingram et al.* [1996], in which water $\delta^{18}\text{O}_{\text{w}}$ and δD values were found to be well correlated with salinity and showed a linear mixing relationship between seawater and river freshwater.

[22] Phosphate concentrations, however, are not linearly correlated with salinity (Figure 3). Maxima in phosphate

concentrations at the mid-salinity stations are detected in January, June and August and low phosphate concentrations at these sites in October (Figure 3). This relationship has also been observed by other workers and was attributed to uptake of nutrients by phytoplankton [*Peterson et al.*, 1985; *Hager and Schemel*, 1992]. The nonconservative nature of phosphate makes it difficult to use concentrations alone to identify the influence of specific phosphate sources to the bay. However, we demonstrate that $\delta^{18}\text{O}_{\text{p}}$ provides a means of identifying point sources of P and rates of P cycling within the estuary.

[23] Our $\delta^{18}\text{O}_{\text{p}}$ data indicate that phosphate is largely out of equilibrium with the surrounding water for each of the months sampled (Figure 4), implying that the biological community is not extensively cycling phosphate within the euphotic zone (relative to DIP availability). This was expected because phosphate does not limit primary productivity within the North Bay [*Peterson et al.*, 1985] and phosphate concentrations are high throughout the bay (Figure 3). If phosphate $\delta^{18}\text{O}_{\text{p}}$ values were determined solely by two end-member mixing between the Pacific Ocean and the Delta, our data would have fallen along a mixing line (Figure 6, solid curved line; stars indicate end-members). If phosphate $\delta^{18}\text{O}_{\text{p}}$ values were determined solely by phosphate cycling, our data would have fallen along the expected equilibrium mixing line calculated from equation (7) (Figure 6, dotted line). Our data fit neither case,

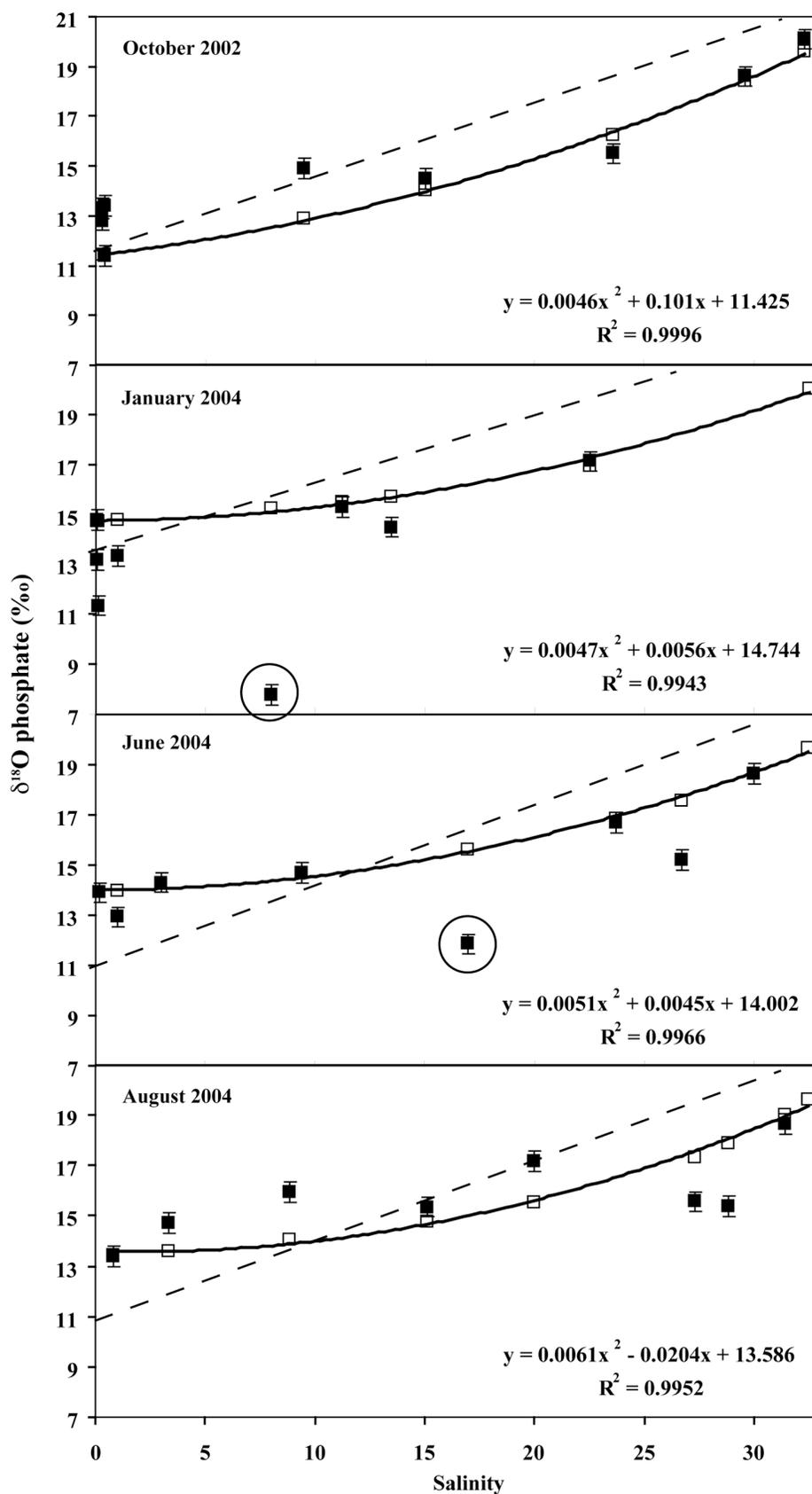


Figure 5. Mixing models for the San Francisco Bay using end-member values listed in Table 1a (solid lines) and observed $\delta^{18}\text{O}_p$ values (squares) for each month sampled: October 2002, January 2004, June 2004, and August 2004. Station 11 is highlighted in January and June. Equilibrium mixing model for phosphate generated from equation (7) (dashed line). Error bars indicate the 0.4‰ error.

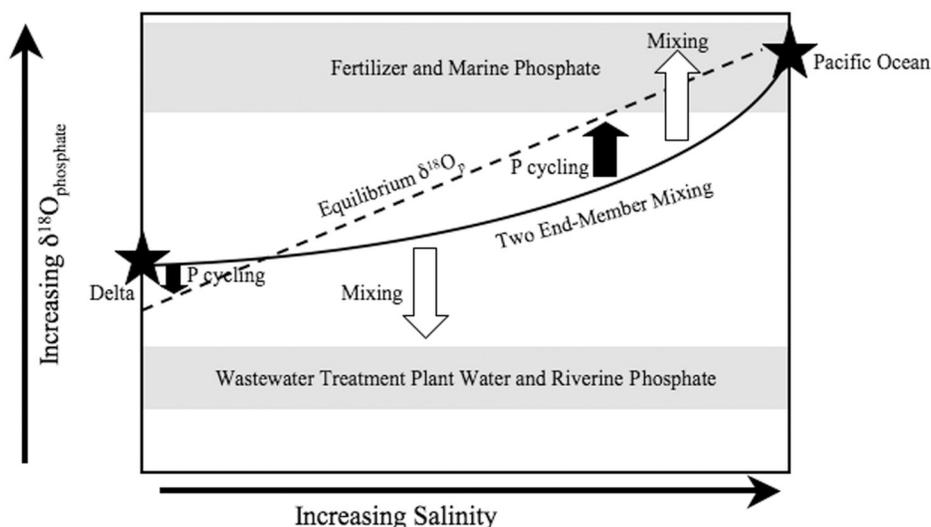


Figure 6. Diagram indicating two end-member mixing and the expected equilibrium mixing line. Deviations below the two end-member mixing (white down-facing arrow) indicate mixing with either a riverine or wastewater treatment plant effluent. Deviations which move off the two end-member mixing line in the direction of equilibrium mixing may be indicative of phosphate cycling, though they may also represent mixing with fertilizer phosphate. Deviations which fall off the two-end-member mixing line in the direction of equilibrium, but in excess of equilibrium, are indicative of mixing with fertilizer phosphate or treatment plant effluent depending on where along the salinity gradient the deviation occurs.

so we examined other potential sources of phosphate to the bay. First, deviations from two end-member mixing toward equilibrium mixing are indicative of some phosphate cycling within the bay (Figure 6, black arrows), but not enough cycling such that equilibrium is attained. Second, deviations either away from equilibrium or in excess of equilibrium reflect the contribution of another phosphate source (Figure 6, white arrows). These deviations may reflect mixing with either riverine or water treatment plant effluent (a deviation toward lower $\delta^{18}\text{O}_p$) or they may reflect mixing with fertilizer phosphate (a deviation toward higher $\delta^{18}\text{O}_p$). Deviations from mixing and isotopic equilibrium can also be explained by sorption onto particles or the precipitation of apatite. Phosphate oxygen isotopic fractionations associated with these mechanisms have not been characterized for San Francisco Bay. However, it has been suggested that only minimal isotopic fractionation is associated directly with these processes [Blake *et al.*, 2005].

[24] Significant deviations from the equilibrium $\delta^{18}\text{O}_p$ mixing line are seen at Station 11 during January (8.0‰) and June (4.5‰) 2004, the highest deviation recorded for the North Bay in this data set (Figure 7). At this station, the $\delta^{18}\text{O}_p$ values were significantly lower than predicted from both the two end-member mixing model and the equilibrium mixing model, with values similar to, but lower than, the Sacramento River water $\delta^{18}\text{O}_p$. The water discharge at the Napa River is higher in January and June than during the other two transect dates (<http://waterdata.usgs.gov/nwis>), suggesting a significant, seasonally active, source of riverine phosphate present at Station 11. A smaller but seasonally persistent deviation in $\delta^{18}\text{O}_p$ (~4‰) is also observed near Station 16, which is in close proximity to two, high-discharge, municipal wastewater treatment outlets. Devia-

tions from the mixing line, other than at station 11, are typically less than 4‰ (Figure 7 and Tables 1a and 1b).

[25] Using the $\delta^{18}\text{O}_p$ mixing models from Figure 5, we calculated the deviation of each station from the mixing line by taking the difference between the expected $\delta^{18}\text{O}_p$ calculated for simple two end-member mixing and the measured $\delta^{18}\text{O}_p$ (Figure 7). Values near zero, within analytical error, represent either mixing with an additional, locally derived phosphate source or a location where there is some degree of phosphate cycling by the biomass. The expected equilibrium value was calculated for each station at each sampling period using equation (2). If deviations from the linear mixing line are due to phosphate cycling, we expect values to fall off the mixing line in the direction of the equilibrium value for each individual station. Stations that deviated from the mixing line in a direction opposite that of equilibrium or in excess of equilibrium are explained by local phosphate sources entering the bay. However, stations that fall off the mixing line in the direction of equilibrium may not necessarily reflect cycling because a deviation toward equilibrium could also indicate the presence of an additional source of phosphate with a $\delta^{18}\text{O}_p$ that lies between the equilibrium value and the mixing line value. For example, Stations 1 through 8 in January fall off the mixing line in the direction of equilibrium, but in most cases exceed the expected equilibrium value. This suggests that these deviations are due to another source of phosphate with a lower $\delta^{18}\text{O}_p$, probably freshwater phosphate from local streams and rivers, rather than cycling.

[26] During January and June 2004, when discharge from the Napa, Sacramento, and San Joaquin Rivers and other local streams and small rivers is greatest, deviations from the mixing line are toward lower $\delta^{18}\text{O}_p$ values (Figure 7).

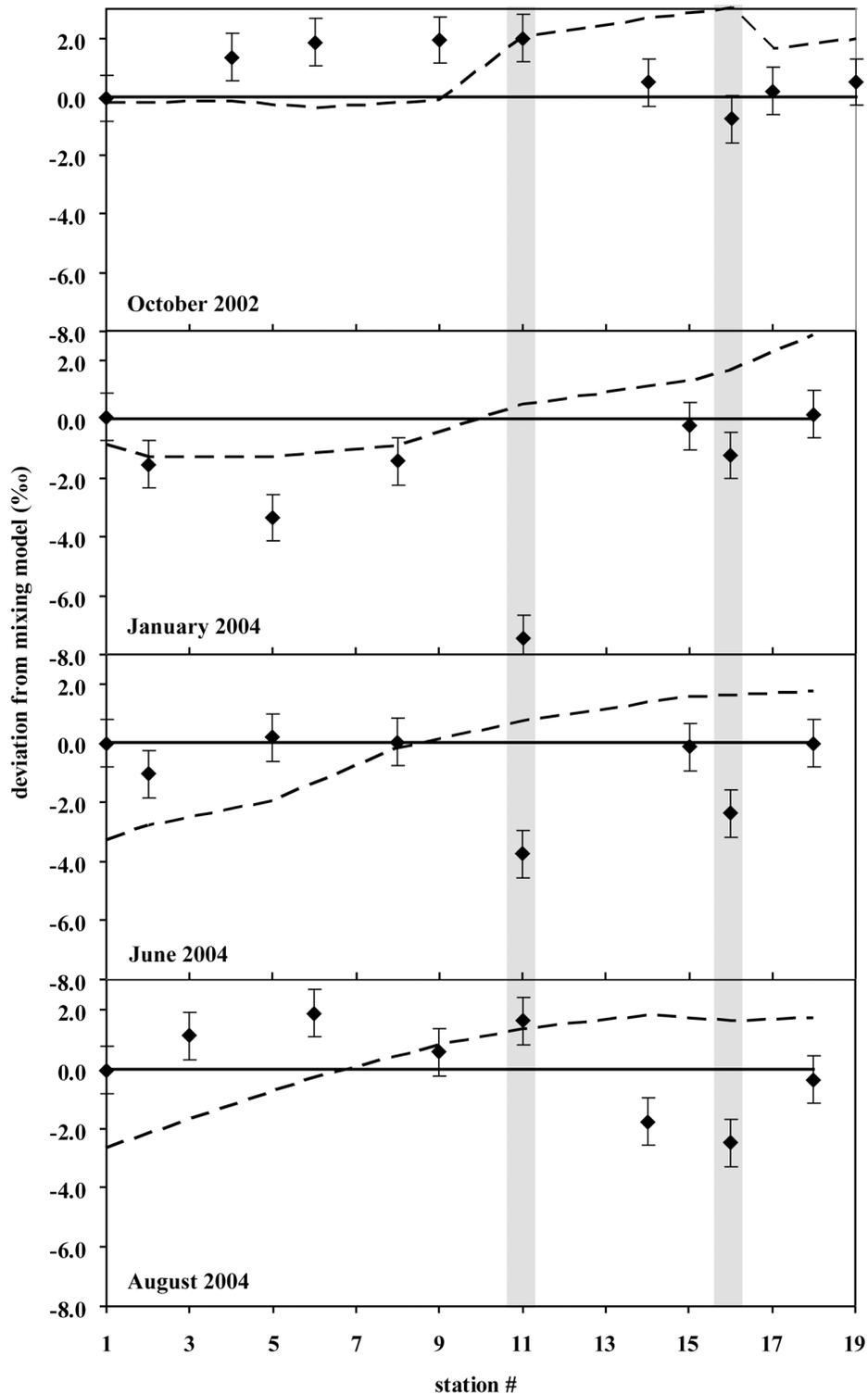


Figure 7. The $\delta^{18}\text{O}_p$ deviations (diamonds) from those expected from the two end-member mixing models (solid line) from Figure 6 for each station and month sampled: October 2002, January 2004, June 2004, and August 2004. Deviations from the mixing line were calculated by taking the difference between the expected $\delta^{18}\text{O}_p$ calculated for each salinity measurement using the mixing models from Figure 5 and the measured $\delta^{18}\text{O}_p$. Deviations of the expected equilibrium $\delta^{18}\text{O}_p$, calculated using equation (5) for each station temperature and $\delta^{18}\text{O}_w$, from the two end-member mixing models are represented by the dashed line in each plot. The mixing model value in each of the above plots is represented by a deviation of 0‰. Vertical highlighting shows the largest deviations observed at Station 11 in January 2004 and June 2004 and the most persistent deviations at Station 16 in all months. Error bars indicate the error propagated through the mixing models.

Table 1b. Potential Phosphate Source Values

Source	$\delta^{18}\text{O}_p$, ‰
Oct 2005 PARWQCP – high flow	8.4
Oct 2005 PARWQCP – low flow	11.1
Fertilizer- Elkhorn Slough, CA [McLaughlin, 2005]	14.8–27.0
Fertilizer- France [Gruau et al., 2005]	19.6–23.1

These values are similar to or lower than those observed within the Sacramento River. Thus, during these rainy months when stream discharge is high, multiple local phosphate point sources can be identified by phosphate oxygen isotope ratios. This was most notable at Station 11, which sits at the confluence of the Napa River and the North Bay.

[27] The seasonally persistent deviation from the equilibrium mixing line is present at Station 16, which deviates from the mixing line toward a lower value between 14.5‰ and 15.5‰. Because this deviation is seasonally persistent, it is probably not due to the influence of local streams with seasonally variable discharge, which would produce a seasonally variable pattern like that seen at Station 11. Station 16, however, does lie between two municipal wastewater treatment outlets with high flow rates (Figure 1). In October 2005 we collected wastewater effluent from the Palo Alto Regional Water Quality Control Plant (PARWQCP), which receives a mixture of residential and industrial wastewater from several communities in South San Francisco Bay. During high sewage outflow the $\delta^{18}\text{O}_p$ of the sewage water was 8.4 ± 0.2 ‰, and during low outflow it was 11.1 ± 1.3 ‰ (Table 1b). Thus it is possible that the observed deviation from mixing is a result of the influence of a local phosphate source from one or both of these outlets.

[28] Samples from the head of the estuary (near the Delta) typically deviate from the equilibrium mixing line toward lower values, whereas samples from stations near the mouth of the estuary deviate toward higher values (Figure 7). As previously mentioned, lower values may reflect equilibrium with freshwater with low $\delta^{18}\text{O}_w$. However, as noted at Station 16, lower values could also be from wastewater treatment outlets. Municipal wastewater treatment plant outlets and industrial wastewater discharge sites are abundant throughout the North Bay (Figure 1). Wastewater treatment plant water in the South Bay has been found to lie between 8.4‰ and 11.1‰. Fertilizer phosphate (both locally applied compost and commercial fertilizers) has been found to range between 14.8‰ and 25.0‰ (Table 1b) [Gruau et al., 2005; McLaughlin, 2005]. Therefore addition of fertilizer and wastewater effluent to the head of North Bay may yield deviations toward higher values, but additions of these sources near the mouth may actually yield deviations toward lower values.

6. Conclusion

[29] North San Francisco Bay is characterized by a two end-member mixing model between Pacific Ocean waters and the freshwaters of the San Joaquin and Sacramento Rivers. This mixing model can be adapted to represent a mixing line for $\delta^{18}\text{O}_p$ expected if phosphate is being cycled

through the biomass such that the source $\delta^{18}\text{O}_p$ signature is modified by the equilibrium exchange. While this mixing model does match the overall trend in the measured data, it does not fully explain the variations observed throughout the Bay. Thus deviations from the equilibrium $\delta^{18}\text{O}_p$ mixing line are most likely the result of the contribution of phosphate with unique $\delta^{18}\text{O}_p$ signatures at various point and nonpoint locations.

[30] The general lack of equilibrium indicates that phosphate cycling is not rapid compared to phosphate input (low utilization rate), and that source phosphate $\delta^{18}\text{O}$ contributes to the observed $\delta^{18}\text{O}_p$ at most, if not all, stations. Therefore deviations from the $\delta^{18}\text{O}_p$ mixing model represent inputs of phosphate from local phosphate sources within the North Bay. We demonstrate that it is possible to use $\delta^{18}\text{O}_p$ to identify point source phosphate inputs to aquatic systems and suggest that this may be applied in other impacted systems to identify specific anthropogenic sources, such as fertilizer and sewage phosphate, or natural sources of phosphate. This information is crucial for mitigation of pollution impacts and successful restoration of estuaries and other aquatic systems.

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