

Nitrogen sources and cycling in the San Francisco Bay Estuary: A nitrate dual isotopic composition approach

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Abstract

We used the dual isotopic composition of nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) within the estuarine system of San Francisco (SF) Bay, California, to explore the utility of this approach for tracing sources and cycling of nitrate (NO_3^-). Surface water samples from 49 sites within the estuary were sampled during July–August 2004. Spatial variability in the isotopic composition suggests that there are multiple sources of nitrate to the bay ecosystem including seawater, several rivers and creeks, and sewage effluent. The spatial distribution of nitrate from these sources is heavily modulated by the hydrodynamics of the estuary. Mixing along the estuarine salinity gradient is the main control on the spatial variations in isotopic composition of nitrate within the northern arm of SF Bay. However, the nitrate isotopic composition in the southern arm of SF Bay exhibited a combination of source mixing and phytoplankton drawdown due mostly to the long residence time during the summer study period. Very low $\delta^{18}\text{O}_{\text{NO}_3}$ values (as low as -5.0‰) at the Sacramento–San Joaquin River delta region give rise to a wide range of $\delta^{18}\text{O}_{\text{NO}_3}$ values in the SF Bay system. The range in $\delta^{18}\text{O}_{\text{NO}_3}$ values is more than twice that of $\delta^{15}\text{N}_{\text{NO}_3}$, suggesting that $\delta^{18}\text{O}_{\text{NO}_3}$ is an even more sensitive tool for tracing nitrate sources and cycling than $\delta^{15}\text{N}_{\text{NO}_3}$.

San Francisco Bay (SF Bay) is one of the most anthropogenically altered estuaries in the United States (Nichols et al. 1986) and some of the world's largest ecosystem restoration efforts are currently under way to mitigate these alterations (Jassby and Cloern 2000; Kimmerer 2004). Changes that have been recorded in the SF Bay estuary over the past decades include dramatic reductions in the area of tidal marshland (by $\sim 95\%$), reduction in the amount of freshwater inflow (by $\sim 65\%$), and high loading of agricultural, industrial, and domestic waste (Nichols et al. 1986; SFBWQCB 1995). Although nutrient loading to the estuary is quite high, it is remarkable that so little eutrophication has occurred as a result of this loading (Cloern 2001). In particular, SF Bay receives

significant annual nitrogen (N) loads, yet does not experience large-scale eutrophic or hypoxic conditions. Thus, an understanding of how the SF Bay estuary functions to moderate the effects of nutrient loading represents an important research area for those focusing on coastal and estuarine restoration and rehabilitation worldwide.

Tracing the sources of nutrients and determining spatial mixing patterns of different sources within an estuarine hydrodynamic regime represent fundamental goals for estuarine researchers. Such information can help in identifying point and nonpoint input sources and in assessing nutrient cycling and dynamics within the ecosystem. Mixing diagrams of nutrient concentrations, such as nitrate or phosphate, along salinity gradients can shed light on mixing between water masses with different nutrient characteristics. However, in using this approach, only sources with distinct salinities and nutrient concentrations can be distinguished. Moreover, this approach can be further complicated by the fact that nutrients do not necessarily behave conservatively. Using the isotopic composition of nutrients adds another dimension to the identification of sources and mixing as well as to the evaluation of nutrient cycling within the system.

Previous research using NO_3^- isotopic composition has shed light on sources of NO_3^- to estuaries, but has only been able to take advantage of the N isotopic composition (Mariotti et al. 1984; Cifuentes et al. 1989; McClelland and Valiela 1998). A NO_3^- dual isotopic approach (i.e.,

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Acknowledgments

We thank the SFEI and the RMP, and those involved with the research cruise including Sarah Lowe, Paul Salop, David Bell, and the crew of the RV *Endeavor*, Nick Sakata and Gordon Smith. Steve Hager, Steve Silva, and Larry Miller provided helpful reviews during the preparation of the manuscript. We also thank John Radyk for the analyses of $\delta^{18}\text{O}$ of water.

This work was supported in part by a NOAA National Estuarine Research Reserve–Elkhorn Slough graduate fellowship to S.D.W., the USGS National Research Program for C.K., an NSF grant (MCB-0433804) to C.A.F., and an NSF grant (ECS-0308070) to A.P. Preparation of this manuscript also benefited significantly from comments provided by two anonymous reviewers.

simultaneous analysis of both N and O isotopes in NO_3^- has, to our knowledge, never been investigated in an estuarine environment. Because of the complexity of the N cycle, N isotopes alone cannot easily delineate the multiple biological processes in the water column involving nitrate (denitrification, nitrification, assimilation, etc.). A multiple isotope approach offers an additional tool to investigate NO_3^- sources and N cycling and may result in better understanding of the ecosystem. Furthermore, NO_3^- dual isotopic composition can also be utilized as a tool for understanding how nutrient enrichment might interact with other ecosystem stressors such as toxic contaminants or hydrologic manipulations, thus facilitating rehabilitation efforts. For example, important processes such as denitrification and phytoplankton uptake cause isotopic fractionations that may impart distinctive isotopic signatures to the remaining nitrate pool (Sebilo et al. 2003; Granger et al. 2004; Needoba et al. 2004). Nitrate stable isotopic composition could therefore potentially be used to identify areas where such reactions are occurring, thus providing a spatial indicator of nitrate reduction and the relation of this process to other parameters (e.g., specific pollutants, seasonality, hydrology, etc.).

In addition, measurement of the $\delta^{18}\text{O}$ of NO_3^- within an estuarine system may shed light on the source of oxygen atoms incorporated during nitrification. There is currently some uncertainty surrounding the controls of the oxygen isotopic composition of nitrate ($\delta^{18}\text{O}_{\text{NO}_3}$). Although several decades of freshwater research has shown that NO_3^- oxygen originates both from dissolved oxygen (O_2) and from water during nitrification (Hollocher et al. 1981; Andersson and Hooper 1983; Hollocher 1984), recent evidence has implied that the process of nitrification in an open-water marine environment incorporates oxygen atoms almost entirely from water (Casciotti et al. 2002). Hence, the factors determining the $\delta^{18}\text{O}$ signature of NO_3^- may actually vary between freshwater and marine systems and may be even more complex in an estuary. An understanding of the specific controls of the $\delta^{18}\text{O}$ composition of nitrate is essential to maximize interpretation of $\delta^{18}\text{O}_{\text{NO}_3}$ data in any system.

Key questions addressed by this research are: What are the sources of nitrate to SF Bay and how are they spatially distributed? What further information can we discern about patterns of N sources and cycling from the NO_3^- dual isotopic composition? Are there areas where denitrification or phytoplankton uptake (or both) might play a relatively important role in mitigating nutrient loading? To address these questions, we use the dual isotopic system of nitrate along with nitrate concentration, salinity, and the oxygen isotopic composition of water. Measurement of the spatial distribution of the nitrate isotopic composition at various sites within the SF Bay provides insights to the spatial heterogeneity of N and O isotopic composition of nitrate, helping to identify nitrate sources, aid in our ability to make comparisons among different regions within SF Bay, improve our understanding of nutrient and ecosystem dynamics, and augment rehabilitation efforts.

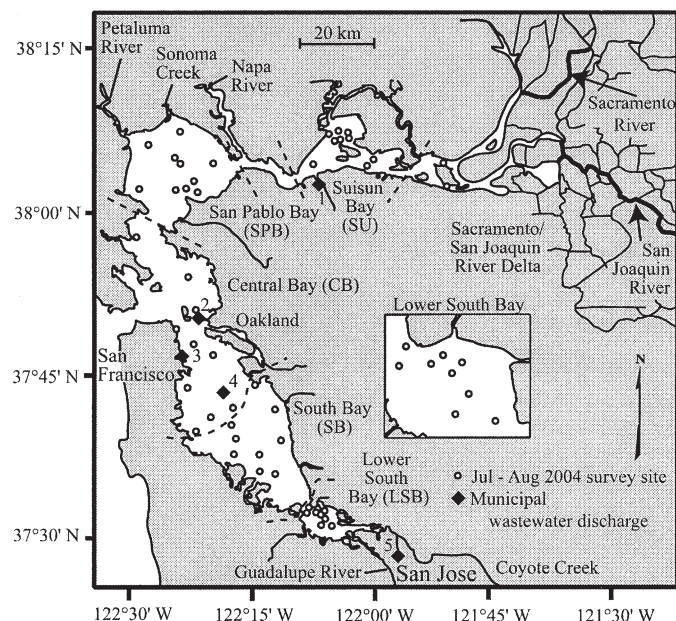


Fig. 1. Map of San Francisco Bay and San Joaquin-Sacramento Delta complex. Sites from the July-August 2004 survey are shown as circles. Locations of wastewater treatment plants with discharges $>1.0 \text{ m}^3 \text{ s}^{-1}$ in SF Bay are shown as diamonds. See text for detailed descriptions of discharge loads.

Materials and methods

Site description—SF Bay is a highly urbanized estuary, with a population of approximately 7 million in the surrounding area. The SF Bay ecosystem is effectively comprised of two estuarine systems (Fig. 1), each with different hydrodynamic and hydrologic regimes (Conomos et al. 1985). Northern SF Bay, considered a partially mixed estuary, connects the Pacific Ocean to the San Joaquin and Sacramento River delta. Southern SF Bay, branching off the main stem of northern SF Bay, is a tidally oscillating tributary lagoon with density-driven exchanges with Central Bay (CB) (Walters et al. 1985). Although salinities in North SF Bay may vary from 0 to 30 depending primarily on discharge of water through the San Joaquin/Sacramento Delta (and distance from the ocean), salinities in the South SF Bay generally remain between 26 and 30 (Nichols et al. 1986).

The Sacramento-San Joaquin River delta is a hydrodynamically complex system comprised of an intensely managed network of natural and human-made levees and lakes, diked agricultural fields, and relicts of tidal marshlands. The watershed comprises approximately 40% of the area of California (Jassby and Cloern 2000). On average, the Sacramento and San Joaquin rivers contribute 84% and 13%, respectively, of the freshwater inflow to the delta (CDWR 2005). During the low flow conditions typical of late summer, the dominant input of nutrients to the northern arm of SF Bay is from the Sacramento River because of export pumping within the delta. The important nutrient sources within the Sacramento River are agricultural drains and wastewater inputs (Hager and Schemel

1992). Approximately 92% of the freshwater flowing to the SF Bay from the delta originated in the Sacramento River during this study period (CDWR 2005).

Southern SF Bay receives only minimal annual freshwater input, with an average freshwater inflow of about $24.5 \text{ m}^3 \text{ s}^{-1}$ (Hager and Schemel 1996). By far the largest proportion ($\sim 75\%$) of the freshwater input comes from effluent of wastewater treatment plants (WWTPs), particularly to Lower South Bay (LSB) (Hager and Schemel 1996). The largest WWTP in LSB is the San Jose/Santa Clara WWTP located in the southeast end of LSB (No. 5 in Fig. 1), with an average discharge of $5.26 \text{ m}^3 \text{ s}^{-1}$ (SFBWQCB 1995). Other substantial contributors to South Bay (SB) and CB include the East Bay Municipal Utilities District ($3.13 \text{ m}^3 \text{ s}^{-1}$; No. 2 in Fig. 1), the San Francisco southeast WWTP ($2.93 \text{ m}^3 \text{ s}^{-1}$; No. 3 in Fig. 1), and a deepwater outfall north of the San Bruno Shoal (East Bay Dischargers Authority; EBDA), which consolidates wastewater effluent from cities in the southeastern SF Bay region ($2.19 \text{ m}^3 \text{ s}^{-1}$; No. 4 in Fig. 1) (SFBWQCB 1995). LSB receives an average of $3.9 \text{ m}^3 \text{ s}^{-1}$ of streamwater flow, whereas SB receives only $2.3 \text{ m}^3 \text{ s}^{-1}$ and CB only $0.7 \text{ m}^3 \text{ s}^{-1}$ (Hager and Schemel 1996).

Hydraulic residence times within the southern arm of SF Bay are on the order of 100 d (Walters et al. 1985; Kimmerer 2004) and mixing of CB water with SB water is limited. Mixing of water between the two branches of SF Bay is generally controlled by density-driven exchange and is largely influenced by the amount of discharge from the San Joaquin/Sacramento Delta. In general, the most important factor influencing the flushing of southern SF Bay is the magnitude of the delta outflow (Conomos et al. 1985; Walters et al. 1985). Hydrodynamic conditions in the SF Bay estuary system during this study ($615 \text{ m}^3 \text{ s}^{-1}$) can be described as typical of late summer for a year of below-normal Sacramento/San Joaquin River discharge (Peterson et al. 1985; CDWR 2004).

Sample collection—Surface water samples (0.5 m depth) were collected at 49 sites in summer 2004 (29 July through 03 August) as part of a SF Bay Regional Monitoring Program (RMP) cruise aboard the RV *Endeavor* (SFEI 2005). Sampling locations were chosen on the basis of a random sampling design. The SF Bay estuary was divided into the following sections: LSB, SB, CB, San Pablo Bay (SPB), and Suisun Bay (SU) (Fig. 1). Nine to ten sites were

chosen at random within each subdivided section to facilitate comparisons among the different sections (Table 1). Water depths ranged from 1.0 m to 19.6 m, averaging 5.1 m. Twenty of the 49 sites were in water shallower than 3 m. Additionally, two samples were collected from the San Joaquin/Sacramento Delta at the western side of the delta complex.

Analytical methods—Samples were immediately filtered through a $0.2\text{-}\mu\text{m}$ filter and frozen. Surface water (~ 0.50 m depth) was collected for nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}) concentrations, as well as for oxygen isotopic composition of water ($\delta^{18}\text{O}_{\text{water}}$) and for nitrogen and oxygen isotopic composition of NO_3^- ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$). $\text{NO}_3^- + \text{NO}_2^-$ concentrations were measured using a modification of the colorimetric method of Armstrong et al. (1967). NO_2^- was measured separately by omitting the cadmium reduction step, whereas NO_3^- was calculated as the difference between these two measurements. Dissolved ammonium was analyzed using the indophenol blue method modified from the ALPKEM RFA methodology (USEPA 1983). Phosphate concentrations were measured using a modification of the molybdenum blue procedure (Bernhardt and Wilhelms 1967).

Isotopic analyses of NO_3^- were carried out using the denitrifier method (Sigman et al. 2001; Casciotti et al. 2002). Analyses of $\delta^{15}\text{N}_{\text{NO}_3}$ were corrected using an internal lab nitrate standard, calibrated against international nitrate isotopic standards IAEA-N3 ($\delta^{15}\text{N} = +4.7\text{‰}$) and USGS-34 ($\delta^{15}\text{N} = -1.8\text{‰}$). Analyses of $\delta^{18}\text{O}_{\text{NO}_3}$ were corrected for exchange, fractionation, and blank against international nitrate isotopic standards USGS-34 ($\delta^{18}\text{O} = -27.9\text{‰}$) and USGS-35 ($\delta^{18}\text{O} = +57.5\text{‰}$) (Böhlke et al. 2003). Analytical precision (1σ) was generally 0.2‰ for $\delta^{15}\text{N}$ and 0.7‰ for $\delta^{18}\text{O}$.

It should be pointed out that the denitrifier method implicitly measures the isotopic composition of $\text{NO}_3^- + \text{NO}_2^-$, but that the contribution of NO_2^- is generally ignored and reported as NO_3^- . If NO_2^- is present at significant concentrations, the reported isotopic composition of NO_3^- may be offset. The error will be significant for $\delta^{18}\text{O}_{\text{NO}_3}$ since data are corrected for the loss of five of six oxygen atoms in the denitrifier method (conversion of NO_3^- to N_2O). In the case of NO_2^- there will be an 'over-correction' (for NO_3^- reduction that did not occur) and

Table 1. Summary of average physicochemical parameters from each section of San Francisco Bay. Number of samples indicated as (n).

| Region | Salinity | Temp ($^{\circ}\text{C}$) | Dissolved oxygen (mg L^{-1}) | Dissolved oxygen (% sat) |
|--|----------|-----------------------------|--|--------------------------|
| Lower South Bay (9) | 26.95 | 20.67 | 5.60 | 67.25 |
| South Bay (9) | 30.16 | 20.65 | 6.31 | 75.81 |
| Central Bay (10) | 30.08 | 19.47 | 6.65 | 79.80 |
| San Pablo Bay (10) | 23.58 | 20.03 | 7.31 | 87.73 |
| Suisun Bay (9) | 7.81 | 21.39 | 7.90 | 94.87 |
| San Joaquin/Sacramento River delta (2) | 0.41 | 22.08 | 6.60 | 79.24 |

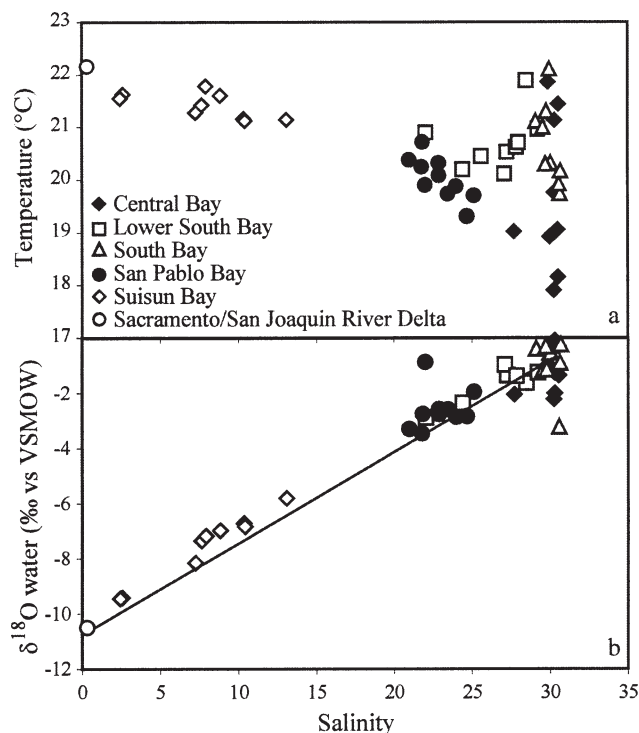


Fig. 2. (a) Temperature versus salinity in San Francisco Bay. (b) Water $\delta^{18}\text{O}$ versus salinity ($r^2 = 0.97$).

hence the resultant $\delta^{18}\text{O}_{\text{NO}_3}$ will be reported as lower than its true value. The magnitude of this offset will therefore depend on both the isotopic composition of the NO_2^- and the fractionation factor for NO_3^- reduction to NO_2^- in the denitrifier species used, which is currently unknown. While we recognize this limitation, NO_2^- in SF Bay surface water samples comprised less than 4% of the oxidized N pool ($\text{NO}_3^- + \text{NO}_2^-$) and for the purposes of this paper, this discrepancy is disregarded.

Water samples were analyzed for oxygen isotopic composition ($\delta^{18}\text{O}_{\text{water}}$) using the standard CO_2 equilibration technique (Epstein and Mayeda 1953). Hydrographic parameters were measured using a standard Seabird CTD package deployed from the research vessel. Parameters measured included conductivity, temperature, dissolved oxygen, salinity, and optical backscatter.

Results and discussion

Hydrographic parameters—A summary of the hydrographic data for the different regions of SF Bay is given in Table 1. Salinities ranged from near seawater (~ 31.4) to near freshwater values (0.3), while water temperatures varied between 18.0°C and 22.5°C , with colder values generally indicative of seawater influence. A plot of salinity versus temperature (Fig. 2a) illustrates the separation of southern SF Bay (LSB and SB) from the main portion of northern SF Bay (CB, SPB, and SU). The southern arm of SF Bay, which receives significantly less freshwater input, clearly has a steeper salinity gradient than the northern arm. The high salinity and temperature of the samples from

southern SF Bay are also consistent with a relatively long residence time and minimal mixing between the two arms of the estuary (Walters et al. 1985; Kimmerer 2004).

Water isotopes ($\delta^{18}\text{O}_{\text{water}}$)—The oxygen isotopic composition of water ($\delta^{18}\text{O}_{\text{water}}$) ranged from -10.6‰ to -0.1‰ (vs. Vienna Standard Mean Ocean Water [VSMOW]). A plot of salinity versus $\delta^{18}\text{O}$ of water (Fig. 2b) demonstrates the generally good correlation of these two conservative tracers within the estuary, with low values in the delta and high values in CB.

Nutrient distributions and mixing lines—Plotting nutrient concentrations against salinity, a conservative tracer of estuarine water mixing, minimizes spatial variation in concentrations due solely to tidal excursion and emphasizes deviations from mixing, thus allowing identification of additional local sources or cycling. For instance, a nutrient distribution falling above a mixing line generally indicates the presence of an additional source, whether a point source or the product of a more diffuse and widespread biological transformation (e.g., remineralization, nitrification, etc.). Conversely, a distribution falling below a mixing line suggests nonconservative behavior such as the presence of a nutrient sink (e.g., denitrification, assimilation, etc.) or the presence of an additional source.

Figure 3 illustrates this concept, highlighting the different behaviors of the two arms of the estuary and also the evidence for nonconservative mixing or multiple sources throughout the SF Bay estuary (see following discussion). Mixing between CB (seawater) and LSB is represented by the solid line, whereas mixing between CB and the delta is represented by the dashed line (see Table 2 for endmember definitions). Endmembers for creating these mixing lines were chosen as follows (Table 2). The delta endmember was chosen as the average of the two most freshwater (salinity = 0.3) sites in the channels of the San Joaquin and Sacramento rivers at the far western side of the delta complex. The CB (seawater) endmember was chosen as the sample with the highest salinity (31.4).

The freshwater endmember for LSB was not explicitly sampled during this study. However, because it is documented that by far the most significant freshwater source to southern SF Bay is WWTP effluent, especially during summer, we used the values reported by Hager and Schemel (1996) for average NO_3^- ($\sim 1,000 \mu\text{mol L}^{-1}$) and PO_4^{3-} ($140 \mu\text{mol L}^{-1}$) (concentrations in the San Jose/Santa Clara WWTP effluent) as the freshwater endmember. In addition, samples of WWTP effluent from this facility were sampled at a later date (under normal operating conditions), showing concentrations of NO_3^- and PO_4^{3-} consistent with the values in Hager and Schemel (1996). This sample also provided a measurement of the NO_3^- isotopic composition of this endmember. Although we cannot be entirely certain how representative the isotopic measurements are, we believe that because the facility typically operates under consistent and tightly regulated conditions throughout the year, the isotopic values can be used to approximate this endmember (Table 2).

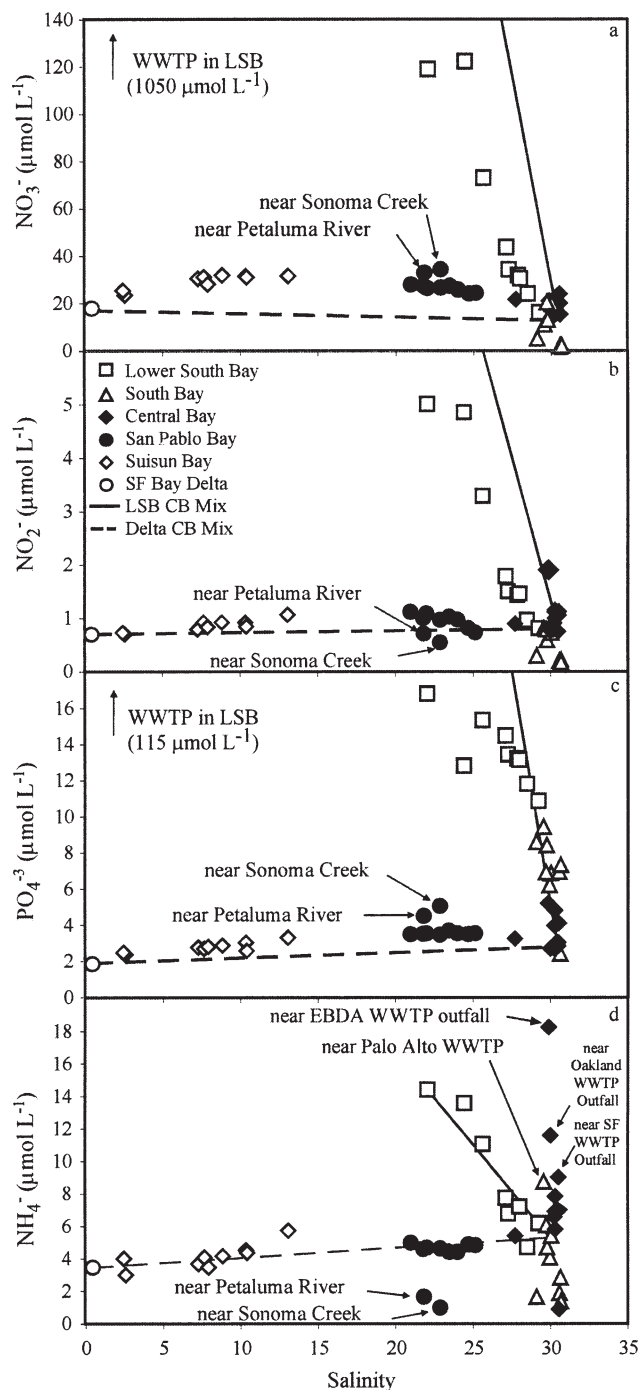


Fig. 3. Nutrients versus salinity in San Francisco Bay. (a) NO_3^- versus salinity, (b) NO_2^- versus salinity, (c) PO_4^{3-} versus salinity, (d) NH_4^+ versus salinity. Southern San Francisco Bay calculated mixing line between LSB and CB is denoted by the solid line. Calculated mixing in northern San Francisco Bay between the delta and CB is denoted by the dashed line. See Table 2 for endmember definitions.

Because the southern SF Bay is essentially hydrodynamically separated from influence by northern SF Bay (Fig. 2a), the two basins are treated separately in the following more detailed discussion of the distribution of nutrients and NO_3^- isotopic compositions.

Southern SF Bay

Nutrient concentrations in southern SF Bay are the highest in LSB, with maximum concentrations of NO_3^- , NO_2^- , and PO_4^{3-} reaching $122.3 \mu\text{mol L}^{-1}$, $5.0 \mu\text{mol L}^{-1}$, and $16.8 \mu\text{mol L}^{-1}$, respectively (Fig. 3a–c). With increasing salinity toward the more marine endmember (CB), concentrations of these nutrients were significantly lower and more typical of a marine source, having concentrations of NO_3^- , NO_2^- , and PO_4^{3-} of $12.7 \mu\text{mol L}^{-1}$, $0.8 \mu\text{mol L}^{-1}$, and $2.8 \mu\text{mol L}^{-1}$, respectively. However, in SB, the middle of the mixing gradient between LSB and CB, concentrations of NO_3^- and NO_2^- were generally lower, with minimum concentrations of $1.0 \mu\text{mol L}^{-1}$ and $0.1 \mu\text{mol L}^{-1}$, respectively.

Although high concentrations of NH_4^+ are generally also associated with the high NO_3^- , NO_2^- , and PO_4^{3-} in LSB, the highest NH_4^+ concentrations are found at some sites in CB (Fig. 3d). These sites are all located near major WWTP discharges (Fig. 1) and likely reflect elevated levels of NH_4^+ (primarily or secondarily) from sewage effluent. Notably, the sites with elevated NH_4^+ concentrations appear to be relatively spatially isolated, suggesting that NH_4^+ has a short residence time (hydraulically flushed) and is not widely distributed by these point sources. NH_4^+ is generally the preferred form of N for assimilation by phytoplankton and therefore is rapidly taken up within SF Bay (Hogue et al. 2003). Alternatively, NH_4^+ can also be rapidly oxidized by nitrifying bacteria and archaea to NO_2^- (Francis et al. 2005). Evidence for this may be indicated by the slightly higher NO_2^- concentrations at the site near the EBDA outfall (No. 4 in Fig. 1).

The freshwater endmember in LSB (WWTP effluent) clearly dominates the local source of nutrients, increasing concentrations of NO_3^- , NO_2^- , PO_4^{3-} , and NH_4^+ (Fig. 3). Regarding NO_3^- specifically (Fig. 3a), the mixing line suggests that even at the highest concentrations observed in LSB, NO_3^- is not conservatively mixed. Effluent is discharged directly into a tidal salt marsh environment that may represent a significant sink for NO_3^- during transport to LSB.

In Fig. 4, $\delta^{15}\text{N}_{\text{NO}_3}$ is plotted against its corresponding $\delta^{18}\text{O}$ for all sites. Nitrogen isotopic composition of nitrate, $\delta^{15}\text{N}_{\text{NO}_3}$, for the entire SF Bay system in the summer of 2004 ranged from +6.5‰ to +13.9‰ (vs. Air), whereas the oxygen isotopic composition ($\delta^{18}\text{O}_{\text{NO}_3}$) ranged from –5.0‰ to +11.6‰ (vs. VSMOW) (Fig. 4). Notably, the range of $\delta^{18}\text{O}$ compositions found within this system is more than twice that of $\delta^{15}\text{N}$.

In southern SF Bay, $\delta^{15}\text{N}$ values ranged from $\sim +7$ ‰ in CB, representing a marine nitrate source consistent with nearshore environments of coastal California (Altabet et al. 1999; Wankel unpubl. data), up to $\sim +14$ ‰ found in LSB. These high $\delta^{15}\text{N}$ values are consistent with a dominance of inputs of WWTP effluent (Shearer et al. 1974; Aravena et al. 1993; Fogg et al. 1998). Values for the $\delta^{18}\text{O}_{\text{NO}_3}$ in the LSB region ranged from +0.2‰ up to +4.5‰, whereas marine (CB) values cluster near $\sim +4$ ‰. The coincidence of high $\delta^{18}\text{O}_{\text{NO}_3}$ values (up to +11.6‰) in the SB with low

Table 2. Endmember definitions used in calculating mixing lines for Figs. 3, 5, and 6.

| Endmember | NO ₃ ⁻ (μmol L ⁻¹) | NO ₂ ⁻ (μmol L ⁻¹) | PO ₄ ⁻³ (μmol L ⁻¹) | NH ₄ ⁺ (μmol L ⁻¹) | δ ¹⁸ O _w (‰) | δ ¹⁵ N _{NO₃} (‰) | δ ¹⁸ O _{NO₃} (‰) | Salinity |
|-------------------------------------|---|---|--|---|---------------------------------------|--|--|----------|
| Lower South Bay | | | | | | | | |
| Lowest salinity sample | 122.3 | 4.9 | 16.8 | 13.6 | -1.3 | +13.9 | +0.2 | 22.0 |
| San Jose/Santa Clara WWTP effluent* | 1050 | NA | 115 | NA | NA | +13.8 | +0.4 | ~0 |
| Central Bay (highest salinity) | 12.7 | 0.8 | 2.8 | 5.6 | -1.3 | +7.7 | +4.3 | 30.8 |
| San Francisco Bay delta | 17.0 | 0.7 | 1.9 | 3.5 | -10.4 | +7.5 | -4.6 | 0.4 |

* Composition of San Jose/Santa Clara WWTP effluent was measured at a later date (29 Nov 2005); values may not be entirely representative on an annual basis. Values for NO₃⁻ and PO₄⁻³ concentrations, however, are consistent with Hager and Schemel (1996).

nutrient concentrations is suggestive of an uptake signature (see following discussion).

Figure 5a,b demonstrates isotopic mixing of two different sources (LSB and CB) of water with differing salinities and containing nitrate of differing concentration and isotopic composition (Table 2). Mixing on such a plot is represented by the heavy solid curve, which is calculated as the hypothetical salinity and nitrate isotopic composition of various proportions of the endmembers. The high δ¹⁵N_{NO₃} values of the LSB are consistent with the dominance of a sewage source (δ¹⁵N = +13.7‰; Table 2). Although the curve in Fig. 5a approximates the δ¹⁵N data quite closely and offers perhaps a simple explanation of mixing alone for the observed pattern, the δ¹⁵N_{NO₃} values of LSB and SB samples do fall slightly above the line. This could suggest either the contribution of an additional source with a high δ¹⁵N_{NO₃} or the influence of fractionation by nitrate consumption (photosynthetic uptake or denitrification). δ¹⁸O_{NO₃} values of LSB nitrate at lower salinities (22–27) are also well described by this mixing curve (Fig. 5b). However, higher-salinity LSB and SB samples have significantly higher δ¹⁸O_{NO₃} values that fall well above the mixing curve, clearly indicating nonconservative behavior of NO₃⁻ in this region. Thus, in this case the added perspective of δ¹⁸O_{NO₃} illustrated an effect that

δ¹⁵N_{NO₃} could not. The higher δ¹⁸O_{NO₃} and δ¹⁵N_{NO₃}, both coinciding with decreasing NO₃⁻ concentrations, seem to suggest that NO₃⁻ is being consumed, as uptake causes both δ¹⁵N_{NO₃} and δ¹⁸O_{NO₃} values to increase.

Comparison of NO₃⁻ concentrations versus δ¹⁵N_{NO₃} and δ¹⁸O_{NO₃} can also be used to distinguish mixing from biological processing, since mixing patterns fall along a hyperbola, whereas fractionation is an exponential process. This concept is illustrated in Fig. 6a,b. A simple mixing curve between CB and LSB is represented by a heavy solid line (as in Fig. 5), whereas a Rayleigh fractionation model for uptake (assumed fractionation factor ε = 5‰ for both δ¹⁵N_{NO₃} and δ¹⁸O_{NO₃}, typical of

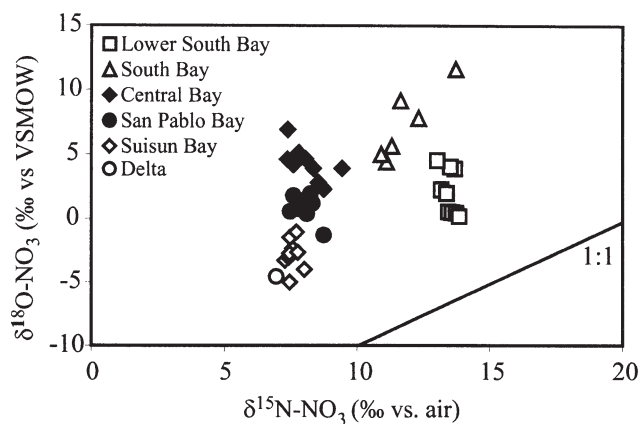


Fig. 4. NO₃⁻ dual isotopic composition of nitrate in San Francisco Bay (δ¹⁸O_{NO₃} versus δ¹⁵N_{NO₃}). Mixing of two sources on this plot is linear. The distribution suggests evidence for at least three major sources. Note the linear pattern suggestive of NO₃⁻ consumption within SB. Assimilative uptake will cause the composition to increase along a slope of 1 (shown) (Granger et al. 2004).

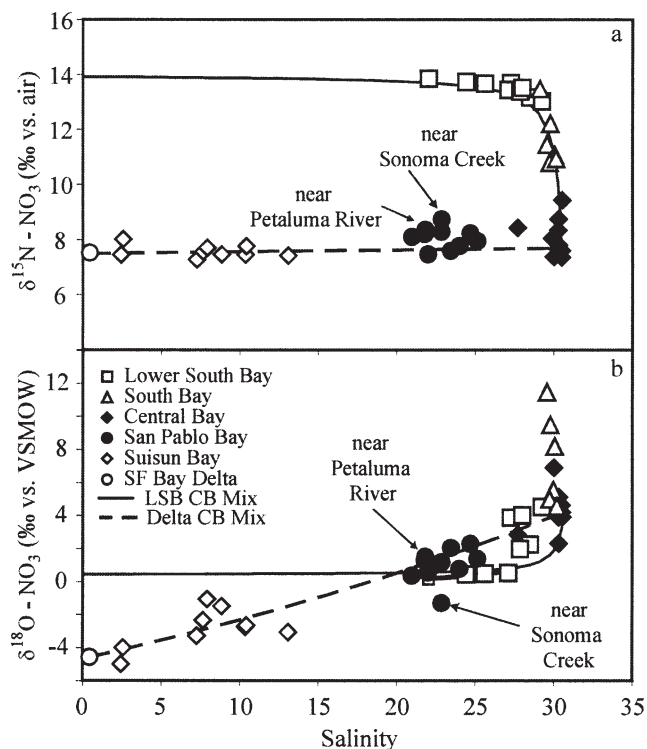


Fig. 5. NO₃⁻ isotopes versus salinity in San Francisco Bay. See Table 2 for endmember definitions: (a) δ¹⁵N_{NO₃} versus salinity. (b) δ¹⁸O_{NO₃} versus salinity. Southern San Francisco Bay calculated mixing curve between San Jose/Santa Clara WWTP effluent (LSB) and CB is denoted by solid line. Calculated mixing between delta and CB is denoted by the dashed line. In SPB, potential point sources, the Petaluma River and Sonoma Creek, are also highlighted.

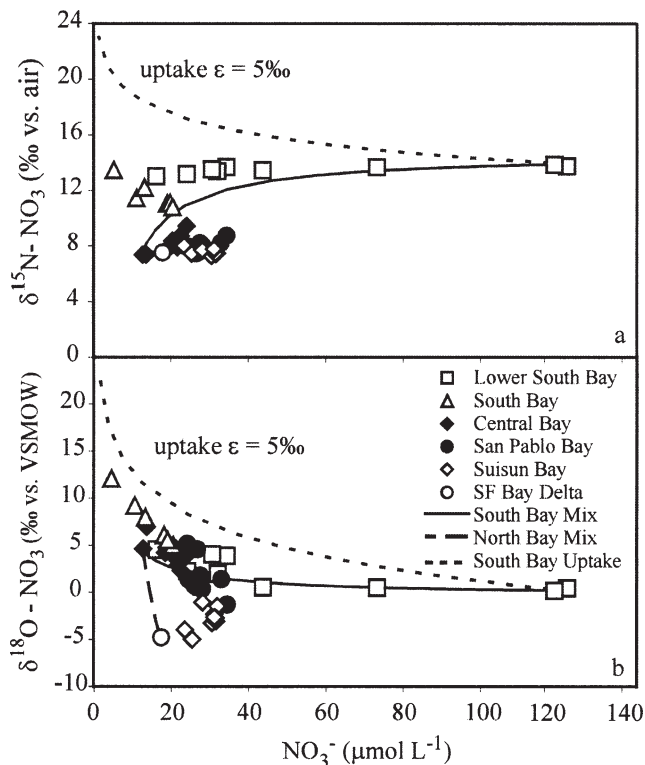


Fig. 6. NO_3 isotopes versus NO_3^- concentration in San Francisco Bay. See Table 2 for endmember definitions: (a) $\delta^{15}\text{N}_{\text{NO}_3}$ versus NO_3^- concentration. (b) $\delta^{18}\text{O}_{\text{NO}_3}$ versus NO_3^- concentration. Southern San Francisco Bay calculated mixing curve between San Jose WWTP effluent and CB is denoted by solid line. Calculated mixing between delta and CB is obscured by the similarity in concentration and $\delta^{15}\text{N}$ values. The progressive isotopic composition resulting from Rayleigh fractionation via photosynthetic uptake ($\epsilon = 5\text{‰}$) is illustrated by the dotted line.

phytoplankton uptake [Granger et al. 2004]) is shown as a dotted line. Note that mixing within the northern bay is obscured in Fig. 6a because the endmembers have very similar NO_3^- concentrations and $\delta^{15}\text{N}_{\text{NO}_3}$ values. In the southern bay, as NO_3^- concentrations decline, either through uptake or mixing with a third lower-concentration source, $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values increase accordingly (Fig. 6a,b). This can be seen especially well in the $\delta^{18}\text{O}_{\text{NO}_3}$ of the SB samples. A significant third source would be required to have a low NO_3^- concentration and a salinity of ~ 28 , and hence is highly improbable. Since samples from LSB fall between the mixing and uptake lines, this pattern may be the result of a combination of mixing and uptake.

Alternatively, different values for ϵ could also cause changes in the relative proportions of mixing and uptake calculated from Fig. 6a,b. It should be pointed out that, although mixing and uptake both cause increases in $\delta^{18}\text{O}_{\text{NO}_3}$ in this system, changes in $\delta^{15}\text{N}_{\text{NO}_3}$ due to mixing and uptake are opposite in direction. This highlights the utility of the dual isotope approach, allowing separation of processes from mixing in cases where the resulting isotopic compositions (of either $\delta^{15}\text{N}_{\text{NO}_3}$ or $\delta^{18}\text{O}_{\text{NO}_3}$) of the two phenomena may overlap.

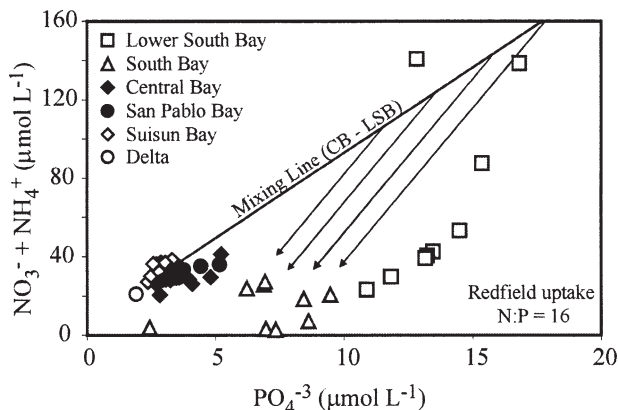


Fig. 7. DIN versus DIP in San Francisco Bay. The concave-up pattern in the southern arm of San Francisco Bay (LSB, SB) is typical of late summer conditions and suggests the combined effects of mixing with uptake along the gradient. Nutrient uptake by phytoplankton at the Redfield ratio (16 : 1) is denoted by the arrows. WWTP values to LSB are $1,050 \mu\text{mol L}^{-1}$ for NO_3^- and $115 \mu\text{mol L}^{-1}$ for PO_4^{-3} .

Dissolved N : P ratios throughout SF Bay are consistently less than 16 (Redfield), indicating that the ecosystem is N-limited with regard to nutrient demand. Because of differences in the stoichiometry of nutrient uptake relative to supply, nutrient/nutrient plots can also be helpful for differentiating mixing from uptake. Figure 7 shows the relation of dissolved inorganic nitrogen (DIN) ($\text{NO}_3^- + \text{NH}_4^+$) relative to PO_4^{-3} for SF Bay. The concave up-distribution of values within southern SF Bay (SB and LSB) is a consistent feature during late summer conditions (Hager and Schemel 1996), and was interpreted as representing the presence of either a NO_3^- sink (denitrification) or a PO_4^{-3} source. However, an unknown point source of PO_4^{-3} causing a trend of this magnitude is unlikely. Moreover, the smooth nature of the deviation from the PO_4^{-3} mixing line in Fig. 3c suggests a more diffusive sedimentary source from organic matter regeneration. Indeed, late summer increases in water column concentrations of PO_4^{-3} in estuaries have been documented (Froehlich 1988; Jordan et al. 1991).

Whereas Fig. 3a suggests a sink of NO_3^- in southern SF Bay, Fig. 3c suggests a net production of PO_4^{-3} in much of the region. The NO_3^- sink may be a loss to the sediment since benthic flux studies in southern SF Bay have shown that NO_3^- and NO_2^- fluxes are variable in both magnitude and direction (Caffrey et al. 1996). Benthic denitrification, generally a heterotrophic process, can contribute to a negative NO_3^- flux and a positive PO_4^{-3} flux. However, because benthic denitrification does not exhibit a strong fractionation (Brandes and Devol 1997; Lehmann et al. 2004), and since no evidence exists for suboxic conditions in the water column during this study, which would promote water column denitrification and a strong isotopic fractionation, it seems that denitrification cannot account for the increases in $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ with decreasing concentrations in LSB and SB. Although we cannot discount the possibility that benthic denitrification could be enhanced by heavy bioturbation, which occurs through-

out the shallow shoals of SF Bay, Lehmann et al. (2004) demonstrated that even in environments where NO_3^- transport across the surface–water interface is eased by bioirrigation, the effective N and O isotope effects are essentially not expressed in the overlying water column.

Whereas the nitrate endmember within LSB has a high concentration and $\delta^{15}\text{N}_{\text{NO}_3}$ at lower salinities (Fig. 5a), it clearly is not simply mixed conservatively northward (Fig. 6) since the SB samples do not have intermediate values. Given the increase in residence time of water during summer in southern SF Bay (Walters et al. 1985), the negative correlation of $\delta^{15}\text{N}_{\text{NO}_3}$ and NO_3^- concentration could best be explained by a combination of mixing between LSB with CB plus nutrient drawdown by phytoplankton. Drawdown of N and P by phytoplankton will follow a slope of ~ 16 according to a Redfield stoichiometry (Fig. 7). A combination of mixing with phytoplankton drawdown could result in the patterns seen in Fig. 7, as illustrated by the arrows. Indeed, in southern SF Bay, although a spring phytoplankton bloom is a recurrent feature that draws down nutrient concentrations significantly, drawdown of nutrients by phytoplankton is substantial all year (Cole and Cloern 1984). Thus, the increases in $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ above that expected from simple mixing are primarily due to the consumption of nitrate by photosynthetic uptake.

During NO_3^- assimilation by phytoplankton the remaining NO_3^- pool becomes simultaneously enriched in both ^{15}N and ^{18}O , because the fractionation factor (ϵ) for N is equal to that of O during uptake of NO_3^- by phytoplankton (Granger et al. 2004). Marine denitrification has also been shown to follow this pattern (Granger et al. 2004). Thus, a pool of NO_3^- affected by phytoplankton uptake or denitrification should theoretically progress along a slope of 1 on a plot of $\delta^{15}\text{N}$ versus $\delta^{18}\text{O}$ (Fig. 4). Although the $\delta^{18}\text{O}_{\text{NO}_3}$ from SB (Fig. 6b) suggests uptake, the data do not follow a slope of 1 (Fig. 4) because of a larger enrichment in the oxygen isotopes than in the nitrogen isotopes. Although the $\delta^{15}\text{N}_{\text{NO}_3}$ data from SB do not fall dramatically above the mixing line, the $\delta^{18}\text{O}_{\text{NO}_3}$ data fall far above the mixing line (Fig. 5). This decoupling of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ may be due to a high degree of water column regeneration of organic nitrogen and nitrification which, if significant, may result in nitrate isotopic compositions falling above a slope of 1 (Granger et al. 2004; Wankel and Paytan 2004). Indeed, high amounts of N regeneration are reported by Hammond et al. (1985) and Hager and Schemel (1996). Careful combination of such nutrient isotopic studies with hydrodynamic models might further aid in the differentiation of photosynthetic uptake, denitrification, source identification, or mixing.

Northern SF Bay

Nutrient concentrations in northern SF Bay also vary significantly along the salinity gradient from the Pacific Ocean to the Sacramento/San Joaquin River delta. In the freshwater endmember of the delta, concentrations of NO_3^- , NO_2^- , PO_4^{3-} , and NH_4^+ were relatively low at $16.9 \mu\text{mol L}^{-1}$, $0.7 \mu\text{mol L}^{-1}$, $1.9 \mu\text{mol L}^{-1}$, and

$3.5 \mu\text{mol L}^{-1}$, respectively. Although nutrient concentrations of the marine endmember are similar to those found emanating from the delta, there appears to be a mid-salinity source of NO_3^- , NO_2^- , and PO_4^{3-} that causes concentrations to increase along the salinity gradient. Generally, the highest concentrations of NO_3^- ($\sim 32 \mu\text{mol L}^{-1}$) were found in SU near salinities of 7–13, whereas the highest PO_4^{3-} concentrations ($\sim 3.5 \mu\text{mol L}^{-1}$) were found in SPB near higher salinities of 21–25.

Within SPB, two sites stand out of the distribution along the salinity gradient (Fig 3). Slightly higher NO_3^- concentrations (32.9 and $34.4 \mu\text{mol L}^{-1}$) and PO_4^{3-} concentrations (4.5 and $5.1 \mu\text{mol L}^{-1}$) were found near the mouths of the Petaluma River and the Sonoma Creek, respectively. In addition, these two sites also showed lower NO_2^- concentrations (0.7 and $0.5 \mu\text{mol L}^{-1}$) and NH_4^+ concentrations (1.6 and $1.0 \mu\text{mol L}^{-1}$), respectively. These data suggest that sites reflect local riverine sources of NO_3^- and PO_4^{3-} and dilution of NO_2^- and NH_4^+ .

Nitrate $\delta^{15}\text{N}$ values at the freshwater end of the northern arm of SF Bay (delta) have a composition ($\sim +7\%$) similar to the marine endmember, resulting in minimal $\delta^{15}\text{N}$ variation along this salinity gradient (Fig. 5a). The lowest $\delta^{18}\text{O}_{\text{NO}_3}$ values measured along the estuarine gradient cluster within the freshwater endmembers of the delta and SU, ranging from -6% to -2% (Fig. 5b). Seawater $\delta^{18}\text{O}_{\text{NO}_3}$ values (represented by samples with salinities near 31) cluster near a value of $+4\%$. Thus, mixing within the northern arm between these two endmembers can be elucidated using $\delta^{18}\text{O}_{\text{NO}_3}$, emphasizing the added benefit of measuring both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

Interestingly, the seawater endmember in this case has a $\delta^{18}\text{O}_{\text{NO}_3}$ value ($+4.3\%$) considerably higher than the near 0.0% $\delta^{18}\text{O}_{\text{NO}_3}$ of deepwater marine NO_3^- (Casciotti et al. 2002). This seawater endmember likely comes from within the euphotic zone of coastal California waters. Whereas the depth of the euphotic zone within the estuary is limited because of high turbidity, euphotic zone depths in coastal California waters are generally 30 m or deeper. Nitrate in surface seawater entering SF Bay could be partially consumed by phytoplankton, explaining the slightly higher $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values for the seawater endmember compared with open-ocean deepwater values. Future studies of nitrate dynamics within SF Bay should include samples from closer to or outside of the Golden Gate.

Although southern SF Bay does not exhibit a strong salinity gradient, northern SF Bay exhibits a large gradient, allowing an even wider perspective on determining mixing relations using salinity. Mixing between the two salinity endmembers in the northern SF Bay (Table 2) is illustrated in Figs. 3, 5, and 6 by the heavy dashed line. In Fig. 5a, elevated $\delta^{15}\text{N}_{\text{NO}_3}$ values within SPB fall above the mixing line, whereas those within SU are consistent with mixing. Because $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ both increase with decreasing NO_3^- concentrations (Fig. 6) along the downstream gradient from SU to SPB, these data are consistent with phytoplankton uptake (see southern SF Bay discussion).

However, other evidence appears to support the presence of additional nitrate sources in the northern bay. Nitrate

$\delta^{18}\text{O}_{\text{NO}_3}$ values within both SU and SPB do not plot along the mixing line (Fig. 6b), suggesting the presence of an additional midrange salinity nitrate source. Also, the highest $\delta^{15}\text{N}_{\text{NO}_3}$ values in SPB (+8.2‰ and +8.7‰) are close to the two most significant riverine inflows, the Petaluma River and Sonoma Creek, respectively. Furthermore, the site nearest the Sonoma Creek also has the lowest $\delta^{18}\text{O}_{\text{NO}_3}$ value for SPB of -1.3‰. Additionally, NO_2^- and NH_4^+ concentrations from these two sites are lower, whereas PO_4^{3-} concentrations are higher (Fig. 3), offering further evidence of these riverine point sources. Though flows are very low during this period ($<0.1 \text{ m}^3 \text{ s}^{-1}$), it seems likely that the increases in $\delta^{15}\text{N}_{\text{NO}_3}$ within SPB are indicative of local influence by contributions from these two riverine sources.

Central Contra Costa Sanitary District discharges wastewater ($1.54 \text{ m}^3 \text{ s}^{-1}$; No. 1 in Fig. 1) near the western end of SU and offers another potential point source, though $\delta^{15}\text{N}_{\text{NO}_3}$ values do not increase as might be expected for significant sewage inputs. Additionally, the Napa River enters SF Bay between SPB and SU. Phosphate oxygen isotopic composition has suggested that during summer the Napa River may contribute a significant amount of phosphate to SF Bay (McLaughlin et al. in press).

During the summer, phytoplankton productivity exerts strong control on NH_4^+ distribution but much less on NO_3^- and PO_4^{3-} . Indeed, historical data demonstrate that the nutrient sink by phytoplankton uptake in SF Bay is not as strong as in other estuaries, mainly due to high turbidity, which limits productivity (Cole and Cloern 1984). Our data are consistent with these results and emphasize the influence of river discharge on nutrient distribution in northern SF Bay (which leads to near conservative distributions of nutrients) (Peterson et al. 1985). However, although input from the delta is important, nitrate isotopic compositions suggest considerable contributions of NO_3^- to northern SF Bay from local sources, including but not limited to the Petaluma River and Sonoma Creek.

The low values for $\delta^{18}\text{O}_{\text{NO}_3}$ (as low as -5.0‰, Figs. 4–7) emanating from the Sacramento–San Joaquin Delta region deserve some attention, as the origin of the $\delta^{18}\text{O}_{\text{NO}_3}$ in marine systems is the subject of some recent debate (Casciotti et al. 2002). Earlier studies showed that the oxygen atoms of NO_3^- formed during the process of nitrification originate from both water and dissolved oxygen (Hollocher et al. 1981; Andersson and Hooper 1983; Hollocher 1984). During the first step of nitrification (NH_4^+ oxidation to NO_2^-), one O atom from dissolved O_2 is incorporated via ammonia monooxygenase while one O atom from water is incorporated via hydroxylamine oxidoreductase. During the final step of nitrite oxidation to nitrate, an additional O atom from water is incorporated. Thus, assuming no kinetic fractionation upon incorporation, the final NO_3^- product should have an isotopic signature equal to 2/3 $\delta^{18}\text{O}$ of water and 1/3 $\delta^{18}\text{O}$ of dissolved oxygen.

The $\delta^{18}\text{O}$ of water in SF Bay will vary depending on the mixture of seawater ($\sim 0.0\text{‰}$) and freshwater (mostly meltwaters from the Sierra Nevada with $\delta^{18}\text{O}$ values near -16‰ to -12‰; [Kendall and Coplen 2001; Kendall

unpubl. data]). The $\delta^{18}\text{O}$ of dissolved O_2 will reflect the balance between respiration, photosynthesis, and gas exchange with atmospheric O_2 . Because dissolved oxygen was only rarely supersaturated during this study (Table 1), $\delta^{18}\text{O}$ of O_2 should range between atmospheric equilibrium (+24‰) to potentially higher values caused by respiration (Quay et al. 1995; Brandes and Devol 1997). Thus, the contribution of dissolved O_2 atoms to NO_3^- isotopic composition should be +24‰ or higher. If 2/3 of the oxygen atoms are from water and 1/3 from dissolved O_2 , nitrate having a $\delta^{18}\text{O}$ value near 0‰ (as in LSB) must have been formed in water with a $\delta^{18}\text{O}$ of near -12‰. This value is consistent with the municipal water supply in the SF Bay area, which is a blend of waters originating from the Central Valley and the Sierra Nevada.

On the other hand, nitrate from the Sacramento/San Joaquin Delta has a low $\delta^{18}\text{O}$ value of near -5‰ (and even lower, unpubl. data), which would require it to have been formed in waters of approximately -19‰ or lower. This value is much too low to be representative of freshwaters from California (Kendall and Coplen 2001). Alternatively, the low $\delta^{18}\text{O}_{\text{NO}_3}$ found within the northern arm of SF Bay could be indicative of increased nitrite-catalyzed nitrite–water–oxygen isotopic exchange (Andersson and Hooper 1983). Casciotti et al. (2002) showed that in marine environments, the $\delta^{18}\text{O}_{\text{NO}_3}$ in deep waters was very close to the $\delta^{18}\text{O}$ of seawater and suggested that ultimately less than 1/6 of the oxygen atoms in NO_3^- may originate from dissolved O_2 . Thus, a similar situation may hold true for tidally influenced or estuarine environments resulting in lower $\delta^{18}\text{O}_{\text{NO}_3}$ than expected if 1/3 of the $\delta^{18}\text{O}$ of nitrate were incorporated from dissolved O_2 . The $\delta^{18}\text{O}_{\text{NO}_3}$ in much of northern SF Bay (and the delta—unpubl. data) are lower than would be predicted (2/3 water + 1/3 dissolved O_2). This discrepancy may be the result of varying degrees of isotopic exchange with water during NO_3^- utilization, regeneration, and nitrification. As nitrate is utilized and recycled, the value for $\delta^{18}\text{O}_{\text{NO}_3}$ is expected to approach the $\delta^{18}\text{O}_{\text{water}}$, thus losing its original source signature. Hence, in LSB where inputs and concentrations are relatively high, the $\delta^{18}\text{O}_{\text{NO}_3}$ values seem to represent a more conservative mixing distribution, whereas the low values for the $\delta^{18}\text{O}_{\text{NO}_3}$ emanating from the delta region may reflect a high degree of NO_3^- cycling. If indeed rapid N cycling interferes with an original NO_3^- source $\delta^{18}\text{O}$ signature, use of $\delta^{18}\text{O}_{\text{NO}_3}$ as an expected conservative tracer of NO_3^- mixing may be questionable, especially in areas with lower concentrations, where rapid turnover is possible. On the other hand, the combined use of $\delta^{18}\text{O}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{water}}$ could be developed to potentially constrain N cycling along an estuarine gradient.

The combined use of salinity, nutrient concentrations, and both water and nitrate isotopic composition revealed several sources and elucidated mixing patterns of nitrate in the SF Bay estuarine system. This first-time use of $\delta^{18}\text{O}_{\text{NO}_3}$ demonstrates the utility of the dual isotopic approach in an estuarine environment. Significant variations in both $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values occur for endmembers within SF Bay, allowing more detailed assessment of their significance. The data also reveal that key microbial

processes within the N cycle may be identified. For example, nitrate sinks such as uptake by phytoplankton or denitrification and nitrate production via nitrification may impart distinctive patterns.

This work also demonstrates the potential range of variability in nitrate isotopic composition that is to be expected within an estuarine system. Indeed, the $\delta^{18}\text{O}_{\text{NO}_3}$ range was more than twice that of the $\delta^{15}\text{N}_{\text{NO}_3}$ and perhaps reflects the large range of $\delta^{18}\text{O}_{\text{water}}$ values found in estuaries. Generally high rates of regeneration and nitrification, common to estuarine ecosystems, may enhance the incorporation of water oxygen, limiting the use of $\delta^{18}\text{O}_{\text{NO}_3}$ as a conservative tracer of source, but perhaps making it a desirable tool for the study of nitrate cycling in estuarine systems, where $\delta^{18}\text{O}_{\text{water}}$ ranges can be large. Thus, the large range in $\delta^{18}\text{O}_{\text{NO}_3}$ may be a common characteristic of such systems, making the $\delta^{18}\text{O}$ of both water and NO_3^- useful adjuncts to the more commonly applied $\delta^{15}\text{N}_{\text{NO}_3}$ in studies of nitrate within estuaries.

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Received: 2 August 2005
Accepted: 7 January 2006
Amended: 8 March 2006