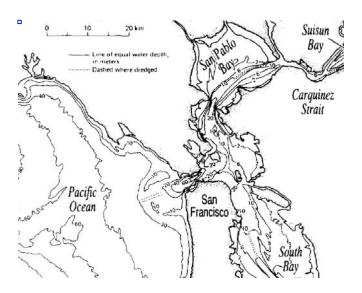
External Nutrient Loads to San Francisco Bay:

Assessing the Flux of Nutrients from Ocean to Bay

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1. INTRODUCTION

In an assessment of nutrient loading to San Francisco Bay (SFB, Fig. 1) one needs to account for loading via freshwater inflow through the Delta, stormwater inflow, wastewater inflow, and exchange with the coastal ocean – and to resolve loading for each sub-basin. To-date, good progress has been made in quantifying nutrient loads through the Delta, and monthly/seasonal/interannual changes in this loading over the past 35 years. Also, progress has been steady in compiling data and quantifying nutrient loads from wastewater as a sum of discharges from individual "publicly-owned treatment works" (POTWs); estimates are being refined based on historic and new data characterizing effluents to each sub-basin. Stormwater loading is less well defined as inflow is episodic and loading exhibits high temporal variability with concomitant high uncertainty. Quantifying variability and uncertainty in all terms is a necessary part of a nutrient loading assessment.



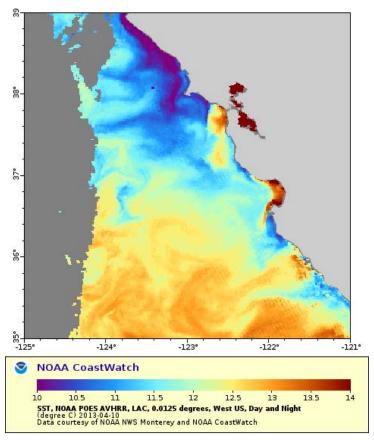
<u>Figure 1.</u> Outline of San Francisco Bay (SFB), showing ebb tide bar and bathymetry.

Nutrient exchange between San Francisco Bay and the coastal ocean remains a major unknown – at times accounting for export of nutrients from the Bay, but at other times this exchange may represent an important source. This report is in response to recent concerns that ocean-bay exchange could represent a large source of nitrate for the Bay. On a daily basis, a quarter of the water in the Bay moves to and from the coastal ocean through tidal action. Given that newly upwelled water in the Gulf of Farallones (GoF) can exhibit nitrate concentrations as high as ~35 μ mol L⁻¹ (0.5 mg N L⁻¹), it is clear that ocean waters may represent a major potential source of nitrogen for the Bay.

Here we characterize ocean-bay nutrient exchange with a view to providing a more complete picture of oceanic nutrient loading to San Francisco Bay and how it varies through the seasons and in response to upwelling events along the coast. Specifically, we present a conceptual model, develop order-of-magnitude estimates of nutrient loading, and identify key factors that need further attention.

2. CONCEPTUAL MODEL

The coastal ocean off San Francisco Bay is enriched with nutrients owing to wind-driven upwelling of deep, cold waters. Upwelling is strongest along the open coast north of Point Reyes, with surface temperatures as low as 8° C and nitrate levels as high as 35μ M observed at the surface (Largier et al 2006; Wilkerson et al 2006). While surface-breaking upwelling is generally less evident in the northern Gulf of Farallones, which is sheltered from southbound winds and currents by Point Reyes, this cold and nutrient-rich water is typically observed at shallow depths in the Gulf (unpublished data: WEST and RTC/SFSU) and at times is seen to break the surface along the shoreline between Drakes Estero and Bolinas Lagoon (e.g., see 10° C surface waters in Fig. 2).



<u>Figure 2.</u> An example of sea surface temperature off San Francisco Bay during active upwelling (10 April 2013): waters colder than 10°C break the surface north of Point Reyes and also in the Gulf of Farallones, along the shore north of Bolinas. Southward flow past Point Reyes is evident from the anti-clockwise flow pattern marked by surface temperatures in the north/central Gulf.

This upwelled nutrient-rich water can be imported to the Bay by tidal inflows, intruding well into the Bay due to tidal jets and buoyancy forcing (i.e., cold and salty ocean water is denser than Bay waters and it can spread landward as a salinity intrusion underneath Bay waters). While much of the inflowing water returns to the ocean on the subsequent ebb tide, some portion of the oceanic water and nutrients remain in the Bay.

The importance of oceanic nitrate loading to the Bay thus depends on 3 sets of factors:

• Concentration of nitrate in oceanic source waters.

The presence of cold/deep, high-nitrate water inside the tidal bar (Fig. 1) depends primarily on upwelling processes, including

- Large-scale seasonal setup of the thermocline in the NE Pacific, bringing highnitrate waters to the depth from which waters are upwelled;
- Strength of northerly winds that upwell waters the strength of winds and ocean stratification determine the depth from which waters are upwelled and the persistence of winds determines the persistence of high-nitrate waters near the surface;
- Interaction of shelf currents and winds with Point Reyes, which in turn controls the presence of upwelled waters in the northern Gulf of Farallones;
- Local wind and tidal effects in affecting the thermocline depth relative to the crest of the bar and whether upwelled waters are brought to within a tidal excursion of the mouth of the Bay.

Tidal influx of oceanic waters to San Francisco Bay.

Once shallow enough and close enough to Golden Gate (within the tidal withdrawal zone), oceanic waters will be drawn into the Bay with each flood tide. The volume delivered to the bay will depend on the strength of the tide (tidal excursion) as well as the strength of stratification coupled with the strength of the longitudinal density gradient – strong stratification will allow oceanic waters to intrude further into the Bay. This in turn affects what proportion of the imported oceanic water remains in the Bay following the subsequent ebb tide. Thus intrusion of oceanic nutrients into the Bay will be modulated by changes in freshwater inflow and surface heating, as well as tides.

• Intrusion of oceanic waters into the Bay and uptake of nitrate in the Bay.

The importance of nutrients retained in the Bay after ebb tide depends on the length of time that these high-nitrate waters remain in the bay, how far they penetrate into the bay, and how effectively they are taken up in primary production. These processes depend on estuarine circulation and phytoplankton dynamics.

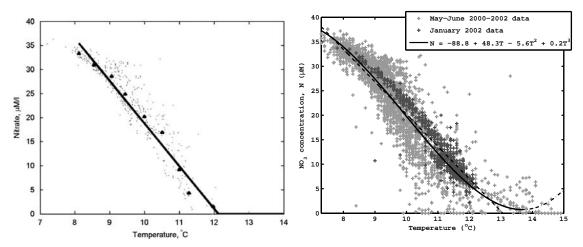
In this preliminary scoping of the oceanic nitrate loading to San Francisco Bay, we focus on the first 2 factors and only briefly address the 3rd factor.

3. NUTRIENT LOADING ESTIMATES

3-1. Nitrate concentration in oceanic source waters.

Upwelled waters originate at great depth in the ocean, where remineralization of organic matter leads to waters being enriched in dissolved inorganic material, including

carbon dioxide, nitrate, phosphate and silicate (and a deficiency in dissolved oxygen). Most attention has been directed at phytoplankton blooms that result from availability of nitrate in the euphotic zone following upwelling of these deep waters (e.g., Wilkerson et al 2006). Upwelled waters are cold and there is a strong relationship between temperature and nitrate concentration, as shown by Dever et al (2006) and Garcia-Reyes et al (2014) for data collected immediately north of Point Reyes, a region which has similar deep-water characteristics as the Gulf of Farallones and which is thought to be the source of the deep waters present in the north/central Gulf. Data from Tomales Bay (Kimbro et al 2009) and limited unpublished data available from the northern Gulf and outer Bay are consistent with this general pattern of highest nitrate in coldest water and negligible nitrate in waters with temperatures >12°C.



<u>Figure 3.</u> The relationship between nitrate concentration and ocean water temperature obtained from many data collected immediately north of Point Reyes during WEST surveys, 2000-2003: left panel from Dever et al (2006) – peak upwelling season; right panel from Garcia-Reyes et al (2014) – upwelling and winter seasons. Data for Tomales Bay is shown in Kimbro et al (2009) and a more general NE Pacific analysis is in Palacios et al (2013).

Similar relationships between temperature and silicate or phosphate are found, with higher concentrations in deeper/colder waters. As nitrate is considered the limiting nutrient for photosynthesis and plankton productivity (in general), the silicate and phosphate levels have not received as much attention. Typical levels of silicate in upwelled waters are reported by Wilkerson et al (2006), showing an approximately linear relationship with nitrate and a regression slope between 1.1 and 1.5 (when both concentrations are reported in μ M). Maximum silicate levels of 50 μ M were observed off Bodega Bay in 8°C waters in June 2002. Phosphate levels are lower, with phosphate levels about 1/10 of nitrate (when both expressed in μ M), although the slope of the line is probably closer to theoretical 1:16 Redfield ratio (Traganza et al 1980) – in the coldest waters, when nitrate is exceeding 30 μ M one expects phosphate levels less then 3 μ M. Finally, ammonium levels are typically low in upwelled waters, with concentrations less than 1 μ M in cold waters with high nitrate and silicate levels, although higher values may

be observed in warmer waters where lower concentrations of other nutrients are observed (e.g., Wilkerson et al 2006; Dugdale et al 2006).

3-2. Total mass of nitrate contained in a tidal prism.

The total mass of nutrients imported to San Francisco Bay with the tide can be estimated from the tidal prism (intertidal volume $^{\sim} 2*10^{9} m^{3}$) and the ocean nitrate concentration. High loading will occur when the inflow is composed entirely of deep upwelled waters (nitrate concentration $^{\sim} 35 \mu M$), and the mass of nitrate imported to the Bay can be estimated as follows:

$$(2*10^9 \text{m}^3)*(35*10^{-6} \text{mole}/10^{-3} \text{m}^3) = 7*10^7 \text{mole} = 4.34*10^6 \text{kg} = 4,340 \text{ ton NO}_3$$

This mass is much greater than the average daily discharge from all POTWs bay-wide (~11.8 ton per day) or from stormwater (average of ~10 ton per day) or from Delta inflows (average ~10.4 ton per day) and far outweighs the ~0.97 ton per day DIN from refineries (Senn et al 2013). While this mass is the equivalent of half a year of nitrate loading from all other sources, only a small fraction typically remains in the Bay). Further, this oceanic loading is strongest in the outer Bay whereas terrigenous loading (Delta/stormwater/wastewater) is typically stronger in the inner Bay.

While it is unusual for the entire tidal prism to be comprised of high-nitrate newly upwelled waters, and much of the water that enters the Bay on the flood tide is removed on the ebb tide (see discussion in section 4.2), this estimate gives an upper-bound estimate and demonstrates that ocean nutrients may have a huge impact in the Bay. Even if only 1% of the mass of nitrate in upwelled water is retained in the Bay (see section 4.2), the loading is 43 tons on a single tidal inflow.

Similarly, given oceanic phosphate concentration of $2.5\mu M$, one can estimate an upper bound of 470 tons phosphate entering SFB on an inflowing tide. This is compared with an annual average ~4 tons per day discharged by bay-wide POTWs and ~1.3 ton per day from stormwater (on average). For ammonium, ocean waters with a concentration of $1\mu M$ will represent a tidal import of 36 tons, a value comparable with an annual daily average of ~34.4 tons from POTW and ~6 tons from Delta inflows. The same inflowing tide may also import 9,200 tons of silicate.

4. QUANTIFYING OCEAN-BAY EXCHANGE

While the dynamics of upwelling and circulation in the Gulf of Farallones will determine the concentration and distribution of nutrients at the mouth of San Francisco Bay (loading of source waters), here we make estimates of the net tidal exchange between ocean and Bay and the resultant delivery of those nutrients to the Bay. By 'net tidal exchange' we mean the exchange averaged over multiple tidal cycles; the exchange on timescales of hours is much larger due to tidal transport, but much of that exchange is 'undone' on the following tidal phase.

The appropriate approach for analyzing net exchange depends on the details of the concentration field adjacent to the mouth of the Bay. If the event that delivers nutrients to the mouth of the Bay is relatively long-lived (several days), then a diffusive approach

can be used to quantify the net exchange – this approach is outlined in the following subsection. If, however, the coastal ocean nutrient concentration is varying on timescales on the order of a single day, then a different approach is required, since the diffusive limit is unlikely to be reached. That approach, which is based on quantifying the tidal exchange ratio, is outlined in the following section.

4-1. Upwelling events spanning several tidal cycles – the diffusive approach

In this section, we describe a method for quantifying nitrate fluxes between the ocean and the bay that is valid for upwelling events that span multiple tidal cycles. Our approach is to use a diffusive flux formulation, where the flux coefficient has been evaluated by Fram et al. (2005). In that work, observations of velocity and salinity were analyzed to determine the net diffusive flux of salt into the bay, and a diffusion coefficient was obtained from relating that flux to the local salinity gradient. To estimate the flux of nutrients F_N we combine that diffusion coefficient K with the local nutrient gradient $\partial N/\partial x$:

$$F_N = -K \, \partial N / \partial x \tag{1}$$

where the minus sign assures that the flux is directed from high concentration to low. The measurements of the diffusion coefficient were made in three distinct seasons: during high river flow (winter/spring), during coastal upwelling (spring/summer), and at other times (fall). The results demonstrated that tidal exchange processes dominate transport at the ocean-bay interface. These exchanges are modified seasonally by a complex three-dimensional structure induced by the density field, leading to increased exchange in the late winter and spring and reduced exchange in the fall. The annual variability of the diffusion coefficient constructed from that study is shown in Figure 4.

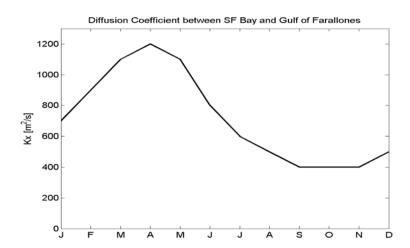


Figure 4: Estimation of the bay-ocean diffusion coefficient based on Fram et al. (2005).

The other factor that determines the net nutrient flux between the ocean and the bay is the local gradient in the nutrient concentration. If that gradient is directed into the bay (higher concentrations in the ocean), then the net flux is landward; if the gradient is reversed, so is the flux. Using a single value for the net flux can be misleading, however, as there is continuous two-way exchange between the ocean and the bay. To address this, we will consider two separate fluxes: (i) the flux of ocean nutrients into the Bay, in which case we consider the Bay to have zero concentration, and (ii) the flux of Bay nutrients to the ocean, for which we define the ocean concentration to be zero. Because of the linear nature of the flux calculations, the net flux of nutrients can be calculated as the difference between these two fluxes. Mathematically, if we define the distance between the ocean and the bay to be *L* (considered one tidal excursion, or about 20 km at the Golden Gate), the magnitudes of these two fluxes are defined as:

$$F_{oceanbay} = K N_o / L \tag{2}$$

$$F_{bayocean} = K N_b / L \tag{3}$$

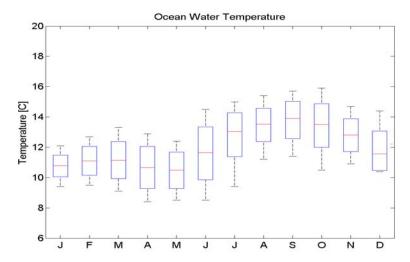
where N_o is nitrate concentration in the ocean and N_b is nitrate concentration in the Bay. We emphasize that these are just the magnitudes of those fluxes; $F_{bayocean}$ is directed seaward and $F_{oceanbay}$ is directed landward.

4-1a. Fluxes from Ocean to Bay

We first consider the flux of nutrients from the ocean to the Bay (equation 2). We use the annual cycle of K from Figure 4 and L = 20 km, but we require an annual cycle for the ocean nutrient concentration N_o , which varies in response to the seasonal cycle in upwelling along the California coast. Observations in the coastal ocean (Figure 3) demonstrate that there is a high correlation between nitrate concentration and ocean water temperature, with water of ~8°C exhibiting nitrate concentrations of ~35 μ M and a linear decrease in nitrate concentration with increasing temperature until reaching a concentration of ~0 μ M at a temperature of ~12°C. As done by Dever et al (2006), Kimbro et al (2010) and Garcia-Reyes et al (2013), here we use temperature data (Figure 5) to estimate monthly data that describe the annual cycle of oceanic nitrate concentration (Figure 6).

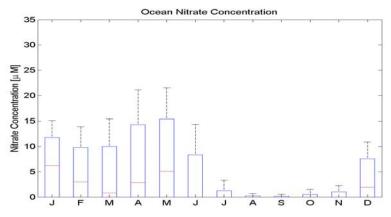
Time-series data on surface temperature are available from several locations outside San Francisco Bay, but there are no ongoing records of bottom temperature (which would be more representative of the coldest waters, i.e., most nitrate enriched) and further effort is needed to collate and interpret shorter historical data sets (e.g., Largier 1996, Figure 16). Here we use 5 years of surface data from the NDBC buoy 46237, which is deployed on the crest of the ebb-tide bar, about 10km west of Golden Gate (http://www.ndbc.noaa.gov/station_page.php?station=46237). Daily minimum values provide a preliminary index of the presence of nitrate-rich waters at the mouth of the Bay – minimum values represent ocean waters whereas higher values may be more representative of Bay outflow. The seasonal cycle is similar to that described by Largier et al (1993) and Garcia-Reyes & Largier (2012) for shelf waters off northern California. Coolest waters are seen in late spring and early summer due to wind-driven upwelling and cool waters are also seen in winter due to surface cooling. Warmest waters are observed in the fall, when upwelling is weak (Garcia-Reyes & Largier 2012). Importantly, ocean temperature is frequently <12°C and monthly means for the 5-year period (2008-

2012) only exceed 12°C during weak upwelling months from July to November (indicating low ocean nitrate values in fall).



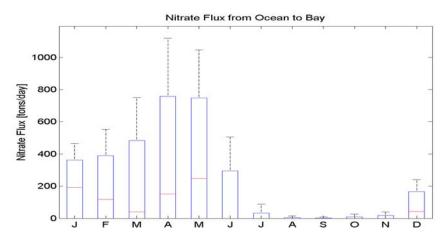
<u>Figure 5</u>: The annual cycle of surface temperature in the Gulf of Farallones, showing monthly mean (red line), plus/minus one standard deviation (blue box), and maximum/minimum (whisker) values for 2008-2012. Data are daily minima from NDBC buoy 46237, deployed on the bar.

Using the Dever et al (2006) bi-linear relation between nitrate concentration and temperature shown in Figure 3, daily temperature data are readily converted into daily nitrate estimates and an annual cycle of monthly nitrate statistics is shown in Figure 6. The annual cycle of oceanic nitrate is the inverse of that of temperature, with highest concentrations and most variability during the late spring and early summer upwelling months (as described more generally for this region by Garcia-Reyes & Largier 2012 and Garcia-Reyes et al 2014, who found maximum nitrate values in May and June). Lowest concentrations occur during the fall when upwelling is weak. During winter, there is a greater uncertainty in nitrate values because temperature and nitrate data are not as well correlated (Garcia-Reyes et al 2014; unpublished data).



<u>Figure 6</u>: The annual cycle of nitrate concentration in the Gulf of Farallones inferred from temperature observations (Figure 5), using an empirical relation (Dever et al 2006).

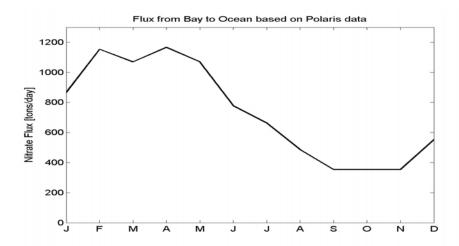
Using these monthly-mean nitrate concentrations for N_o we use equation (2) to determine the flux of oceanic nitrate to the Bay (Figure 7). This ocean-to-bay flux is strongly dependent on the seasonal upwelling cycle and the resultant concentration of nitrate in coastal ocean waters. It also depends on the seasonal cycle in the diffusion coefficient K that peaks in April (Figure 3). Maximum ocean-bay fluxes occur in the late spring (April-May), with a mean flux of ~200 tons/day and maximum values of 1000 tons/day (note that maximum values are not sustained, occurring as brief events). For these data from 2008-2012, the estimated mean flux is near-zero for June to November, although significant influxes are expected in other years, based on a 30-year description of the seasonality of upwelling (Garcia-Reyes and Largier, 2012). High values in winter months (notably 200 tons/day in January) exhibit less variability than in spring as ocean temperatures are persistently cool in winter (although never as cold as during upwelling events) – however, this does not account for high variability in both the diffusion coefficient K and the relationship between temperature and nitrate, such that these winter estimates have a high uncertainty.



<u>Figure 7</u>: Monthly nitrate flux from ocean to bay expressed as tons/day (assuming zero nitrate in the bay). Red lines represent values based on monthly mean nitrate values, blue boxes extend to the flux based on nitrate concentration that is one standard deviation above/below the mean, and whiskers represent the flux that would result from the maximum nitrate concentration (Figure 6).

4-1b. Fluxes from Bay to Ocean

Just as the tide mixes oceanic nutrients into the Bay, tides also mix Bay nutrients out to the ocean – with both processes acting simultaneously. The rate of diffusive exchange from Bay to ocean is calculated using equation (3) and the flux is linearly related to Bay nitrate concentration N_b . We use monthly mean nitrate values from San Pablo Bay obtained from monthly USGS surveys (station s15) from 2006 to 2011 (monthly values from Senn et al 2013; source data at http://sfbay.wr.usgs.gov/access/wqdata). The monthly Bay-to-ocean flux can then be estimated with zero nitrate concentration in the ocean (just as done for ocean-to-bay estimates in section 4.1a).



<u>Figure 9</u>: Monthly nitrate flux from bay to ocean expressed as tons/day (assuming zero nitrate in the ocean). Monthly mean nitrate concentrations in the Bay from 2006-2011 USGS survey data.

These fluxes are significant all year, and typically larger than ocean-to-bay fluxes due to the persistence of moderate to high nitrate concentration in San Pablo Bay, with monthly means varying between 25-30 μ M in winter months and 15-20 μ M in spring/summer/fall months. Seasonality in bay-to-ocean flux is primarily due to seasonality in the diffusion coefficient K (Figure 3).

4-1c. Net Fluxes of Nitrate from Ocean to Bay

Given that ocean and bay nitrate are ecologically equivalent, we can compare ocean-to-bay and bay-to-ocean values to obtain an estimate of net nitrate flux (Figure 10). Outward fluxes dominate in every month, so that there is a net efflux in all months. Months with lower efflux are in the fall (low diffusion coefficient and low bay concentrations) and in late spring (annual maximum in ocean concentrations with decreased Bay concentrations). Ultimately, the direction of flux is determined by the difference between ocean and bay concentrations and monthly mean concentrations in San Pablo Bay are higher than monthly mean ocean concentrations in every month – so that on average there is no month with a net influx of nitrate from ocean to Bay.

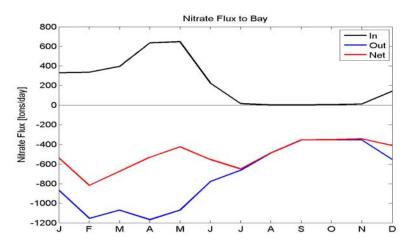
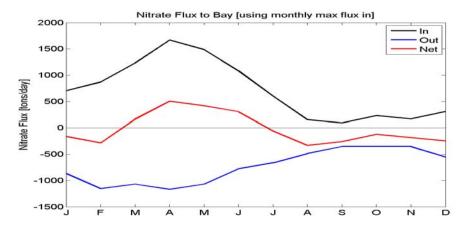


Figure 10: Monthly mean ocean to Bay (black), Bay to ocean (blue) and net (red) nitrate fluxes.

Although the flux of nitrate out of the Bay dominates influx from the ocean, this is not the same as zero ocean loading. One can see that the flux of nitrate from ocean to Bay is important in reducing nitrate efflux from the Bay (compare blue and red lines in Figure 10) and thus will result in higher nitrate levels in the Bay.

Monthly mean values tell only part of the story, given that ocean nitrate concentrations are very variable in response to wind-driven upwelling events and circulation patterns in the Gulf of Farallones, whereas the Bay concentrations are expected to be less variable. To explore fluxes during maximum upwelling, we choose maximum ocean nitrate values for each month of the year and recalculate fluxes (Figure 11), which show that during strong upwelling events in March-June one can expect a net influx of nitrate. In contrast, even during upwelling events in late summer and fall, the net flux is outward.



<u>Figure 11</u>: Monthly ocean to Bay (black), Bay to ocean (blue) and net (red) nitrate fluxes based on monthly-mean nitrate values in San Pablo Bay and monthly-maximum nitrate values derived from water temperatures observed near-surface at NDBC Buoy 46237..

4-2. Brief upwelling events – the tidal exchange ratio approach

The approach in the previous section relies on an assumption that multiple tidal cycles are involved in the delivery of nutrients from the ocean to the bay, which is valid only if the ocean nitrate concentration varies little over a period of several days. For shorter upwelling events, or for cases when the delivery of upwelling-sourced nutrients is intermittently brought to the vicinity of the mouth, an alternative approach is needed. Here we follow previous analyses of bay-ocean exchange (e.g., Parker et al 1972; Largier 1996; Chadwick and Largier 1999) and use the "tidal exchange ratio" (TER) which defines the fraction of "new" ocean waters that enter the Bay on a flood tide, as opposed to waters that exited the estuary on the preceding ebb tide and are simply re-entering. If the entire tidal inflow were comprised of "new" ocean water (TER=1), one would have a mass of nitrate as estimated in section 3.2 being delivered to the Bay on every day that upwelling was delivering high-nitrate water to the mouth of the Bay. However, TER is always much less than one and for San Francisco Bay it is estimated to be ~0.1 (Fram et al 2007) such that the mass of nitrate delivered to the Bay is only 10% of the mass

calculated in section 3.2. Further, a necessary assumption in applying the TER is that flood-tide waters mix completely with waters in the Bay. In reality, mixing is not complete and partial mixing of flood tide waters leads to a further reduction in the effective Tidal Exchange Ratio, since ebb-tide waters exiting the Bay consist of a fraction of unmixed (or less mixed) oceanic waters together with outflowing Bay waters.

Using the TER approach, the flux of oceanic nitrate to the bay is estimated as a fraction of the total potential mass of nitrate delivered to the Bay every tidal cycle, so that the mass of oceanic nitrate delivered to Bay is given by $V_{tide}*N_o*TER$ where V_{tide} is the volume of water exchanging tidally (i.e., tidal prism). The ocean-to-bay nitrate flux is then given by:

$$F_{oceanbay} = V_{tide} * N_o * TER/T_{tide}$$
 (4)

where T_{tide} is the tidal period. And the efflux of nitrate from the Bay to ocean is calculated in a similar way as mass/(tidal period) so that:

$$F_{bayocean} = V_{tide} * N_b * TER/T_{tide}$$
 (5)

With TER~0.1 and a total potential mass of 4,340 tons nitrate in a tidal prism during peak upwelling (section 3.2), one obtains an ocean-to-bay flux of 434 tons/tidal cycle or about 850 tons/day. These values are similar to the maximum values obtained from the diffusive exchange estimates (section 4.1a), although in reality the net flux is likely to be smaller when one accounts for the incomplete mixing and retention of "new" ocean water carried into the Bay on the flood tide. Nevertheless, this is a large nitrate flux because if only 10% of that mass of nitrate remains in the Bay, this still represents ~85 tons/day which is much larger than other nitrate loading to the Bay and an order of magnitude larger than other direct loading to Central Bay.

With reference to Figures 10 and 11, it may be that late-season upwelling events have the largest impact on the Bay: short upwelling events are observed in late summer and fall (Garcia et al 2013, Figure S1) and they may result in a major nitrate input at a time when Bay concentrations and terrigenous loading are lowest. The likelihood of such events is greater earlier in summer, but their impact will vary from year to year depending on runoff and terrigenous loading. Upwelling and oceanic nitrate delivery also varies internannually (Garcia-Reyes et al 2014), with differences in concentration, persistence and seasonality of high-nitrate waters in the Gulf of Farallones from year to year.

5. DISCUSSION

5-1. Net Ocean-Bay Flux

Although the flux of nitrate out of the Bay may dominate influx from the ocean much of the time, non-zero nitrate concentrations in the ocean and associated non-zero ocean loading are important to the Bay. Typically high-nutrient and productive estuarine waters are "flushed" out by less productive ocean waters, but for San Francisco Bay and comparable estuaries/bays coupled to upwelling systems, this flushing is reduced (and at times reversed) owing to the high-nutrient and productive nature of ocean waters. In

the end, whether one views non-zero nitrate levels in the ocean as a source of nitrate for the Bay or as a reduction in ocean flushing of Bay waters, the effect is a higher level of nitrate in the Bay than would be found in absence of upwelled nitrate in the coastal ocean.

5-2. Transport, mixing and uptake in the Bay

Once delivered to the Bay, oceanic nitrate is transported by tidal currents and estuarine circulation, moving through Central Bay and into San Pablo and South Bays. In Central Bay, transport is dominated by tidal dynamics and interactions of strong tidal flows with the complex topography of the basin result in mixing such that Central Bay tends to be less stratified than the other sub-basins. Thus we expect that oceanic nitrate will be relatively well mixed in Central Bay, even if it is introduced primarily at depth through the Golden Gate. Although the colder and saltier Central Bay water should stratify as it intrudes under less dense waters in San Pablo and South Bays, we expect that oceanic nitrate will be taken up rapidly in Central Bay (where it is mixed into the euphotic surface waters). Oceanic nutrients may then have much less impact on South or San Pablo Bays. This speculation needs further investigation, based on an analysis of existing data and (if needed) collection of new data.

At times, however, an exception to this well-mixed scenario occurs. When tidal forcing is weak (neap tides), winds are minimal and density forcing is strong (due to either salinity or temperature), dense ocean waters may intrude into the Bay as a well-defined lower layer. This appears to have occurred in April 2011, when a layer of cold, salty, oxygen-deficient ocean water was observed extending from Golden Gate into South Bay during the monthly USGS survey. Similar events appear to have occurred in summer 2013, with low-oxygen events observed in the Bay following upwelling of very low oxygen waters along the coast (unpublished data). Also, in fall 2010 these conditions appear to have existed during development of a red tide in Central Bay (high temperatures, no winds, neap tides). When mixing (tidal and wind) is weak and density forcing (salinity or temperature) is strong, vertical stratification can develop in Central Bay, so that waters that enter the mouth at depth (nutrient-rich and sometimes hypoxic) are retained at depth, below the euphotic zone. In this instance, nutrients will not be utilized and oxygen will not be replenished so that oceanic waters that enter at the Golden Gate may be able to retain their identity into South and San Pablo Bays, where the nitrate may be entrained into the euphotic zone and thus impact productivity in those basins.

The impact of oceanic nitrate on the Bay depends on the retention of this nitrogen in the Bay, either through retention of oceanic waters (at least through the subsequent ebb tide) and/or through uptake of this nitrate in the Bay. The uptake of oceanic nitrate also depends on the availability of nitrate from other sources and the nature of the phytoplankton community. A data-based analysis is needed to explore the interplay of nitrate deliveries from oceanic and terrigenous sources with the relative rates of uptake through photosynthesis and efflux through mixing to the ocean. Here we explore the

relative effect of these four key terms in a nitrate mass balance for the Bay, as illustrated in Figure 12.

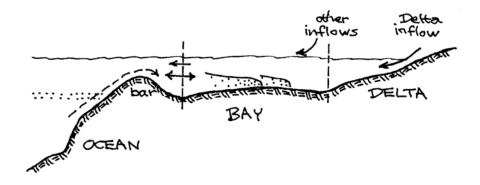


Figure 12: Cartoon of conceptual model (section 2), showing the delivery of deep cold waters over the bar (dashed arrow on left side), tidal mixing into the Bay through Golden Gate (double-headed arrow) and possible intrusion as a sub-surface layer (dotted shape in Bay). This influx of ocean waters interacts with inflow of freshwater from the Delta and other sources (arrows on right side) and associated net outflow through Golden Gate. Dashed vertical lines indicate the boundaries for the nitrate mass-balance model expressed in Equation (6) below.

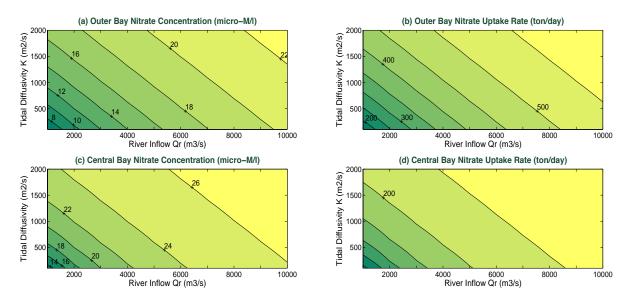
We use a steady-state, one-box, mass-balance model for a preliminary exploration of the effect of three rate parameters (K for ocean-bay mixing, Q_r for river inflow rate, k_r for reaction rate) and two nutrient loading concentrations (N_o for ocean and N_r for inflows) on Bay nitrate concentration N_b . The steady-state Bay nitrate concentration is given by:

$$N_b = (A.K.N_o/L + Q_rN_r) / (k_rV + A.K/L + Q_r)$$
(6)

where A is the mouth cross-sectional area at Golden Gate and V is the Bay volume. There are five key terms, comprised of two loading terms and three loss terms. Loading is via tidal mixing of oceanic nitrate into the Bay, given by $A.K.N_o/L$, and via inflow of terrigenous nitrate (wastewater, Delta, and stormwater combined), given by Q_rN_r . Loss is via uptake of nitrate in the Bay, given by $k_r.V.N_b$ and via tidal flushing of nitrate from the Bay, given by diffusive and advective terms $A.K.N_b/L$ and Q_rN_b . Loss terms depend on Bay nitrate concentration that will increase until the sum of loss terms can balance the sum of loading terms, which is when a steady state occurs.

In Figures 13(a) and 13(c) we show how Bay nitrate concentration N_b depends on the rate of river inflow Q_r and the strength of tidal mixing that accounts for ocean-bay exchange K (assuming constant nitrate loading of $30\mu M$ in both freshwater inflow and oceanic waters, and a value for k_r that represents a 10-day doubling time). Recognizing that the impact of nitrate on Bay ecology depends on how much nitrate is taken up, we also show how the uptake rate k_r . $V.N_b$ depends on the delivery of oceanic and terrigenous nitrate (Figs. 13(b) and 13(d)). This one-box model is applied to a small-volume Bay representing just Central Bay (Figs. 13(c) and 13(d)) and a large-volume Bay representing the combination of Central/South/San Pablo Bays, known as Outer Bay

(Figs. 13(a) and 13(b)). Bay nitrate concentrations are lower for weaker inflow and tidal mixing, when uptake through photosynthesis draws down Bay levels. Bay nitrate concentrations approach source water levels in the small-volume Bay when inflow and tidal mixing are strong. Given the larger volume of water in Outer Bay, there is a longer residence time and more effective uptake resulting in lower concentrations, but the larger volume holds more phytoplankton and results in a faster rate of uptake of nitrate. For the small-volume Bay representing Central Bay, uptake rates are ~200 tons/day and don't vary much with changes in river inflow and tidal mixing.



<u>Figure 13</u>: (a) Nitrate levels in outer San Francisco Bay for a range of tidal diffusion coefficient values (y-axis: $100 \text{ to } 2000\text{m}^2/\text{s}$) and a range of river inflow rates (x-axis: $1000 \text{ to } 10,000\text{m}^3/\text{s}$) – concentrations are in units of μM and contoured with an interval of $2\mu\text{M}$.

- (b) Nitrate uptake rates for outer Bay under the same conditions rates in units of tons/day and contoured with an interval of 50ton/day.
 - (c) Nitrate levels for Central Bay, with contour interval of 2μM.
 (d) Uptake rates for Central Bay, with contour interval of 20ton/day.

With the parameter values used in Figure 13, oceanic influx ranges from 40 to 800 tons/day whereas terrigenous influx ranges 160 to 1600 tons/day. However, in this "continuously stirred tank reactor" model, the source of nitrate does not have an effect on Bay concentrations or uptake rates, only the total input rate – hence the contours are straight lines that represent equivalent loading scenarios. Meanwhile, uptake rates that range from 200 to over 500 tons/day (for a reaction coefficient that represents a 10-day doubling time) are typically more important than tidal mixing losses that range from 27 to 270 tons/day for this model scenario.

This bulk, bay-wide box-model approach is useful in exploring balances between nitrate loading and loss terms (as done in Tomales Bay; Largier et al 1997), however it needs refinement, including demarcation of separate boxes for Central Bay, San Pablo Bay and South Bay. One can include a parallel model for phytoplankton levels, with

phytoplankton also being taken up by benthic grazing and exported from the Bay by tidal action (cf., Lucas et al 2009). Further, seasonal variability in loading, upwelling and reaction rate (photosynthesis rate) can be explored as well as management options for maintaining lower nitrate or phytoplankton concentrations in the Bay. Although more complex models exist for San Francisco Bay, this reduced-complexity mass balance approach allows one to explore the essential trade-offs in nutrient management.

In parallel with this quasi-steady approach, attention should also be given to short-lived events. An initial review of historical data suggests that there are times when upwelled water may flow continuously into the Bay at depth (e.g., Largier 1996), accounting for a non-tidal influx of several hundred tons of nitrate that is not immediately removed by tidal outflow. If such an event occurred in fall, when Bay residence times are longer and terrigenous loading is typically low, this may result in a marked and aseasonal algal bloom in the Bay.

5-2. Key issues and uncertainties.

As discussed above, the key terms in Bay nitrate concentrations are inputs from land and ocean and loss of nitrate via mixing from Bay to ocean and also via uptake in photosynthesis. While terrigenous inputs are increasingly well defined and quantified, the strength, timing and penetration of oceanic inputs are poorly known. Following the conceptual model, there are three key issues:

- (i) processes controlling nitrate concentration in tidal inflow source waters,
- (ii) processes controlling the import and retention of oceanic waters in the Bay,
- (iii) processes controlling the uptake of nitrate in the Bay.

Collation and analysis of existing data is a first step to better quantifying each of these unknowns, which will also better isolate those processes that are most critical and least known. To properly quantify oceanic loading and Bay responses, it is anticipated that new field studies will be required that address:

- (i) circulation and water properties in the inner Gulf of Farallones,
- (ii) tidal inflow and mixing in Central Bay, and
- (iii) photosynthesis rates in San Francisco Bay at different location/depth/season.

Ultimately, a nitrate mass balance may be developed with a fine-resolution numerical model, but only after analysis of field data has revealed the dominant processes and time and space scales of nitrate delivery to the Bay ecosystem. The benefit of a high-resolution numerical model is the ability to project future scenarios that result from climate change and/or changes in water and nutrient management on land.

6. LITERATURE CITED

- Chadwick, D. B. and J. L. Largier, 1999. Tidal exchange at the bay-ocean boundary. *Journal of Geophysical Research*, 104 (C12), 29901-29919.
- Dever, E. P., C. E. Dorman, J. L. Largier, 2006. Surface boundary layer variability off northern California, USA during upwelling. *Deep Sea Research II*, 53(25-26), 2887-2905.
- Dugdale, R. C., F. P. Wilkerson, A. Marchi and V. E. Hogue, 2006. Nutrient controls on new production in the Bodega Bay, California, coastal upwelling plume. *Deep Sea Research II*, 53(25-26), 3049-3062.
- Fram, J. P., M. A. Martin and M. T. Stacey, 2007. Dispersive fluxes between the coastal ocean and a semienclosed estuarine basin. *Journal of Physical Oceanography*, 37, 1645-1660.
- Garcia-Reyes, M. and J. L. Largier, 2012. Seasonality of coastal upwelling off central and northern California: new insights including temporal and spatial variability. *Journal of Geophysical Research*, 117, C03028: doi:10.1029/2011JC007629.
- Garcia-Reyes, M., J. L. Largier and W. J. Sydeman, 2014. Synoptic-scale upwelling indices and predictions of phyto- and zooplankton populations. *Progress in Oceanography*, doi: 10.1016/j.pocean.2013.08.004.
- Kimbro, D. L., J. Largier, E. D. Grosholz, 2009. Coastal oceanographic processes influence the growth and size of a key estuarine species, the Olympia oyster. *Limnology and Oceanography*, 54(5), 1425-1437.
- Largier, J. L., B. A. Magnell and C. D. Winant, 1993. Subtidal circulation over the northern California shelf. *Journal of Geophysical Research*, 98(C10), 18147-18179.
- Largier, J. L., 1996. Hydrodynamic exchange between San Francisco Bay and the ocean: the role of ocean circulation and stratification. In: *San Francisco Bay: The Ecosystem*. J.T.Hollibaugh (editor). Pacific Division AAAS, 69-104.
- Largier, J. L., S. V. Smith and J. T. Hollibaugh, 1997. Seasonally hypersaline estuaries in mediterranean-climate regions. *Estuarine Coastal and Shelf Science*, 45, 789-797.
- Largier, J. L., C. A. Lawrence, M. Roughan, D. M. Kaplan, E. P. Dever, C. E. Dorman, R. M. Kudela, S. M. Bollens, F. P. Wilkerson, R. C. Dugdale, L. W. Botsford, N. Garfield, B. Kuebel-Cervantes, D. Koracin, 2006. WEST: A northern California study of the role of wind-driven transport in the productivity of coastal plankton communities. *Deep Sea Research II*, 53(25-26), 2833-2849.
- Lucas, L. V., J. K. Thompson, and L. R. Brown, 2009. Why are diverse relationships observed between phytoplankton biomass and transport time? *Limnology & Oceanography*, 54(1), 381-390.

- Palacios, D. M., E. L. Hazen, I. D. Schroeder and S. J. Bograd, 2013. Modeling the temperature-nitrate relationship in the coastal upwelling domain of the California Current. *Journal of Geophysical Research*, 118, 3223-3239.
- Parker, D. S., D. P. Morris and A. W. Nelson, 1972. Tidal exchange at Golden Gate. Proceedings of the ASCE Journal of Sanitary Engineering, 98:305-323.
- Senn, D. and E. Novick, 2013. Nutrient Conceptual Model (Draft).
- Wilkerson, F. P., A. M. Lassiter, R. C. Dugdale, A. Marchi and V. E. Hogue, 2006. The phytoplankton bloom response to wind events and upwelled nutrients during the CoOP-WEST study. *Deep Sea Research II*, 53(25-26), 3023-3048.