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Stoichiometry of C, N, P, and Si fluxes in a temperate-climate embayment

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ABSTRACT

Dissolved C, N, P, and Si budgets for Tomales Bay, California, have been used to solve simultaneous stoichiometric equations which describe a plausible material balance for net organic matter reactions in the bay. Dissolved Si and P were both exported hydrographically. Dissolved C and fixed N were imported hydrographically. If we assume that C, N, P, and Si were supplied to the bay as organic detritus and remineralized at a rate required to balance dissolved Si and P exports, we can calculate reasonable rates of denitrification and CO₂ gas evasion across the air-water interface. The system is thus interpreted to have been net heterotrophic at the time of our investigation.

Fluxes attributed to individual components in the system (benthic respiration, water-column material turnover, biochemical transformations between fixed and gaseous N) were of sufficient magnitude to account for the system-wide net fluxes, although too noisy to allow piecewise derivation of net system fluxes.

Denitrification and limitation of primary production by dissolved fixed N in aquatic ecosystems may be symptoms of other system-scale constraints on net C metabolism, rather than themselves being system-level controls of net C metabolism.

1. Introduction

Conservation of mass is a fundamental characteristic of nature. Therefore, attention to the net fluxes of biogeochemically active materials to or from biological systems at any scale can define constraints on the internal function of those systems. We have imposed constraints on net fluxes based on independent budgets and inferred chemical stoichiometry of C, N, P, and Si in a temperate-climate marine embayment (Tomales Bay, California; Fig. 1), in order to calculate plausible internal net biogeochemical reactions.

The study was originally designed to test the hypothesis posed by Smith (1984): The

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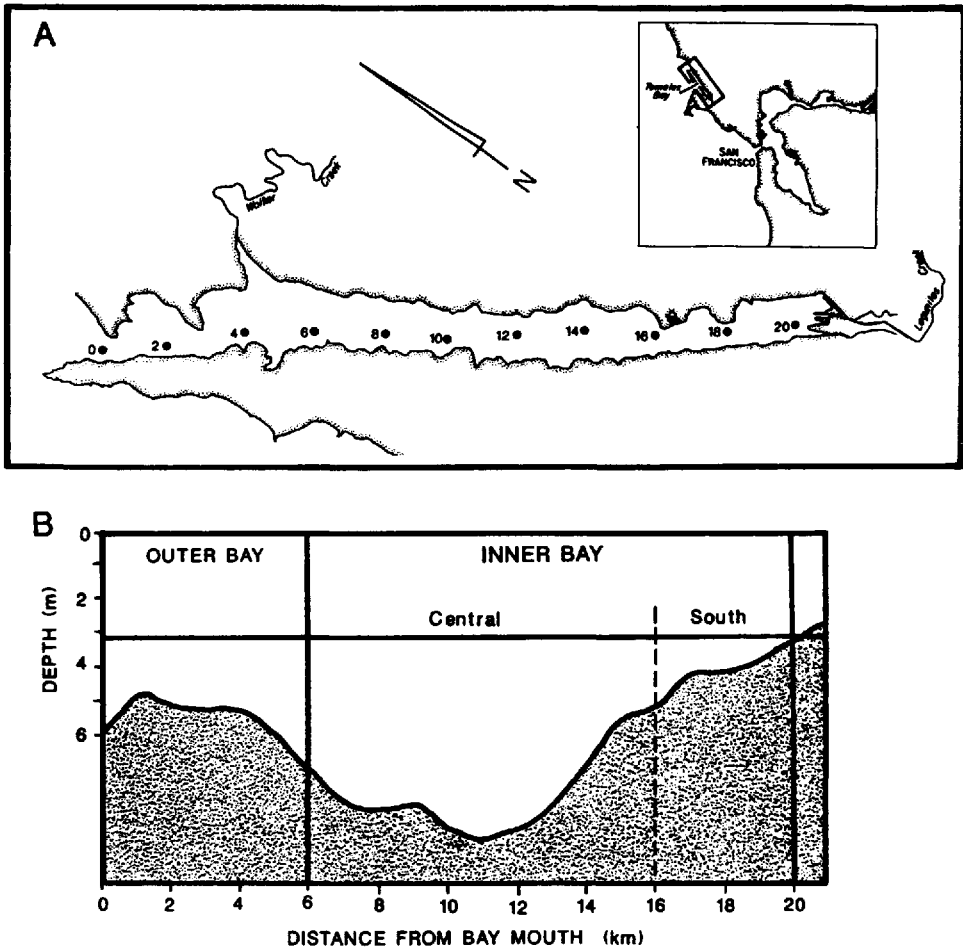


Figure 1. (a) Index map of Tomales Bay, California, showing locations of primary transect sampling stations. The station numbers denote distance, in km, from the bay mouth. (b) Longitudinal cross section through Tomales Bay, showing mean depth along the axis of the bay.

net organic production of marine ecosystems with restricted water exchange is limited by the availability of P, rather than N, as is more commonly supposed for coastal marine ecosystems in general (e.g., Ryther and Dunstan, 1971). It is important to emphasize that the hypothesis deals with net organic production of the entire system, not net primary production uncorrected for heterotrophic respiration. The hypothesis was based on studies in tropical and subtropical oligotrophic systems; Tomales Bay was chosen as a site to extend that hypothesis into temperate coastal ecosystems.

Tomales Bay receives more dissolved and particulate terrigenous input than the sites previously examined and also derives materials from coastal upwelling. We will

Table 1. Dimensions of the major sectors of Tomales Bay.

Sector	Length m	Width m	Depth m	Area 10 ⁶ m ²	Volume 10 ⁶ m ³
Outer	6000	1700	2.2	10.2	22.4
Inner					
Central	10000	1400	4.4	14.0	61.6
South	4000	1000	1.0	4.0	4.0
Total	20000	1410	3.1	28.2	88.0

demonstrate that these inputs rendered the intended hypothesis untestable in Tomales Bay, at least at the time of our study. Nevertheless, we derive important conclusions about ecosystem-scale nutrient dynamics and biochemical pathways in the bay. We do so by addressing the following questions.

Was this embayment a net producer or net consumer of organic carbon at the time of our study? What were the relationships of N, P, and Si fluxes to C metabolism? Finally, we have compared inferences drawn from the system-scale budgets with smaller-scale experiments designed to evaluate benthic fluxes, water-column nutrient turnover, and biochemical transformations between fixed and gaseous N. The purpose of these experiments was to verify that reactions along the inferred biogeochemical pathways were of sufficient magnitude to account for net baywide fluxes.

We have attempted to be comprehensive in establishing the hydrographic and biogeochemical fluxes of nongaseous dissolved forms of each element analyzed (C, N, P, and Si). The budgets also deal implicitly with gas flux (N₂, N₂O, CO₂) across the air-water interface and with particle flux, as consequences of stoichiometry inferred from the dissolved-load budgets. We emphasize that our investigation does not resolve the significance of annual or longer-term variation in the mass balances of biogeochemically active materials.

2. Study site—Tomales Bay

Tomales Bay (Fig. 1) is well suited for mass balance studies of a relatively unperturbed system. The watershed (an area of about 600 km²) has a population of about 3000 persons; human pressures, in the form of nutrient pollution, other environmental degradation, or fishing pressure, are relatively minor. Runoff from pasture land may significantly affect the wet-season nutrient budgets, but was minimal during our study.

The geological setting and physiography of Tomales Bay have been described by Daetwyler (1966). The bay, which occupies a rift valley formed by the San Andreas Fault, approximates a long, narrow rectangle (20 km by 1.4 km). The average depth is 3.1 m (z_{\max} = 19 m). About 30% of the area is shallower than 2 m, with shoals near the mouth, the head, and the northeast shoreline. Between 4 and 16 km from the mouth is a silled basin.

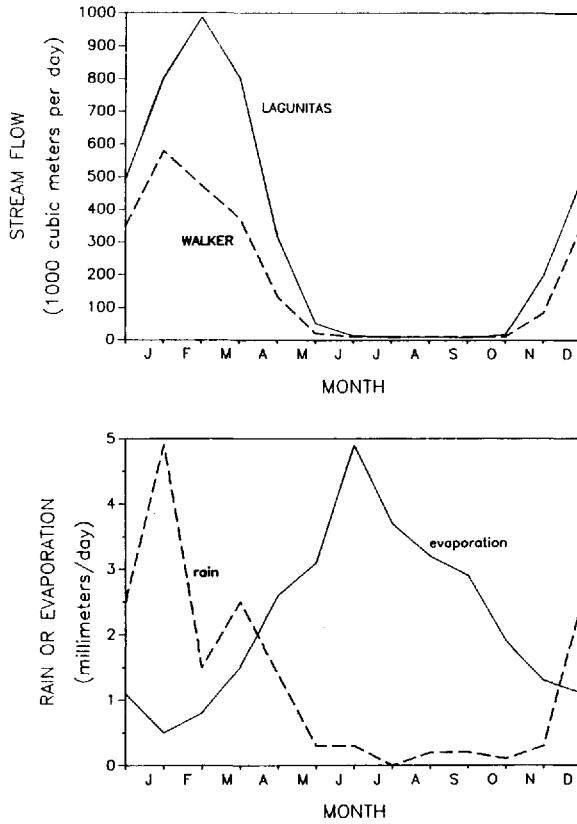


Figure 2. Summary of long-term mean stream flow (Lagunitas and Walker Creeks), evaporation, and rainfall in the Tomales Bay watershed; data summarized from various sources.

The shoals near the mouth support extensive eelgrass (*Zostera marina*) beds; limited eelgrass and benthic algae persist along the northeastern shore, approximately 16 km into the bay. Benthic plant populations are not conspicuous below about 2 m (except for some giant kelp, *Macrocystis pyrifera*, in the Outer Bay). Benthic diatoms may be present on much of the bay floor, especially on the shoals near the southern end of the bay. However, based on suspended chlorophyll levels, we believe that phytoplankton dominate the submerged plant biomass of the Inner Bay. The bay floor supports abundant infauna. Macrozooplankton were abundant at the mouth of the bay; except for localized swarms of the jellyfish, *Aurelia*, macrozooplankton were rare within the Inner Bay during the present study.

E. H. Smith *et al.* (1971) discussed aspects of water composition and circulation. Exchange with the ocean is predominantly tidal, with wind-induced mixing in the Inner Bay. The mean semidiurnal tidal range is 1.1 m.

Two major streams enter the bay (Fig. 1). Walker Creek flows into the north end of

the bay along the eastern shore; its effects on salinity are minor, episodic, and localized (Smith *et al.*, 1971). Lagunitas Creek, which flows into the southern end of the bay, can substantially depress surface salinity of the Inner Bay during the rainy season. During the dry season, bay salinity is near oceanic values, with insignificant vertical salinity stratification. Information on long-term rainfall, evaporation, and stream flow is summarized in Figure 2. Major stream flow occurs from about November to April, with little runoff and significant net evaporation during the remainder of the year.

Coastal upwelling is strong in the vicinity of the mouth of the bay, bringing nutrient-rich water to the sea surface. The upwelling is episodic, tied to strength and persistence of northerly winds, but is strongest between April and September (Bakun, 1975; Abbott and Zion, 1985).

3. Experimental design

We have used a steady-state, one-dimensional box model to calculate material mass balances in Tomales Bay. The model is intermediate between the river-dominated model employed by Boyle *et al.* (1974), Wollast (1978), Officer (1979), Kaul and Froelich (1984), and others, and the meteorologically dominated model of Smith and Jokiel (1978) and Smith and Atkinson (1983).

Consider a system of constant volume (V), open to exchange of ocean water by advection and mixing, with freshwater advection (F) from land, and with net evaporation minus rainfall (E) across the system. Let $d\bar{S}/dt$ = salinity change with time; S_o = oceanic salinity; S_f = stream salinity; S_e = salinity of rain water and water removed by evaporation; dS/dX = longitudinal salinity gradient (positive into bay); A_x = cross sectional area of the system perpendicular to X ; and K_x = longitudinal mixing coefficient. E , K_x , A_x , and S are all functions of X :

$$V \cdot d\bar{S}/dt = (E - F) \cdot S_o + E \cdot S_e + F \cdot S_f - K_x \cdot A_x \cdot dS/dX \quad (1)$$

= 0 (at steady state).

If we assume that streams and rainfall minus evaporation both involve water flux of salinity = 0, the equation simplifies:

$$V \cdot d\bar{S}/dt = (E - F) \cdot S_o - K_x \cdot A_x \cdot dS/dX = 0. \quad (2)$$

If all other terms in Eq. 6 are known:

$$K_x = ((E - F) \cdot S_o / A_x) \cdot dX/dS. \quad (3)$$

A general term (B_y) can be added for any material (Y) which has fluxes that are not conservative with respect to salinity; both B_y and Y are functions of X . Other notation is analogous to that presented for salinity. The following equation can be derived (assume $Y_e = 0$, but make no such assumption for Y_f):

$$V \cdot d\bar{Y}/dt = (E - F) \cdot Y_o + F \cdot Y_f - K_x \cdot A_x \cdot dY/dX + B_y = 0. \quad (4)$$

It follows from Eqs. (3) and (4):

$$(E - F) \cdot (Y_o - S_o \cdot dY/dS) + F \cdot Y_f + B_y = 0. \quad (5)$$

This equation can be broken into nonconservative processes (B_y), advection of Y in ocean water ($(E - F) \cdot Y_o$) and river water ($F \cdot Y_f$), and mixing ($-(E - F) \cdot S_o \cdot dY/dS$).

For evaluating \bar{B}_y , Eq. 5 is scaled by map area (A_m):

$$\bar{B}_y = ((E - F) \cdot (S_o \cdot dY/dS - Y_o) - F \cdot Y_f) / A_m. \quad (6)$$

Eq. 6 describes \bar{B}_y in an embayment between the oceanic salinity isopleth and the bay head. E and F are obtained landward of that isopleth. Values for \bar{B}_y can be derived landward of any isopleth, and the solution within any bay sector follows by integration between isopleths. The appropriate gradient, dY/dS , is the gradient in the vicinity of the isopleth which bounds the flux between the embayment and ocean (Officer, 1979).

Calculation of B_y is sensitive to the form of the equation used to describe Y as a function of S (Boyle *et al.*, 1974). This limitation has its most severe effect in examining variation of B_y along the bay; we restrict calculations to bay-wide fluxes, rather than sector fluxes.

Net hydrographic exchange time in the system (T) can be calculated from the system volume (V), daily water flux ($E - F$), average bay salinity (\bar{S}_b), and incoming oceanic salinity (S_o) (modified from Smith and Jokiel, 1978; Pilson, 1985):

$$T = V \cdot (\bar{S}_b - S_o) / ((E - F) \cdot S_o). \quad (7)$$

Our sampling period (29 September–9 October 1985) was chosen to be near the end of the dry season in order to minimize advection and maximize the effect of B_y on horizontal concentration gradients (Eq. 6). We recognize that such a “snapshot in time” does not characterize temporal trends in a seasonal system (e.g., Kaul and Froelich, 1984), and we plan to extend the study to an annual cycle.

4. Materials and methods

This investigation consisted of five coordinated efforts: (1) hydrographic sampling for budgetary analyses; (2) field studies of benthic nutrient flux; (3) water-column primary productivity measurements; (4) water-column N and P turnover experiments; (5) nitrogen fixation and denitrification measurements.

a. Hydrographic studies. Figure 1 shows the primary stations for transect sampling (numbered by distance, in km, from the bay mouth). Primary sampling, undertaken 5 times over a 10-day period, included salinity, temperature, dissolved inorganic and organic nutrients, pH, and total alkalinity (TA). The normal sampling suite included

stations 0 through 18, in the navigable portion of the bay. Station 20 was sampled only once. We also sampled once for dissolved organic carbon (DOC) and chlorophyll *a*. Samples were also collected for establishing the C:N:P ratio of particulate matter in the water column, major submerged benthic plants in the system, and sediments. In addition to the bay samples, we once collected water from the two streams flowing into the bay.

Salinity and temperature profiles (obtained with an Applied Microsystems STD) established the lack of vertical stratification. Subsequently, surface temperatures were taken with a bucket thermometer; surface samples were taken for measurement with a Plessey model 6230N laboratory salinometer standardized against a secondary standard ($\pm 0.01\%$). Samples for all analyses were collected by subsampling from a bucket.

pH was measured with a Cole Parmer model 5985-00 pH meter and Orion model 8166BN Ross combination electrode, within two hours of sample collection. pH of water samples held in air-tight containers near collection temperature showed negligible drift over this period. Alkalinity (TA) was measured with the same system, generally following the technique of Smith and Kinsey (1978). Precision within analysis sessions was better than 0.006 pH units for both pH and TA. pH, not explicitly reported here, varied between 8.0 and 8.3. pH and TA were used to calculate dissolved inorganic C (DIC) and CO₂ partial pressure. Lyman's dissociation constants (in Skirrow, 1975) and Weiss's (1974) CO₂ solubility data were used.

Samples for DOC were filtered into Teflon-capped quartz test tubes and frozen until analysis. After persulfate oxidation, samples were analyzed on an Oceanography International model 700 TOC analyzer, according to procedures in the instrument manual.

Dissolved N, P, and Si analyses were conducted by the U.S. Geological Survey, Menlo Park (USGS), and the Hawaii Institute of Marine Biology Analytical Services group (UH). Automated analysis procedures by the two laboratories were similar, generally following the Technicon procedures for NO₃⁻, NO₂⁻, NH₄⁺, PO₄³⁻, and Si, as locally modified by those laboratories (details available from SVS [UH] and SWH [USGS]). Both laboratories use ultraviolet oxidation (Armstrong *et al.*, 1966) for total dissolved N and P analyses. Dissolved organic N and P (DON, DOP) are calculated by difference between total and inorganic (DIN, DIP) nutrient concentrations.

Pre-analysis sample handling differed between laboratories. The 30 September samples and a set of samples collected on 3 October for intercalibration were analyzed by the USGS. Other nutrient analyses reported were analyzed by UH only. USGS samples were held on ice in 2-liter Nalgene containers for 3–6 hours before filtration. After filtration through 0.45 μ m Nuclepore filters, samples were refrigerated until analysis within one day of collection. UH samples were immediately filtered through glass fiber filters, into acid-washed, sample-rinsed polyethylene bottles. Samples were held on ice for up to an hour, then frozen for 2–3 weeks until analysis. Agreement

between laboratories ranged from about 2% (Si and PO_4^{3-}), to 10% ($\text{NO}_3^- + \text{NO}_2^-$, NH_4^+). The USGS data for 30 September were adjusted by regression analysis for intercomparison with the UH data.

Particulate C and N analyses were conducted with a Hewlett Packard model 185B CHN analyzer. One aliquot of each sample was held at 480–500°C for 4 hours in a muffle furnace to remove organic C, for subsequent analysis of $\text{CaCO}_3\text{-C}$; this value was subtracted from the total C measured on an unmuffled aliquot, to yield organic C. A third aliquot was analyzed for total P after ashing (as above) and digestion of the ash in 6N HCl.

b. Benthic flux studies. Benthic nutrient fluxes were measured at two sites within each bay sector. Measurements were made in cube-shaped opaque fiberglass chambers 30 cm on a side, and open on the bottom. A hard rubber flange rimming the chamber bottoms penetrated 8 cm into the sediment. Lead collars anchored the chambers. Six replicate incubations were conducted at each site. Battery-powered stirrers in each chamber prevented water stagnation.

Chambers were lowered to the bay floor from a boat; divers positioned the chambers in smooth areas approximately 2–3 m deep and devoid of sea grass. Divers extracted water from each chamber into plastic syringes via a stopcock, temporarily opening a second stopcock to replace the sample water volume with ambient bay water. Dark bottles with bottom water served as water-column controls. Samples were extracted a few minutes after chamber deployment, then approximately 8 and 24 hours later.

Samples were collected for pH, TA, and dissolved nutrients; analytical procedures followed those used for transect studies. Because of sediment resuspension during chamber emplacement, fluxes were calculated with the 8 and 24 hour data.

c. Primary productivity. Samples for productivity analyses were collected from surface waters at one site in each of the bay sectors. After inoculation with 5 μCi of $\text{NaH}^{14}\text{CO}_3$ in each 150 ml bottle, 24 hr incubations were undertaken in incubation chambers floating nearshore. Samples were exposed to 8 intensities of ambient irradiance (100, 55, 30, 15, 8, 3, 1, 0%), by placing bottles in tubes of different mesh screen. Following incubation, 3 ml aliquots from each bottle were placed in scintillation vials. To remove residual ^{14}C , 0.1 ml of 0.2N HCl was added to each vial, which was shaken uncapped for 30–60 minutes. The activity of each sample was measured by liquid scintillation. Data were corrected for dark-bottle uptake.

Daily productivity through the water column was calculated as discussed by Cole and Cloern (1984), fitting the light versus productivity data to a hyperbolic tangent function. 24-hour chlorophyll-specific respiration rate was assumed to be 10% of the maximum carbon assimilation rate. Net primary productivity was calculated as the

sum of water-column productivity minus integral respiration over the mean water depth for the corresponding sector of the bay (Table 1).

d. Water-column N and P cycling. Samples for P and N regeneration experiments were collected by immersing clean 20 liter plastic carboys to a depth of 10 cm. The carboys were returned to the laboratory and held in dim light ($100 \mu\text{E m}^{-2}\text{s}^{-1}$ PAR from Cool-white fluorescent tubes) until experiments were run later on the collection day. To initiate experiments, water was mixed by swirling the carboy, and subsamples were poured through a $100 \mu\text{m}$ mesh screen into 1 liter or 10 liter plastic bottles.

The 1 liter bottle was spiked with carrier-free $^{32}\text{P-PO}_4^{3-}$ (approx. $10 \mu\text{Ci}$; exact spike determined by radioassaying a 1.0 ml subsample). P regeneration rates were determined by following the time course of PO_4^{3-} specific activity. At various times during a four-hour time course, 100 ml samples were filtered and frozen for PO_4^{3-} analysis. Filters were rinsed three times with 10 ml portions of unlabelled sample, placed in vials, and radioassayed by liquid scintillation.

Specific activity of PO_4^{3-} was determined by extracting the phospho-molybdate complex formed in the standard PO_4^{3-} analysis with isobutanol (Strickland and Parsons, 1972). ^{32}P in the extract was determined by assaying a 1 ml portion. Extract absorbance was measured by spectrophotometer, in order to determine concentration. P uptake and regeneration were measured in one subsample per carboy, and one sample was filtered at each time point. Specific activity determinations at each time point were made in triplicate. Uptake and regeneration were calculated from linear (type 1) regressions, using log-transformed specific activity data. Calculations followed Harrison (1983).

Incubations for NH_4^+ uptake and regeneration were carried out in the 10 liter carboy, spiked with enough $^{15}\text{N-NH}_4^+$ to raise NH_4^+ concentration by approximately 5%. Subsamples were withdrawn after tracer addition and after 1, 2, and 4 hours.

The relative abundance of ^{15}N in NH_4^+ was determined on filtrates (GF/F Whatman filters) by conversion of $\text{NH}_4^+\text{-N}$ to indophenol-N and subsequent extraction of the indophenol into dichloromethane. After evaporation of the solvent, the atom percent ^{15}N of the samples was determined by emission spectrometry (after Dudek *et al.*, 1986). Rates of NH_4^+ regeneration were calculated according to Blackburn (1979) if there was a significant change in NH_4^+ during the incubation, and Glibert *et al.* (1982) if there was not. Rates of NH_4^+ uptake were calculated as the sum of the change in concentration and the rate of regeneration (Blackburn, 1979).

e. Nitrogen fixation—denitrification studies. Preliminary screening incubations were conducted for N_2 fixation and denitrification. Samples for screening included sediments, rooted *Zostera*, and drift grass or algae. Incubations on undisturbed

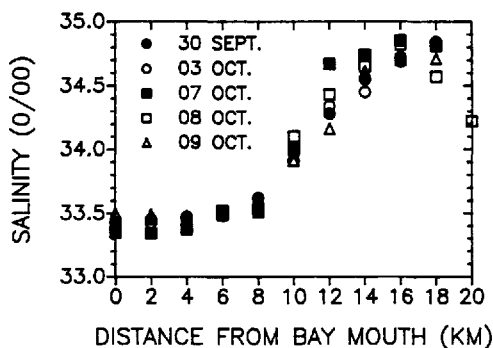


Figure 3. Salinity as a function of distance from the mouth of Tomales Bay. September–October 1985.

sediment cores were conducted in small glass cylinders stoppered at both ends; grass or algae incubations were conducted in larger cylinders.

Nitrogen fixation measurements generally followed Webb *et al.* (1975). Ten replicates were run for each site. Acetylene reduction was measured on an A.I.D. Instruments gas chromatograph equipped with a 6-foot column packed with Poropak R and a flame ionization detector. Only relative rates of N_2 fixation are reported. Potential denitrification (i.e., the ability of the microbial community to utilize NO_3^- present in a concentration of approximately 1 mM) was measured in one of two ways. First, NO_3^- loss was measured, with the assumption that all NO_3^- loss could be attributed to denitrification. Six samples were run by this method at one site. Second, N_2O was added to samples in the presence of acetylene to block N_2O reductase (Oremland *et al.*, 1984); N_2O loss was measured on a Carle gas chromatograph with an 18 foot Poropak Q column. A time course was run with 8 samples.

5. Results

a. Hydrographic data. Between 0 and 6 km (Outer Bay), there was little gradient in salinity (Fig. 3) (mean \pm std. dev. = $33.44 \pm 0.06\text{‰}$), because K_x is large relative to $E - F$ (Eq. 3). Over the next 10 km (central sector), salinity rose to 34.7‰ , reflecting long water residence time and net evaporation. Salinity in the south sector reached 34.8‰ due to net evaporation ($E > F$), and then dropped slightly due to runoff from Lagunitas Creek ($E < F$). Salinity was constant ($\pm 0.05\text{‰}$) with depth; samples transverse to the longitudinal profile showed only minor variation. The salt-balance model is not applicable in the Outer Bay because $dS/dX = 0$, so we restrict calculations of nonconservative fluxes to that portion of the bay inside the 33.5‰ isopleth (approximately station 6). Volume-weighted average Inner Bay salinity was 34.07‰ .

Water temperature averaged 14.5°C in the Outer Bay, 17.0°C in the central sector, and 18.4°C in the southern sector during our study. Area-weighted Inner Bay average temperature (used for calculating evaporation rate, Table 2) was 17.2°C .

Table 2. Weather, water temperature, and stream runoff into Tomales Bay, September-October 1985.

A. Mean weather conditions

Variable	Pt. Reyes* ALERT sta.	Marshall**	Bodega*** Coast Guard	Mean
Wind (m s^{-1})	5	4	3	4
Humidity (%)	80	90	—	85
Air temp. ($^{\circ}\text{C}$)	15	17	—	16
Rain (mm d^{-1})	0.1	—	—	—
Inner Bay				
Water temp. ($^{\circ}\text{C}$)†				17.2
Evap. (mm d^{-1})††				1.6

B. Inner bay water budget

Net evaporation—rainfall‡	$2.88 \cdot 10^4 \text{ m}^3 \text{ d}^{-1}$
Lagunitas Creek stream flow‡‡	$1.30 \cdot 10^4 \text{ m}^3 \text{ d}^{-1}$
Net ocean-water replacement	$1.58 \cdot 10^4 \text{ m}^3 \text{ d}^{-1}$

*Remote recorder, National Weather Service. Data from 25 September through 9 October 1985.

**Private obs., 2–3 obs./day; NE side of bay. Data from 1 September through 9 October.

***6 obs./day. Data available from National Weather Service.

†Data from 30 Sept.; 3, 7, 8, 9 Oct.

††Formula in Smith and Jokiel (1978), Sverdrup *et al.* (1942).

‡Calculated for area of $18 \cdot 10^6 \text{ m}^2$ (Table 1).

‡‡Data from U.S. Geological Survey.

Table 3. Cubic regression equations for nutrients as functions of salinity in Tomales Bay. The equations are of the form $Y = a + b \cdot S + c \cdot S^2 + d \cdot S^3$, where Y is the nutrient and S is salinity. Values and slopes of Y at $S = 33.5 \text{ ‰}$ and the concentration of Y in Lagunitas Creek water (Y_f) (October 1985) are also given for modelling purposes.

Material (Y)	a	b	c	d	r^2	$Y_{33.5}$ μM	dY/dS $\mu\text{M}/\text{‰}$	Y_f μM
Si	-31693.70	835.84	32.2495	-0.863820	0.98	23.30	88.29	190
PO_4^{3-}	-821.23	20.740	0.8475	-0.021886	0.99	1.85	3.84	0.5
DOP	-76.73	1.942	0.0805	-0.002082	0.96	0.39	0.33	0.3
NO_3^-	3125.64	-79.759	-3.2917	0.086303	0.95	4.20	-9.74	1.1
NO_2^-	171.20	-4.527	-0.1723	0.004631	0.98	0.29	-0.48	0.0
NH_4^+	737.00	-23.049	-0.4811	0.015399	0.78	3.88	-3.44	0.7
DON	-1055.41	27.192	1.0313	-0.026727	0.99	8.09	6.31	8.1
TA	38638	-1094.80	-33.914	1.0228	0.97	2355	76	1980
DIC	32113	-997.40	-22.085	0.7509	0.85	2146	51	2010
DOC	838	-20.06	-1.726	0.0485	0.93	52	28	260

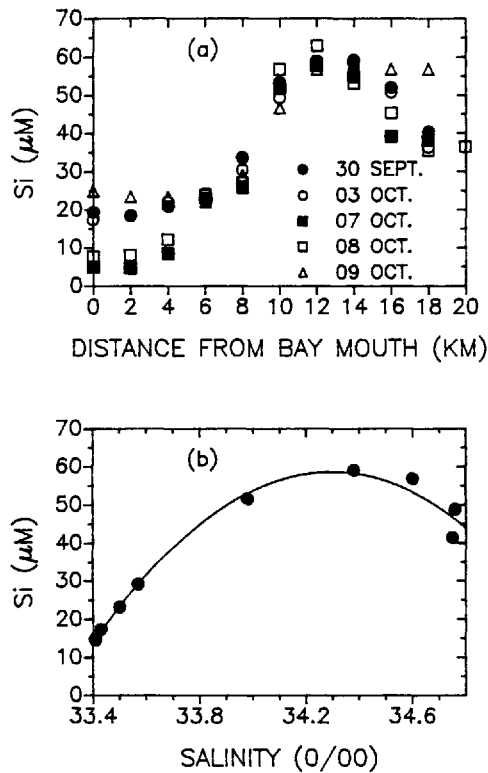


Figure 4. Si in Tomales Bay, September–October 1985. (a) Daily data as a function of distance from mouth. (b) Mean Si at each station as a function of salinity, with cubic regression line.

Station mean nutrient versus salinity data were fitted with cubic regression equations. The cubic equations allowed for curvature in some data sets. The regression coefficients and nutrient concentrations (Y_o) and slopes at 33.5‰ (dY/dS) are presented in Table 3. Values for stream concentrations (Y_f) are also tabulated.

There was no spatial Si gradient in the Outer Bay, but there was day-to-day variation (Fig. 4a) (mean \pm std. dev. = $18 \pm 7 \mu\text{M}$). This variation apparently reflected variable delivery of upwelled water to the bay. From 6 km southward, Si showed a general increase to about 60 μM (at 12 km), then decreased. The volume-weighted mean Si concentration in the Inner Bay was 44 μM . When station means Si data between 0 and 18 km are presented as a function of salinity, the data are well approximated by the cubic regression line (Fig. 4b). Station 20 (where stream runoff lowered salinity slightly) is excluded from the Si-salinity regression analysis, as it is for other regression analyses.

The PO_4^{3-} trend (Fig. 5) was similar to Si, although without a prominent decrease at the southern end of the bay. Outer Bay PO_4^{3-} was also temporally, but not spatially,

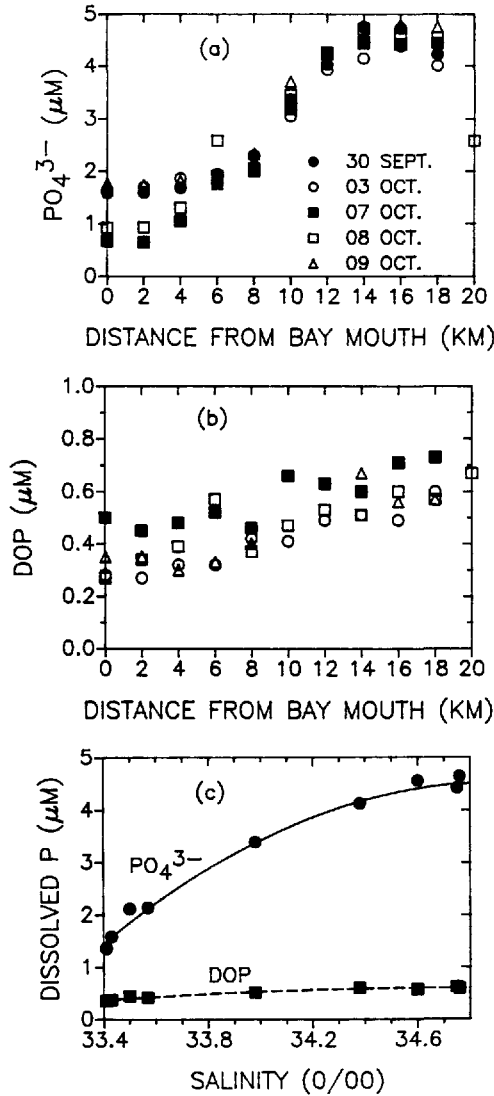


Figure 5. P in Tomales Bay, September–October 1985. (a) Daily PO_4^{3-} as a function of distance from mouth. (b) As for (a), but DOP. (c) Mean PO_4^{3-} and DOP as functions of salinity, with cubic regression lines.

variable ($1.5 \pm 0.5 \mu M$), again apparently reflecting variation in coastal upwelling. PO_4^{3-} increased with increasing salinity, to about $4.5 \mu M$. Inner bay volume-weighted PO_4^{3-} concentration was $3.3 \mu M$. DOP increased from 0.4 to $0.6 \mu M$ (volume-averaged mean = $0.5 \mu M$).

Four N species are shown as functions of location (Fig. 6a–d) and salinity (Fig. 6e,

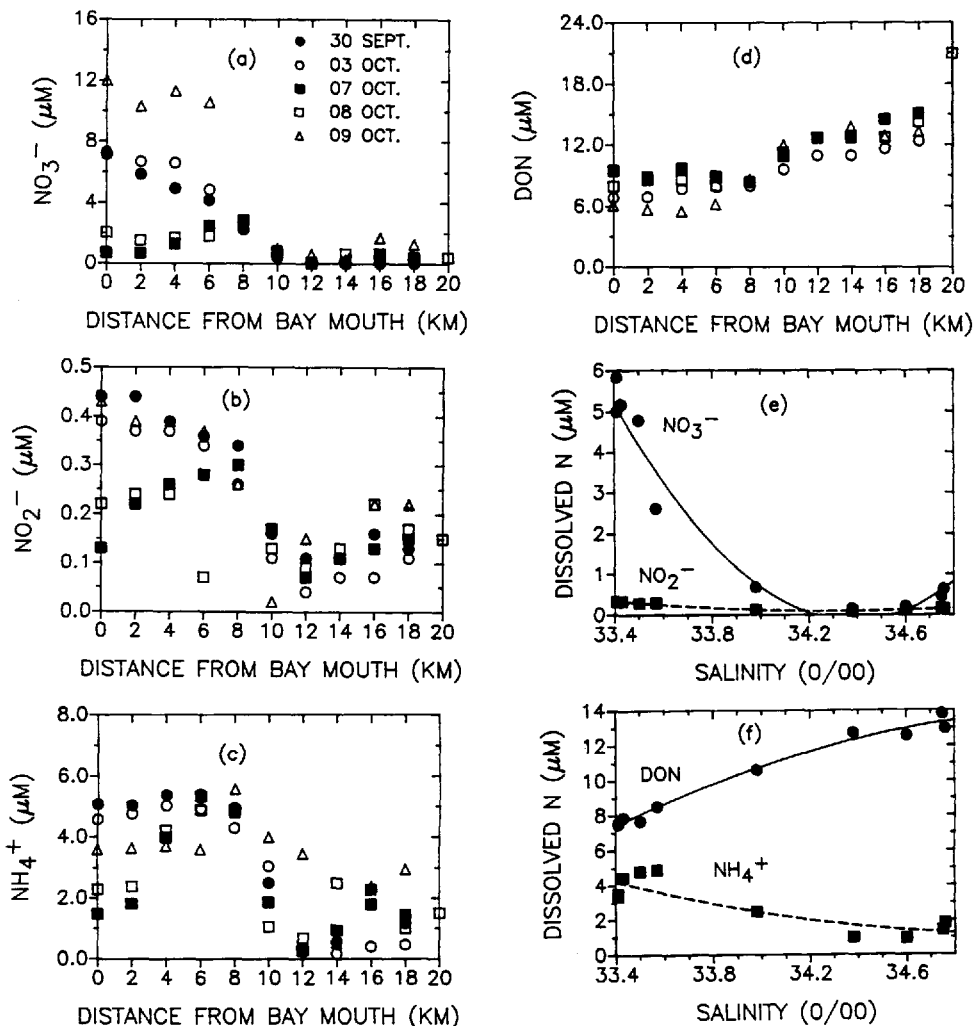


Figure 6. N in Tomales Bay, September–October 1985. (a) Daily NO_3^- as a function of distance from mouth. (b) As for (a), but NO_2^- . (c) As for (a), but NH_4^+ . (d) As for (a), but DON. (e), (f) mean N species as functions of salinity, with cubic regression lines.

f). NO_3^- , NO_2^- , and NH_4^+ were elevated and variable in the Outer Bay ($\text{NO}_3^- = 5.1 \pm 3.7 \mu\text{M}$; $\text{NO}_2^- = 0.34 \pm 0.13 \mu\text{M}$; $\text{NH}_4^+ = 3.9 \pm 1.1 \mu\text{M}$). The high and variable NO_3^- values also apparently reflect the variable influence of upwelling. Evidence of rapid cycling of fixed N is seen in the tendency of both NH_4^+ and NO_2^- to be elevated in Outer Bay water samples. All forms of DIN decreased in the central sector, with some increase in the southern sector (volume-weighted mean: $\text{NO}_3^- = 1.6 \mu\text{M}$;

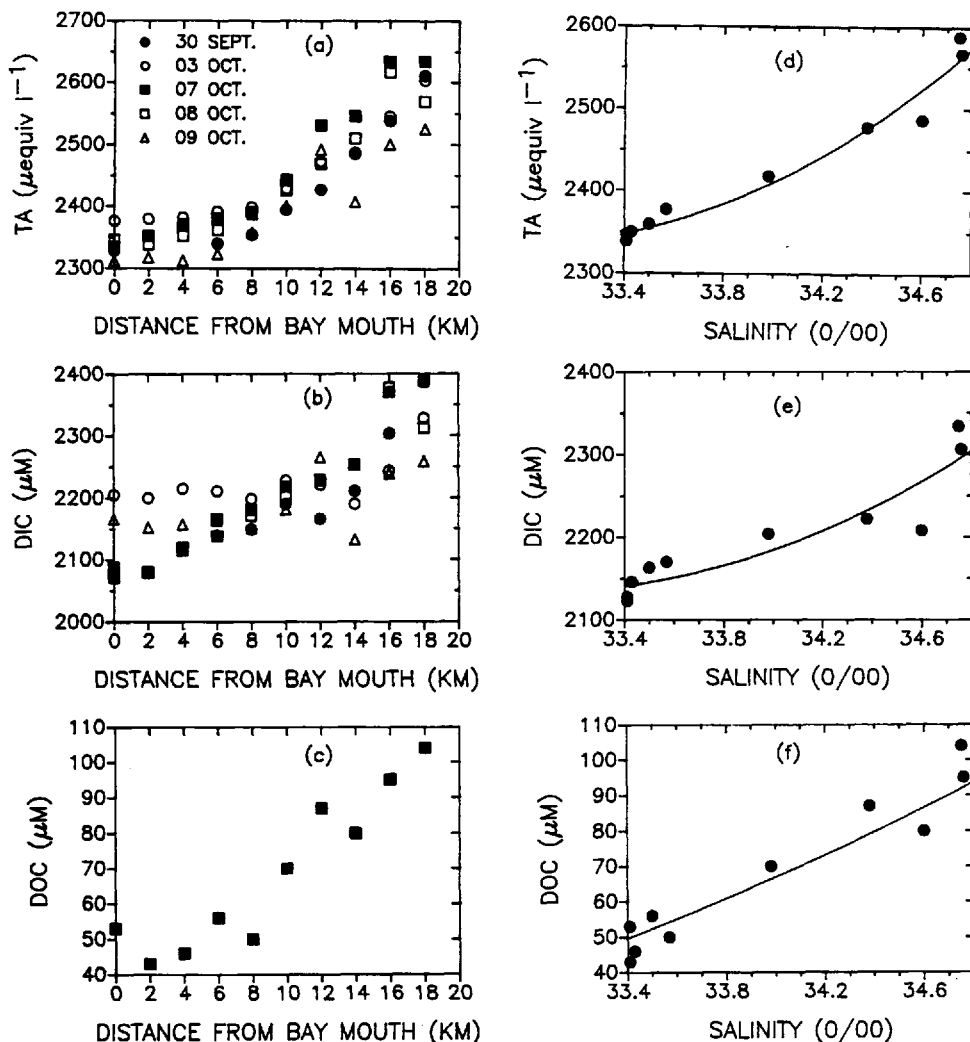


Figure 7. C in Tomales Bay, September–October 1985. (a) Daily TA as a function of distance from mouth. (b) As for (a), but DIC. (c) As for (a), but DOC. (d), (e), (f) Mean TA, DIC, DOC as functions of salinity, with cubic regression lines.

$\text{NO}_2^- = 0.2 \mu\text{M}$; $\text{NH}_4^+ = 2.5 \mu\text{M}$). Salinity-DIN trends are summarized in Table 3. DON increased from $7 \mu\text{M}$ in the Outer Bay to $13 \mu\text{M}$ (mean = $10.8 \mu\text{M}$).

When the Si, PO_4^{3-} , and DIN data are viewed together, the upwelling influence is even more apparent. Water samples from the Outer Bay show positive correlations between all combinations of these materials ($r > 0.95$), with the concentration ratios being about the expected ratios for variable fractions of upwelled water along the west

Table 4. Calculated steady-state net fluxes of dissolved Si, P, N, and C, Inner Tomales Bay, late summer 1985. Values are in mol d⁻¹ (mmol m⁻² d⁻¹). See text for detailed explanation.

Material	Advection				
	River	Ocean	Mixing	Nonconservative	
Si	+2470.0	+368.1	-46731.9	+43893.8	(+2.439)
PO ₄ ³⁻	+6.5	+29.2	-2032.5	+1996.8	(+0.111)
DOP	+3.9	+6.2	-174.7	+164.6	(+0.009)
tot. P	+10.4	+35.4	-2207.2	+2161.4	(+0.120)
NO ₃ ⁻	+14.3	+66.4	+5155.4	-5236.0	(-0.291)
NO ₂ ⁻	+0.0	+4.6	+254.1	-258.6	(-0.014)
NH ⁺	+9.1	+61.3	+1820.8	-1891.2	(-0.105)
DIN	+23.4	+132.3	+7230.3	-7385.8	(-0.410)
DON	+105.3	+127.8	-3339.9	+3106.8	(+0.172)
tot. N	+128.7	+260.1	+3890.4	-4279.2	(-0.238)
TA	+25740	+37209	-40227	-22722	(-1.262)
DIC	+26130	+33906	-26994	-33043	(-1.836)
DOC	+3380	+822	-14820	+10618	(+0.590)
tot. C	+29510	+34728	-41814	-22425	(-1.246)

coast of North America (Park, 1967; Fehler, 1981). There were negative correlations between each inorganic nutrient and water temperature in the Outer Bay.

The data for TA, DIC, and DOC are shown in Figure 7. TA increased from 2300 to 2600 $\mu\text{eq l}^{-1}$ (mean = 2435 $\mu\text{eq l}^{-1}$). DIC increased from 2100 to 2300 μM (mean = 2203 μM). DOC increased from about 40 to 100 μM with increasing salinity (mean = 70 μM). CO₂ partial pressure (not illustrated) did not show a clear spatial trend, but averaged about 470 μatm throughout the bay.

b. Budgetary calculations. The water budget defining *E* and *F* is summarized in Table 2. Table 4 presents calculated fluxes (from Eqs. 5 and 6) for each nutrient south of the 33.5‰ isopleth.

The water budget was dominated by evaporation (Table 2), resulting in salinity elevation in the Inner Bay. The margin of *E* over *F* was $1.6 \cdot 10^4 \text{ m}^3 \text{ d}^{-1}$ (0.02% of the Inner Bay volume). Inner Bay hydrographic exchange time during this "diffusive regime" driven by tidal and wind mixing was about 78 d (Eq. 7). *E* altered salinity sufficiently that water exchange could be estimated, but was insufficient to affect the exchange rate. The cross-sectional area at station 6 is 5800 m², and the local salinity gradient was $1.6 \cdot 10^{-5} \text{‰ m}^{-1}$. Eq. 3 yields a longitudinal mixing coefficient of $5.7 \cdot 10^6 \text{ m}^2 \text{ d}^{-1}$. If, instead of station 6 statistics, we use Inner Bay average statistics ($dS/dX = 8.1 \cdot 10^{-5} \text{‰ m}^{-1}$; $\bar{A}_x = 4700 \text{ m}^2$), *K_x* decreases to $1.4 \cdot 10^6 \text{ m}^2 \text{ d}^{-1}$.

During the wet season, *F* can exceed $10^6 \text{ m}^3 \text{ d}^{-1}$ (Fig. 2), a flow rate which would

directly affect water exchange. Conservative exchange time would decrease (e.g. Pilson, 1985), and advection would decrease the system signal from B_y (Eq. 5).

Variability of Y_o in response to upwelling might introduce apparently nonconservative behavior in conservative properties of the system (Loder and Reichard, 1980; Officer and Lynch, 1981). Inspection of Figures 3–7 suggests that this variability is largely damped out from station 6 southward for most variables.

The Inner Bay showed hydrographic export of dissolved Si, implying a dissolved Si source within the bay. We assume that there is no significant aerial Si source or sink. The net release rate was $2.44 \text{ mmol m}^{-2}\text{d}^{-1}$ during our study (Table 4). PO_4^{3-} was also exported hydrographically, at a rate of approximately $0.11 \text{ mmol m}^{-2}\text{d}^{-1}$ (Table 4). Again, we assume no significant aerial source or sink. DOP export was an additional $0.01 \text{ mmol m}^{-2}\text{d}^{-1}$.

Unlike Si and P, which were being exported from the Inner Bay, DIN was imported hydrographically (Table 4). Net DIN influx totalled $0.41 \text{ mmol m}^{-2}\text{d}^{-1}$, with NO_3^- accounting for about 70% and NH_4^+ most of the remainder. NO_3^- was taken up before NH_4^+ (Fig. 6). DON export ($0.17 \text{ mmol m}^{-2}\text{d}^{-1}$) accounted for about 40% of the DIN import; there must have been a net dissolved fixed N sink totalling $0.24 \text{ mmol m}^{-2}\text{d}^{-1}$. There can be aerial input of fixed N (via fixation of N_2 gas) and a dissolved fixed N sink other than organic matter (denitrification of NO_3^-).

Inner Tomales Bay showed net hydrographic input of TA and DIC, and net export of DOC (Table 4). The total C budget includes the additional term of CO_2 gas flux driven by the CO_2 partial pressure differential. The observed air-to-sea CO_2 partial pressure differential (340–470 μatm) indicated CO_2 gas loss from the water to the atmosphere.

c. Stoichiometric implications of the biogeochemical budgets. The system-scale budgets are now considered simultaneously in order to derive a plausible stoichiometry of biogeochemical reactions involving C, N, P, and Si. Nixon and Pilson (1984) and Hammond *et al.* (1985) have presented similar derivations.

Export of dissolved Si and PO_4^{3-} suggests that the Inner Bay (water column plus sediments) was heterotrophic at the time of our study, showing net P release from particulate organic matter and Si release from diatom frustules. Alternative explanations might be that P was released from inorganic matter by redox-mediated desorption, and that Si was released by silicate mineral dissolution. However, Si and PO_4^{3-} concentrations for all samples in the bay were correlated ($r = 0.87$; $n = 63$), suggesting that the source for Si and P was similar. The high CO_2 partial pressure of the water indicates that CO_2 gas escaped to the atmosphere, consistent with regeneration from biogenic material.

Organic matter supporting this nutrient regeneration might have come from land (during winter runoff), from organic production sedimented earlier in the season, or from input of organic matter across the Outer Bay sill. A time series of budgets would be needed to resolve among these alternatives.

There are possible complications to the general model we propose. Martens *et al.* (1978) and Klump and Martens (1981) observed that there can be differential loss of dissolved P to mineral phases or to adsorption during oxidation of organic matter. Krom and Berner (1981) argued that much of the P released from sediments is derived from inorganic material. However, Watanabe and Tsunogai (1984) pointed out that, while the immediate source of P released from the sediments may be desorbed inorganic P in response to varying redox conditions, the P is likely to have originated from organic material deposited in the sediments and oxidized there. Sediment profiles or benthic flux measurements capture the immediate time scale of release, which may not be directly coupled to organic oxidation. The 78-day residence time of water in Tomales Bay provided a record of net reactions integrated through much of the summer.

Si concentration decreased at the south of the bay (Fig. 4), while PO_4^{3-} concentration did not (Fig. 5). This difference may reflect preferential settling of diatoms in deep water immediately south of the sill; less dense, Si-free material may have drifted further into the bay before settling. There must also have been local Si uptake in the southernmost portion of the bay, by diatoms or localized emergent salt-marsh plants, in order for the high Si concentration of stream water not to elevate the Si concentration of the lower salinity water at station 20.

We infer the Si:P ratio of the material being regenerated from the Si:P export ratio ($2.4/0.12 = 20:1$; Table 4). Grill and Richards (1964), Park (1967), Webb (1981), Kaul and Froelich (1984), and Watson and Whitfield (1985) have derived Si:P ratios of plankton, planktonic uptake, and planktonic regeneration between 20 and 24. Brzezinski (1985) suggested that marine diatoms have a lower average Si content than we have derived. Although he did not report Si:P ratios, the Si:N and Si:C ratios he reported for diatoms grown in cultures are about half the value suggested by our data. We acknowledge this discrepancy without having a ready explanation for it.

Decrease of DIN as water entered the bay could suggest N assimilation into organic matter. This interpretation is not consistent with biogenic release of C, Si, and P, so we look for an alternative. The most plausible alternative DIN sink is loss to gaseous N_2 or N_2O by denitrification. Autotrophic uptake of DIN often favors NH_4^+ uptake over NO_3^- (e.g. McCarthy, 1981; Wheeler, 1983). In fact, autotrophic NO_3^- assimilation can be inhibited by the presence of NH_4^+ (e.g. Falkowski, 1983). The budgets (Table 4) indicate that net NO_3^- utilization preceded net NH_4^+ utilization. This pattern can be interpreted to imply that NO_3^- may have been consumed by denitrification and replenished by nitrification of NH_4^+ until the NH_4^+ was largely consumed. NO_2^- , an intermediate product of both denitrification and nitrification, was present throughout the bay, suggesting active transport through this reservoir.

Suspended material, sediments, and selected benthic plant samples were analyzed for particulate C, N, and P (Table 5). The organic C:N:P molar ratio of suspended material in the water column averaged 85:9:1, close to Ryther and Dunstan's (1971)

Table 5. C, N, P composition of suspended material, sediments and benthic plants in Tomales Bay. Suspended load data are in μM ; plant data are in mmol g^{-1} ; sediment data are in $\mu\text{mol g}^{-1}$ (mean \pm std. dev.).

Material	Organic C	Total N	Total P	C:N:P
Suspended load ($n = 11$)	61 \pm 30	6.8 \pm 3.6	0.72 \pm 0.39	85:9:1
Sediments ($n = 15$)	873 \pm 592	74 \pm 50	14 \pm 6	62:5:1
Benthic plants				
<i>Zostera</i> ($n = 4$)	25.6 \pm 3.1	2.2 \pm 0.9	0.12 \pm 0.03	213:18:1
<i>Ulva</i> ($n = 1$)	25.2	2.6	0.07	360:37:1

modified N:P ratio for coastal plankton. The organic C:N:P ratio of sediments was 62:5:1. The sediment C:P ratio is reasonably close to the ratio in suspended material, but the sediments have a lower N content, relative to either P or C, than does the suspended material. The C:N:P ratio of a small selection of benthic plants was about 240:20:1, lower in N and especially P, relative to C, than suspended material. This observation is consistent with the general composition of benthic plants (Atkinson and Smith, 1983). We therefore assume that plankton-derived material is the major contributor to the sediment C:N:P ratio, with some differential N loss in the sediments.

To test for internally consistent stoichiometry, we build a model with suspended material being the fuel for net reactions. Table 6 summarizes the results of the inferred total-system stoichiometry, scaled to C. The total dissolved C flux (ΔC_t) is the sum of

Table 6. Partitioning total dissolved C, fixed N, P, and Si fluxes among component processes.

Rates in $\text{mmol m}^{-2} \text{d}^{-1}$. Numerical values for calculations are in Table 4; see text for detailed explanation.

Process	How estimated	Total C	Fixed N	Total P	Total Si
CaCO_3 precip. (ΔC_c)	eq 9	-0.731	0.000	0.000	0.000
Oxic resp. (ΔC_r)	eqs 12, 13	+7.668	+0.812	+0.090	0.000
Denitrification (ΔC_d)	eqs 12, 13	+1.761	-1.222	+0.021	0.000
CO_2 gas flux (ΔC_g)	eq 8	-10.534	0.000	.000	0.000
Silica dissolution	eq 6	0.000	0.000	0.000	+2.439
Dissolved organic release (ΔDOC)	eq 6	+0.590	+0.172	+0.009	0.000
Total non-conservative flux (ΔC_t)	eq 6	-1.246	-0.238	+0.120	+2.439

“oxic respiration” (ΔC_r), DIC release by denitrification (ΔC_d), CaCO_3 reactions (ΔC_c), gas flux (ΔC_g) across the air-water interface, and DOC flux (ΔDOC):

$$\Delta C_t = \Delta C_r + \Delta C_d + \Delta C_c + \Delta C_g + \Delta\text{DOC}. \quad (8)$$

Organic oxidation by sulfate reduction is not directly budgeted, although this process is likely to be important in the sediments. H_2S released to an oxygenated water column would become oxidized back to SO_4^{2-} (e.g. Jørgensen, 1977; Hansen *et al.*, 1978). “Oxic respiration” therefore includes both direct oxic respiration and sulfate reduction resulting in H_2S release to the water column. Any S bound into a mineral sulfide will result in net *TA* elevation (e.g. Berner *et al.*, 1970). Mineral (e.g. Fe) sulfide deposition would result in an underestimate of CaCO_3 precipitation and organic oxidation.

ΔC_t is known directly (Table 4). ΔTA (also known) is a response to CaCO_3 reactions and inorganic nitrogen flux (and, of course, sulfate reduction). NO_3^- and NO_2^- depress *TA*, while NH_4^+ raises it (Brewer and Goldman, 1976; Kinsey, 1978). Thus:

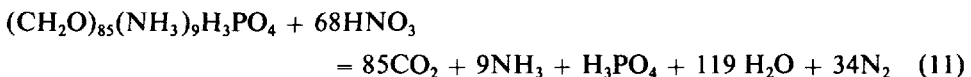
$$\Delta TA = 2 \cdot \Delta C_c + \Delta\text{NH}_4^+ - \Delta\text{NO}_3^- - \Delta\text{NO}_2^-. \quad (9)$$

This equation is re-arranged and solved for ΔC_c (Table 6). Any error in the total C budget from mineral sulfide reactions should be small, because net *TA* flux is small.

The stoichiometric relationship among C, N, and P from oxic respiration and denitrification can be described by the equations of Richards (1965), modified to reflect the C:N:P ratio of suspended organic matter in Tomales Bay. Oxic respiration:



Denitrification:



Oxidation of NH_3 to NO_3^- by nitrification is left out of these equations, because this process results in no net gain or loss of DIN. It is instructive to show fixed N release from organic matter to DIN during denitrification, rather than writing the reaction to show the net change in fixed N.

It follows algebraically that inorganic P was released according to the P:C molar ratio (P/C) of organic matter being oxidized by both oxic respiration and denitrification. There was also release of DOP from the organic matter:

$$\Delta P = (\Delta C_r + \Delta C_d) \cdot \text{P/C} + \Delta\text{DOP}. \quad (12)$$

Also by algebra, fixed N is released by oxic respiration and denitrification, according to the N:C ratio (N/C) of the organic matter; NO_3^- in the water is consumed in a 0.8:1 ratio with organic C oxidized by denitrification. The net change in

dissolved fixed N (ΔN) includes N release from organic matter, NO_3^- utilization by denitrification, and direct release of DON:

$$\Delta N = (\Delta C_r + \Delta C_d) \cdot N/C - 0.8 \cdot \Delta C_d + \Delta \text{DON}. \quad (13)$$

Eqs. 12 and 13 can be solved simultaneously to yield estimates of ΔC_r and ΔC_d (Table 6). Oxic respiration plus denitrification released about $9 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$.

Net C release by denitrification totalled $1.8 \text{ mmol m}^{-2} \text{ d}^{-1}$, only about 23% of the net system carbon oxidation (Table 6). Fixed N consumed by denitrification totalled $1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$, and there was $0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ of fixed N released by that denitrification. Thus, the net fixed N consumption by denitrification totalled $1.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 6), 150% of fixed N released during oxic respiration. The 50% excess dissolved inorganic N required to support denitrification was imported from the ocean. Billen (1978), Teal and Valiela (1978), Boynton *et al.* (1980), Nixon (1981), Hopkinson and Wetzel (1982), Seitzinger *et al.* (1984), Jørgensen and Sørensen (1985), and Hammond *et al.* (1985) have estimated estuarine and coastal denitrification rates between 0.7 and $5 \text{ mmol m}^{-2} \text{ d}^{-1}$. The calculated Tomales rate is towards the low end of this range.

Eq. 8 is now rearranged and solved for ΔC_g (Table 6). CO_2 flux across the air-water interface ($-10.5 \text{ mmol m}^{-2} \text{ d}^{-1}$) provides a check on the realism of the stoichiometric derivation. Gas flux is a function of solubility ($\alpha = 0.036 \text{ mmol m}^{-3} \mu\text{atm}^{-1}$ for CO_2 at the salinity and temperature of Tomales Bay), CO_2 partial pressure difference between the air and water ($P_a - P_w = 340 - 470 \mu\text{atm}$), and the piston coefficient (k) (Smith, 1985):

$$\Delta C_g = k \cdot \alpha \cdot (P_a - P_w). \quad (14)$$

By re-arrangement, $k = 2.2 \text{ m d}^{-1}$. This value is higher than the value of 1 m d^{-1} derived from the empirical equation of Hartman and Hammond (1985) for a wind speed of 4 m s^{-1} , but within the scatter of the data which those authors summarize.

d. Sediment nutrient fluxes. Table 7 summarizes the sediment flux data. A few obvious statistical outliers were removed, leaving 10–12 measurements in each sector. Tabulated uncertainties are based on variability among incubations, and do not account for uncertainties associated with depth (probably primarily substratum).

Across the Inner Bay, the benthic fluxes of PO_4^{3-} and Si were 2–5 times the system-wide net fluxes (Table 4). The sediments showed release of NH_4^+ —a reversal of the bay-wide net flux. TA flux was higher in the Inner Bay than the Outer Bay, we suspect due to localized sulfate reduction (see section on stoichiometry). DIC release was high, relative to the Inner Bay budget. DON flux was high, but variable; DOP flux was low; DOC flux was not measured but is assumed on the basis of bay-wide net DOC:DON:DOP flux ratios to be small relative to DIC flux. These results are

Table 7. Nutrient fluxes from sediments, as measured with chamber incubations. Fluxes in $\text{mmol m}^{-2}\text{d}^{-1}$ ($\text{meq m}^{-2}\text{d}^{-1}$ for TA). Mean \pm std. dev. (n).

Material (Station)	Outer (3, 5)	Central (10, 10)	South (16, 18)	Inner-bay mean*
Si	5.94 \pm 5.10 (12)	5.75 \pm 2.20 (11)	1.16 \pm 5.28 (12)	4.73 \pm 3.16
PO ₄ ³⁻	0.22 \pm 0.15 (10)	0.29 \pm 0.21 (10)	-0.18 \pm 0.26 (12)	0.19 \pm 0.22
DOP	0.15 \pm 0.27 (12)	-0.09 \pm 0.09 (12)	0.05 \pm 0.08 (12)	-0.06 \pm 0.09
tot. P	0.37 \pm 0.31	0.20 \pm 0.23	-0.13 \pm 0.27	0.13 \pm 0.24
NO ₃ ⁻	-0.10 \pm 0.20 (11)	0.03 \pm 0.07 (9)	0.06 \pm 0.08 (12)	0.04 \pm 0.07
NO ₂ ⁻	0.02 \pm 0.05 (12)	0.00 \pm 0.06 (12)	0.03 \pm 0.05 (12)	0.01 \pm 0.06
NH ₄ ⁺	2.12 \pm 1.70 (12)	2.17 \pm 1.01 (10)	1.64 \pm 0.91 (11)	2.05 \pm 0.99
DON	0.06 \pm 1.79 (11)	3.25 \pm 3.23 (12)	2.07 \pm 1.21 (12)	2.99 \pm 2.91
tot. N	2.10 \pm 2.48	5.45 \pm 3.39	3.80 \pm 1.52	5.09 \pm 3.08
TA	0.7 \pm 9.1 (6)	14.3 \pm 12.1 (9)	14.2 \pm 5.6 (10)	14.3 \pm 11.0
DIC	28.2 \pm 28.6 (6)	35.6 \pm 24.6 (12)	53.9 \pm 11.0 (10)	39.7 \pm 22.3
DOC**	0.0	0.0	0.0	0.0
tot. C	28 \pm 29	36 \pm 25	54 \pm 11	40 \pm 23

*Area-weighted means; data from Table 1.

**Assumed = 0; not measured.

consistent with other studies of benthic flux (e.g. Elderfield *et al.*, 1981; Callender and Hammond, 1982; Hopkinson and Wetzel, 1982; Hammond *et al.*, 1985).

A particularly interesting aspect of the chamber flux data is that the north sector (Outer Bay, Table 1), and the central sector resemble one another more so than do the central and southern sectors: the major difference (to the water chemistry) between the Inner and Outer Bay is apparently one of water exchange, not rates of benthic regeneration. Si and PO₄³⁻ fluxes were rapid in the two northern sectors and then decreased to the south, introducing large standard deviations into the calculated Inner Bay rates. Mean PO₄³⁻ flux in the southern sector was negative. Rapid Si and PO₄³⁻ release in the north, decreasing to the south, is consistent with the general shapes of the bay-wide Si and PO₄³⁻ concentration gradients (Figs. 4, 5).

Because the benthic chambers were opaque, photo-autotrophic processes are not likely to account for the lower Si release and reversal of PO₄³⁻ flux in the southern

Table 8. Estimates of water-column net primary production based on ^{14}C uptake experiments. Station productivity has been weighted by sector mean depth and light distribution through the water column. Estimates of nutrient uptake are scaled by the estimated net C:N:P:Si flux ratio. Also included are estimates of productivity in the Inner Bay in samples receiving NH_4^+ spike.

Station	2 (Outer)	8 (Central)	16 (South)	Inner bay mean*
Photic depth (m)	6.9	5.0	5.2	
Sector mean depth (m)	2.2	4.4	1.0	
Sector net production (station productivity weighted by sector mean depth and light distribution through the water column)				
(mmol C $\text{m}^{-2}\text{d}^{-1}$)	23.6	53.8	11.8	44.5
(mmol N $\text{m}^{-2}\text{d}^{-1}$)	2.50	5.70	1.25	4.71
(mmol P $\text{m}^{-2}\text{d}^{-1}$)	0.28	0.63	0.14	0.52
(mmol Si $\text{m}^{-2}\text{d}^{-1}$)	5.55	12.66	2.78	10.46
Station net productivity with NH_4^+ spike				
(mmol C $\text{m}^{-2}\text{d}^{-1}$)	—	178	62	—

*Weighted by sector area, Table 1.

sector. The lower Si flux to the south might result from the previously suggested preferential sedimentation of diatom frustules as water crosses the sill, into the Inner Bay. We suspect that the reversal of the P flux might represent local inorganic P adsorption or precipitation (as discussed above), perhaps because of the Fe content and sorptive capacity of seasonally deposited terrigenous sediments. This phenomenon appears to be of limited significance to the bay-wide budget because of the relatively small area of the southern sector (Table 1).

We also calculated diffusion-supported fluxes for four cores, using nutrient concentration gradients in the upper 2 cm of the cores, average measured porosity (70%), and molecular diffusivity (from Li and Gregory, 1974, for Si, H_2PO_4^- , and NH_4^+ ; and Lerman, 1979, for NO_3^-). Mean diffusion-supported fluxes (in $\text{mmol m}^{-2}\text{d}^{-1}$) were: Si = 0.18; PO_4^{3-} = 0.06; NH_4^+ = 0.31; NO_3^- = 0.004. These diffusion-supported fluxes are low (by 3–30 times) in comparison to measured fluxes (Table 7). Such discrepancies have been repeatedly noted in other systems; we are inclined to favor the view of Kemp *et al.* (1982), that much of the benthic nutrient release is from a surface flocculant layer, rather than from the sediment column.

e. Water-column primary production. Table 8 summarizes phytoplankton net primary production. The table indicates the estimated photic-zone depth (consistently greater than sector mean depth) and integrated net production over mean water depth in each sector. Inner-bay primary production can be used to estimate the incorporation of N, P, and Si into phytoplankton biomass. The estimates of nutrient uptake by

Table 9. Summary of water-column PO_4^{3-} cycling measurements. Details of uptake and regeneration calculations are explained in text.

Date	Station	PO_4^{3-}		Uptake $\mu\text{M}/\text{hr}$	Regeneration $\mu\text{M}/\text{hr}$
		μM^*	$\mu\text{M}/\text{hr}^{**}$		
7 Oct	2	0.57	n.s.***	0.013	n.s.
	12	3.81	n.s.	0.012	n.s.
	16	4.56	n.s.	0.010	n.s.
8 Oct	2	0.89	n.s.	0.011	n.s.
	12	4.26	n.s.	0.010	n.s.
	18	4.60	n.s.	0.018†	n.s.
9 Oct	0	1.89	n.s.	0.005	n.s.
	12	4.38	n.s.	0.015†	n.s.
	16	4.93	n.s.	0.012†	n.s.
Mean \pm std. dev	Outer			0.010 \pm 0.004	0.010‡
	Central			0.012 \pm 0.003	0.012‡
	South			0.013 \pm 0.004	0.013‡

*Initial concentration.

**Regression slope.

***n.s. = not statistically significant ($P = 0.05$).

†Based on $^{32}\text{P}\text{-PO}_4^{3-}$ uptake from first hour only. Time trend becomes non-linear thereafter.

‡Assumed not different from uptake, as discussed in text.

phytoplankton are based on the C:N:P:Si flux ratio which we have previously established (85:9:1:20). If Brzezinski's (1985) Si data for diatoms were used instead of our flux-derived estimate, phytoplankton uptake of Si would be reduced by approximately one half. The point to note is that estimated phytoplankton uptake rates are all higher than the absolute baywide net fluxes (Table 4), but of similar magnitude to the benthic fluxes (Table 7).

In addition to the incubations of unmodified water samples, samples at the two Inner Bay sites (where DIN was low) were spiked to approximately $20 \mu\text{M NH}_4^+$, prior to incubation. There was a substantial increase in productivity in bottles spiked with NH_4^+ , suggesting that phytoplankton primary production at the time of these incubations was limited by the availability of DIN.

f. Water-column N and P cycling. Table 9 summarizes data from the water-column PO_4^{3-} cycling experiments. There was insignificant net change in PO_4^{3-} concentrations over the 4-hour incubations, so gross PO_4^{3-} regeneration rates cannot be distinguished from 0 (Harrison, 1983; Eq. 1). Because there is no significant net change in PO_4^{3-} , gross regeneration is also indistinguishable from uptake. Gross uptake of PO_4^{3-} can be measured even though regeneration cannot, because uptake is

Table 10. Summary of water-column NH_4^+ cycling measurements. Details of uptake and regeneration calculations are explained in text.

Date	Station	NH_4^+		Uptake $\mu\text{M/hr}$	Regeneration* $\mu\text{M/hr}$
		μM^{**}	$\mu\text{M/hr}^{***}$		
7 Oct	2	2.11	-0.105	0.142	0.037
	12	0.90	-0.165†	0.301	0.136
	16	2.81	-0.110†	0.110	n.s.
8 Oct	2	3.44	-0.086	0.301	0.215
	12	1.16	n.s.‡	0.132	0.063
	18	1.16	-0.165	0.165	n.s.
9 Oct	0	4.06	n.s.	n.s.	n.s.
	12	5.68	0.083	n.s.	0.083
	16	2.90	0.003	n.s.	0.003
Mean \pm std. dev	Outer			0.148 \pm 0.151	0.084 \pm 0.115
	Central			0.144 \pm 0.151	0.094 \pm 0.038
	South			0.110 \pm 0.055	0.001 \pm 0.002

*Using Blackburn (1979) if significant change in NH_4^+ ; otherwise Glibert *et al.* (1982).

**Initial concentration.

***Regression slope.

†0-2 hr data only. Time trend non-linear thereafter.

‡n.s. = not statistically significant ($P = 0.05$); use value of 0 for calculating means.

based on incorporation of ^{32}P into particulate matter (Harrison, 1983; Eq. 2), analytically a sensitive measurement.

Both uptake and regeneration of NH_4^+ are individually calculable (Table 10). NH_4^+ uptake clearly exceeded regeneration in the south sector and showed such a tendency elsewhere. NH_4^+ uptake and regeneration data show considerable variability, both among sites and among days. We suspect that the variability primarily reflects variable amounts of wind-stirred resuspended material in the water column.

Several conclusions about water-column nutrient turnover can be derived when 24-hour uptake rates for NH_4^+ and PO_4^{3-} are averaged over the Inner Bay (Table 11). The $\text{NH}_4^+ : \text{PO}_4^{3-}$ uptake ratio is about 12:1, in reasonable agreement with the 9:1

Table 11. Estimates of daily water-column PO_4^{3-} and NH_4^+ uptake (based on assumption of 24-hour uptake). Uptake data from Tables 11 and 12 and hypsographic data from Table 1.

Sector	$\text{mmol m}^{-3} \text{d}^{-1}$		$\text{mmol m}^{-2} \text{d}^{-1}$		N:P
	PO_4^{3-}	NH_4^+	PO_4^{3-}	NH_4^+	
Outer	0.24	3.55	0.53	7.8	15
Central	0.29	3.46	1.28	15.2	12
South	0.31	2.64	0.31	2.6	8
Inner-Bay mean			1.22	14.4	12

Table 12. Potential denitrification and relative nitrogen fixation in various materials.

Location	Material	Process	Rate mmol m ⁻² d ⁻¹
Sta. 5	sediment	Denit. (NO ₃ ⁻ loss) (90 min)	37
	sediment	Denit. (NO ₃ ⁻ loss) (200 min)	47
Sta. 8	sediment	Denit. (N ₂ O uptake) (16 hr)	48
Sta. 3	sediment	N ₂ fix.	0
	grass	N ₂ fix.	0
Sta. 6	sediment	N ₂ fix.	0
	grass/algae	N ₂ fix.	0
Sta. 10	sediment	N ₂ fix.	low
	grass	N ₂ fix.	low
Sta. 18	sediment	N ₂ fix.	low

suspended N:P ratio in the bay (Table 5). When NH₄⁺ and PO₄³⁻ uptake rates are compared with the nutrients inferred to be required for primary production (Table 8), the N and P fluxes are 2–3 times as high as predicted from primary production.

We assume that this difference in part reflects the difference between gross uptake (for N and P) and net uptake (for C). A second consideration is the role of heterotroph uptake in accounting for the observed uptake. Inventories of fluxes to and from all of the N and P reservoirs would be required to address this point. The independently performed primary production and nutrient turnover experiments may also individually contain artifacts which preclude close comparison. The important point to note is that the water-column turnover rates are substantially more rapid than the system net rates (Table 4).

g. Biochemical nitrogen transformation reactions. An examination of N₂ fixation and denitrification was conducted in order to establish whether these processes could be demonstrated in zones consistent with the system-wide analyses.

Denitrification potential, shown in Table 12, was high at both station 5, which was in the region of high NO₃⁻ concentrations (Fig. 6) and station 8, in the region of low NO₃⁻ concentrations. As demonstrated by a NO₃⁻ uptake experiment at station 5, rates obtained over 90 minutes were about as fast as rates over 200 minutes. This observation suggests that there was little or no initial lag period of slow denitrification once NO₃⁻ was added to the incubation chambers. Results of a 16-hour N₂O uptake experiment for sediments at station 8 yielded about the same rates as those obtained at

station 5, suggesting that the microbial community is capable of high rates of denitrification throughout much of Tomales Bay. It should be emphasized that the rates obtained are *potentials* only, and should not be construed to represent *in situ* rates.

Sediment N₂ fixation was assayed at four stations. One Outer Bay station (3) and one transition station (6), where DIN concentrations were fairly high but variable, showed negligible N₂ fixation. Two Inner Bay stations (10, 18), where DIN concentrations were generally low, showed low but measurable N₂ fixation. Pieces of drift seagrass and algae showed much the same pattern. N₂ fixation seems likely to occur at low but significant rates throughout much of the Inner Bay.

We are aware of the discussion surrounding the acetylene blockage technique and NO₃⁻ uptake as measures of denitrification (e.g. Seitzinger *et al.*, 1984) and with concerns over the stoichiometry for conversion from acetylene reduction to N₂ fixation (e.g. Capone, 1983). We emphasize that we have used these field assays to establish a preliminary understanding of the potential for these N transformation reactions in Tomales Bay, and some idea as to the distribution of that potential.

6. Discussion

This study was designed to test the generality of Smith's (1984) hypothesis that P, not N, limits organic carbon production in confined aquatic systems. It was assumed that Tomales Bay would be net autotrophic, hence to have a net demand for N and P to support the production of new organic carbon. That assumption proved to be incorrect at the time of this investigation, so questions about the supply of nutrients to support net ecosystem production remain unaddressed by the investigation. Hypotheses to explain inorganic nutrient limitation of net ecosystem organic production cannot be addressed in a system which consumes, rather than produces, organic carbon.

We approached the question of net ecosystem metabolism from both a total-system mass-balance analysis and analyses of major component fluxes. Figure 8 is a summary of the total-system budgets and major component fluxes. While the component-flux studies were not as comprehensive as the analysis of total-system fluxes, these component studies were sufficient to make the following point. There is no problem in accounting for net ecosystem fluxes by the rates of nutrient turnover through component cycles within the system.

Our data address several scales of turnover cycles embedded within the net ecosystem fluxes. Water-column nutrient turnover (Table 11) was more rapid than net nutrient uptake by phytoplankton production (Table 8). The cycle between net water-column uptake (Table 8) and net sediment release (Table 7) was rapid in comparison with net nutrient exchange between the Inner Bay and adjacent reservoirs (Tables 4, 6). Transformations between fixed and gaseous N were not quantified (Table 12), but were apparently capable of rates which were rapid in comparison with net exchange (Table 6). It is statistically difficult to evaluate slow net system

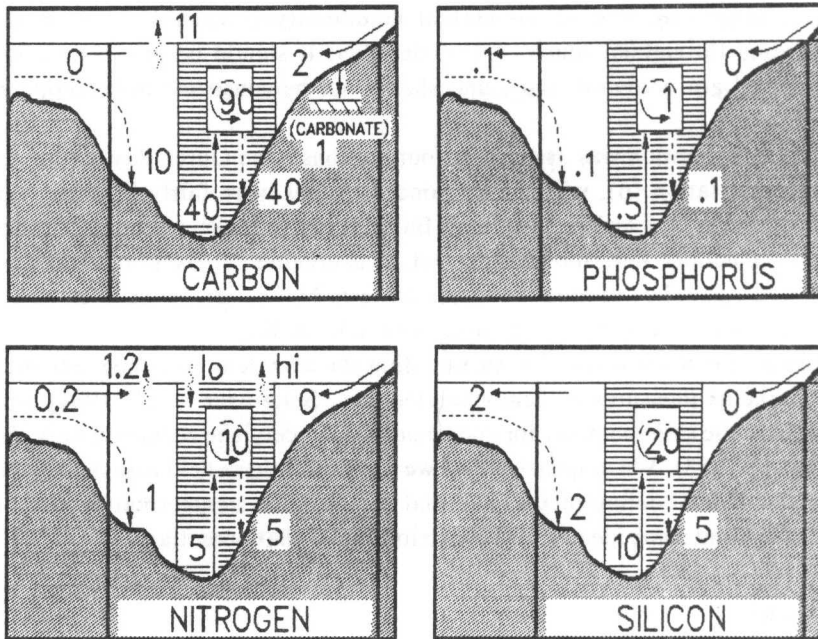


Figure 8. Simplified summary diagrams of C, N, P, and Si fluxes in Inner Tomales Bay. The cross-hatched column represents the component flux calculations, with the inner box being the water-column fluxes. Solid arrows are dissolved-load fluxes; dashed arrows are particle fluxes; and dotted arrows are gas fluxes. Arrows not in contact with the hatched area represent total-system budgetary calculations; arrows to, from, or within the hatched areas are based on the component budgets. Note that the component fluxes do not "add up" to the net system fluxes or necessarily reflect their direction; nevertheless the component fluxes are of sufficient magnitude to account for those net fluxes.

performance as the sum of rapid, cyclical fluxes. Had we only approached this system component by component, it would have been difficult to evaluate rates, or even directions, of net fluxes for the entire ecosystem.

The budgetary analyses integrate temporal and spatial characteristics of the system. We conclude with some confidence that Inner Tomales Bay was exporting dissolved P and Si, exporting gaseous CO_2 , and importing dissolved fixed N at the time of our study. Regeneration of dissolved nutrients from organic matter, loss of fixed N to gaseous N, and gas evasion are consistent with these fluxes. This net system performance is neither apparent from nor inconsistent with the component studies.

Reservoirs of particulate organic matter outside Tomales Bay and hydrographic characteristics of the Inner Bay as a settling basin give the bay potential to trap organic matter, become heterotrophic, and release nutrients. Without data over an annual cycle, we cannot be sure whether the particle supply supporting the calculated

heterotrophy represents ongoing (tidal) particle delivery; a seasonal sequence of net production and sedimentation, followed by regeneration; or regeneration from previously sedimented terrigenous input. However our "snapshot in time" did have an "exposure time" of about 80 days (i.e. about 20% of the year; 40% of the dry, upwelling season). Thus the heterotrophy describes a substantial fraction of an annual cycle.

It would be inappropriate to apply the box model used here to estimate particle fluxes. Longitudinal gradients of particle concentration are not reliable indicators of net fluxes for materials which are readily sedimented and resuspended in response to spatially and temporally varying turbulence. The low mixing coefficient and deep basin of Inner Tomales Bay are qualitative clues that deposition might be expected there; but extensive measurements of particle transport, sedimentation, and resuspension would be required to quantify this deposition. Welsh *et al.* (1982) observed: "The prospects for securing estimates (of net particulate transport) with any degree of precision appear to be dim, given the methodological problems."

Hopkinson (1985) recognized the difficulties of inferring trophic status from detrital flux. He advocated the "recipient system" approach: "By measuring the level at which community respiration exceeds primary production, the import of allochthonous material is directly observed." Hydrographic budgets for dissolved materials are recipient-system analyses of the entire system at once. The budgets yield unambiguous statements about net fluxes of materials; simultaneous stoichiometric analyses of C, N, P, and Si provide more insight into biogeochemical processes than would separate budgets.

An estimate of net organic C metabolism for the ecosystem was the "desired product" of the hydrographic budgets, but DIC changes include CaCO_3 reactions and gas flux as well as C metabolism. CaCO_3 reactions can often be unambiguously deciphered by changes in TA (e.g. Smith and Jokiel, 1978; Smith and Atkinson, 1983). In this system, CaCO_3 reactions were not unambiguously separable from mineral sulfide deposition, but CaCO_3 precipitation seemed to be minor. CO_2 gas flux can be a quantitatively important term in a total C budget, and this flux cannot be directly derived from hydrographic analysis of C flux alone. In order to constrain organic C metabolism, either CO_2 gas flux must be estimated directly (e.g. Hartman and Hammond, 1985) or organic metabolism must be constrained by stoichiometric considerations (this study; Nixon and Pilson, 1984).

A dissolved P budget scaled by the organic C:P ratio is probably the simplest single measure of ecosystem net metabolism, an idea which has been aired previously (e.g. Postma, 1954; Smith and Jokiel, 1978; Atkinson, 1981). Elevated summertime P concentrations in other estuaries (Taft and Taylor, 1976) may also represent local heterotrophy on some time scale, although abiotic P reactions cannot be ruled out by a P budget alone.

Dissolved Si budgets can also be useful in deciphering biogeochemical fluxes, despite

the potential importance of mineral-water reactions. Concordance between biochemically expected (Grill and Richards, 1964; Webb, 1981) and environmentally calculated (Park, 1967; Kaul and Froelich, 1984; Watson and Whitfield, 1985; this study) Si:P ratios is circumstantial evidence that biochemical processes dominate both Si and P fluxes.

Hydrographic budgets for fixed N alone contain ambiguous information about system-level net organic C metabolism. Some autotrophic ecosystems largely meet their demand for N to assimilate into net organic production by fixation of N_2 gas (e.g. Smith, 1984). Heterotrophic systems can also have their N budgets dominated by gas transfer. Even the modest rate of organic C oxidation by denitrification for Inner Tomales Bay apparently converted available dissolved and particulate fixed N to gaseous N. Sulfate reduction probably occurs in most shallow-water marine environments, yet denitrification is energetically favored over sulfate reduction (e.g. Reeburgh, 1983). Such ecosystems should therefore show a tendency towards heterotrophic consumption of available fixed N.

Denitrification may be limited by availability of either organic substrate (Kaspar, 1982) or NO_3^- (Oremland *et al.*, 1984). Altering the supply of either organic substrate or dissolved fixed N by changing the hydrographic regime can therefore alter the denitrification rate. However, it is difficult to imagine that greatly altering the system-wide denitrification rate (a relatively slow rate of fixed N consumption) would have much effect on fixed N utilization by primary production (a much more rapid process relying largely on recycled nutrients). Denitrification and limitation of primary production by dissolved fixed N in aquatic ecosystems may therefore be symptoms of other system-scale constraints on net C metabolism, rather than themselves being system-level controls of net C metabolism.

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