Title
Organic Carbon in the Marine Enviornment: Redox State as a Measure of the Health of California Estuaries

Author
Nilsen, Elena B.

Publication Date
2004-11-29

Organic Carbon in the Marine Enviornment: Redox State as a Measure of the Health of California Estuaries

Elena Brennan Nilsen, UC Santa Cruz

Current contact information: (650) 329-4799; enilsen@usgs.gov

Graduate Advisor: Peggy Delaney, Ocean Sciences

FINAL PROJECT STATUS:

The California Environmental Quality Initiative program funded me to investigate redox state as an indicator of ecosystem health using an automated Combustion Oxygen Demand Instrument (CO_xD) that I had proposed to build. Due to engineering and personnel challenges that were outside of my control, the CO_xD instrument did not come online fast enough for me to use it as a tool in my dissertation (although it is now nearing completion at UCSC and will hopefully be of use to future graduate students there). As a result, I modified my analytical methods while addressing the same general environmental issue: assessing the health and function of the base of the food web in California estuaries by investigating organic carbon and redox state. I submitted the findings of this project to the peer-reviewed journal *Estuaries*, where it will be published, pending minor edits (reviews received 11/23/04). This project also makes up a substantive portion of my PhD dissertation, completed 9/1/04. In addition, I presented this work orally at two scientific meetings, resulting in two published abstracts and two separate awards for outstanding student contribution. Detailed citations of all the publications pertaining to my CEQI-funded project are presented in the next section. A summary of the project (pp. 3-17), figure captions (pp. 18-19), and budget (p. 20) follow. Figures and tables are attached separately.

PUBLICATIONS

Nilsen, E.B., 2004. Studies of Carbon Cycling, Climate Change and Nutrient Dynamics in Pelagic and Coastal Ecosystems Using Sediment Geochemical Techniques. PhD dissertation for UC Santa Cruz.

Nilsen, E.B. and Delaney, M.L., 2004. Particulate Organic Matter in the San Francisco Bay/Sacramento-San Joaquin Delta: Surface Sediments Provide Clues on Sources and Composition. In review at *Estuaries*.

Nilsen, E.B., K.H. Coale and M.L. Delaney, 2002. Biogeochemistry of sedimentary carbon, phosphorus and redox-sensitive trace metals in the San Francisco Bay / Sacramento-San Joaquin Delta Estuary. *EOS* Transactions, Oral presentation at the AGU Fall Meetings, **Outstanding Student Paper Award**, December 10, San Francisco, CA.

Nilsen, E.B. and M.L. Delaney, 2002. Biogeochemistry of sedimentary carbon and phosphorus in the Sacramento Delta. Oral presentation at the Society of Wetland Scientists, Western Chapter Meetings, **Best Student Paper Award**, $100, September 20, Tiburon, CA.

Factors influencing the biogeochemistry of sedimentary carbon and phosphorus in the San Francisco Bay/Sacramento-San Joaquin Delta

E. B. Nilsen and M. L. Delaney

University of California, Santa Cruz

ABSTRACT

Particulate organic matter (POM) derived from phytoplankton provides the dominant pelagic food source to the Sacramento-San Joaquin Delta (Delta), California, despite its relatively small contribution to total POM. In contrast, a large percentage of detrital organic matter does not appreciably participate in the food web. This study characterizes organic carbon ($C_{organic}$) and phosphorus (P) geochemistry to investigate the sources and composition of POM buried in surface sediments of the Delta. Sediment cores were collected from five sites on a sample transect from the edge of the San Francisco Bay eastward to the freshwater Consumnes River. The top 8 cm of each core were analyzed for $C_{organic}$, concentrations of four P fractions and redox-sensitive trace metals (uranium and manganese). Sedimentary $C_{organic}$ concentrations and $C_{organic}$/P ratios decreased, while reactive P concentrations increased moving inland in the Delta. The fraction of total P represented by organic P increased inland, while that of authigenic P was higher bayward than inland reflecting increased diagenetic alteration of organic matter bayward. The redox indicator metals are consistent with decreasing sedimentary suboxia inland. Sediment C and P geochemistry is influenced by site-specific POM sources, the sorptive power of the sedimentary material present, physical forcing, and by early diagenetic transformations presumably driven by $C_{organic}$ oxidation. The distribution of P fractions and C/P ratios may reflect the presence of labile OM in upstream surface and near-surface sediments. Observed

distributions of sedimentary constituents may indicate that the upstream habitats constitute an important source of high food value POM to the Delta food web and serve a disproportionately important role in fueling secondary trophic level survival in the system.

INTRODUCTION TO SCIENTIFIC ISSUES AND PROJECT GOALS

The San Francisco Bay/Sacramento-San Joaquin Delta (Bay-Delta) is arguably California's most important aquatic ecosystem (Cain and Thomas, 2001) and is the hub of its water delivery system (Fox et al. 1990). The Bay-Delta is a highly modified estuarine wetland that has experienced decades of water diversion, agriculture and urbanization. Because of its important location at the land-estuary interface, the Sacramento-San Joaquin Delta (Delta) serves as a transition between the San Francisco Bay and its watershed. Organic matter (OM) produced in and/or transported through the Delta makes up the primary food supply to the downstream food web of the San Francisco Bay, thus understanding OM sources, transformation and storage within the Delta is an important undertaking (Conomos et al. 1979; Jassby and Cloern 2000).

Phytoplankton productivity in the Bay-Delta is light limited owing to high turbidity (Alpine and Cloern 1988), and the system is eutrophic due to sewage inputs and non-point source agricultural and urban runoff. Low biomass yields of net primary production result from a combination of influences, including high turbidity (Murrell et al. 1999) and rapid filtration of the water column by two invasive clam species, *Potamocorbula amurensis* (Alpine and Cloern 1992) and *Corbicula fluminea* (Lucas et al 2002). Zooplankton have shown declines concomitant with those of phytoplankton (Kimmerer and Orsi 1996; Orsi and Mecum 1996), as have many native species of fish (Bennett and Moyle 1996).

Although there are many sources of organic matter to this system, POM derived from phytoplankton provides the dominant pelagic food source and is integral to the success of primary consumers (Murrell et al. 1999; Müeller-Solger et al. 2002), and presumably to higher trophic levels. The key role of phytoplankton production in the food web is surprising given that it provides < 15% of the total organic matter budget for the Delta waters, compared to roughly 70% provided by tributary-born total $C_{organic}$ (TOC) (Jassby and Cloern 2000), and that phytoplankton carbon makes up < 10% of total POC in the upper San Francisco Bay Estuary (Murrell and Hollibaugh 2000). A large percentage of detrital organic matter does not appreciably participate in the food web because of its low bioavailability and/or nutritional value (Canuel et al. 1995; Wehr et al. 1998; Finlay 2001; Müeller-Solger et al. 2002). It is important therefore to characterize the composition of organic matter in the Bay-Delta, and investigators interested in this ecosystem have recently focused attention on this issue (Canuel et al. 1995; Jassby and Cloern 2000; Cloern et al. 2002; Sobczak et al. 2002).

These studies have primarily examined organic matter dynamics within the water column. We analyzed organic matter in surface sediments at sites on a sample transect within the Delta to characterize the spatial pattern of POM composition in surface sediments. The advantages of this approach are that seasonal and recent interannual variability are smoothed providing a time-averaged map of spatial trends in the system. This produces valuable information because practical constraints dictate that many water column studies are not conducted on timescales sufficient to capture the temporal variability inherent in natural primary productivity (Jassby et al. 2002), and because episodic high intensity pulses of organic matter may constitute an important component of the Delta carbon budget (Murrell and Hollibaugh 2000). Disadvantages are that surface and near-surface sediments record the composition of

POM that was in the water column as altered by early diagenesis, and that the processes occurring within the water column are not uniquely quantified using this approach.

The purpose of this study was to characterize $C_{organic}$ and nutrient P delivery to sediments and explore their relevance to ecosystem function and the food web in the San Francisco Bay-Delta. We focus on five major themes regarding $C_{organic}$ and nutrient burial along the study transect. We examine the importance of phytoplankton POM in Delta sediments. We investigate $C_{organic}$ and P evidence about sources of POM. We apply this evidence to evaluating the extent of diagenetic alteration in surface sediments, and we explore how this issue relates to the redox state of sediments as reflected by trace metals Mn and U. Finally, we comment on how these diagenetic factors influence $C_{organic}$ and P burial. In this delta transect, we find that some organic matter sources are site-specific (e. g., peat), some are not as important as anticipated (e. g., macrophytes) and some are more significant than anticipated (e. g., phytoplankton), with important implications for ecosystem function.

SITE DESCRIPTION AND SAMPLING APPROACH

The Sacramento/San Joaquin Delta sits between the San Francisco Bay and Pacific Ocean to the west, and the Sierra Madre to the East. Five sites were sampled from the edge of the San Francisco Bay, bounded by the confluence of the Sacramento and San Joaquin Rivers, eastward to the freshwater Consumnes River (Fig. 1). Sediment cores were collected from the five sites. The top 8 cm of each core were analyzed (in 1-cm intervals) for organic carbon ($C_{organic}$), reactive and detrital phosphorus (P) concentrations and redox-sensitive trace metals (uranium and manganese). The sample transect encompasses mostly freshwater habitat, though depending on precipitation and river inflow, water diversion and tidal influence, the westward Sherman

Island site can reach salinities approaching 10 (Byrne et al. 2001; SFEI, 1999). During drought conditions, saline waters can intrude up the rivers (Goman and Wells 2000). Typically salinity varies seasonally from 0 – 5 near the confluence of the two rivers (Conomos 1979).

The tule bulrush, *Scirpus lacustris*, which densely covered the islands before reclamation began over a century ago, is the main component of expansive Delta peat deposits that extend as deep as 18 m at maximum thickness under Sherman Island (Shlemon and Begg 1975). Peat is present in two of the cores (Table 1). Tributary-borne loading is the largest source of $C_{organic}$ to Delta waters, predominantly in the form of DOC (Table 2). Sample sites were selected as depositional environments.

RESULTS

Sedimentary $C_{organic}$ concentrations are very high at Sherman Island (roughly 20 wt %) and decreases inlad (Fig. 2A). The same trend is apparent in $C_{organic}$/Ti ratios (Fig. 2B). Ratios are higher and more variable at Sherman Island, which may reflect lower and more variable Ti concentrations (and sediment accumulation rates) relative to the other sites, and/or larger grain size (Table 1). The presence of peat in the cores of the bayward sites appears to be the major factor contributing to high sedimentary concentrations of $C_{organic}$ at those sites (Table 3). However, with $C_{organic}$ concentrations in the range of 3-7% even at the inland sites, the entire study region is rich in particulate organic matter (POM) reaching the sediments.

P_{total} concentrations increase inland on the sample transect (Fig. 3A), showing the opposite trend to that of $C_{organic}$ (Figs. 2A and 3A; Table 4). $P_{reactive}$ concentrations increase inland (range: ~5 – 49 μmol g^{-1} sediment), while the $P_{detrital}$ fraction does not exhibit a clear trend with direction along the site transect (range: ~0 – 9 μmol g^{-1} sediment; Fig. 3). As with $C_{organic}$, normalization to the detrital component does not appreciably affect sedimentary P trends (Fig. 3B).

Dissolved P released to pore spaces during diagenesis of organic matter can become oxide-associated (adsorbed to grain surfaces or captured by reducible Fe- and Mn-containing minerals) during early sedimentary transformations. P is subsequently lost from the oxide-associated phase during reduction and is incorporated into an authigenic mineral phase at greater sediment depths and ages (Filipek and Owen 1981; Ruttenberg and Berner 1993; Lucotte et al. 1994; Filippelli and Delaney 1996; Slomp et al. 1996; Filippelli 2001; Anderson et al. 2001). The trends in $P_{oxide\text{-}associated}$, $P_{authigenic}$, and $P_{organic}$ along the sample transect are consistent with younger, less altered material at the inland Consumnes River site and increasing diagenetic alteration toward the bayward Sherman Island site.

$P_{organic}$ constitutes a relatively large portion of the $P_{reactive}$ fraction at the inland Consumnes River site (~25%; Fig. 4), which is consistent with recently deposited organic matter that has not experienced advanced diagenesis. $P_{organic}$ as a percentage of $P_{reactive}$ decreases bayward to ~13% at Sherman Island (Fig. 4). The secondary $P_{oxide\text{-}associated}$ pool makes up approximately 43% of total $P_{reactive}$ at Consumnes River, roughly 60% at Potato Slough, Mandeville Slough and Frank's Track, then falls again to ~43% at Sherman Island (Fig. 4). This pattern is consistent with more conversion of $P_{organic}$ to $P_{oxide\text{-}associated}$ at Potato Slough, Mandeville Slough and Frank's Track than at Consumnes River, and more conversion of $P_{oxide\text{-}associated}$ to $P_{authigenic}$ at Sherman Island than at any of the other sites. $P_{authigenic}$ as a percentage of $P_{reactive}$ decreases from ~32% at the inland Consumnes River site to ~20% of $P_{reactive}$ at Mandeville Slough, then increases to ~44% at the furthest bayward site (Fig. 4). Given that $P_{authigenic}$ is the most diagenetically advanced phase measured, this pattern is again consistent with increasing diagenetic alteration of sedimentary P bayward. We attribute this trend to larger contribution of labile phytoplankton-derived POM to sediments of the inland sites (Table 3), discussed further below.

The observed patterns in sedimentary carbon and P yield a very clear trend of decreasing $C_{organic}/P_{organic}$ ratios inland (Fig. 5). Ratios exceed 1000 at Sherman Island and Frank's Track, owing to peat accumulation at those sites (Table 3). Mandeville Slough has $C_{organic}/P_{organic}$ ratios close to the range expected for OM derived from aquatic phytoplankton, Potato Slough has $C_{organic}/P_{organic}$ ratios lower than those estimated for freshwater but close to Redfield, while Consumnes River has $C_{organic}/P_{organic}$ ratios below those of marine and aquatic plants (Fig. 5). Molar ratios of $C_{organic}$ to $P_{reactive}$ also decrease inland, from ~500 at Sherman Island down to ~10 at the Consumnes River site.

Manganese (Mn) concentrations range from close to 2 to nearly 30 μmol g^{-1} sediment (Table 4). Mn concentrations increase inland following the general trend seen in $P_{reactive}$ concentrations, except at Consumnes River (Fig. 6A). The trend in Mn concentrations agrees fairly well with that of $P_{oxide\text{-}associated}$ based on their relative patterns of enrichment (Figs. 4 and 6A). This is consistent with expectation since P is known to sorb to Mn-oxides, which constitute a large portion of the $P_{oxide\text{-}associated}$ fraction. The pattern of Mn enrichment factors (EFs) is similar to that of Mn concentrations, and sediments at all sites are depleted in Mn relative to source rock estimate because of oxidation of Mn oxides during organic matter diagenesis (Fig. 6B). The study range for U is approximately 4 – 33 μmol U g^{-1} sediment (Table 4). Uranium concentrations follow the trend seen in $C_{organic}$, decreasing inland, except for the low U values found at Sherman Island (Fig. 6A). Uranium enrichment results from suboxic or anoxic pore waters at or near the sediment-water interface. U EFs reflect sedimentary reducing conditions at

Frank's Track, Mandeville Slough and Potato Slough (U EFs > 1; Fig. 6B), consistent with grain size and depth of methane bubble formation observed during sampling (Table 1).

SUMMARY AND CONCLUSIONS

Sedimentary $C_{organic}$ concentrations and $C_{organic}$/P ratios decreased, while reactive P concentrations increased, moving inland in the Delta. The fraction of total P represented by organic P increased inland, while that of authigenic P was higher bayward than inland reflecting increased diagenetic alteration of organic matter bayward. The geochemistry of sediment C and P is influenced by site-specific POM sources, by the Delta's historical function as a tidal marsh, by the sorptive power of the sedimentary material present throughout the transect and by early diagenetic transformations presumably driven by $C_{organic}$ oxidation. Observed distributions of sedimentary constituents reflect predominance of labile, phytoplankton-derived OM in upstream sediments.

We initiated this study with the intention of determining whether $C_{organic}$ and nutrient P would be delivered to the sediments in a predictable manner along a transect in the Delta, and thus provide insight into organic matter dynamics in this important ecosystem. Carbon and P show striking patterns along the site transect. Sedimentary $C_{organic}$ and $C_{organic}$ /P ratios decreased, while P_{total} and $P_{reactive}$ increased moving inland in the Delta. The geochemistry of sediment C is influenced by POM sources, often site-specific, and by the Delta's historical function as a tidal marsh. Sediment P geochemistry appears to be governed by POM sources, the sorptive power of the sedimentary material present throughout the transect and early diagenetic transformations presumably driven by $C_{organic}$ oxidation.

Phytoplankton productivity may be the most important contributor of sedimentary $C_{organic}$ at the inland sites. The distribution of P fractions may reflect the dominance of labile, phytoplankton-derived OM in upstream surface and near-surface sediments due to an important source of phytoplankton in these habitats. Similarly, $C_{organic}$/P ratios indicate that sedimentary OM is dominated by phytoplankton at Mandeville Slough and Potato Slough, and by peat at Sherman Island and Franck's Track. These results indicate that the upstream habitats may constitute an important source of high food value phytoplankton to the Delta food web and may serve a disproportionately important role in supplying organic matter to fuel higher trophic level survival in this system. The sedimentary tools employed in this study are especially valuable given that phytoplankton production is extremely variable and thus difficult to measure in the water column.

Literature Cited

Alpine, A. E. and J. E. Cloern, 1988. Phytoplankton growth rate in a light-limited environment, San Francisco Bay. *Marine Ecology Progress Series* 44: 167-173.

Alpine, A. E. and J. E. Cloern, 1992. Trophic interactions and direct physical effects control phytoplankton biomass and production in an estuary. *Limnology and Oceanography* 37(5): 946-955.

Anderson, L. D., M. L. Delaney and K. L. Faul, 2001. Carbon to phosphorus ratios in sediments: implications for nutrient cycling. *Global Biogeochemical Cycles* 15(1): 65-79.

Bennett, W. A. and P. B. Moyle, 1996. Where have all the fishes gone? Interactive forces producing fish declines in the Sacramento-San Joaquin Estuary. *In* J. T. Hollibaugh (ed.), San Francisco Bay: The Ecosystem. Pacific Division, American Association for the Advancement of Science, San Francisco, pp. 519-542.

Byrne, R., B. L. Ingram, S. Starratt and F. Malamud-Roam, 2001. Carbon-isotope, diatom, and pollen evidence for late Holocene salinity change in a brackish marsh in the San Francisco Estuary. *Quaternary Research* 55: 66-76.

Cain, J. and G. Thomas, 2001. National Heritage Institute. Bay-Delta restoration: Development of short- and long-term programs to protect and restore the Delta and make it sustainable. http://www.n-h-i.org/Projects/RestorationBiodiversity/BayDelta/BayDelta.html

CANUEL, E. A., J. E. CLOERN, D. B. RINGELBERG, J. B. GUCKERT AND G. H. RAU, 1995. Molecular and isotopic tracers used to examine sources of organic matter and its incorporation into the food webs of San Francisco Bay. *Limnolology and Oceanography* 40(1): 67-81.

CLOERN, J. E., E. A. CANUEL AND D. HARRIS 2002. Stable carbon and nitrogen isotope composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. *Limnology and Oceanography* 47(3): 713-729.

CONOMOS, T. J., 1979. Properties and circulation of San Francisco Bay waters. *In* T. J. Conomos (ed.), San Francisco Bay: The Urbanized Estuary. Pacific Division of the American Association for the Advancement of Science, San Francisco, pp. 47-84.

CONOMOS, T. J., R. E. SMITH, D. H. PETERSON, S. W. HAGER AND L. E. SCHEMEL, 1979. Processes affecting seasonal distributions of water properties in the San Francisco Bay estuarine system. *In* T. J. Conomos (ed.), San Francisco Bay: The Urbanized Estuary. Pacific Division of the American Association for the Advancement of Science, San Francisco, pp. 115-142.

FILIPEK, L. AND R. M. OWEN, 1981. Diagenetic controls of phosphorus in outer continental-shelf sediments from the Gulf of Mexico. *Chemical Geology* 33: 181-204.

FILIPPELLI, G. M., 2001. Carbon and phosphorus cycling in anoxic sediments of the Saanich Inlet, British Columbia. *Marine Geology* 174(1-4): 307-321.

FILIPPELLI, G. M. AND M. L. DELANEY, 1996. Phosphorus geochemistry of equatorial Pacific sediments. *Geochimica et Cosmochimica Acta* 60(9): 1479-1495.

FINLAY, J. C., 2001. Stable-carbon-isotope ratios of river biota: Implications for energy flow in lotic food webs. *Ecology* 82(4): 1052-1064.

FOX, J. P., T. R. MONGAN AND W. J. MILLER, 1990. Trends in freshwater inflow to San Francisco Bay from the Sacramento-San Joaquin Delta. *Water Resources Bulletin* 26(1): 101-116.

GOMAN, M. AND L. WELLS, 2000. Trends in river flow affecting the northeastern reach of the San Francisco Bay Estuary over the past 7000 years. *Quaternary Research* 54(2): 206-217.

JASSBY, A. D. AND J. E. CLOERN, 2000. Organic matter sources and rehabilitation of the Sacramento-San Joaquin Delta (California, USA). *Aquatic Conservation* 10(5): 323-352.

KIMMERER, W. J. AND J. J. ORSI, 1996. Changes in the Zooplankton of the San Francisco Bay Estuary since introduction of the clam *Potamucorbula amurensis*. *In* J. T. Hollibaugh (ed.), San Francisco Bay: The Ecosystem. Pacific Division, American Association for the Advancement of Science, San Francisco, pp. 403-424.

LUCAS, L. V., CLOERN, J. E., THOMPSON, J. K., AND N. E. MONSEN. 2002. Functional variability of habitats within the Sacramento-San Joaquin Delta: restoration implications. *Ecological Applications*, 12(5): 1528-1547

LUCOTTE, M., A. MUCCI, C. HILLAIRE-MARCEL AND S. TRAN, 1994. Early diagenetic processes in deep Labrador Sea sediments; reactive and nonreactive iron and phosphorus. *Canadian Journal of Earth Sciences* 31(1): 14-27.

MÜLLER-SOLGER, A., A. D. JASSBY AND D. C. MÜLLER-NAVARRA, 2002. Nutritional quality of food resources for zooplankton (Daphnia) in a tidal freshwater system (Sacramento-San Joaquin Delta). *Limnology and Oceanography* 47(5): 1468-1476.

MURRELL, M. C. AND J. T. HOLLIBAUGH, 2000. Distribution and composition of dissolved and particulate organic carbon in northern San Francisco Bay during low flow conditions. *Estuarine Coastal and Shelf Science* 51(1): 75-90.

MURRELL, M. C., J. T. HOLLIBAUGH, M. W. SILVER AND P. S. WONG, 1999. Bacterioplankton dynamics in northern San Francisco Bay: Role of particle association and seasonal freshwater flow. *Limnology and Oceanography* 44(2): 295-308.

ORSI, J. J. AND W. L. MECUM, 1996. Food limitation as the probable cause of a long-term decline in the abundance of Neomysis mercedis the Opossum Shrimp in the Sacramento-San Joaquin estuary. *In* J. T. Hollibaugh (ed.), San Francisco Bay: The Ecosystem. Pacific Division, American Association for the Advancement of Science, San Francisco, pp. 375-401.

RUTTENBERG, K. C. AND R. A. BERNER, 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochimica Et Cosmochimica Acta* 57(5): 991-1007.

SFEI, 1999. San Francisco Estuary Institute. 1999 Regional Monitoring Program Annual Results. http://www.sfei.org/rmp/1999/RMP_99_datatables.pdf

SHLEMON, R. J. AND E. L. BEGG, 1975. Late Quaternary evolution of the Sacramento-San Joaquin Delta, California. *In* R. P. Suggate and M. M. Cresswell (eds.), Quaternary Studies. The Royal Society of New Zealand, Wellington, pp. 259-266.

SLOMP, C. P., E. H. G. EPPING, W. HELDER AND W. VAN RAAPHORST, 1996. A key role for iron-bound phosphorus in authigenic apatite formation in North Atlantic continental platform sediments. *Journal of Marine Research* 54: 1179-1205.

SOBCZAK, W. V., J. E. CLOERN, A. D. JASSBY AND A. B. MÜLLER-SOLGER, 2002. Bioavailability of organic matter in a highly disturbed estuary: The role of detrital and algal resources. *PNAS* 99(12): 8101-8105.

WEHR, J. D., D. A. HOLEN, M. M. MACDONALD AND S. P. LONERGAN, 1998. Effects of different organic carbon sources on a freshwater plankton community. *Canadian Journal of Fisheries and Aquatic Sciences* 55: 2150-2160.

FIGURE LEGENDS

Fig. 1. Area map showing the study site transect. Sediment cores were recovered from each study site. The top 8 cm of a core from each site were processed and analyzed for chemical composition in 1-cm increments. The sample transect encompasses mostly freshwater habitat. Typically salinity varies seasonally from 0 – 5 at Sherman Island (Conomos 1979).

Fig. 2. ~~Percent~~ S~~s~~edimentary $C_{organic}$ in sediment samples from study site transect as means ± standard deviation of shallowest 8 samples (1-cm increments)~~measured at each study site~~. Results are expressed as weight percent of sediments in panel A, and as molar ratios of sedimentary $C_{organic}$ to Ti ($C_{organic}$/Ti) in panel B. Ti is an indicator of the detrital component of sediments (Schroeder et al. 1997), and these ratios are used to normalize for differences in detrital input between sites since sediment accumulation rates were not determined. Ti concentrations in sediment samples are shown in panel B.

Fig. 3. P_{total} (black bars), $P_{reactive}$ (light gray bars) and $P_{detrital}$ (dark gray bars) in sediment samples from the study site transect as means ± standard deviation of shallowest 8 samples (1-cm increments). Results are expressed as concentration in sediments in panel A, and as molar ratios of sedimentary P to Ti (P/Ti) in panel B.

Fig. 4. Three sedimentary P components~~phases~~ that sum to $P_{reactive}$ at each site as means of shallowest 8 samples (1-cm increments): $P_{authigenic}$ (black bars), $P_{oxide\text{-}associated}$ (light gray bars) and

$P_{organic}$ (dark gray bars). Numbers associated with bar subdivisions denote the percentage of $P_{reactive}$ represented by each P pool at each site.

Fig. 5. $C_{organic}$/P ratios in sediment samples from study site transect as means ± standard deviation of shallowest 8 samples (1-cm increments): $C_{organic}/P_{organic}$ ratios (white bars; fine error bars) and $C_{organic}/P_{reactive}$ ratios (gray bars; bold error bars). There is a break in the vertical axis from 1450 to 5000. Resolution of the vertical axis is 200 from 0 to 1450 and 1000 from 5000 to 6000. Error bars for $C_{organic}/P_{organic}$ at Sherman Island exceed the figure scale; the mean ± standard deviation for that site is noted above the graph. Dashed gray line denotes the characteristic Redfield $C_{organic}/P_{organic}$ ratio of marine phytoplankton: ~117:1 (Anderson and Sarmiento 1994). Solid gray line denotes the estimated $C_{organic}/P_{organic}$ molar ratio of decomposing autochthonous organic matter in freshwater lakes: ~222:1 (Likens 1985).

Fig. 6. Mn (black bars) and U (dark gray bars) in sediment samples from study site transect as means ± standard deviation of shallowest 8 samples (1-cm increments). Results are expressed as concentrations in sediments in panel A, and as enrichment factors (EFs) normalized to detrital component (see Methods for explanation) in panel B.