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Abstract

We report measurements of seasonal variability in the C-N stable isotope ratios of plants collected across the habitat mosaic of San Francisco Bay, its marshes, and its tributary river system. Analyses of 868 plant samples were binned into 10 groups (e.g., terrestrial riparian, freshwater phytoplankton, salt marsh) to determine whether C-N isotopes can be used as biomarkers for tracing the origins of organic matter in this river–marsh–estuary complex. Variability of $\delta^{13}C$ and $\delta^{15}N$ was high (~5–10‰) within each plant group, and we identified three modes of variability: (1) between species and their microhabitats, (2) over annual cycles of plant growth and senescence, and (3) between living and decomposing biomass. These modes of within-group variability obscure any source-specific isotopic signatures, confounding the application of C-N isotopes for identifying the origins of organic matter. A second confounding factor was large dissimilarity between the $\delta^{13}C$-$\delta^{15}N$ of primary producers and the organic-matter pools in the seston and sediments. Both confounding factors impede the application of C-N isotopes to reveal the food supply to primary consumers in ecosystems supporting diverse autotrophs and where the isotopic composition of organic matter has been transformed and become distinct from that of its parent plant sources. Our results support the advice of others: variability of C-N stable isotopes within all organic-matter pools is high and must be considered in applications of these isotopes to trace trophic linkages from primary producers to primary consumers. Isotope-based approaches are perhaps most powerful when used to complement other tools, such as molecular biomarkers, bioassays, direct measures of production, and compilations of organic-matter budgets.

Two fundamental questions of ecosystem science are (1) ''What sources of organic matter provide energy and nutrient resources to heterotrophs?'' and (2) ''What are the trophic pathways through which the chemical energy of organic matter is transferred within food webs?'' The first question is straightforward in the upper ocean where the only source of organic matter to sustain pelagic food webs is phytoplankton photosynthesis (Michener and Schell 1994). The problem becomes more complex in lakes where littoral producers (vascular plants, epiphytes) contribute to system primary production (France 1995), and the complexity of the problem grows further in those lakes, rivers, and estuaries where exogenous sources of organic matter also supply energy to heterotrophs. The pervasive supersaturation of CO_2 in lakes, rivers, and estuaries (e.g., Frankignoulle et al. 1998) has been interpreted as an indicator of net ecosystem heterotrophy, implying that metabolism of these aquatic ecosystems is fueled by exogenous supplements to autochthonous primary production (Smith and Hollibaugh 1997). The question of energy supply to these complex ecosystems has persisted as a challenge to estuarine scientists for decades because there is no single assay for directly measuring the relative contribution of different plant communities, or exogenous versus autochthonous sources, to the pools of organic matter that supply energy to primary consumers (Kling et al. 1992).

Ecologists and geochemists use an array of indirect methods to infer sources and use pathways of organic matter, and since the pioneering works of Parker (1964), Haines (1976), Hedges and Parker (1976), and others, one important approach uses the isotopic composition of light elements (C, N, or S) in biota and organic-matter pools to identify these sources and pathways. This approach is often based on fundamental assumptions that (a) consumers fractionate carbon and nitrogen in predictable ways that allow for the identification of the isotopic composition of their food resource(s) (DeNiro and Epstein 1978, 1981) and (b) the relative contributions of some groups of primary producers can be distinguished because the carbon isotopic composition of plants varies, in a systematic manner, with differences in growth

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environment and the biochemical pathways of photosynthesis and biosynthesis (Maberly et al. 1992).

Ecological application of natural isotopic tracers has become a powerful tool for identifying food web linkages in rivers (e.g., Finlay 2001), flood plains (Lewis et al. 2001), salt marshes (Currin et al. 1995), lakes (Kling et al. 1992; Vander Zanden and Rasmussen 1999), estuaries (Deegan and Garritt 1997), and marine systems (Michener and Schell 1994). Stable isotopes have also been widely used in biogeochemical and organic geochemical studies for tracing the dominant sources of carbon in the environment (Hedges et al. 1988; Canuel et al. 1995), for elucidating the sources of organic matter fueling heterotrophy (Coffin and Cifuentes 1999), and for identifying the sources of carbon accumulating in sediments (Hedges and Parker 1976; Goñi and Thomas 2000). Unambiguous application of isotopic information to reveal organic-matter sources is possible when (a) only a few sources are important and (b) those sources have distinct isotopic signatures (e.g., Rau 1980). But can the sources of organic matter be inferred with isotopic tools in complex river–marsh–estuary systems where multiple plant communities and diverse exogenous inputs collectively sustain system metabolism, and where the relative contribution of each of these sources is difficult to measure directly? There has been considerable effort to characterize the C and N isotopic composition of plants from different habitats of watershed–marsh–river–estuary–marine continua (Currin et al. 1995 and references therein). However there have been few, if any, systematic assessments of all plant communities within one complex ecosystem to test the assumptions inherent in the application of C and N isotope ratios as source-specific biomarkers of organic-matter origin. Here we report results of a comprehensive study designed to measure the patterns and magnitudes of variability in the C and N stable isotopic composition of plants collected from all the habitat types of one complex ecosystem. We include comparisons with the C-N isotopic composition of soils in the river–estuary watershed and in the pools of organic matter from which primary consumers derive their nutrition—the suspended particulate organic matter (POM) and the bottom sediments.

This study is part of a team effort, using multiple approaches (Jassby et al. 1993; Jassby and Cloern 2000; Canuel et al. 1995), to identify the sources of energy that support secondary production in San Francisco Bay and its tributary river network. Here, we specifically ask ''Within this complex ecosystem, do primary producers from different habitats have distinct C-N isotopic signatures, and can these be used as biomarkers to reveal the origins of the organic matter constituting the primary food supply to this ecosystem?''

Methods

Study site and sample design—The San Francisco Bay Estuary (SFBE) comprises a set of estuarine–marine tidal embayments linked to a network of tidal freshwater channels, wetlands, and marshes of the Sacramento–San Joaquin River Delta (Fig. 1). Our study was designed to measure temporal fluctuations in plant isotopic composition associated with seasonal cycles of growth and environmental variability. Ten species of vascular plants common to wetlands of northern California were sampled biweekly for one year (1999) along a gradient of habitats (salt-marsh creek, freshwater–brackish marsh, seasonal wetland) within the San Francisco Bay National Wildlife Refuge (Fig. 1). Additional spatial variability was measured from seasonal sampling in the freshwater–brackish marshes, river channels, tidal lakes, and riparian corridors of the Sacramento–San Joaquin River Delta and from salt marshes and mudflats of the other marine embayments of San Francisco Bay (Fig. 1). Target plant communities included terrestrial woody perennials of riparian habitat (e.g., *Populus fremontii, Acer negundo, Alnus oregona, Salix* spp., *Rubus vitifolius*); emergent vascular plants of freshwater and brackish marshes (*Typha* spp., *Juncus balticus, Scirpus* spp., *Phragmites australis*); floating (*Eichornia crassipes, Hydrocotyle ranunculoides*) and submerged (*Egeria densa, Myriophyllum* sp.) vascular plants and multicellular freshwater algae (*Chara* sp., *Mougeotia* sp.); benthic diatoms from intertidal mudflats; and C_3 (*Salicornia* spp., *Grindelia stricta*) and C_4 (*Spartina foliosa, Distichlis spicata*) salt-marsh plants. We did not sample sea grasses or macroalgae because their distributions are limited in this turbid ecosystem and their contributions to total system production are minor (Jassby et al. 1993). We collected seston samples during algal blooms in river/lake habitats and San Francisco Bay to provide surrogate measures of the isotopic signatures of freshwater and estuarine–marine phytoplankton. Sampling was conducted between September 1998 and July 2000. A total of 868 plant samples were analyzed to determine C and N mass and $^{13}C:{}^{12}C$ and $^{15}N:{}^{14}N$ ratios by mass spectrometry.

Sample collection and analyses—Plant tissue (mostly apical foliage, but also including some flower, root, or stem) samples were collected and frozen until processed in the laboratory. At the sites of biweekly sampling, we collected both fresh green foliage and standing dead foliage from plants produced the previous year. Samples were rinsed vigorously in tap water, washed in 5% HCl, and rinsed in distilled water to neutral pH. Cleaned samples were dried to constant weight at 50°C and then powdered with a Wiley Mill. Aliquots of the powdered sample (~2–3 mg dry weight) were weighed into tin capsules and held in a desiccator until analyzed.

Benthic diatoms were collected from surficial mud samples scraped from mudflats in three different embayments (Fig. 1). Mud samples were mixed gently, spread to a depth of ~1 cm in trays, covered with a 64-μm mesh Nytex screen, and then covered with a gel prepared from silica powder and filtered seawater (Couch 1989). The trays were kept in a lighted incubator, and diatoms were harvested after they migrated vertically from the mud into the silica gel layer. The silica gel was gently scraped and sieved with 64-μm Nytex mesh to separate diatoms from the silica powder. Benthic diatoms were suspended in filtered seawater and then processed as seston samples.

Seston was analyzed from water samples collected in open-water habitats along the salinity gradient from the tidal river system throughout San Francisco Bay (Fig. 1). Water samples were collected by peristaltic pump and screened

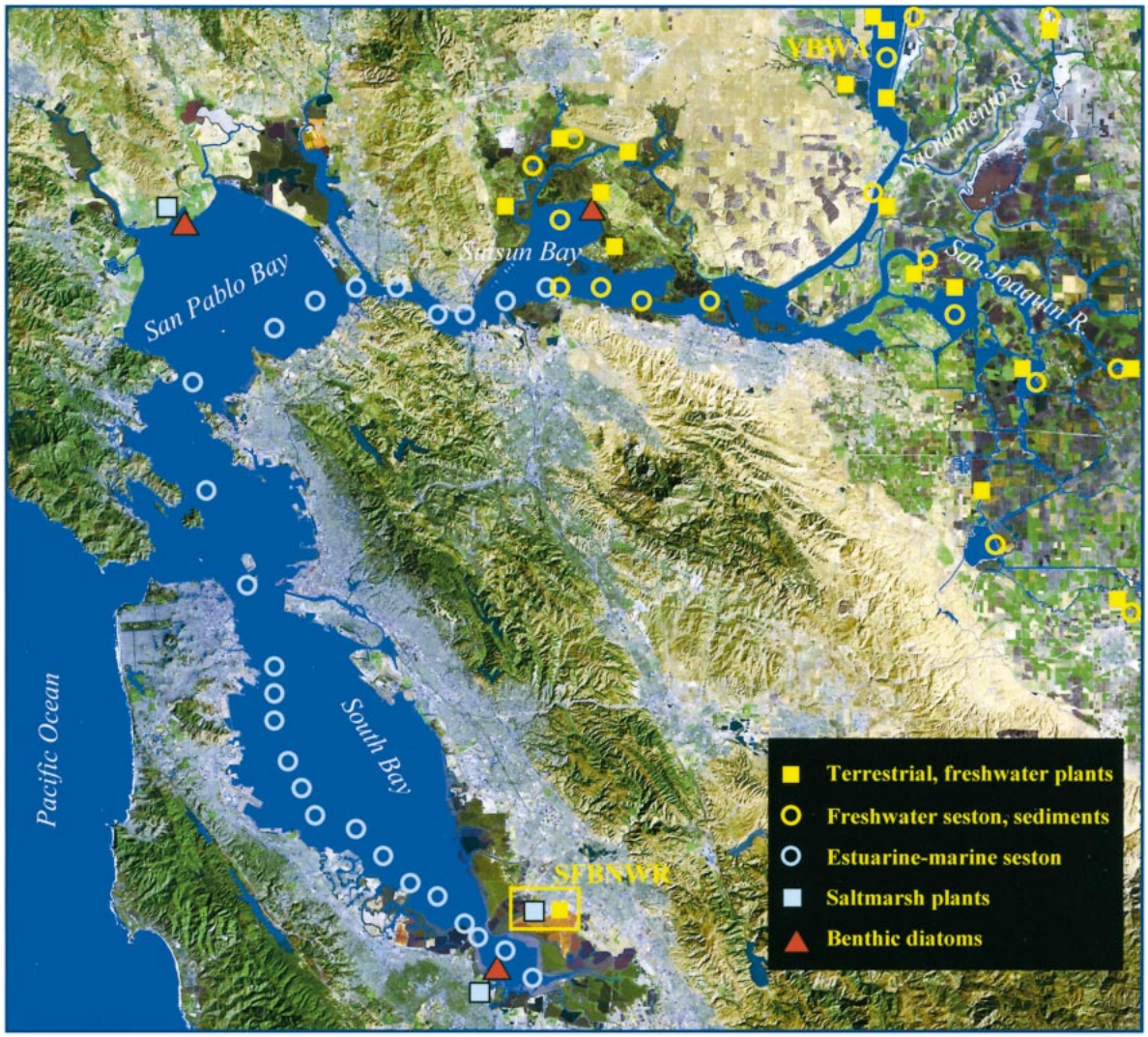

Fig. 1. The San Francisco Bay estuarine system, including the Sacramento–San Joaquin River Delta. Labels identify the locations of plant collections in aquatic and terrestrial habitats, fresh/brackish marshes and mudflats, and locations of seston and sediment sampling in freshwater (salinity <2 psu) and estuarine–marine waters (salinity >10 psu). YBWA = Yolo Bypass Wildlife Area on the Sacramento River floodplain. SFBNWR is the study site in the San Francisco Bay National Wildlife Refuge where 10 species of vascular plants were sampled biweekly for 1 yr. The map combines Landsat TM satellite imagery with a digital elevation model of San Francisco Bay (http://www.sfbayquakes.org/mapview.html).

through 125-μm Nytex mesh to remove coarse particulates. At the time of sampling, salinity was measured with a Sea-Bird 9/11 CTD. Seston was collected onto precombusted 13-mm GF/F filters and fumed in a desiccator with HCl to remove carbonates, and filters were placed in tin capsules and held in a desiccator until analyzed for C and N isotope ratios. Separate aliquots of water were filtered onto 25-mm GF/F filters to determine chlorophyll *a* concentration fluorometrically (Eaton et al. 1995). We distinguish here those samples having high chlorophyll content (>10 μg Chl *a* L^{-1} in fresh water; >5 μg Chl *a* L^{-1} in estuarine–marine waters) and low C : N ratios (<9 g C g^{-1} N in fresh water and ≅7 in estuarine–marine waters), indicative of phytoplankton-rich seston. We supplemented results from 302 seston samples collected in this study with results from 90 seston samples collected in San Francisco Bay from 1990 to 1992 (Cloern et al. 1993).

Soil samples were collected in October 1999 from cultivated/pasture lands throughout the delta and flood plains of the lower Sacramento and San Joaquin Rivers, including the Yolo Bypass Wildlife Area (Fig. 1). Agricultural sites were chosen to represent the dominant crops. Surficial soils were collected using a clean spatula and placed in muffled (450°C for 4–5 h) glass vials. Visible plant fragments were removed from the soil samples with forceps, and soils were sieved to remove additional plant fragments then dried at 60°C and ground with mortar and pestle until homogeneous. Bottom sediments were collected seasonally in a diversity of freshwater habitats of the delta (Fig. 1) using a van Veen grab. Sediments from the upper 0.5 cm were placed in muffled

glass jars, frozen on dry ice, and returned to the lab where they were similarly dried and ground with mortar and pestle until homogeneous. Samples were acidified to remove inorganic carbon with high-purity HCl (10% by volume) until CO_2 release was no longer visible. Samples were redried without rinsing (to minimize losses of DOM) and ground and aliquots (generally 10–20 mg) were weighed into acetone-rinsed tin capsules.

Isotope ratios and C and N mass of each plant, seston, soil, and sediment sample were determined at the Stable Isotope Facility, University of California, Davis, using a Europa Scientific Hydra 20/20 continuous flow isotope ratio mass spectrometer and Europa ANCA-SL elemental analyzer to convert organic C and N into CO_2 and N_2 gas. Results are presented as deviations from standards, expressed as $\delta^{13}C$ and $\delta^{15}N$:

$$\delta X = [R_{sample}/R_{standard} - 1] \times 10^3$$

where X is ^{13}C or ^{15}N and R is $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The standard for C is Peedee Belemnite, and for N it is atmospheric diatomic nitrogen. Instrument precision was 0.1‰ for carbon and 0.3‰ for nitrogen based on replicate analyses of standard reference materials. Two aliquots of most sediment and soil samples and 102 plant samples were analyzed.

Results

Analytical precision and sampling error—We measured analytical precision by comparing $\delta^{15}N$ and $\delta^{13}C$ of paired aliquots of plant samples. We separated the results for (n = 55) aquatic plant (benthic diatoms, submerged vascular plants, algae) samples and (n = 57) aerial (terrestrial or marsh) vascular plants. The analytical precision of $\delta^{15}N$, taken as the median difference between paired aliquots, was 0.36‰ for samples of aquatic plants and 0.13‰ for samples of aerial plants (Fig. 2). The analytical precision of $\delta^{13}C$ was 0.12‰ for aquatic plants and 0.06‰ for aerial plants. We also assessed sampling error as the difference between replicate samples of the same plant species collected within the same microhabitat (e.g., replicate sampling of leaves from one tree or collections of apical foliage from the same stand of emergent marsh plants). These differences between samples were larger than the differences between aliquots of individual samples: the median difference of $\delta^{15}N$ was 0.58‰ for (n = 21) aquatic plant samples and 0.33‰ for (n = 42) aerial plant samples. The median difference of $\delta^{13}C$ was 0.32‰ for aquatic plants and 0.18‰ for aerial plants (Fig. 2). These results verify the high analytical precision for determining stable carbon isotope ratios of terrestrial/marsh vascular plant samples. They also show that analytical precision of $\delta^{15}N$ is lower (by a factor of 2–3) than for $\delta^{13}C$; variability in the isotope ratios among aliquots and replicate samples of both $\delta^{15}N$ and $\delta^{13}C$ is systematically higher for aquatic plants than for aerial plants (Fig. 2); and small-scale variability among samples adds a component of error to the analytical error. The lower analytical precision of $\delta^{15}N$ is likely due to the smaller masses of this element (1–5% dry weight but typically 1–2%). The root mean square deviations between $\delta^{15}N$ and $\delta^{13}C$ of replicate samples and the sample means (estimators of the standard deviations of individual measurements) were 0.53 and 0.37‰, respectively.

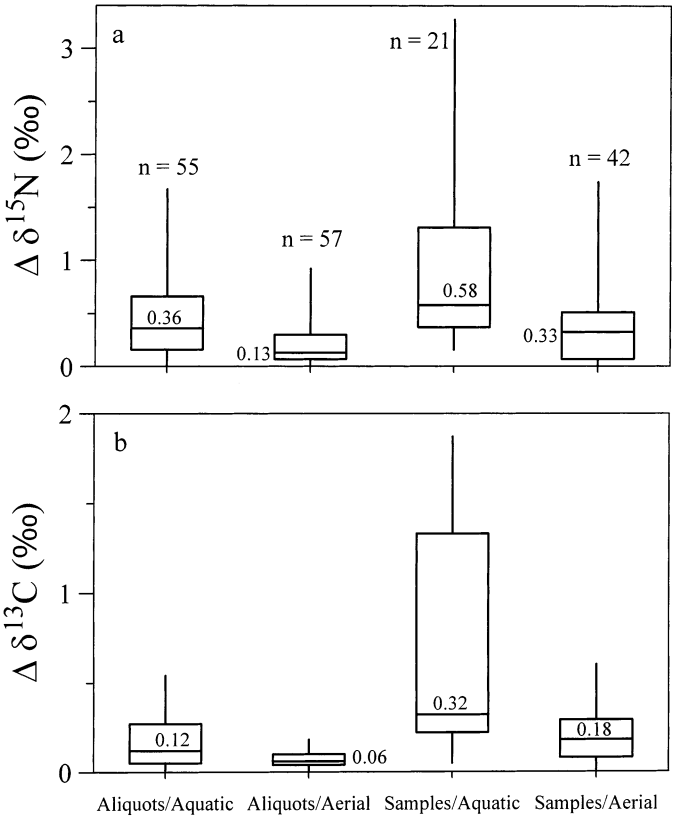

Fig. 2. Box plots showing the median (labeled horizontal lines inside boxes), interquartile range (25th to 75th percentiles as box ends), and range from the 5th to 95th percentile of (a) $\Delta\delta^{15}N$ and (b) $\Delta\delta^{13}C$, the differences between analyses of paired aliquots of the same plant samples or replicate samples of the same plant type. Separate measures of analytical precision were done for samples of aquatic (benthic diatoms, floating and submerged vascular) plants and aerial (marsh and terrestrial) plants. n = sample number for each comparison type.

Variability of plant isotopic composition—Our results showed large variability in the isotopic composition of primary producers collected across the habitat matrix of SFBE: $\delta^{15}N$ ranged from −3.4 to +17.4‰, and $\delta^{13}C$ ranged from −32.0 to −12.4‰. These ranges encompass the variability among 39 species of vascular plants or freshwater algae, 51 samples of benthic diatoms, and 61 samples of high-chlorophyll seston. We binned the samples into 10 groups based on plant habitat, morphology, and photosynthetic pathway. Analysis of variance (ANOVA) shows significant ($P < 0.001$) differences in the mean $\delta^{13}C$ and $\delta^{15}N$ among the 10 plant groups, confirming that the isotopic composition of plants reflects, in a general way, differences in the sources and biochemical pathways through which inorganic C and N are assimilated and incorporated into biomass. Ecological applications of C and N isotopes often start with the measurement or prescription of source-specific isotopic signatures, depicted as discrete domains within plots of plant $\delta^{15}N$ versus $\delta^{13}C$ (e.g., Deegan and Garritt 1997). There was a

Table 1. Plant-group comparisons showing those having different mean $\delta^{15}N$ (upper half) and $\delta^{13}C$ (lower half). Results are from the Scheffé test, a post-ANOVA procedure of group contrasts for identifying those plant-group pairs having significantly ($P < 0.05$) different means (+) and means that are not significantly different (−). BD = benthic diatoms, C3SM = C_3 saltmarsh, C4 = C_4 saltmarsh, EMP = estuarine–marine phytoplankton, EV = emergent vascular, FV = floating vascular, FWP = freshwater phytoplankton, SV = submerged vascular, T = terrestrial woody plants. Algae were excluded because of small sample size.

	BD	C3SM	C4SM	EMP	EV	FV	FWP	SV
$\delta^{15}N$								
BD								
C3SM	+							
C4SM	+	−						
EMP	−	+	−					
EV	−	+	+	−				
FV	+	−	−	−	+			
FWP	−	+	+	+	+	+		
SV	+	−	−	+	+	−	+	
T	+	+	+	+	+	+	−	+
$\delta^{13}C$								
BD								
C3SM	+							
C4SM	+	+						
EMP	+	+	+					
EV	+	−	+	+				
FV	+	−	+	+	−			
FWP	+	+	+	+	−	−		
SV	−	+	+	+	+	+	+	
T	+	−	+	+	−	−	+	+

coarse pattern in the distribution of isotope measurements among the 10 groups (Fig. 3). The largest $\delta^{15}N$ values were measured in salt-marsh and submerged vascular plants, the smallest $\delta^{15}N$ values were measured in terrestrial plants, and intermediate values were measured in freshwater marsh plants and estuarine microalgae. Variability along the *x*-axis (C isotope) corresponded to differences in photosynthetic pathway and source of carbon dioxide, with C_4 salt-marsh plants having the least negative $\delta^{13}C$ (−17.7 to −12.8‰), C_3 terrestrial and salt-marsh plants having the most negative $\delta^{13}C$ (−31.3 to −22.1‰), and large variability among plants that obtain inorganic carbon from solution—filamentous algae, phytoplankton, and submerged vascular plants.

Isotope ratios of each plant group were distributed as diffuse clusters of $\delta^{13}C$–$\delta^{15}N$ pairs, with the centroids of each cluster falling in a different region of Fig. 3. We used the Scheffé test as a conservative procedure (Snedecor and Cochran 1974) to identify those specific pairs of plant groups having significantly ($P < 0.05$) different mean $\delta^{13}C$ and $\delta^{15}N$ (Table 1). The mean $\delta^{15}N$ of terrestrial plants was significantly different from all other plant groups except freshwater phytoplankton; C_4 salt-marsh plants, as expected, had significantly different mean $\delta^{13}C$ from all other groups. Among all possible permutations, there were 15 plant-group pairs having significantly different mean $\delta^{13}C$ and $\delta^{15}N$, so distinct plant-group signatures exist as mean C-N isotope ratios. However, there was considerable overlap in the distributions of C-N isotope ratios among the 10 plant groups, and no one plant group occupied a unique region of $\delta^{13}C$–$\delta^{15}N$ space. Even the large separation of $\delta^{13}C$ between C_3 and C_4 marsh plants was bridged by the highly variable $\delta^{13}C$ of aquatic plants (Fig. 3). Frequency distributions of $\delta^{13}C$ and $\delta^{15}N$ (Fig. 4) show the overlapping ranges of isotope measurements: for both C and N isotope ratios, the interquartile range (spanning the 25th to 75th percentiles) of any one plant group overlapped the interquartile ranges of at least two other groups. The clearest separation was between the $\delta^{13}C$ of C_4 salt-marsh plants (mean −14.9‰) and C_3 vascular plants (mean −27.2‰). However, the distributions of $\delta^{15}N$ measurements were similar in C_4 and C_3 salt-marsh plants, and their mean $\delta^{15}N$ values were not different (Table 1). As a bulk indicator of plant biochemical composition, the C : N ratio was also highly variable, ranging from 3.7 to 169 (g C g^{-1} N) with highest ratios measured in terrestrial and marsh vascular plants and consistently low ratios in the aquatic plants (Fig. 4).

The large sample sizes of this study reveal inherent high variability of both C and N isotope ratios within all the plant groups. Comparable variability existed at the level of species, where individual species were collected over different seasons and in different geographic regions of the SFBE complex. As extreme examples, the $\delta^{15}N$ of alkalai bulrush (*Scirpus maritimus*), water hyacinth (*Eichornia crassipes*), common cattail (*Typha latifolia*), and California blackberry (*Rubus vitifolius*) each varied by more than 10‰ (Table 2). Variability of $\delta^{13}C$ in aquatic species was of comparable magnitude, and even among terrestrial plant species the $\delta^{13}C$ varied by 4 to 5‰ (Table 2). The C : N ratios of terrestrial and marsh vascular plants ranged from minima of 10 to 20 to maxima of 40 to >100 (Table 2), again showing large variability, at the species level, in biochemical composition.

Isotopic composition of organic-matter pools—Riverine inputs of particulate organic matter to the SFBE system include a large component of soil organic matter that is mobilized during periods of heavy precipitation and runoff (Schemel et al. 1996). The isotope ratios of soils collected across the Sacramento–San Joaquin River Delta landscape varied 8.7‰ for $\delta^{15}N$ and 8.3‰ for $\delta^{13}C$ (Table 3), and this variability was associated with differences in land use. The most ^{13}C-enriched soil sample ($\delta^{13}C$ of −19.8‰) was collected in a corn (C_4 plant) field and the least ^{13}C-enriched soils were from uncultivated grasslands. The most ^{15}N-depleted soils were from diverse croplands (asparagus and corn fields, orchards) and the most ^{15}N-enriched soils were from pastures with grazing cattle. Isotopic compositions of surficial sediments collected in a diversity of freshwater habitat types (deep river channels, shallow tidal lakes, narrow marsh sloughs; Fig. 1) had smaller variability but similar mean $\delta^{15}N$ and $\delta^{13}C$ to the soil samples (Table 3). The isotopic composition of seston collected in the same freshwater habitats was much more variable: $\delta^{15}N$ varied 16.3‰ and $\delta^{13}C$ varied 11.3‰. Isotopic composition of seston collected in San Francisco Bay was equally variable, but the mean isotopic composition of estuarine–marine seston was more enriched in ^{15}N (by 2.9‰) and ^{13}C (by 4.2‰; Table 3) than the seston collected in fresh waters.

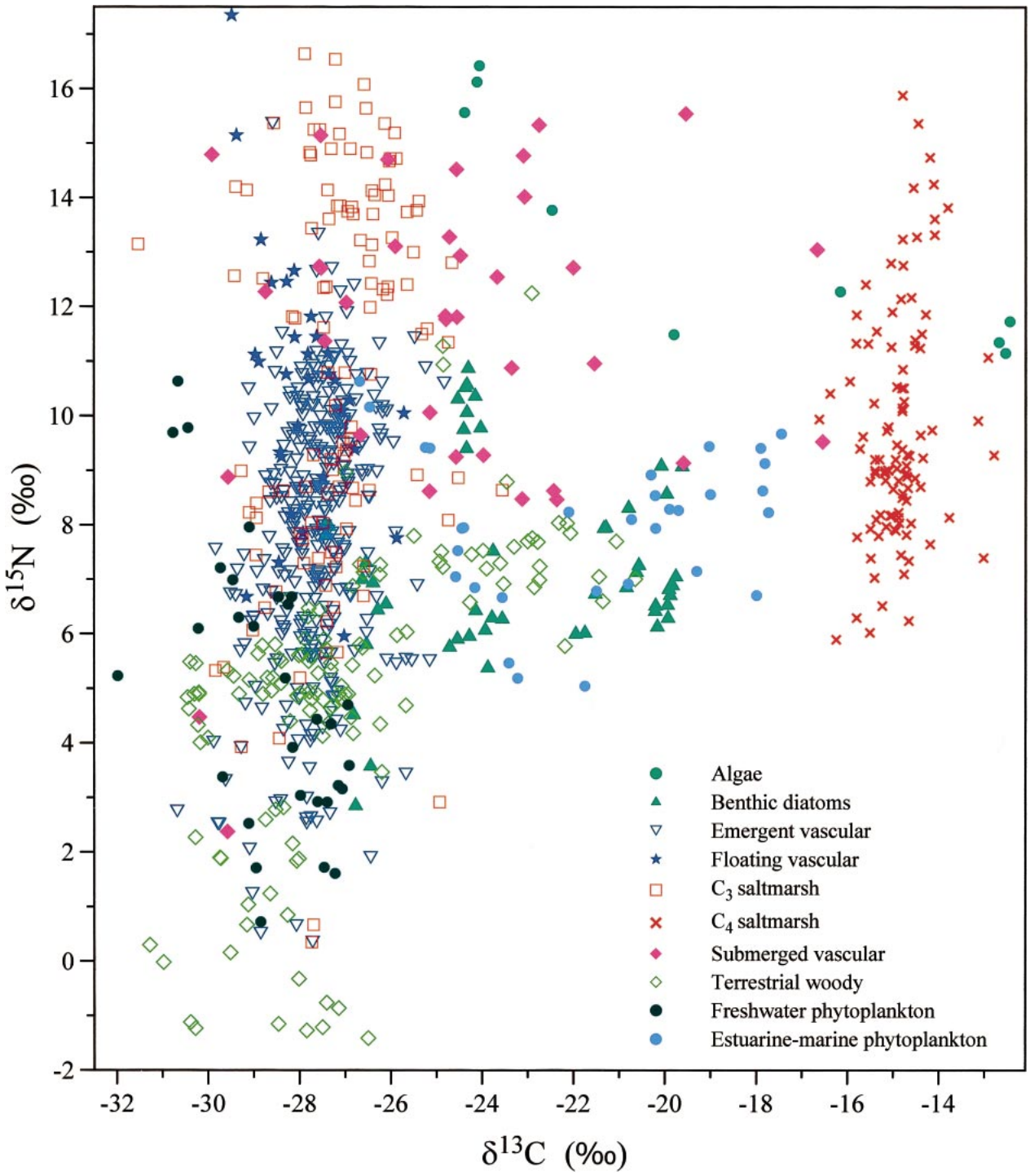

Fig. 3. δ^{15}N and δ^{13}C of 868 plant samples collected within the SFBE system, binned into 10 groups on the basis of habitat, class, and photosynthetic pathway. These data are available in Web Appendix 1 http://www.aslo.org/lo/toc/vol_47/issue_3/0713a1.pdf.

Discussion

Source-specific isotopic signatures?—Although coarse patterns of distribution exist in the isotopic compositions of different plant groups, and differences exist in mean δ^{13}C and δ^{15}N between plant groups, we found a high degree of overlap in the distributions of C-N isotope ratios of those groups. This data set, produced from a study designed to measure the combined spatial and temporal variability within a complex ecosystem, does not reveal distinct combinations of δ^{13}C and δ^{15}N that can be used to identify the source, or the potential source mixture, of the different pools of organic matter (seston, sediments, biota) in the SFBE river–marsh–estuary system. We can explore this data set to reveal three

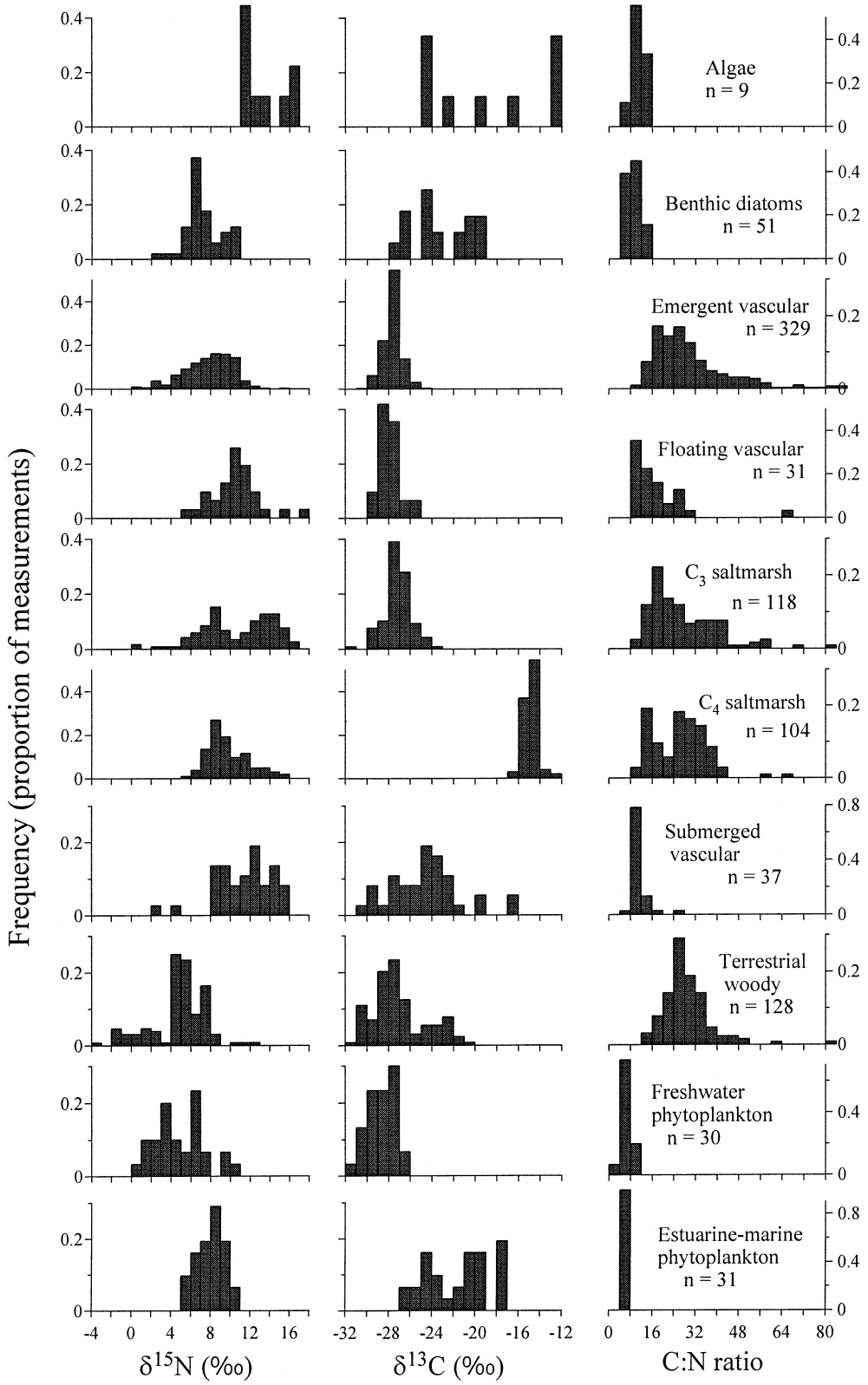

Fig. 4. Frequency distributions (proportion) of $\delta^{15}N$, $\delta^{13}C$, and C:N ratio of 10 plant groups sampled in the SFBE system.

Table 2. Summary statistics of the N- and C-isotopic composition ($\delta^{15}N$ and $\delta^{13}C$, ‰) and C:N mass ratio (g C g^{-1} N) of 25 primary producers collected in the San Francisco Bay estuarine system. n = sample number. Codes of plant groups given in Table 1.

Plant group	Plant common name	Genus species	$\delta^{15}N$			$\delta^{13}C$			C:N			
			Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	n
BD	Benthic diatoms (<5 psu)		6.6	6.1	7.0	−20.0	−20.2	−19.8	6.1	5.9	6.4	9
BD	Benthic diatoms (>10 psu)		7.5	2.8	10.9	−24.0	−27.4	−19.6	9.7	7.1	14.7	42
C3SM	Alkalai bulrush	*Scirpus maritimus*	9.2	0.4	15.6	−26.4	−27.9	−23.6	51.0	25.1	169.1	13
C3SM	Marsh gum	*Grindelia stricta*	7.9	3.9	10.2	−27.7	−29.3	−26.6	20.3	11.2	69.1	33
C3SM	Pickleweed	*Salicornia*	12.8	4.1	16.6	−27.0	−29.8	−25.2	29.2	14.5	57.1	57
C3SM	Sea arrowgrass	*Triglochin maritima*	11.4	8.0	13.2	−28.3	−31.5	−27.0	22.1	12.9	43.4	7
C4SM	Cordgrass	*Spartina foliosa*	10.5	5.9	15.9	−14.8	−16.6	−12.8	22.0	11.7	65.1	56
C4SM	Salt grass	*Distichlis spicata*	8.8	6.2	11.9	−15.0	−15.7	−14.2	31.4	15.5	56.1	48
EMP	Estuarine-marine phytoplankton		8.0	5.0	10.6	−21.5	−26.7	−17.4	6.0	5.1	7.0	31
EV	California bulrush	*Scirpus californicus*	8.3	2.6	13.3	−27.4	−29.2	−25.9	35.3	17.7	83.8	34
EV	Common cattail	*Typha latifolia*	7.0	0.4	15.4	−28.2	−29.9	−25.5	34.9	11.6	96.3	79
EV	Common reed	*Phragmites australis*	7.0	1.9	11.4	−26.4	−28.0	−24.8	27.0	13.3	80.2	16
EV	Narrow-leaved cattail	*Typha angustifolia*	7.9	2.6	12.7	−27.3	−28.3	−25.9	29.4	14.2	54.8	45
EV	Olney's bulrush	*Scirpus olneyi*	8.9	5.6	11.2	−27.3	−28.3	−26.3	24.2	14.6	52.0	44
EV	Rush	*Juncus balticus*	5.6	4.0	8.8	−27.6	−28.5	−25.7	25.5	21.5	30.0	19
EV	Tule	*Scirpus acutus*	8.7	2.5	12.4	−27.7	−29.8	−26.2	31.5	15.3	108.1	80
FV	Marsh pennywort	*Hydrocotyle ranunculoides*	9.8	7.8	11.8	−26.9	−27.9	−25.7	11.6	9.4	14.7	7
FV	Water hyacinth	*Eichhornia crassipes*	10.7	6.0	17.4	−28.2	−29.5	−27.0	19.2	9.4	65.1	24
FWP	Freshwater phytoplankton		5.0	0.7	10.6	−28.6	−32.0	−26.9	6.6	3.7	8.9	30
SV	Brazilian waterweed	*Egeria densa*	11.7	8.5	15.1	−25.4	−29.9	−22.0	11.1	8.9	16.1	24
SV	Parrots feather	*Myriophyllum brasiliense*	12.2	9.1	15.5	−22.2	−27.4	−16.5	9.8	8.0	11.3	11
T	California blackberry	*Rubus vitifolius*	6.5	−0.8	12.2	−24.7	−29.2	−20.7	30.9	12.8	89.4	46
T	Fremont cottonwood	*Populus fremontii*	2.4	0.0	4.7	−29.0	−31.3	−25.7	24.3	19.7	41.1	6
T	Red alder	*Alnus oregana*	−1.5	−3.4	−0.9	−28.5	−30.4	−27.1	31.8	21.0	39.2	7
T	Yellow tree willow	*Salix lasiandra*	4.9	−0.3	6.5	−28.3	−30.4	−26.4	28.6	14.4	47.9	52

Table 3. Summary statistics of the N- and C-isotopic compositions (δ^{15}N and δ^{13}C, ‰) of seston, soils, and sediments collected in the Sacramento–San Joaquin River Delta, its local watershed, and in San Francisco Bay. *n* = sample number. SD = standard deviation.

	δ^{15}N				δ^{13}C				
Organic matter pool	Mean	Min	Max	SD	Mean	Min	Max	SD	*n*
Freshwater seston	3.7	−5.7	10.6	2.8	−28.3	−35.2	−23.9	1.9	226
Estuarine–marine seston	6.6	−1.2	10.6	2.0	−24.1	−28.2	−17.4	2.2	166
Soils	4.5	1.5	10.2	1.9	−25.1	−28.1	−19.8	2.0	33
Freshwater sediments	5.4	2.1	7.5	1.3	−25.4	−27.2	−23.3	1.0	32

modes of variability that obscure source-specific isotopic signatures.

Some applications of stable isotopes in ecosystem studies are based on the assumption that primary producers growing within general habitat categories (e.g., terrestrial woody, C_4 salt-marsh, freshwater phytoplankton) have distinct isotopic compositions. This assumption is not valid for the San Francisco Bay Estuary complex where variability of plant isotope ratios within habitats is as large as variability between some habitat types (Fig. 5). For example, biweekly sampling of *Grindelia stricta* and *Salicornia virginica* showed very different distributions of δ^{15}N (Fig. 5a), even though these two species were sampled within 20 m on the same salt-marsh plain: the median δ^{15}N was 8‰ for *Grindelia* (which grows at higher elevation in the salt marsh) compared to 14‰ for *Salicornia.* Biweekly sampling in one small brackish pond showed different distributions of δ^{13}C for two species of *Typha* collected from stands separated by only 50 m (Fig. 5b). Two species of woody perennial plants, *Rubus vitifolius* and *Salix lasiandra,* had different distributions of both δ^{15}N and δ^{13}C (Fig. 5a,b), although these plants were separated by only 20 m within one seasonal wetland. Each of these cases, comparing species within the groups of C_3 salt-marsh, emergent vascular, and terrestrial woody plants, illustrates high within-habitat variability. We cannot determine the relative contributions to this variability of (a) genetically based differences between species in their assimilation, biosynthesis, and isotopic fractionations of inorganic elements, and (b) microscale gradients in the environmental factors and biogeochemical processes that alter the isotopic composition of inorganic C-N or the plant fractionations of these isotopes (Handley and Scrimgeour 1997 describe the concept of ''N-niche,'' where plants exploit N as multiple resources in space and time). As examples of isotopic variability at small spatial scales, Guy et al. (1988) measured 6‰ changes in δ^{13}C of the perennial grass *Puccinellia nuttalliana* along 10 m of a soil salinity gradient, and Leavitt and Long (1988) measured 2–3‰ differences in δ^{13}C of wood from individual trees (*Pinus edulis*) in one stand. This variability between species or individuals and their microhabitats is one source of natural variability that tends to obscure any distinctions in the isotopic compositions of plants growing in general habitat types.

A second mode of isotopic variability occurs over annual cycles of plant growth and senescence. We used biweekly measurements of the C : N ratio as an indicator of changes in plant biochemical composition (Fig. 6). Some species of vascular plants (*Salix, Salicornia, Typha* spp., *Scirpus olneyi*) had large seasonal fluctuations in the C : N ratio of living biomass; other species (*Spartina*) did not. The most common seasonal pattern was low C : N ratio of foliage in March when leaves/shoots first emerged, gradual increase in C : N during the spring–summer growth season, and a rapid increase in C : N in November–December when the new biomass died. The individual series of C : N (Fig. 6) show patterns of seasonal change in the bulk biochemical composition of vascular plants that likely reflect species-specific changes in the synthesis of structural (high C : N) and metabolic (low C : N) components of biomass and the timing of die off. Seasonal changes in the C : N ratios were accompanied by seasonal changes in C and N isotopic composition of some species (Fig. 6). The δ^{13}C of living biomass either declined nearly monotonically during the growth season (*Distichlis, Typha* spp., *Scirpus californicus*), increased during the growth season (*Rubus*), or varied during the year but showed no pronounced seasonal trend or periodicity (*Spartina, Scirpus olneyi*). Seasonal fluctuations in δ^{15}N were even larger (2 to 10‰) and showed the same diversity of patterns: nearly monotonic decline of δ^{15}N during the growth season (*Spartina, Typha* spp., *Scirpus californicus*), low-frequency seasonal oscillations (*Grindelia*), or no strong seasonal trend or periodicity (*Rubus, Salix, Distichlis*). These species-specific patterns of seasonal variability in wetland plants are similar to those reported in a study of terrestrial vegetation by Handley and Scrimgeour (1997), who concluded that plant elemental composition ''is not necessarily correlated with δ^{15}N or with leaf age and that patterns of δ^{15}N through the growing season, among plant parts and between taxa are not predictable.''

A third mode of variability that obscures habitat-specific isotopic signatures is the change in isotopic composition of plant biomass as it decomposes. For most species of wetland vascular plants sampled here, the C : N ratio of year-old dead biomass was usually higher than the C : N ratio of new living biomass sampled at the same time (Fig. 6). However, this age distinction disappeared over the growing season for *Salix, Typha* spp., and *Scirpus olneyi* because the C : N ratio of their living biomass increased while the C : N ratio of senescent biomass decreased. The seasonal increase of C : N in living biomass probably reflects increases in the proportional biosynthesis of structural versus metabolic components over the growing season. The trend of decreasing C : N in senescent biomass probably reflects changes as the residual structural components are colonized and transformed into plant–microbe composites by fungal and bacterial decomposers (Currin et al. 1995; Goñi and Thomas 2000). Given the large and species-specific differences in the seasonal changes of C : N ratio between living and dead biomass, and the poten-

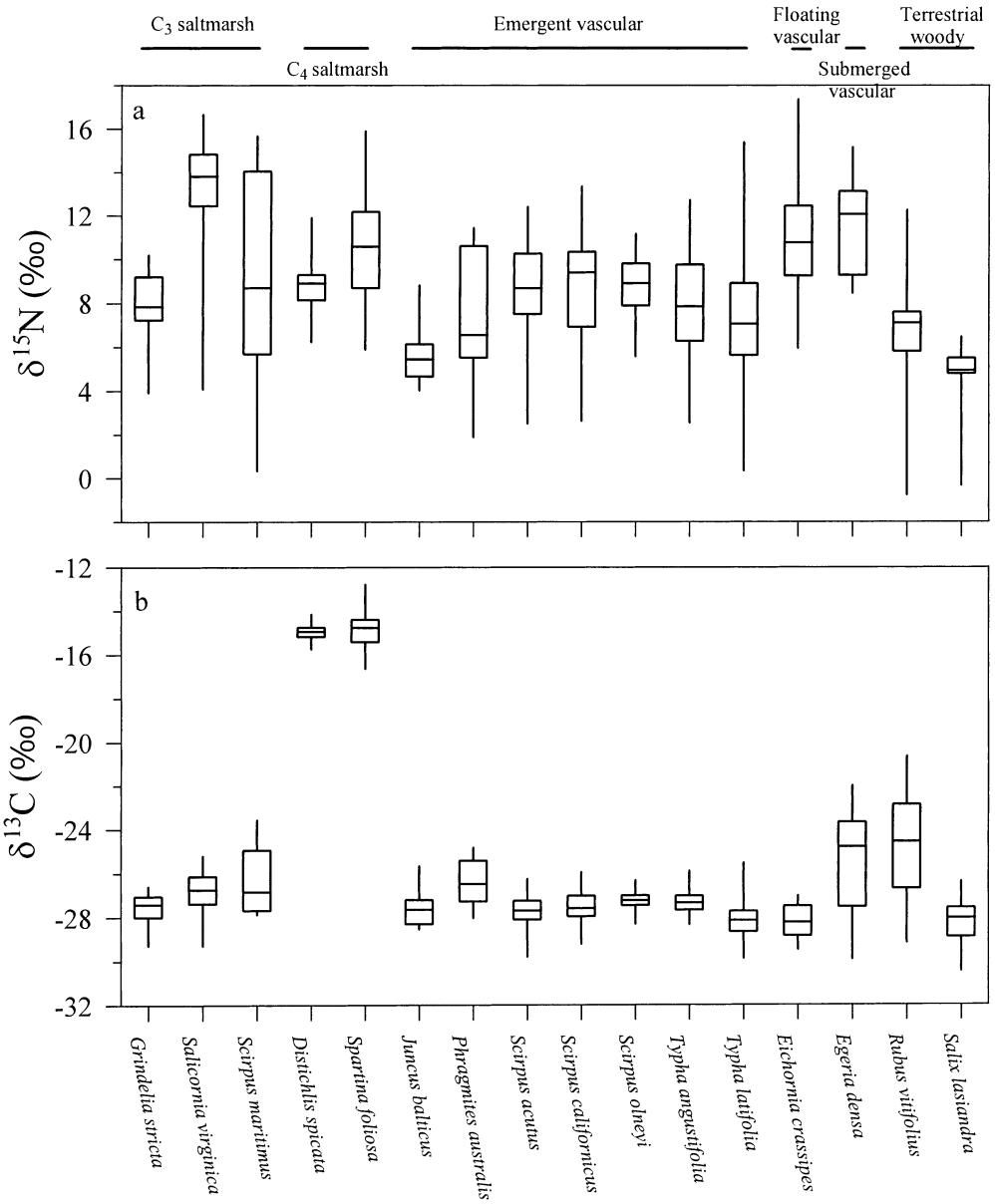

Fig. 5. Box plots showing the median (horizontal line inside boxes) and variability (box ends show interquartile range, vertical lines the full range) of $\delta^{15}N$ and $\delta^{13}C$ measured in 16 species of vascular plants collected from the SFBE system. Species are arranged by habitat group, showing that variability of plant isotopic composition within groups is of the same magnitude as variability between groups.

tial effects of different degradation pathways (e.g., denitrification, sulfate reduction, methanogenesis) and differential C isotope fractionations of C_3 and C_4 plant carbohydrates by basidiomycete fungi (Henn and Chapela 2000), it is not surprising to see a diversity of patterns in the seasonal distinction between $\delta^{13}C$ and $\delta^{15}N$ of living and dead biomass (Fig. 6). For example, the $\delta^{15}N$ of dead biomass was consistently lower (by up to 4–5‰) than the $\delta^{15}N$ of living biomass in both species of *Typha*. The $\delta^{15}N$ of decomposing *Spartina* leaves (collected on the marsh surface) was always higher than the $\delta^{15}N$ of living leaf biomass (Fig. 6). Covariations between the seasonal changes in C-N mass and C-N isotope ratios differed among species. Three patterns are illustrated in Fig. 7: (1) highest C : N ratio and highest $\delta^{15}N$ of dead biomass (*Spartina*), (2) highest C : N ratio but lowest $\delta^{15}N$ of dead biomass (*Typha angustifolia*), and (3) no clear covariation of $\delta^{15}N$ with seasonal changes in C : N ratio (*Salix*). These different patterns of isotopic change over annual cycles of growth and senescence explain why we cannot identify clear habitat-specific isotopic signatures, even when the data are binned by season.

The seasonal patterns and range of C-N isotope ratios in *Spartina foliosa* collected in San Francisco Bay salt marshes were completely different from those of *S. alterniflora* in a

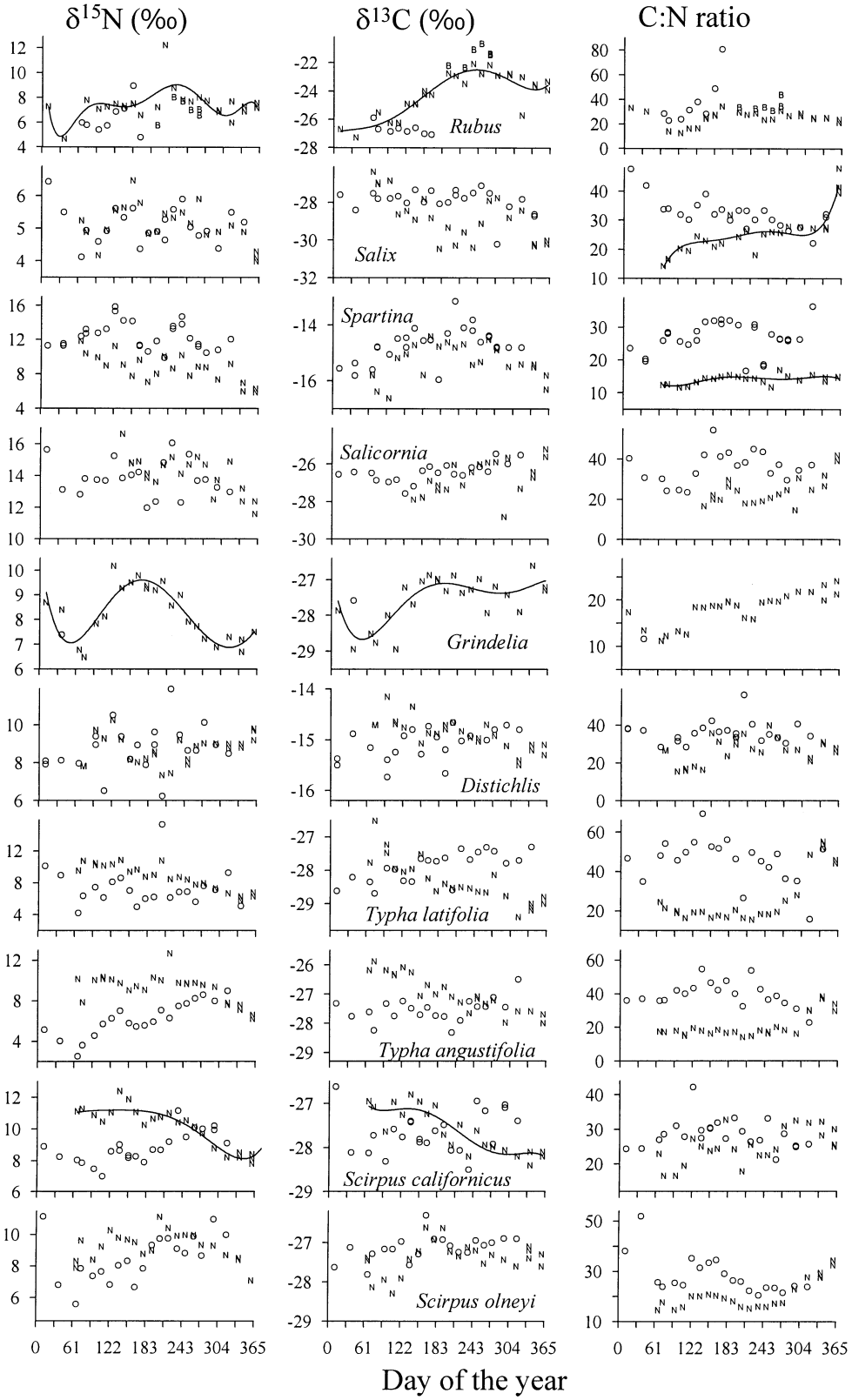

Fig. 6. Seasonal changes in the $\delta^{15}N$, $\delta^{13}C$, and C : N ratio of 10 species of wetland plants collected across a gradient of habitats, illustrating variability in the magnitudes and patterns of change over an annual cycle (1999). N = newly produced living foliage; O = year-old dead foliage. Solid lines are polynomial curves fitted by least squares to highlight different patterns of seasonality.

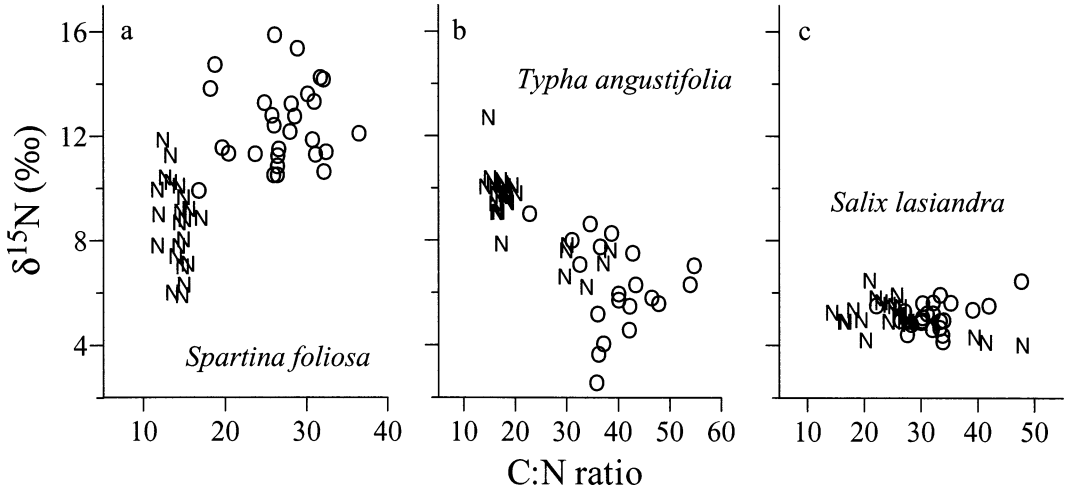

Fig. 7. Seasonal and age changes in bulk C-N mass and isotopic composition vary among species of wetland vascular plants. Three different patterns of association between the C : N ratio and δ^{15}N of living and dead plant biomass: (a) cordgrass *Spartina foliosa,* (b) cattail *Typha angustifolia,* and (c) yellow tree willow *Salix lasiandra.* N = newly produced living foliage; O = year-old dead foliage.

North Carolina salt marsh (Currin et al. 1995): δ^{13}C of *S. alterniflora* ranged from −12.3 to −13.1‰ and varied little seasonally or between living–dead tissues (compared to *S. foliosa* δ^{13}C, ranging from −13 to −17‰ and varying seasonally in SFBE); δ^{15}N of *S. alterniflora* ranged from 0 to 6‰ (compared to 6 to 16‰ for *S. foliosa* in SFBE). These contrasting results suggest a fourth mode of variability, between ecosystems, and illustrate the danger of applying isotopic data from one species/ecosystem to congeneric species of plants in different ecosystems.

Mechanisms of plant isotope variability—The coarse patterns of difference in the δ^{15}N and δ^{13}C among different plant groups (Figs. 3, 4) are consistent with our general understanding of the mechanisms of variability in plant isotopic composition. The smallest values of δ^{15}N were measured in riparian vegetation (including red alder, *Alnus oregona*): foliage of woody perennials is often depleted in ^{15}N relative to soil N, through multiple mechanisms including microbial N_2 fixation or plant use of NH_4-N (Handley and Scrimgeour 1997). High δ^{15}N was measured in salt-marsh (C_3 and C_4) and submerged vascular plants that assimilate inorganic N from aquatic sediments where microbial mineralization and nitrification/denitrification produce ^{15}N-enriched inorganic nitrogen (Cline and Kaplan 1975). The broad range of δ^{15}N in aquatic plants and algae, from 0.7 to 17.4‰ in this study, reflects the large seasonal changes in the ^{15}N content of dissolved inorganic N (potentially up to 30‰; Cifuentes et al. 1989) resulting from variability in N isotope fractionation by algal uptake and microbial processes such as nitrification. During phytoplankton blooms the δ^{15}N of seston can decrease 10‰ in less than a week because algal uptake discriminates against the heavy isotope ^{15}N (Nakatsuka et al. 1992).

The C_4 photosynthetic pathway yields photosynthate enriched in ^{13}C relative to the C_3 pathway, so the mechanism separating C_3 and C_4 plants along the *x*-axis of Fig. 3 is well established (Smith and Epstein 1971). Among the C_3 plants and algae, there was also a general difference in the δ^{13}C of those that acquire CO_2 from the atmosphere (most <-22‰) or from water (δ^{13}C from −32 to −12‰). Aquatic plants have a broad range of δ^{13}C (from −8 to −30‰; Ehleringer and Rundel 1988), and this variability reflects changes in (1) the δ^{13}C of dissolved inorganic carbon (DIC) along estuarine salinity gradients (from about −10‰ in the Sacramento River to zero in marine waters of San Francisco Bay; Spiker and Schemel 1979); (2) concentration and isotope ratio of DIC caused by C isotope fractionations of photosynthesis and heterotrophic respiration (Fogel et al. 1992); (3) nutrient-regulated changes in phytoplankton growth rate (Gervais and Riebesell 2001); and (4) differences between aquatic plants and phytoplankton that fix CO_2 or HCO_3 (Maberly et al. 1992). Recent evidence shows that marine diatoms can use both C_3 and C_4 pathways of carbon fixation (Reinfelder et al. 2000), so there can be high variability in the ^{13}C discrimination within individual species depending on the degree of DIC-limitation of photosynthesis or nutrient limitation of growth rate (Gervais and Riebesell 2001).

General mechanisms of variability in C and N isotope fractionation have also been identified for terrestrial plants. For example, $^{13}CO_2$ discrimination varies seasonally and spatially with fluctuations in soil moisture and water use efficiency (Farquhar et al. 1989) and with changes in photosynthetic capacity as foliage senesces (Mackerron and Jefferies 1994). Different patterns of ^{13}C discrimination have been observed among genotypes, perennial and annual species, early- and late-flowering species, monocots and dicots, and along altitudinal gradients (Lajtha and Marshall 1994). Whole-plant δ^{13}C varies with the growth cycle because some structural components (lignin, Benner et al. 1987) are ^{13}C depleted and some metabolic components (sugars, Pate and Arthur 1998) are ^{13}C enriched. This mechanism probably explains why the δ^{13}C of *Rubus* increased over the growth season and peaked at the time of berry ripening (Fig. 6). The

whole-plant $\delta^{13}C$ of C_3 halophytes varies (up to 10‰) with substrate salinity, and the responses differ among species depending on their strategies for osmotic adjustment to salinity change (Guy et al. 1988). This mechanism may partly explain the seasonal changes of $\delta^{13}C$ in *Salicornia* and *Grindelia* (Fig. 6) as soil salinity of the salt marsh fluctuated between the wet winter–spring and the dry summer–autumn.

Foliar N isotopic composition changes with the seasonal timing of leaf emergence; the amount and periodicity of soil wetting, soil age, and rooting depth (Lajtha and Marshall 1994); N content of soils (Martinelli et al. 1999); ^{15}N ratio of atmospheric N inputs (Koopmans et al. 1997); and the relative contributions of remobilized N, soil-derived N, and recently fixed atmospheric N_2 in new plant biomass (Handley and Scrimgeour 1997). These mechanisms may explain the rapid decline of $\delta^{15}N$ in *Grindelia* during February–March (Fig. 6), a period of heavy rainfall, and, presumably, changes in the atmospheric component of inorganic N within the root zone. Specific mechanisms of isotopic variability have not been established for most species of wetland and estuarine plants (but *see* Benner et al. 1987; Currin et al. 1995), although the multiplicity of patterns in Fig. 6 suggests multiple mechanisms depending on species and growth habitat.

C, N isotopes as tracers of organic-matter origin—The inherent large variability and absence of clear plant-specific isotopic signatures confounds the application of C-N isotopes to identify the sources of organic matter in the SFBE system. A second complication is revealed when we compare the isotopic compositions of POM with the characteristic compositions of individual plant groups, defined as the interquartile ranges of $\delta^{15}N$ and $\delta^{13}C$ measured here. We compared separately the seston collected in the freshwater Sacramento–San Joaquin River Delta and estuarine–marine waters of San Francisco Bay because these domains provide habitats for different primary producers, because they have different proximity to the riverine inputs of watershed-derived organic matter (Jassby et al. 1993; Canuel 2001), and because the $\delta^{13}C$ of DIC and POM vary along the river–estuary salinity gradient (Spiker and Schemel 1979). From an isotopic perspective, most of the seston samples collected in the freshwater tidal river system did not overlap aquatic or terrestrial plant sources, local soils, or sediments (Fig. 8a). There was some overlap with the signatures of terrestrial/woody plants and with freshwater phytoplankton during algal blooms when the seston (based on chlorophyll content and C : N ratio) was dominated by phytoplankton biomass. However 134 of the 226 freshwater seston samples had isotopic compositions that were more depleted in either ^{15}N or ^{13}C than the plant groups and soils in the local watershed. Therefore, with the exceptional cases of high phytoplankton biomass during blooms, the origins of the seston organic matter cannot be identified from C-N isotope ratios alone. This finding suggests that the seston likely includes a large signal from nonliving organic matter and/or that bacterial processes leave a diagenetic overprint that makes it difficult to relate the seston to its original plant source(s).

The isotopic dissimilarity of seston and the presumed sources of organic matter show that POM in this river system is not simply a mixture of recently produced plant biomass/detritus and local soils. This dissimilarity, and particularly the relative ^{13}C depletion of seston, is consistent with the emerging concept that riverine POM includes large components of old (~1,000 yr) recalcitrant terrestrial organic matter (Onstad et al. 2000; Raymond and Bauer 2001) whose structure has been altered by selective degradation operating over long periods as POM transport is retarded by multiple cycles of deposition/suspension. The ^{13}C depletion of seston relative to plants is consistent with a refractory origin because microbial degradation selectively removes labile ^{13}C-enriched components such as proteins and carbohydrates and leaves behind more refractory ^{13}C-depleted biochemicals such as cellulose, lipid, and lignin (Benner et al. 1987). Our findings suggest that applications of stable carbon and nitrogen isotopes for tracing organic-matter sources are confounded by the effects of a diagenetic (microbial) overprint. These processes should be given greater consideration in assessing the potential for using stable isotopes in organic geochemical studies designed to identify the sources of sedimentary organic matter.

The isotopic composition of freshwater seston was highly variable ($\delta^{15}N$ ranged from −5.7 to +10.6 and $\delta^{13}C$ ranged from −35.2 to −23.9‰), but representative of the seston isotopic variability in large river systems (Kendall et al. 2001). We can only speculate about processes producing seston highly depleted in ^{13}C and ^{15}N, but these samples were collected during specific events. Seston with the most negative $\delta^{13}C$ (−32 to −35.2‰) was collected during the first winter storm and runoff event in January 1999. Organic matter this depleted in $\delta^{13}C$ could reflect riverine inputs of organic matter produced in wetlands, including rice fields in the upper Sacramento River watershed, where methanogenesis and methane oxidation produce ^{13}C-depleted organic carbon (e.g., Goñi and Thomas 2000). These very negative $\delta^{13}C$ values could also reflect inputs of organic matter originally produced by phytoplankton blooms in the upstream reservoirs on the Sacramento River system (Kendall et al. 2001). Seston samples with negative $\delta^{15}N$ were all collected during July 2000 when cyanobacteria (*Synechocystis* sp., *Synechococcu*s sp., *Aphanothece* sp., *Aphanizomenon* sp., *Cyanobium* sp.) comprised a high proportion of phytoplankton biomass. In the ocean, cyanobacterial nitrogen fixation introduces isotopically light nitrogen (Minagawa and Wada 1986), which can subsequently be converted to isotopically light nitrate. Fertilizers are another potential source of ^{15}N-depleted nitrate (Macko and Ostrom 1994). The isotopic composition of the seston varies in response to changes in NH_4^+ or NO_3^- assimilation as well as variations in the isotopic signature of NH_4^+ or NO_3^- (McClusker et al. 1999). Regardless of the mechanisms, these extreme seston isotope ratios illustrate that the character of POM in the tidal river system changes at the scale of events, both hydrologic and biological, further confounding attempts to link the POM pool to specific plant sources.

Of the 166 seston samples collected in the downstream estuary, 56 fell within the interquartile ranges of primary producers (Fig. 8b) and, again, most of these occurrences were during algal blooms. Many of the other estuarine–marine seston samples had isotopic compositions depleted in

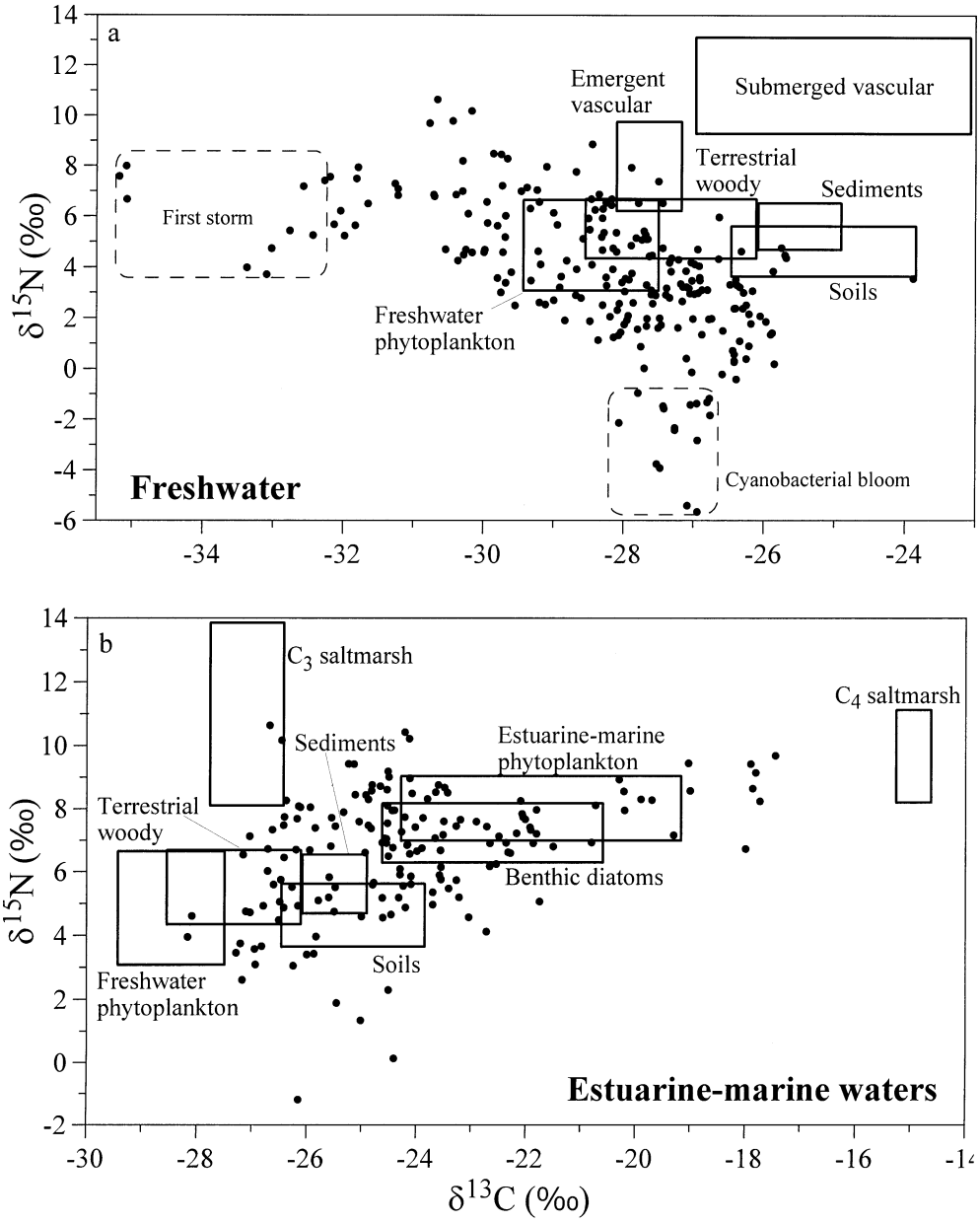

Fig. 8. Comparisons of the isotopic compositions (δ^{15}N vs. δ^{13}C) of soils, seston, sediments, and plants collected in (a) tidal freshwater domains and (b) estuarine–marine domains of SFBE (*see Fig. 1*). Rectangles show the interquartile ranges of δ^{15}N and δ^{13}C measured in each plant group (Fig. 4) and in soils and sediments collected in freshwater domains.

^{15}N or ^{13}C relative to the estuarine–salt-marsh primary producers. Because of the high variability in the isotopic composition of freshwater seston, simple mixing models that specify a fixed isotopic composition of POM at the riverine end member cannot be applied to the SFBE system as a tool for interpreting isotopic variability of seston within the estuary (Fig. 8b).

C, N isotopes as tracers of food sources—Results of this study illustrate two factors that confound the use of C-N stable isotopes to identify the ultimate origins of organic matter contained in the seston and sediments: (1) nonspecific, overlapping isotope ratios among the primary producer groups and (2) selective degradation and gradual transformation of organic matter over the duration of its retention within the watershed–surface water system, displacing the isotopic composition of organic matter from that of its parent plant source. These confounding factors (recognized by Sherr in 1982) are general and suggest that we should reconsider the conceptual model that organic matter has isotopic signals linking it to specific plant sources. The most profitable approach for identifying the food web base of complex ecosystems might be to probe the consumer biota directly and ask whether their isotopic composition is similar

to any primary producer groups (e.g., Peterson et al. 1985). This approach circumvents the second confounding factor because consumers selectively assimilate and extract essential elements and energy from the labile components of the POM (e.g., Lewis et al. 2001). However this approach does not overcome the confounding factor of nonspecific plant isotopic signatures. For example, the $\delta^{13}C$ of the clam *Potamocorbula amurensis* overlaps the $\delta^{13}C$ of both freshwater phytoplankton and terrestrial vegetation, so carbon isotope ratios cannot distinguish the relative contributions of the exogenous and autochthonous food supplies to this primary consumer in San Francisco Bay. However, when used to complement other biomarkers such as fatty acids, the isotopic composition of consumers is a useful corroborating measurement. The tissues of *Potamocorbula amurensis* in northern San Francisco Bay are enriched in algal-specific (polyunsaturated C_{20} and C_{22}) fatty acids but not in lipid biomarkers of terrestrial plants, suggesting that this suspension-feeder selectively consumes and assimilates available phytoplankton, even when phytoplankton biomass is a small proportion of the bulk POM (Canuel et al. 1995).

This example illustrates that stable isotopic information is perhaps most powerful when used as one component of a multicomponent attack on questions of energy supply to the food web base and/or studies assessing the origins (sources) of organic matter in aquatic environments. Natural isotopes of C and N do provide information as constraints on the energy supply to the food web base of the San Francisco Bay ecosystem. Seston, on average, has different isotope ratios in the freshwater and estuarine–marine domains (Fig. 8), which suggests that POM in the tidal river system has different sources or pathways of transformation than POM in the downstream estuary. This is consistent with lipid biomarker data showing differences in the sources and reactivity of POM in these two regions of the estuary (Canuel et al. 1995; Canuel 2001). This result is also consistent with carbon budgets (Jassby et al. 1993) showing that riverine inputs contribute ~90% of the total organic carbon supply to the upper estuary (Suisun Bay, Fig. 1), but autochthonous primary production contributes ~90% of the supply to South San Francisco Bay.

Isotopic information also provides clues about those plant groups most likely to contribute to the organic-matter supply. Within the Sacramento–San Joaquin River Delta, seston isotopic composition is farthest removed from the isotopic compositions of submerged and emergent vascular marsh plants but nearest to freshwater phytoplankton and terrestrial vascular plants (Fig. 8a). These results are consistent with compilations of carbon inputs and primary production in different habitat areas (Jassby and Cloern 2000), showing that the supply of organic carbon to the Delta is dominated by riverine inputs, much of the labile component of riverine loading comprises freshwater phytoplankton, autochthonous production is dominated by phytoplankton, and exports from freshwater marshes and production by submerged vascular plants are of secondary importance. Similarly, isotopic composition of seston in the estuary suggests that export of organic matter produced in salt marshes by C_3 and C_4 vascular plants is not an important source of POM (Fig. 8b), a conclusion reached by Spiker and Schemel (1979) in the first application of stable isotopes in this estuary; this conclusion is consistent with the large-scale filling and diking of San Francisco Bay's salt marshes. The organic carbon budget of South San Francisco Bay indicates that primary production in this marine lagoon subsystem is dominated by phytoplankton and benthic microalgae; this conclusion is supported by the overlapping isotope ratios of seston with both estuarine–marine phytoplankton and benthic diatoms. The relative contributions of these two microalgal sources cannot be distinguished, however, because of their similar isotope ratios (Fig. 8b).

Finally, comparisons in Fig. 8 suggest that POM in the riverine and estuarine–marine domains of SFBE is not simply a mixture of recently produced plant biomass and detritus (except during phytoplankton blooms). Rather, the bulk POM appears to be a highly variable matrix of aged and recalcitrant organic matter that masks the smaller components of labile POM (including phytoplankton) from which consumers extract materials and energy. An independent approach, using long-term incubations to measure the microbial assimilation of organic C, suggests that only about 10–35% of the POM is biologically available and that this labile component is correlated with phytoplankton biomass (W.S. Sobczak pers. comm.). If this interpretation is correct, then bulk POM is not a good indicator of the food resource used by the primary consumers.

Conclusions—Where secondary production is fueled by one or a few sources of organic matter having distinct isotopic signatures, natural isotopes can be valuable biomarkers for determining the relative importance of individual sources and for tracing trophic linkages at the food web base (Rau 1980). Where many plant communities and exogenous inputs supply organic matter, natural isotopes may not provide definitive information about the source(s) of energy that fuel heterotrophy because (a) the isotopic composition of primary producers is so variable in time and space that source-specific signatures become obscured (Sherr 1982; Hedges et al. 1988), (b) biogeochemical transformations in soils and sediments can operate over centuries/millennia to displace isotopic signatures of their organic matter from those of their plant sources, and (c) the labile components of POM can be masked by larger components of recalcitrant organic matter. Our results reinforce the practical advice of others (e.g., Michener and Schell 1994; Handley and Scrimgeour 1997): isotopic information, alone, cannot definitively reveal or measure the dominant sources of organic matter or the food supply to primary consumers in ecosystems having multiple and time-varying sources of autochthonous and exogenous organic matter. In complex ecosystems, answers to these fundamental questions can only be patched together with information from combined approaches, including measurement of multiple isotopes in organic matter and biota (Peterson et al. 1985; Currin et al. 1995; Deegan and Garritt 1997); isotopic composition of C and N in all the pools through which these elements cycle (Cifuentes et al. 1989); other biomarkers such as lipids, amino acids, or lignin compounds (Hedges et al. 1988; Canuel et al. 1995; Goñi and Thomas 2000); isotopic composition of specific compounds such as pigments, lipids, and lignin (Benner et al. 1987); direct mea-

surements of organic-matter sources (Coffin and Cifuentes 1999), production rates of consumers (Lewis et al. 2001), and food web dynamics (Finlay 2001); compilations of organic-matter budgets (Jassby and Cloern 2000); simulation models of C and N cycling (Koopmans et al. 1997); and manipulative experimentations (Hughes et al. 2000).

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