

# Study of East Matagorda Bay Productivity Final Report

By:

Luis A. Cifuentes and James E. Kaldy

Department of Oceanography

Texas A&M University

College Station, TX 77843

(409) 845-3380 (work phone)

(409) 862-3172 (fax)

cifuentes@ocean.tamu.edu

kaldy@nitro.tamu.edu

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Ms. Carla Guthrie

Texas Water Development Board

1700 N. Congress Ave.

Austin, TX 78711-3231

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# Introduction

Organic carbon, both allochthonous and autochthonous, is the currency of estuarine ecosystem processes. Although nitrogen and phosphorous are often factors limiting production (Howarth 1988), organic carbon is the basis of metabolism. In an estuary, the largest carbon pools are the dissolved inorganic and organic carbon (DIC & DOC, respectively). Measurements of pool size (i. e., concentration) are relatively easy to make; however, valuable ecological information comes from stable carbon isotope ( $\delta^{13}\text{C}$ ) measurements. Although comparatively more difficult to perform,  $\delta^{13}\text{C}$  allow us to determine the sources and sinks of the carbon, providing insight on the relative importance of specific processes within the system (Fogel and Cifuentes 1993). Additionally, the large DIC and DOC pools tend to integrate biological processes over periods similar to the residence time of a system (Cifuentes and Eldridge 1998), making them ideal tracers for biological and geochemical processes.

Stable isotope data combined with basic ecological data (i. e., residence time, input rates, etc.) provides a powerful measure of the relative importance of a particular source or sink. This information is critical to the description of complex food webs (Peterson and Fry 1987), which can define the function and ecosystem structure of an estuary. Isotope measurements can now be made more quickly and with greater precision as a result of advances in isotope ratio mass spectrometry (IRMS). We developed a method that couples a DOC analyzer with and IRMS (TOC-IRMS). Using a similar type of approach (GC-c-IRMS), our lab has previously developed a rapid and precise method for measuring the concentration and isotope ratio of DIC ( $\delta^{13}\text{C}$ -DIC; Salata et al. 2000). Using both these new methods, we are able to collect and analyze a large number of data points, which will greatly enhance the spatial and temporal resolution as well as the predictive capacity of food web analysis.

Organic carbon is the ultimate currency for ecosystem processes since it is the metabolic energy source. Because most organisms assimilate carbon and specific carbon flows are often characterized by well known isotopic fractionations, isotopic

measurements of multiple carbon pools can be used to define the mechanistic linkages between watershed resources and ecosystem processes. For example, the largest isotope fractionation results from photosynthetic carbon fixation due to preferential uptake of  $^{12}\text{C}$ -DIC ( $\epsilon = -10$  to  $-20$  ‰; Fogel and Cifuentes 1993). In contrast, heterotrophic DOC assimilation by bacteria ( $\epsilon = -2$  to  $+2$  ‰; Coffin et al. 1994) and trophic level transfers ( $\epsilon = +1$  ‰; Peterson and Fry 1987) have a much smaller fractionation. Thus, while fractionation results in a shift in the isotope ratio of the assimilating organism,  $\delta^{13}\text{C}$  data from various carbon reservoirs can provide information on the major sources of carbon to an ecosystem. Although large geochemical pools such as DIC and DOC have been ignored in most food web studies, these pools have the advantage of integrating processes over periods more similar to the residence time of the system (Cifuentes and Eldridge 1998A). Moreover, Coffin et al. (1993) showed that there is a strong relationship between  $\delta^{13}\text{C}$ -DIC and  $\delta^{13}\text{C}$ -DOC and  $\delta^{13}\text{C}$  in biotic pools. Based on these concepts, Eldridge and Cifuentes (2001) have shown that isotope-balance models of DIC and DOC can be used to establish the sources and sinks of these materials.

Estuarine energy relationships based on  $\delta^{13}\text{C}$  of DOC are better than those based on POC (particulate organic carbon; Eldridge and Cifuentes 2001). Stable isotopic analysis has recently been used to determine why estuarine  $^{13}\text{C}$ -POC is not representative of “edge” habitat (i. e., marsh and non-point sources). The relative contribution of edge material to the DOC is much greater than to the POC because of selective processes (i. e., sedimentation) within the estuary. Additionally, POC tends to be more labile relative to DOC. As a result, the edge signal is generally not manifested in the isotope ratio of the POC. Equal fluxes of edge POC and DOC (Fig. 1) to the estuary when mixed with phytoplankton sources result in different isotope ratios. Even at low levels of primary production ( $<100 \text{ gC m}^{-2} \text{ y}^{-1}$ ), substantial edge outwelling (i. e., high edge to estuarine area) is required before a edge signal appears in the estuarine POC. In fact, at typical primary production rates ( $200\text{-}300 \text{ gC m}^{-2} \text{ y}^{-1}$ ) edge values are not predicted even with exceptionally high edge export. The opposite result is observed in the DOC analysis. That is, an edge DOC signal is seen in the estuarine  $\delta^{13}\text{C}$ -DOC at edge:estuarine areas as low as 0.8.

To determine the major sources of carbon into the system, we sampled East Matagorda Bay (Fig. 1) for the concentration and isotope ratio of the DIC and DOC pools as well as for making measurements of total suspended solids (TSS) nutrients (i. e., nitrogen, phosphorus and silicate) and pigment composition (with HPLC). Accessory data was provided by TWDB. Selected other isotopic measurements were also performed. Sampling took place in December 2000, June 2001 and December 2003.

## Study Area

East Matagorda Bay is approximately rectangular (Fig. 2) with an average width of 6 km and length of about 37 km (see Kraus and Militello 1999). Caney Creek discharges into the system at the eastern border while the Colorado River channel forms the western boundary. Originally, this bay was part of the larger Matagorda Bay system, but was cut off by a rapidly prograding delta that formed during the 1930's. Today, East Matagorda Bay has a mean surface area of 155.6 km<sup>2</sup> and volume of 1.71x10<sup>8</sup> m<sup>3</sup>. Depths typically range from 0.6 to 1.2 m. Exchange with GOM water occurs to a limited extent at Mitchell's Cut on the eastern side of the bay. Another channel, SW Cut has been permitted by the US Army Corp of Engineers. Local runoff may derive from various small creeks, but associated wetlands are separated from the bay by the GIWW. The extent to which East Matagorda Bay relies on the Colorado River (partly through the GIWW) versus local runoff for freshwater input is not known. Consequently, the impact that these inputs have on the productivity of the system is also not well understood.

## Methods

### *Sampling*

Sampling was performed in December 2000, June 2001 and December 2003. Sixteen stations were occupied over a two-day period with an additional station deployed in June 2001 (Table 1). Owing to problems with the stable carbon isotope analyses of DOC in the first two samplings, and additional set of samples was collected in December 2003. The same stations were deployed in both December samplings. All water samples

were collected from a depth of about 0.5 m with a peristaltic pump. Sub-samples for analyses were drawn from the cubitainers and filtered as appropriate. All sub-sampling was conducted in the field. Triplicate sub-samples for DIC (30 ml) were transferred to quorpak™ bottles, fixed with mercuric chloride, sealed and placed on ice. For pigment samples, water was filtered through GFF filters, placed in appropriately labeled petri dishes and stored in liquid nitrogen. The amount of sample filtered was noted for quantification. Samples for TSS analyses were collected similarly. Triplicate sub-samples of filtrate (5-10 ml) were placed in clean (i.e. acid washed & combusted) scintillation vials, and frozen immediately on dry ice. These were used for DOC concentration and stable carbon isotopes measurements. For nutrient analyses, a portion of the filtrate (30 ml) was transferred to Nalgene™ sample bottles and frozen on dry ice. Samples were returned to TAMU and stored in freezers prior to analyzes.

#### *T°C, Salinity, pH, and Dissolved Oxygen*

Staff of the Texas Water Development Board (TWDB) at each sample collection station using a Hydrolab H20 made temperature, salinity, pH and dissolved oxygen measurements. Depths of measurement were usually approximately mid-depth for this shallow bay.

#### *Total Suspended Solids*

Total suspended solids were determined gravimetrically by standard methods. In December 2003 we measured the elemental composition of suspended material using a standard elemental analyzer.

#### *Dissolve Inorganic Carbon (DIC) and $\delta^{13}\text{C}$ -DIC*

The concentration and stable carbon isotope ratio of DIC were measured according to Salata et al. (2000).

### *Dissolved Organic Carbon (DOC) and $\delta^{13}\text{C}$ -DOC*

DOC concentrations were determined with a Shimadzu TOC 5000 analyzer following standard analytical procedures. For the  $\delta^{13}\text{C}$ -DOC analyses an OI TOC 1010 was connected to the Finnigan-MAT IRMS (Fig. 3A). Briefly, the method consisted of  $\text{CO}_2$  production by oxidation of the DOC using sodium persulfate. This gas then flows through an elemental copper trap to remove halogens and into a cold trap to remove the  $\text{CO}_2$  from the carrier flow (Fig. 3B). The cold trap consists of 5 turns of 1/8<sup>th</sup> inch tubing with approximately 0.5g Porapak Q (50-80mesh) (Alltech Associates, Deerfield, IL.). During trapping mode the trap is held at  $-80^\circ\text{C}$  and the valves are configured to allow the carrier flow to pass through the trap and out to the atmosphere. Once trapping is complete the valves are reconfigured so that carrier flow passes straight to the atmosphere and the trap is isolated to the inlet system of the IRMS. The trap is then heated to release and expand the  $\text{CO}_2$  into the bellows system of the IRMS where it is analyzed in dual inlet mode.

### *Nutrients*

Nutrients were measured with an auto-analyzer by marine technicians at the Department of Oceanography, Texas A&M University according to Biggs et al. (1982).

### *HPLC Pigments*

High performance liquid chromatography (HPLC) was used to quantify photopigment concentrations in water samples. Aliquots (0.1 to 0.5 L) of water were filtered under a gentle vacuum ( $<50$  kPa) onto 2.5 cm diameter glass fiber filters (Whatman GF/F), immediately frozen, and stored at  $-80^\circ\text{C}$ . For analyses, frozen filters were placed in 100% acetone (1.00 ml), sonicated, and extracted at  $-20^\circ\text{C}$  for 12 - 20 h. Filtered extracts were be injected into a Shimadzu HPLC equipped with a single monomeric (Rainin Microsorb-MV, 0.46 x 10 cm, 3 mm) and a polymeric (Vydac 201TP, 0.46 x 25 cm, 5 mm) reverse-phase  $\text{C}_{18}$  column in series. A nonlinear binary gradient was used for pigment separations (Pinckney et al. 1996). Absorption spectra and chromatograms (440 nm) were acquired using a Shimadzu SPD-M10av photodiode array

detector. Pigment peaks were identified by comparison of retention times and absorption spectra with pure standards, including chlorophylls *a*, *b*, B-carotene, fucoxanthin, lutein, canthaxanthin, echinenone, gyroxanthin, peridinin, alloxanthin, and zeaxanthin (DHI, Denmark). Other pigments were identified by comparison to extracts from phytoplankton cultures and quantified using the appropriate extinction coefficients (Jeffrey et al. 1997).

We used CHEMTAX (CHEMical TAXonomy), a matrix factorization program, to calculate algal class abundances based on the concentrations of algal photopigments (Mackey et al. 1996). The program uses a steepest descent algorithm to determine the best fit based on an initial estimate of pigment ratios for algal classes. Input for the program consisted of a raw data matrix of photopigment concentrations obtained by the HPLC analyses and an initial pigment ratio file. The data matrix was subjected to a factor minimization algorithm that calculated a best-fit pigment ratio matrix and a final phytoplankton class composition matrix. The class composition matrix is expressed as relative or absolute values for specified photopigments. The absolute chlorophyll *a* (Chl *a*) contribution of each class is particularly useful because it partitions the total Chl *a* into major phytoplankton groups. Full discussions, validation, and sensitivity analyses of CHEMTAX are provided in Mackey et al. (1996).

## Results

The Hydrolab and chemical data for samples taken in December 2000, June 2001 and December 2003 are found in Tables 2, 3 and 4, respectively. The HPLC pigment data for December 2000 and June 2001 are shown in Tables 6 and 7, respectively. CHEMTAX results for both dates are given in Table 8. No pigment data is reported for December 2003.

In the original scope of work, we intended to measure the concentration and isotopic ratio of DOC under low (summer) and high (winter) flow conditions. Due to unforeseen problems with the isotope ratio mass spectrometer, we were not able to measure the isotopic ratio of DOC for samples taken in June and December 2001. As

discussed below, the DOC samples taken in December 2001 were contaminated and will henceforth be excluded from further discussions. By the time the analytical system was functional, we determined the June 2001 samples had been stored too long and were unsuitable for measurement. It was decided in consultation with Dr. David Brock, contract manager, to conduct additional sampling. Fiscal constraints, however, only allowed for one additional set of samples, which were taken in December 2003. Therefore, stable isotope data for DOC will only be reported for one season.

### *Hydrographic Data*

As expected mean temperature was significantly higher in June compared with December (Table 5). Averages were 30.58°C in June 2001 and 11.33°C and 12.60°C in December 2001 and 2003, respectively. There was relative little variation within system. In contrast, mean salinity (Table 5) was similar between June and December 2001, as expected in view of the generally low rainfall in the months previous to sampling. In December 2003, however, average salinity was about 5 ‰ lower. In contrast, pH (Table 5) did not vary significantly between seasons, with mean values close to 8, or just slightly less than typical seawater numbers. Average dissolved oxygen (Table 5) was lower in June, 6.25 mg/L compared with 9.53 mg/L and 9.28 mg/L in December 2001 and 2003, respectively.

### *Total Suspended Solids*

The TSS ranged from 17 to 298 mg/L in December and from 35 to 215 mg/L in June (Table 5). Mean values were close to 100 mg/L in both 2001 samplings, but was lower in December 2003 – 73.41 mg/L. Generally, higher TSS was observed at higher salinities (Fig. 4).

### *Dissolved Inorganic Carbon*



We observed DIC values greater than typical seawater concentrations (2.2 mM) in much of East Matagorda Bay (Fig. 5). No DIC data was available for December 2003. Concentrations ranged from 1.7 to 3.9 mM, with average numbers being quite similar in December and June (Table 5).

The  $\delta^{13}\text{C}$  of DIC ranged from  $-9.36$  to  $-0.74\text{‰}$  (Table 5). No isotopic data was available for December 2003. Mean values were more negative in December compared with June, but this difference was not statistically significant. With the exception of two outliers in June, the  $\delta^{13}\text{C}$  of DIC was generally more negative at lower salinities (Fig. 6).

#### *Dissolved Organic Carbon*

As state above, the DOC data taken during December 2001 was likely contaminated and will be excluded from subsequent discussions. The DOC ranged from 135 to 454  $\mu\text{M}$  in December 2003 (Table 5). The mean DOC was 259  $\mu\text{M}$ . In June, values were higher, ranging from 135 to 899  $\mu\text{M}$  and averaging 310  $\mu\text{M}$ . The typical conservative trend with salinity (i. e., straight line) with higher values at low salinities was not observed (Fig. 7).

Stable carbon isotope data for DOC taken in December 2003 are depicted in Figure 8. Values ranged from  $-26.4$  to  $-23.7\text{‰}$ . Contrary to typical estuarine systems, the most negative  $\delta^{13}\text{C}$  were observed at high salinities where the freshwater input was lowest.

#### *Nutrients*

With the exception of one station, a possible outlier, dissolved inorganic nitrogen (nitrate+nitrite+ammonium) was below 10  $\mu\text{M}$  in summer (Fig. 9). Higher values were generally observed in December (Fig. 9) and this was evident in the average concentrations of ammonium, nitrate and nitrite (Table 5). Nitrate was the dominant

nitrogenous nutrient in both seasons. In contrast, phosphate had similar averages in December and June (Table 5) , but there was significant scatter throughout the system (Fig. 10). Higher mean silicate values were seen in June with typically elevated values at lower salinities (Fig. 11).

### *Biomass*

Chlorophyll a, a proxy for biomass was similar at both sampling times (Table 5). Data was not available for December 2003. Values ranges from 2 to 23 µg/L and showed no obvious trend with salinity (Fig.12). CHEMTAX analysis indicated that diatoms and cryptophytes were dominant in December, whereas more cyanobacteria and prochlorophytes were present in June (Fig. 13).

## Discussion

We originally planned to sample East Matagorda Bay twice with the intent of sampling during low and high inflow to the bay. There was low inflow during much of 2001. Not surprisingly salinity and DIC were similar during the June and December 2001 sampling periods making the primary objective of the project difficult to meet. After recognizing that DOC samples had been contaminated during December 2001, we changed the scope of work and added another field effort in December 2003. In the 2003 sampling, we encountered freshwater (0.30 ‰) and encountered lower salinity throughout the bay. The lower mean salinity in December 2003 (15.67 ‰) compared with June 2001 (19.08 ‰) suggested the bay was about 15 % fresher.

In typical estuaries, higher DOC concentrations are associated with river inputs and not coastal water – higher salinity waters. With the exception of a few high numbers, winter and summer values were consistent with DOC concentrations reported for other estuarine systems. Generally, DOC concentrations are higher in the inflow to estuaries compared with the coastal mixing waters. In contrast, higher DOC values were observed at estuarine salinities and not in the river inputs. Although there was more fresh water in

East Matagorda Bay during December 2003, we measured less DOC in winter compared with summer (less freshwater). These observations suggest either edge inputs or significant turnover of carbon in the sediments releasing DOC to overlying water.

We successfully measured  $\delta^{13}\text{C}$  of DOC in December 2003. Throughout the bay, isotopic data were consistently in the range of values (-26.4 to -23.7 ‰) reported for terrestrial C3 material. At this time, C:N of suspended material ranged from 9.1 to 24.8. These C:N – much greater than typical marine organic matter, imply terrestrial organic matter also contributed to the particulate organic matter in the bay during winter. It must be noted, however, that the most negative  $\delta^{13}\text{C}$  measured in DOC occurred at the highest salinities (Fig. 8). It is not likely that phytoplankton production in these waters, incorporating DIC in the range of -3 ‰ (see Fig. 6) would produce algal carbon in the range of -26 ‰ (see Fogel and Cifuentes 1993). This fact, in consideration of the low biomass measured in the previous December sampling (Chlorophyll a was not measured in December 2003, but was in December 2001) - 2.13 to 22.98  $\mu\text{g/L}$  – lead us to conclude that the DOC in East Matagorda Bay during December 2003 was of terrestrial origin. Most likely DOC was entering the bay from its margins in addition to sources from river inflow. As we did not measure the isotopic ratio of DOC diffusing from sediments, we cannot exclude sediments as another possible source of DOC.

DIC concentrations higher than seawater values (2.2 mM) imply either calcium carbonate dissolution (rivers with limestone rich draining basins) or that respiration dominates algal production in the system. Many measured DIC concentrations in East Matagorda Bay were above seawater values. Moreover, the linear relationship often seen with salinity was not observed in the data (Fig. 5). Combined with the significant scatter in the data, we interpret this to mean that respiration from sediments was a dominant process in this system. The  $\delta^{13}\text{C}$  of DIC (Fig. 6) were consistent with this interpretation.

Biomass in East Matagorday Bay was not particularly high, averaging close to 10  $\mu\text{g/L}$  (Table 5). The DIN was low (< 2  $\mu\text{M}$ ) throughout much of the bay. This is not unexpected as conditions for high phytoplankton production are not ideal in the bay.

First, the TSS was typically above 50 mg/L with values reaching high levels at the higher salinities (Fig. 4). Second, DIN concentrations were often low ( $< 2 \mu\text{M}$ ) in the bay (Fig. 9) and N deficit was more evident in June 2001. Finally, based on N:P, the system was N limited during both seasons (N:P  $< 10$ ) (Table 5). It is likely both low light levels and relatively low nitrogen concentrations limited biomass accumulation.

Diatoms dominated both in June and December 2001, accounting for about 60 to 70 % of the biomass – as estimated by CHEMTAX analysis (Fig. 13). Silicate was available throughout the bay during both seasons, supporting the diatom population. Chryptophytes were the only other dominant alga in December 2001, whereas cyanobacteria and prochlorophytes were present at similar levels in June 2001. Two freshwater stations were measured in June 2001 and diatoms were dominant there also. Finally, it appears the presence of cyanobacteria and prochlorophytes were related to availability of N and P.

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Table 1. Description of sampling sites in East Matagorda Bay and GPS coordinates for the December and June samplings.

Site	Description	GPS		GPS	
		Latitude	Longitude	Latitude	Longitude
		Dec-00		Jun-01	
1	Colorado River above GIW	28 41.27	95 58.56	28 41.27	95 58.56
2	Colorado River near mouth	28 38.04	95 58.17	28 38.04	95 58.17
3	GIW at Old Gulf	28 42.98	95 53.53	28 42.98	95 53.53
4	East Matagorda Bay	28 41.62	95 53.15	28 41.62	95 53.15
5	East Matagorda Bay	28 39.31	95 54.00	28 39.31	95 54.00
6	Little Boggy	28 42.62	95 54.84	28 42.62	95 54.84
7	East Matagorda Bay	28 43.30	95 49.31	28 43.30	95 49.31
8	East Matagorda Bay	28 41.11	95 49.33	28 41.11	95 49.33
9	Chinquipin	28 45.19	95 46.21	28 45.19	95 46.21
10	East Matagorda Bay	28 44.15	95 46.29	28 44.15	95 46.29
11	East Matagorda Bay	28 42.33	95 46.29	28 42.33	95 46.29
12	East Matagorda Bay	28 43.32	95 44.15	28 43.32	95 44.15
13	East Matagorda Bay	28 44.10	95 42.61	28 44.10	95 42.61
14	Mitchell's Cut	28 45.03	95 39.49	28 45.03	95 39.49
15	Caney Creek at 457	28 55.11	95 41.54	28 55.11	95 41.54
16	Old GIW	28 45.41	95 40.04	28 45.41	95 40.04
1*	Colorado River at Bay City			28 59.05	95 00.02

Table 2. Hydrographic and chemical data for samples collected December 2000. Depth is total station depth, not depth of measurement. NA = not available, BDL = below detection limits.

Site	Depth (ft)	T°C	pH	DO	Salinity	DIC (mM)	$\delta^{13}\text{C}$ (‰)	DOC (uM)	TSS (ppm)	Nitrate (uM)	Nitrite (uM)	Ammonium (uM)	Urea (uM)	Phosphate (uM)	Silicate (uM)
Dec-00															
1	NA	12.7	8.34	9.18	10.5	3.91	-8.56	1288	17.7	238.67	0.88	BDL	BDL	5.89	89.32
2	ca 11	13.058	8.23	8.95	25.0	2.63	-3.21	1637	164.0	40.24	0.40	0.12	BDL	2.98	39.04
3	ca 15	11.57	8.23	9.53	23.2	2.36	-3.10	1197	56.3	14.36	0.16	BDL	0.23	1.41	15.95
4	3	11.24	8.27	9.27	23.2	2.08	-2.94	1340	50.3	1.44	BDL	BDL	BDL	0.64	5.79
5	3	11.37	8.02	8.7	24.1	1.89	-3.38	1663	65.0	0.73	BDL	0.47	BDL	0.41	15.03
6	1.5	12.54	8.21	8.88	25.4	2.29	-2.77	1455	72.0	19.38	0.28	0.42	0.30	1.53	25.72
7	3	11.34	8.29	9.31	22.3	1.92	-2.80	1269	38.0	0.55	BDL	BDL	BDL	0.42	3.36
8	3.5	11.93	8.13	8.52	23.3	2.08	-3.56	1213	297.5	1.14	0.19	5.02	4.80	1.78	22.84
9	NA	11.03	8.5	11.93	9.6	1.70	-4.06	1980	52.0	22.64	2.18	7.22	0.56	4.84	38.56
10	2	11.6	8.16	9.41	22.5	2.19	-3.37	1536	262.0	1.44	0.12	0.29	BDL	0.99	24.22
11	3	11.24	8.17	9.63	22.4	2.07	-3.28	2483	86.7	0.76	0.08	0.11	BDL	0.48	18.28
12	2	10.83	8.26	9.6	22.8	1.97	-2.71	1888	94.8	0.91	0.06	0.09	BDL	0.49	15.56
13	1.5	10.5	8.23	9.7	23.2	1.99	-2.68	1370	50.5	0.45	BDL	BDL	BDL	0.61	10.96
14	ca 8	10.29	8.21	9.76	21.2	1.94	-3.06	1338	94.6	1.57	0.19	BDL	BDL	0.51	27.54
15	ca 6	10.83	8.15	9.45	11.7	2.19	-7.85	1412	46.2	NA	NA	NA	NA	NA	NA
16	1	9.2	8.33	10.71	23.2	2.20	-2.94	1469	52.8	0.51	BDL	BDL	0.31	0.83	16.22

Table 3. Hydrographic and chemical data for samples collected in June 2001. Depth is total station depth, not depth of measurement. NA = not available, BDL = below detection limits.

Site	Depth (ft)	T°C	pH	DO	Salinity	DIC (mM)	$\delta^{13}\text{C}$ (‰)	DOC (uM)	TSS (ppm)	Nitrate (uM)	Nitrite (uM)	Ammonium (uM)	Urea (uM)	Phosphate (uM)	Silicate (uM)
Jun-01															
1	NA	31.29	7.89	7.47	10.6	2.93	-4.50	NA	20.0	BDL	BDL	0.37	BDL	1.85	60.29
2	NA	30.3	7.81	6.6	20.5	2.28	-2.38	187	87.3	0.87	0.16	0.10	BDL	0.38	36.00
3	NA	29.6	7.76	5.55	20.7	2.24	-2.16	248	181.0	1.22	0.49	0.37	BDL	1.09	44.77
4	4.5	29.84	7.94	6.81	19.0	2.26	-1.69	266	65.3	1.03	BDL	0.51	BDL	1.74	44.10
5	5	29.06	7.79	5.00	20.2	2.12	-2.22	433	78.0	2.02	0.18	2.62	0.46	1.92	32.38
6	NA	31.27	7.67	4.5	19.7	2.52	-3.23	135	171.0	2.98	0.74	4.25	0.22	1.86	50.18
7	4.66	29.1	7.85	6.02	21.0	2.10	-1.88	374	100.0	BDL	BDL	0.05	BDL	1.00	54.17
8	4.33	29.1	7.88	5.88	22.8	1.98	-1.06	171	54.3	BDL	0.01	0.03	BDL	1.15	51.50
9	5.5	29.42	7.82	3.00	13.1	2.59	-3.87	564	64.0	1.73	0.07	0.28	BDL	1.85	43.50
10	3.75	31.11	7.97	6.97	22.0	2.20	-1.47	245	215.0	BDL	0.04	0.72	BDL	1.12	55.25
11	4.8	30.5	7.98	6.97	22.7	2.18	-1.04	249	144.3	BDL	0.03	0.24	BDL	1.32	60.36
12	4.25	30.76	7.98	5.85	22.8	2.32	-1.84	293	77.5	BDL	0.03	0.35	0.10	1.05	58.74
13	1.5	32.46	8.09	7.30	22.6	2.19	-1.39	252	106.2	BDL	0.01	0.22	BDL	1.04	56.96
14	9	31.51	8.18	6.38	23.5	2.09	-0.74	169	94.5	BDL	BDL	0.04	BDL	0.12	2.00
15	NA	31.54	8.78	9.22	0.5	2.09	-1.42	166	83.5	BDL	BDL	0.13	BDL	BDL	0.50
16	3.3	32.38	8.15	6.51	23.5	2.20	-9.36	899	58.5	97.50	4.13	0.42	0.50	8.48	184.49
1*	NA	31.92	8.224	7.45	0.3	2.99	-6.44	263	35.0	1.37	0.20	2.40	0.29	1.48	66.99



Table 4. Hydrographic and chemical data for samples collected December 2003. Depth is total station depth, not depth of measurement. NA = not available, BDL = below detection limits.

Site	Depth (ft)	T°C	pH	DO	Salinity	DOC (uM)	DOC <sup>13</sup> (‰)	TSS (ppm)	Nitrate (uM)	Nitrite (uM)	Ammonium (uM)	Urea (uM)	Phosphate (uM)	Silicate (uM)	Elemental Data		
															%N	%C	C/N
Dec-03																	
1	16.0	12.9	8.10	8.54	21.34	219	-25.8	68.67	3.39	0.33	0.88	0.48	1.26	33.83	1.3	16.2	14.0
2	18	12.9	7.88	8.99	1.89	281	-24.8	20.00	83.41	1.38	8.81	3.08	9.34	32.20	0.7	10.4	16.4
3	7.0	12.4	8.01	8.91	20.85	210	---	50.00	0.97	0.18	0.59	0.48	1.08	25.75	1.2	11.9	11.6
4	1.0	12.2	7.95	9.90	4.39	355	-25.0	44.50	14.83	0.67	6.02	0.77	2.72	45.52	0.8	10.4	15.7
5	5.0	12.8	8.04	8.87	20.53	260	-23.9	71.33	0.51	0.13	0.69	0.45	1.66	40.76	2.0	15.7	9.1
6	4.0	12.8	8.01	8.77	21.06	244	-23.8	66.33	0.48	0.10	0.50	0.50	1.22	39.58	0.9	11.9	16.2
7	3.0	12.5	7.99	11.01	3.61	431	-23.7	92.00	18.50	0.57	0.58	0.38	1.37	46.41	2.0	16.9	9.7
8	8.0	12.8	8.11	9.71	21.13	235	-25.5	43.25	17.77	0.51	1.18	0.56	2.76	28.81	1.2	13.6	13.6
9	3.5	13.0	8.16	9.97	25.18	221	-26.4	26.75	0.60	0.14	0.79	0.56	0.94	20.36	0.7	10.6	16.7
10	9.0	13.9	7.63	7.94	0.14	454	-24.2	56.00	21.85	2.81	3.13	1.23	8.03	44.17	0.4	7.4	23.1
11	NA	12.3	7.94	9.63	0.28	203	-24.8	19.00	133.86	0.75	2.94	0.60	9.16	40.49	0.5	11.3	24.8
12	5	12.3	8.22	9.18	22.00	224	-24.1	92.33	0.28	0.11	0.75	0.46	1.14	26.10	0.9	10.3	13.1
13	3.0	12.6	8.20	9.19	23.16	188	-25.4	177.00	0.13	0.10	0.50	0.46	0.96	24.10	1.0	11.2	13.2
14	2	13.2	8.25	9.21	23.05	186	-23.7	84.00	0.05	0.11	0.45	0.45	0.92	26.04	0.9	11.7	15.0
15	5	12.0	8.21	9.2	21.31	207	-23.9	166.67	0.03	0.10	0.42	0.41	1.23	29.50	1.2	16.0	15.6
16	3.5	11.7	8.27	9.45	20.82	223	-24.0	96.67	0.08	0.08	0.45	0.36	0.87	13.48	1.5	16.4	12.6

Table 5. Minimum, maximum, average and standard deviations for parameters measured in East Matagorda Bay in December 2000 and June 2001. Ave. = average; Std. = standard deviation; NA = not available; Ex = data excluded.

Parameter	Minimum			Maximum			Ave.	Std.	Ave.	Std.	Ave.	Std.
	Dec. '01	Dec. '03	June '01	Dec. '01	Dec. '03	June '01	Dec. '01		Dec. '03		June '01	
T°C	9.20	11.7	29.06	13.06	13.90	32.46	11.33	0.96	12.60	0.50	30.58	1.18
Salinity (‰)	9.60	0.14	0.30	25.40	25.18	23.50	20.85	5.20	15.67	9.60	19.08	7.47
pH	8.02	7.63	7.67	8.50	8.27	8.78	8.23	0.11	8.06	0.17	7.97	0.26
DO (mg/L)	8.52	7.94	3.00	11.93	11.01	9.22	9.53	0.82	9.28	0.69	6.25	1.39
TSS (mg/L)	17.71	19.00	35.00	297.50	177.00	215.00	93.77	79.94	73.41	45.79	100.03	50.86
DIC (mM)	1.70	NA	1.98	3.91	NA	2.99	2.21	0.50	NA	NA	2.27	0.25
δ13C (‰)	-8.56	NA	-9.36	-2.68	NA	-0.74	-3.77	1.77	NA	NA	-2.51	2.27
DOC (µM)	Ex	186	135	Ex	454	899	Ex	Ex	259	82.6	310	193
Nitrate (µM)	0.45	0.03	0.00	238.67	133.86	97.50	22.99	60.81	18.55	37.19	6.71	24.21
Nitrite (µM)	0.00	0.08	0.00	2.18	2.81	4.13	0.30	0.57	0.50	0.71	0.37	1.02
Ammonium (µM)	0.00	0.42	0.03	7.22	8.81	4.25	0.92	2.16	1.79	2.40	0.67	1.21
Urea (µM)	0.00	0.36	0.00	4.80	3.08	0.50	0.41	1.23	0.70	0.67	0.08	0.17
Phosphate (µM)	0.41	0.87	0.00	5.89	9.34	8.48	1.59	1.69	2.79	3.07	1.62	1.92
Silicate (µM)	3.36	13.48	0.50	89.32	46.41	184.49	24.56	20.62	32.32	9.71	52.20	39.93
N:P	0.61	0.45	0.03	40.68	15.01	12.04	7.02	10.28	4.37	4.99	1.86	3.06
Chla (µg/L)	2.13	NA	3.48	22.98	NA	17.11	7.99	5.73	NA	NA	8.24	3.65

Table 6. HPLC pigment data for December 2000. Abbreviations: Perid = Peridin; 19'Bfuco = 19'-butanoyloxyfucoxanthin; Fuco = fucoxanthin; 19'HFuco = 19'-hexanoyloxyfucoxanthin; Viola = Violaxanthin; Myxo = Myxoxanthophyll; Diad = Diadinoxanthin; Allox = Alloxanthin; Diat = Diatoxanthin; Zeax = Zeaxanthin; BChla; Canth = Canthaxanthin; Chl b = Chlorophyll b; Chl a = Chlorophyll a; Total Chla = Chlorophyll a+Chlorophyllide a; Echin = Echinone; B-Car = B-Carotene; Gyrox = Gyroxanthin.

Site	Perid	19'BFuco	Fuco	19'HFuco	Viola	Myxo	Diad	Allox	Diat	Lutein	Zeax	BChla	Canth	Chl b	Chl a	Total Chla	Echin	B-Car	Gyrox
Dec-00																			
1	0.000	0.000	0.338	0.000	0.000	0.000	0.000	2.349	0.763	0.569	0.752	0.000	0.000	0.562	7.522	7.683	0.788	0.000	0.000
2	0.000	0.000	4.584	0.000	0.000	0.000	1.694	1.942	0.454	0.000	0.185	0.000	0.000	0.000	11.869	11.869	0.000	0.000	0.000
3	0.000	0.000	2.899	0.000	0.000	0.000	0.482	0.660	0.373	0.000	0.681	0.000	0.000	0.000	5.736	5.736	0.000	0.000	0.000
4	0.000	0.000	1.327	0.000	0.000	0.000	0.268	0.238	0.211	0.000	0.266	0.000	0.000	0.140	2.229	2.229	0.000	0.000	0.000
5	0.000	0.000	1.415	0.000	0.000	0.000	0.229	0.372	0.000	0.000	0.000	0.000	0.000	0.000	3.925	3.925	0.000	0.000	0.000
6	0.000	0.822	3.631	0.000	0.000	0.000	0.719	0.758	0.287	0.000	0.946	0.000	0.000	0.000	7.552	8.267	0.000	0.000	0.000
7	0.000	0.000	1.419	0.000	0.000	0.000	0.364	0.216	0.000	0.000	0.000	0.000	0.000	0.533	2.285	2.430	0.000	0.000	0.000
8	0.000	0.000	1.589	0.000	0.000	0.000	0.340	0.515	0.000	0.000	0.424	0.000	0.000	0.000	2.812	2.812	0.000	0.000	0.000
9	4.771	0.000	1.532	0.000	1.226	0.000	6.335	0.888	0.300	1.142	0.164	0.000	0.000	1.795	22.985	22.985	0.247	0.579	0.000
10	0.000	0.000	1.312	0.000	0.000	0.000	0.453	0.268	0.000	0.000	0.000	0.000	0.000	0.978	2.659	2.659	0.000	0.000	0.000
11	0.000	0.000	4.237	0.000	0.000	0.000	1.578	0.834	0.000	0.000	0.000	0.000	0.000	0.373	8.982	8.982	0.000	0.000	0.000
12	0.000	0.000	7.155	0.000	0.000	0.000	2.752	0.845	0.283	0.000	0.000	0.000	0.000	0.477	14.542	14.542	0.175	0.000	0.000
13	0.166	0.000	4.489	0.000	0.000	0.000	2.846	0.614	0.228	0.000	0.000	0.000	0.000	0.314	9.932	5.652	0.151	0.257	0.000
14	0.255	0.000	4.297	0.000	0.000	0.000	1.974	0.620	0.176	0.000	0.914	0.000	0.000	0.333	9.715	9.715	0.000	0.000	0.000
15	0.000	0.000	0.775	0.000	0.000	0.000	0.439	0.252	0.761	0.552	0.638	0.000	0.000	0.000	2.126	2.126	0.000	0.000	0.000
16	0.563	0.518	5.132	0.000	0.197	0.000	4.354	0.957	0.263	0.157	0.477	0.000	0.000	0.593	12.979	13.679	0.169	0.424	0.000

Table 7. HPLC pigment data for June 2001. Abbreviations: Perid = Peridin; 19'Bfuco = 19'-butanoyloxyfucoxanthin; Fuco = fucoxanthin; 19'Hfuco = 19'-hexanoyloxyfucoxanthin; Viola = Violaxanthin; Myxo = Myxoxanthophyll; Diad = Diadinoxanthin; Allox = Alloxanthin; Diat = Diatoxanthin; Zeax = Zeaxanthin; Bchla; Canth = Canthaxanthin; Chl b = Chlorophyll b; Chl a = Chlorophyll a; Total Chla = Chlorophyll a+Chlorophyllide a; Echin = Echinone; B-Car = B-Carotene; Gyrox = Gyroxanthin.

Site	Perid	19'BFuco	Fuco	19'HFuco	Viola	Myxo	Diad	Allox	Diat	Lutein	Zeax	BChla	Canth	Chl b	Chl a	Total Chla	Echin	B-Car	Gyrox
Jun-01																			
1	0.370	0.479	61.974	0.000	0.000	0.000	2.341	0.397	0.000	0.000	0.363	0.000	0.000	0.467	11.199	11.199	0.000	0.000	0.000
2	0.211	0.687	4.385	0.000	0.000	0.000	1.915	1.452	0.635	0.000	1.224	0.731	0.000	0.624	9.649	11.661	0.000	0.388	0.000
3	0.138	0.000	3.146	0.000	0.000	0.000	1.581	0.832	0.151	0.000	1.119	0.000	0.000	0.518	8.323	8.323	0.000	0.291	0.000
4	0.000	0.000	2.716	0.000	0.000	0.000	1.175	0.460	0.000	0.000	0.850	0.000	0.000	0.334	6.749	6.749	0.000	0.243	0.000
5	0.000	0.000	1.443	0.000	0.000	0.000	0.497	0.230	0.000	0.000	0.443	0.000	0.000	0.125	3.483	3.483	0.000	0.000	0.000
6	0.000	0.000	0.675	0.000	0.000	0.000	0.185	0.172	0.000	0.387	1.868	0.000	0.000	0.375	5.164	5.164	0.000	0.382	0.000
7	0.000	0.000	1.853	0.000	0.000	0.000	0.768	0.354	0.717	0.113	1.316	0.000	0.000	0.146	5.636	5.636	0.000	0.159	0.000
8	0.159	0.000	1.712	0.000	0.000	0.000	0.631	0.243	0.000	0.000	1.236	0.000	0.000	0.217	5.145	5.267	0.000	0.284	0.000
9	0.219	0.253	5.335	0.000	0.000	0.000	1.667	0.586	0.157	0.183	1.760	0.000	0.000	0.482	11.598	13.326	0.000	0.219	0.000
10	0.000	0.000	1.139	0.000	0.000	0.000	0.556	0.280	0.000	0.000	2.186	0.000	0.000	0.499	5.375	5.375	0.000	0.247	0.000
11	0.223	0.000	0.824	0.288	0.150	0.000	0.733	0.515	0.123	0.857	1.998	0.000	0.000	0.530	6.418	6.418	0.000	0.438	0.000
12	0.223	0.000	2.645	0.000	0.000	0.000	1.448	0.493	0.000	0.000	2.431	0.000	0.000	0.732	8.470	8.470	0.000	0.585	0.000
13	0.243	0.000	1.316	0.000	0.778	0.000	0.664	0.292	0.112	0.665	2.840	0.000	0.000	0.929	8.361	8.372	0.000	0.562	0.000
14	0.556	0.279	6.757	0.000	0.000	0.000	1.964	0.484	0.484	0.157	0.350	0.000	0.000	0.247	11.667	12.769	0.000	0.124	0.000
15	0.000	0.000	0.513	0.000	0.000	0.000	0.346	0.495	0.649	0.513	6.179	0.000	0.000	0.362	11.138	12.687	0.147	0.374	0.000
16	0.000	0.000	0.556	0.000	0.000	0.000	35.123	2.544	0.728	1.527	1.843	0.000	0.526	3.722	13.541	13.541	0.875	0.852	0.000
1*	0.383	0.000	0.563	0.185	0.759	0.000	0.124	6.649	0.346	5.285	0.617	0.999	0.170	4.311	17.115	19.600	0.249	0.220	0.428

Table 8. CHEMTAX results based on pigment data in Tables 4 and 5 for December and June samplings. Abbreviations: Cyano = Cyanobacteria; Proch = Prochlorophytes; Eugle = Euglenophytes; Chlor = Chlorophytes; Prasi = Prasinophytes; Dino = Dinoflagellates; Hapto = Prymnesiophytes; Crypt = Cryptophytes; Diato = Diatoms; Chrys = Chrysophytes; Pelag = Pelagophytes.

Site	Dec-00											Jun-01										
	Cyano	Proch	Eugle	Chlor	Prasi	Dino	Hapto	Crypt	Diato	Chrys	Pelag	Cyano	Proch	Eugle	Chlor	Prasi	Dino	Hapto	Crypt	Diato	Chrys	Pelag
1	0.0	8.3	0.0	11.6	0.0	0.0	0.0	51.5	28.6	0.0	0.0	0.3	2.9	2.0	0.0	0.0	1.7	0.4	2.8	80.1	8.9	0.9
2	0.0	6.1	0.0	0.2	0.0	0.0	0.0	10.1	81.8	1.8	0.0	12.4	15.8	0.0	9.9	0.0	0.2	0.2	9.1	48.9	3.6	0.0
3	0.1	5.7	0.0	0.2	0.0	0.0	0.0	8.6	84.4	0.0	0.9	18.1	21.5	0.0	18.9	0.0	0.4	0.3	6.8	28.6	5.4	0.0
4	0.2	3.5	0.0	0.0	0.0	0.0	0.0	15.8	78.5	0.0	1.8	14.7	15.1	0.0	11.9	0.0	0.4	0.3	8.0	46.7	2.8	0.0
5	0.1	2.8	0.0	0.0	0.0	0.0	0.0	14.2	81.9	0.0	0.9	11.6	7.3	0.0	5.4	0.0	0.2	0.2	10.8	63.5	1.0	0.0
6	0.0	1.0	0.0	0.0	0.2	0.0	0.0	6.6	92.2	0.0	0.0	10.2	12.5	0.0	2.7	0.0	1.1	0.0	9.9	61.7	2.0	0.0
7	0.7	1.6	0.0	0.0	0.2	0.0	0.0	16.2	81.3	0.0	0.0	8.4	19.8	0.0	0.3	0.0	2.8	0.0	7.9	55.7	5.1	0.0
8	1.5	3.6	0.0	0.0	0.0	0.0	0.0	30.9	63.9	0.0	0.0	8.6	19.7	0.0	3.3	0.0	2.1	0.0	8.5	54.5	3.1	0.1
9	0.8	2.0	0.0	5.2	3.9	13.1	0.0	18.5	56.5	0.0	0.0	13.7	23.7	0.0	3.2	0.0	0.4	0.0	8.6	50.2	0.0	0.1
10	0.1	1.0	0.0	11.6	0.0	0.0	0.1	38.4	48.7	0.0	0.1	3.8	11.9	0.7	0.0	0.0	2.3	0.1	13.2	66.7	0.0	1.1
11	0.1	1.9	0.0	0.0	0.0	0.0	0.2	28.2	69.3	0.0	0.3	4.2	13.4	2.9	0.0	0.0	3.0	0.0	14.3	61.6	0.0	0.5
12	0.2	0.9	0.0	0.0	0.0	0.0	0.3	23.7	74.5	0.0	0.4	5.0	15.8	2.9	0.0	0.0	2.0	0.0	14.9	59.3	0.0	0.0
13	0.2	0.3	0.0	0.0	0.0	0.0	0.6	18.8	79.5	0.0	0.6	5.2	16.2	0.4	0.0	0.5	1.0	0.0	13.2	63.5	0.0	0.0
14	0.1	0.3	0.0	0.0	0.0	0.0	0.4	15.7	82.9	0.0	0.6	5.4	15.9	0.0	0.0	0.8	0.0	0.0	11.4	66.5	0.0	0.0
15	0.1	0.0	0.0	0.0	0.0	0.0	0.0	11.9	87.7	0.0	0.4	5.5	14.3	0.0	0.0	0.3	0.0	0.0	10.2	69.7	0.0	0.0
16	0.0	2.1	0.0	0.0	0.0	0.0	0.0	15.1	80.9	1.8	0.1	6.2	10.5	0.0	0.0	0.0	0.0	0.0	10.1	73.2	0.0	0.0
1*												2.3	8.1	2.4	0.0	0.0	2.0	0.5	9.0	65.7	8.9	1.0

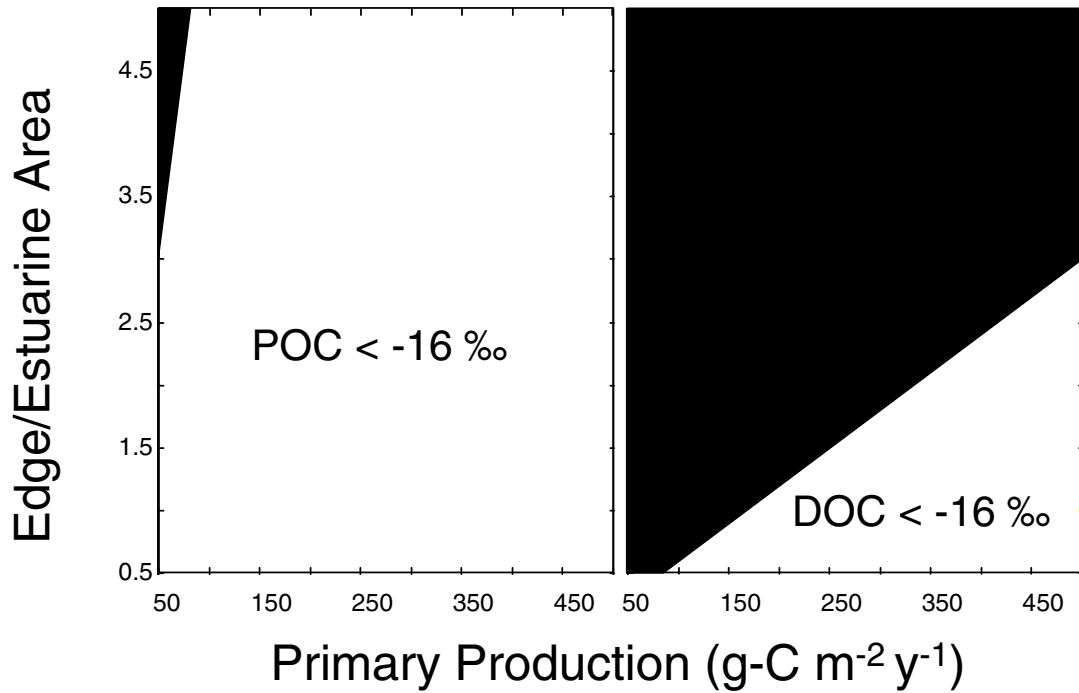


Figure 1. Results of simple model showing the dependence of estuarine POC and DOC isotope ratio on edge outwelling and phytoplankton primary production. Edge outwelling for both POC area indicates regions where the edge signature dominates, and DOC is a function of edge:estuary area (assumes export rate of 50 gC m<sup>-2</sup> yr<sup>-1</sup>). The shaded

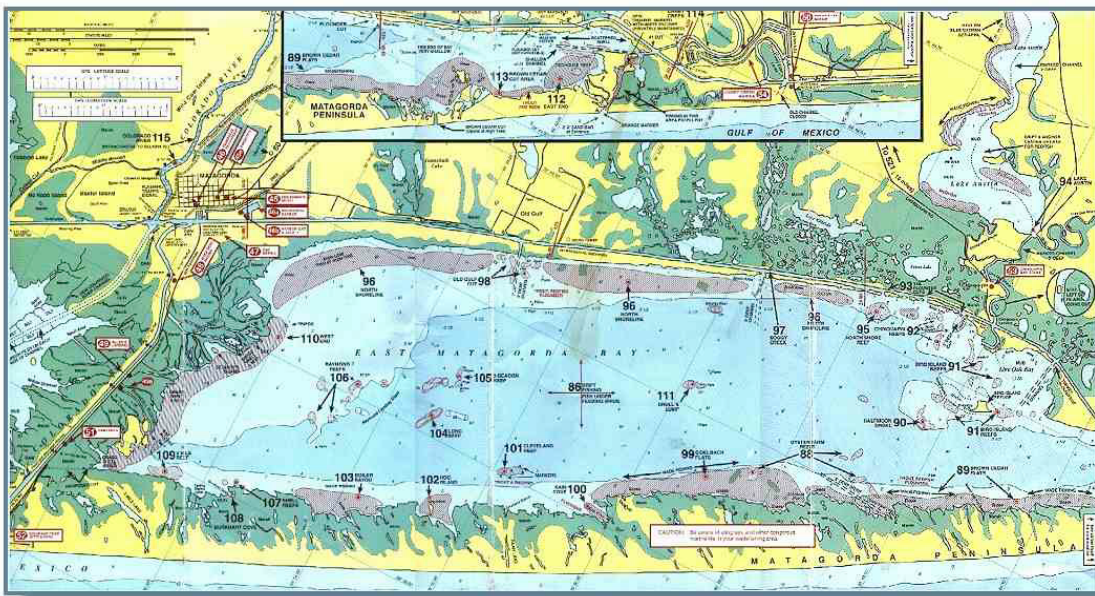


Figure 2. Map of East Matogorda Bay.

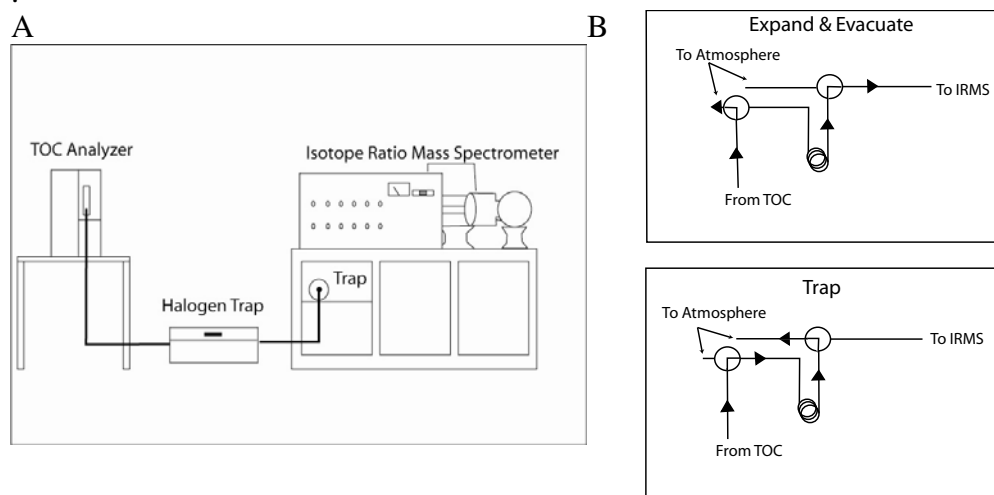


Figure 3A. Schematic diagram showing the direct coupling of the OI TOC 1010 analyzer to the Finnigan-MAT 252 IRMS. 3B. Schematic diagram of the valves and flow paths used to trap the CO<sub>2</sub> and expand the gas into the bellows system for analysis.

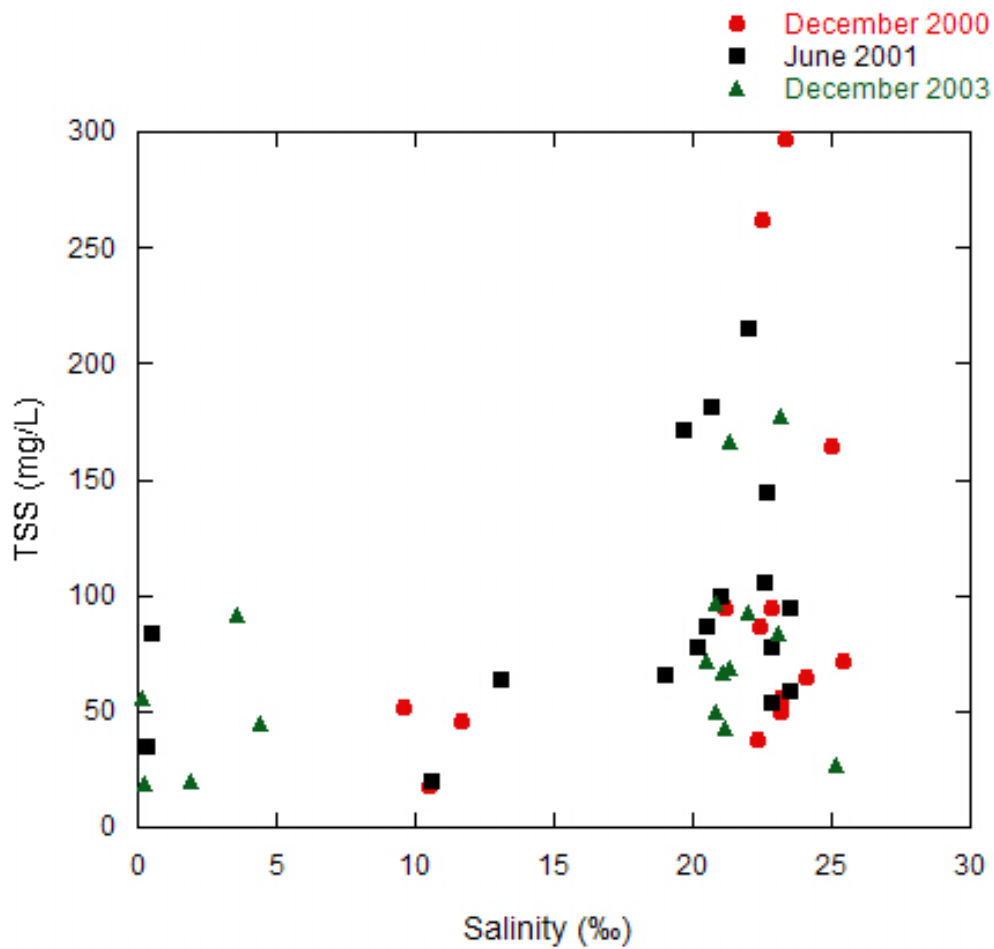


Figure 4. Total suspended solids (TSS; mg/L) versus salinity (‰) for samples taken in December 2000, June 2001 and December 2003.



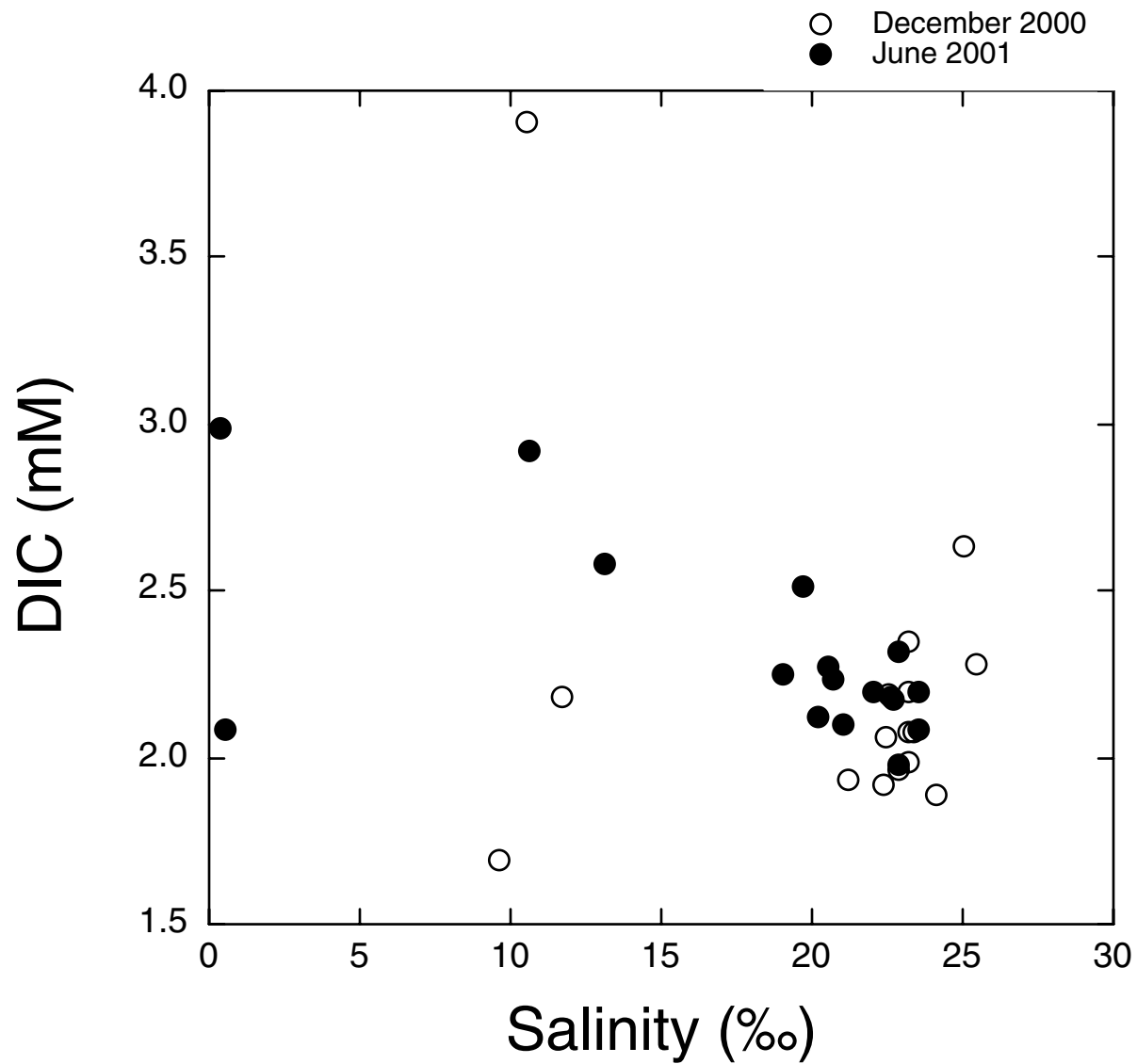


Figure 5. Dissolved inorganic carbon (DIC; mM) versus salinity (‰) for samples taken December 2000 and June 2001.

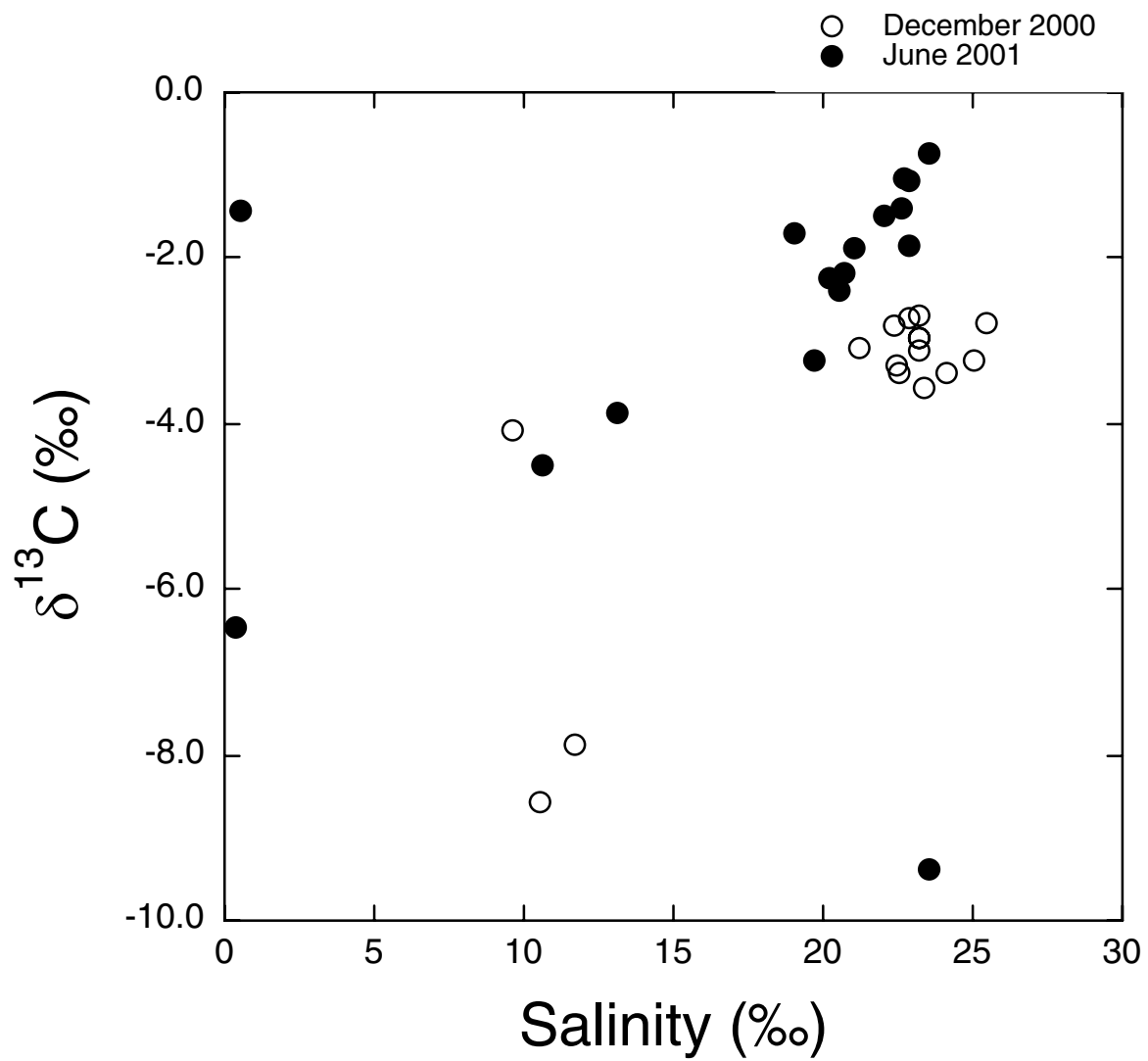


Figure 6. Stable carbon isotope ratio of DIC ( $\delta^{13}\text{C}$ ; ‰) versus salinity (‰) for samples taken December 2000 and June 2001.

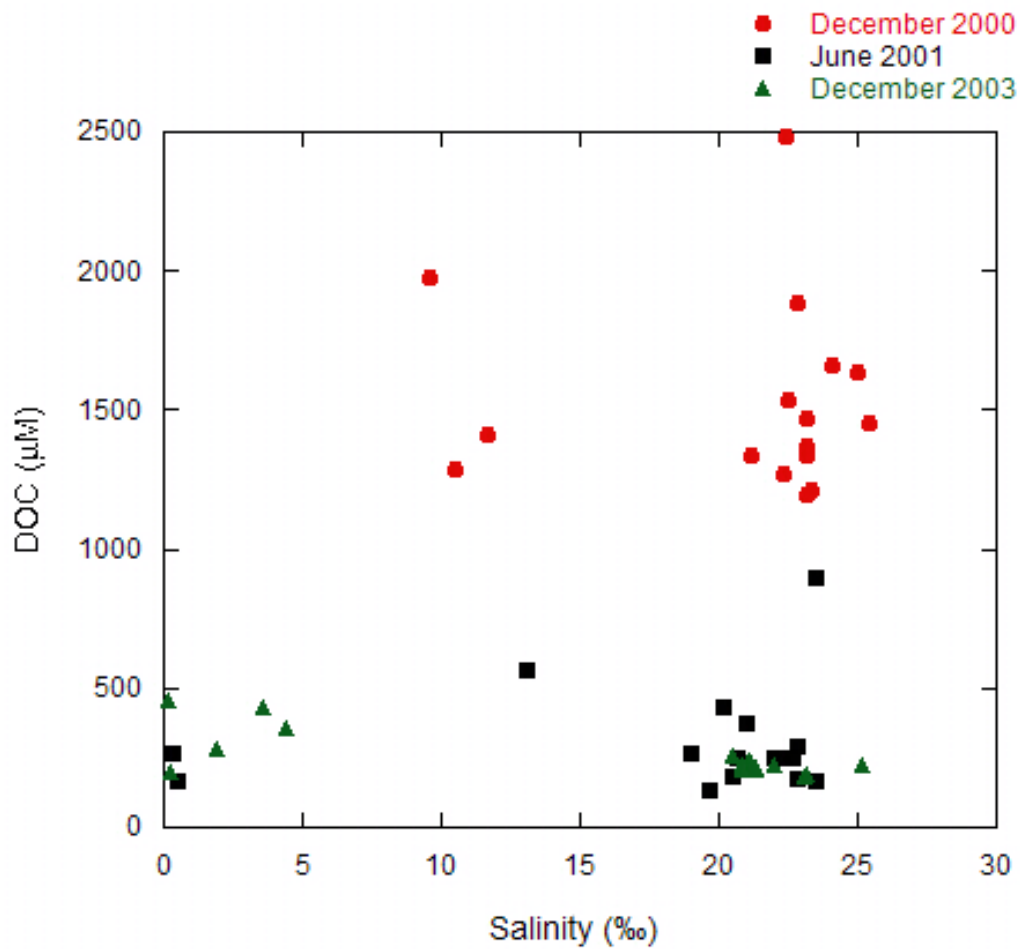


Figure 7. Dissolved organic carbon (DOC;  $\mu\text{M}$ ) versus salinity ( $\text{‰}$ ) for samples taken in December 2000, June 2001 and December 2003. The December 2001 data was obviously contaminated.

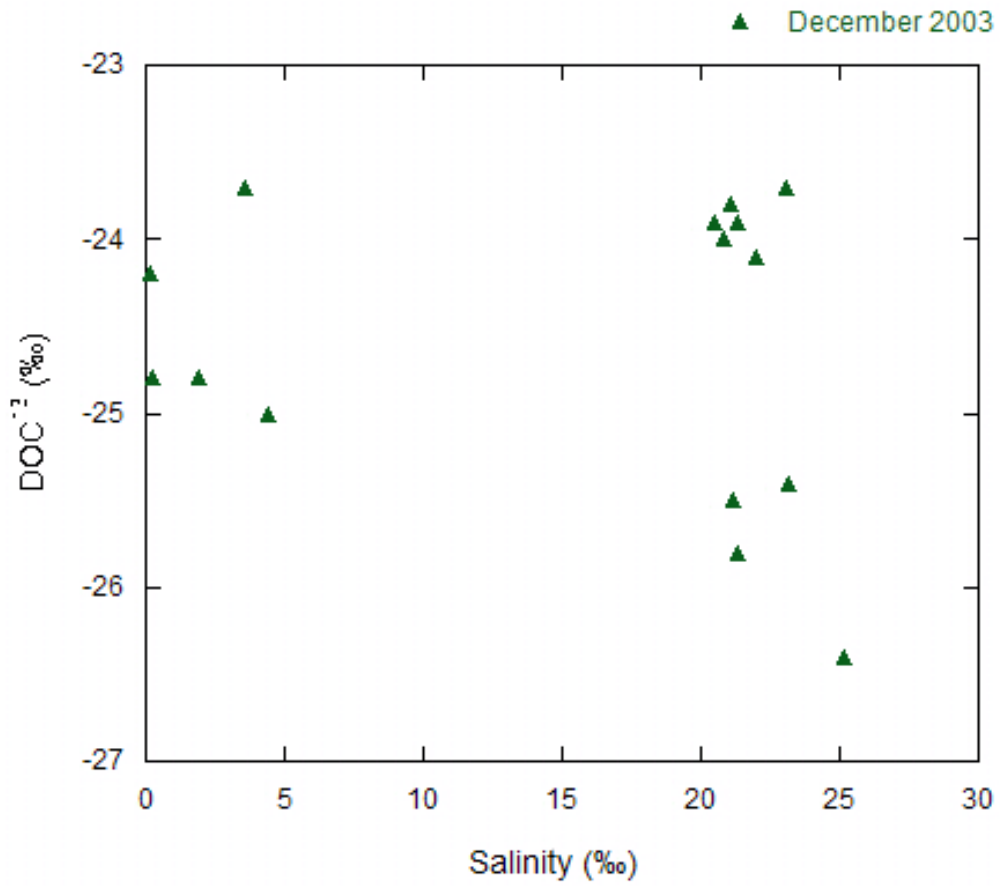


Figure 8. Stable carbon isotope ratio of DOC ( $\text{DOC}^{13}\text{‰}$ ) versus salinity ( $\text{‰}$ ) for samples taken December 2003.

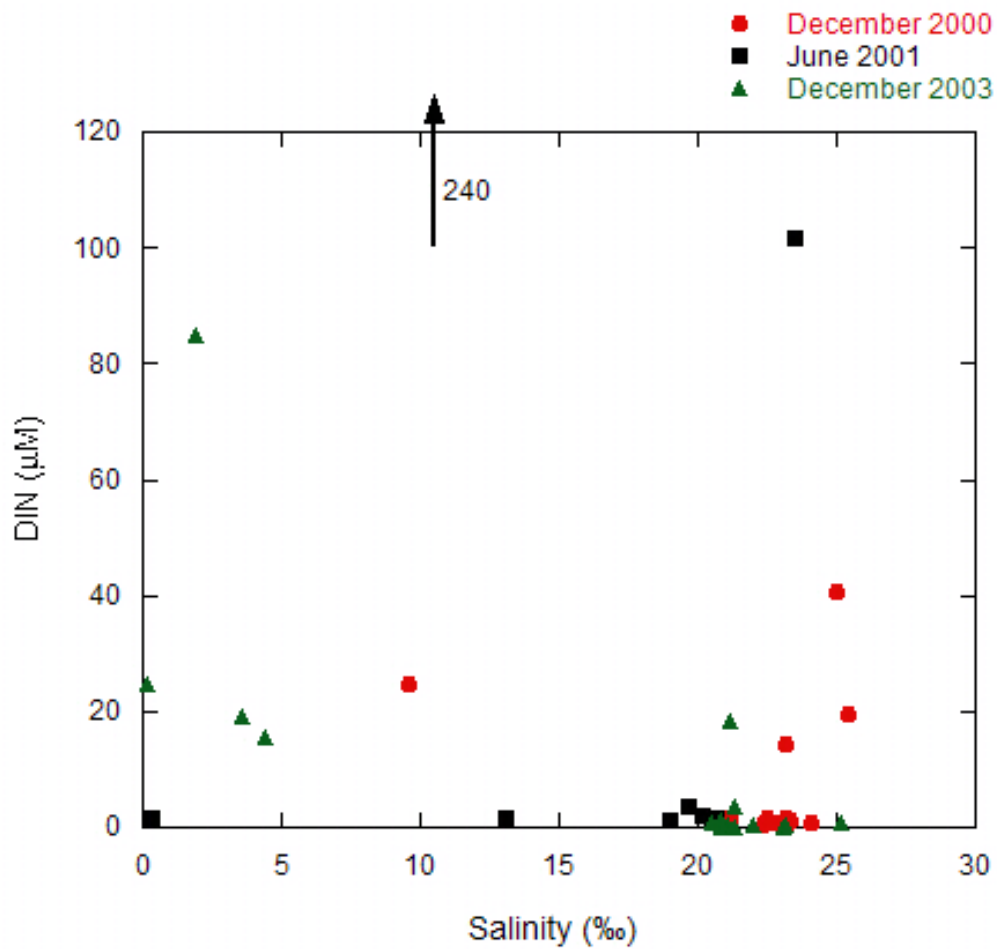


Figure 9. Dissolved inorganic nitrogen (DIN;  $\mu\text{M}$ ) versus salinity ( $\text{‰}$ ) for samples taken in December 2000, June 2001 and December 2003.

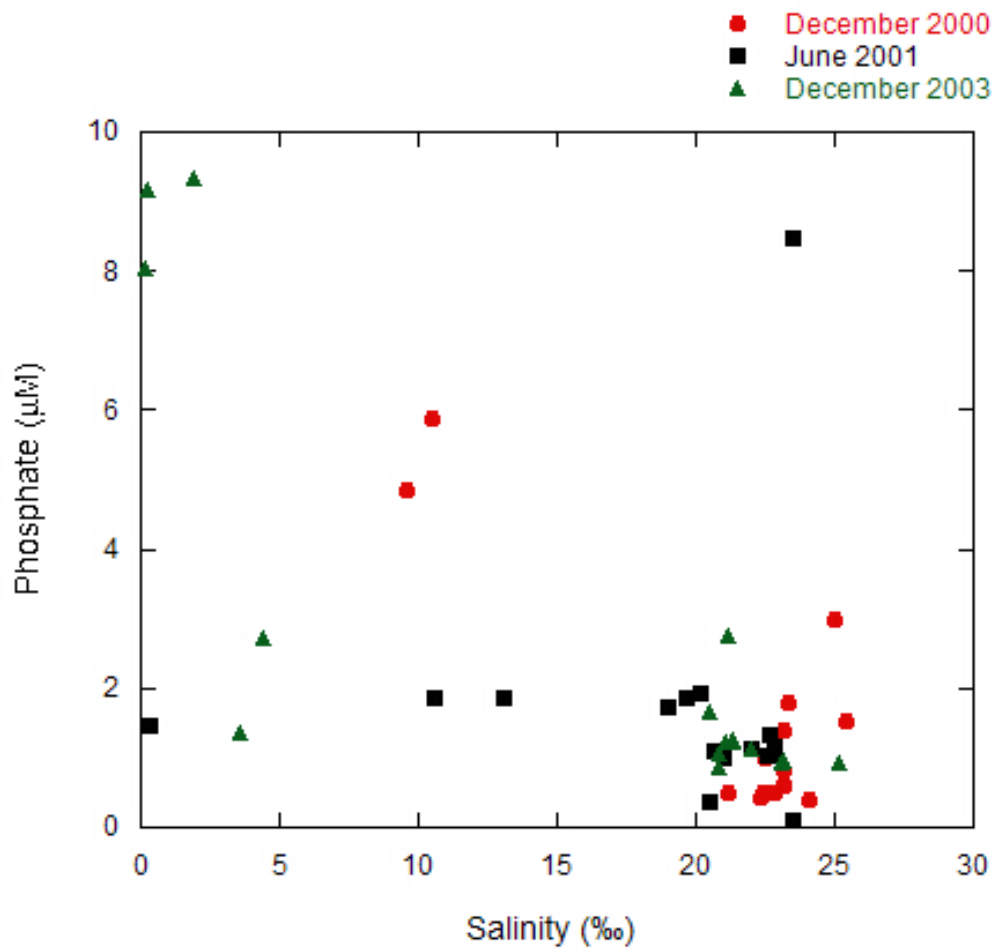


Figure 10. Phosphate ( $\mu\text{M}$ ) versus salinity ( $\text{‰}$ ) samples taken in December 2000, June 2001 and December 2003.

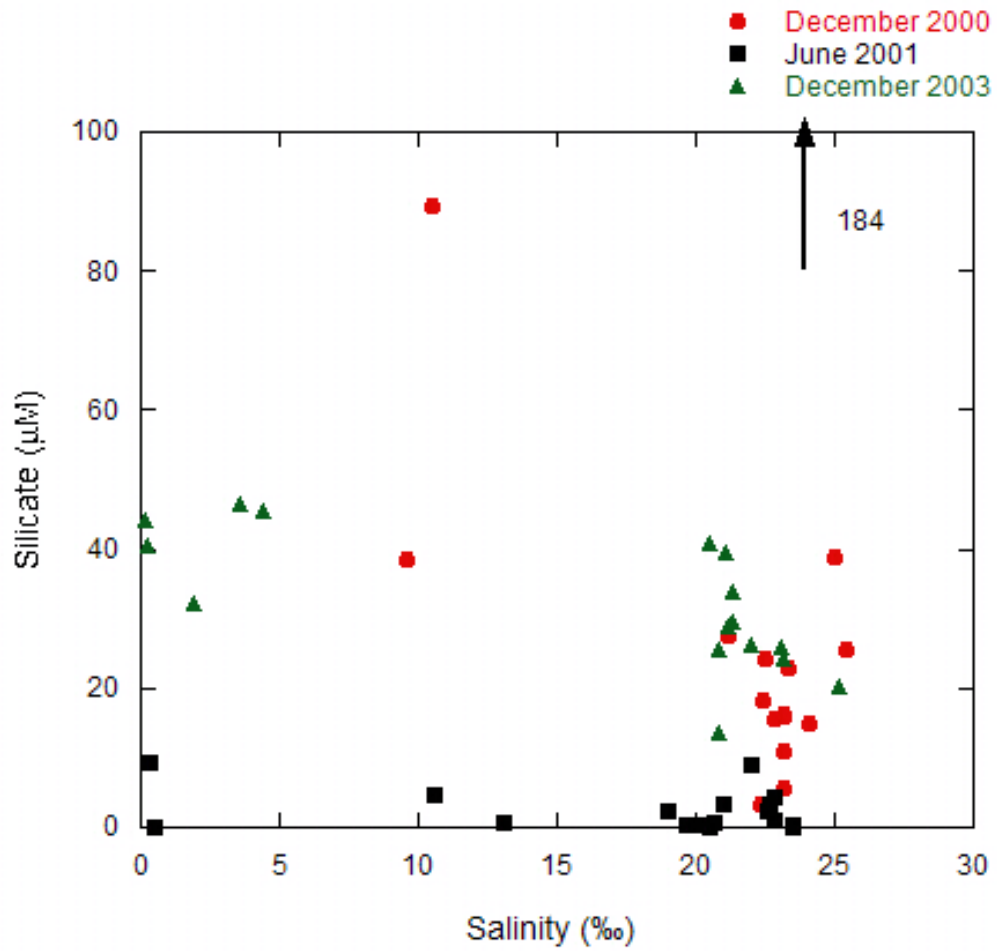


Figure 11. Silicate ( $\mu\text{M}$ ) versus salinity ( $\text{‰}$ ) for samples taken in December 2000, June 2001 and December 2003

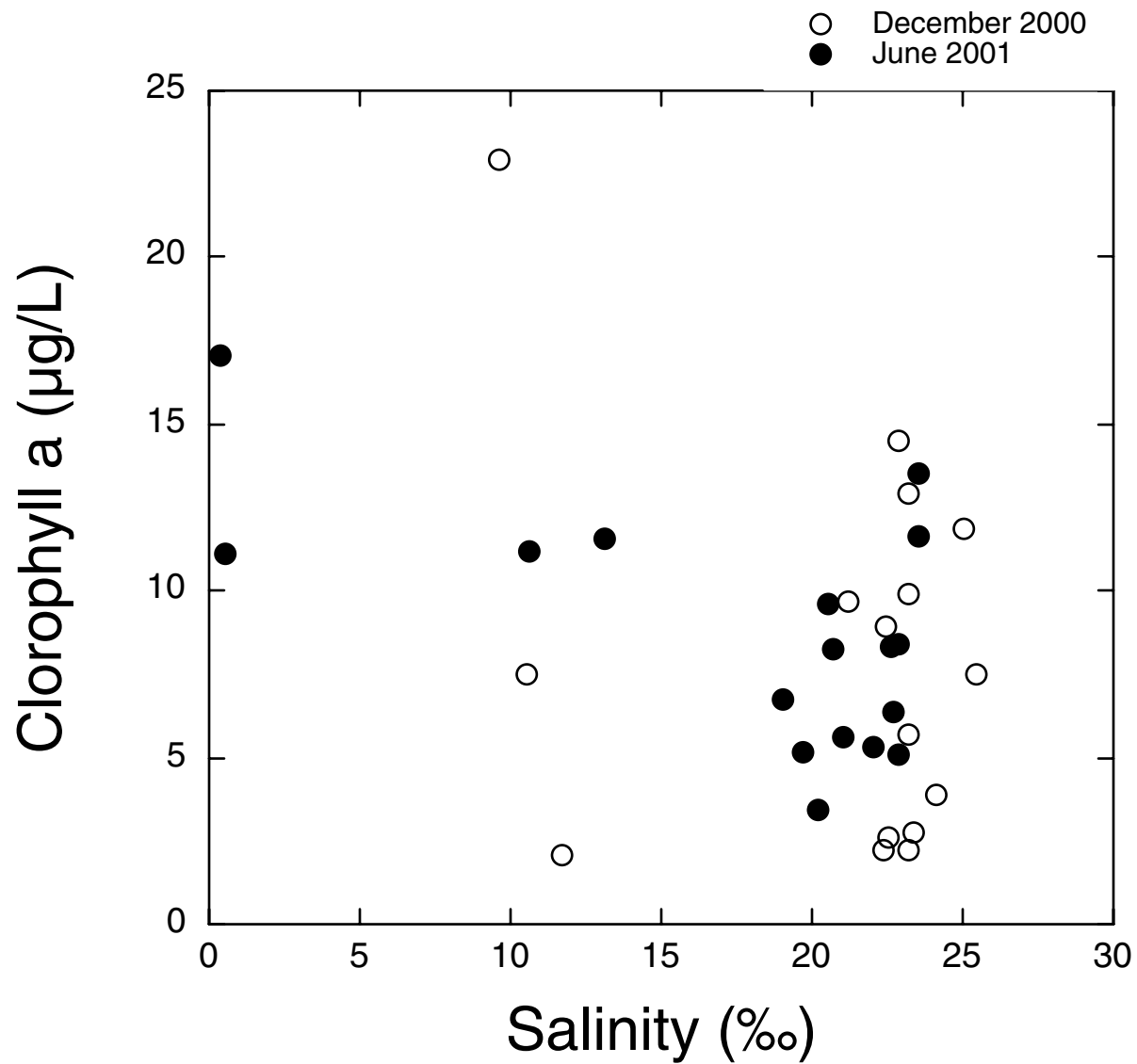


Figure 12. Chlorophyll a ( $\mu\text{g/L}$ ) versus salinity ( $\text{‰}$ ) for samples taken in December 2000 and June 2001.



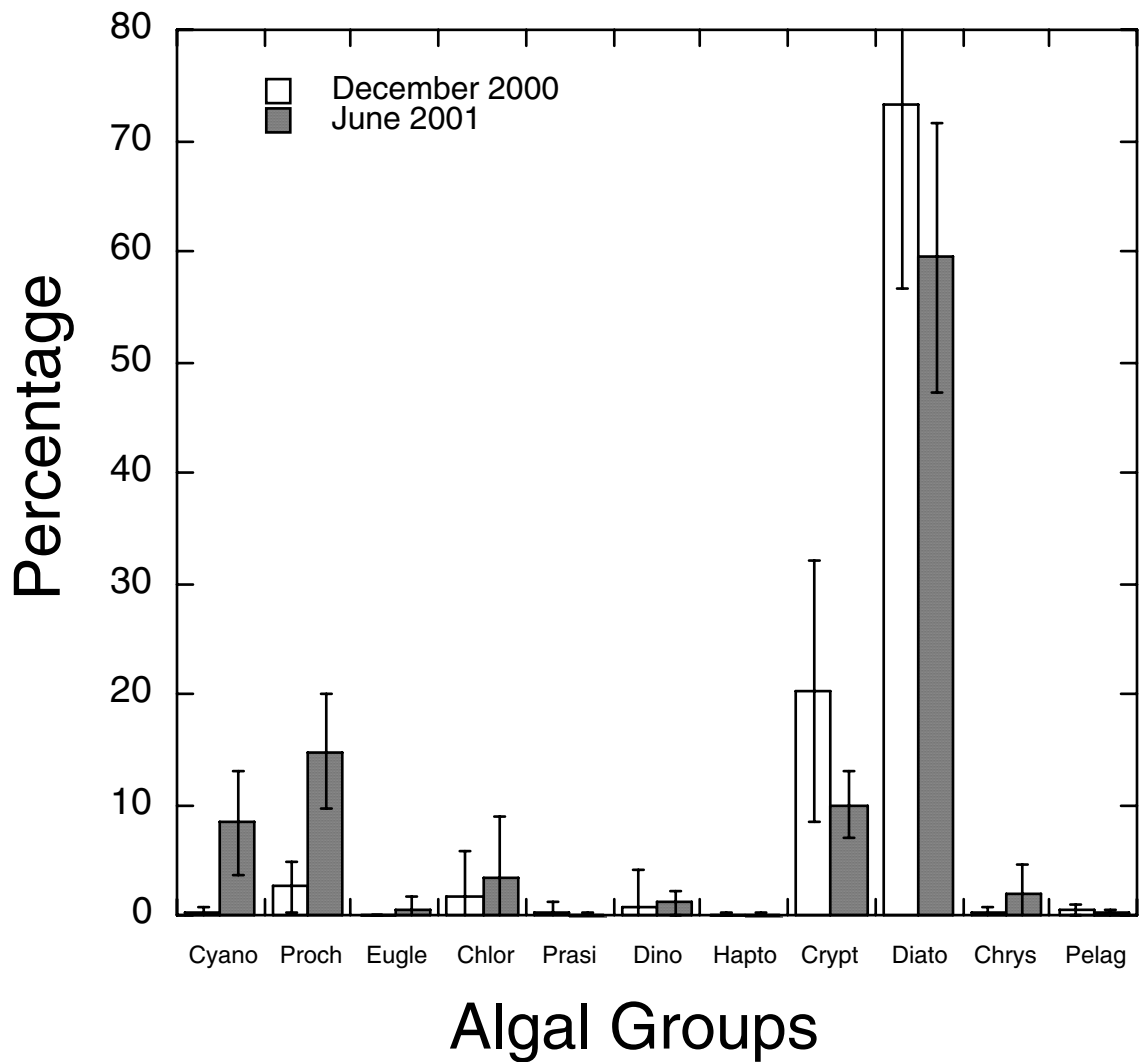


Figure 13. Percentage contribution (average and standard deviation) of various algal groups based on pigment data in Tables 4 and 5 for December 2000 and June 2001 samplings. Abbreviations: Cyano = Cyanobacteria; Proch = Prochlorophytes; Eugle = Euglenophytes; Chlor = Chlorophytes; Prasi = Prasinophytes; Dino = Dinoflagellates; Hapto = Prymnesiophytes; Crypt = Cryptophytes; Diato = Diatoms; Chrys = Chrysophytes; Pelag = Pelagophytes.