

Preliminary Study of Seasonal Variation of Carbon and Nitrogen in Sediments off Point Loma

Environmental scientists have identified numerous chemical and biological markers or indicators of sources of contaminants (Simoneit and Kaplan 1980, Eganhouse *et al.* 1983, Eganhouse and Kaplan 1985, Readman *et al.* 1986, Colombo *et al.* 1989, Venkatesan and Kaplan 1990). These studies have enhanced our knowledge of geochemical cycling and the impact of humans on the environment. Total organic carbon (TOC) and total nitrogen (TN) are used to identify and trace the sources of organic compounds in the marine environment (Gadel *et al.* 1990, Pocklington *et al.* 1991, SCCWRP 1992). The organic carbon/nitrogen ratio (C/N) is an indicator of the terrigenous or marine origin of organic material in the marine environment, although the usefulness of TOC and TN data is enhanced when used in conjunction with other chemical indicators.

The impact of organic matter on the marine ecosystem is correlated with the rate of accumulation and degradation, which may reflect the extent of physico-chemical, microbiological, or other activities. In dynamic areas,

changes in organic chemical composition may be so rapid that information is lost if the interval between sampling times is long. For example, Canual and Martens (1993) measured the seasonal signal in the input of organic matter to the sediments in Cape Lookout Bight (North Carolina). They suggested that *in situ* microbial processes control the composition of the preserved organic matter more than temporal changes in the delivery of allochthonous materials.

We report on the first year of a multi-year survey of the seasonal variation in organic carbon and nitrogen in surface sediments near the recently extended Point Loma outfall (San Diego). The work, which was part of a pre-discharge monitoring program for the outfall extension, was contracted by the City of San Diego. The objective was to measure TOC and TN concentrations quarterly in sediments in an area not strongly influenced by human activities. Since we have only completed four quarters of sampling, the conclusions in this report are tentative and further investigations are underway.

Materials and Methods

Sampling Site

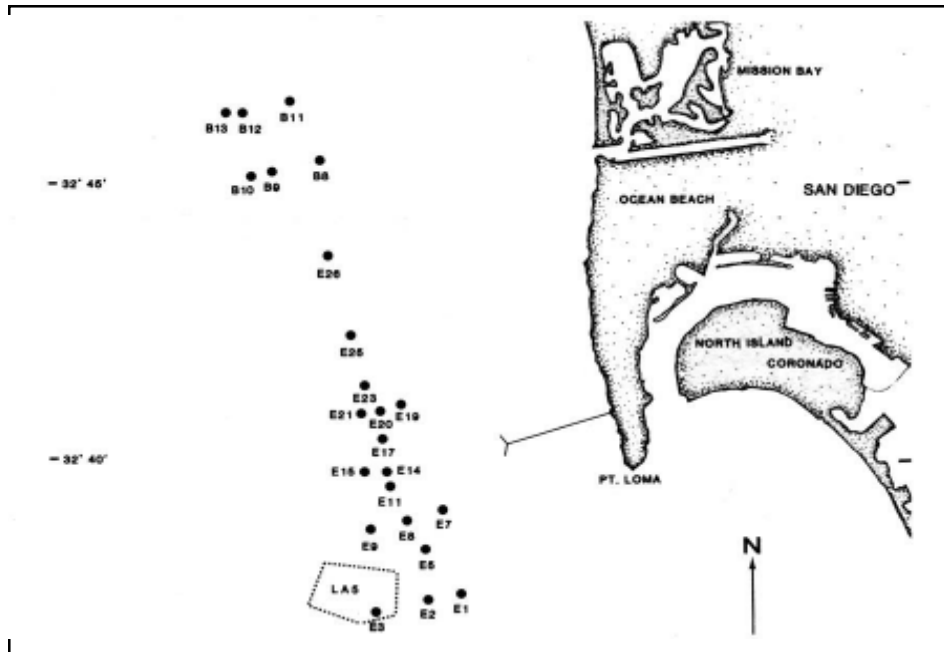
Twenty-three stations were divided into two groups: those near the Point Loma outfall extension, labeled E, and those in a remote area, labeled B (Figure 1, Table 1). Some stations were located near (E1, E2, E5, E8, and E9) or at (E3) a dredge material dumpsite (LA-5). Sediments were collected by the staff of the City of San Diego with a 0.1 m² chain-rigged van Veen grab (City of San Diego 1991) in October 1992 and January, April, and July 1993. Surface sediments (top 2 cm) were collected from the grab, frozen, and delivered to SCCWRP where they were stored at temperatures below -4°C until further treatment.

Sample Analysis

The analytical method developed by SCCWRP has been used to measure TOC and TN in wastewater effluent, marine sediments, sediment trap particles, and surface runoff. The procedures were described in detail in SCCWRP (1992) and only a brief description is given here. Quality control measures and

Figure 1.

Locations of sampling stations.



evaluation of the method detection limit are presented in the Appendix.

Sediment samples were thawed and homogenized at room temperature and dried at 60°C overnight. An aliquot (25-40 mg) of each sample was weighed in a silver boat, placed on a Teflon plate, and exposed to concentrated hydrochloric acid vapors (in a closed desiccator) for at least 18 h to remove inorganic carbon. The acidified samples were dried at 60°C overnight and each was crimped in a tin boat.

The TOC and TN measurements were made with a Carlo Erba 1108 CHN Elemental Analyzer with an AS/23 autosampler. Combustion occurred in a quartz tube

containing layers of chromium oxide and silver cobaltous-cobaltic oxide with oxygen as an oxidizing agent. The reaction products flowed into another quartz tube filled with active copper granules where nitrogen oxide was reduced into elemental nitrogen. The gas mixture (CO₂, N₂, and water) was separated by a 2m (6 mm o.d. and 4 mm i.d.) stainless steel column packed with Poropack QS and detected by a thermal conductivity detector. The data acquisition and processing were automated using a Carlo Erba EAGER 100 data system running on an IBM-compatible PC. The carrier gas was helium with a flow rate of 100 mL/min. Quantitation was done using acetanilide as

an external standard. The experimental conditions were as follows: combustion temperature: 1050°C; reduction temperature: 650°C; chromatographic column temperature: 65°C; and run time: 10 min.

Materials

Acetanilide standards, silver cobaltous-cobaltic oxide, and quartz turnings were purchased from Fison Instruments (Paramus, NJ); reduction copper and chromium oxide from Conrey Scientific (Costa Mesa, CA); silver cups from Sanda, Inc. (Philadelphia, PA); tin cups from Isotech, Inc. (Miamisburg, OH); reduction and combustion tubes from Micro Analysis (Manchester, MA).

Results

The TOC concentrations ranged from 0.2 to 0.79% (dry weight) except for Stations B12 in July 1992 (1.04%), and B13 in October 1992 (1.38%) and July 1993 (1.40%) (Table 1). The average TOC was 0.53% (SD=0.18). The largest seasonal variations occurred in sediments at Stations B12 (0.38-1.04%), B13 (0.21-1.40%), and E2 (0.23-0.43%). These sediments were generally coarse (Table 1) and the distribution of organic matter was variable. The dredge material dumpsite (LA-5) may have influenced the TOC and TN distributions

Table 1.

Results of a pre-discharge survey of TOC and TN in surface sediments near the recently extended Point Loma outfall. TOC=total organic carbon; TN=total nitrogen; C/N=carbon/nitrogen ratio; Cl=% clay; Si=%silt; Sa=%sand. Grain size data for 1992 were adopted from the City of San Diego (1992); data for 1993 were unpublished results from the City of San Diego.

STATION	DEPTH (m)	SAMPLING DATE	TOC (%)	TN (%)	C/N	(Cl+Si)/ Sa (%)
B8	88.4	10/6/92	0.69	0.064	10.8	136
		1/4/93	0.71	0.041	17.3	169
		4/12/93	0.69	0.056	12.3	208
		7/12/93	0.70	0.066	10.6	145
B9	97.5	10/13/92	0.53	0.050	10.7	86
		1/21/93	0.53	0.033	16.2	83
		4/12/93	0.57	0.040	14.2	102
		7/15/93	0.63	0.060	10.6	88
B10	115.8	10/13/92	0.46	0.044	10.5	43
		1/21/93	0.47	0.021	22.6	52
		4/12/93	0.49	0.026	18.8	58
		7/15/93	0.55	0.049	11.2	53
B11	88.4	10/12/92	0.76	0.074	10.3	108
		1/20/93	0.61	0.032	19.0	97
		4/21/93	0.68	0.051	13.3	162
		7/13/93	0.79	0.060	13.1	95
B12	97.5	10/12/92	0.63	0.068	9.2	61
		1/20/93	0.70	0.054	13.0	58
		4/21/93	0.38	<0.01	-	76
		7/13/93	1.04	0.044	23.6	46
B13	115.8	10/12/92	1.38	0.030	45.9	50
		1/20/93	0.21	<0.01	-	46
		4/21/93	0.35	<0.01	-	42
		7/13/93	1.40	0.033	42.3	22
E1	88.4	10/6/92	0.50	0.043	11.7	92
		1/13/93	0.46	0.024	19.0	70
		4/8/93	0.64	0.047	13.6	144
		7/9/93	0.57	0.048	11.9	121
E2	97.5	10/6/92	0.23	0.016	14.3	294
		1/13/93	0.43	0.024	18.1	80
		4/8/93	0.41	0.025	16.3	105
		7/9/93	0.43	0.032	13.3	70
E3	115.8	10/6/92	0.23	0.017	13.3	51
		1/13/93	0.23	0.006	38.0	61
		4/8/93	0.20	0.013	15.6	47
		7/9/93	0.27	0.017	15.6	101
E5	97.5	10/19/92	0.41	0.035	11.7	60
		1/27/93	0.41	0.023	17.8	68
		4/20/93	0.48	0.054	8.9	85
		7/20/93	0.43	0.032	13.5	81

(Table 1. continued)

STATION	DEPTH (m)	SAMPLING DATE	TOC (%)	TN (%)	C/N	(Cl+Si)/ Sa (%)
E7	88.4	10/19/92	0.52	0.049	10.6	98
		1/26/93	0.50	0.019	26.5	100
		4/16/93	0.56	0.041	13.6	116
		7/20/93	0.57	0.046	12.3	92
E8	97.5	10/18/92	0.43	0.039	11.1	53
		1/26/93	0.44	0.019	23.1	65
		4/16/93	0.51	0.033	15.4	83
		7/20/93	0.47	0.037	12.8	67
E9	115.8	10/19/92	0.52	0.041	12.6	63
		1/26/93	0.42	0.016	26.4	65
		4/16/93	0.49	<0.01	-	136
		7/20/93	0.53	0.037	14.3	76
E11	97.5	10/14/92	0.50	0.045	11.0	58
		1/26/93	0.45	0.019	23.8	74
		4/20/93	0.45	0.031	14.4	73
		7/19/93	0.57	0.046	12.3	70
E14	97.5	10/14/92	0.45	0.039	11.4	44
		1/26/93	0.46	0.025	18.3	65
		4/20/93	0.39	0.019	20.3	61
		7/19/93	0.49	0.038	12.8	63
E15	115.8	10/14/92	0.44	0.041	10.7	47
		1/22/93	0.42	0.018	23.1	49
		4/16/93	0.46	0.027	17.1	59
		7/19/93	0.44	0.035	12.5	48
E17	97.5	10/17/92	0.44	0.039	11.3	50
		1/22/93	0.46	0.025	18.3	54
		4/20/93	0.44	0.027	16.3	54
		7/19/93	0.47	0.037	12.7	59
E19	88.4	10/14/92	0.55	0.052	10.5	84
		1/27/93	0.61	0.036	16.8	113
		4/14/93	0.56	0.043	13.0	126
		7/16/93	0.53	0.045	11.7	94
E20	97.5	10/14/92	0.43	0.038	11.2	56
		1/27/93	0.49	0.025	19.4	72
		4/22/93	0.56	0.040	13.9	75
		7/16/93	0.51	0.042	12.2	64
E21	115.8	10/14/92	0.45	0.039	11.4	35
		1/15/93	0.44	0.017	25.9	58
		4/13/93	0.50	0.036	13.9	63
		7/16/93	0.51	0.044	11.7	54
E23	97.5	10/14/92	0.49	0.044	11.1	49
		1/15/93	0.52	0.034	15.4	99
		4/13/93	0.55	0.038	14.6	83
		7/16/93	0.69	0.060	11.6	80

(Table 1. continued)

STATION	DEPTH (m)	SAMPLING DATE	TOC (%)	TN (%)	C/N	(Cl+Si)/ Sa (%)
E25	97.5	10/13/92	0.45	0.041	11.0	48
		1/21/93	0.45	0.028	16.2	78
		4/13/93	0.57	0.044	12.8	104
		7/15/93	0.55	0.048	11.5	85
E26	97.5	10/13/92	0.57	0.052	10.9	77
		1/21/93	0.57	0.039	14.7	107
		4/13/93	0.61	0.050	12.3	105
		7/15/93	0.62	0.053	11.7	91
		Mean	0.53	0.038	15.4	
		SD	0.18	0.014	6.5	

at nearby stations (E2, E3, E7, E8, and E9). Station E3, which was located in the dumpsite, had consistently low TOC concentrations ($<0.27\%$). The sample from Station E2 in October 1992 also had a low TOC concentration (0.23%).

The TN concentrations ranged from non-detectable to 0.074% with an average of 0.038% ($SD=0.014$). Non-detectable TN concentrations occurred in samples from Stations B12 in April 1993, B13 in January and April 1993, and E9 in April 1993. TN concentrations in sediments at Station E3 were also consistently low ($<0.017\%$). These stations were either had coarse sediments (B12 and B13) or were near the dredge material dumpsite (E3 and E9). Since the detection limit for TN was about 0.01% (see Appendix), measurements of samples with concentrations approaching this limit could possess large

errors. If the TN concentration was below the detection limit, the C/N ratio could not be calculated.

The C/N ratios generally varied between 10 and 25 with a few exceptions; the mean was 15.4 ($SD=6.5$). The high C/N ratios in sediments of Station B13 in October 1992 and July 1993 were due to the relatively high TOC concentrations. The high C/N ratio at Station E3 in January 1993 was due to a low TN concentration.

The TOC and TN concentrations in sediments were closely correlated (Figure 2). The relationship for July and October was different compared to the relationship for January and April; the slopes were the same, but the intercepts were significantly different. At a given TOC concentration, TN concentrations were higher in summer and fall compared to winter and spring. The three outliers in July and October were

samples from Stations B12 and B13; excluding these points, the r^2 values were almost identical for the two regressions.

The TOC concentrations were fairly constant at most stations regardless of season. The low TN concentrations in January and April 1993 resulted in higher C/N ratios (Figure 3). The mean seasonal concentrations were:

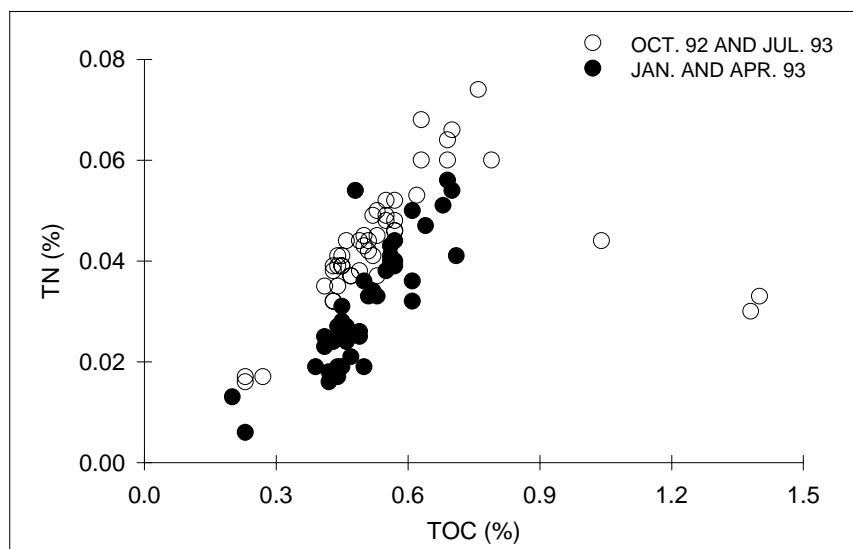
	TOC (%)	TN (%)
October 92	0.52	0.044
January 93	0.48	0.026
April 93	0.50	0.038
July 93	0.60	0.044

Discussion

The TOC and TN measurements separated stations into three groups: 1) stations distant from the outfall (B12 and B13) with coarse sediments and variable TOC and TN concentrations; 2) stations near a dredge material dumpsite (E2, E3, and E9)

Figure 2.

Correlation between TOC and TN in sediments near the Point Loma outfall extension.



with generally low TOC and TN concentrations; and 3) stations near the recently extended Point Loma outfall with similar TOC and TN concentrations. The sediments in the first two groups of stations were generally nitrogen-poor (Table 1). The TOC and TN values were within the range of nearshore marine sediments (Hendricks and Eganhouse 1992, SCCWRP 1992) and the C/N ratios were generally in the range of marine humic material (10-15; Rashid 1985).

A previous study near the old Point Loma outfall obtained a mean TOC content of 0.59% (SD=0.07) for 15 stations (Hendricks and Eganhouse 1992), SCCWRP 1992), which is similar to the present study (0.53%, SD=0.18). The broader

range of TOC measurements in the present study was due to the inclusion of stations with coarse sediments (B12 and B13) and stations near a dredge material dumpsite (E2, E3, and E9). If those stations were excluded from the calculation, the range of TOC concentrations (mean=0.53%, SD=0.09) was similar to the previous study.

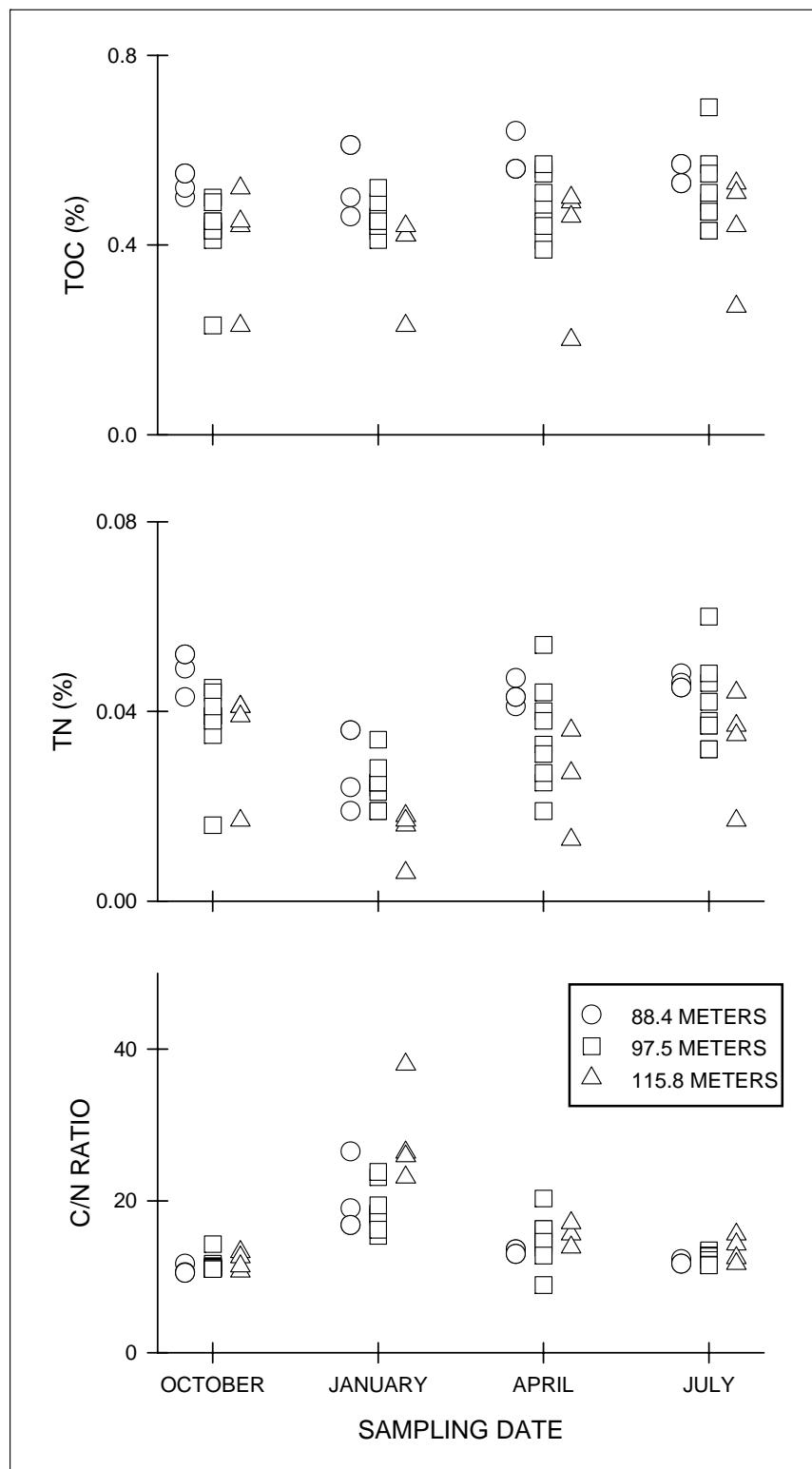
The upper sections of two sediment cores in the Hendricks and Eganhouse (1992) study had higher C/N ratios (mean=12.9, n=2) than did surface sediments collected by van Veen grabs (mean=8.5, n=2). The authors thought that the corer may have blown away a significant portion of the surface sediments, which usually have lower C/N ratios than older deposits. The TOC

concentrations in the cores (mean=0.88%) were higher than TOC concentrations in van Veen grab samples (mean=0.59%); however, cores and grab samples had similar TN concentrations (0.064% and 0.071%). Samples collected by van Veen grab in the present study had similar TOC concentrations, lower TN concentrations (mean 0.038%), and therefore higher C/N ratios (mean =15.4). Since the stations in the present study were 3-5 km farther offshore, higher C/N ratios may indicate either that newly deposited sediments in deeper water lack nitrogen-containing material or there was a fundamental discrepancy between the two sampling techniques. More work is required to answer this question.

With the limited data available, the mechanisms that result in low TN concentrations and seasonal variation in sediments off Point Loma cannot be determined. We can only speculate that the seasonality is associated with marine microbial activities occurring in water column before the particles are deposited, or occurring in the sediments after the particles are deposited. Additional measurements of organic components (especially microbially mediated by-products) in sediments and water column particles are needed to resolve this problem.

Figure 3.

Seasonal variation of TOC, TN, and C/N ratio in sediments near the Point Loma outfall extension.



Conclusions

Seasonality in C/N ratios (and TN concentrations) in the sediments near the recently extended Point Loma outfall indicated a marine-dominated source of organic deposits, although some effects of dredge material dumping or terrestrial inputs may have been present. The low TN concentrations in samples collected in January 1993 cannot be explained with the limited data. Additional measurements of microbially mediated products in sediments and water column particles are needed to provide better understanding of the seasonal variation. This study provides a TOC and TN baseline against which the effects of future municipal wastewater discharges can be measured.

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Appendix

Quality Assurance/Quality Control

Detailed QA/QC measures for sample handling and preparation were described in SCCWRP (1992); similar procedures were used in the present study. The CHN analyzer was initially calibrated with acetanilide standard (71.09% carbon and 10.36% nitrogen) prepared in five concentrations. The response factors (K factor) for carbon and nitrogen were consistent for five calibration levels (Table 2), indicating the linearity of the instrument was acceptable. Instrument calibration was performed daily before sample analysis. Three acetanilide standards were analyzed to obtain an mean K factor for quantitation.

The precision of the measurements was assured by analyzing acetanilide standards during and at the end of sample analyses. Twenty-eight acetanilide samples (five of which went through the sample preparation process) were analyzed during the study. The precision of the method was good (Table 3). In addition to analyzing acetanilide standards, one sediment sample was analyzed in duplicate for approximately every 10 samples.

Method Detection Limit

Method detection limit (MDL) is the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Glaser *et al.* 1980). In practice, the method detection limit can be determined by analyzing seven replicates of the analyte(s) in the matrix of interest at a concentration near (1-5 times) the estimated MDL. The method detection limit is equal to the product of 3.14 times the standard deviation of the seven measurements (American Public Health Association 1989).

The difficulty in determining MDL in our case was finding a matrix similar to the sediments. Instead, MDLs were based on pure solid standards whose matrix may not have been comparable to actual samples. However, high-temperature combustion in the analyzer should eliminate almost all kinds of matrix interference.

We analyzed seven acetanilide standards weighing from 0.1446 to

0.2780 mg with a mean value of 0.227 mg. The mean carbon contents were 0.161 mg ($SD=3.01 \times 10^{-3}$) and the mean nitrogen contents were 0.0235 mg ($SD=9.05 \times 10^{-4}$). The method detection limits are:

$$\begin{aligned} \text{MDL (carbon)} &= 3.14 \times 3.01 \times 10^{-3} \text{ mg} = 9.45 \times 10^{-3} \text{ mg} \\ \text{MDL (nitrogen)} &= 3.14 \times 9.05 \times 10^{-4} \text{ mg} = 2.84 \times 10^{-3} \text{ mg} \end{aligned}$$

The results of TOC and TN measurements are usually expressed in percent of dry sample weight. Assuming the sample weight is 30 mg, the MDLs was converted into:

$$\text{MDL (carbon)} = 100\% \times 9.45 \times 10^{-3} / 30 = 0.032\%$$

$$\text{MDL (nitrogen)} = 100\% \times 2.84 \times 10^{-3} / 30 = 0.0095\%$$

Some of the nitrogen concentrations were close to the MDL (Table 1).

Table 2.

Initial response (K) factors for carbon and nitrogen.

	WEIGHT (mg)	AREA	Kx10 ⁶ (mg/area)	MEAN Kx10 ⁶ (mg/area)	RSD (%)
<u>Carbon</u>	0.1599	113830	1.405	1.489	3.4
	0.3938	265110	1.485		
	0.8195	545280	1.503		
	1.5574	1025323	1.519		
	3.1735	2072003	1.532		
<u>Nitrogen</u>	0.0233	6247	3.73	4.00	3.9
	0.0574	14207	4.04		
	0.1194	28953	4.12		
	0.2270	55485	4.09		
	0.4625	115230	4.01		

Table 3.

Recoveries and standard deviations of acetanilide. N=number of analyses.

	DATE	N	RECOVERY (%)	RSD (%)
<u>Carbon</u>	October 1992	4	97.8	2.9
	January 1993	8	99.6	1.8
	April 1993	7	100.3	0.53
	July 1993	4	101.2	3.1
	July 1993	5 ^a	103.8	2.1
<u>Nitrogen</u>	October 1992	4	99.8	1.9
	January 1993	8	98.6	3.1
	April 1993	7	100.4	1.3
	July 1993	4	99.7	3.9
	July 1993	5 ^a	02.8	2.2

^aAcetanilide standards that went through the sample preparation process.