

# Total Organic Carbon and Total Nitrogen in Marine Sediments, Sediment Trap Particles, Municipal Effluents, and Surface Runoff

lemental carbon and nitrogen are the basic components of organic matter entering the marine environment. Their measurement may provide a gross assessment of the origin and accumulation of organic material in marine sediments, and possibly the transport and fate of contaminants. The ratio of carbon to nitrogen (C/N) is used to identify the source of organic material. Humic substances originating from marine organisms are rich in nitrogen, hence their C/N ratios are lower than those derived from terrestrial vegetation. Typical C/N ratio of marine humic material ranges from 10 to 15, although ratios of 5 to 10 are not unusual, especially for compounds originating from algal sources. Coastal environments also have high C/N ratios as a result of microbial mineralization of organic nitrogen. Terrestrial materials generally have C/N ratios between 10 and 35 (Rashid 1985).

Organic carbon and nitrogen can be measured in sediments by wet chemistry or instrumental methods. The latter is the more prevalent technique because of better accuracy and precision, and shorter analysis time. The objectives of this study were: 1) to develop instrumental methods to measure organic carbon and nitrogen in wastewater effluent, marine sediment, sediment trap particles, and surface runoff, and 2) to examine the usefulness of



Running samples on the CHN analyzer

the C/N ratio for distinguishing among sources of organic material in the marine environment.

# Materials and Methods

Effluents were collected from the County Sanitation Districts of Los Angeles County Joint Water Pollution Control Plant (JWPCP), the County Sanitation Districts of Orange County Wastewater Treatment Plant (CSDOC), and the City of San Diego Point Loma Treatment Plant (PLTP). Sediment trap particles were collected near each of the three ocean outfalls. Surface sediments were collected near the CSDOC and PLTP ocean outfalls. Sample collection and analysis was conducted over a 12-month period. Water samples were collected from the Los Angeles River in Long Beach during a winter storm.

#### **Effluents**

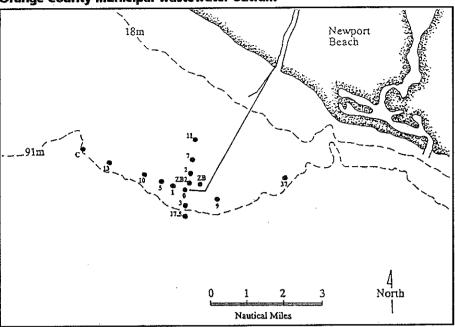
Final effluents were collected from JWPCP, CSDOC, and PLTP every other month from January to November 1990. Twenty-four- hour composite samples were collected by treatment plant personnel in two bottles: 1) an amber glass bottle (for determination of total suspended solids), and 2) an acidrinsed 2 L polyethylene bottle sealed with Teflon-lined cap (for determination of TOC and TN). The samples were placed on ice, returned to the laboratory within 12 hr of collection, and analyzed immediately.

About 100 ml of the effluent from the glass bottle was measured using a graduated cylinder, and filtered in an all-glass filtration assembly using pre-combusted, pre-weighed 25 mm or 47 mm Whatman GF/C glass fiber filter. The filter was washed with distilled water and transferred to a previously kilned Petri dish and dried in a vacuum desiccator for two days. Total suspended solids were determined by reweighing the dry filter on a Cahn 31 microbalance.

About 100 ml of the effluent were removed from the polyethylene bottle, filtered, dried as described above, and exposed to hydrochloric acid vapor for 18 hr to remove inorganic carbon. This is a modification of the acid vaporization technique described by Hedges and Stern (1984). The filter was then dried in an oven at 60°C for 4-6 hr to remove excess acid and water, crimped in a tin combustion boat (Carlo Erba), and analyzed for TOC and TN. We calculated particulate organic carbon (POC) and particulate nitrogen (PN) based on the amount of total suspended solids measured in the effluent.

Figure 1.

Surface sediment sampling sites near the County Sanitation Districts of Orange County municipal wastewater outfall.



# **Sediment Trap Particles**

Sediment traps were deployed off the Palos Verdes Peninsula, Orange County (Huntington Beach), and Point Loma from October 1989 to November 1990 at elevations of 0.5, 2.0, and 5.0 m above the sea floor in 60 m of water and 1 km downcurrent from each of the outfalls (JWPCP, CSDOC, PLTP). The traps were retrieved monthly, although some moorings were lost. Particles were collected in glass centrifuge bottles in the trap. The bottles were transported to the laboratory and stored at -20°C until the particles were analyzed.

The frozen sediment trap particles were thawed at room temperature and homogenized with a glass rod. The wet sample was transferred in an acid-rinsed glass jar and dried at 60°C overnight. A 20-30 mg aliquot of the dry sample was weighed into a silver boat (Carlo Erba) using a

Cahn 31 microbalance, placed in a Teflon plate, exposed to acid for 18 hr, and dried as described above. The silver boat was crimped and loaded in a tin combustion boat for analysis.

#### **Sediments**

Surficial sediments were collected near the CSDOC outfall in May 1989 (Figure 1) and near the Point Loma outfall (Figure 2) in April 1989 by Van Veen grab (Stubbs et al. 1987). Subsamples of the upper 2 cm of the sediments were collected in precombusted glass jars covered with Teflon-lined caps, transported on ice to the laboratory, and stored at -20°C until analyzed.

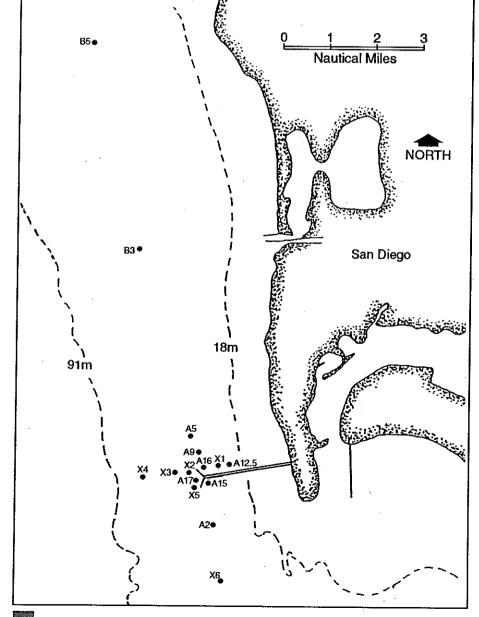
The frozen sediments were thawed at room temperature and homogenized with a glass rod. The wet sediment sample was dried in an aluminum pan at 60°C overnight and stored in a glass

vial. An aliquot of the dry sample was weighed and the carbonate removed as described for the sediment trap samples.

#### **River Runoff**

Water samples were collected from the Los Angeles River at Willow Street in Long Beach during a storm in January 1990. Samples were collected at 15-30 min intervals for 6 hr. Flow measurements at the time of sampling were obtained from the Los Angeles Department of Public Works. The sampler and sampling method are described in SCCWRP (1990a). Water samples were stored in polyethylene bottles and refrigerated at 5°C until analyzed. Subsamples of 15-25 ml were filtered in the same

Figure 2.
Surface sediment sampling sites near the Point Loma Treatment Plant municipal wastewater outfall.



way as effluent samples and the carbonate was removed as described for sediment trap samples.

## Instrumental Analysis

Carbon, hydrogen and nitrogen (CHN) were determined by flash combustion on a Carlo Erba EA 1108 CHN Elemental Analyzer equipped with an AS/23 autosampler, Porapak OS column, and a thermal conductivity detector. The sample was crimped in a tin combustion boat, placed in a quartz combustion tube packed with chromium oxide and silvered cobaltous-cobaltic oxide catalyst. and combusted at 1050°C with oxygen as the oxidizing agent. The oxides pass through a reduction tube filled with copper to convert nitrogen oxides to elemental nitrogen. The resulting compounds are separated and eluted as CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O by gas chromatography. Helium was used as a carrier gas at a flow rate of 100 ml/min. Total analysis time was 10 min per sample.

The instrument was calibrated daily with standard acetanilide using a three-point calibration curve. The same standard was also processed daily as a sample to determine TOC and TN recovery. Data were acquired and processed with a DP 110 integrator and later with a Carlo Erba 100 data system that uses an IBM-compatible computer. Quality control and quality assurance data are presented in the Appendix.

# Results Effluent Particles

There were no significant differences in TOC concentrations (ANOVA, F<sub>2,16</sub>=0.346, p=0.71) and TN concentrations

Table 1

Elemental composition of effluent particles from County Sanitation Districts of Los Angeles County Joint Water Pollution Control Plant (JWPCP), County Sanitation Districts of Orange County (CSDOC), and City of San Diego Point Loma Treatment Plant (PLTP). TOC = total organic carbon, TN = total nitrogen, TSS = total suspended solids, POC = particulate organic carbon, PN = particulate nitrogen, SD = standard deviation, and CV = coefficient of variation.

	Collection Date	TOC (%)	TN (%)	C/N	TSS <sup>a</sup> (mg/L)	POC (mg/L)	PN (mg/L)
JWPCP	1/17/90	30.7	3.29	9.33	82.9	25.4	2.73
	3/17/90	28.7	4.02	7.14	76.1	21.8	3.06
	4/12/90	31.6	4.16	7.6	70.7	22.3	2.94
	7/6/90	35.0	4.32	8.10	61.8	21.6	2.67
	10/1/90	39.4	4.68	8.42	49.4	19.5	2.32
	11/1/90	37.2	3.90	9.54	71.6	26.6	2.79
	11/21/90	<u>25.3</u>	2.96	8.55	89.7	22.7	2.66
	Mean	32.6	3.90	8.38	71.7	22.8	2.74
	SD	4.9	0.59	0.86	13.3	2.4	0.24
	CV(%)	15	15	10	18	11	9
CSDOC	1/17/90	30.1	3.80	7.92	56.0	16.8	2.13
	3/9/90	28.7	4.04	7.11	60.8b	17.4	2.46
	5/17/90	38.5	5.79	6.65	49.8b	19.2	2.88
•	7/5/90	39.9	5.75	6.94	54.5	21.7	3.13
	9/24/90	41.4	5.47	7.57	42.4	17.6	2.32
	<u>11/21/90</u>	<u>22.2</u>	<u>3.38</u>	6.57	<u>79.0</u>	17.5	2.67
	Mean	33.5	4.71	7.12	57.1	18.4	2.60
	SD	7.6	1.08	0.53	12.4	1.8	0.37
	CV (%)	23	23	7	22	10	14
PLTP	1/18/90	24.8	3.19	7.77	81.7	20.3	2.61
	3/12/90	32.9	5.06	6.5	94.8b	31.2	4.8
	<i>5/</i> 24/90	35.3	3.55	9.94	100.9ъ	35.6	3.58
	7/6/90	32.3	5.13	6.3	101.9	32.9	5.23
	9/17/90	35.5	4.07	8.72	117.2	41.6	4.77
	11/19/90	<u>23.0</u>	<u>2.45</u>	9.39	120.3b	27.7	<u>2.95</u>
	Mean	30.6	3.91	8.10	102.8	31.6	3.99
	SD	5.4	1.06	1.51	14.3	7.2	1.09
	CV (%)	18	27	19	14	23	27

<sup>\*</sup>TSS measured on 47 mm Whatman GF/C glass fiber filter

(ANOVA, F<sub>2,16</sub>=1.540, p=0.25) among effluent samples from the three municipal wastewater treatment plants (Table 1). The variability of TOC and TN measurements was moderate; coefficients of variation (CV) ranged from 15 to 30%.

Total suspended solids were significantly different among the three effluents (ANOVA on log-transformed data, F<sub>2,16</sub>=15.94, p<0.001). The CSDOC effluent had the lowest concentration; PLTP effluent had the highest

concentration, and hence the highest concentrations of POC and PN. The average POC concentration in the PLTP effluent was about 40% greater than the JWPCP effluent and 70% higher than the CSDOC effluent.

bTSS measured on 25 mm Whatman GF/C glass fiber filter

# **Sediment Trap Particles**

The concentrations of TOC and TN in sediment trap particles generally increased with trap elevation above the sea floor (Figure 3). Particles collected 5 m above the bottom had 5-20% higher average TOC concentrations, and 4-30% higher average TN concentrations, than particles collected 0.5 m above the bottom. Particles collected 2 m above the bottom had 1-12% higher average TOC concentrations, and 0-10% higher average TN concentra-

tions, than particles collected 0.5 m off the bottom.

Sediment trap particles collected 5 m above the bottom off Palos Verdes had a 70% higher average TOC concentration, and a 60% higher average TN concentration, than particles collected 5 m above the bottom off Orange County and Point Loma.

The variability of TOC and TN concentrations was greater for particles collected off Orange County and Point Loma (CV<sub>TOC</sub>= 9-34%, CV<sub>TN</sub>=10-53%) than par-

ticles collected off Palos Verdes ( $CV_{TOC}$ =5-8%,  $CV_{TN}$ =8-9%) (Figure 3). The coefficients of variation were about twice as large for the 5 m traps compared to the 0.5 m traps at Orange County and Point Loma.

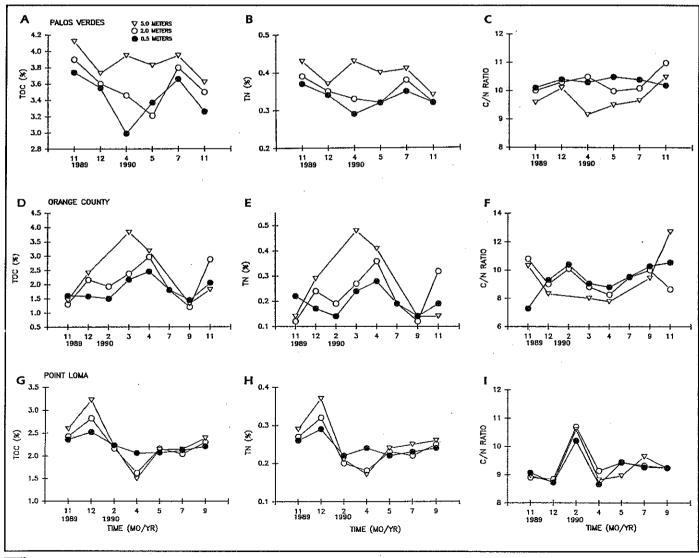
The C/N ratios were consistent (CV range 1-3%) across all trap elevations at the three sites (Figure 3).

### **Sediments**

Off Orange County, TOC and TN concentrations in surficial

Figure 3.

Total organic carbon (TOC), total nitrogen (TN), and C/N ratios of sediment trap particles collected at three elevations above the seafloor in 60 m of water off the Palos Verdes Peninsula (A-C), Orange County (D-F), and Point Loma (G-I).



sediments were highest at the station closest to the end of the outfall and lowest at the station farthest downcoast (Table 2, Figure 1). The C/N ratio had a substantial range (4.7), but the variability was low (CV=11%).

The TOC and TN concentrations in surficial sediments off Point Loma were about twice those off Orange County (Table 2). The concentrations were highest at several stations upcoast and downcoast from the outfall, and lowest at two stations farthest upcoast (Figure 2). The C/N ratio had a narrow range (1.9) and low variability (CV=6%).

#### **River Runoff**

The organic content of suspended particles collected in the Los Angeles River declined as the storm progressed (Figure 4). River flow was inversely correlated with the concentrations of TOC (Spearman r<sub>s</sub>= -0.83, p<0.002) and TN (r<sub>e</sub>= -0.85, p<0.001), but was not correlated with the C/N ratio. During the early part of the storm when flows were less than 10 m<sup>3</sup>/s, the TOC concentration averaged 12%, the TN concentration averaged 1.2%, and the C/N ratio was 10.8. During the storm when flows were greater than 20 m<sup>3</sup>/s, the TOC concentration averaged 6%, the TN concentration averaged 0.5%, and the C/N ratio was 12.1.

# Discussion Effluents

Effluent particles from the three municipal wastewater treatment plants had similar TOC and TN concentrations, but because of differences in level

Table 2
Concentration of total organic carbon (TOC) and total nitrogen (TN), and the C/N ratio in surficial sediments (0-2 cm) near the County Sanitation Districts of Orange County (Figure 1) and Point Loma Treatment Plant (Figure 2) outfalls.

	Station	TOC (%)	TN (%)	C/N
Orange	OC-0	0.54	0.058	9.3
County	OC-1	0.33	0.031	10.6
County	OC-2	0.31	0.033	9.4
•	OC-3	0.32	0.033	9.7
	OC-5	0.37	0.041	9.0
	OC-7	0.34	0.036	9.4
	OC-9	0.26	0.026	10.0
	OC-10	0.38	0.039	9.7
	OC-11	0.29	0.027	10.7
-	OC-13	0.33	0.034	9.7
	OC-17.5	0.32	0.031	10.3
	OC-37	0.17	0.013	13.1
	OC-ZB	0.32	0.031	10.3
	OC-ZB2	0.38	0.045	8.4
	OC-control	0.31	0.033	9.4
Point Loma	SD A-2	0.70	0.100	7.0
	SD A-5	0.70	0.083	8.4
	SD A-9	0.60	0.070	8.6
	SD A-12.5	0.54	0.065	8.3
	SD A-15	0.63	0.072	8.8
	SD A-16	0.57	0.066	8.6
	SD A-17	0.54	0.061	8.8
	SD B-3	0.46	0.058	7.9
	SD B-5	0.48	0.057	8.4
	SD X-1	0.55	0.067	8.2
	SD X-2	0.65	0.073	8.9
	SD X-3	0.65	0.079	8.2
	SD X-4	0.57	0.067	8.5
	SD X-5	0.57	0.067	8.5
	SD X-6	0.62	0.076	8.2

of treatment, TSS (and POC and PN) concentrations were significantly different. Effluent at PLTP received advanced primary treatment and had the highest TSS concentration. More than 50% of the effluents from JWPCP and CSDOC receive secondary treatment (SCCWRP 1990b).

Our measurements of effluent TSS were significantly higher than effluent TSS measurements

reported by CSDOC (Mann-Whitney U test, p<0.02) and PLTP (U test, p<0.001), but not by JWPCP (U test, p>0.10) (see Characteristics of Effluents from Large Municipal Wastewater Treatment Plants in 1990 in this report). This may be a function of differences in filter pore sizes used by the laboratories. SCCWRP and JWPCP use Whatman GF/C filters with a

particle retention size of 1.2 µm; CSDOC and PLTP use Whatman 934-AH filters with a particle retention size of 1.5 µm. Filters with smaller pore diameter may retain more of the suspended particles and have higher TSS concentrations<sup>1</sup>.

Because of improved wastewater treatment practices and increased source control, effluent concentrations of suspended solids are 60-70% lower today than in 1978 (Schafer 1980, SCCWRP 1990b). Effluent particle concentrations of organic carbon and nitrogen, however, have not changed in nearly two decades. The concentration of TOC in present-day JWPCP effluent particles (25-39%) is similar to concentrations measured by Myers (1974; 28-42%), Sweeney and Kaplan (1980; 31-32%), and Venkatesan and Kaplan (1990; 25%). The range of TN concentrations measured in the present study (2.5-5.8%) was higher than concentrations measured by Sweeney and Kaplan (1980; 2.4%).

The C/N ratios of effluent

particles (7.1-8.4) from the three municipal wastewater treatment plants are comparable to the C/N ratios of effluent (8.3) from South Essex District in Massachusetts (Eganhouse 1986) and the combined sewer overflow effluent (6.5-8.9) discharged to Boston Harbor (Eganhouse and Sherblom 1991).

#### **Sediment Traps**

The organic content of sediment trap particles collected off Palos Verdes, Orange County, and Point Loma was substantially less than the organic content of effluent particles from the corresponding sites. Sediment trap particles had 6-11% of the TOC concentration, and 4-9% of the TN concentration, of effluent particles. The C/N ratios of sediment trap particles (9.1-10.3) were 13-34% higher than the C/N ratios of effluent particles (7.1-8.4) from the corresponding sites.

The lower TOC and TN concentrations, and higher C/N ratios, of sediment trap material suggest that effluent particles undergo rapid biodegradation upon discharge to the marine environment (Myers

1974, Eganhouse and Kaplan 1988), and perhaps dilution with plankton and terrestrial lithogenic particles transported into the area. The higher TOC and TN concentrations of particles at the higher trap elevations suggest accumulation of sinking sewage material.

The TOC concentrations of sediment trap particles collected off the Palos Verdes Peninsula during the present study (3.0-4.1%) are comparable to TOC concentrations of flocculent material collected in shallow water off Palos Verdes by Myers (1974; 1.8-3.2%) and Sweeney and Kaplan (1980; 0.8-5.2%). The C/N ratios of their samples (8-12) are comparable with present data.

#### Sediments

The concentrations of TOC and TN in surface sediments off Orange County and Point Loma were at or below levels of TOC (mean=0.72% dry weight, sd=0.22, n=11) and TN (mean=0.04% dry weight, sd=0.02, n=11) in surface sediments at the 60 m Reference Survey stations (SCCWRP 1992). There was some evidence, however, for the effect of effluent discharge on sediments near the outfalls. Sediment concentrations of TOC and TN near the CSDOC outfall were 200-300% higher than concentrations at the most distant stations. Sediment concentrations of TOC and TN near the PLTP outfall were about 50% higher than concentrations at the most distant stations.

The organic content of sediments collected off Orange

Table 3
The average concentration of total organic carbon (TOC) and total nitrogen (TN), and the average C/N ratio of municipal wastewater effluents, surface runoff, sediment trap particulates, and sediments.

	Effluent <sup>a</sup>	Runoff	Sediment trap <sup>c</sup>	Sediments
TOC (%)	32	8.4	2.7	0.46
TN (%)	4	0.75	0.28	0.05
C/N	8	11	10	9

<sup>\*</sup>from County Sanitation Districts of Los Angeles County Joint Water Pollution Control Plant (JWPCP), County Sanitation Districts of Orange County Wastewater Treatment Plant (CSDOC), and City of San Diego Point Loma Treatment Plant (PLTP)

<sup>&</sup>lt;sup>b</sup>from the Los Angeles River

<sup>°</sup>from sediment traps deployed near JWPCP, CSDOC, and PLTP outfalls

<sup>&</sup>lt;sup>d</sup>from sediment samples collected near CSDOC and PLTP outfalls

<sup>&</sup>lt;sup>1</sup> County Sanitation Districts of Los Angeles County compared the GF/C and 934AH filters in 1992 and found no significant difference in estimates of TSS concentrations (J. Stull, County Sanitation Districts of Los Angeles County, personal communication, September 1992).

County and Point Loma was substantially less than the organic content of effluent particles from the corresponding sites. Sediments off Orange County had 10-30% of the TOC and TN concentration of sediment trap particles and <1-2% of the TOC and TN concentration of effluent particles from the same site. Sediments off Point Loma had 20-30% of the TOC and TN concentration of sediment trap particles and 1-2% of the TOC and TN concentration of effluent particles from the same site.

The patterns of C/N ratios of sediments around the outfalls were not consistent between the two sites. The high C/N ratio at station OC-37, which is located near Newport Canyon, is probably due

to dilution of the sediment with terrigenous debris low in nitrogen.

No current TOC data by this method are available for sediments off Palos Verdes. A decade ago, the TOC concentration in the upper 1 cm of sediment was 6.8-8.7% (Kettenring 1981). Background levels for sediments near the JWPCP outfalls are about 1% TOC and 0.1% TN (Eganhouse and Kaplan 1988).

#### **River Runoff**

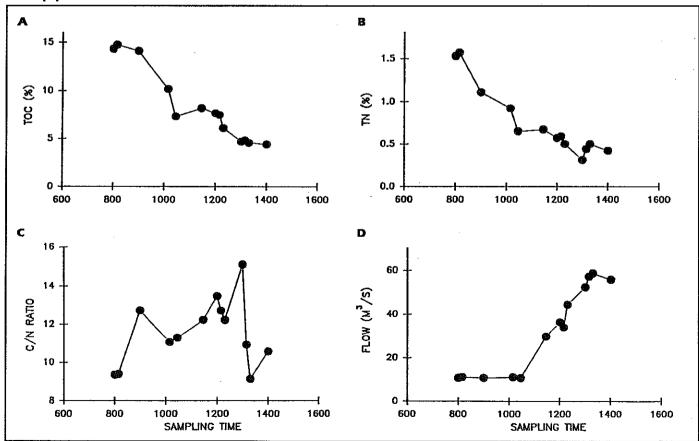
The concentrations of TOC and TN in particles collected from the Los Angeles River during a storm declined as flow increased. The C/N ratio was variable and did not correlate with flow. This was not unexpected since the source of

organic material, and its removal by scouring, is probably not consistent throughout a storm. At low flow, sand-filtered, secondary effluents from three water reclamation plants make up 80-90% of stream flow (SCCWRP 1990a). The decline in the organic content and the increase in C/N ratio as river discharge increased suggests that the municipal effluents were being diluted by surface runoff.

Particles collected in the Los Angeles River during low flow had, on average, about 40% of the TOC concentration and 30% of the TN concentration of effluent particles. Particles collected in the river during high flow had, on average, about 20% of the TOC and 10% of the TN concentration of effluent

Figure 4.

Total organic carbon (A), total nitrogen (B), and C/N ratios (C) of surface runoff particles collected in the Los Angeles River (D).



**Table 4**Precision and accuracy of elemental analyses of effluent particles, sediments, and sludge. CV = coefficient of variation.

		Carbo	on (%)	Nitrog	gen (%)	Hydrogen (%)	
	N	mean	CV	mean	CV	mean	CV
Effluent <sup>a</sup>	5	41.2	4	4.79	2	7.31	3
Sediment-1 <sup>b</sup>	10	11.4	2	0.42	29	1.85	2
Sediment-2°	10	1.1	4	-	-	0.37	10
Sludge-1d	5	35.0	1	3.09	3	_	_
Sludge-2	5	40.0	3	3.62	2	7.38	2
PACS-1a <sup>e</sup>	5	3.59	1	0.28	1	0.88	3
PACS-1b	3	3.48	1				
PACS-1c	3	3.61	1				
Certified value		3.69	3.0				

<sup>\*</sup>from County Sanitation Districts of Los Angeles County Joint Water Pollution Control Plant

Table 5.
Recovery of standards.

	Recovery (%)						
	N	Carbon	Nitrogen	Hydrogen			
Acetanilide-1	3	100	99	103			
Acetanilide-2	3	101	98	100			
Cyclohexanone-1 <sup>a</sup>	3	101	100	96			
Cyclohexanone-2	6	101	101	103			
Phenanthrene-1	3	101	_	100			
Phenanthrene-2	6	100	-	99			
PACS-1ab	3	98					
PACS-1b	3	95					

cyclohexanone-2,4-dinitrophenylhydrazone

particles. The average C/N ratio of particles in runoff was about 30% higher than effluent at low flow and 40% higher than effluent at high flow.

### Conclusions

We compared the organic material associated with effluent, sediment, sediment trap, and surface runoff particles by elemental analysis of organic carbon and nitrogen. Effluents had the highest organic carbon and nitrogen content and sediments had the lowest (Table 3). The results for sediment trap material and sediments suggest that effluent particles undergo rapid biodegradation, and perhaps dilution with plankton and terrestrial particles, in the marine environment.

The C/N ratio data collected in this study were not very helpful for differentiating sources of the particles, but offered some insight into areas enriched by municipal wastewater discharge. Marine organic matter is rich in N and has a C/N ratio of 5-9; terrestrial organic matter is poor in N and has a C/N ratio of at least five or six times that of terrestrial organic matter (e.g., Macdonald et al. 1991). Other indicators such as stable isotopes or molecular markers need to be examined to draw more definitive conclusions.

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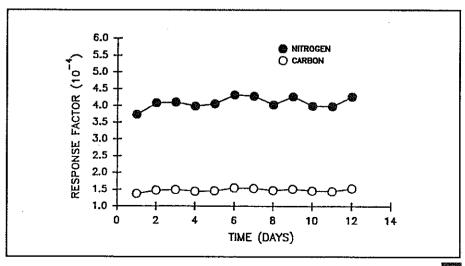
# Appendix:

#### Quality Control/Quality Assurance

Samples of final effluent particles, sediments, and raw sludge were used to bring the method online. Analytical standards used were acetanilide, cyclohexanone, phenanthrene, and a sediment reference material (PACS-1) obtained from the Canadian Research Council.

The final effluent sample was a 24-hr composite obtained from JWPCP. A 100 ml subsample was homogenized and filtered on a 25

Figure 5.
Response factors for carbon and nitrogen based on calibration data.



mm Whatman GF/C glass fiber filter; suspended particles on the filter were transferred to a glass Petri dish and dried under vacuum for two days. The filter was then exposed to hydrochloric acid vapor for 18 hr in a desiccator to remove inorganic carbon, dried, crimped in a tin boat, and loaded in the CHN analyzer. Five replicate subsamples were analyzed to determine the variability of TOC and TN measurements.

Primary sludge was also obtained from JWPCP. The sample was thoroughly mixed in a polytron homogenizer. A 75 µl subsample was pipetted directly into a silver boat, dried at 60°C, and weighed to obtain 2-3 mg of sample. The boat was placed in a Teflon plate and acid-exposed in a desiccator for 24-48 hr, dried at 60°C, and crimped

into a tin boat. Five replicate samples were prepared.

Surface sediment samples were collected from Station HR 51-1 and HR 6-1 in Santa Monica Bay. A 50 g wet subsample was dried and pulverized, and an aliquot was ground in an agate mortar and pestle, and stored in glass vials. The optimum sample size required for TOC and TN analysis was determined from 10 replicate analyses of sediments (1-50 mg) from each station.

The glass fiber filters used to filter effluents and surface runoff samples were kilned at 425 °C for 4 hr and stored in glass jars sealed with Teflon-lined caps. For effluent particle analysis, blanks of kilned filter paper were processed as samples at a rate of two per eight samples. Empty silver boats were

processed as blanks for the sediments and sediment trap particles. Duplicate analyses were run every 10 samples.

The precision of TOC and TN measurements was high for all sample types (Table 4). Carbon and nitrogen recoveries were consistently high for standards and sediment reference material (Table 5) The response factors, calculated daily from the standard data, was constant over time for carbon and nitrogen (Figure 5) The minimum sample size required to quantitate total nitrogen and carbon simultaneously in sediments varied with TOC content. For sediment from HR 51-1 with TOC of 11%, optimum sample size was 10-15 mg; for sediment from HR 6-1 with a TOC of 1%, optimum sample size was 35-40 mg (Figure 6).

**Figure 6.**Effect of sample size on carbon (A,C) and nitrogen (B,D) concentrations in sediment samples collected in Santa Monica Bay.

