Boulder Creek Ecology: An Instream Experimental Examination of Total Organic Carbon

Kate Campbell

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Abstract

The purpose of this experiment was to determine the effects of instream processes on the total organic carbon content in a stream such as Boulder Creek, diurnally as well as over an extended period of time. These processes were experimentally tested in two ways. An aluminum and Plexiglas box 15" x 30" x 24" was constructed to be placed in Boulder Creek, Boulder, Colorado, in order to create an isolated natural environment with the same characteristics as the Creek. The box was placed on open space property near the junction of 61st street and Boulder Creek. From 12:00 am to 10:00 pm on December 30, 1995, samples from Boulder Creek were taken every two hours, and samples from the box were also taken every two hours from 12:00 pm to 4:00 pm. However, due to a flux of water consisting of 150 cfs from the hydroelectric plant at approximately 10:00 pm every evening, the experiment had to be moved from the site into two aquaria and transported. There were three aquaria: one containing sediment, algae, benthic macroinvertebrates and Creek water taken directly from the box; one containing only Creek water taken from the site; and a third containing a distilled water control. Samples from the aquaria were collected at 4:00 pm every day over a period of eight days, and all samples were analyzed for total organic carbon (TOC), absorbance at 254 nanometers and 400 nanometers (color), total dissolved solids (TDS), pH, dissolved oxygen (DO), and temperature. The diurnal samples revealed a bimodal flux of TOC in the Creek. In conjunction with the box in the Creek, the TOC in the aquarium with the sediment, etc. increased over the duration of the experiment, most likely due to agal production. The aquarium containing only Creek water experienced a decrease in TOC, which could most probably be attributed to bacterial consumption. While the biological

activity in the water alone consumed carbon, the entire natural system including sediment, benthic macroinvertebrates, and plant matter leached and/or produced TOC.

Acknowledgments

I would like to thank the following people for their time and assistance on this science fair project.

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Mr. Rich Smith, Park Ranger Supervisor, for saving the day! When the experiment had been destroyed twice, he helped make it possible to complete the project by allowing me to utilize Open Space property.

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Introduction

The study of organic chemistry is one that is crucial to understanding life on Earth. Virtually everything is comprised of carbon, the building block of life and a focal point in the study of organic chemistry. Organic matter is consequently an important factor in stream ecosystems. However, to characterize organic matter in its entirety is a lengthy and difficult process, if indeed it is possible. Organic carbon, on the other hand, is measured with practicality and yields an effective analysis of approximately 50% of the total organic matter content in water. Therefore, this study has utilized total organic carbon (TOC) as a base analysis for the measurement of the organic matter content.

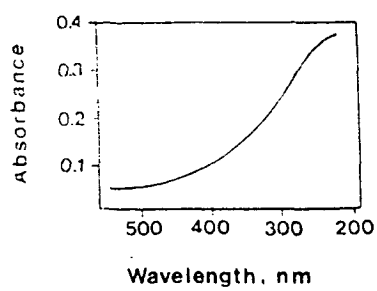
"Measurement of DOC [dissolved organic carbon] is one of the simplest and most important determinations in organic geochemistry. This measurement tells us the amount of organic carbon in the water and is the starting point for understanding the complex nature of organic constituents" (Thurman 7). TOC is simply the sum of the POC (particulate organic carbon) and DOC. Although neither DOC nor POC were analyzed in this experiment, it has been shown (Barber, unpublished data) that in streams similar to and including Boulder Creek the TOC and DOC are almost the same, and the POC is negligible. Therefore, TOC was analyzed in this study.

The majority of organic carbon, 50% - 70%, has been shown to consist of polymeric organic acids, known as humic substances (Thurman 2, 283). This major class of organic compounds has several essential functions and specific characteristics that justify the use of TOC as a useful indicator. Humic substances are divided into humic acids and fulvic acids. Fulvic

acids comprise about 85% of humic substances, while humic acids constitute about 15%. Since humic substances are long organic acid compounds, they consist of several elements: on average, carbon at 52%, hydrogen at 5%, oxygen at 40%, nitrogen at 2%, sulfur at 0.4%, phosphorus at < 0.2%, and other trace elements (Thurman 287-294).

Humic substances also possess various qualities that allow for several important functions. Firstly, humic substances constitute 5%-10% of all anions in streams, like Boulder Creek (Thurman 3). This anionic character gives humic substances aqueous solubility, buffer capacity, surfactant (soaps) character, and binding sites for pesticides and the like as well as metals. Humic substances in general affect water quality, taste, odor, color, and toxicity (Thurman 418). Since humic substances comprise most of the carbon content of natural water, TOC also reflects these characteristics to a certain degree.

Another carbon-related measurement is visible absorbance at 400 nanometers (absorbance at 254 nanometers was also measured), known as color in Cobalt/Platinum units (Thurman 314-316). Measured by means of a spectrophotometer, this analysis is basically a comparison of levels of humic substances in water samples. It is slightly more specific than TOC, but it also has another advantage. Algae produce certain types of carbon compounds that tend to have a low absorbance. Color may be useful in identifying whether or not carbon is produced by algae. It was measured at two frequencies, 400 nanometers and 254 nanometers, chosen because of UV-VIS (ultraviolet - visible) spectrum of aquatic humic substances, shown in the following figure, taken from Thurman's book, *Organic Geochemistry of Natural Waters*, pp. 314:



The most absorbance occurs at the 254 nanometer wavelength, and therefore, absorbance at 254 nanometers is measured.

In general terms, carbon that enters a system from the land, or any source outside the aquatic system, is called allochthonous, while the carbon produced by instream processes is called autochthonous. In every system, allochthonous and autochthonous carbon is present. The production of autochthonous carbon is a fundamental process of every stream ecosystem. This study is an attempt to determine how much autochthonous carbon is produced, using Boulder Creek as a "lab" for investigating this phenomena.

Purpose

The purpose of this experiment was to determine the effects of instream processes on the total organic carbon (TOC) content in a stream such as Boulder Creek, diurnally as well as over an extended period of time.

Hypothesis

The instream processes will either:

- create a system in which the TOC remains in equilibrium, or in other words, the carbon production and consumption will be equal, or
- consume TOC, if the consumption is greater than production, or
- produce TOC, if the production is greater than consumption,

diurnally, as well as over an extended period of time.

The null hypothesis is that the TOC will remain constant, diurnally as well as over an extended period of time.

Materials

TOC:

Oceanographic International Model 700 Carbon Analyzer

DO:

Orion 820 Dissolved Oxygen Meter

Temperature:

Orion 820 Dissolved Oxygen Meter

pH:

Hach Company pH Pocket Pal tester
pH Buffer Powder Pillows pH 7.00

TDS:

Total Dissolved Solids Pocket Pal tester
Conductivity buffer 108 mS

Box:

Aluminum frame 15" x 30" x 24"
silicon aquarium sealant
Plexiglas side panels

Aquaria:

3 uniform aquaria: glass and silicon sealant

Color:

Spectrophotometer:
Bausch and Lomb Spectronic 710, Tungsten and Deuterium lamps
cuvette

Methods

Sample Site

Sample sites were chosen based on a habitat assessment taken from an EPA publication, *Rapid Bioassessment Protocols for use in Streams and Rivers* (Plafkin et al. 1989). Also see Table 2. By the criteria set forth in *Protocols*, a high rating is equivalent to good quality habitat in the stream. A perfect rating would have been a 135. The chosen sites were upstream of the Waste Water Treatment Plant effluent merging with the Creek above 75th street. The first site was near Folsom Field, located approximately midway in the Creek's route through Boulder. This site rated very high in terms of habitat from the assessment (a score of 130), but was also unfortunately a local residence for transients who subsequently vandalized the box within a day of its placement in Boulder Creek. A second site was chosen at 75th street, which also rated very high for habitat with a score of 110. The box was placed in the Creek before there was any knowledge of a large release of water at night from the hydroelectric plant located in Boulder Canyon. This pulse had a flow of approximately 150 cfs at its peak, as compared with the normal flow of the Creek in winter, which is approximately 10 cfs. The water level during the peak flow increased up to 18 inches from the base flow water level. At around 6:00 pm every evening the hydroelectric plant released water in order to operate their generators for about 3-4 hours. This pulse of water destroyed the box at 75th street, although it was not known at that time that the water pulse was the cause. A new site was chosen on City of Boulder Open Space property at

61st street, which scored 130 on the habitat assessment. This site at 61st street was the last site, and the final experimentation and samples were taken at this site.

Experimental Design

In order to obtain quality results, the experimental design of the apparatus had to meet certain criteria. An isolated controlled aquatic microcosm needed to be created, and a box was the most practical design for this purpose. However, since groundwater could not be allowed to enter the system, the box needed to have a bottom, which also meant that the sediment from the Creek had to be disturbed in order for it to be placed in the box. Since macroinvertebrates and algae required a period of time to reestablish within the box, two sides opposite each other were left open for the flow to pass through the box (see figure 3). A period of at least two weeks was required for the re-establishment of macroinvertebrates and algae inside the box, after which the sides were to be attached, thus creating a controlled and isolated microcosm. On the top surface, two rectangular holes were left open for aeration, although they were covered with a screen to prevent the introduction of any large particles that could possibly contain carbon into the system.

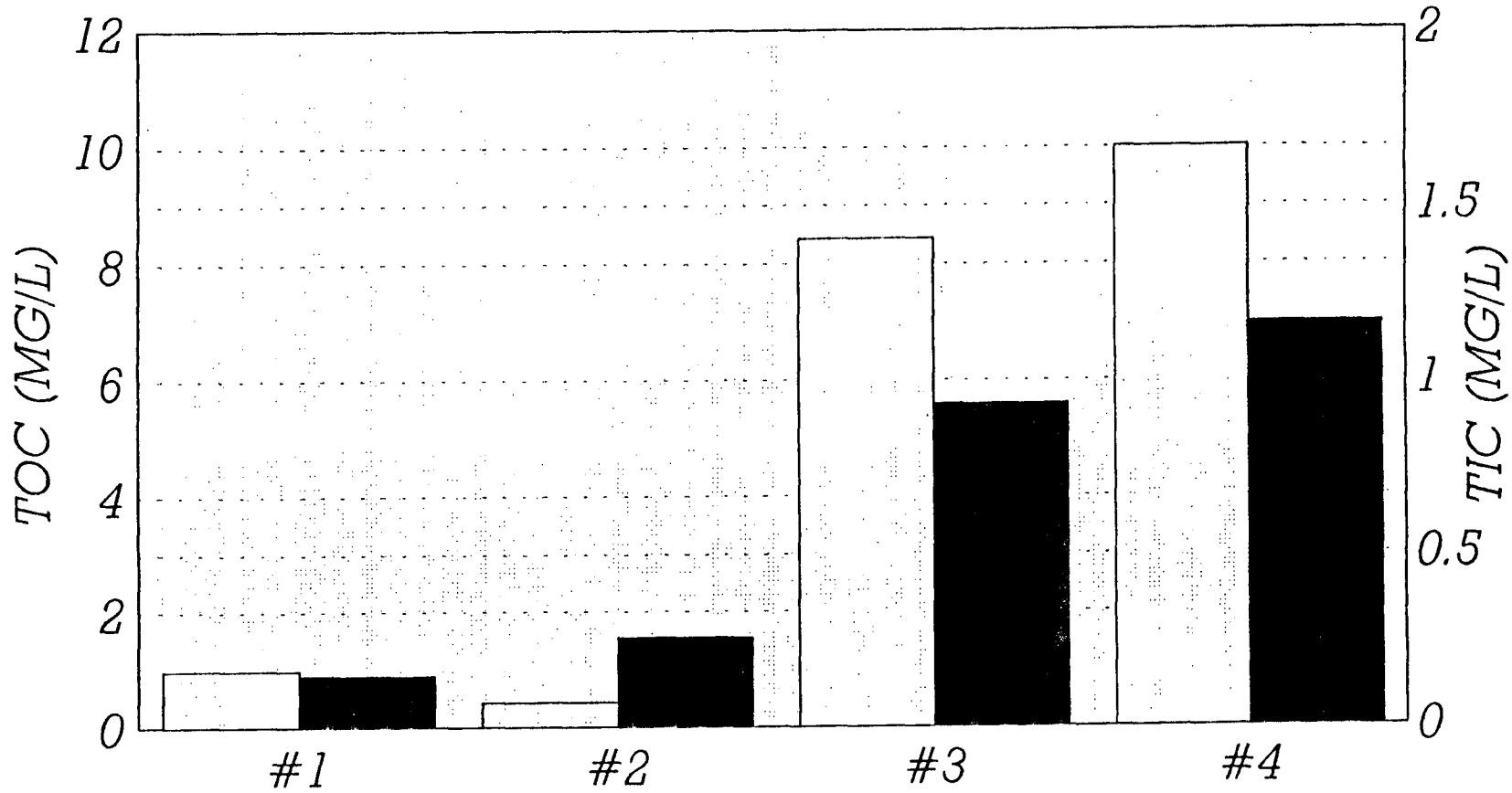
The purpose of experimentation was to measure the TOC of a controlled microcosm. The construction of an apparatus was feasible, but the materials used could not produce carbon by leaching into the sample water. An experiment was performed by placing a piece of Plexiglas and aluminum (proposed materials) in a beaker with 100 mL of distilled water. Another piece of Plexiglas and aluminum was prepared with cork gasket material and also placed in 100 mL of distilled water. The gasket material was to be used for sealing the removable sides of the box,

since they could not be glued under water once the box was placed in the Creek. Duplicate pieces of both aluminum and Plexiglas as well as aluminum, Plexiglas, and gasket material were placed in separate beakers in the same manner. After a week, the aluminum and Plexiglas pieces leached no significant amount of TOC into the water, on average 0.71 mg/L TOC. Also, total inorganic carbon (TIC) compounds were not leached into water in any significant amounts, on average 0.21 mg/L TIC. On the other hand, the gasket material leached significant amounts of both TOC and TIC. The average TOC was 9.13 mg/L and the average TIC was 1.05 mg/L. From this experiment it became evident that gasket material was not suitable for the planned experiment, but a box constructed of Plexiglas sides with an aluminum frame would be acceptable because the apparatus would not leach carbon into the sample water. In addition, the two week stabilization period would allow any carbon to be removed from the box materials.

The box was replicated three times, one box for each site, although this was not foreseen by the original plan. Due to the high flow pulse of water, the box was not strong enough to withstand the flow without being staked with three large stakes to the Creek bed, which was done at 61st street. This prevented it from being washed downstream and destroyed, as it had been at 75th street. Nevertheless, during one high flow period, large chunks of ice approximately 1.5 meters wide by 10 cm thick deformed the box. Also, the water level increased over the top of the box, thus preventing a closed system due to the aeration holes on the top surface. A modification was made to the original plan by removing the sediment from the bottom of the box into an aquarium, which was removed from the site after the diurnal samples were taken.

LEACHING EXPERIMENT

Materials test



#1 = aluminum and plexiglas
#2 = duplicate of #1
#3 = #1 with gasket material
#4 = duplicate of #3

Preservation

Two 40 mL bottles of samples were taken at every sample time and date. One was left as taken from the Creek, box, or aquarium. The other duplicate bottle was preserved with 10 drops of (0.66 mL) a 2 normal solution of Phosphoric Acid (H_3PO_4). With phosphoric acid, the pH of the sample was dropped to 2 to prevent bacterial and other biological activity, which might have consumed a portion of the carbon content in the sample. Phosphoric Acid was chosen because it was used in the carbon analyzer method. Other acids, e.g. Hydrochloric Acid, would have interfered with the carbon analyzer method.

Diurnal Samples: 30 Dec., 1995

The box was placed in the Creek two weeks prior to the 24 hour sampling period.

Ideally, the box was to be closed at midnight and remained closed for a week while samples were taken from the box and Creek. However, due to the high-flow pulse of water from the hydroelectric plant, this plan had to be modified. The box with ends attached could not stand the water pressure of high flow, plus the peak water level was above the top surface of the box. At noon on 30 Dec., 1995 local time the sides were attached and samples taken from the box every two hours until 4:00 pm 30 Dec., 1995. The setting sun, lack of light, and impending water release of water from the hydroelectric plant prevented sampling from the box after this time.

Samples from Boulder Creek were taken from 61st street in the same spot where the box was located. The first sample was taken on 30 Dec., 1995 at 12:00 am (00:00 hours). Samples were collected every two hours until 10:00 PM on 30 Dec., 1995. Two 40 mL samples were

taken from the Creek and the box when possible, and one was preserved with 2N phosphoric acid (H_3PO_4). Both were placed in a cooler for further preservation.

At the lab, TOC, TIC, and color were analyzed as a set, along with the extended period samples.

Samples over an extended period: 31 Dec., 1995 - 7 Jan, 1996

After the samples from the box were completed at 4:00 PM on 30 Dec., 1995, the contents of the box were removed and placed in an aquarium. Although the aquarium was smaller than the box, a proportional amount of sediment and water was placed in the aquarium. Another aquarium was filled with Creek water without any sediment. The aquarium with sediment, macroinvertebrates, and plant matter was labeled #1 and the aquarium with Creek water was labeled #2. A third aquarium was filled with distilled water as a control, and labeled #3. The aquaria were transported off site so that the water would not freeze at night.

Every day from 31 Dec., 1995 to 7 Jan, 1996 two samples were collected at 4:00 PM, one of which was preserved. At this time, pH, DO, temperature, and TDS were also measured.

At the lab, TOC, TIC, and color at 400 nm and 254 nm were analyzed as a set along with the diurnal samples.

Carbon Analysis: Total Organic Carbon (TOC)

Although there are many methods for analyzing organic carbon, the following is a fairly common method that can be found in *Standard Methods for the Examination of Water and Wastewater*, method # 505, Organic Carbon Combustion-Infrared Method. To meet specific requirements of the analyzer, etc., the method was modified accordingly.

TOC was measured by heated persulfate oxidation using an Oceanographic International Model 700 Carbon Analyzer. This method involved acidifying a 1 mL water sample with a 0.8 mL 2 N phosphoric acid (H_3PO_4) to convert inorganic carbon to carbon dioxide (CO_2) and sparging with nitrogen gas (N_2 - medical grade). The N_2 sparge gas passed through a molecular sieve where the CO_2 was trapped. The trapped CO_2 was thermally desorbed at 200°C and measured by Infrared detector. After removal of inorganic carbon, 0.5 mL of saturated sodium persulfate ($Na_2S_2O_8$) was added and the sample was heated to 100°C to oxidize the organic carbon to CO_2 which is then measured in the same way as inorganic carbon. The reagent grade sodium persulfate and phosphoric acid were obtained from J.T. Baker. Each sample was analyzed in duplicate, and concentrations were calculated using a 6 point calibration curve prepared from potassium hydrogen phthalate as the carbon standard. Distilled water blanks and quality assurance standards were analyzed approximately every 10 samples. The detection limits for this method was about 0.1 mg/L.

For the diurnal samples, 4 sets of duplicates were run for the following times: midnight, preserved, unpreserved; 8:00 AM, preserved, unpreserved; 4:00 PM, preserved, unpreserved; box at 4:00 PM, preserved, unpreserved. Duplicates were also run for the extended period samples for the following dates: 31 Dec., aquaria 1, 2, 3, preserved, unpreserved; 5 Jan, aquaria 1, 2, 3,

preserved, unpreserved. Duplicates allowed a standard deviation and a student t-test to be calculated.

Color

Absorbance was measured with a Bausch and Lomb Spectronic 710 spectrophotometer with Tungsten and Deuterium lamps. The spectrophotometer utilized UV-VIS spectra. Using the Tungsten lamp, absorbance at 400 nanometers was measured, and absorbance at 254 nanometers was measured with the Deuterium lamp. The sample was placed in a cuvette with a path link of 1 cm, constructed of quartz. Along with the samples, standards of 5, 10, 25, and 50 in Platinum/Cobalt units were analyzed at 400 nm wavelength.

Dissolved Oxygen

Dissolved Oxygen was analyzed using an battery operated Orion 820 Dissolved Oxygen Meter. It consisted of a two electrode system that was separated from the sample by an oxygen permeable Teflon membrane. When a polarizing voltage was imposed across the system through the electrode, the Dissolved Oxygen in the sample caused a measurable current to flow between the silver anode and the gold cathode. The current varied directly with diffusion of dissolved oxygen across the membrane, which is proportional to the partial pressure of oxygen outside the membrane. Because the percent saturation of oxygen in water is dependent upon the temperature

(i.e., as the temperature increases, the less dissolved oxygen the water is able to absorb), two thermistors were also incorporated for the temperature compensation of percent saturation.

Temperature

Temperature was also measured with the Orion DO meter. Since the percent saturation of dissolved oxygen was calculated based upon the temperature of the water, the DO probe included two thermistors. It was accurate to a tenth of a degree Celsius.

pH

The pH was measured with a Hach Company pH Pocket Pal pH tester, and is a measure of the hydrogen ion activity. The probe consisted of a glass half cell, and a reference half cell. The glass half cell separated the sample from an inner solution with a known pH. An electrical potential was developed on both sides of the glass, and it varies based on the pH of the sample. The reference electrode had a constant electrical potential, allowing the meter to adjust the pH based on the temperature of the water. Accuracy was to a tenth of a unit.

Total Dissolved Solids (TDS)

TDS was measured using a Hach Company TDS Pocket Pal tester. The probe consisted of two electrodes. As an electrical current was passed through one, the dissolved solids in the

sample conduct the current to the second electrode. The strength of the current depended upon the amount of TDS in the water. The accuracy was to 10 mg/L.

Statistical Analysis

$$\text{Mean} = \frac{\sum x}{n}$$

Where: x is the measured value and n is the number of samples

$$\text{Standard deviation} = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n}} = \sigma$$

$$\text{Relative Standard Deviation} = \frac{\sigma}{mean}$$

$$\text{correlation coefficient} = \frac{\sigma_{xy}}{\sigma_x * \sigma_y}$$

linear regression: $y = mx + b$, where m is the slope, and b is the y-intercept

t-test = $\frac{M_1 - M_2}{\sqrt{\left(\frac{\sum x_1^2 + \sum x_2^2}{n_1 + n_2 - 2}\right)\left(\frac{n_1 + n_2}{n_1 n_2}\right)}}$ where M_1, M_2 are the mean values if set 1 and

2

median = y_m if n is odd where m = (n-1)/2

mean of y_m and y_{m-1}

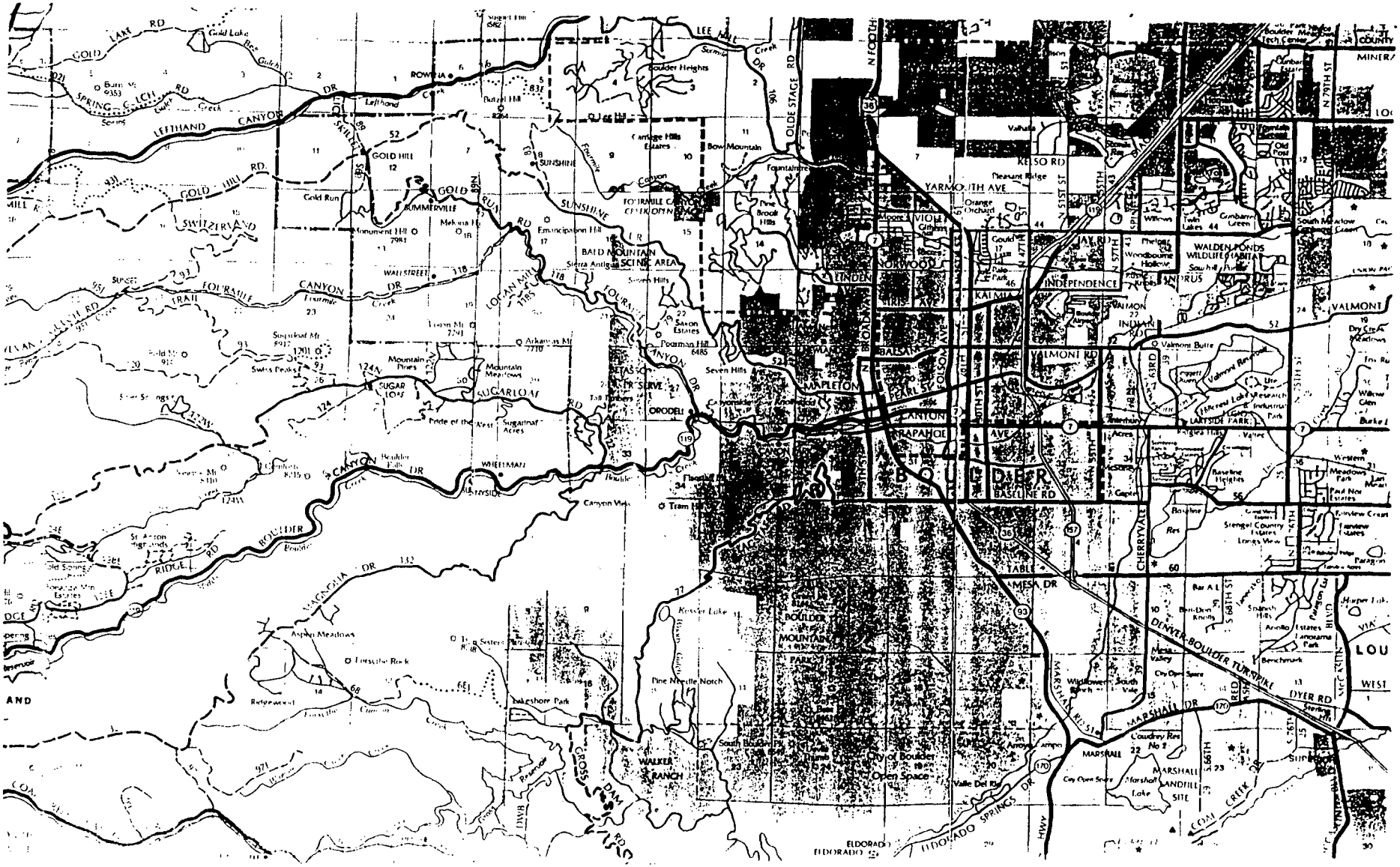


Figure 1: A map of Boulder, Colorado. The sample site was located at 61st Street, above the confluence with the Waste Water Treatment Plant effluent.

HABITAT ASSESSMENT FIELD DATA SHEET

Habitat Parameter	Category			
	Excellent	Good	Fair	Poor
1. *Bottom substrate available cover[a]	Greater than 50% rubble, gravel, submerged logs, undercut banks, or other stable habitat. 16-20	30-50% rubble, gravel or other stable habitat. Adequate habitat. 11-15	10-30% rubble, gravel or other stable habitat. Habitat availability less than desirable. 6-10	Less than 10% rubble gravel or other stable habitat. Lack of habitat is obvious. 0-5
2. Embeddedness[b]	Gravel, cobble, and boulder particles are between 0 and 25 % surrounded by fine sediment 16-20	Gravel, cobble, and boulder particles are between 25 and 50 % surrounded by fine sediment 11-15	Gravel, cobble, and boulder particles are between 50 and 75 % surrounded by fine sediment 6-10	Gravel, cobble, and boulder particles are over 75 % surrounded by fine sediment 0-5
3. ≤0.15 cms (5 cfs) * *Flow[a] at rep. low flow	Cold >0.05 cms (2 cfs) Warm >0.15 cms (5 cfs) 10-20	0.03-0.05 cms (1-2 cfs) 0.05-0.15 cms (2-5 cfs) 11-15	0.01-0.03 cms (.5-1 cfs) 0.03-0.05 cms (1-2 cfs) 6-10	<0.01 cms (.5 cfs) <0.03 cms (1 cfs) 0-5
or >0.15 cms (5cfs) * Velocity/depth	Slow (<0.3 m/s), deep (>0.5 m); slow, shallow (<0.5 m); fast (>0.3 m/s), deep; fast, shallow habitats all present. 16-20	Only 3 of the 4 habitat categories present (missing riffles or runs receive lower score than missing pools). 11-15	Only 2 of the 4 habitat categories present (missing riffles/runs receive lower score). 6-10	Dominated by one velocity/depth category (usually pool). 0-5
4. * Channel alteration[a]	Little or no enlargement of islands or point bars, and/or no channelization. 12-15	Some new increase in bar formation, mostly from coarse gravel; and/or some channelization present. 8-11	Moderate deposition of new gravel, coarse sand on old and new bars; pools partially filled w/silt; and/or embankments on both banks. 4-7	Heavy deposits of fine material, increased bar development; most pools filled w/silt; and/or extensive channelization. 0-3
5. Bottom scouring and deposition[a]	Less than 5% of the bottom affected by scouring and deposition. 12-15	5-30% affected. Scour at constrictions and where grades steepen. Some deposition in pools. 8-11	30-50% affected. Deposits and scour at obstructions, constrictions and bends. Some filling of pools. 4-7	More than 50% of the bottom changing nearly year long. Pools almost absent due to deposition. Only large rocks in riffle exposed. 0-3

(a) From Ball 1982.
(b) From Platts et al. 1983.
Note: * = Habitat parameters not currently incorporated into BIOS.

Figure 2: Habitat Assessment taken from EPA publication. A habitat assessment was done for each site to ensure high quality

HABITAT ASSESSMENT FIELD DATA SHEET (cont.)

Habitat Parameter	Category: Excellent	Good	Fair	Poor
6. Pool/riffle, run/bend ratio[a] (distance between riffles divided by stream width)	5-7. Variety of habitat. Deep riffles and pools. 12-15	7-15. Adequate depth in pools and riffles. Bends provide habitat. 8-11	15-25. Occassional riffle or bend. Bottom contours provide some habitat. 4-7	>25. Essentially a straight stream. Generally all flat water or shallow riffle. Poor habitat. 0-3
7. Bank stability[a]	Stable. No evidence of erosion or bank failure. Side slopes generally <30%. Little potential for future problem. 9-10	Moderately stable. Infrequent, small areas of erosion mostly healed over. Side slopes up to 40% on one bank. Slight potential in extreme floods. 6-8	Moderately unstable. Moderate frequency and size of erosional areas. Side slopes up to 60% on some banks. High erosion potential during extreme high flow. 3-5	Unstable. Many eroded areas. Side slopes >60% common. "Raw" areas frequent along straight sections and bends. 0-2
8. Bank vegetative stability[b]	Over 80% of the streambank surfaces covered by vegetation or boulders and cobble. 9-10	50-79% of the streambank surfaces covered by vegetation, gravel or larger material. 6-8	25-49% of the streambank surfaces covered by vegetation, gravel, or larger material. 3-5	Less than 25% of the streambank surfaces covered by vegetation, gravel, or larger material. 0-2
9. Streamside cover[b]	Dominant vegetation is shrub. 9-10	Dominant vegetation is of tree form. 6-8	Dominant vegetation is grass or forbes. 3-5	Over 50% of the streambank has no vegetation and dominant material is soil, rock, bridge materials, culverts, or mine tailings. 0-2
Column Totals	____	____	____	____

Score _____

Figure 2: continued.

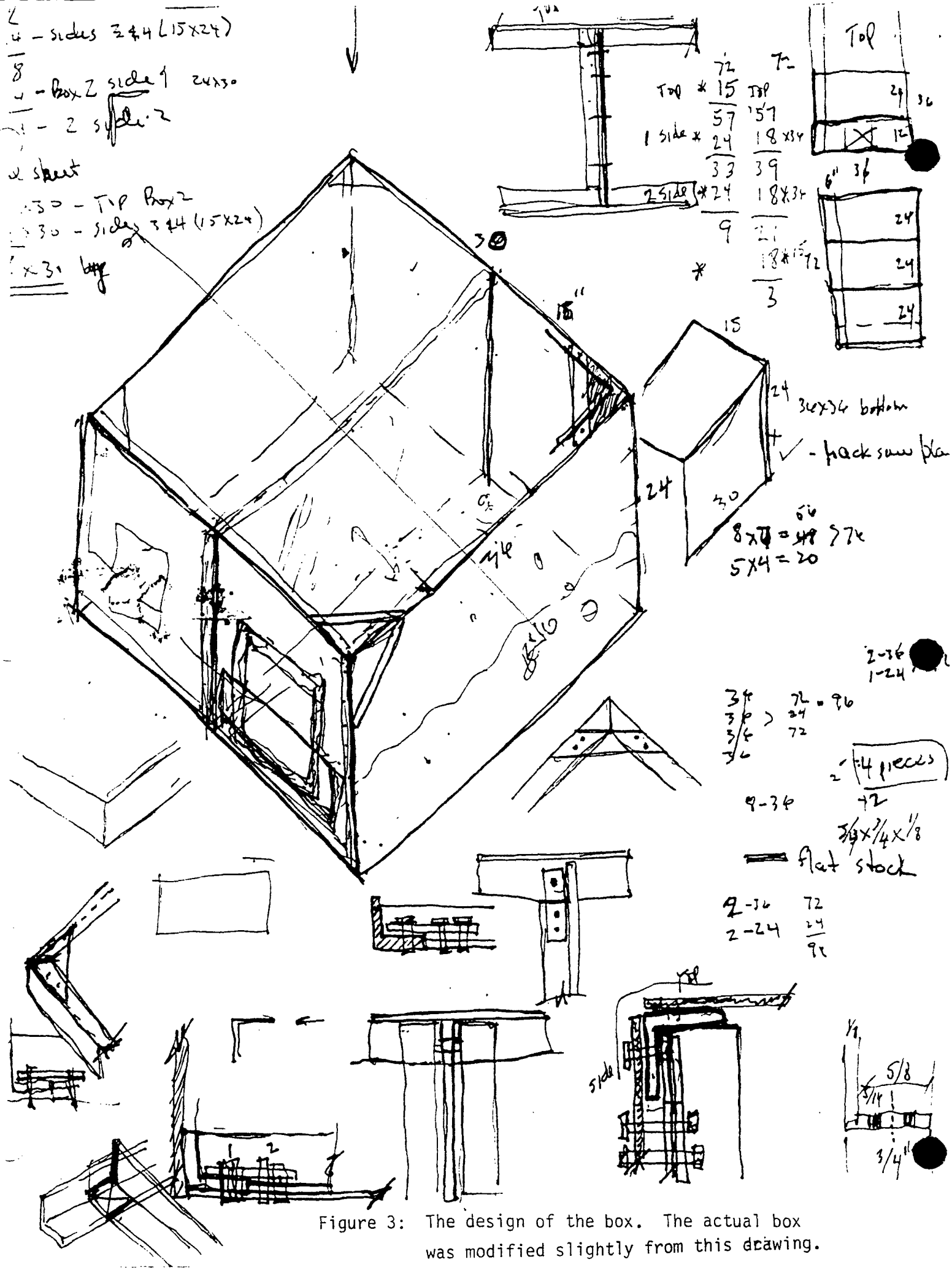


Figure 3: The design of the box. The actual box was modified slightly from this drawing.

Results

Quality assurance/Quality control

	# of samples	min	max	mean	median	std dev	rsd
DIW	10	0.06	0.22	0.14	0.13	0.06	0.43
1 std	5	1.11	1.51	1.27	1.14	0.18	0.14
3 std	6	3.04	3.29	3.2	3.24	0.09	0.03

LEACHING EXPERIMENT

	TOC (MG/L)	TIC(MG/L)
#1: ALUM+PLEXIGLA	0.99	0.15
#2: W/ GASKET	8.42	0.93
#3: DUP #1	0.43	0.26
4: DUP #2	10.01	1.16

FILENAME: 01-11-96.WKS

NUMBER	SAMPLE	TOC1	TOC2	TIC1	TIC2
SPL# 00001	RB	3.20	3.20	2.93	2.93
SPL# 00002	DIW	3.73	3.73	2.67	2.40
SPL# 00003	0.5	9.92	10.19	4.81	4.54
SPL# 00004	1	16.97	17.25	3.73	3.47
SPL# 00005	3	41.74	42.02	4.54	4.27
SPL# 00006	5	68.41	68.41	5.07	5.34
SPL# 00007	7	91.37	93.53	5.61	6.15
SPL# 00008	10	127.87	129.18	6.68	5.34
SPL# 00009	15	201.14	193.81	6.42	4.27
SPL# 00010	10 DIC	6.15	6.68	128.86	128.20
SPL# 00011	30	6.68	6.15	402.33	399.41
SPL# 00012	DIW	4.54	4.27	3.47	4.00
SPL# 00013	INITIAL A	31.05	30.21	108.87	105.71
SPL# 00014	INITIAL B	31.05	31.88	111.09	108.87
SPL# 00015	HIGH FLOW A	28.54	29.10	84.64	87.38
SPL# 00016	HIGH FLOW B	29.37	30.77	84.94	86.16
SPL# 00017	BC61 12:00AM U	33.56	34.12	114.28	111.09
SPL# 00018	BC61 12:00 AM P	29.37	29.37	59.59	60.46
SPL# 00019	BC61 2:00AM U	32.72	33.84	123.63	123.31
SPL# 00020	BC61 2:00AM P	32.44	31.05	57.25	59.29
SPL# 00021	BC61 4:00AM U	33.84	34.96	157.38	150.55
SPL# 00022	BC61 4:00AM P	39.47	81.30	75.57	81.60
SPL# 00023	BC61 6:00AM U	38.06	37.49	188.01	183.34
SPL# 00024	BC61 6:00AM P	36.37	36.37	77.67	80.69
SPL# 00025	BC61 8:00AM U	36.09	37.49	194.18	197.83
SPL# 00026	BC61 8:00AM P	35.24	34.68	90.45	91.68
SPL# 00027	BC61 10:00AM U	34.40	34.40	210.79	208.18
SPL# 00028	BC61 10:00AM P	32.16	33.56	78.28	78.28
SPL# 00029	BC61 12:00PM U	33.56	34.12	193.45	188.73
SPL# 00030	BC61 12:00PM P	30.77	31.32	71.68	72.58
SPL# 00031	BOX 12:00PM U	32.72	34.68	184.41	192.72
SPL# 00032	BOX 12:00PM P	33.00	33.56	53.19	55.51
SPL# 00033	BC61 2:00PM U	33.00	33.28	193.45	193.81
SPL# 00034	BC61 2:00PM P	31.88	32.16	70.79	71.98
SPL# 00035	BOX 2:00PM U	34.40	33.84	198.20	190.18
SPL# 00036	BOX 2:00PM P	33.84	34.40	53.19	56.38
SPL# 00037	DIW	5.61	5.88	3.73	3.73
SPL# 00038	1 DOC STD	22.18	21.63	4.00	3.73
SPL# 00039	3 DOCSTD	45.72	44.30	3.47	3.73
SPL# 00040	3 DOC STD	43.73	45.72	3.73	3.73
SPL# 00041	BC61 4:00PM U	34.68	34.96	196.00	203.73
SPL# 00042	BC61 4:00PM P	30.77	31.05	49.73	51.75

SPL# 00043 BOX 4:00PM U	36.37	37.21	195.27	201.88
SPL# 00044 BOX 4:00PM P	33.00	34.40	39.19	41.17
SPL# 00045 BC61 6:00PM U	33.00	33.28	200.40	207.81
SPL# 00046 BC61 6:00PM P	35.24	34.12	46.29	48.01
SPL# 00047 BC61 8:00PM U	29.65	29.93	219.08	218.70
SPL# 00048 BC61 8:00PM P	31.32	31.88	33.00	34.12
SPL# 00049 BC61 10:00PM U	30.77	30.77	81.60	84.33
SPL# 00050 BC61 10:00PM P	32.72	32.44	14.79	15.07
SPL# 00051 (DUP)BC61 12:00AMU	37.78	37.78	107.92	108.55
SPL# 00052 (DUP)BC61 12:00AMP	30.77	30.77	13.71	13.98
SPL# 00053 (DUP)BC61 8:00AMU	35.81	36.09	197.10	196.73
SPL# 00054 (DUP)BC61 8:00AMP	32.72	32.44	29.10	29.93
SPL# 00055 (DUP)BC61 4:00PMU	34.96	34.96	198.20	197.83
SPL# 00056 (DUP)BC61 4:00PMP	31.60	31.88	20.53	20.81
SPL# 00057 (DUP) BOX 4:00PM U	37.49	36.65	197.47	197.83
SPL# 00058 (DUP)BOX 4:00PM P	32.72	34.40	26.04	27.43
SPL# 00059 DIW	5.61	5.88	3.47	3.47
SPL# 00060 AQ1 12/30/5 U	40.04	39.75	205.21	212.67
SPL# 00061 (DUP)AQ1 12/30/5 U	40.04	39.19	207.06	202.25
SPL# 00062 AQ1 12/30/5 P	45.15	44.58	26.60	27.43
SPL# 00063 (DUP)AQ1 12/30/5 P	46.01	44.58	22.73	23.28
SPL# 00064 AQ2 12/30/5 U	39.19	38.91	200.77	204.47
SPL# 00065 DIW	5.34	5.61	3.73	3.73
SPL# 00066 1 STD	22.18	22.18	3.20	3.47
SPL# 00067 3 STD	44.30	44.87	3.47	3.20
SPL# 00068 5 STD	72.58	73.18	3.20	3.20
SPL# 00069 (DUP)AQ2 12/30/5 U	38.62	40.04	202.99	202.25
SPL# 00070 AQ2 12/30/5 P	38.06	38.06	20.53	21.08
SPL# 00071 (DUP) AQ2 12/30 P	40.32	38.62	19.43	19.43
SPL# 00072 AQ3 12/30/5 U	9.92	9.92	6.42	6.42
SPL# 00073 (DUP)AQ3 12/30 U	9.92	9.92	6.42	6.42
SPL# 00074 AQ3 12/30/5 P	8.57	8.30	2.93	2.93
SPL# 00075 (DUP) AQ3 12/30 P	8.57	8.84	3.73	3.20
SPL# 00076 AQ1 1/1/6 U	38.91	40.32	208.18	211.92
SPL# 00077 AQ1 1/1/6 P	40.60	39.47	13.71	14.79
SPL# 00078 AQ2 1/1/6 U	34.96	34.96	203.36	201.14
SPL# 00079 AQ2 1/1/6 P	39.75	40.32	13.71	14.25
SPL# 00080 AQ3 1/1/6 U	16.97	17.25	6.15	6.15
SPL# 00081 AQ3 1/1/6 P	15.34	15.07	2.67	2.67
SPL# 00082 AQ1 1/2/6 U	41.17	42.02	209.67	208.55
SPL# 00083 AQ1 1/2/6 P	45.72	46.87	11.81	12.35
SPL# 00084 AQ2 1/2/6 U	37.49	38.06	200.77	200.77
SPL# 00085 DIW	4.54	4.54	2.13	2.40
SPL# 00086 1 STD	17.52	17.52	4.00	3.73
SPL# 00087 3 STD	42.87	42.30	4.27	4.27
SPL# 00088 DIW	4.54	4.00	2.13	2.13

FILENAME: 01-11-96

Sample	Avg TOC mv	TOC (mg/L)	Avg TIC mv
RB	3.20	0.02	2.93
DIW	3.73	0.07	2.53
0.5	10.05	0.56	4.67
1	17.11	1.11	3.60
3	41.88	3.04	4.40
5	68.41	5.12	5.21
7	92.45	6.99	5.88
10	128.53	9.81	6.01
15	197.48	15.20	5.34
10 DIC	6.42	0.27	128.53
30	6.42	0.27	400.87
DIW	4.40	0.12	3.73
INITIAL A	30.63	2.17	107.29
INITIAL B	31.46	2.23	109.98
HIGH FLOW A	28.82	2.02	86.01
HIGH FLOW B	30.07	2.12	85.55
BC61 12:00AM U	33.84	2.42	112.69
BC61 12:00 AM P	29.37	2.07	60.02
BC61 2:00AM U	33.28	2.37	123.47
BC61 2:00AM P	31.74	2.25	58.27
BC61 4:00AM U	34.40	2.46	153.96
BC61 4:00AM P	60.38	4.49	78.58
BC61 6:00AM U	37.78	2.72	185.67
BC61 6:00AM P	36.37	2.61	79.18
BC61 8:00AM U	36.79	2.65	196.01
BC61 8:00AM P	34.96	2.50	91.06
BC61 10:00AM U	34.40	2.46	209.49
BC61 10:00AM P	32.86	2.34	78.28
BC61 12:00PM U	33.84	2.42	191.09
BC61 12:00PM P	31.05	2.20	72.13
BOX 12:00PM U	33.70	2.41	188.57
BOX 12:00PM P	33.28	2.37	54.35
BC61 2:00PM U	33.14	2.36	193.63
BC61 2:00PM P	32.02	2.27	71.39
BOX 2:00PM U	34.12	2.44	194.19
BOX 2:00PM P	34.12	2.44	54.79
DIW	5.74	0.22	3.73
1 DOC STD	21.91	1.48	3.87
3 DOCSTD	45.01	3.29	3.60
3 DOC STD	44.72	3.27	3.73
BC61 4:00PM U	34.82	2.49	199.86
BC61 4:00PM P	30.91	2.19	50.74

BOX 4:00PM U	36.79	2.65	198.58
BOX 4:00PM P	33.70	2.41	40.18
BC61 6:00PM U	33.14	2.36	204.11
BC61 6:00PM P	34.68	2.48	47.15
BC61 8:00PM U	29.79	2.10	218.89
BC61 8:00PM P	31.60	2.24	33.56
BC61 10:00PM U	30.77	2.18	82.97
BC61 10:00PM P	32.58	2.32	14.93
(DUP)BC61 12:00AMU	37.78	2.72	108.24
(DUP)BC61 12:00AMP	30.77	2.18	13.84
(DUP)BC61 8:00AMU	35.95	2.58	196.92
(DUP)BC61 8:00AMP	32.58	2.32	29.51
(DUP)BC61 4:00PMU	34.96	2.50	198.02
(DUP)BC61 4:00PMP	31.74	2.25	20.67
(DUP) BOX 4:00PM U	37.07	2.67	197.65
(DUP)BOX 4:00PM P	33.56	2.40	26.74
DIW	5.74	0.22	3.47
AQ1 12/30/5 U	39.89	2.89	208.94
(DUP)AQ1 12/30/5 U	39.61	2.87	204.66
AQ1 12/30/5 P	44.87	3.28	27.01
(DUP)AQ1 12/30/5 P	45.29	3.31	23.01
AQ2 12/30/5 U	39.05	2.82	202.62
DIW	5.48	0.20	3.73
1 STD	22.18	1.51	3.33
3 STD	44.58	3.26	3.33
5 STD	72.88	5.47	3.20
(DUP)AQ2 12/30/5 U	39.33	2.85	202.62
AQ2 12/30/5 P	38.06	2.75	20.81
(DUP) AQ2 12/30 P	39.47	2.86	19.43
AQ3 12/30/5 U	9.92	0.55	6.42
(DUP)AQ3 12/30 U	9.92	0.55	6.42
AQ3 12/30/5 P	8.43	0.43	2.93
(DUP) AQ3 12/30 P	8.70	0.45	3.47
AQ1 1/1/6 U	39.61	2.87	210.05
AQ1 1/1/6 P	40.04	2.90	14.25
AQ2 1/1/6 U	34.96	2.50	202.25
AQ2 1/1/6 P	40.04	2.90	13.98
AQ3 1/1/6 U	17.11	1.11	6.15
AQ3 1/1/6 P	15.20	0.96	2.67
AQ1 1/2/6 U	41.59	3.02	209.11
AQ1 1/2/6 P	46.29	3.39	12.08
AQ2 1/2/6 U	37.78	2.72	200.77
DIW	4.54	0.13	2.27
1 STD	17.52	1.14	3.87
3 STD	42.59	3.10	4.27
DIW	4.27	0.11	2.13

FILENAME:01-11-96

TIC (mg/L)
0.15
0.12
0.29
0.20
0.27
0.33
0.38
0.39
0.34
9.96
31.23
0.21
8.30
8.51
6.64
6.60
8.72
4.61
9.57
4.47
11.95
6.06
14.42
6.11
15.23
7.03
16.28
6.04
14.85
5.56
14.65
4.17
15.04
5.50
15.09
4.20
0.21
0.22
0.20
0.21
15.53
3.89

Calibration Curve

Conc	Avg mv	Avg mv - RB	DOC mg/l
0.5	10.05	6.85	0.56
1	17.11	13.91	1.11
3	41.88	38.68	3.04
5	68.41	65.21	5.12
7	92.45	89.25	6.99
10	128.53	125.33	9.81
15	197.48	194.28	15.20

Regression Output:

Constant		-0.02384
Std Err of Y Est		0.133806
R Squared		0.999452
No. of Observations		7
Degrees of Freedom		5
X Coefficient(s)	0.078099	
Std Err of Coef.	0.000818	

15.43
3.06
15.86
3.60
17.02
2.54
6.40
1.09
8.38
1.00
15.30
2.23
15.39
1.54
15.36
2.01
0.19
16.24
15.91
2.03
1.72
15.75
0.21
0.18
0.18
0.17
15.75
1.55
1.44
0.42
0.42
0.15
0.19
16.33
1.04
15.72
1.01
0.40
0.13
16.25
0.87
15.60
0.10
0.22
0.26
0.09

FILENAME: 01-12-96.WKS

NUMBER	SAMPLE	TOC1	TOC2	TIC1	TIC2
SPL# 00001	RB	2.93	3.20	2.40	2.40
SPL# 00002	DIW	4.27	4.00	2.67	2.93
SPL# 00003	0.5	10.46	10.19	4.27	4.00
SPL# 00004	1	17.52	17.25	3.47	3.73
SPL# 00005	3	42.59	42.59	3.73	3.73
SPL# 00006	5	69.30	66.93	4.27	4.27
SPL# 00007	7	92.61	91.99	4.54	4.54
SPL# 00008	10	130.17	128.86	4.27	4.27
SPL# 00009	15	193.09	190.91	4.00	3.73
SPL# 00010	10 DIC	5.88	5.88	126.57	126.24
SPL# 00011	30	6.68	6.42	396.98	399.41
SPL# 00012	DIW	4.27	4.00	2.67	2.67
SPL# 00013	AQ2 1/2/6 P	38.06	37.21	143.45	151.22
SPL# 00014	AQ3 1/2/6 U	13.71	14.52	6.42	6.42
SPL# 00015	AQ3 1/2/6 P	14.79	15.07	4.54	4.27
SPL# 00016	AQ1 1/3/6 P	42.02	41.45	224.02	222.88
SPL# 00017	AQ1 1/3/6 U	54.35	53.48	139.10	144.12
SPL# 00018	AQ2 1/3/6 U	36.09	36.09	200.04	198.57
SPL# 00019	AQ2 1/3/6 P	36.37	37.78	118.14	124.61
SPL# 00020	AQ3 1/3/6 U	17.25	17.52	7.22	7.76
SPL# 00021	AQ3 1/3/6 P	18.34	18.89	4.27	4.00
SPL# 00022	AQ1 1/4/6 U	44.87	45.72	223.64	227.09
SPL# 00023	AQ1 1/4/6 P	48.01	49.16	123.31	126.89
SPL# 00024	AQ2 1/4/6 U	39.19	39.47	211.17	211.54
SPL# 00025	AQ2 1/4/6 P	35.81	35.81	99.12	101.31
SPL# 00026	AQ3 1/4/6 U	18.07	17.79	7.22	7.22
SPL# 00027	AQ3 1/4/6 P	22.18	21.91	3.73	3.47
SPL# 00028	AQ1 1/5/6 U	47.15	46.01	222.88	225.94
SPL# 00029	(DUP) AQ1 U	46.87	47.15	225.94	224.02
SPL# 00030	AQ1 1/5/6 P	45.15	45.44	99.12	101.00
SPL# 00031	(DUP) AQ1 P	46.87	46.87	92.30	95.39
SPL# 00032	AQ2 1/5/6 U	37.49	36.93	201.88	207.06
SPL# 00033	(DUP) AQ2 U	36.93	37.21	200.40	204.47
SPL# 00034	AQ2 1/5/6 P	36.37	35.24	69.30	71.98
SPL# 00035	(DUP) AQ2 P	36.09	35.81	67.53	68.12
SPL# 00036	AQ3 1/5/6 U	19.98	19.43	7.76	7.76
SPL# 00037	DIW	5.07	5.07	2.93	3.20
SPL# 00038	1 STD	19.98	19.71	3.20	3.20
SPL# 00039	3 STD	44.30	43.16	2.67	2.67
SPL# 00040	3 STD	44.01	42.87	2.67	2.67
SPL# 00041	(DUP) AQ3 U	19.71	19.16	7.76	7.76
SPL# 00042	AQ3 1/5/6 P	21.63	22.18	3.20	3.20

SPL# 00043 (DUP) AQ3 P	21.63	21.63	3.20	2.93
SPL# 00044 AQ1 1/6/6 U	48.30	47.72	220.98	221.36
SPL# 00045 AQ1 1/6/6 P	47.15	48.58	47.44	48.58
SPL# 00046 AQ2 1/6/6 U	37.78	37.49	198.93	197.83
SPL# 00047 AQ2 1/6/6 P	36.93	37.49	42.59	43.73
SPL# 00048 AQ3 1/6/6 U	20.81	20.26	6.42	6.95
SPL# 00049 AQ3 1/6/6 P	23.83	23.28	2.93	3.20
SPL# 00050 AQ1 1/7/6 U	50.02	49.45	222.88	222.50
SPL# 00051 AQ1 1/7/6 P	49.73	48.30	42.87	44.58
SPL# 00052 AQ2 1/7/6 U	36.37	37.21	201.51	203.73
SPL# 00053 AQ2 1/7/6 P	36.65	36.65	33.28	34.96
SPL# 00054 AQ3 1/7/6 U	19.43	19.71	7.49	7.76
SPL# 00055 AQ3 1/7/6 P	20.53	20.53	3.20	3.20
SPL# 00056 DIW	6.15	6.68	2.93	2.93
SPL# 00057 DIW	5.07	5.07	2.93	2.67
SPL# 00058 1 STD	18.34	18.07	3.20	2.93
SPL# 00059 3 STD	44.58	44.30	2.67	2.67
SPL# 00060 DIW	4.81	5.07	3.20	3.20

FILENAME: 01-12-96.WKS

Sample	Avg TOC mv	TOC (mg/L)	Avg TIC mv
RB	3.07	-0.09	2.40
DIW	4.14	-0.00	2.80
0.5	10.32	0.49	4.14
1	17.38	1.06	3.60
3	42.59	3.08	3.73
5	68.12	5.12	4.27
7	92.30	7.06	4.54
10	129.51	10.04	4.27
15	192.00	15.04	3.87
10 DIC	5.88	0.14	126.40
30	6.55	0.19	398.19
DIW	4.14	-0.00	2.67
AQ2 1/2/6 P	37.64	2.68	147.34
AQ3 1/2/6 U	14.11	0.80	6.42
AQ3 1/2/6 P	14.93	0.86	4.40
AQ1 1/3/6 U	41.74	3.01	223.45
AQ1 1/3/6 P	53.92	3.98	141.61
AQ2 1/3/6 U	36.09	2.56	199.30
AQ2 1/3/6 P	37.07	2.63	121.37
AQ3 1/3/6 U	17.38	1.06	7.49
AQ3 1/3/6 P	18.61	1.16	4.14
AQ1 1/4/6 U	45.29	3.29	225.36
AQ1 1/4/6 P	48.59	3.56	125.10
AQ2 1/4/6 U	39.33	2.82	211.36
AQ2 1/4/6 P	35.81	2.53	100.21
AQ3 1/4/6 U	17.93	1.10	7.22
AQ3 1/4/6 P	22.04	1.43	3.60
AQ1 1/5/6 U	46.58	3.40	224.41
(DUP) AQ1 U	47.01	3.43	224.98
AQ1 1/5/6 P	45.29	3.29	100.06
(DUP) AQ1 P	46.87	3.42	93.84
AQ2 1/5/6 U	37.21	2.65	204.47
(DUP) AQ2 U	37.07	2.63	202.44
AQ2 1/5/6 P	35.81	2.53	70.64
(DUP) AQ2 P	35.95	2.54	67.82
AQ3 1/5/6 U	19.71	1.24	7.76
DIW	5.07	0.07	3.07
1 STD	19.85	1.26	3.20
3 STD	43.73	3.17	2.67
3 STD	43.44	3.14	2.67
(DUP) AQ3 U	19.43	1.22	7.76
AQ3 1/5/6 P	21.91	1.42	3.20

(DUP) AQ3 P	21.63	1.40	3.07
AQ1 1/6/6 U	48.01	3.51	221.17
AQ1 1/6/6 P	47.87	3.50	48.01
AQ2 1/6/6 U	37.64	2.68	198.38
AQ2 1/6/6 P	37.21	2.65	43.16
AQ3 1/6/6 U	20.53	1.31	6.68
AQ3 1/6/6 P	23.56	1.55	3.07
AQ1 1/7/6 U	49.73	3.65	222.69
AQ1 1/7/6 P	49.02	3.59	43.73
AQ2 1/7/6 U	36.79	2.61	202.62
AQ2 1/7/6 P	36.65	2.60	34.12
AQ3 1/7/6 U	19.57	1.23	7.63
AQ3 1/7/6 P	20.53	1.31	3.20
DIW	6.42	0.18	2.93
DIW	5.07	0.07	2.80
1 STD	18.20	1.12	3.07
3 STD	44.44	3.22	2.67
DIW	4.94	0.06	3.20

FILENAME: 01-12-96.WKS

TIC (mg/L)
0.06
0.09
0.20
0.16
0.17
0.21
0.23
0.21
0.18
9.99
31.75
0.08
11.67
0.38
0.22
17.76
11.21
15.83
9.59
0.47
0.20
17.91
9.88
16.79
7.89
0.45
0.16
17.84
17.88
7.88
7.38
16.24
16.08
5.52
5.30
0.49
0.11
0.12
0.08
0.08
0.49
0.12

Calibration Curve

Conc	Avg mv	Avg mv - RB	DOC mg/l
0.5	10.32	5.81	0.49
1	17.38	12.87	1.06
3	42.59	38.08	3.08
5	68.12	63.61	5.12
7	92.30	87.79	7.06
10	129.51	125.00	10.04
15	192.00	187.49	15.04

Regression Output:

Constant		-0.02718
Std Err of Y Est		0.042978
R Squared		0.999943
No. of Observations		7
Degrees of Freedom		5
X Coefficient(s)	0.080074	
Std Err of Coef.	0.000269	

0.11
17.58
3.71
15.75
3.32
0.40
0.11
17.70
3.37
16.09
2.60
0.48
0.12
0.10
0.09
0.11
0.08
0.12

STANDARD DEVIATION

24 HOUR SAMPLES

UNPRESERVED

BC 61 12:00 AM	0.154448
BC61 8:00 AM	0.051561
BC61 4:00 PM	0.009489
BOX 4:00 PM	0.034774

PRESERVED

BC 61 12:00 AM	0.054385
BC61 8:00 AM	0.094599
BC61 4:00 PM	0.034465
BOX 4:00 PM	0.060658

AQUARIUM SAMPLES

UNPRESERVED

AQ1

12/30/95	0.02705
1/5/96	0.037543

AQ2

12/30/95	0.041302
1/5/96	0.018706

AQ3

12/30/95	0
1/5/96	0.02453

PRESERVED

AQ1

12/30/95	0.045611
1/5/96	0.063443

AQ2

12/30/95	0.07237
1/5/96	0.03329

AQ3

12/30/95	0.014881
1/5/96	0.01907

COLOR: 24 HOUR SAMPLES

QA/QC

		400 nm
5 STD		0.005
	10	0.009
	25	0.023
	50	0.045
SRFA		0.016

SAMPLE

UNPRESERVED

			BOX	
	400 nm	**254 nm**	**400 nm**	**254 nm**
12:00 AM	0.011	0.075		
02:00 AM		0.075		
04:00 AM		0.077		
06:00 AM		0.074		
08:00 AM	0.014	0.078		
10:00 AM		0.058		
12:00 PM		0.066		0.066
02:00 PM		0.072		0.06
04:00 PM	0.01	0.075	0.012	0.071
06:00 PM		0.068		
08:00 PM		0.05		
10:00 PM		0.059		

PRESERVED

			BOX	
	400 nm	**254 nm**	**400 nm**	**254 nm**
12:00 AM	0.01	0.068		
02:00 AM		0.077		
04:00 AM		0.076		
06:00 AM		0.083		
08:00 AM	0.007	0.077		
10:00 AM		0.064		
12:00 PM		0.059	0.074	0.066
02:00 PM		0.071		0.079
04:00 PM	0.009	0.069	0.008	0.081
06:00 PM		0.081		
08:00 PM		0.074		
10:00 PM		0.099		

OTHER ANALYSES: 24 HOUR SAMPLES

CREEK

	pH	TDS	DO	DO: %	TEMP
01:30 AM	7.2	40			
02:00 AM	7.7	40			
04:00 AM	7.1	50	11.9		-0.2
06:00 AM	7.7	50	10.9	90	-0.1
08:00 AM	7.9	60	11.2	92	0
10:00 AM	8.2	70	12.3	104	0.1
12:00 PM	8.2	60	12.3	100	0.2
14:00	8.4	70	12	101	1.1
04:00 PM	8.5	70	12	100	0.6
06:00 PM	8.4	80	11.2	94	0.1
08:00 PM	8.4	80	12.2	104	0.2
10.00 PM	8.7	30	12.9	105	-0.2

BOX

	pH	TDS	DO	DO: %	TEMP
01:30 AM					
02:00 AM					
04:00 AM					
06:00 AM					
08:00 AM					
10:00 AM					
12:00 PM	8.3	70	12.9	104	0.2
14:00	8.4	70	12.5	102	0.9
04:00 PM	8.6	70	12	102	0.6
06:00 PM					
08:00 PM					
10.00 PM					

OTHER ANALYSES: AQ SAMPLES

AQ1

	TDS	pH	DO: mg/L	DO:%	TEMP
12/31	90	7.3	10.6	111	8.6
1/1	90	7.1	6.6	68	8.9
1/2	90	7.2	5	51	7.4
1/3	90	7	6.1	63	7
1/4	100	7	3.9	40	8.2
1/5	100	6.9	3.4	37	6.4
1/6	100	6.9	3.5	36	6
1/7	90	6.9	4.5	45	5.9
1/8	100	6.9	6.6	73	10.3
1/9	100	6.8	7.8	81	7.5

AQ2

12/31	90	7.6	12.9	132	8
1/1	90	7.4	10.3	108	8.4
1/2	90	7.3	9.6	97	6.8
1/3	90	7.5	10.1	104	6.6
1/4	90	6.9	9.2	95	7.7
1/5	90	7.1	8.9	88	6.4
1/6	90	6.8	8.8	87	5.6
1/7	90	6.8	8.7	84	5.5
1/8	100	7.1	8.7	99	10.2
1/9	90	7.1	8.9	89	7.1

AQ3

12/31	0	7.1	7.7	92	15.1
1/1	0	7.3	8.4	89	8.6
1/2	0	7.2	9.2	93	6.9
1/3	0	7.3	9.5	105	10.1
1/4	0	7.4	8.9	95	8.5
1/5	0	7.7	8.2	93	6.2
1/6	0	7.7	9.7	95	5.8
1/7	0	8.2	9.2	94	7.5
1/8	0	7.7	9.4	103	9.9
1/9	0	8	9.1	98	9.7

COLOR: AQ SAMPLES

SAMPLE

UNPRESERVED
AQ1

	254 nm	400 nm
12/30	0.075	0.01
1/1	0.073	
1/2	0.068	
1/3	0.057	
1/4	0.067	
1/5	0.075	0.01
1/6	0.071	
1/7	0.064	

PRESERVED
AQ1

	254 nm	400 nm
12/30	0.082	0.01
1/1	0.089	
1/2	0.077	
1/3	0.07	
1/4	0.091	
1/5	0.076	0.009
1/6	0.084	
1/7	0.063	

UNPRESERVED
AQ2

	254 nm	400 nm
12/30	0.075	0.01
1/1	0.055	
1/2	0.078	
1/3	0.068	
1/4	0.058	
1/5	0.067	0.009
1/6	0.066	
1/7	0.054	

PRESERVED
AQ2

	254 nm	400 nm
12/30	0.162	0.007
1/1	0.086	
1/2	0.111	
1/3	0.133	
1/4	0.062	
1/5	0.074	0.011
1/6	0.074	
1/7	0.059	

UNPRESERVED
AQ3

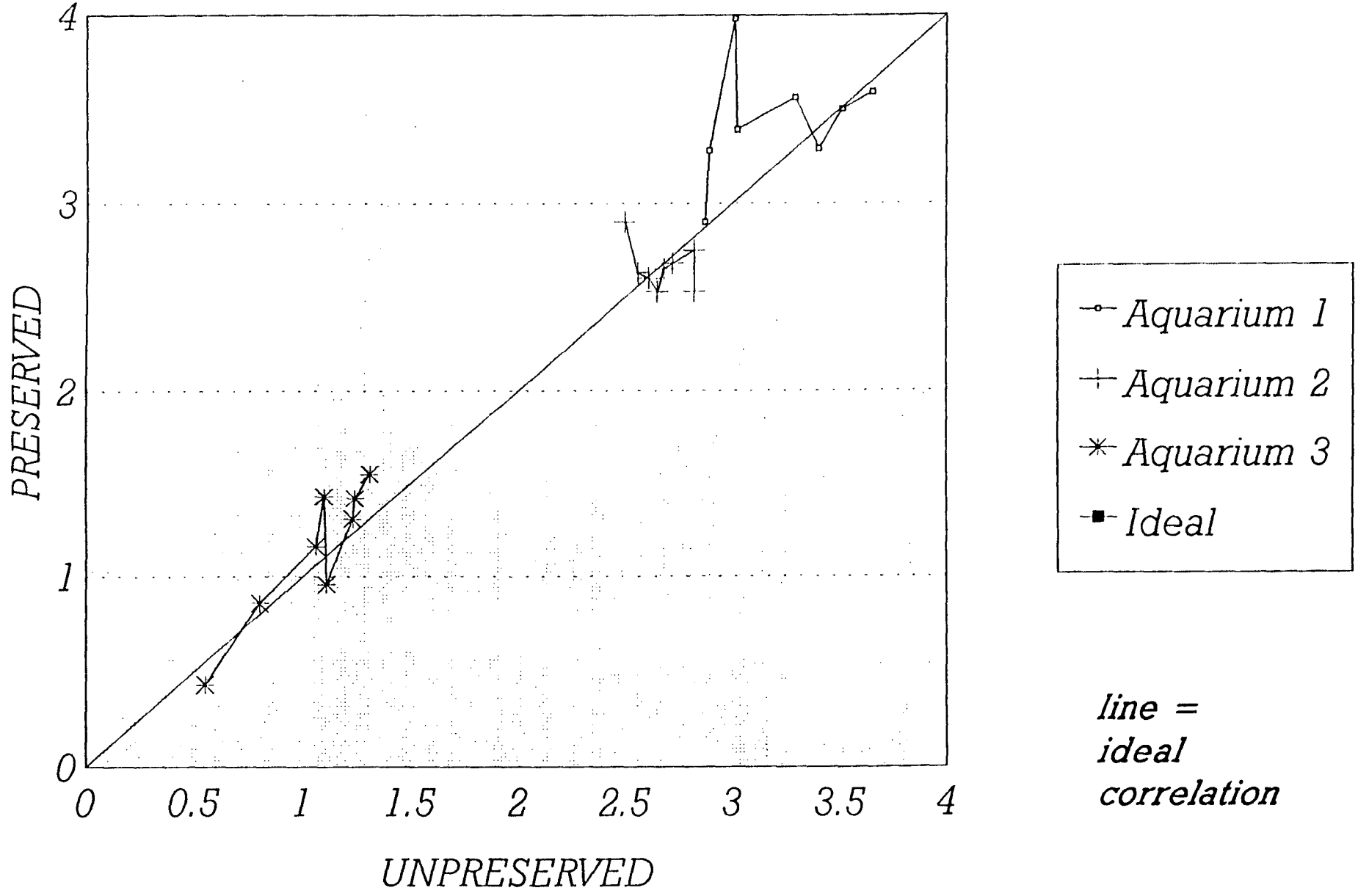
	254 nm	400 nm
12/30	0.022	0.003
1/1	0.035	
1/2	0.016	
1/3	0.034	
1/4	0.021	
1/5	0.032	0.004
1/6	0.031	
1/7	0.016	

PRESERVED
AQ3

	254 nm	400 nm
12/30	0.019	0.002
1/1	0.021	
1/2	0.014	
1/3	0.027	
1/4	0.026	
1/5	0.03	0.001
1/6	0.021	
1/7	0.022	

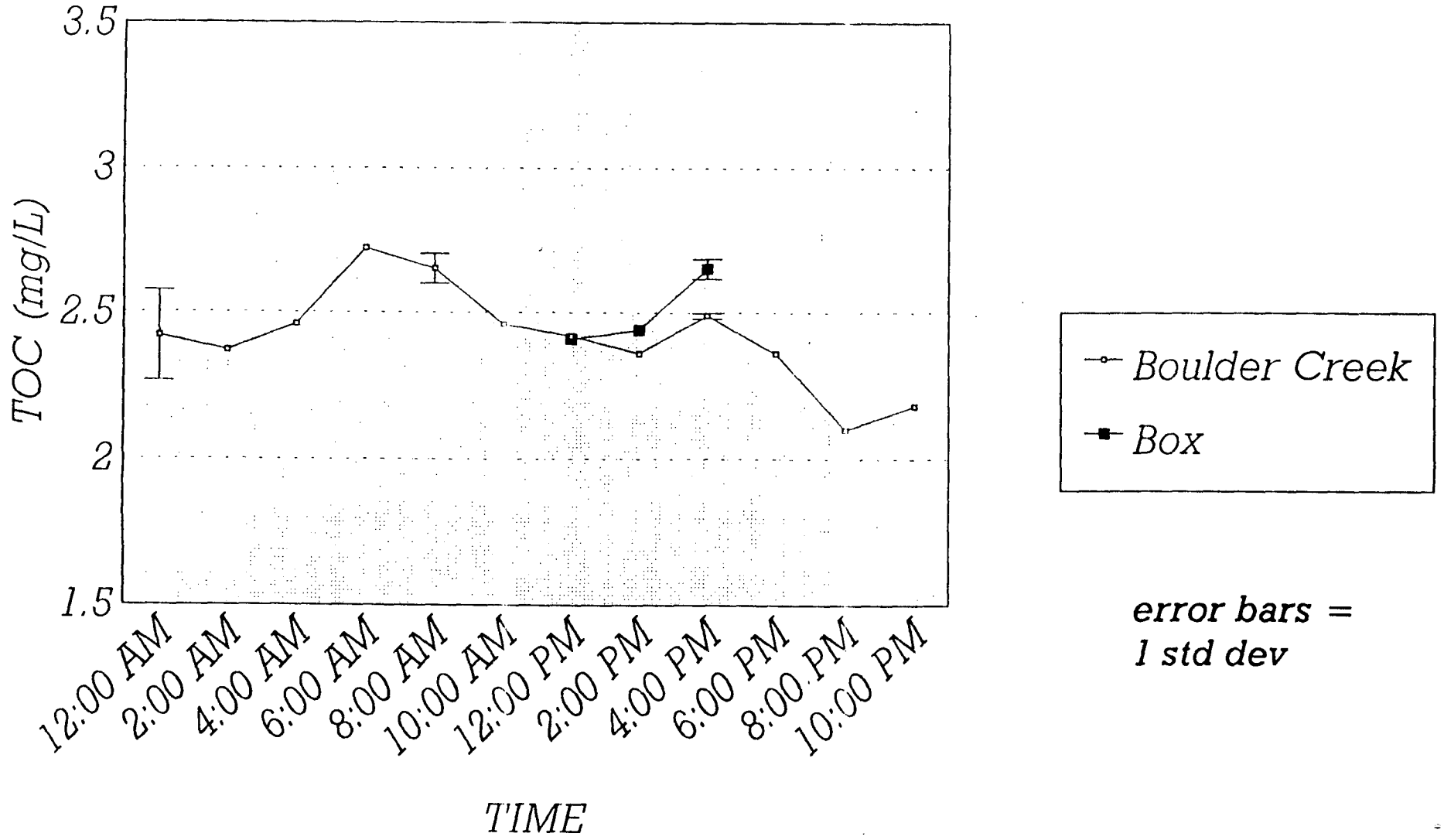
AQUARIA MICROCOSM: comparison of preserved and unpreserved

Ave TOC



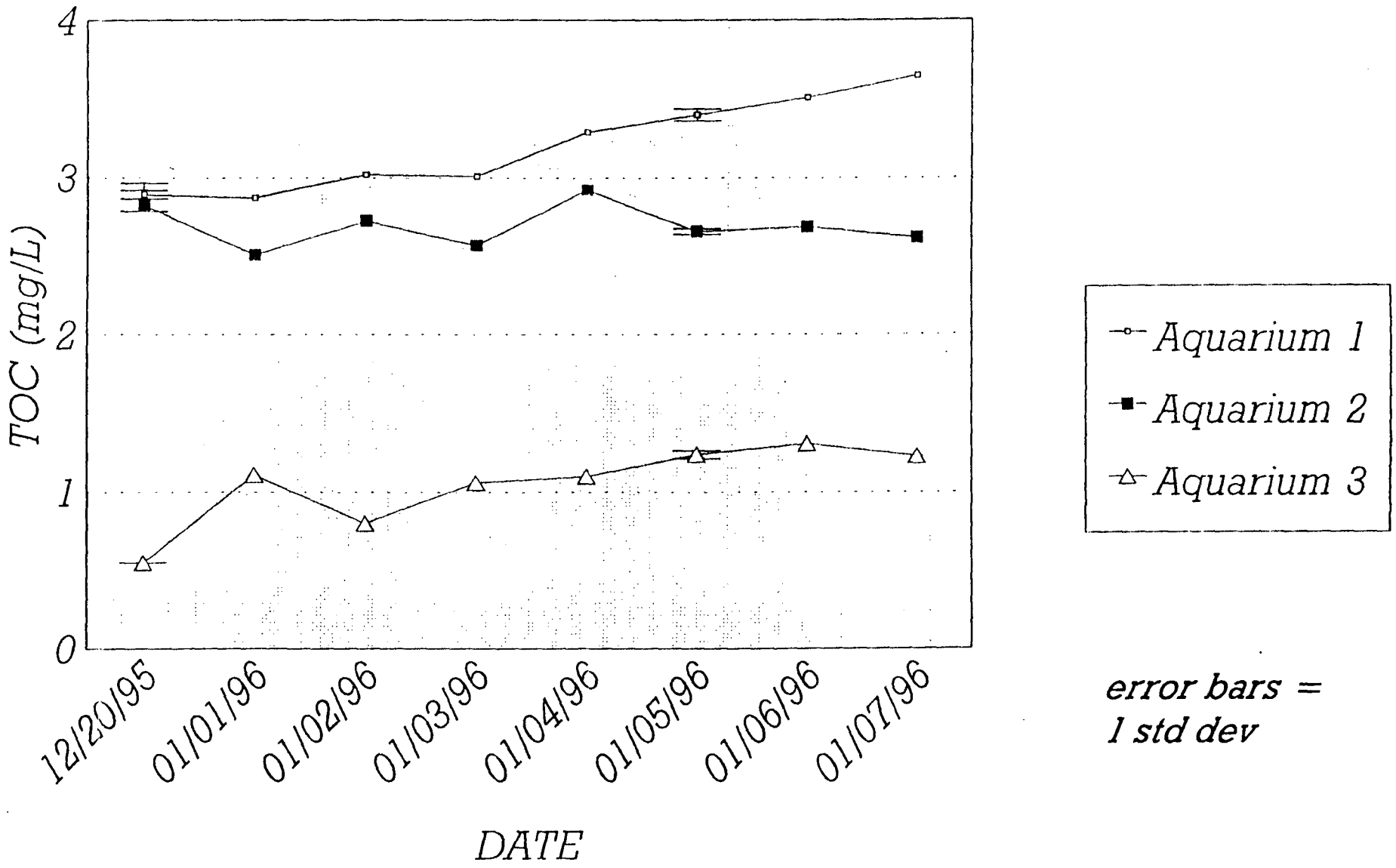
DIURNAL SAMPLES

TOC UNPRESERVED



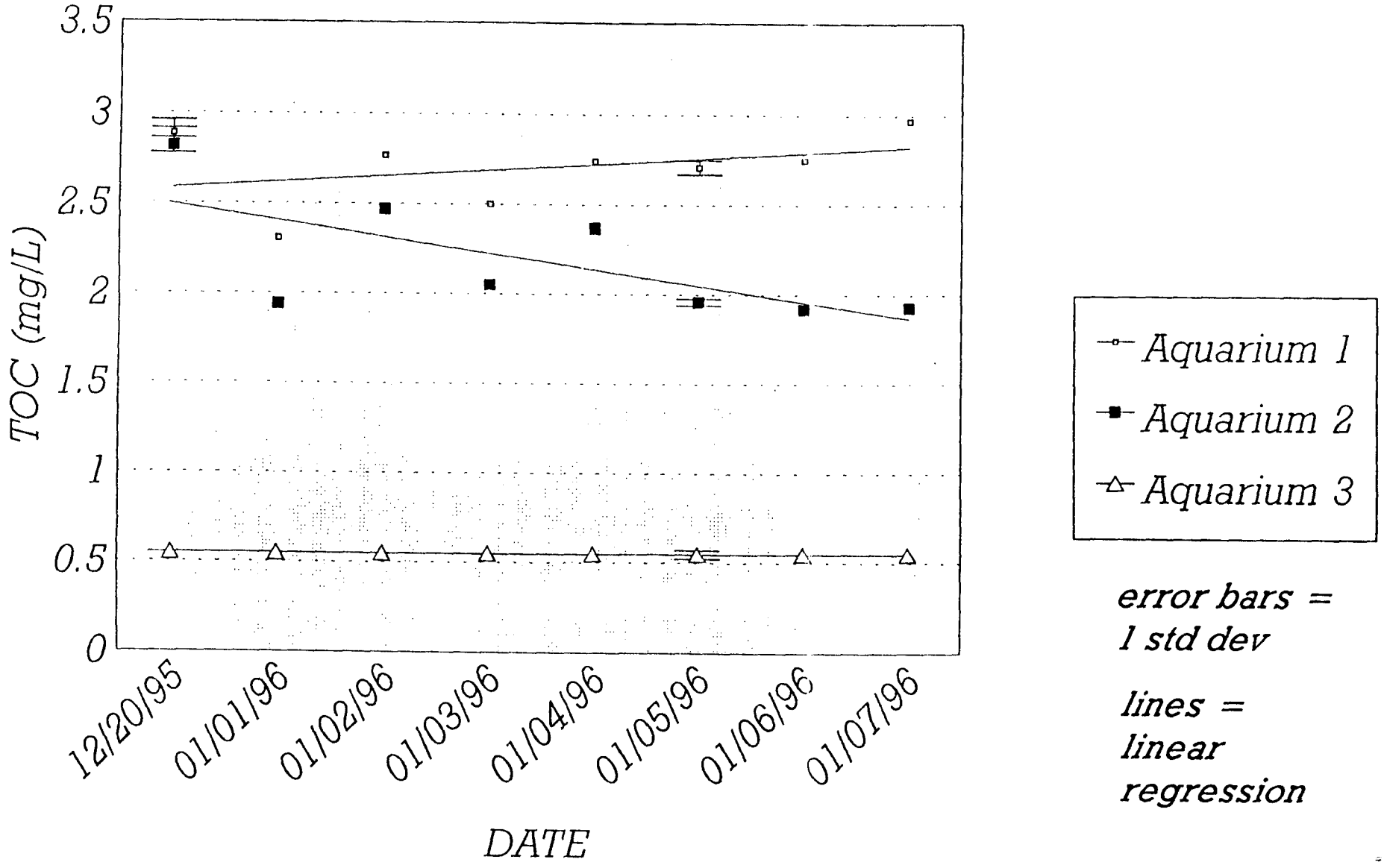
AQUARIA MICROCOSM: measured values

Ave TOC unpreserved



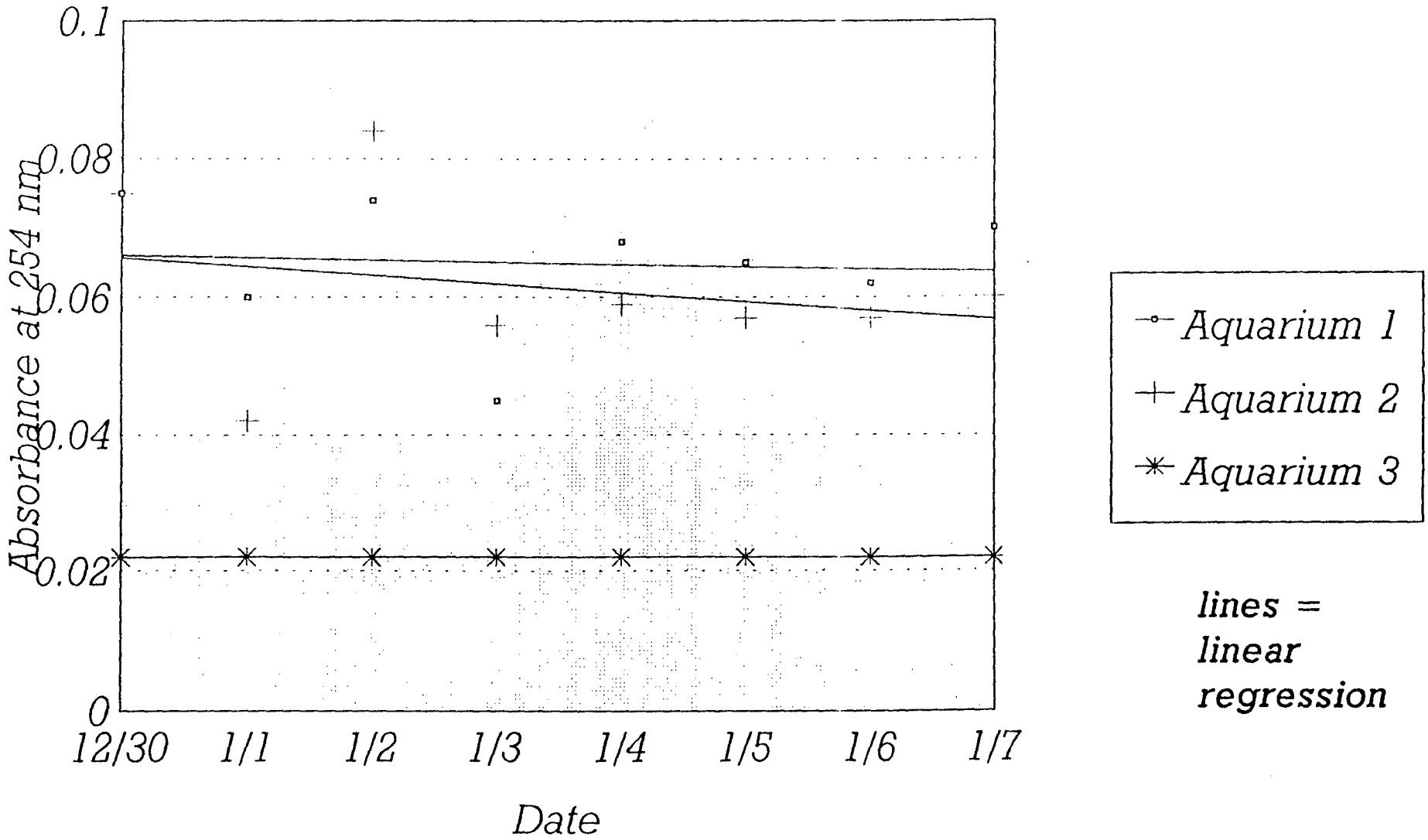
AQUARIA MICROCOSM: normalized values

Ave TOC unpreserved

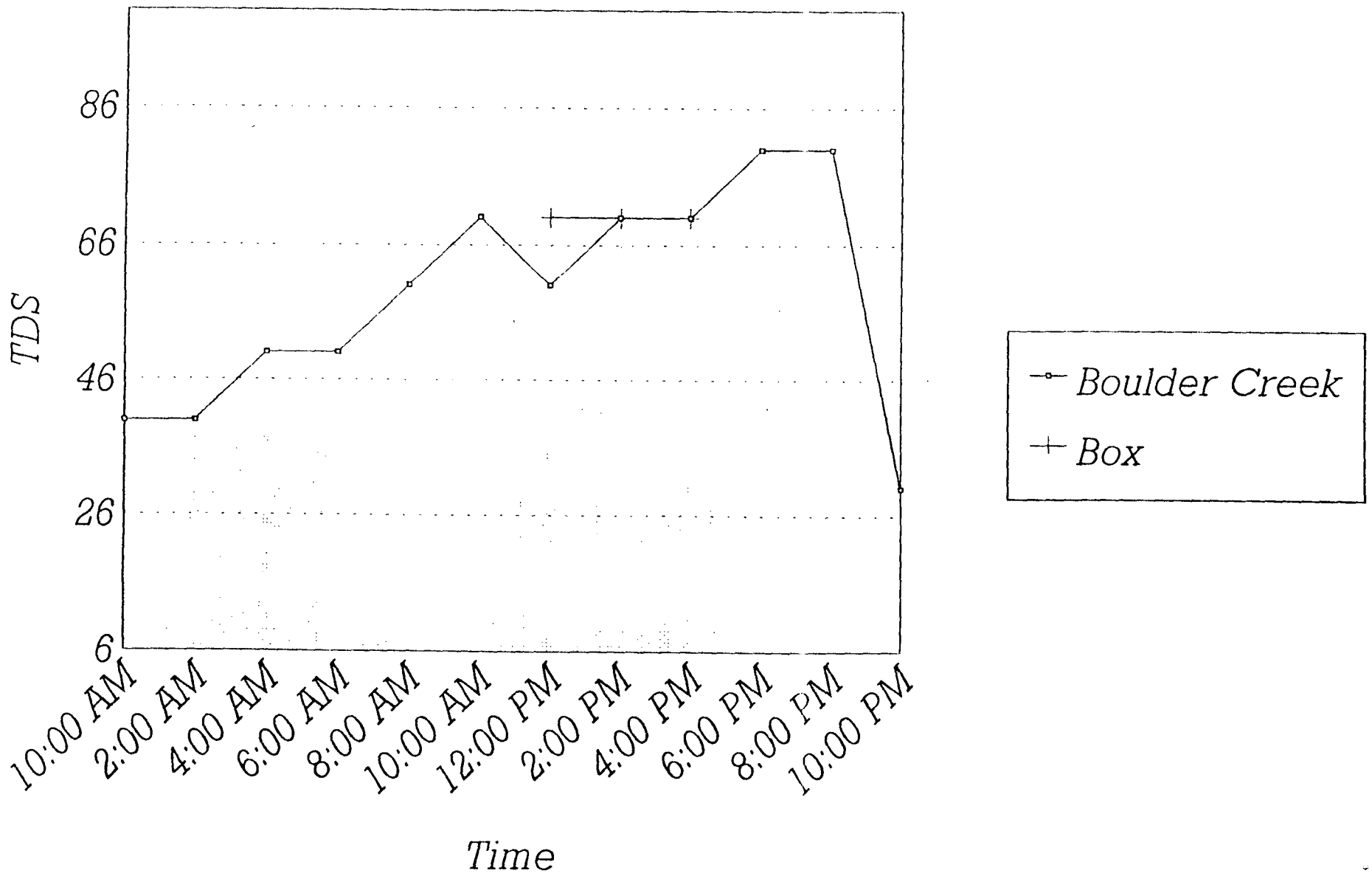


COLOR normalized values

absorbance at 254 nm wavelength

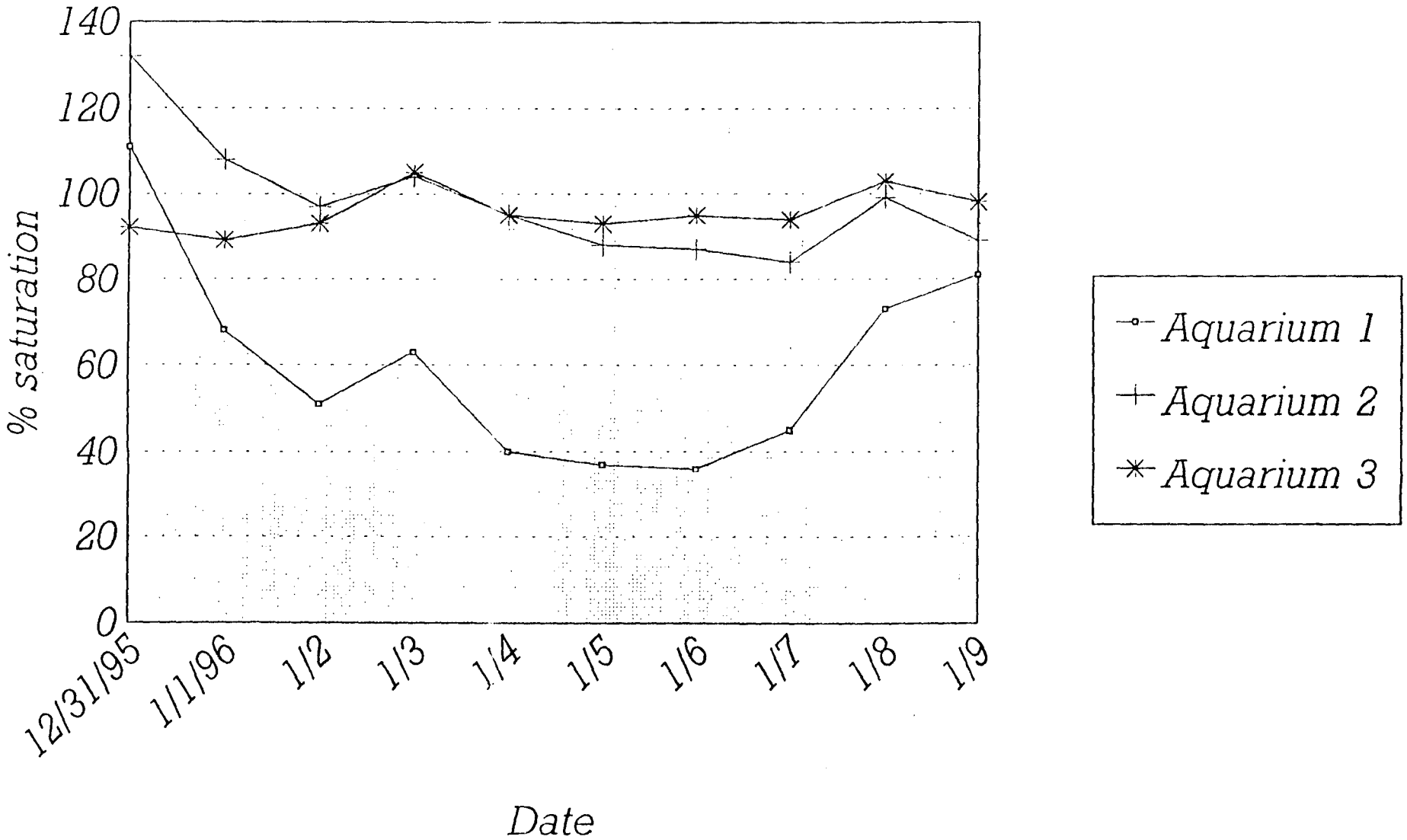


DIURNAL SAMPLES: Total Dissolved Solids



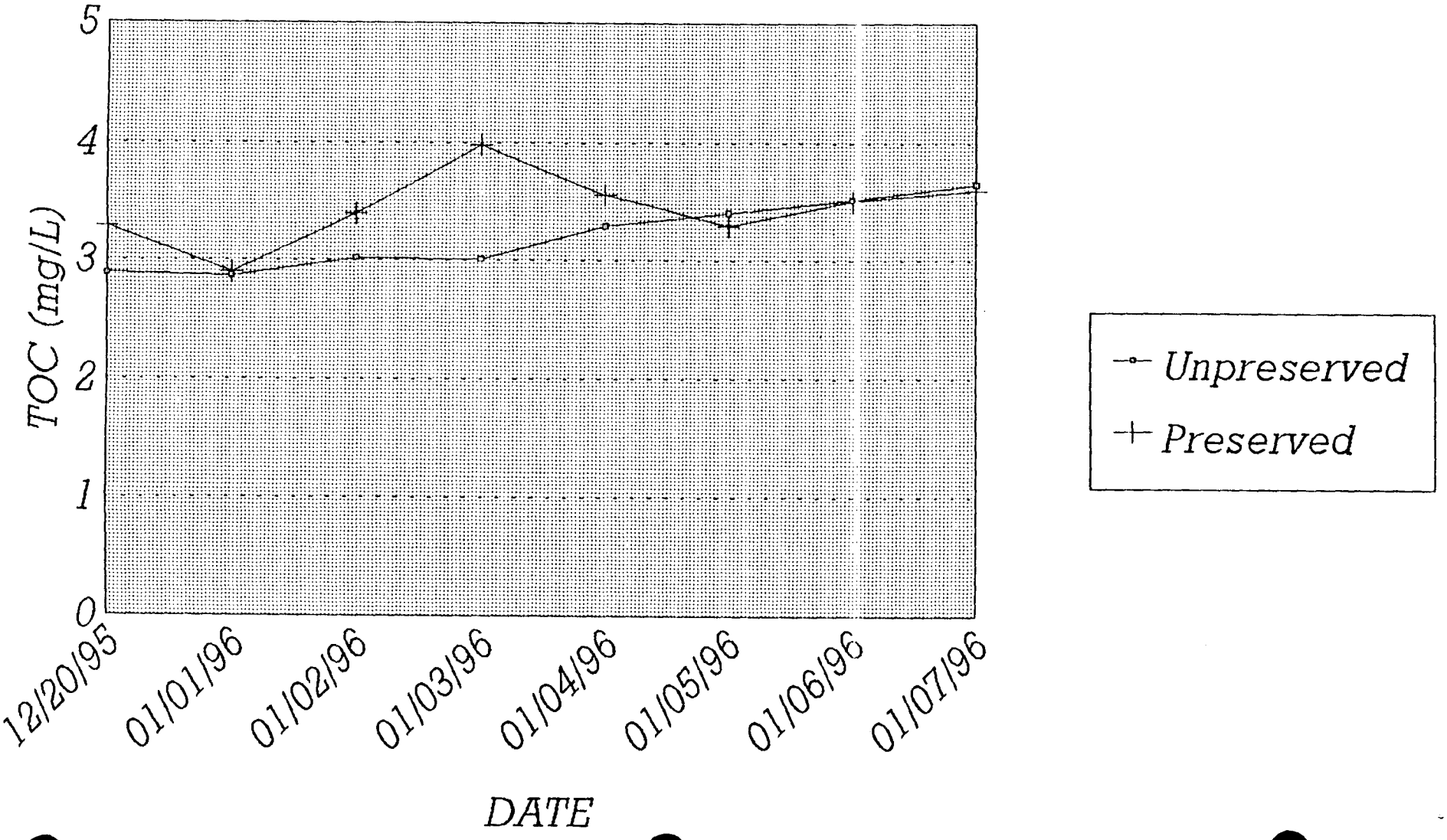
MICROCOSM: Dissolved Oxygen

Percent Saturation



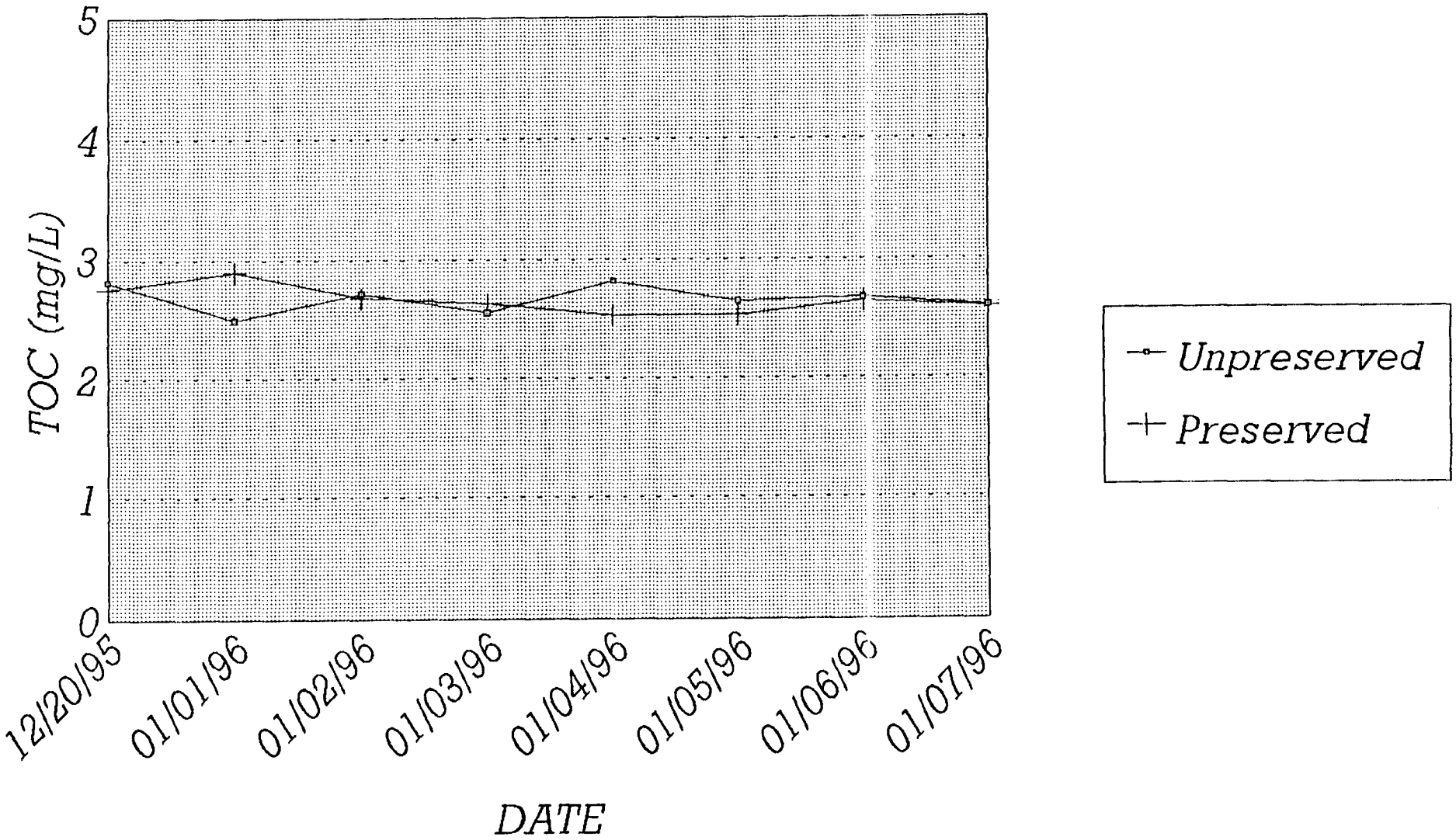
MICROCOSM: Aquarium 1

AVE TOC



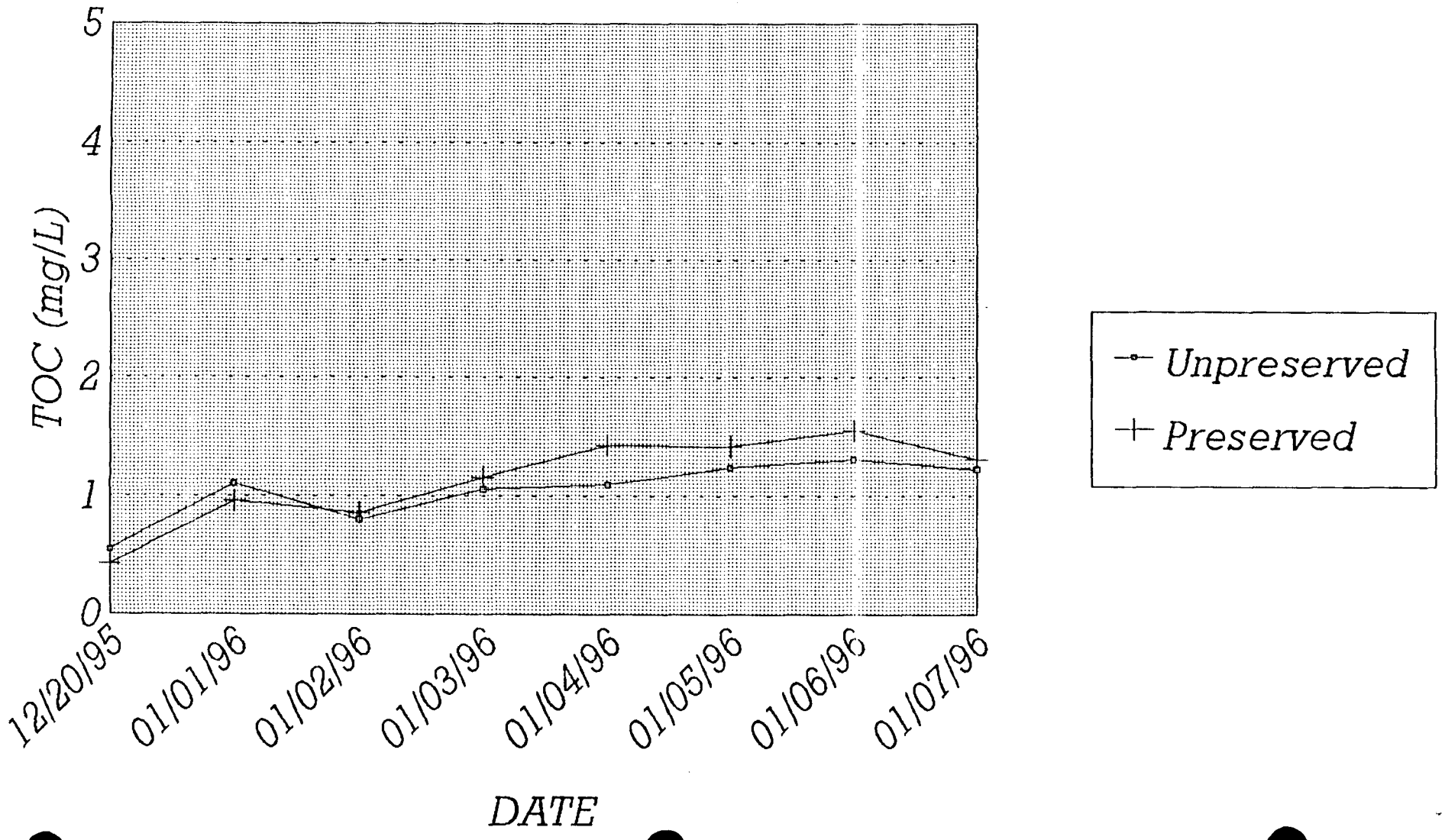
MICROCOSM: Aquarium 2

AVE TOC



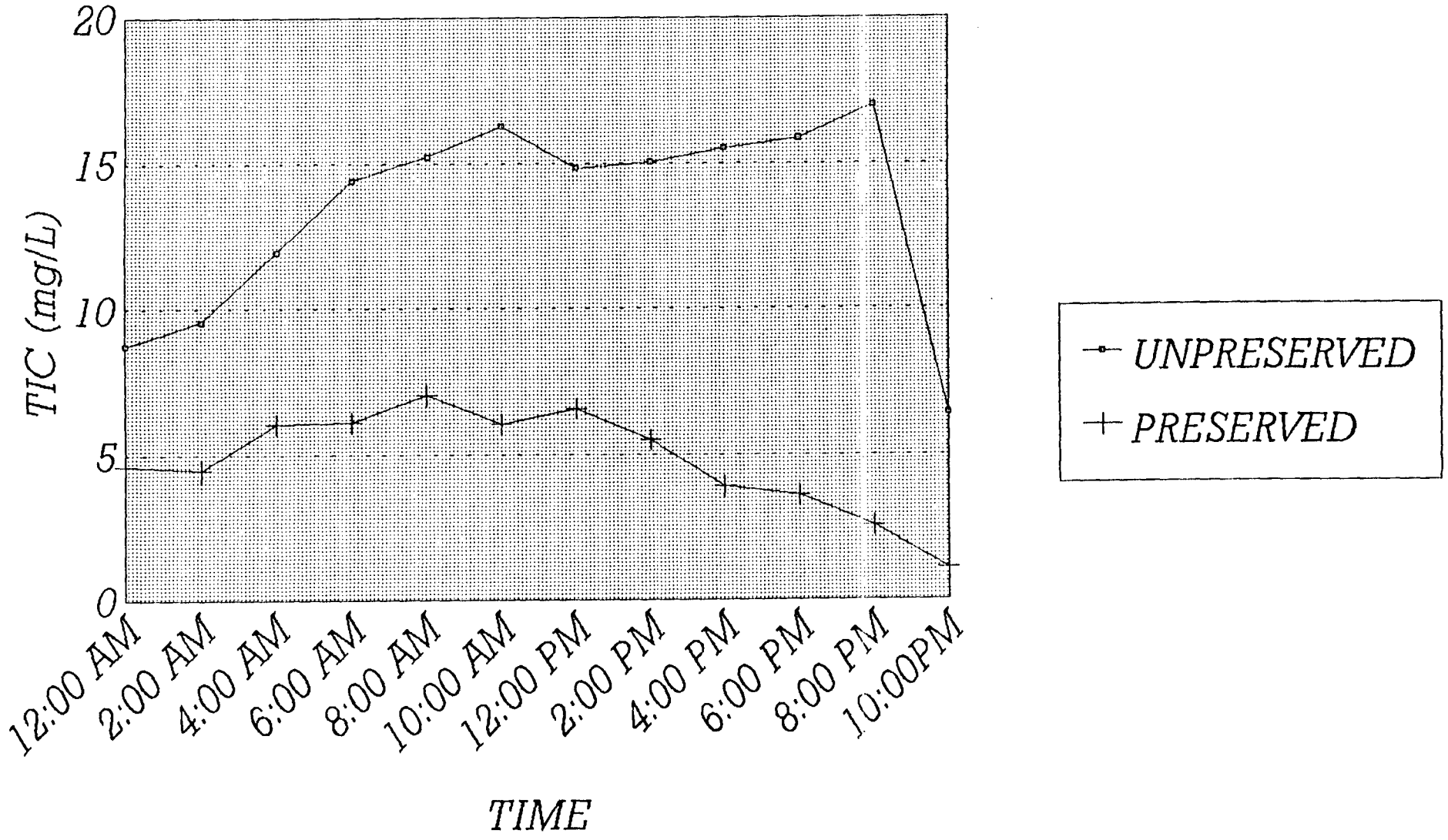
MICROCOSM: Aquarium 3

AVE TOC



DIURNAL SAMPLES

AVE TIC



Conclusion/Discussion

Design Evaluation

In order to create an controlled natural aquatic microcosm in which changes in TOC could be evaluated, a box was designed. The site selected had good quality habitat for biological life, which was necessary to obtain a representative of a high water quality stream, like Boulder Creek. The box that was designed and built three times had several advantages. The materials used, aluminum and Plexiglas, did not leach any significant amounts of carbon into the system as shown by the leaching experiments. When the box was in prime condition, it was water-tight, as well as being fairly economical. It was large enough to obtain a representative sample in terms of water volume, but it was also small and light enough to be transported easily. It was constructed out of Plexiglas, which allowed sunlight to enter into the box, which was necessary for algae and other biological organisms' survival. Finally, it allowed oxygen from the air to enter the box, also essential for the survival of organisms inside. The aquaria used for the extended samples were all uniform, removing any variation based on equipment.

However, in this case, designing a feasible and reliable experiment proved to be a great challenge. The pulse of water from the hydroelectric plant created serious problems since the author was not aware of it before the actual field experiment began. The box was not strong enough to withstand the high flow periods during the night. The base flow during winter was approximately 10 cfs, while the water released from the plant was 150 cfs based on hydroplant estimates. The flow was forceful enough to wash the box with the sediment downstream, as in

the case of 75th street. At 61st street, stakes were attached to prevent this effect, but the stakes were bent out of shape even though they held the box in place for two weeks. Also, the water level rose approximately 18 inches, which was about 12 cm above the top of the box. During the high flow period, ice fragments, branches, and other debris were carried down the stream, and the box was consequently damaged. The ice fragments, which were up to 1.5 m wide and 10 cm thick, bent the frame of the box and cracked the Plexiglas along the bottom and sides.

The aquaria also presented some disadvantages. The aquaria leached carbon, as shown by the increasing trend in TOC in aquarium 3, the distilled water control. Although this was not a major problem, it was a flaw in the materials used for carbon analysis. Also, the aquaria did not experience the range of temperatures exactly similar to a natural system due to freezing air temperatures, but they did experience enough variation to replicate the Creek as much as possible.

In general, the greatest challenge was making experimental design adjustments and box replacements after the discovery of a nightly water pulse from the hydroelectric plant. The magnitude and force of the flow, including its destructive capabilities, had never been completely understood until the diurnal samples were taken. If it had been known that there was a pulse of water every night with a magnitude of 150 cfs, the entire design of the box would have been changed to withstand the flow. Therefore, it is necessary to evaluate the dynamics of a system before the initiation of an experiment or a sample set. This "dynamic assessment" is similar to a habitat assessment in that it evaluates the physical characteristics of a system, but should have five "dimensions" as follows, as concluded from this project.

Topography

1. elevation

2. width of stream

3. depth of stream

Time

4. annual changes in flow, natural and unnatural

5. diurnal changes in flow, natural and unnatural

The awareness of these factors could significantly alter designs of experiment, sampling techniques, and interpretations of results. It could also save time, money, and effort.

Quality Assurance/Quality Control

Distilled water, 1 mg/L and 3 mg/L standards were included in the analysis of the samples for TOC. Distilled had a low standard deviation, 0.06, and the median and mean were the same within the accuracy of the carbon analyzer, although the relative standard deviation was 43%. The relative standard deviation was high due to the relatively little amount of carbon in distilled water. The RSD decreased as the quantity of carbon increased. The 1 standard had an RSD of 14%, and the 3 standard had an RSD of 3%. Since most of the samples from the Boulder Creek and the aquaria were in the 3 mg/L range, it can be assumed that the values measured also had an RSD of approximately 3%. This means that the carbon analyzer measured precisely, with a 3% variation between duplicate samples in the 3 mg/L range. In addition, the actual measured values were accurate, by the examination of the 3 standard. The carbon analyzer measured a mean value of 3.2 mg/L, and a mean distilled water value of 0.1. Since the standards were made by diluting a

more concentrated amount of carbon in distilled water, the analyzer measured accurately to within 0.1 mg/L, which is its analytical error.

Preservation

As described in the methods section, two samples were taken at every date/time. One was preserved, and one was left raw. Diurnally, there was not a significant difference between the preserved and unpreserved samples, only random variation. As shown by the comparison graph, preserved versus unpreserved for diurnal samples. the slope of the line is near 1, thus demonstrating that there is not substantial difference between preserved and unpreserved samples.

The aquaria samples also confirmed this conclusion. When all three aquaria are graphed in comparison to the ideal one-to-one correlation, aquaria 1, 2, and 3 generally lie near the line of perfect correlation. Since there are no significant differences between the preserved and the unpreserved samples for diurnal samples and samples from aquaria 1, 2, and 3, it was shown that the unpreserved samples could be used for further analysis.

Diurnal samples

TOC

Boulder Creek demonstrated a bimodal trend in TOC, with a peak at 6:00 am and another at 4:00 pm. In perspective, however, the peaks at these times reflect an event or combination of events that occurred several hours previously upstream of 61st street.

Samples were not collected from the box for a full 24 hours, but the box experienced a significant increase in the TOC as compared with the Creek. This suggests a production of TOC from instream processes because the water inside the box was not being transported downstream at 10 cfs like the Creek outside the box. In the Creek, any carbon that was produced was immediately swept away by the stream current. All carbon in the box, on the other hand, remained inside for all four hours, thus increase on TOC demonstrated a production of TOC from instream processes. However, it must also be noted that the box at the time of sampling was damaged and not completely water-tight. Although leakage was kept at a minimum, the data were not accurate to as great a degree as desired. The change in TOC inside the box cannot reasonably be assumed to be caused by leaching from the box materials, and Creek water infiltrating through the cracks could have possibly diluted the box water.

TIC

TIC did not appear to follow the TOC trend, although is was also bimodal. The two peaks occurred at 10:00 am and 8:00 pm. The Creek also tended to possess 3 times more TIC than TOC in general. There are several explanations for this phenomena. CO_2 can be absorbed from the air, like oxygen, which is then part of the TIC content. Also, TOC is degraded into TIC through various processes. Therefore, TIC is not as useful a measurement of instream carbon production of as TOC.

Aquaria samples

Several trends were clearly defined in the aquaria samples. The TOC values in aquarium 3, the distilled water control, were consistently lower than aquaria 1 or 2.. Also, aquarium 1 was consistently higher than aquaria 2 and 3. On closer examination of aquarium 3, it is evident that leaching from the aquarium material occurred, and since all the aquaria were identical, leaching most likely occurred in all aquaria. Because of this, the measured values were recentered based on the change in aquaria 3. From the recentered values, the TOC in aquarium 1 increased, as shown by the linear regression with a slope of 0.03 on a preserved versus unpreserved graph. aquarium 2 decreased, again based on a linear regressional slope of -0.09.

Color was also an indicator of trends in TOC for the aquaria samples. Again, the measured values were normalized for the variation in aquarium 3, and it was shown that both aquaria 1 and 2 decreased over time. However, there are several possible reasons for the trends seen in TOC and color, discussed in the following section.

Discussion

As seen by the trends in TOC in aquaria 1 and 2 after recentering the values for materials leaching, the factors involved in the production of the majority of carbon are present in the sediment, but not in the Creek water alone. Also, carbon consumption is performed in the water itself. While this does not preclude consumption in the sediment, it is evident that the sediment produces more carbon than can be consumed by the system as a whole. In the absence of this

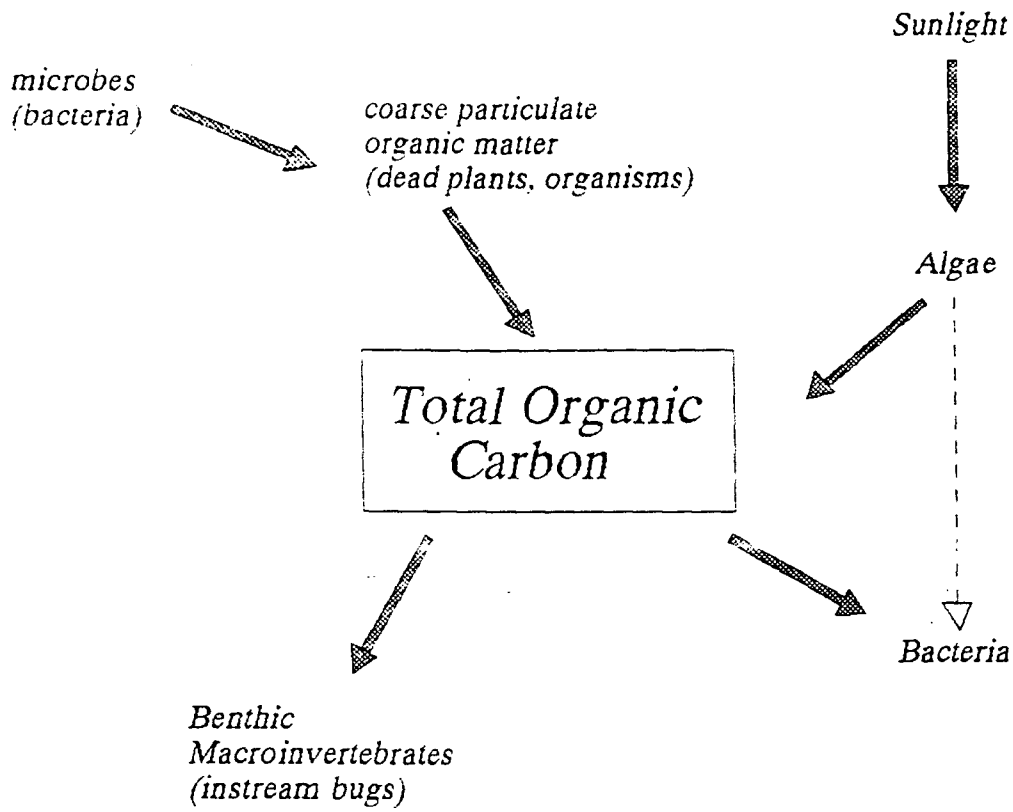
major source of carbon, activity in the water continually consumes more carbon than is produced by instream processes.

While the TOC in aquarium 1 increased over time, the color in aquarium 1 did not follow the same trend. Carbon produced by algae very often does not have a high absorbance at 254 nm unlike other forms of carbon in a system. This supports the hypothesis that most carbon is produced by algae, which would account for the production of TOC in aquarium 1, but not in aquarium 2, and the discrepancy in the TOC and color trends for aquarium 1. It must also be noted that the spectrophotometer may possibly have a lower sensitivity, as compared to the carbon analyzer.

Another interesting trend was noticed in aquarium 2. Unlike aquarium 1, carbon consumption occurred over an extended period of time. A large quantity of carbon production can be attributed to algal processes that leach carbon at a greater rate than consumption, but this source was not present in aquarium 2. Bacteria and other suspended organisms appeared to consume carbon. It has been proposed that there are heterotrophic bacteria that live in a symbiotic relationship with algae: the bacteria consume the carbon produced by the algae. Although the experiment does not support this symbiosis, it can by hypothesized that bacteria in the water consume carbon, and more specifically, carbon produced by algae based on the color data for aquarium 2.

In the sediment, algae are not the only residents. Specific taxa of benthic macroinvertebrates, of instream bugs, contribute to the carbon cycle by decomposing decaying matter, which is composed mainly of carbon. In this way, macroinvertebrates consume carbon in

the stream. The following chart represents part of the carbon cycle as hypothesized from the experiment:



In summary, the instream processes that contribute carbon are complex, but several hypotheses can be postulated. Firstly, the instream processes as a whole contribute carbon to the system. Even though allochthonous carbon may not be a large portion of the entire carbon content in a stream, it is present nevertheless. Secondly, algae may be the major producer of allochthonous carbon. Finally, bacteria in the water in conjunction with the macroinvertebrates in the sediment consume the carbon produced by the algae, although the amount of carbon produced is greater than the amount consumed.

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