# COMPARISON STUDY OF FIVE INSTRUMENTS MEASURING DISSOLVED ORGANIC CARBON FOR THE CHESAPEAKE BAY MONITORING PROGRAM

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ACKNOWLEDGEMENTS

This study would not have been feasible without the endeavors of the personnel at CBL, ODU, DHMH, and DCLS who analyze for dissolved organic carbon. They took time in their busy schedule to analyze the samples within the necessary time frame and forward the data.

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# COMPARISON OF DISSOLVED ORGANIC CARBON INSTRUMENTS AND EVALUATION OF THE EFFECT OF SALINITY

## INTRODUCTION

The Chesapeake Bay Monitoring Program (CBMP) was initiated by the U.S. Environmental Protection Agency, together with Maryland, Pennsylvania, Virginia and the District of Columbia in the summer of 1984. Water Quality monitoring has been performed on the Chesapeake Bay and its tributaries at least monthly since the program started. Dissolved Organic Carbon (DOC) has been measured from the beginning of the program.

The monitoring program was designed to develop a data base which would allow scientists 1) to determine trends in water quality over time and 2) to formulate a model of water quality processes. In order to provide continuity of data, a record of all methodology and instrument changes must be maintained.

The purpose of this study was two-fold:
1) Comparison of the DOC results from different instruments used in the program in order to provide a baseline for comparison of DOC data and historical data if these instruments are replaced.
2) Examination of salinity interference, if any, in of the results.

## HISTORY

An interlaboratory study conducted at VIMS with two other laboratories suggested that DOC concentrations differed with the type of instrument used. Zimmermann (1991) suggested that these differences may have been due to salinity interference. In addition, samples which have been split between laboratories participating in the program have shown statistically significant differences. A study done in 1991 reported a significant difference in DOC when split samples were analyzed by two methods (Salley, 1991). The salinities of the samples were mesohaline to polyhaline.

In 1988, the international marine scientific community

became aware that a new DOC instrument was measuring much higher DOC concentrations than had been reported previously in open ocean water samples. This has led to intensive comparison of instruments and methodologies. An entire issue of Marine Chemistry (January, 1993) was devoted to the details of DOC measurement.

Due to this interest in and concern about DOC measurements, The Analytical Methods and Quality Assurance Workgroup (AMQAW) recommended that a comparison study be conducted between the DOC instruments involved in the Chesapeake Bay Monitoring Program at that time. The DOC study was also expanded to include an investigation to determine if the varying salinities of samples influenced or interferred with DOC measurements.

**STUDY DESIGN**

The study was designed to compare DOC recoveries by different instruments/methodologies. Since salinity possibly affected carbon recovery, the samples used for comparison were prepared in graduated salinities. Two carbon concentrations were used. The carbon concentrations chosen approximated the range encountered in the Chesapeake Bay. The five different instruments included in the study were used in the three mainstem Laboratories and two Tributary Laboratories. These instruments presently report DOC measurements to the Chesapeake Bay Monitoring Program (CBMP).

Sargasso Sea (SS) water was used for the high salinity diluent and Distilled and Deionized (DDI) water was used for the zero salinity diluent. The samples were prepared by combining the two waters to obtain the salinity required for the sample. For the low concentration DOC samples, the zero salinity carbon concentration was simply the residual carbon in the DDI water. Since the SS water contained more organic carbon than the DDI water, the carbon concentrations of the intermediate salinities were incrementally intermediate between those of the DDI and SS water. SS water and DDI water which had been separately adjusted to 8 mgC/L with glucose were used to prepare the high concentration DOC samples in the desired salinity range. Each sample was to have seven replicates analyzed. The replicates gave the statistical power for detection of differences in method and instrument variability.

**INSTRUMENTS, METHODS, AND SAMPLE HANDLING**

The procedures used in sample preparation, setting the blank, and standard curve were important parts of the results. Therefore, the method for each instrument is described in detail below.

1. Astro, Model 1850, Total Organic Carbon Analyzer

   A 15 mL sample, pH <3, is purged with nitrogen and injected into the instrument. The sample is mixed with sodium persulfate and exposed to ultraviolet light. The resultant $CO_2$ is measured with a non-dispersive infrared cell. The standard curve is calculated using one standard and the instrument zero.

   Low concentration samples were not analyzed on the Astro.

   The study samples were acidified with 6 N $H_2SO_4$, transported, and stored at 4°C until analyzed.

2. Dohrmann, Model 180

   A 5 mL sample is used. Phosphoric acid is added and the sample is sparged to remove the $CO_2$. Sodium persulfate is added and the sample is exposed to ultraviolet light. The instrument is zeroed with a millipore water blank. Five standards are analyzed and the data calculations are performed by the instrument.

   The study samples were acidified with 6 N $H_2SO_4$, transported, and stored at 4°C until analyzed.

3. Oceanographic International Carbon Analyzer (OI) - Ampule method

   A 5 ml sample, pH <3, is placed in an ampule and purged with ultrapure oxygen to remove the Dissolved Inorganic Carbon (DIC). One ml of saturated potassium persulfate and 200 µL of 10% phosphoric acid are added. The ampule is sealed and autoclaved at 130°C for four hours. The resultant $CO_2$ is carried through a Non-Dispersive Infrared Detector (NDIR) by nitrogen gas.

   The NDIR is calibrated with blanks, standards and standard reference material (SRM) before the samples are analyzed. Check standards and spikes are interspersed throughout the analyses for internal quality control. The standards are reduced by linear regression and the intercept set to zero.

The study samples were acidified with 6 N $H_2SO_4$ and chilled to 4°C, for preservation and transport. On arrival, they were frozen until prepared for analysis. Since the pH was less than 3, no further acid was added before purging.

4. Oceanographic International Analytical, Model 700 TOC - Automated

   The automated OI uses zero grade nitrogen as the carrier gas. All reagents (potassium persulfate and sodium phosphoric acid) are added automatically by the instrument. The $CO_2$ is purged from the digestion vessel with the nitrogen gas after phosphoric acid is added. In order to compensate for any possible salt interference in the oxidation, the volume of oxidant and the reaction time is increased when analyzing saline samples. Reagent blanks are run until instrument is stabilized. The standard curve is set with a one-point calibration where the standard concentration is 10 mgC/L. The zero point is set electronically. A scaling factor is calculated from this curve and used to calculate the sample values.

   The study samples were not acidified, but frozen and transported. They remained frozen until analysis.

5. Shimadzu TOC 500, ASI-502, Automated

   The Shimadzu method employs high temperature (680°C) combustion with a platinum catalyst. The carrier and sparge gas is zero-grade air. A sample, pH <3, is sparged for 6 minutes to remove DIC. An 80 µL sample is autoinjected into the TC port. The resultant carbon is oxidized to $CO_2$, dehumidified, and measured with a NDIR.

   The instrument has an internal microprocessor. Each sample is injected at least three separate times. A coefficient of variation is calculated. If the coefficient is unacceptable, then instrument makes additional injections until the maximum of five injections is reached. An internal decision of which injections to use for the calculation is made by the microprocessor and the mean peak area, the standard deviation, and CV are printed out.

   Instead of using the two point curve generated by the microprocessor, five internal standards are used with each set of analyses (18 samples) to calculate a linear regression with the intercept set at zero. Spikes, standards, and standard reference material are

interspersed throughout the analyses for quality control.

The study samples were acidified to pH <3 with HCl, stored at 4°C and analyzed within 30 days.

**RESULTS AND DISCUSSION**

Comparison of the instruments and any interference from salinity will be discussed separately. Since there was no means to determine the absolute true value for the carbon in the samples in this study, there was no single correct value. In order to provide a common baseline for comparing the instruments, a DDI blank sample was prepared and sent with the samples. The blank was the same water sample as the low carbon concentration, zero salinity sample, except that it was in a separate container. All concentrations used in the comparison have had this DDI water blank value subtracted from each sample value reported.

As previously noted, the Astro instrument did not analyze the low concentration samples. The laboratory personnel considered the instrument unable to correctly measure low levels of DOC in saline samples. Plans were made to replace both the Astro and Dohrmann instruments shortly after this study.

Comparison of Instruments and Data

The results from the four instruments that analyzed the low carbon concentration samples were very similar with the exception of one instrument. It was noted that the Dohrmann instrument analyzed each sample twice versus the seven replicates for the other instruments. In Figure 1, the Dohrmann values appear to differ from the others. When using the mean combined value for each sample from the Shimadzu and OI instruments, the maximum and minimum differences from this mean by the Dohrmann is 1.32 and 0.19 mgC/L respectively. The average difference between the Dohrmann and the mean of the other instruments' values is 0.68 mgC/L.

When the data from the Shimadzu and the two OI instruments were compared, there was a maximum difference between the nine low carbon concentration samples of 0.35 mgC/L and a minimum difference of 0.02 mgC/L. In general, the difference increased slightly as the salinity increased. In most instances the values of the three instruments were within one standard deviation of each other. The minimal concentration of these samples does not encourage great

variability. If the blank sample value had not been subtracted from each sample mean, the difference would have been greater.

The high carbon concentration samples analyzed by the five instruments showed wider variability. Because the concentration of samples was 8 mgC/L or higher, there was a greater potential for differences in the absolute recovery than there was when comparing the absolute recoveries of the low carbon concentration samples. All five instruments' high carbon concentration determinations are plotted in Figure 2. The Dohrmann and Astro sample values showed a greater variability than the Shimadzu and the two OI results. In order to clarify the graph, two additional plots were made: Figure 3 which displays only the high carbon concentration determinations from the Shimadzu, OI ampule and OI automated instruments and Figure 4 which displays the mean of these three determinations plotted with the Dohrmann and Astro results. Assuming that the sample values ranged from 8 to 9 mgC/L, increasing with salinity, these two instruments were generally within 1 mgC/L of the mean value of the other instruments. As with the low carbon samples, the Dohrmann only analyzed two replicates as opposed to seven or more by the other instruments.

The standard deviation of the replicates indicates the variability within each instrument. Precision is not an indicator of accuracy, but it is indicative of the instrument's quality control. Using only the high concentration samples to illustrate, all values are in mgC/L;

1.) The Astro standard deviation varied from 0.1 to 0.59.
2.) The Dohrmann with two replicates can not be compared.
3.) The OI ampule standard deviation varied from 0.06 to 0.17.
4.) The OI automated standard deviation varied from 0.03 to 0.14.
5.) The Shimadzu standard deviation varied from 0.05 to 0.18.

When the results from the Shimadzu, OI ampule, and OI automated instrument were compared, the high carbon samples of varying salinities showed as little variability as the low carbon samples. The maximum difference was 0.67 mgC/L and the minimum difference was 0.12 mgC/L. The average difference for the three instruments was 0.32 mgC/L. This is within the Upper Control Limit for precision for some DOC instruments.

Influence of Salinity

Since the Shimadzu, OI ampule, and OI automated data were so comparable, their data were used to access the influence of salinity on the DOC results. The samples had been prepared to allow close examination of the salinity range from 5 to 14 ppt. Previous studies indicated that salinities in this range influenced DOC results. No salinity influence would give a straight line regression of the sample values and salinity for each set. On examination of Figures 1 and 3, each instrument showed some slight variability in the area of 5 to 14 ppt salinity. In order to superimpose the data from the three instruments, the sample set for low carbon concentration was set to zero for the zero salinity (Figure 5) and 8.0 mgC/L for the first high level sample (Figure 6). The rest of the sample means for each set were adjusted accordingly.

This does not address the possiblity of a continual salinity effect, which would give a linear regression, but it allows comparison of the methodologies in analyzing saline samples.

Standards, Blanks, and Curves

Although this study did not include laboratory calibration of instruments and data reduction, the final results were very dependent on these factors. In addition, the problem of carbon contamination was of great interest and was very much a problem in analyzing low level carbon samples. Known sources of carbon contamination include:

C1.) The acid added to lower the pH of samples and standards to <3 before sparging off the inorganic carbon. This is referred to as the Acid Blank.
C2.) The water to prepare the standards. This is referred to as the Standard Blank.
C3.) Carbon in the instrument through which the sample passes. This is referred to as the Instrument Blank.

The samples and standards during analysis are equally contaminated by carbon from sources C1. and C3. Only the standards contain carbon contamination from the Standard Blank (C2.).

In addition to contamination, methods of data reduction for the samples need to be evaluated. Examples of some methods are given below:

S1.) Some instruments use an electronic zero, but not a standard blank. Using this electronic zero and a single high standard, a two point curve is regressed. The sample values are calculated from this curve.

S2.) In some instruments a set of standards containing from four to ten separate values is analyzed and a linear regression calculated using the results. The sample concentrations values are calculated using this curve.

a. This regression is allowed to set its own intercept which is generally above zero and no further adjustment is made. This assumes that any carbon found in the standards is also found in the samples.

b. Dividing the sample peak area by the slope of the regression could be used to calculate the sample values. This sets the curve to zero and assumes that any carbon found in the standards is not found in the samples.

When the method described in S1. is used, the electronic zero assumes no carbon in the Acid or Standard Blank; however, it makes allowance for the Instrument Blank. Therefore, the resultant standard curve would be slightly skewed. The values close to zero may be higher than the true value and the values in the upper range may be slightly lower than the true value due to the presence of carbon in the standard water for which no correction can be made.

When the method described in S2a. is used, there is no allowance in the calculation for the carbon in the Acid Blank, Standard Blank, and Instrument Blank; thus, these would be included in the resultant standard curve. Consequently, a lower sample result than the true value would be obtained.

When the S2b. method is used, the Acid Blank and Instrument Blank are fully considered, but the carbon in the standard water would be included in the resultant standard curve, thus giving sample concentrations which are higher than the true value.

In addition, other factors exist which can result in a bias in very low level carbon analysis. For instance, the standard diluent typically has some carbon contamination present which is difficult to remove and should be considered in the calculations. As the level of carbon in the sample increases, this contamination assumes less importance. Most DDI water contains no more than 0.30 mgC/L, when only polished with Deionization cartridges. When any water (samples, reagents, standards, etc...) is exposed to the atmosphere, it collects carbon. Further consideration is given to these biases in Sharp et al. (1994).

**CONCLUSIONS**

Comparison of the dissolved organic carbon results from the five methodologies/instruments used for the Chesapeake Monitoring Program demonstrated that the consensus was good between all instruments and excellent between three instruments. There was no need to develop a correction factor between instruments. Any problems with the two instruments which yielded the greatest variability was probably due to the age of the instruments and their detectors. That instrument variability has been eliminated as those two instruments have been replaced by high temperature combustion instruments which performed well in this comparison.

Salinity may present a bias in wet oxidation methods, but the instruments in this study were modified in their reagent concentration and reaction time to compensate for salinity. The motion linearity of the curves with the adjusted means for examination of salinity influence is probably an artifact of the addition measurements in that range. It could be argued from these curves that salinity does affect DOC measurements, but if so, the influence is so slight that it can be ignored.

Attention to calibration, blanks, and standards is more important than difference in recovery of dissolved organic carbon by the instruments. All data reported must have an explanation of how this was handled for future data users. However, for the concentrations of carbon found in the Chesapeake Bay Monitoring Program, errors induced in measurement by data reduction are probably less than those normallly associated with intralaboratory variability since all the laboratories involved share a common method of data generation.

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# APPENDICES

A. Tables

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E. Coordinated Split Sample Data from Chespeake Bay Program

# APPENDIX A

## Tables

Contents:

TABLE 1

INSTRUMENT METHODOLOGY

| ITEM | ASTRO | DOHRMANN | OI AMPULE | OI AUTO | SHIMADZU |
|---|---|---|---|---|---|
| SAMPLE SIZE | 15mL | 5 mL | 5 mL | 1.103mL | 80µL |
| ACID ADDED | H2SO4 | H2SO4 | H2SO4 | H3PO4 added internally | H2SO4 |
| METHOD | Sodium Persulfate/ ultraviolet/ NDIR detector | SAME AS ASTRO | Sodium Persulfate/ 10% H3PO4 autoclaved | Sodium persulfate/ H3PO4 100'C | Platinum Catalyst 680'C |
| CALIBRA-TION | ONE POINT CURVE AND INSTRUMENT BLANK | TWO POINT CURVE AND MILLIPORE WATER FOR BLANK | ELEVEN POINTS PLUS MILLIPORE BLANK | ONE POINT CALIBRATION WITH INSTRUMENT BLANK | FIVE POINT CALIBRATION |
| GAS | Nitrogen purge | Nitrogen purge | Nitrogen purge | Zero Grade $N_2$ | Zero Grade Air |
| DATA REDUCTION | Regressed on calibration curve | Calculation by Instrument | Double Regression with intercept at zero | Instrument calculates a scaling factor for samples mVs | Slope of standards calculated & area count of samples divided by slope |

TABLE 2.
**MEANS OF DOC DATA IN MG/L BY SALINITY FOR LOW CONCENTRATIONS corrected for blank value**

| SAMPLE ID | SALINITY | DORHMANN | OI AMPULE | OI AUTOMATED | SHIMADZU TOC 500 |
|---|---|---|---|---|---|
| L7 | 0.03 | 0.90 | 0.02 | -0.04 | 0.06 |
| L1 | 5.20 | 1.54 | 0.21 | 0.19 | 0.26 |
| L2 | 7.18 | 0.92 | 0.19 | 0.25 | 0.31 |
| L9 | 9.23 | 0.58 | 0.19 | 0.32 | 0.27 |
| L5 | 11.36 | 0.87 | 0.32 | 0.33 | 0.34 |
| L6 | 12.99 | 1.00 | 0.31 | 0.35 | 0.44 |
| L4 | 14.97 | 0.65 | 0.44 | 0.44 | 0.50 |
| L3 | 24.53 | 1.15 | 0.77 | 0.68 | 0.84 |
| L8 | 34.66 | 2.14 | 1.00 | 0.88 | 1.23 |

TABLE 3.
**MEANS OF DOC DATA IN MG/L BY SALINITY FOR HIGH CONCENTRATIONS corrected for blank value**

| SAMPLE ID | SALINITY | ASTRO | DORHMANN | OI AMPULE | OI AUTO | SHIMADZU TOC 500 |
|---|---|---|---|---|---|---|
| H8 | 0.06 | 8.78 | 8.72 | 8.12 | 7.80 | 8.03 |
| H6 | 5.15 | 9.65 | 9.36 | 7.91 | 7.99 | 8.14 |
| H3 | 7.25 | 9.39 | 7.37 | 8.53 | 8.14 | 8.27 |
| H2 | 9.22 | 9.31 | 9.38 | 8.28 | 8.23 | 8.16 |
| H5 | 11.27 | 9.90 | 9.33 | 8.11 | 8.25 | 8.41 |
| H1 | 13.40 | 8.54 | 8.29 | 8.29 | 8.31 | 8.43 |
| H4 | 15.40 | 7.97 | 9.65 | 8.53 | 8.35 | 8.37 |
| H7 | 23.72 | 8.23 | 9.36 | 8.76 | 8.42 | 8.83 |
| H9 | 35.50 | 9.39 | 9.96 | 9.35 | 8.68 | 9.19 |

TABLE 4.

**ADJUSTED MEANS OF DOC DATA FOR LOW CONCENTRATIONS BY SUBTRACTION OF ZERO SALINITY VALUE IN MG C/L**

| SAMPLE ID | SALINITY | OI AMPULE | OI AUTOMATED | SHIMADZU TOC 500 |
|---|---|---|---|---|
| L7 | 0.03 | 0.00 | 0.00 | 0.00 |
| L1 | 5.20 | 0.19 | 0.23 | 0.20 |
| L2 | 7.18 | 0.17 | 0.29 | 0.25 |
| L9 | 9.23 | 0.17 | 0.36 | 0.21 |
| L5 | 11.36 | 0.30 | 0.37 | 0.28 |
| L6 | 12.99 | 0.29 | 0.39 | 0.38 |
| L4 | 14.97 | 0.42 | 0.44 | 0.44 |
| L3 | 24.53 | 0.75 | 0.72 | 0.78 |
| L8 | 34.66 | 0.98 | 0.92 | 1.17 |

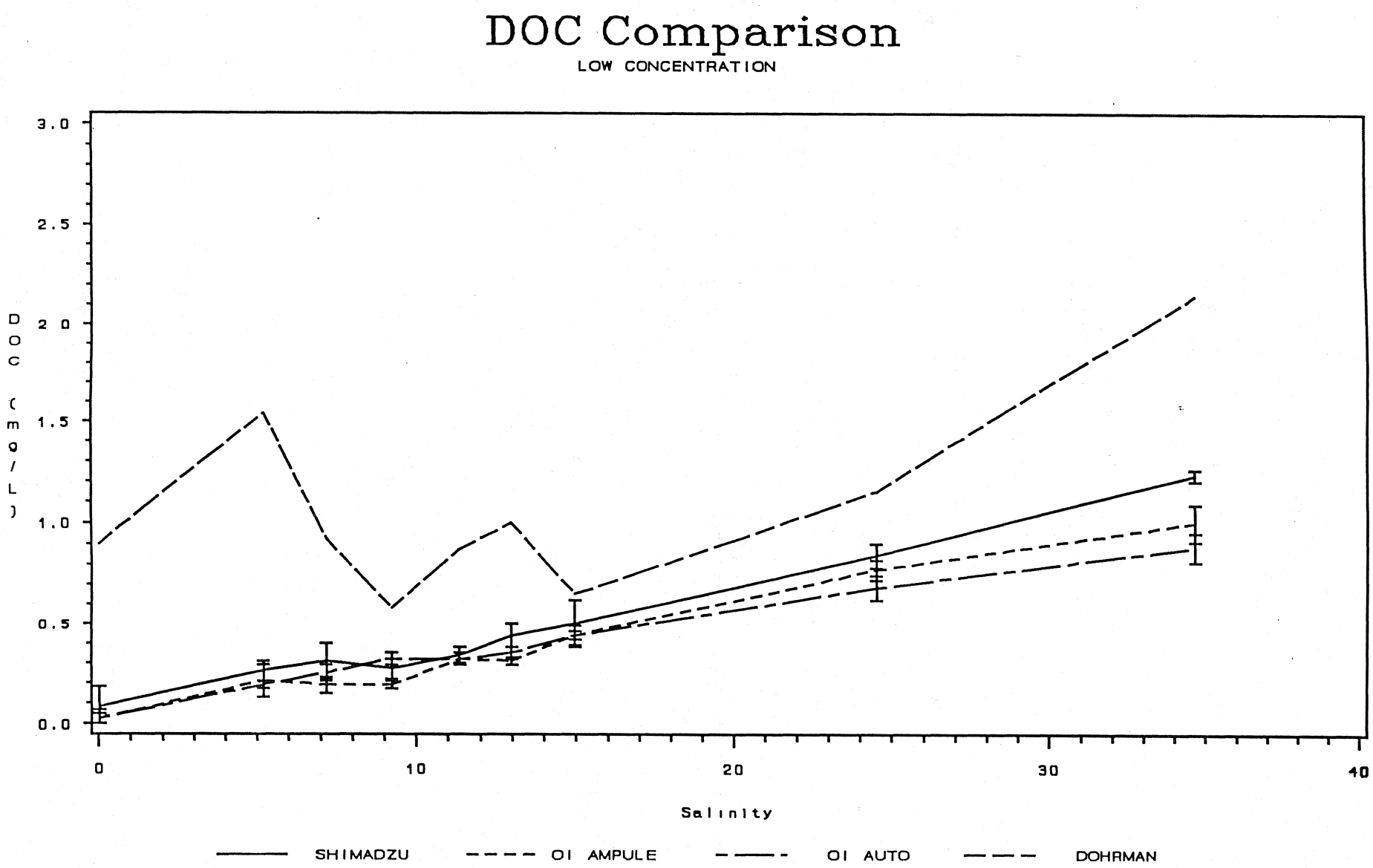
TABLE 5.

**ADJUSTED MEANS OF DOC DATA FOR HIGH CONCENTRATIONS TO 8.0 MG C/L FOR ZERO SALINITY VALUE**

| SAMPLE ID | SALINITY | OI AMPULE | OI AUTO | SHIMADZU TOC 500 |
|---|---|---|---|---|
| H8 | 0.06 | 8.00 | 8.00 | 8.00 |
| H6 | 5.15 | 7.79 | 8.19 | 8.11 |
| H3 | 7.25 | 8.41 | 8.34 | 8.24 |
| H2 | 9.22 | 8.16 | 8.43 | 8.13 |
| H5 | 11.27 | 7.99 | 8.45 | 8.38 |
| H1 | 13.40 | 8.17 | 8.51 | 8.40 |
| H4 | 15.40 | 8.41 | 8.55 | 8.34 |
| H7 | 23.72 | 8.64 | 8.62 | 8.80 |
| H9 | 35.50 | 9.23 | 8.88 | 9.16 |

# Appendix B

## Figures


DOC Comparison
LOW CONCENTRATION
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2.5
2.0
1.5
1.0
0.5
0.0
DOC (mg/L)
0
10
20
30
40
Salinity
SHIMADZU
OI AMPULE
OI AUTO
DOHRMAN

**Figure 1.**

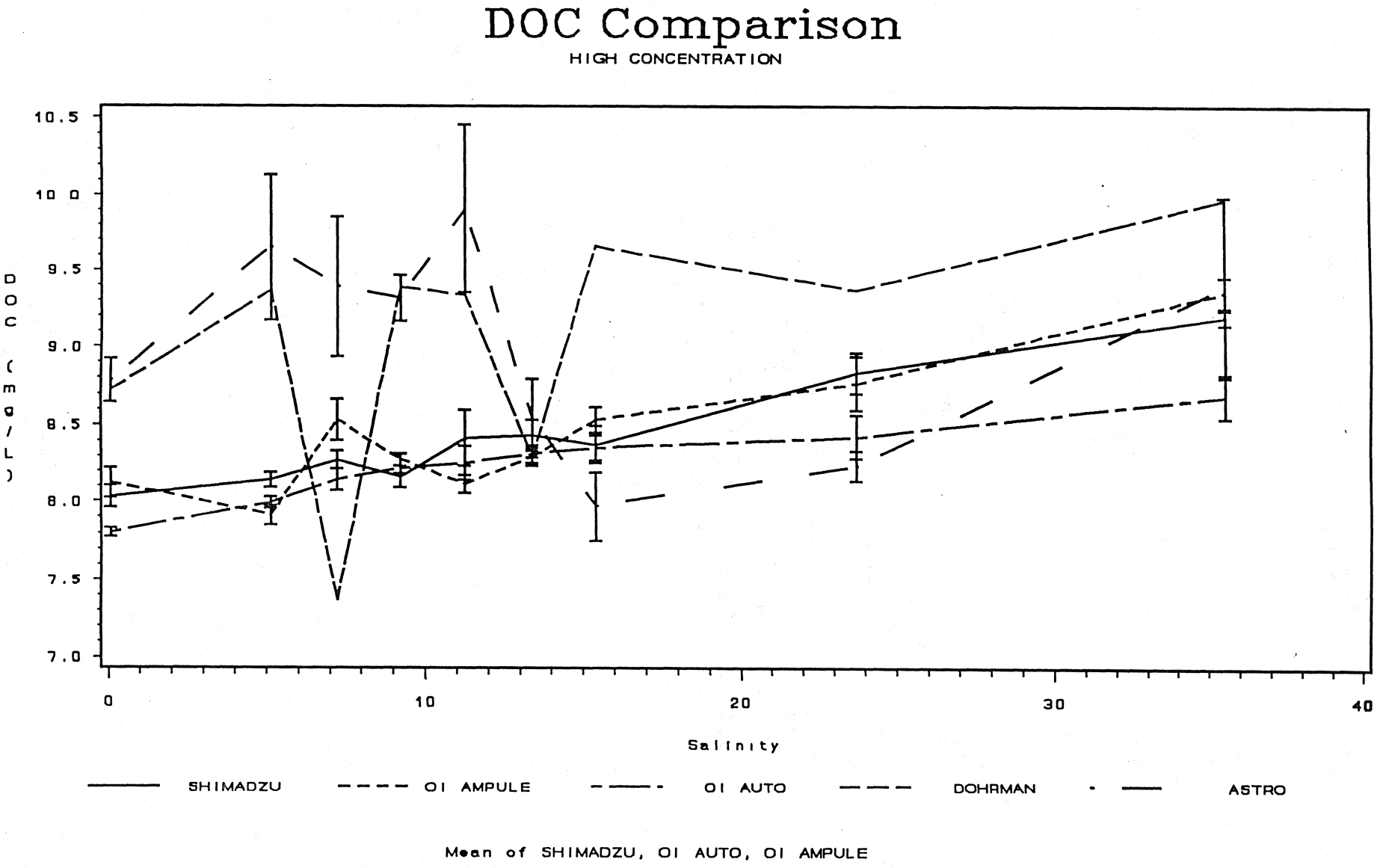

DOC Comparison
HIGH CONCENTRATION
DOC (mg/L)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
0
10
20
30
40
Salinity
SHIMADZU
OI AMPULE
OI AUTO
DOHRMAN
ASTRO
Mean of SHIMADZU, OI AUTO, OI AMPULE

**Figure 2.**

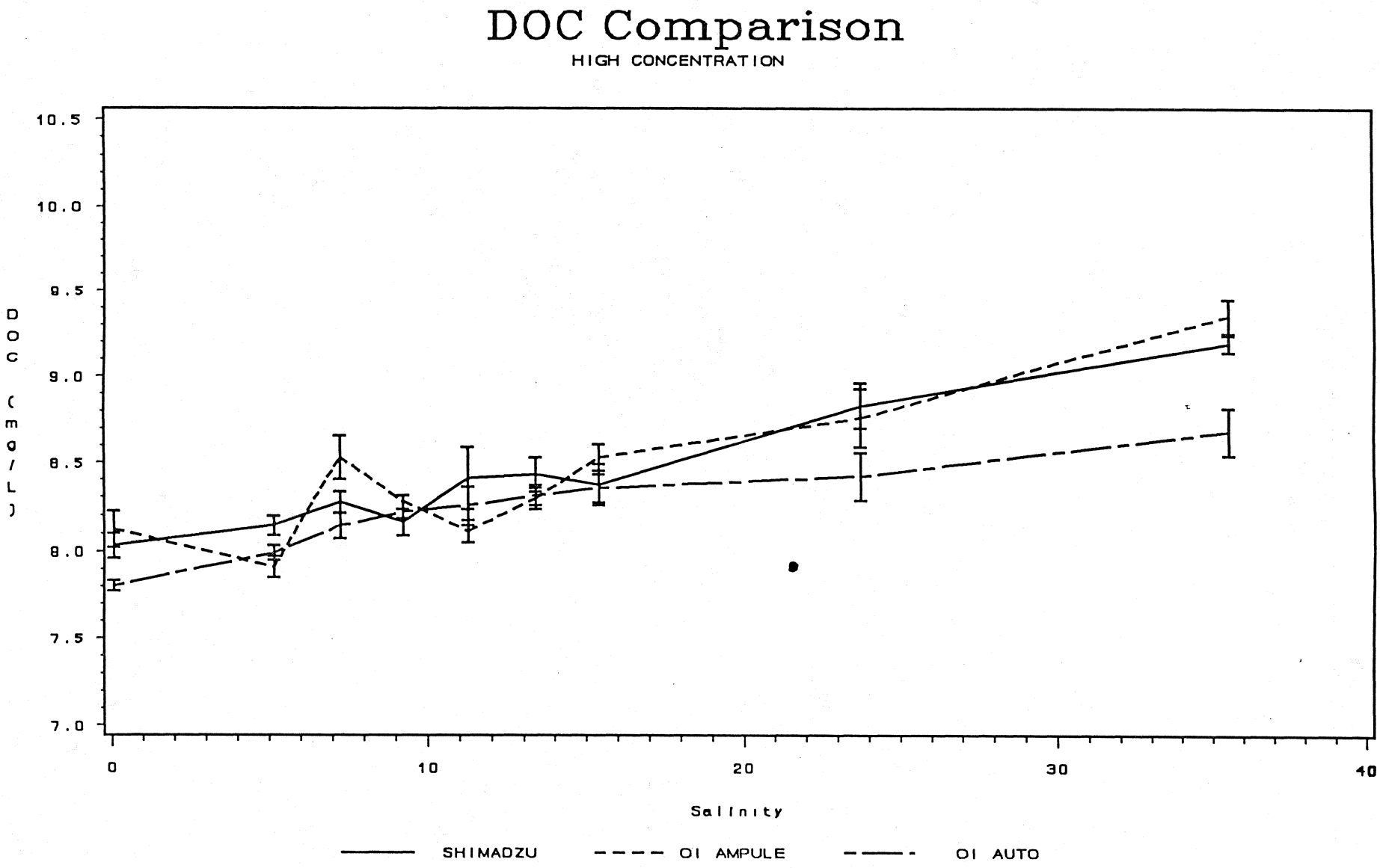
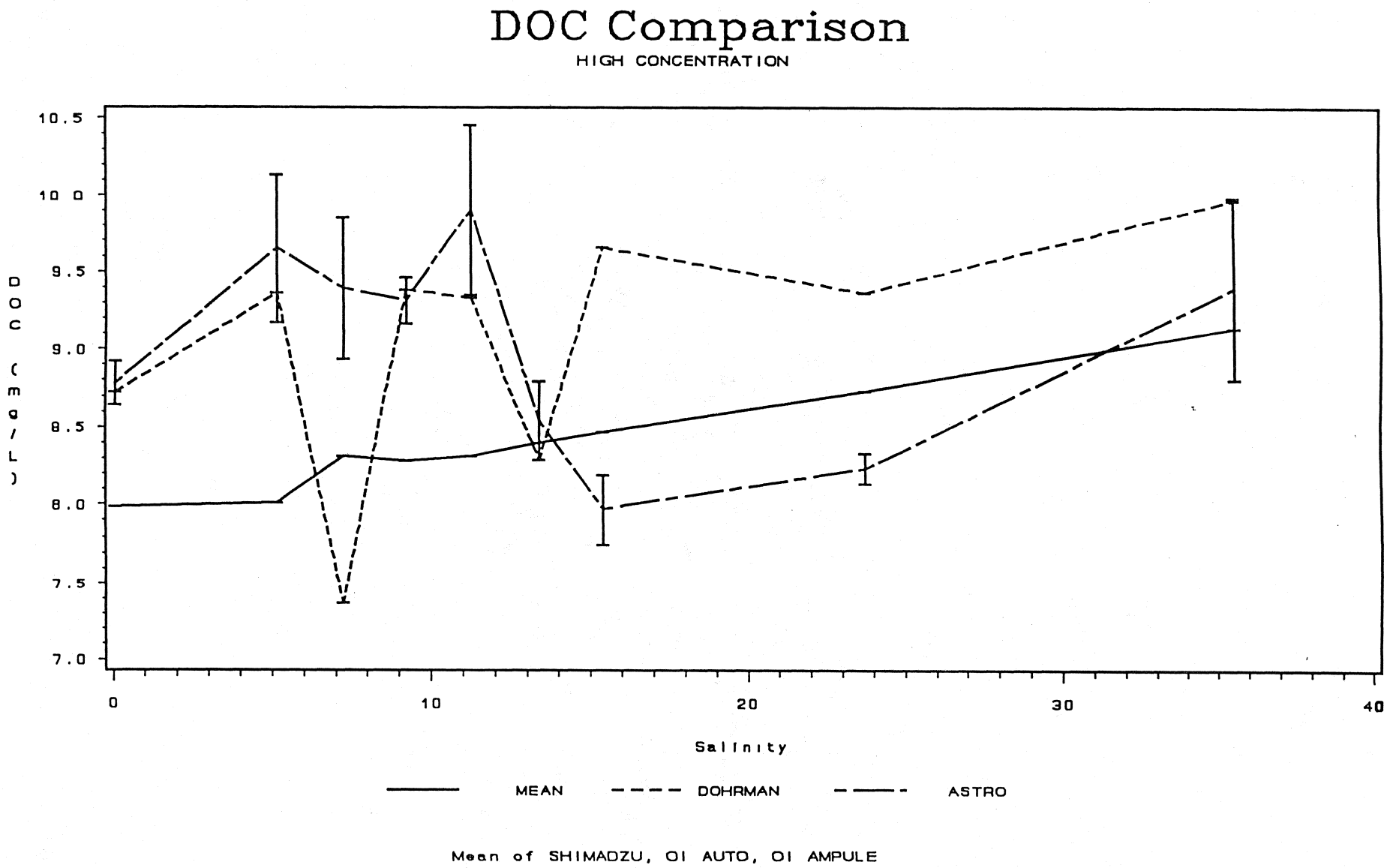

DOC Comparison
HIGH CONCENTRATION
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
DOC (mg/L)
0
10
20
30
40
Salinity
SHIMADZU
OI AMPULE
OI AUTO

**Figure 3.**


DOC Comparison
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
DOC (mg/L)
0
10
20
30
40
Salinity
MEAN
DOHRMAN
ASTRO
Mean of SHIMADZU, OI AUTO, OI AMPULE

**Figure 4.**

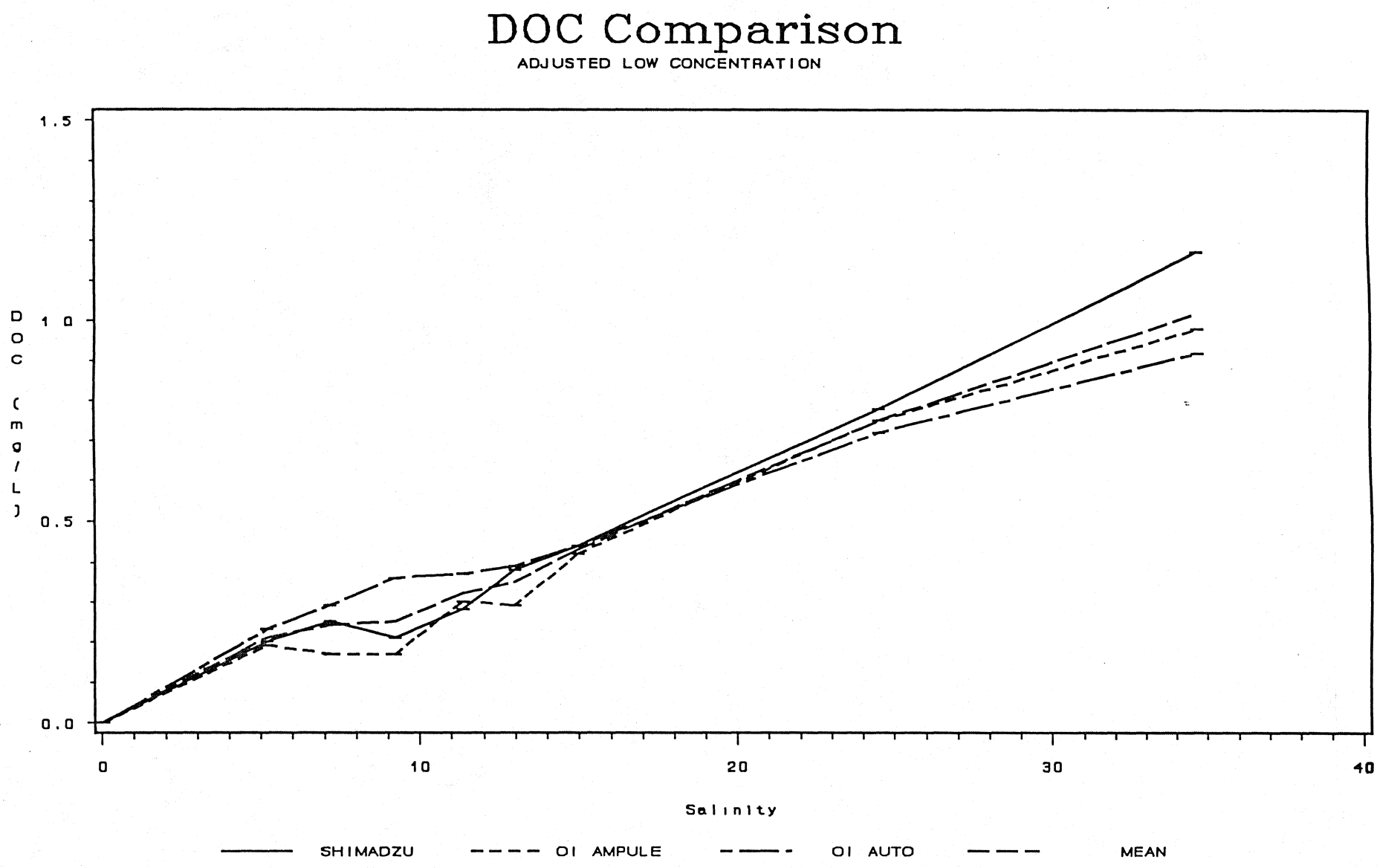

DOC Comparison
ADJUSTED LOW CONCENTRATION
1.5
1.0
0.5
0.0
DOC (mg/L)
0
10
20
30
40
Salinity
SHIMADZU
OI AMPULE
OI AUTO
MEAN

Figure 5

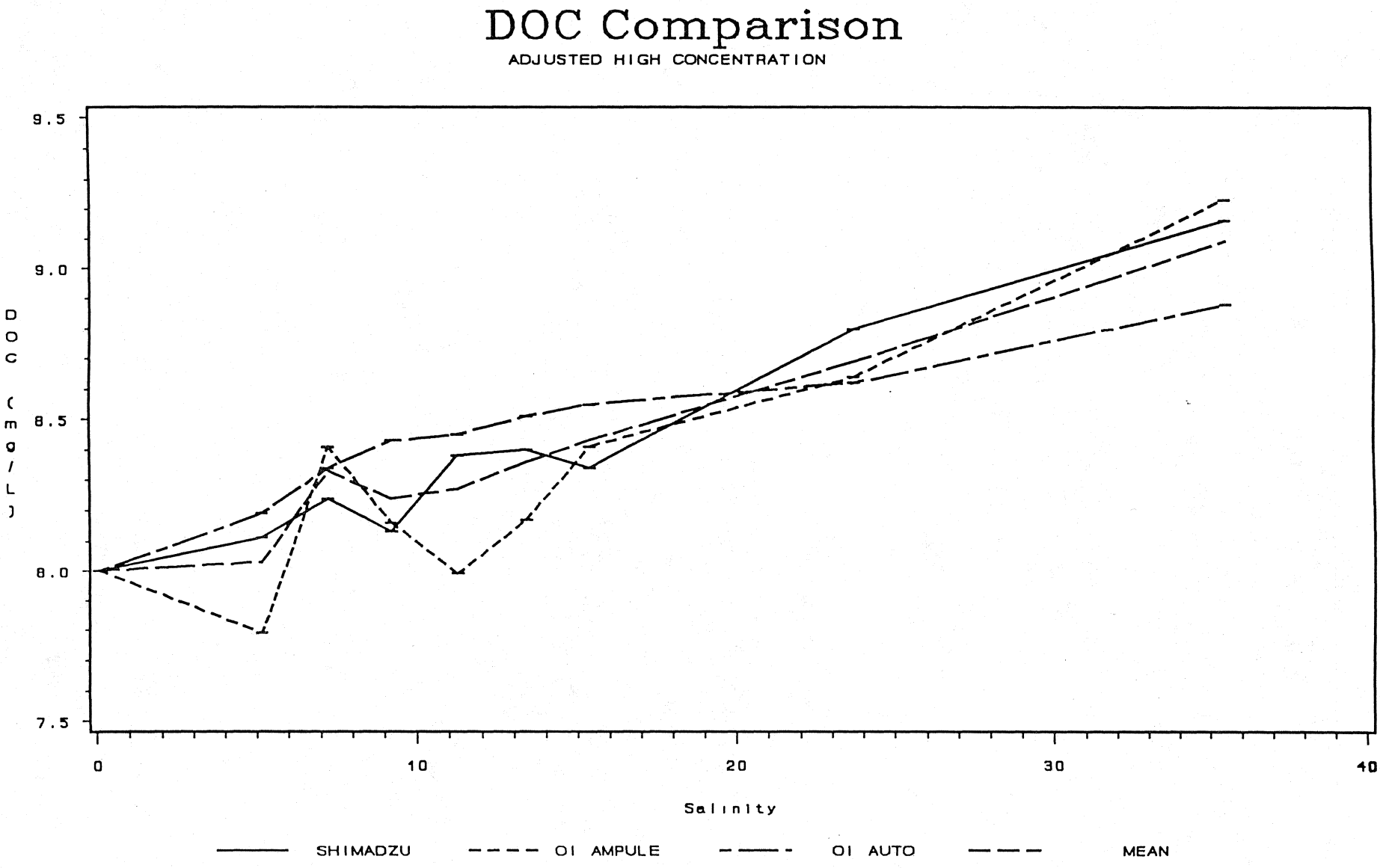

DOC Comparison
ADJUSTED HIGH CONCENTRATION
9.5
9.0
8.5
8.0
7.5
DOC (mg/L)
0
10
20
30
40
Salinity
SHIMADZU
OI AMPULE
OI AUTO
MEAN

Figure 6.

# APPENDIX C
## Raw Data

1. Astro
2. Dohrmann
3. Oceanographic International, Ampule
4. Oceanographic International, Automated
5. Shimadzu

DHMH - Astro

VIMS DOC COMPARISON STUDY
in mg/L

| | DI $H_2O$ BLANK |
|---|---|
| REP 1 | 0.40 |
| 2 | 0.42 |
| 3 | 0.40 |
| 4 | 0.41 |
| 5 | 0.42 |
| 6 | 0.45 |
| 7 | 0.41 |
| MEAN | 0.42 |
| STD | .016 |

| | H1 | H2 | H3 | H4 | H5 | H6 | H7 | H8 | H9 |
|---|---|---|---|---|---|---|---|---|---|
| REP 1 | 8.76 | 9.49 | 9.54 | 8.36 | 9.42 | 11.03 | 9.87 | 9.15 | 9.28 |
| 2 | 9.27 | 9.90 | 9.43 | 8.76 | 10.56 | 9.89 | 8.54 | 9.23 | 9.93 |
| 3 | 9.19 | 9.91 | 10.36 | 8.48 | 10.51 | 10.31 | 8.76 | 9.25 | 9.24 |
| 4 | 9.13 | 9.69 | 9.88 | 8.34 | 9.87 | 10.09 | 8.63 | 9.15 | 9.17 |
| 5 | 8.75 | 9.63 | 9.34 | 8.10 | 10.73 | 9.56 | 8.60 | 9.02 | 9.37 |
| 6 | 8.57 | 9.76 | 9.64 | 8.31 | 10.81 | 9.75 | 8.79 | 9.47 | 10.68 |
| 7 | 9.07 | | 10.50 | | | 9.87 | | 9.13 | 9.28 |
| MEAN | 8.96 | 9.73 | 9.81 | 8.39 | 10.32 | 10.07 | 8.65 | 9.20 | 9.61 |
| STD | 0.247 | 0.148 | 0.457 | 0.218 | 0.549 | 0.483 | 0.099 | 0.140 | 0.588 |
| minus blank | 8.54 | 9.31 | 9.39 | 7.97 | 9.90 | 9.65 | 8.23 | 8.78 | 9.39 |

| | | SPIKES | |
|---|---|---|---|
| | ACTUAL | ORIGINAL | EXPECTED |
| H4 | 13.76 | 9.81 | 14.81 |
| H2 | 14.95 | 9.73 | 14.81 |
| H5 | 14.57 | 10.32 | 15.32 |
| H7 | 13.47 | 8.65 | 13.65 |

| SRM | True Value = 8.2 mg/L |
|---|---|
| 1 | 8.62 |
| 2 | 8.79 |
| 3 | 8.63 |

DCLS - Dorhmann

VIMS DOC COMPARISON STUDY
in mg/L

| | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 |
|---|---|---|---|---|---|---|---|---|---|
| REP 1 | 1.633 | 0.863 | 1.334 | 0.383 | 0.949 | 1.046 | 0.636 | 2.747 | 0.755 |
| 2 | 1.448 | 0.984 | 0.966 | 0.925 | 0.798 | 0.946 | 1.155 | 1.536 | 0.402 |
| MEAN | 1.541 | 0.924 | 1.150 | 0.654 | 0.874 | 0.996 | 0.896 | 2.142 | 0.579 |
| minus blank | 1.437 | 0.820 | 1.046 | 0.550 | 0.770 | 0.892 | 0.792 | 2.038 | 0.475 |

| | H1 | H2 | H3 | H4 | H5 | H6 | H7 | H8 | H9 |
|---|---|---|---|---|---|---|---|---|---|
| REP1 | 7.496 | 9.448 | 8.058 | 9.412 | 9.781 | 9.394 | 9.250 | 8.574 | 9.870 |
| 2 | 9.299 | 9.314 | 6.886 | 10.100 | 9.083 | 9.531 | 9.452 | 9.074 | 10.260 |
| MEAN | 8.398 | 9.381 | 7.472 | 9.756 | 9.432 | 9.463 | 9.463 | 8.824 | 10.065 |
| minus blank | 8.294 | 9.377 | 7.368 | 9.652 | 9.328 | 9.359 | 9.359 | 8.720 | 9.961 |

Blank

| | |
|---|---|
| Rep 1 | 0.113 |
| Rep 2 | 0.095 |
| Mean | 0.104 |

ODU - Oceanographic International, Ampule

VIMS DOC COMPARISON STUDY
in mg/L

| | | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 |
|---|---|---|---|---|---|---|---|---|---|---|
| REP | 1 | 0.58 | 0.42 | 1.06 | 0.63 | 0.53 | 0.52 | 0.24 | 1.36 | 0.36 |
| | 2 | 0.44 | 0.35 | 0.96 | 0.61 | 0.51 | 0.49 | 0.21 | 1.12 | 0.34 |
| | 3 | 0.35 | 0.33 | 0.92 | 0.62 | 0.51 | 0.47 | 0.19 | 1.13 | 0.39 |
| | 4 | 0.34 | 0.40 | 0.92 | 0.59 | 0.50 | 0.47 | 0.18 | 1.15 | 0.35 |
| | 5 | 0.35 | 0.35 | 0.93 | 0.59 | 0.47 | 0.46 | 0.18 | 1.14 | 0.35 |
| | 6 | 0.34 | 0.35 | 0.91 | 0.61 | 0.49 | 0.47 | 0.17 | 1.18 | 0.35 |
| | 7 | 0.35 | 0.30 | 0.91 | 0.63 | 0.45 | 0.47 | 0.17 | 1.09 | 0.37 |
| DUP | 1 | 0.36 | | | | | | | | |
| | 2 | 0.33 | | | | | | | | |
| | 3 | 0.40 | | | | | | | | |
| MEAN | | 0.38 | 0.36 | 0.94 | 0.61 | 0.49 | 0.48 | 0.19 | 1.17 | 0.36 |
| STD | | 0.077 | 0.041 | 0.054 | 0.017 | 0.027 | 0.020 | 0.025 | 0.089 | 0.017 |
| minus blank | | 0.21 | 0.19 | 0.77 | 0.44 | 0.32 | 0.31 | 0.02 | 1.00 | 0.19 |

| | | DI H2O BLANK |
|---|---|---|
| REP | 1 | 0.18 |
| | 2 | 0.15 |
| | 3 | 0.15 |
| | 4 | 0.15 |
| | 5 | 0.19 |
| | 6 | 0.19 |
| | 7 | 0.18 |
| MEAN | | 0.17 |
| STD | | .019 |

ODU(2)

| | H1 | H2 | H3 | H4 | H5 | H6 | H7 | H8 | H9 |
|---|---|---|---|---|---|---|---|---|---|
| REP 1 | 8.46 | 8.39 | 8.42 | 8.57 | 8.21 | 8.07 | 9.27 | 8.18 | 9.55 |
| 2 | 8.38 | 8.45 | 8.64 | 8.66 | 8.22 | 8.07 | 9.19 | 8.31 | 9.56 |
| 3 | 8.37 | 8.55 | 8.67 | 8.67 | 8.25 | 8.01 | 8.85 | 8.26 | 9.44 |
| 4 | 8.54 | 8.46 | 8.81 | 8.74 | 8.27 | 8.05 | 8.86 | 8.31 | 9.31 |
| 5 | 8.51 | 8.43 | 8.74 | 8.79 | 8.29 | 8.08 | 8.86 | 8.48 | 9.58 |
| 6 | 8.49 | 8.42 | 8.76 | 8.71 | 8.31 | 8.19 | 8.74 | 8.21 | 9.56 |
| 7 | 8.48 | 8.43 | 8.77 | 8.78 | 8.40 | 8.10 | 8.99 | 8.28 | 9.59 |
| DUP 1 | | | 8.82 | | | | 8.84 | | 9.58 |
| 2 | | | | | | | 8.82 | | |
| 3 | | | | | | | 8.89 | | |
| MEAN | 8.46 | 8.45 | 8.70 | 8.70 | 8.28 | 8.08 | 8.93 | 8.29 | 9.52 |
| STD | .064 | .051 | .131 | .077 | .064 | .056 | .170 | .097 | .098 |
| minus blank | 8.29 | 8.28 | 8.53 | 8.53 | 8.11 | 7.91 | 8.76 | 8.12 | 9.35 |

SPIKES

| | ACTUAL | ORIGINAL | EXPECTED |
|---|---|---|---|
| L2 | 4.49 | 0.36 | 4.36 |
| L8 | 5.14 | 1.17 | 5.17 |
| H4 | 12.53 | 8.70 | 12.70 |
| H6 | 12.68 | 8.08 | 12.08 |

| | EPA | | |
|---|---|---|---|
| | 3.06 | 9.18 | 6.14 |
| 1 | 2.94 | 9.33 | 6.16 |
| 2 | 2.83 | 9.36 | 6.10 |
| 3 | 2.87 | 9.37 | |
| 4 | 2.86 | 9.41 | |
| MEAN | 2.88 | 9.37 | 6.13 |
| STD | 3.19 | 9.49 | 6.27 |

CBL - Oceanographic International, Automated

VIMS DOC COMPARISON STUDY
in mg/L

| | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 |
|---|---|---|---|---|---|---|---|---|---|
| REP 1 | 0.39 | 0.51 | 0.88 | 0.71 | 0.55 | 0.50 | 0.13 | 1.03 | 0.52 |
| 2 | 0.34 | 0.39 | 0.98 | 0.70 | 0.50 | 0.51 | 0.13 | 1.17 | 0.48 |
| 3 | 0.39 | 0.40 | 0.79 | 0.60 | 0.47 | 0.53 | 0.16 | 1.10 | 0.54 |
| 4 | 0.36 | 0.42 | 0.80 | 0.58 | 0.49 | 0.58 | 0.12 | 1.02 | 0.51 |
| 5 | 0.41 | 0.38 | 0.88 | 0.60 | 0.49 | 0.58 | 0.15 | 1.09 | 0.52 |
| 6 | 0.34 | 0.46 | 0.88 | 0.58 | 0.49 | 0.52 | 0.20 | 1.05 | 0.46 |
| 7 | 0.37 | 0.43 | 0.82 | 0.57 | 0.51 | 0.52 | 0.15 | 0.90 | 0.48 |
| DUP 1 | | 0.43 | | | 0.54 | | 0.11 | 1.07 | |
| 2 | | | | | | | | 1.12 | |
| 3 | | | | | | | | 1.04 | |
| MEAN | 0.37 | 0.43 | 0.86 | 0.62 | 0.51 | 0.53 | 0.14 | 1.06 | 0.50 |
| STD | 0.02 | 0.04 | 0.06 | 0.05 | 0.03 | 0.03 | 0.03 | 0.07 | 0.03 |
| minus blank | 0.19 | 0.25 | 0.68 | 0.44 | 0.33 | 0.35 | -0.04 | 0.88 | 0.32 |

| | DDI H2O BLANK |
|---|---|
| REP 1 | 0.14 |
| 2 | 0.12 |
| 3 | 0.18 |
| 4 | 0.12 |
| 5 | 0.11 |
| 6 | 0.41 |
| 7 | 0.21 |
| DUP 1 | 0.16 |
| 2 | 0.08 |
| 3 | 0.07 |
| MEAN | 0.18 |

CBL (2)

| | H1 | H2 | H3 | H4 | H5 | H6 | H7 | H8 | H9 |
|---|---|---|---|---|---|---|---|---|---|
| REP 1 | 8.50 | 8.35 | 8.31 | 8.41 | 8.34 | 8.12 | 8.58 | 8.00 | 8.68 |
| 2 | 8.47 | 8.52 | 8.34 | 8.49 | 8.53 | 8.23 | 8.64 | 7.97 | 8.94 |
| 3 | 8.54 | 8.38 | 8.31 | 8.50 | 8.32 | 8.20 | 8.37 | 8.02 | 8.66 |
| 4 | 8.44 | 8.39 | 8.29 | 8.67 | 8.60 | 8.15 | 8.82 | 7.99 | 8.80 |
| 5 | 8.38 | 8.41 | 8.26 | 8.57 | 8.30 | 8.19 | 8.50 | 7.93 | 9.03 |
| 6 | 8.53 | 8.40 | 8.26 | 8.60 | 8.39 | 8.18 | 8.72 | 8.00 | 8.68 |
| 7 | 8.54 | 8.40 | 8.29 | 8.48 | 8.50 | 8.11 | 8.58 | 7.98 | 9.00 |
| DUP 1 | | | 8.48 | | | 8.18 | | | 8.80 |
| MEAN | 8.49 | 8.41 | 8.32 | 8.53 | 8.43 | 8.17 | 8.60 | 7.98 | 8.82 |
| STD | 0.06 | 0.05 | 0.07 | 0.08 | 0.11 | 0.04 | 0.14 | 0.03 | 0.14 |
| minus blank | 8.31 | 8.23 | 8.14 | 8.35 | 8.25 | 7.99 | 8.42 | 7.80 | 8.68 |

SPIKES
1/2 SAMPLE + 1/2 5 PPM KHP

| | ACTUAL | ORIGINAL | EXPECTED |
|---|---|---|---|
| L1 | 2.73 | 0.37 | 2.68 |
| L4 | 2.77 | 0.62 | 2.81 |
| L6 | 2.79 | 0.53 | 2.76 |
| L8 | 2.78 | 1.06 | 3.03 |
| L9 | 2.73 | 0.50 | 2.75 |
| H1 | 6.67 | 8.49 | 6.74 |
| H2 | 6.63 | 8.41 | 6.70 |
| H5 | 6.67 | 8.43 | 6.72 |
| H7 | 6.61 | 8.60 | 6.80 |

| | |
|---|---|
| SCALING FACTOR | 0.04637 ugC/mV |
| ORGANIC BLANK | 8.96 mV |
| INORGANIC BLANK | 1.27 mV |

VIMS
Shimadzu TOC 500, ASI 502

VIMS DOC COMPARISON STUDY
in mg/L

| | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 |
|---|---|---|---|---|---|---|---|---|---|
| REP 1 | 0.74 | 0.90 | 1.26 | 1.21 | 0.71 | 0.82 | 0.77 | 1.63 | 0.66 |
| 2 | 0.70 | 0.83 | 1.23 | 0.95 | 0.72 | 1.00 | 0.44 | 1.45 | 0.78 |
| 3 | 0.74 | 0.74 | 1.35 | 0.87 | 0.74 | 0.85 | 0.44 | 1.63 | 0.64 |
| 4 | 0.68 | 0.74 | 1.20 | 0.87 | 0.78 | 0.87 | 0.48 | 1.63 | 0.68 |
| 5 | 0.68 | 0.70 | 1.36 | 0.83 | 0.79 | 0.87 | 0.48 | 1.70 | 0.70 |
| 6 | 0.59 | 0.64 | 1.29 | 0.87 | 0.82 | 0.87 | 0.42 | 1.67 | 0.69 |
| 7 | 0.68 | 0.64 | 1.21 | 0.94 | 0.83 | 0.81 | 0.40 | 1.98 | 0.76 |
| MEAN | 0.69 | 0.74 | 1.27 | 0.93 | 0.77 | 0.87 | 0.49 | 1.66 | 0.70 |
| STD | 0.05 | 0.09 | 0.06 | 0.12 | 0.04 | 0.06 | 0.12 | 0.025 | 0.047 |
| minus blank | 0.26 | 0.31 | 0.84 | 0.50 | 0.34 | 0.44 | 0.06 | 1.23 | 0.27 |

| | DI H2O BLANK |
|---|---|
| REP 1 | 0.39 |
| 2 | 0.47 |
| 3 | 0.47 |
| 4 | 0.44 |
| 5 | 0.45 |
| 6 | 0.39 |
| 7 | 0.42 |
| MEAN | 0.43 |
| STD | .03 |

VIMS(2)

| | H1 | H2 | H3 | H4 | H5 | H6 | H7 | H8 | H9 |
|---|---|---|---|---|---|---|---|---|---|
| REP 1 | 8.85 | 8.68 | 8.64 | 9.03 | 8.69 | 8.61 | 9.37 | 8.54 | 9.59 |
| 2 | 8.81 | 8.68 | 8.67 | 8.92 | 9.17 | 8.63 | 9.06 | 8.50 | 9.56 |
| 3 | 8.80 | 8.59 | 8.84 | 8.72 | 9.00 | 8.58 | 8.06 | 8.45 | 9.59 |
| 4 | 8.90 | 8.54 | 8.66 | 8.74 | 8.96 | 8.63 | 8.39 | 8.32 | 9.58 |
| 5 | 9.05 | 8.48 | 8.64 | 8.70 | 8.72 | 8.53 | 8.29 | 8.45 | 9.63 |
| 6 | 8.70 | 8.59 | 8.72 | 8.78 | 8.65 | 8.49 | 8.30 | 8.54 | 9.69 |
| 7 | 8.88 | 8.74 | 8.70 | 8.71 | 8.73 | 8.53 | 8.38 | 8.43 | 9.67 |
| MEAN | 8.86 | 8.59 | 8.70 | 8.80 | 8.84 | 8.57 | 9.26 | 8.46 | 9.62 |
| STD | 0.10 | 0.07 | 0.06 | 0.12 | 0.18 | 0.05 | 0.130 | 0.07 | 0.05 |
| minus blank | 8.43 | 8.16 | 8.27 | 8.37 | 8.41 | 8.14 | 8.83 | 8.03 | 9.19 |

SPIKES

| | sample | sample + spike | spike (3 mg/L) |
|---|---|---|---|
| L1 | 0.69 | 3.65 | 2.96 |
| L2 | 0.74 | 3.98 | 3.24 |
| L3 | 1.27 | 4.29 | 3.02 |
| L4 | 0.93 | 4.02 | 3.09 |
| L5 | 0.77 | 3.80 | 3.03 |
| L6 | 0.87 | 3.95 | 3.08 |
| L7 | 0.49 | 3.55 | 3.06 |
| L8 | 0.70 | 3.78 | 3.08 |

| Standard Reference Material | | | True Value |
|---|---|---|---|
| DI Blank | 0.04 | 0.38 | 0.14 |
| DI SRM | 3.11 | 3.49 | 3.29 |
| SRM-Blank | 3.07 | 3.11 | 3.15 |
| Salt Blank | 0.13 | 0.69 | 0.76 |
| Salt SRM | 3.19 | 3.98 | 3.83 |
| SRM-Blank | 3.06 | 3.29 | 3.07 |

# Appendix D

DOC Samples List

Instruction for Analyses

## DOC SAMPLES LIST

1. NINE SAMPLE CONTAINERS LABELED:
   H1 H2 H3 H4 H5 H6 H7 H8 H9

2. NINE SAMPLE CONTAINERS LABELED:
   L1 L2 L3 L4 L5 L6 L7 L8 L9

3. DI WATER BLANK WITH SAME PRESERVATION AS ABOVE SAMPLES, LABELED:
   BLANK DI H20

**INSTRUCTIONS**

Analyzing samples

Run seven replicates on each sample. Use the usual quality control for accuracy. If you have any standard reference material from EPA, include this in the analysis. There is no need to run additional duplicates. Please give information of which chemicals are used for the spike and SRM.

Documentation

Send a copy of the instrument standard operating procedures. Detailed information of calibration procedure for instrument is needed. Include the instrument methodolgy, model number, when purchased, gases used by instrument, or for sparging, and any reagents used by instrument, or in samples before loading instrument.

Data

1. Report the data for all seven replicates
2. Report any quality control results.
3. Report the standards used; what the matrix used for dilution (ie, DI water).
4. Include the regression, slope and intercept for the standards and what the chemical that was used for the standards.
5. Please send a hard copy of your results and other information. Also if it is possible to send a floppy disk with the data in an ASCII file; it will facilitate data Handling.

# Appendix E

Results and graphs from Coordinated Split Sampling Program for 1990-1993
Chespeake Bay Program

Table with Median TOC results for CSSP 1990-1991

Table with Median DOC results from CSSP 1990-1991

Figure 11.

Figure 41.

Figure 43.

Median DOC values of split sample reuslts for 1992-1993

1992 Four-Way splits for DOC graph

1993 Four-Way splits for DOC graph

TF5.5 split sample medians with Friedman analysis results, 1990-1991 data. Data from 1991 were analyzed separately where applicable.

| Parameter[1] | N[2] | Laboratory Medians (mg/l) | | | | Friedman results[3] | |
|---|---|---|---|---|---|---|---|
| | | DCLS | HRSD | ODU | VIMS | $X^2$ | P |
| NH4 | 8 | 0.0750 | 0.0950 A | 0.0728 B | 0.0760 | 18.2 | <0.001 |
| NH4[4] | 5 | 0.0800 | 0.1000 | 0.0739 | 0.0800 | 6.1 | <0.20 |
| NO2 | 3 | 0.050 | 0.080 A | 0.046 B | 0.052 | 15.6 | <0.01 |
| NO2 | 2 | 0.035 | 0.055 | 0.027 | 0.032 | 12.7 | <0.01 |
| NO23 | 8 | 0.365 | 0.385 | 0.374 | 0.385 | 1.1 | >0.70 |
| NO23 | 5 | 0.400 | 0.420 | 0.421 | 0.410 | 7.8 | <0.10 |
| TDN | 4 | - | 0.623 B | 0.737 | 0.878 A | 11.2 | <0.01 |
| PN | 3 | - | 0.450 | 0.258 | 0.315 | 1.4 | >0.30 |
| TN | 5 | 0.800 | 0.710 B | 0.799 B | 0.933 A | 26.8 | <0.001 |
| TN | 4 | 1.150 | 1.070 B | 1.072 B | 1.158 A | 21.1 | <0.001 |
| PO4F | 7 | 0.020 C | 0.030 AB | 0.037 A | 0.025 BC | 39.4 | <0.001 |
| PO4F | 4 | 0.020 B | 0.028 | 0.036 A | 0.025 B | 30.0 | <0.001 |
| TDP | 7 | 0.030 B | 0.060 A | 0.036 | 0.033 | 24.5 | <0.001 |
| TDP | 4 | 0.030 | 0.056 | 0.032 | 0.033 | 5.3 | <0.20 |
| PHOSP | 7 | 0.090 A | 0.090 | 0.078 | 0.064 B | 15.1 | <0.01 |
| PHOSP | 4 | 0.110 A | 0.101 | 0.097 | 0.083 B | 15.9 | <0.01 |
| TP | 7 | 0.160 | 0.169 | 0.127 | 0.136 | 8.7 | <0.05 |
| TP | 4 | 0.165 | 0.169 | 0.138 | 0.138 | 13.1 | <0.01 |
| TOC | 5 | 3.87 B | - | 7.18 A | 7.43 A | 21.3 | <0.001 |

| Parameter | N[1] | Laboratory Means (mg/l except CHLA & PHEA) CBL | ODU | VIMS | MDHMH | DCLS | P value[2] |
|---|---|---|---|---|---|---|---|
| PHOSP | 7 | 0.0162 | 0.0176 | 0.0179 | . | . | <0.30 |
| PHOSP | 7 | 0.0162 | 0.0176 | 0.0179 | 0.0175 | . | <0.05 |
| PHOSP | 4 | 0.0157 | 0.0158 | 0.0173 | 0.0117 | 0.0192 | <0.02 |
| TP | 7 | 0.0261 | 0.0267 | 0.0292 | . | . | <0.30 |
| TP | 7 | 0.0261 | 0.0267 | 0.0292 | 0.0329 | . | <0.50 |
| TP | 4 | 0.0272 | 0.0245 | 0.0296 | 0.0348 | 0.0375 | 0.01 |
| DOC | 6 | 2.8194 B | 3.0483 B | 3.5267 A | . | . | <0.001 |
| PC | 8 | 1.3611 A | 1.0688 B | 1.0743 B | . | . | <0.001 |
| TOC | 6 | 4.2482 | 4.1644 B | 4.6867 A | . | . | <0.001 |
| TOC | 3 | 4.1767 | 4.5740 | 3.5067 | . | 3.7822 | <0.02 |
| TSS | 7 | 5.0738 B | 12.0619 A | 12.7905 A | . | . | <0.001 |
| TSS | 7 | 5.0738 B | 12.0619 A | 12.7905 A | 10.1429 A | . | <0.001 |
| TSS | 4 | 5.2875 B | 7.6833 | 7.7750 | 10.5000 A | 12.0000 | <0.001 |
| CHLA[4] | 6 | . | 10.6550 | 12.2033 | 12.3067 | . | <0.10 |
| PHEA[4] | 4 | . | 0.7767 | 1.7842 | 1.1133 | . | <0.10 |
| SI | 7 | 0.5610 B | 0.6705 A | 0.6665 A | . | . | <0.001 |
| SI | 7 | 0.5610 B | 0.6705 A | 0.6665 A | 0.7048 A | . | <0.001 |
| SI | 3 | 0.7789 B | 0.9580 A | 0.8830 | 0.9889 A | 0.8359 | <0.001 |

1 Number of cruises (sample dates) with complete data.

2 Underlined values were statistically significant ($P < 0.01$), based on Friedman two-way ANOVA using three subsamples per cruise. Laboratory means with different letters below them also had statistically significant pairwise differences ($A > B$, $P < 0.01$).

3 Too many values were below the method detection limit to make a comparison.

4 Units are ug/l, not mg/l, for CHLA and PHEA.

FIGURE 11. Split sample data for Dissolved Organic Carbon (DOC), from samples collected at CB5.3 or CB4.4 (Mainstem), showing cruise means with precision bars.

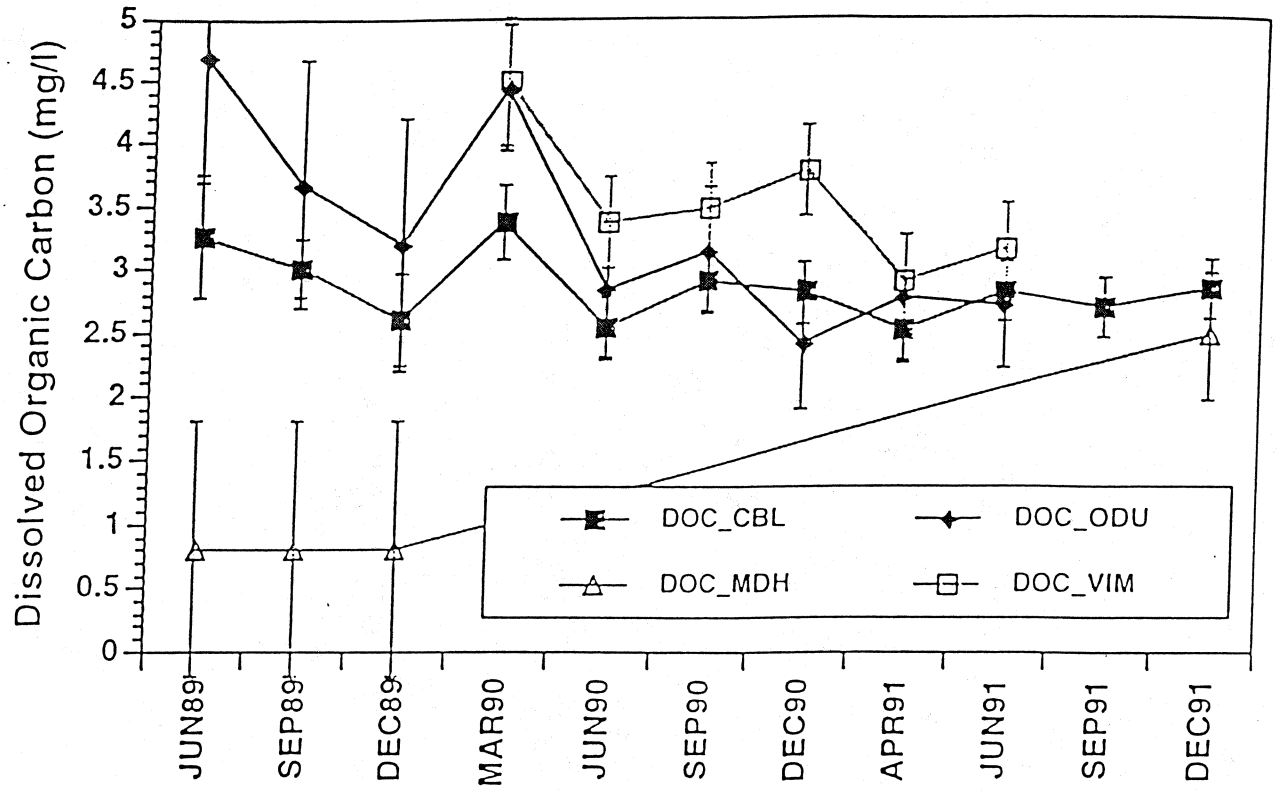


FIGURE 41. Split sample data for dissolved organic carbon (DOC), from Virginia samples collected at TF5.5 showing medians for each sample date with precision bars.

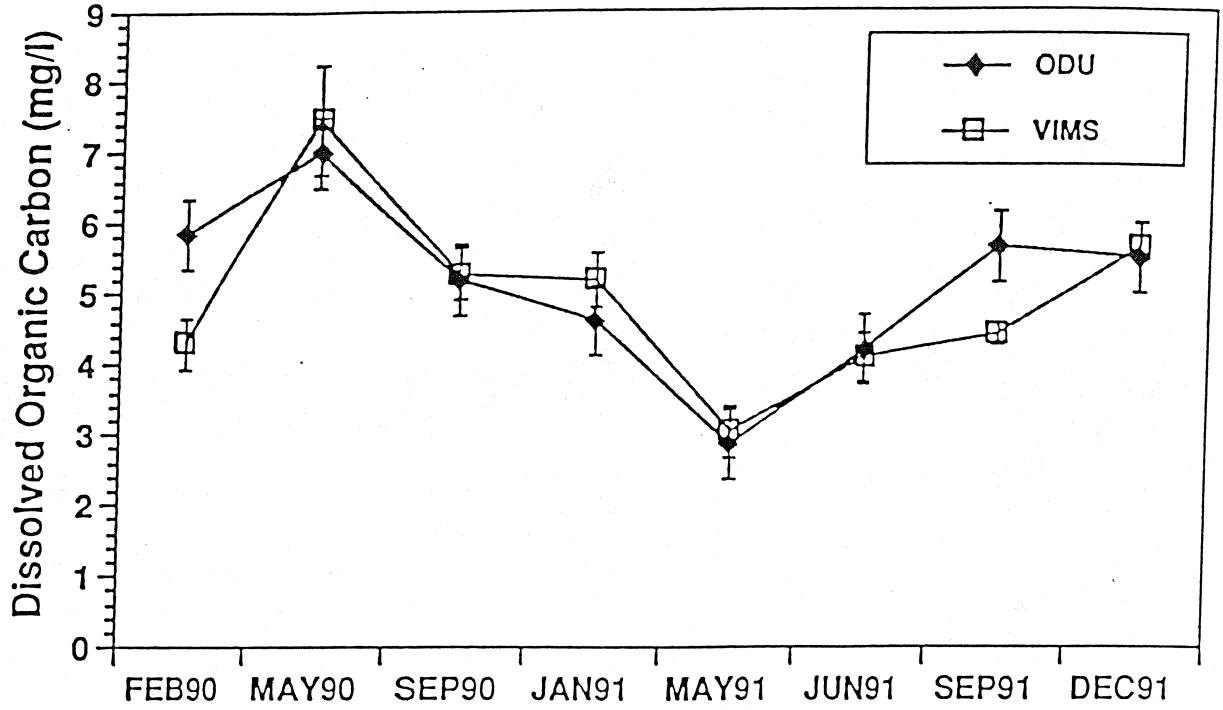
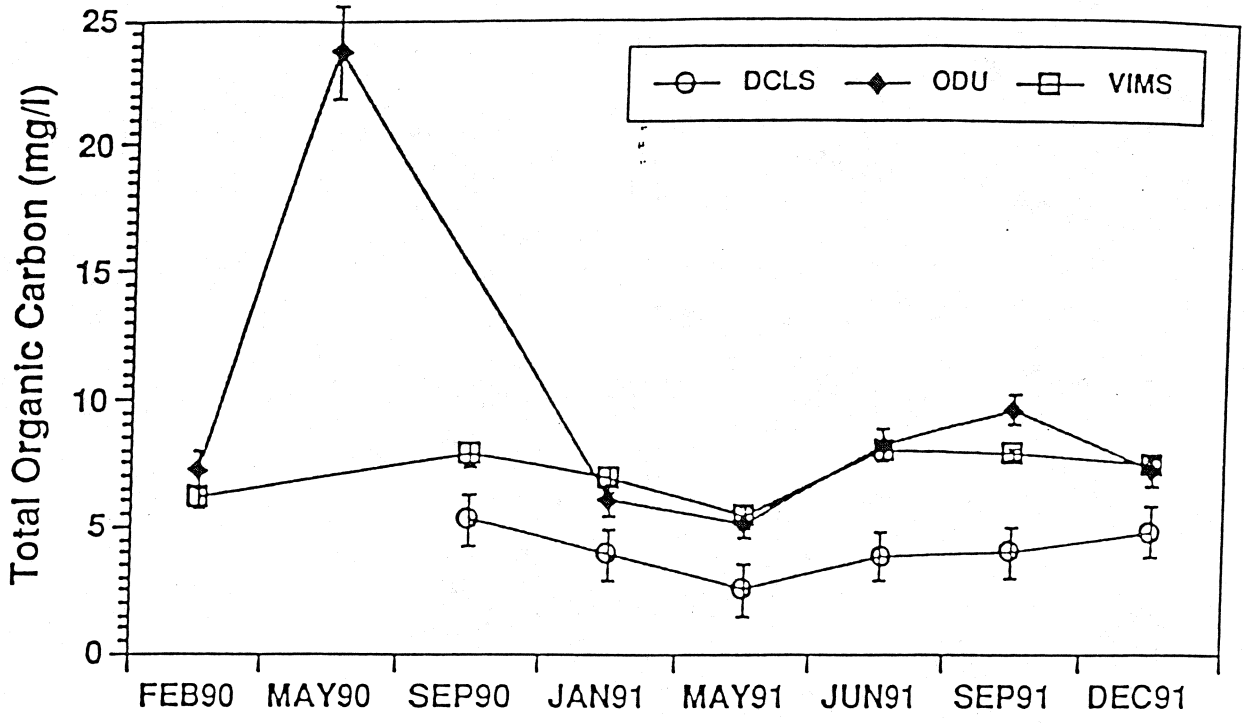
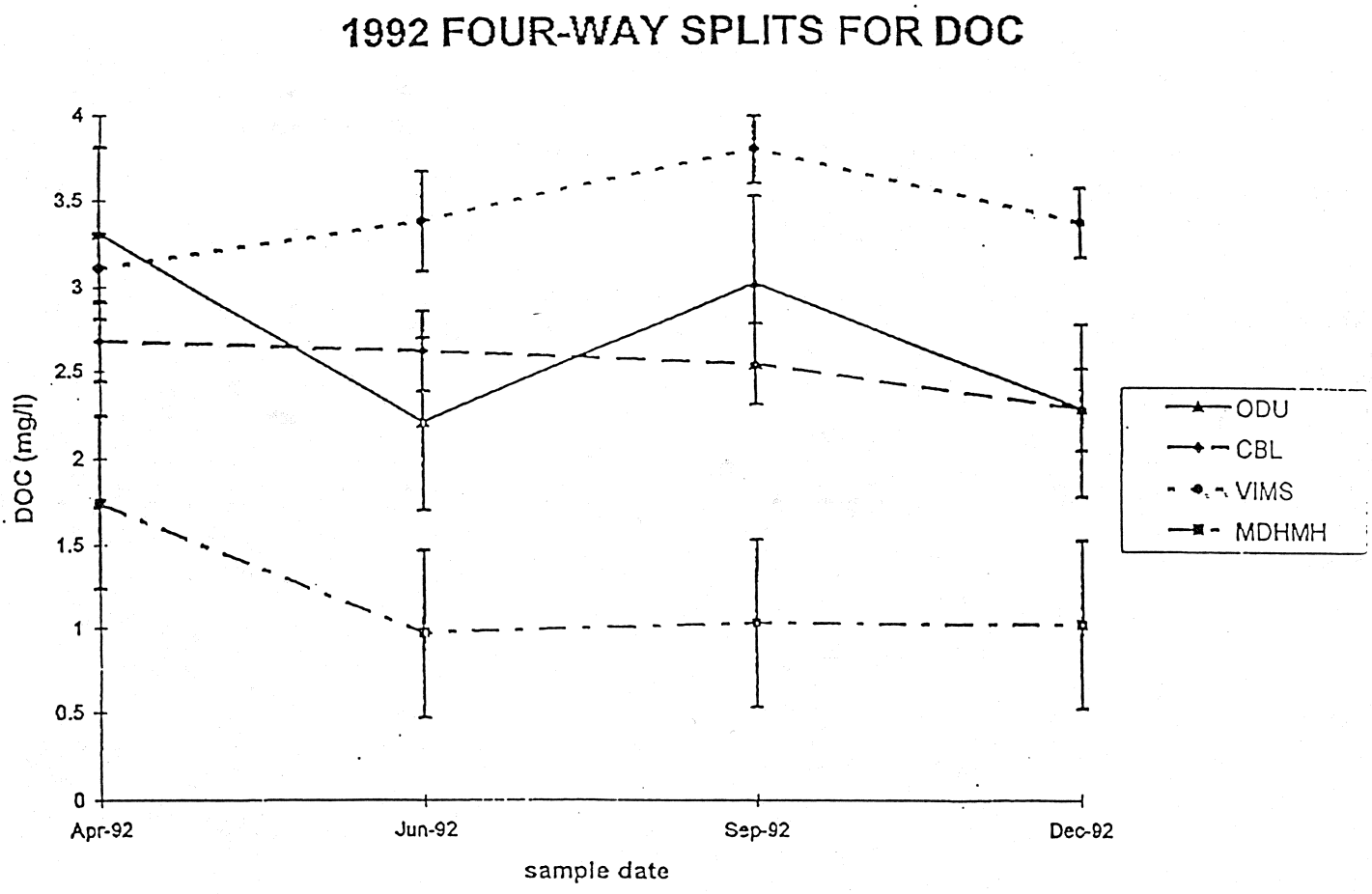
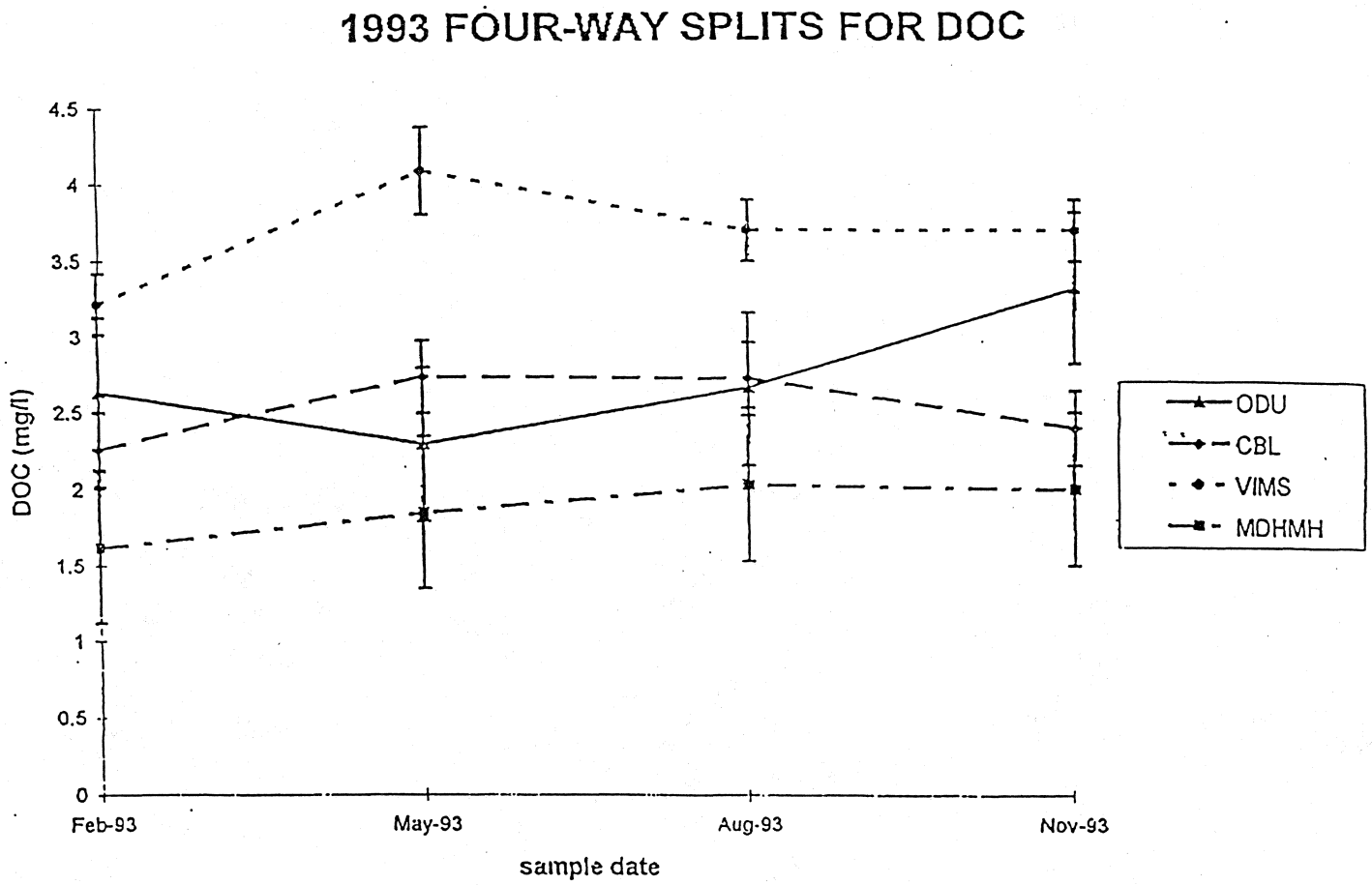


FIGURE 43. Split sample data for total organic carbon (TOC), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.



| | ODU | CBL | VIMS | MDHMH | |
|---|---|---|---|---|---|
| | | | | | |
| Apr-92 | 3.31 | 2.68 | 3.11 | 1.74 | |
| Jun-92 | 2.2 | 2.62 | 3.38 | 0.97 | |
| Sep-92 | 3.015 | 2.54 | 3.79 | 1.03 | |
| Dec-92 | 2.27 | 2.27 | 3.36 | 1.02 | |
| | | | | | |
| | | | | | |
| | ODU | CBL | VIMS | MDHMH | |
| | | | | | |
| Feb-93 | 2.63 | 2.26 | 3.22 | 1.62 | |
| May-93 | 2.3 | 2.74 | 4.1 | 1.85 | |
| Aug-93 | 2.66 | 2.72 | 3.7 | 2.03 | |
| Nov-93 | 3.32 | 2.4 | 3.7 | 2 | |


1992 FOUR-WAY SPLITS FOR DOC
DOC (mg/l)
4
3.5
3
2.5
2
1.5
1
0.5
0
Apr-92
Jun-92
Sep-92
Dec-92
sample date
ODU
CBL
VIMS
MDHMH


1993 FOUR-WAY SPLITS FOR DOC
DOC (mg/l)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Feb-93
May-93
Aug-93
Nov-93
sample date
ODU
CBL
VIMS
MDHMH