A COMPARISON OF TWO METHODS OF MEASURING DISSOLVED ORGANIC CARBON

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INTRODUCTION

During the summer of 1984, Virginia, Maryland, the District of Columbia, and the U.S. Environmental Protection Agency initiated a water quality monitoring program for Chesapeake Bay and its tributaries. Responsibility for sample collection and analysis in the Virginia portion of Chesapeake Bay is shared by the Virginia Institute of Marine Science (VIMS) and Old Dominion University (ODU). Since the beginning of the program, water samples from all Virginia mainstem Chesapeake Bay stations have been analyzed for dissolved organic carbon (DOC) by the Applied Marine Research Laboratory at ODU. The Nutrient Analysis Laboratory at VIMS acquired a dissolved carbon analyzer in late 1989 and began analyzing samples for DOC in January 1990. For the period January through June 1990, all of the water samples collected at VIMS' mainstem Chesapeake Bay monitoring stations were analyzed for DOC by both VIMS and ODU.

One of the stated purposes of the monitoring program is the development of a data base that will allow scientists (1) to determine if there have been changes in water quality with time, and (2) to postulate hypotheses concerning water quality processes. Clearly, methods changes may confound these efforts. The purpose of this study is to examine the data from the period when samples were analyzed using both DOC methods, so that differences related to changes in methods are made apparent to data users. The implications of these differences will be discussed briefly in the Results and Discussion section.

METHODS AND MATERIALS

The two laboratories employed different instruments that used different analytical approaches. ODU used an Oceanographic Instruments (OI) ampule TOC Analyzer. Beginning in January 1990, VIMS used a Shimadzu (Shim) TOC ASI-502, Automated. A description of the instruments, methods, and calibration procedures follows. Procedures for collecting and handling samples and for the analysis of the data also are included in this section.

OI Ampule Method: This OI method used a 5 ml sample, pH < 3, which was placed in an ampule and purged with ultrapure oxygen to remove the dissolved inorganic carbon (EPA, 1983; Method 415.1). One ml of saturated potassium persulfate and 200 ul of 10% phosphoric acid was added, the ampule sealed and autoclaved at 130° C for four hours. The remaining steps were carried out automatically by the instrument. The ampule was opened and the resultant CO_2 was carried through a nondispersive infrared detector (NDIR) by nitrogen gas.

The NDIR was calibrated with blanks, standards, and standard reference materials before samples were analyzed. Spiked samples and standards were interspersed among the field samples for internal quality control. Linear regression with the intercept set at zero was used to establish a standard response.

Shimadzu Automated TOC Analyzer: The Shimadzu method used high temperature (680° C) combustion with a platinum catalyst (Shimadzu, 1989). The sample was placed in a glass cup on a carousel, the carousel was loaded onto the instrument, and the instrument automatically processed the sample. Each sample, pH < 3, was sparged with ultralow carbon air to remove dissolved inorganic carbon (DIC). Then an 80 μl sample was autoinjected into the total carbon port. The resultant carbon was oxidized to CO_2 and carried by ultralow carbon air through the NDIR.

The instrument's microprocessor used a two point curve to calculate the concentration for each sample. Each sample was injected three separate times and a coefficient of variation was calculated. If the coefficient of variation was large, the instrument made an additional injection. If the results were still out-of-bounds, a fifth injection was made. The microprocessor chose which injections were used, and then calculated and printed the mean peak area, the standard deviation, and the coefficient of variation (Shimadzu, 1989).

With each set of samples (18 samples), five internal standards were used. A linear regression was calculated with the intercept set at zero. This regression was used to calculate the concentration of each sample. Spiked samples, standards, and standard reference materials were interspersed throughout the field samples for quality control.

Sample Collection and Handling: The samples were collected at 19 stations in lower Chesapeake Bay (see Figure 1) over a six month period, January through June 1990. Surveys occurred once per month in January, February, and March and twice per month in April, May, and June, for a total of nine cruises. At each station, vertical profiles of water temperature, salinity, pH, and dissolved oxygen were measured. Each water sample was analyzed for suspended solids, chlorophyll, and nutrient concentrations. During this six month period, each sample was analyzed for DOC using both methods.

When possible, the analyses were made on the same sample. That is, the VIMS laboratory withdrew an aliquot for its analysis and then sent the remainder of the field sample to ODU. In other instances the sample was split into two containers in the field, with one container returned to VIMS and the other sent to ODU. All DOC samples had acid added in the field (1 ml 6N H_2SO_4) to lower the pH to < 3.

Statistical Analysis: The data were organized and several statistical tests performed. The mean, maximum, and minimum concentrations and the standard deviation were determined for each DOC method, and for the difference (Shimadzu minus OI) between methods. An analysis of variance (ANOVA) was performed on the Shimadzu concentrations versus the OI concentrations and on the difference between methods (Shimadzu minus OI) versus the OI concentrations. The results were then plotted. The tables of statistics for each of the nine cruises and for

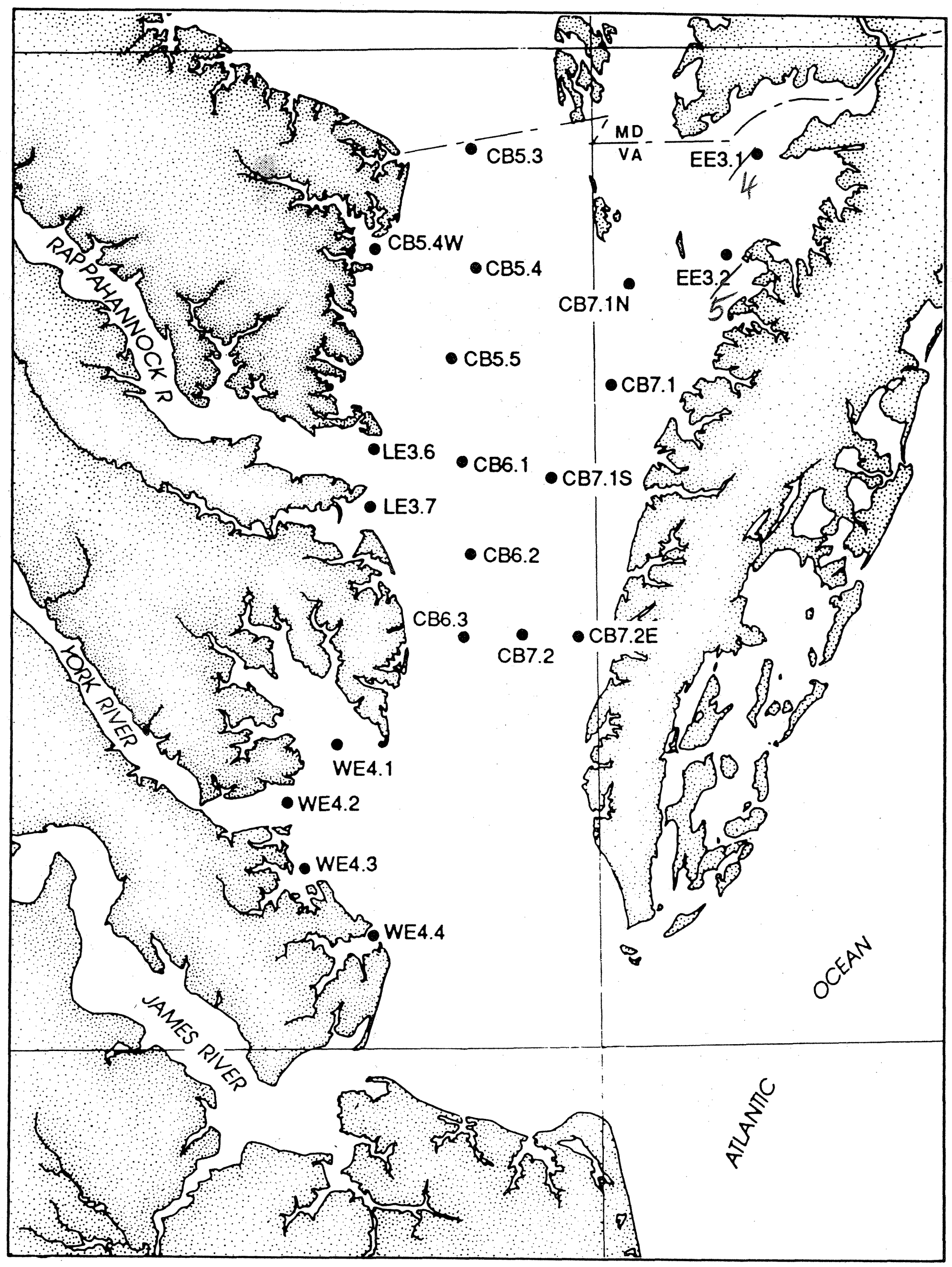


Figure 1. Map of lower Chesapeake Bay showing the 19 sampling stations.

the combined data set are included in Appendix A and the figures presenting the data are included in Appendix B.

The statistics are summarized, along with the mean, maximum, and minimum salinities, in Table 1. For the ANOVA's, the intercept, the slope of the regression, and r-squared values are given; both regressions use the OI DOC concentrations as the independent variable.

In keeping with the considerable attention given to quality control and quality assurance in the Chesapeake Bay monitoring program, about 96% of the OI samples and more than half of the Shimadzu samples were run in duplicate. To assess accuracy, an aliquot of a concentrated solution, or what is commonly referred to as a "spike", was added to water samples. A 3 mg-C/l spike was used with the Shimadzu and a 4 mg-C/l spike was used with the OI method. Relative percent recovery was calculated as:

$$\text{Relative \% Recovery} = 100 \times \{ CSS / (SPK + C) \}$$

where CSS is the concentration of the spiked sample, SPK is the concentration of the spike, and C is the concentration of the sample (unspiked). It is believed that relative recovery allows for a more direct comparison of accuracy data when different spike concentrations are used.

The accuracy and precision data for each cruise and for the combined data set are summarized in Table 2. The number of duplicate analyses, mean difference between duplicates, and standard deviation of the differences are given for both methods, along with the number of spiked samples, mean relative percent recovery, and standard deviation of the recovery values. Maximum and minimum values and the concentration of the spike also are included in the tables in Appendix B.

Table 1: Summary of Salinity and DOC data for each cruise and the combined data set.

CRUISE		112	113	114	116	117	118	119	120	121	ALL
Salinity	min	13.86	14.33	14.25	10.02	12.21	12.99	13.48	12.83	12.41	10.02
	max	24.59	25.82	27.16	23.97	23.84	22.77	26.04	25.52	23.40	27.16
	mean	19.17	18.48	17.76	18.13	17.40	17.48	18.20	17.49	17.69	17.94
Samples	N	50	51	52	53	52	49	48	49	49	453
DOC OI	min	2.680	2.590	2.275	2.475	2.315	2.530	2.620	2.345	2.595	2.275
	max	4.630	4.720	5.015	6.705	4.965	5.330	7.295	8.005	9.820	9.820
	mean	3.459	3.536	3.243	3.731	3.545	3.769	4.122	3.837	4.458	3.737
	std	0.465	0.494	0.463	0.808	0.530	0.598	1.084	1.242	1.411	0.914
DOC SHIMADZU	min	3.060	2.770	3.080	3.005	3.040	3.360	2.950	2.440	2.970	2.440
	max	5.010	5.530	6.015	6.360	5.280	5.885	7.325	9.325	9.235	9.325
	mean	3.897	3.984	3.917	4.041	4.091	4.405	4.372	4.366	4.853	4.208
	std	0.518	0.507	0.483	0.660	0.484	0.519	0.940	1.455	1.389	0.893
Regression Shim/OI	Int	0.477	1.464	0.899	1.624	1.270	1.714	1.398	0.140	0.593	0.938
	Slope	0.989	0.713	0.931	0.648	0.796	0.714	0.727	1.101	0.956	0.875
	r_2	0.7876	0.4813	0.7961	0.6295	0.7606	0.6762	0.7069	0.8846	0.9417	0.8039
Difference (Shim - OI)	min	-0.020	-0.735	0.060	-0.875	0.045	-0.330	-2.945	-1.900	-0.585	-2.945
	max	1.110	1.320	1.135	2.040	1.350	1.445	1.415	1.355	1.180	2.040
	mean	0.439	0.448	0.675	0.310	0.546	0.636	0.273	0.529	0.395	0.473
	std	0.239	0.392	0.220	0.492	0.260	0.341	0.587	0.510	0.341	0.411
Regression Diff on OI	Int	0.477	1.464	0.899	1.624	1.270	1.714	1.398	0.140	0.593	0.938
	slope	-0.011	-0.287	-0.069	-0.352	-0.204	-0.286	-0.273	0.101	-0.044	-0.125
	r_2	0.0005	0.1309	0.0211	0.3345	0.1732	0.2507	0.2538	0.0610	0.0338	0.0766

Table 2: Summary of Quality Control Data.

CRUISE		112	113	114	116	117	118	119	120	121	ALL
Precision (Dup Diff)											
OI	N	46	48	50	50	50	49	46	47	48	434
	mean	0.202	0.221	0.095	0.100	0.082	0.124	0.146	0.083	0.111	0.129
	std	0.141	0.141	0.095	0.120	0.077	0.103	0.126	0.084	0.086	0.119
SHIMADZU	N	10	30	25	35	30	9	27	44	26	236
	Mean	0.090	0.265	0.085	0.138	0.133	0.141	0.130	0.089	0.102	0.132
	Std	0.099	0.161	0.051	0.132	0.135	0.156	0.111	0.076	0.091	0.126
Accuracy % Recovery											
OI	N	8	11	10	9	8	10	11	8	10	85
	mean	101.98	98.80	99.73	99.34	95.60	98.92	99.22	98.68	100.10	99.18
	std	1.668	3.379	3.450	2.823	1.802	3.444	4.464	4.768	5.753	3.891
SHIMADZU	N	6	8	13	7	8	6	10	6	6	70
	Mean	100.92	101.78	102.25	100.16	99.55	98.90	100.30	98.86	98.67	100.40
	Std	3.459	3.360	4.765	3.508	2.097	1.537	4.348	1.655	1.497	3.481

RESULTS AND DISCUSSION

Results: The mid-portion of Chesapeake Bay is mesohaline to polyhaline, and consequently, neither oceanic salinities nor freshwater were encountered. The mean salinity for the six months was just under 18 parts per thousand (ppt; see Table 1). The mean salinity for each cruise was about the same, with only the mean for the January cruise (#112) differing by more than about half a ppt from the overall mean.

The mean DOC concentration was 3.7 mg/l for the OI method and 4.2 for the Shimadzu (see Table 1). For both instruments, DOC concentrations ranged from just over 2 mg/l to just under 10 mg/l. The mean difference between methods was 0.473 mg/l, with the Shimadzu giving higher readings on the average.

A two-tailed t-test indicated that the difference between the means for the two methods was significant (alpha <0.1%). We note that the mean difference between duplicates for both instruments was 0.13 mg/l (see Table 2), whereas the mean instrument difference was 0.5 mg/l. Thus we conclude that the difference observed is in fact one that can be measured reliably.

For most of the individual cruises and the overall data set, the slope of the regression between the two methods is close to 1 and the r-squared values are above 0.7 (see Table 1). Similarly, for most of the individual cruises and the overall data set, the slope of the regression of difference on OI concentrations is close to zero and, as a consequence, the r-squared value is small. These observations suggest that the difference between the two methods is fairly constant.

The range of the differences was large, about 12 standard deviations. Some of these differences were believed to be outliers that should be deleted from the data set. The statistics and regressions were determined for two reduced data sets. For the first case, 3 samples (Difference = 2.040, -2.945, and -1.900 mg/l) were removed, and for the second case 10 samples were deleted from the data set. These ten samples had differences greater than 2.5 standard deviations (± 1.028 mg/l) from the original mean. The statistics for the original and reduced data sets are sumarized in Table 3.

When the outliers were removed from the data set, the variance of the samples of course decreased. In addition, the slope of the regression between methods approached one, the slope of the regression on differences approached zero, and the value of the mean difference increased to 0.5 mg/l. The data points and regression lines for the difference are shown in Figure 2 for each data set; the outliers that were deleted are indicated in the figures.

Table 3. The Effect of Removing Three and Ten Outliers on Statistical Properties and Regressions

	DATA SET	ALL	LESS 3	LESS 10
NUMBER		453	450	443
OI-DOC	Mean	3.737	3.727	3.697
SHIM-DOC	Mean	4.208	4.209	4.198
DIFFERENCE SHIM - OI	Mean	0.473	0.482	0.501
	Std Dev	0.411	0.355	0.324
REGRESSION SHIM on OI	Intercept	0.938	0.808	0.696
	Slope	0.875	0.913	0.947
	r^2	0.804	0.849	0.861
REGRESSION Diff on OI	Intercept	0.938	0.808	0.696
	Slope	-0.125	-0.087	-0.053
	r^2	0.077	0.049	0.019

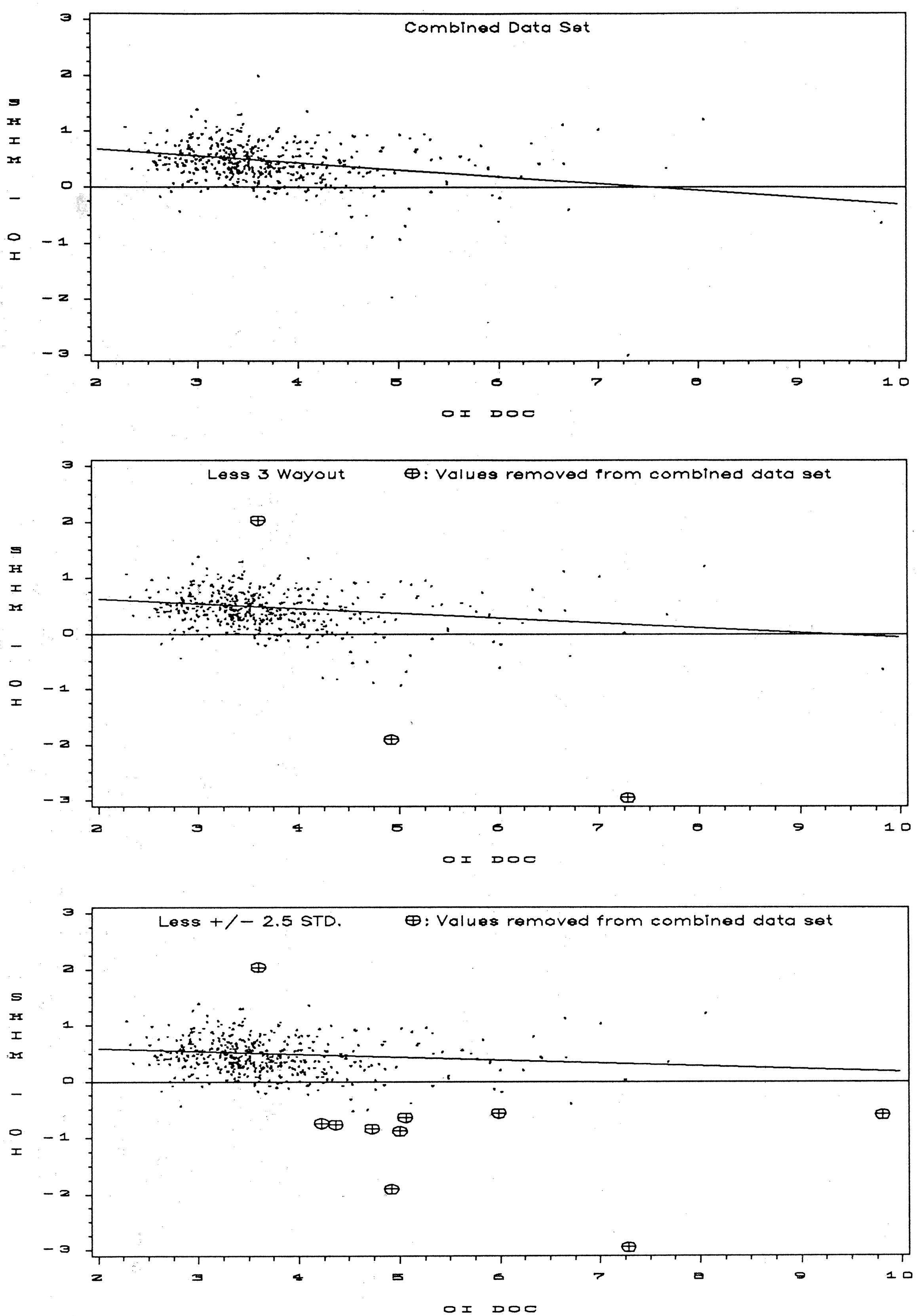


Figure 2. Variation of methods difference with (OI) DOC concentration & the effect of removing outliers

Correlations: The effects of salinity, chlorophyll-a (CHLOR-A), total suspended solids (TSS), and particulate carbon (PC) concentrations on the difference between methods were investigated using ANOVA. The slopes of the regressions for all of the factors were close to zero, and consequently so were the r-squared values. In Table 4 the maximum, minimum and mean concentrations for each variable, and the intercept, slope and r-squared value for the regression are listed. The methods differences versus salinity, chlorophyll-a, total suspended solids, and particulate carbon are plotted in Figure 3.

Note that for chlorophyll-a, TSS, and PC, the intercepts are all close to the mean difference of the complete data set (0.473 mg/l), the slopes are all close to zero and consequently, the r-squared values are small. Although the intercept for salinity (0.820 mg/l) is somewhat larger than those for the other variables, the slope again is very small. When one considers that the lowest salinity observed was about 12 ppt, extrapolation to zero salinity does not seem appropriate.

It appears that the difference between methods is not affected in any consistent manner by the amount of algae, particulate carbon, suspended solids, or salinity in the sample.

Table 4. Ranges and Means of Selected Environmental Variables and the Results of ANOVA Regression of The Variables on the Difference between Methods.

	CONCENTRATIONS			REGRESSION		
VARIABLE	Min	Mean	Max	Int.	Slope	r^2
SALINITY	11.88	17.36	27.17	0.820	-0.020	0.0175
CHLOR-A	0.00	16.11	115.93	0.438	0.002	0.0056
TSS	1.60	15.62	98.67	0.459	0.001	0.0007
PC	0.179	1.170	5.533	0.430	0.037	0.0026

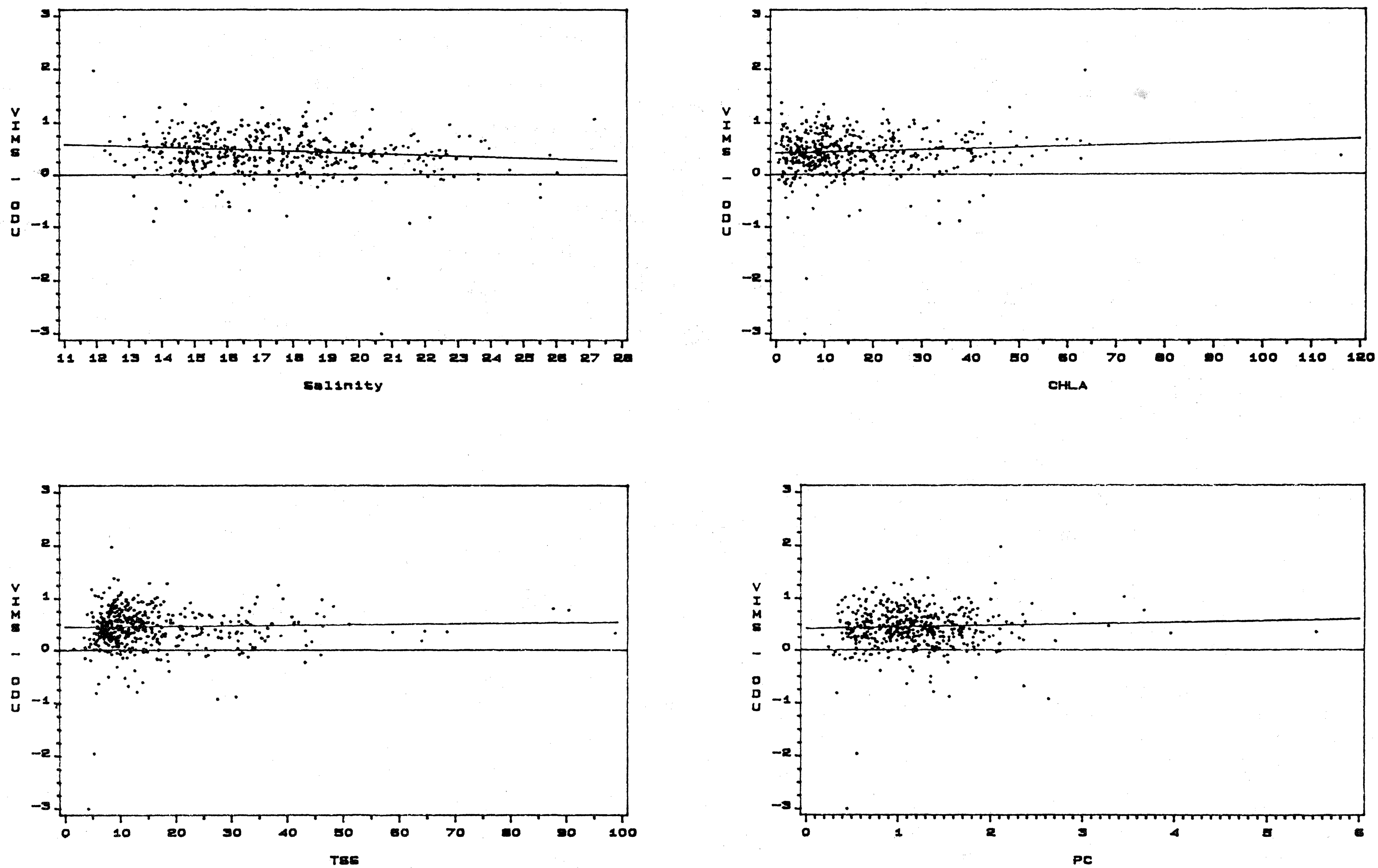


Figure 3. The difference between methods versus Salinity, Chlorophyll-a, Total Suspended Solids, and Particulate Carbon concentrations.

Association: The data indicate that there is a measureable difference between the two analytical methods. Data users must be aware of the change in methods and may want to adjust the data. The need to account for the methods change is clear, but how that should be accomplished is not so clear.

In the preceding sections, the DOC measurements using the Shimadzu TOC analyzer were contrasted with those obtained using the OI instrument and using the OI measurements as the independent variable. Similarly, the difference between methods was contrasted with the OI measurements. This was done primarily because the OI instrument had been used since the beginning of the program. There is, however, no dependency between the two data sets. Rather for each data pair, there are two independent estimates of some unknown "true concentration." The "true concentrations" are random variables in the sense that these are natural samples and no effort was made to select or reject particular samples or types of samples. The data are not normally distributed, however. For this case, the functional regression provides a more appropriate association between the two data sets (Ricker, 1973).

The functional regression line lies between the regression lines obtained when one data set is assumed to depend on the other (See Figure 4). The equations for these three regression lines are given below. The intercept for the functional regression (0.563 mg/l) is somewhat larger than the mean difference (0.473 mg/l) between all 453 sample pairs. The slope of the functional regression is very close to one.

REGRESSION	EQUATION
Functional	SHIM = 0.563 + 0.976 (OI)
Linear - Shimadzu on OI (OI = independent variable)	SHIM = 0.938 + 0.875 (OI)
Linear - OI on Shimadzu (Shimadzu = independent var.)	SHIM = 0.141 + 1.089 (OI)

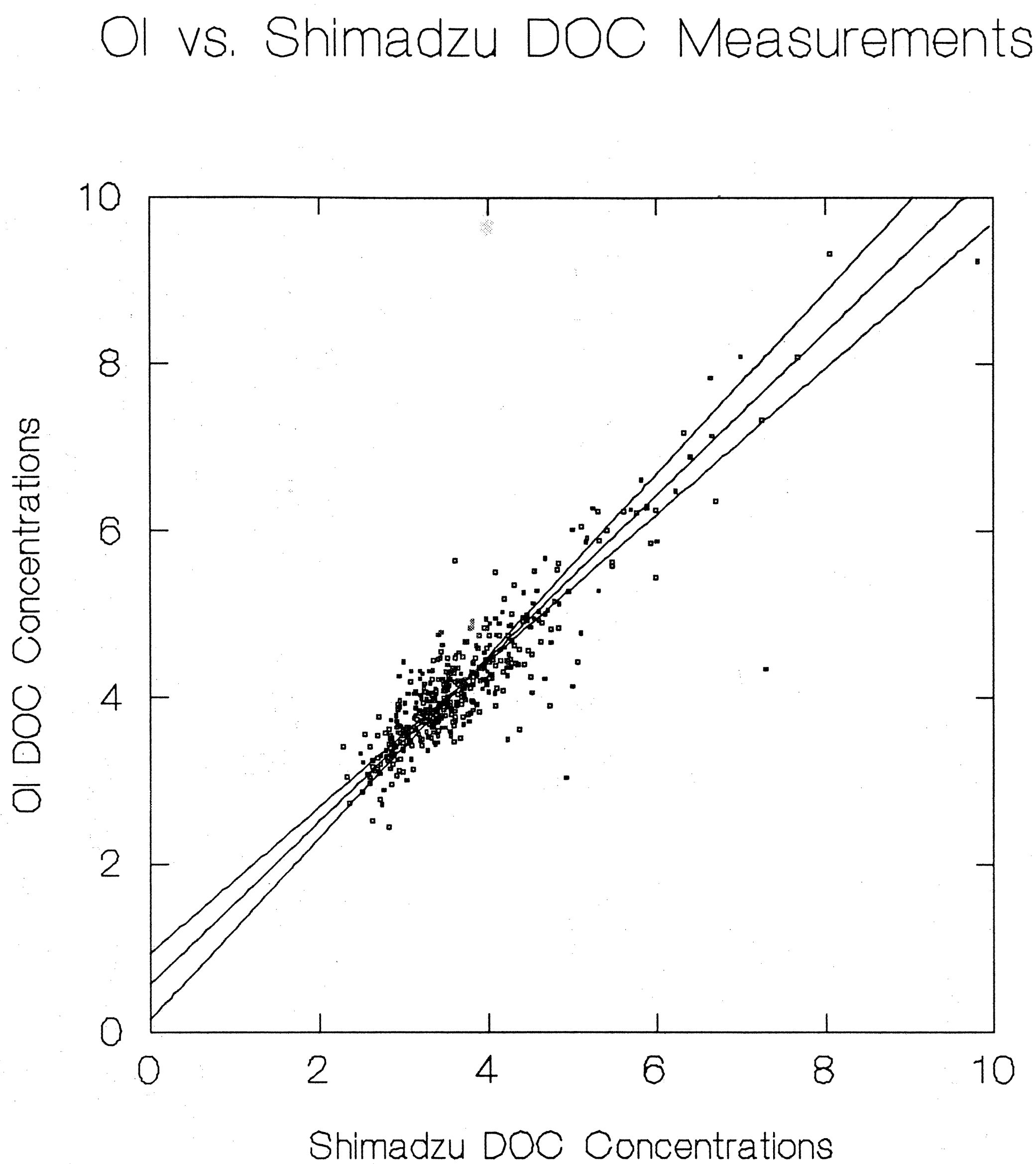


Figure 4. Comparison of Shimadzu and OI DOC measurements showing the functional regression and the two linear regression lines.

Importance: Differences among analytical methods confound use of data sets that involve different methods. A similar change (change of laboratory and method) may have contributed to erroneous interpretation of water quality data for Lake Erie (e.g., Shapiro and Swain, 1983). The limitations of older methodologies for DOC determinations have been made known for many years (Sharp, 1973). Oceanographers are aware that new instruments (e.g., Sugimura & Suzuki, 1988) give higher readings than the older methods, and that this poses difficult questions for scientists working on global carbon budgets (Williams & Druffel, 1988). As best we can tell, no consensus has yet developed within the oceanographic scientific community regarding differences among methods, despite the importance of this issue.

Clearly this issue is important for those working in coastal and estuarine environments as well (Mantoura & Woodward, 1983). Studies at other marine institutions (Sharp, Suzuki, and Munday, 1988) and among the Chesapeake Bay monitoring labs suggest that the differences between methods are small for fresh and olighaline waters. Further study is needed to determine whether this effect is real and the reasons for any methods differences at higher salinities.

A recent workshop, however, suggests that the "variation thus appears to be attributable to operators rather than analyzers" (Williams, 1991). The issue is receiving considerable attention within the oceanographic community and scientists hope to resolve the issue in the near future. Analysts within the Chesapeake Bay water quality monitoring program should keep abreast of developments in the oceanographic community and make appropriate changes once there is consensus.

Data users should be made aware that differences between methods for dissolved organic carbon measurements are real and measureable and they should use the data accordingly.

CONCLUSIONS AND RECOMMENDATION

Determinations of dissolved organic carbon (DOC) concentrations for mesohaline and polyhaline samples will differ depending on the analytical method used. For the case at hand, the Shimadzu TOC analyzer gives results that are about 0.5 mg/l higher than those obtained using the Oceanographic Instruments ampule method. The mean methods difference was several times larger than the mean difference between duplicates for either method. Thus we conclude that the methods difference is measureable and real.

The difference between methods varied little over the time period (January to June, 1990) or with salinity, although the range of salinities encountered in this study was limited (12 to 27 ppt). The difference varied only slightly with the concentrations of DOC (range = 2 to 10 mg-C/l), chlorophyll-a (range = 0 to 116 μg/l), particulate carbon (range = 0.18 to 1.17 mg/l), and total suspended solids (range = 1.6 to 15.6 mg/l). Thus we conclude that the methods difference is constant, at least for the conditions encountered in this study.

If data users wish to adjust either data set, the functional regression is recommended. The equation giving the "best association" between the two methods is:

$$SHIM = 0.563 + 0.976\ (OI),$$

where SHIM is the DOC concentration in mg/l using the Shimadzu analyzer and OI is the DOC concentration in mg/l measured with the Oceanographic Instruments ampule method.

REFERENCES

Mantoura, R. F. C. and E. M. S. Woodward, 1983. Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications. **Geochimica et Cosmochimica Acta**, 47:1293-1309.

Ricker, W. E., 1973. Linear Regressions in Fishery Research. **Journal Fisheries Research Board of Canada**, Vol. 30, No. 3, pp 409-434.

Shapiro, J. & Swain, E. B., 1983. Lessons from the Silica "Decline" in Lake Michigan. **Science** 223:457-459.

Sharp, J. H., 1973. Total organic carbon in seawater - comparison of measurements using persulfate oxidation and high temperature combustion. **Marine Chemistry, 1,** 211-229.

Sharp, J. H., Suzuki, Y. & Munday, W. L. 1988. Inter comparison of dissolved organic carbon analyses in estuarine and coastal waters of the North Atlantic Ocean. **EOS**, 69,1134.

Shimadzu Corporation, 1989. Instruction Manual, Total Organic Carbon Analyzer, Auto Sample Injection, Model ASI-502, CM 393-070 and 638,90887. Kyoto, Japan.

Sugimura, Y. & Suzuki, Y. 1988. A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample. **Marine Chemistry, 24**, 105-131.

US Environmental Protection Agency, 1983. Methods for Chemical Analysis of Water and Wastes. Environmental Reseach Center, Cincinnati, Ohio.

Williams, P. M. and E. R. M. Druffel, 1988. Dissolved Organic Matter in the Ocean: Comments on a Controversy. **Oceanography**, 1:1, 14-17.

APPENDIX A. Tables of Statistics

Tables of statistics are given for each monitoring cruise (Tables A1 - A9) and for the combined data set (Table A10). The information presented in the tables includes:

(1) Statistics on DOC concentrations for each method and for the difference between methods;

(2) Results of ANOVA regressions of Shimadzu measurements on OI DOC measurements;

(3) Results of ANOVA regressions of the difference between methods (Shimadzu - OI) on OI DOC measurements; and

(4) QA/QC information.

Table A1: BAY112; January 8 - 9, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	50	3.897	0.518	3.060	5.010
OI DOC	50	3.459	0.465	2.680	4.630
SHIM - OI	50	0.439	0.239	-0.020	1.110

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	10.347	10.347	177.96
Deviation	48	2.791	0.058	
Total	49	13.137		

Linear Regression: Y = 0.477 + 0.989 * X
Y = SHIM DOC
X = OI DOC
$r^2 = 0.7876$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	0.001	0.001	0.022
Deviation	48	2.791	0.058	
Total	49	2.792		

Linear Regression: Y = 0.477 - 0.011 * X
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r_2 = 0.0005$

QA/QC

Instrument: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	46	0.202	0.141	0.000	0.770
Rel. Per. Recovery	8	101.984	1.668	99.933	103.951
Recovered Conc.	8	4.151	0.128	3.995	4.320

Instrument: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	10	0.090	0.099	0.010	0.340
Rel. Per. Recovery	6	100.925	3.459	96.165	105.928
Recovered Conc.	6	3.077	0.258	2.740	3.460

Table A2: BAY113; February 5 - 6, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	51	3.984	0.507	2.770	5.530
OI DOC	51	3.536	0.494	2.590	4.720
SHIM - OI	51	0.448	0.392	-0.735	1.320

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	6.190	6.190	45.47
Deviation	49	6.670	0.136	
Total	50	12.860		

Linear Regression: Y = 1.464 + 0.713 * X
Y = SHIM DOC
X = OI DOC
$r^2 = 0.4813$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	1.005	1.005	7.380
Deviation	49	6.670	0.136	
Total	50	7.674		

Linear Regression: Y = 1.464 - 0.287 * X
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.1309$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	48	0.221	0.141	0.000	0.470
Rel. Per. Recovery	11	98.799	3.379	92.168	103.194
Recovered Conc.	11	3.901	0.263	3.355	4.225

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	30	0.265	0.161	0.020	0.530
Rel. Per. Recovery	8	101.776	3.360	97.540	106.973
Recovered Conc.	8	3.121	0.230	2.830	3.470

Table A3: BAY114; March 5 - 6, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	52	3.917	0.483	3.080	6.015
OI DOC	52	3.243	0.463	2.275	5.015
SHIM - OI	52	0.675	0.220	0.060	1.135

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	9.462	9.462	195.18
Deviation	50	2.424	0.048	
Total	51	11.886		

Linear Regression: Y = 0.899 + 0.931 * X
Y = SHIM DOC
X = OI DOC
$r^2 = 0.7961$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	0.052	0.052	1.078
Deviation	50	2.424	0.048	
Total	51	2.476		

Linear Regression: Y = 0.899 - 0.069 * X
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.0211$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	50	0.095	0.095	0.000	0.420
Rel. Per. Recovery	10	99.734	3.450	95.334	104.318
Recovered Conc.	10	3.975	0.256	3.630	4.310

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	25	0.085	0.051	0.010	0.260
Rel. Per. Recovery	13	102.247	4.765	96.125	115.920
Recovered Conc.	13	3.147	0.317	2.690	4.030

Table A4: BAY116; April 9 - 13, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	53	4.041	0.660	3.005	6.360
OI DOC	53	3.731	0.808	2.475	6.705
SHIM - OI	53	0.310	0.492	-0.875	2.040

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	14.252	14.252	86.637
Deviation	51	8.390	0.165	
Total	52	22.642		

Linear Regression: $Y = 1.624 + 0.648 * X$
Y = SHIM DOC
X = OI DOC
$r^2 = 0.6295$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	4.217	4.217	25.634
Deviation	51	8.390	0.165	
Total	52	12.607		

Linear Regression: $Y = 1.624 - 0.352 * X$
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.3345$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	50	0.100	0.120	0.000	0.480
Rel. Per. Recovery	9	99.345	2.823	96.190	103.569
Recovered Conc.	9	3.939	0.219	3.700	4.255

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	35	0.138	0.132	0.010	0.520
Rel. Per. Recovery	7	100.155	3.508	96.931	105.933
Recovered Conc.	7	3.016	0.241	2.780	3.410

Table A5: BAY117; April 16 - 17, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	52	4.091	0.484	3.040	5.280
OI DOC	52	3.545	0.530	2.315	4.965
SHIM - OI	52	0.546	0.260	0.045	1.350

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	9.080	9.080	158.87
Deviation	50	2.858	0.057	
Total	51	11.938		

Linear Regression $Y = 1.270 + 0.796 * X$
Y = SHIM DOC
X = OI DOC
$r^2 = 0.7606$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	0.598	0.598	10.471
Deviation	50	2.858	0.057	
Total	51	3.456		

Linear Regression: $Y = 1.270 - 0.204 * X$
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.1732$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	50	0.082	0.077	0.000	0.360
Rel. Per. Recovery	8	95.604	1.802	92.658	97.813
Recovered Conc.	8	3.663	0.141	3.420	3.820

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	30	0.133	0.135	0.010	0.500
Rel. Per. Recovery	8	99.547	2.097	95.759	101.770
Recovered Conc.	8	2.965	0.147	2.690	3.120

Table A6: BAY118; May 14 - 15, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	49	4.405	0.519	3.360	5.885
OI DOC	49	3.769	0.598	2.530	5.330
SHIM - OI	49	0.636	0.341	-0.330	1.445

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	8.742	8.742	98.137
Deviation	47	4.187	0.089	
Total	48	12.929		

Linear Regression: Y = 1.714 + 0.714 * X
Y = SHIM DOC
X = OI DOC
$r^2 = 0.6762$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	1.401	1.401	15.728
Deviation	47	4.187	0.089	
Total	48	5.588		

Linear Regression: Y = 1.714 - 0.286 * X
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.2507$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	49	0.124	0.103	0.000	0.380
Rel. Per. Recovery	10	98.919	3.444	90.340	102.643
Recovered Conc.	10	3.900	0.300	3.120	4.180

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	9	0.141	0.156	0.000	0.480
Rel. Per. Recovery	6	98.900	1.537	96.658	100.949
Recovered Conc.	6	2.917	0.116	2.750	3.070

Table A7: BAY119; May 29 - June 1, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	49	4.372	0.940	2.950	7.325
OI DOC	48	4.122	1.084	2.620	7.295
SHIM - OI	48	0.273	0.587	-2.945	1.415

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	29.178	29.178	110.95
Deviation	46	12.097	0.263	
Total	47	41.275		

Linear Regression: Y = 1.398 + 0.727 * X
Y = SHIM DOC
X = OI DOC
$r^2 = 0.7069$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	4.115	4.115	15.647
Deviation	46	12.097	0.263	
Total	47	16.212		

Linear Regression: Y = 1.398 - 0.273 * X
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.2538$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	46	0.146	0.126	0.010	0.540
Rel. Per. Recovery	11	99.223	4.464	93.298	106.813
Recovered Conc.	11	3.929	0.367	3.375	4.495

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	27	0.130	0.111	0.010	0.420
Rel. Per. Recovery	10	100.295	4.348	94.844	111.078
Recovered Conc.	10	3.011	0.306	2.570	3.750

Table A8: BAY120; June 11 - 13, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	49	4.366	1.455	2.440	9.325
OI DOC	49	3.837	1.242	2.345	8.055
SHIM - OI	49	0.529	0.510	-1.900	1.355

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	89.861	89.861	360.37
Deviation	47	11.720	0.249	
Total	48	101.581		

Linear Regression: $Y = 0.140 + 1.101 * X$
Y = SHIM DOC
X = OI DOC
$r^2 = 0.8846$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	0.761	0.761	3.051
Deviation	47	11.720	0.249	
Total	48	12.481		

Linear Regression: $Y = 0.140 + 0.101 * X$
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.0610$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	47	0.083	0.084	0.000	0.420
Rel. Per. Recovery	8	98.679	4.768	87.324	101.530
Recovered Conc.	8	3.903	0.362	3.055	4.145

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	44	0.089	0.076	0.000	0.310
Rel. Per. Recovery	6	98.864	1.655	96.204	100.753
Recovered Conc.	6	2.907	0.130	2.710	3.050

Table A9: BAY121; June 25 - 26, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	49	4.853	1.389	2.970	9.235
OI DOC	49	4.458	1.411	2.595	9.820
SHIM - OI	49	0.395	0.341	-0.585	1.180

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	87.230	87.230	759.23
Deviation	47	5.400	0.115	
Total	48	92.629		

Linear Regression: Y = 0.593 + 0.956 * X
Y = SHIM DOC
X = OI DOC
$r^2 = 0.9417$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	0.189	0.189	1.644
Deviation	47	5.400	0.115	
Total	48	5.589		

Linear Regression: Y = 0.593 - 0.044 * X
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.0338$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	48	0.111	0.086	0.000	0.370
Rel. Per. Recovery	10	100.096	5.753	90.261	107.869
Recovered Conc.	10	3.992	0.463	3.290	4.615

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	26	0.102	0.091	0.000	0.360
Rel. Per. Recovery	6	98.671	1.497	96.446	100.554
Recovered Conc.	6	2.903	0.109	2.780	3.060

Table A10: Combined Data Set; January - June, 1990

	N	Mean	Std.Dev.	Min.	Max.
SHIM DOC	454	4.208	0.893	2.440	9.325
OI DOC	453	3.737	0.914	2.275	9.820
SHIM - OI	453	0.473	0.411	-2.945	2.040

DOC Methods Comparisions
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	289.439	289.439	1849.16
Deviation	451	70.593	0.157	
Total	452	360.032		

Linear Regression: Y = 0.938 + 0.875 * X
Y = SHIM DOC
X = OI DOC
$r^2 = 0.8039$

DOC Methods Differences
ANOVA

Source	DF	Sum Squares	Mean Square	F
Regression	1	5.859	5.859	37.431
Deviation	451	70.593	0.157	
Total	452	76.451		

Linear Regression: Y = 0.938 - 0.125 * X
Y = DOC Difference (SHIM - OI)
X = OI DOC
$r^2 = 0.0766$

QA/QC

Inst: OI	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	434	0.129	0.119	0.000	0.770
Rel. Per. Recovery	85	99.176	3.891	87.324	107.869
Recovered Conc.	85	3.929	0.308	3.055	4.615

Inst: SHIM	N	Mean	Std.Dev.	Min.	Max.
Duplicate Diff.	236	0.132	0.126	0.000	0.530
Rel. Per. Recovery	70	100.400	3.481	94.844	115.920
Recovered Conc.	70	3.023	0.241	2.570	4.030

APPENDIX B. GRAPHICAL DISPLAY OF STATISTICS

The data have been plotted for each monitoring cruise (BAY 112 to BAY 120) and for the combined data set (January - June, 1990). The figures include:

(1) VIMS DOC concentrations (using the Shimadzu method) versus ODU DOC concentrations (using the OI method);

(2) The difference between methods (VIMS - ODU, that is, Shimadzu - OI) versus ODU DOC concentrations (using the OI method);

(3) Box-and-whisker diagrams showing QA/QC information for both ODU (O) and VIMS (V); The boxes represent +/- one standard deviation from the mean, and the whiskers represent the maximum and minimum values.

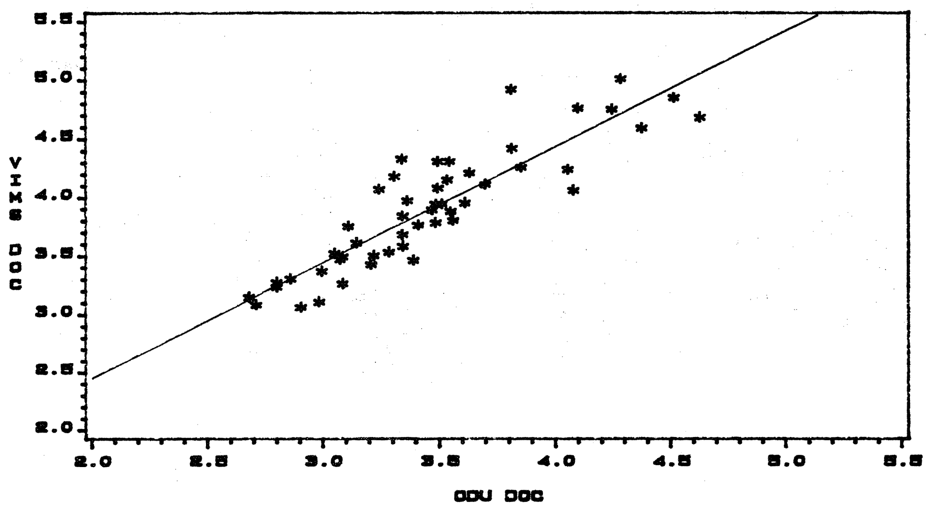
(3a) The difference between duplicate samples;

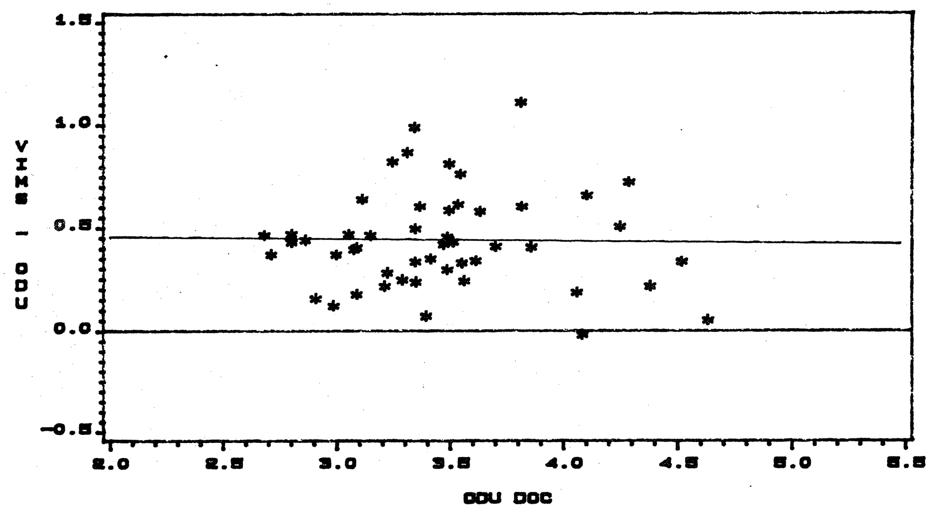
(3b) The relative percent recovery (See text for definition of this term); and

(3c) The recovery of the spike.

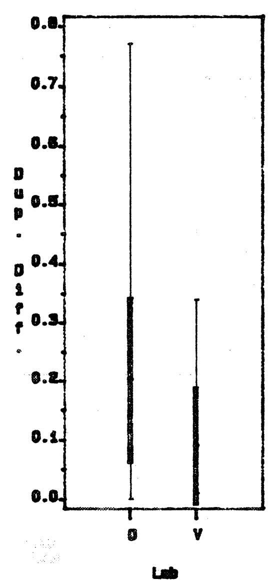
BAY112

Jan. 8 - 9, 1990

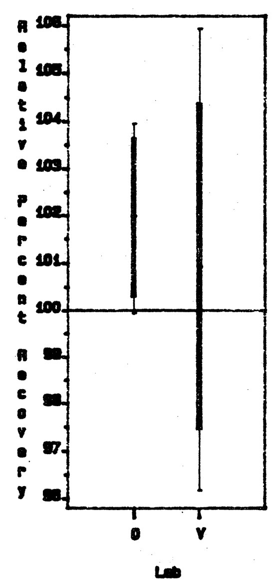




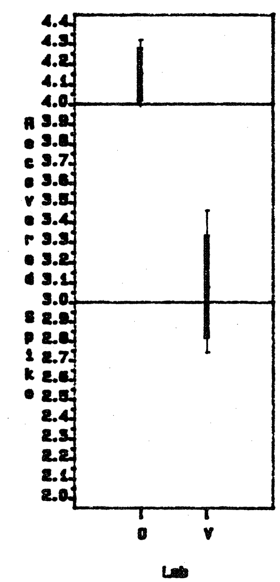
DUP. DIFF.



REL. PER. REC.

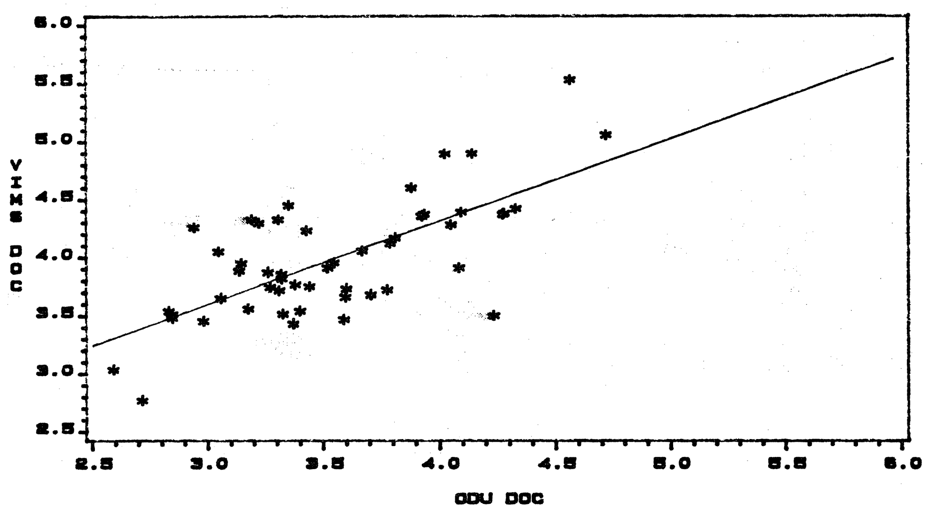


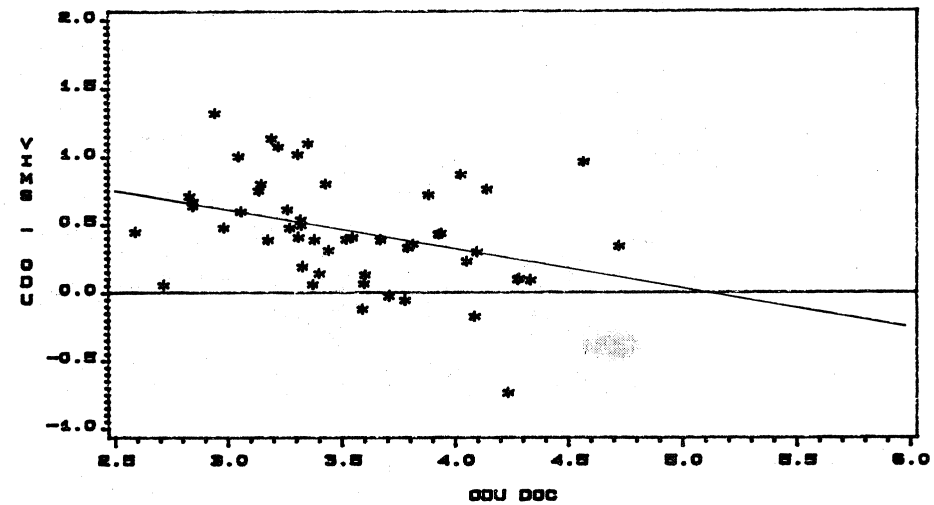
REC. SPIKE



BAY113

Feb. 5 - 6, 1990





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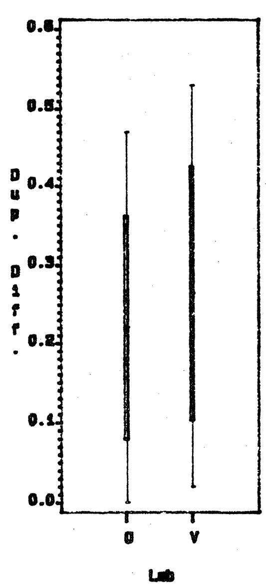

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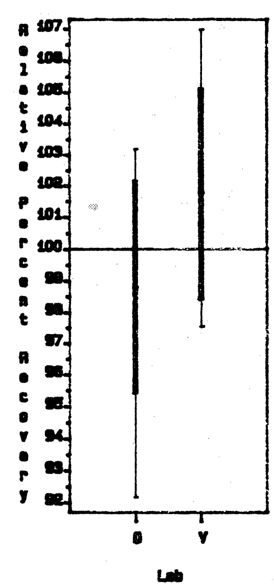

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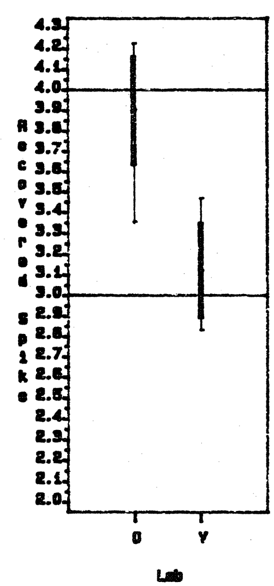
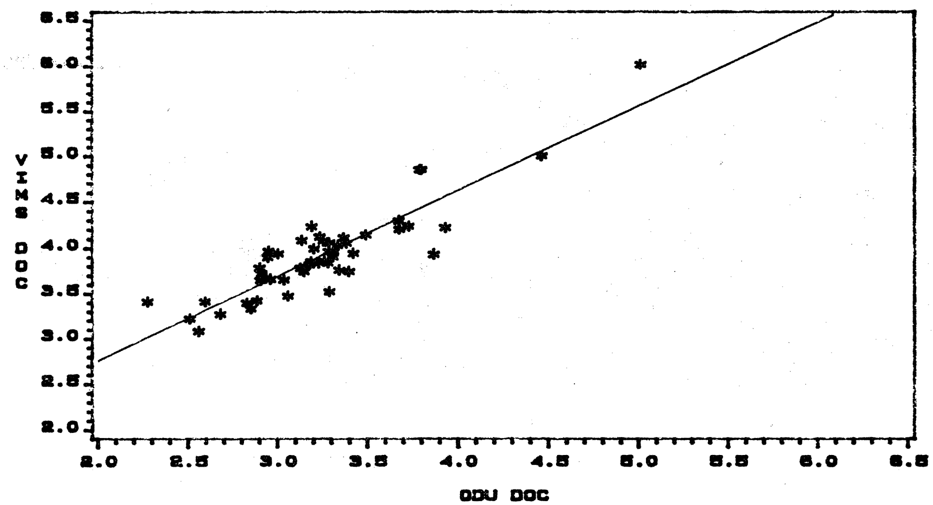
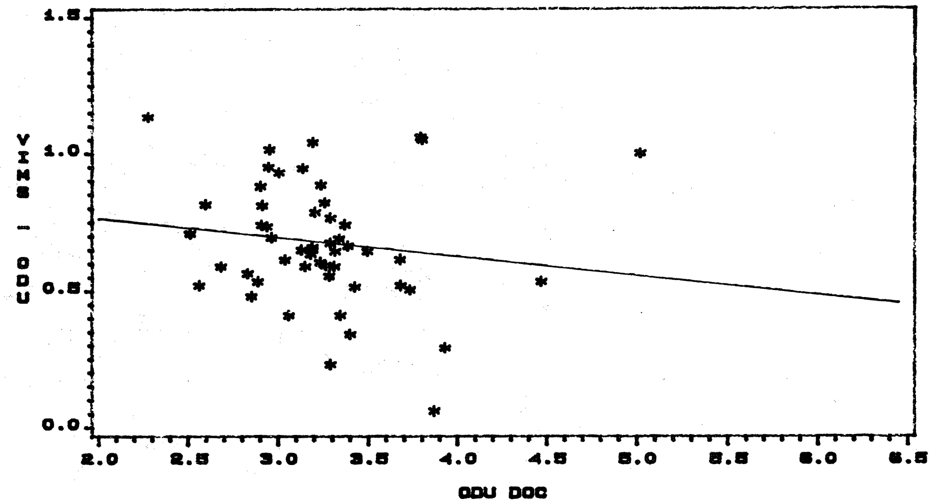


BAY114

Mar. 5 – 6, 1990





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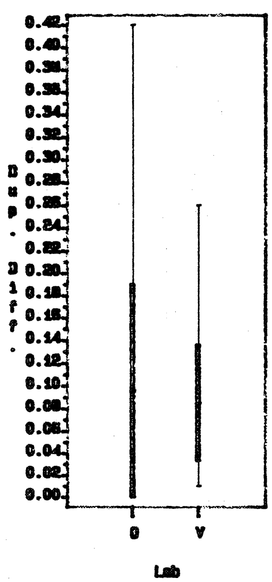
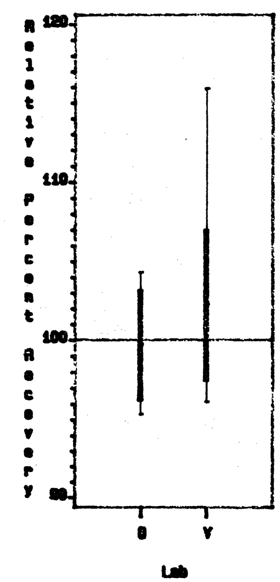
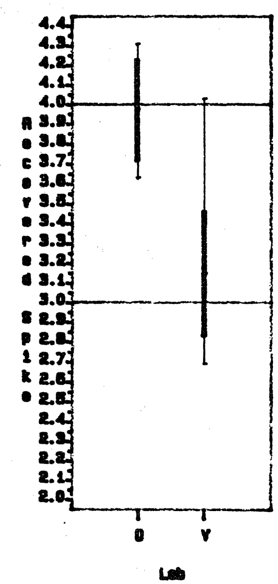


REL. PER. REC.

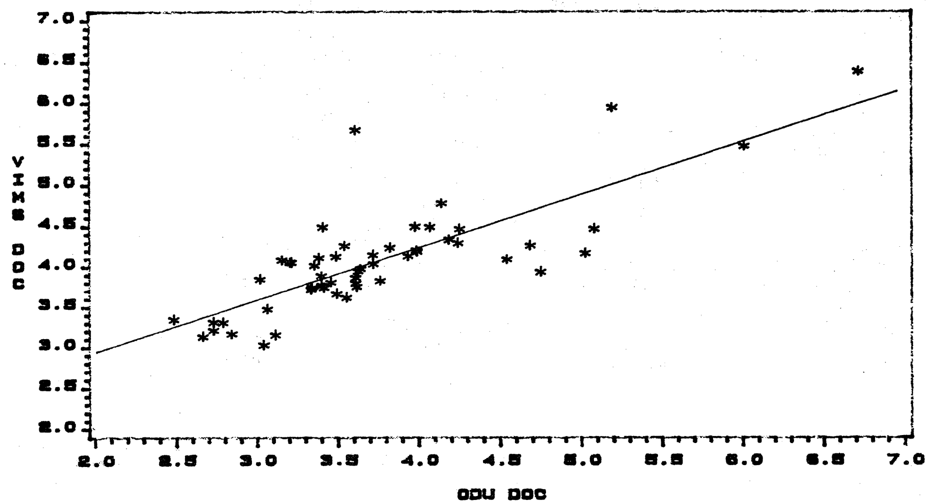


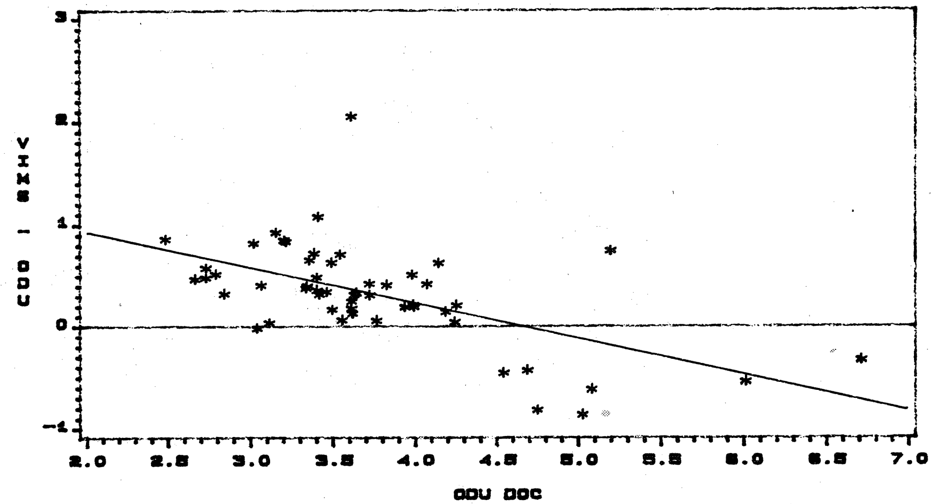
REC. SPIKE



BAY116

April 9 - 13, 1990





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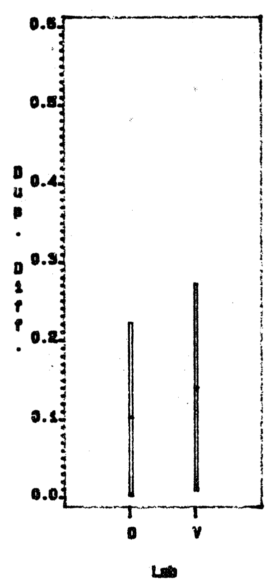
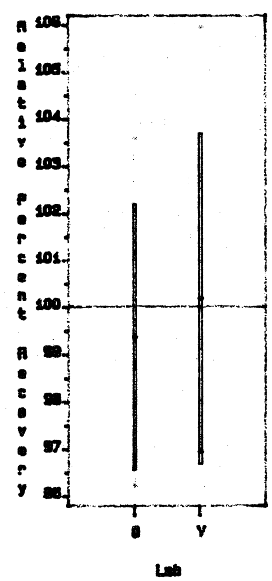


REL. PER. REC.



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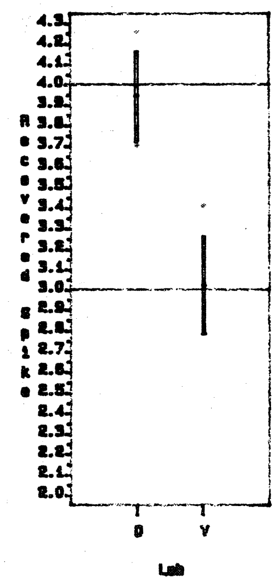
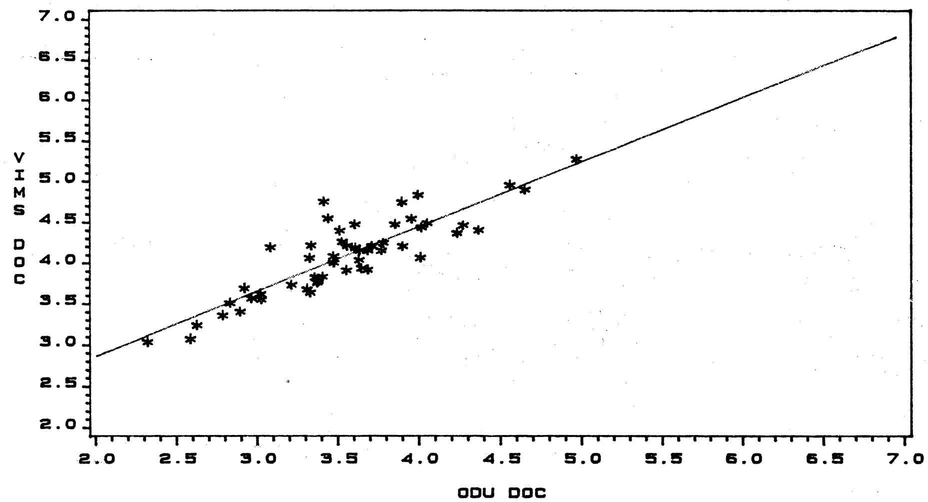
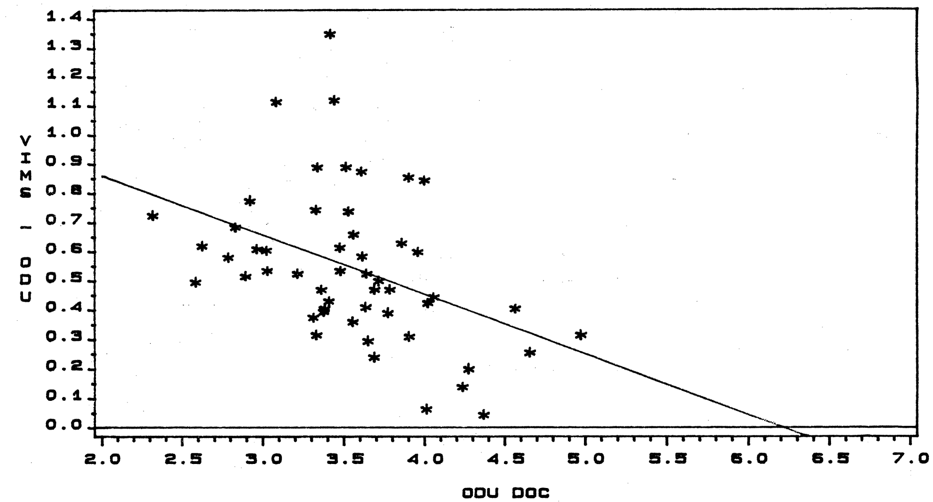


BAY117

April 16 – 17, 1990





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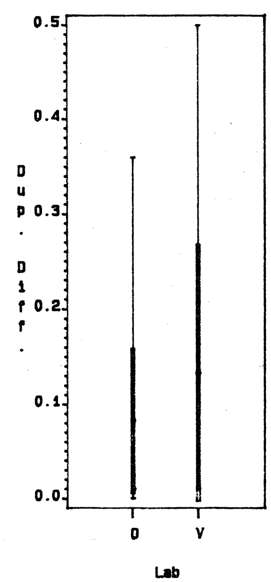
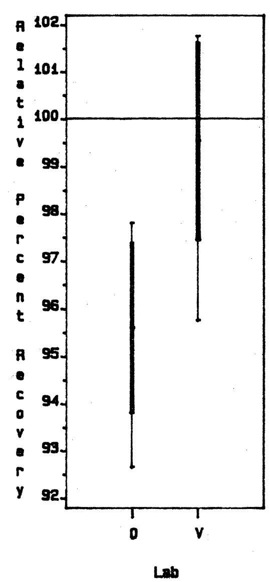


REL. PER. REC.



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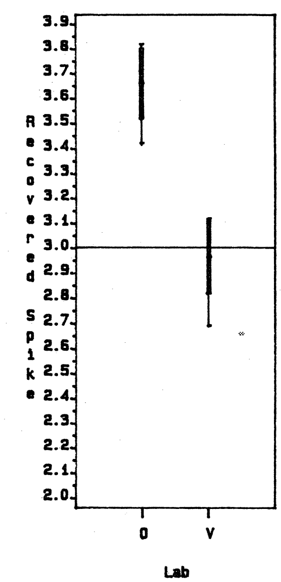
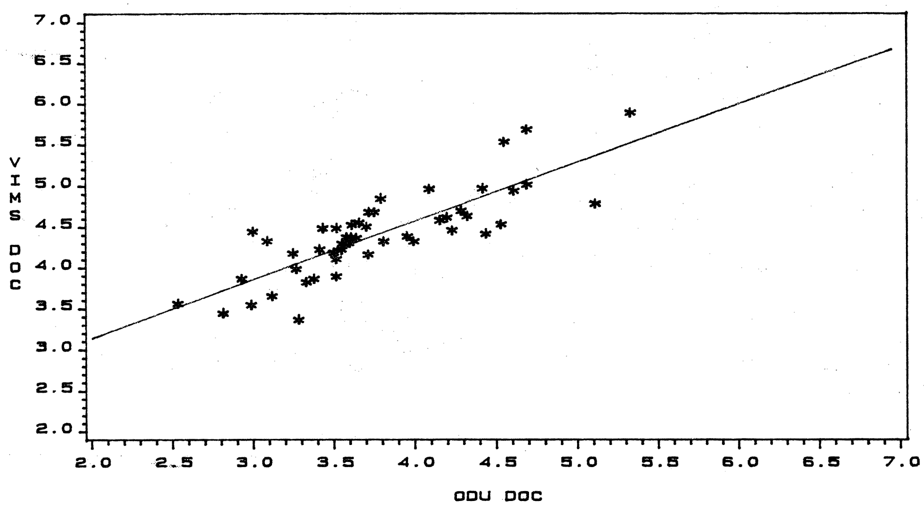
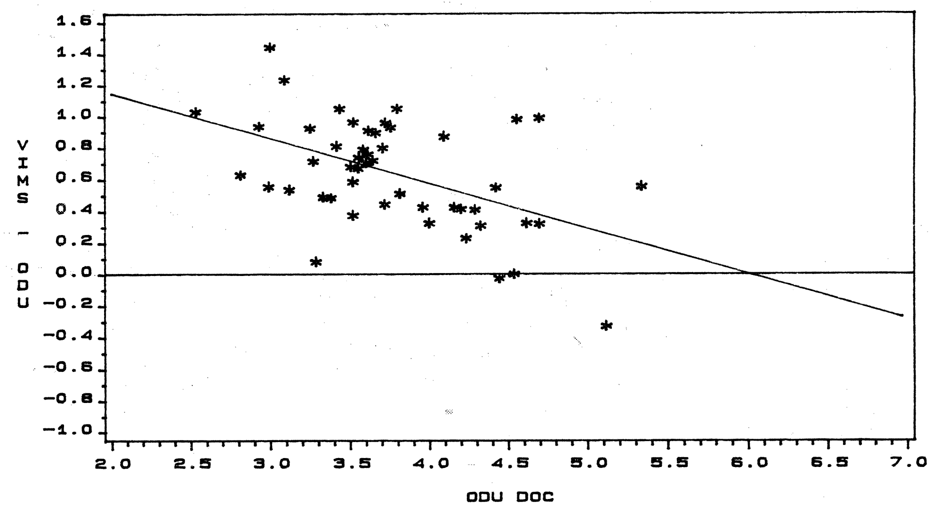


BAY118

May 14 – 15, 1990





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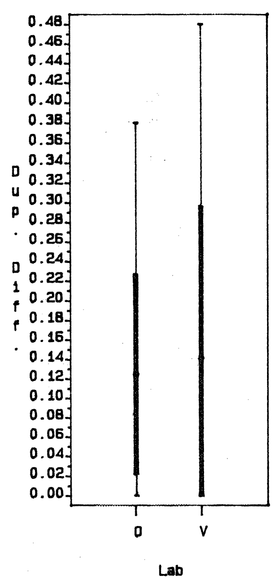
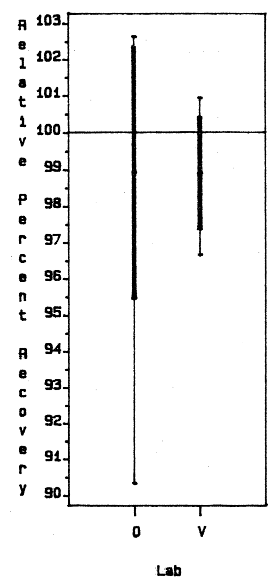


REL. PER. REC.



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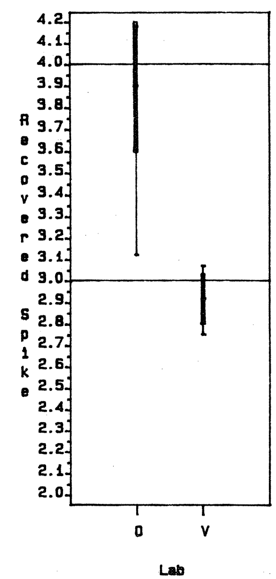
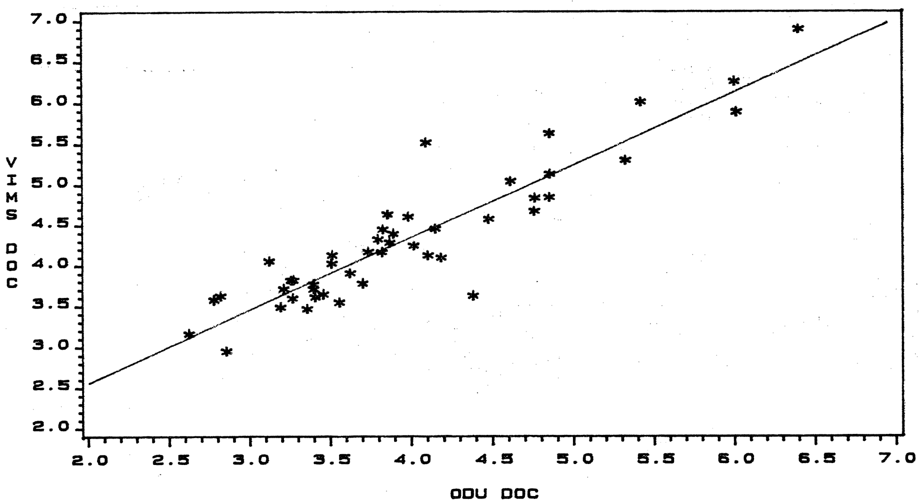
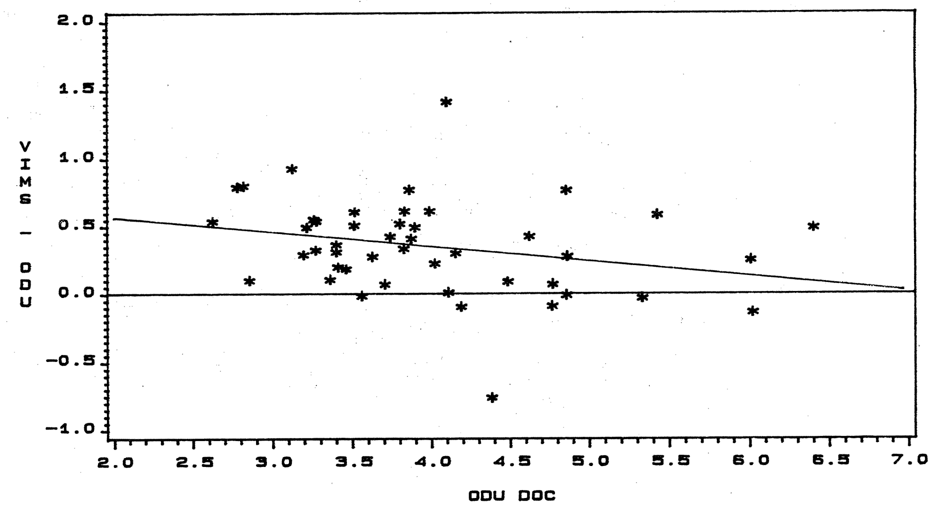


BAY119

May 29 - June. 1, 1990





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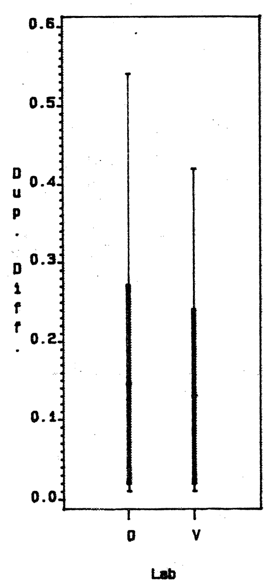

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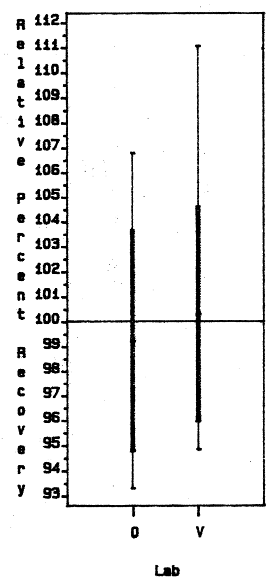

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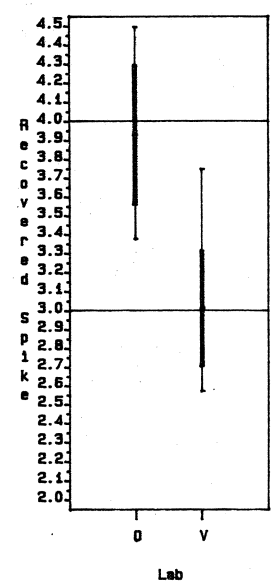
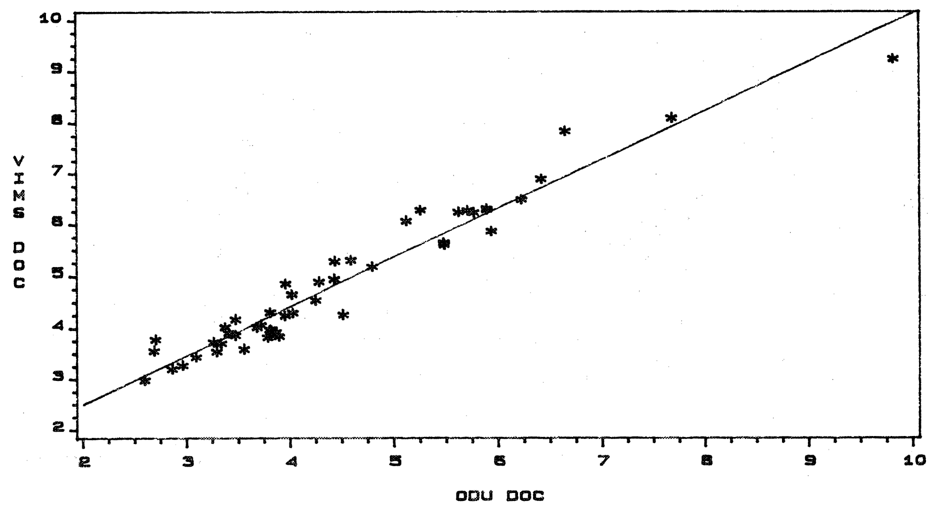
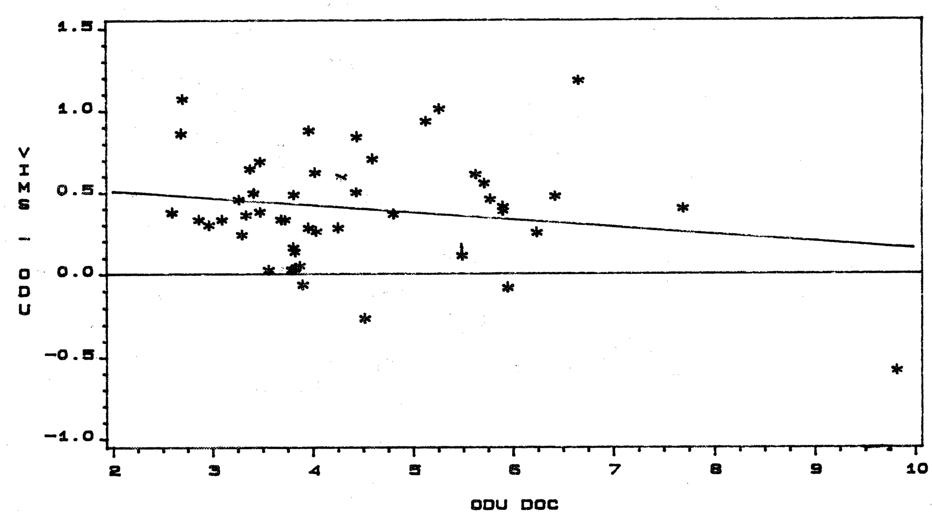


BAY121

June 25 - 26, 1990





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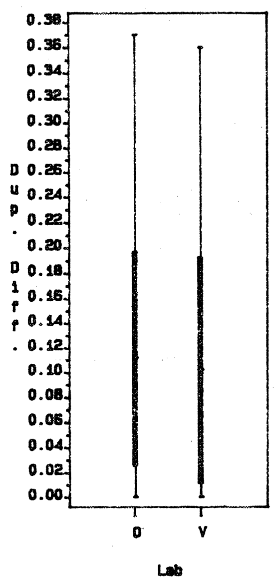
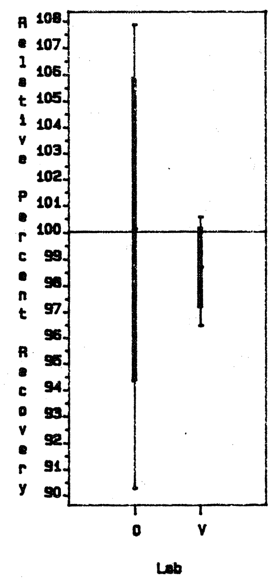
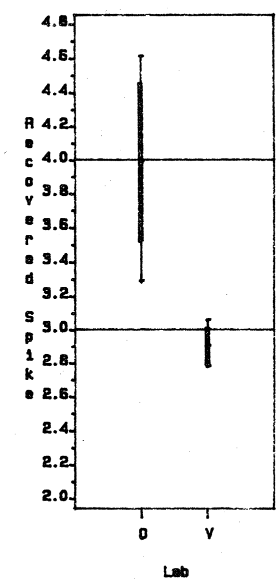


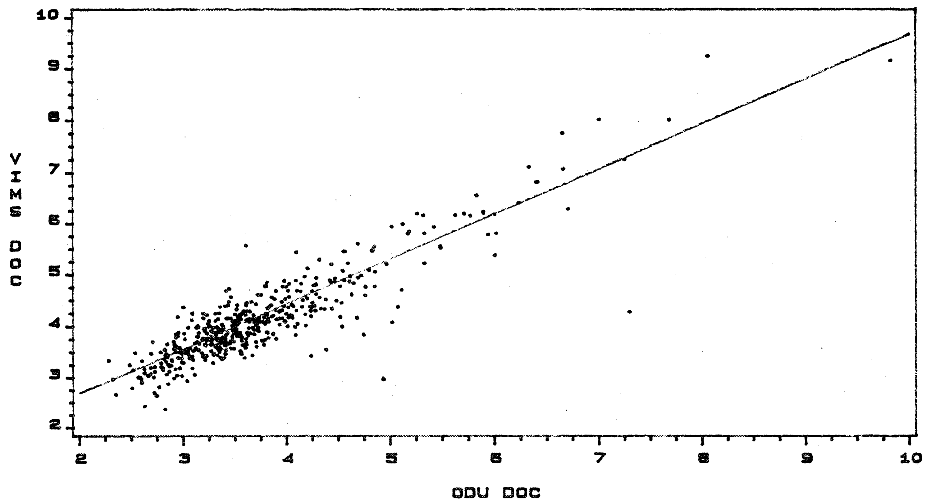
REL. PER. REC.

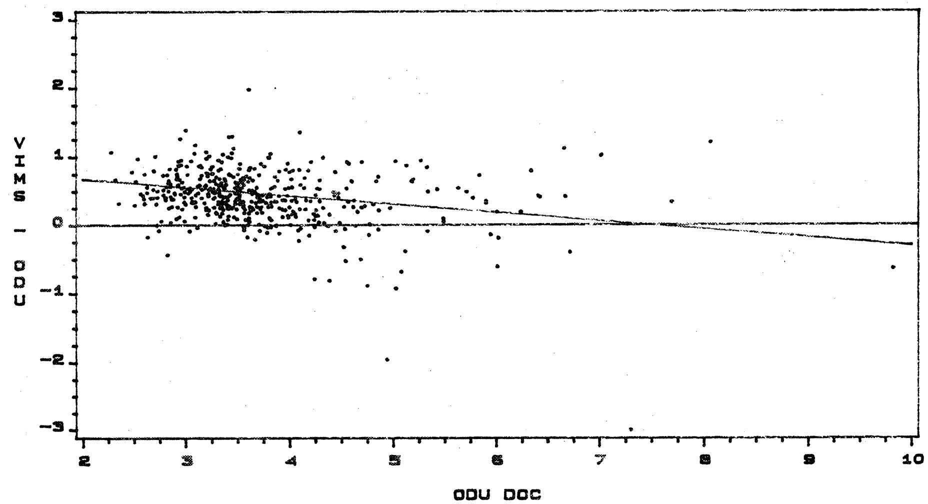


REC. SPIKE



January – June, 1990





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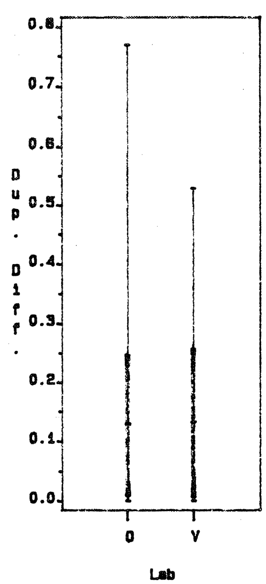

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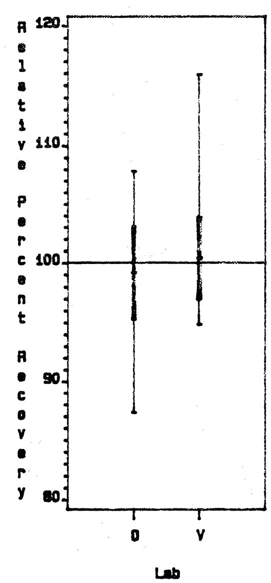

REC. SPIKE