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THE ANALYSIS OF THE TOTAL ORGANIC CARBON IN SEAWATER:

a). DEVELOPMENT OF METHODS FOR THE QUANTIFICATION
OF T.O.C.

b). MEASUREMENT AND EXAMINATION OF THE VOLATILE
FRACTION OF THE T.O.C.

by

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Submitted in partial fulfilment of the requirements

for the Degree of Doctor of Philosophy in Oceanography

at Dalhousie University

February, 1977

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ABSTRACT

A method has been developed for the direct quantification of the volatile organic matter in seawater. The volatile material has been defined by a working definition as that material which is capable of being extracted, concentrated, and measured with the methodology presented in this study. The distribution, sources, and fate of this volatile material in natural waters are discussed. The fraction of the total organic matter which is volatile has been measured. Dry oxidation methods for the measurement of the total organic carbon have been developed and are described. The TOC results by dry oxidation methods are compared to results obtained by a modified standard wet oxidation procedure for identical or simultaneous samples collected in different geographic areas. Besides presenting methods for the analysis of the VOC and TOC in seawater, I have attempted to show many of the potential shortcomings of these and previous methods for the analysis of organic matter in natural waters.

GENERAL INTRODUCTION

The organic matter in the sea is composed of a complex mixture of organic components; only a small fraction of the organic matter has been characterized structurally. The total organic carbon (TOC) is classed into two broad and arbitrary divisions dissolved (DOC) and particulate (POC). Particulate organic material is that material retained by a filter of specific size (0.45-0.8μ), while the filter passing material is classed as dissolved. The physical division of these classes is not rigid (Sharp, 1972, 1973) since the size separation of the particles predicted by the filters is not accurate (Sheldon, 1972) and the efficiency of the separation is dependent on the type of filter (Wangersky, pers. comm.). Similarily, the filter passing materials will contain colloidal as well as dissolved organic matter (Sharp, 1972).

The cycle of organic matter in seawater and the source, pathway, distribution, fate, and analysis of the organic components of seawater have been examined in past studies. General reviews by Provasoli (1963) Duursma (1961, 1965), Wagner (1969), Riley (1970), Riley (1971), Menzel (1974), Williams (1975), Parsons (1975), and Wangersky (1965, 1976) as well as recent symposia edited by Hood (1970, 1971), Faust and Hunter (1971), Woodwell and Pecan (1973), and the

Symposium on Concepts in Marine Organic Chemistry (1976)
have been presented and the role of the organic matter in
the chemistry of the sea has been discussed. The characterized
components of the organic matter have been surveyed by
Vallentyne (1957), Koyama (1962), Duursma (1965), Wagner
(1969), Riley (1971), Josefsson (1973), Duursma and Marchand
(1974), Williams, (1975), and Wangersky (1976) and only a
small fraction (5-10%) of the total organic matter has been
identified. The identification of specific components has
been hampered by difficulties in the extraction, concentration,
and analysis procedures and by the very low concentrations
of organic matter found in seawater. Most qualitative
methods are difficult (Jeffrey and Hood, 1958, Josefsson,
1973) and the results are questionable (Blumer, 1975) or
inconclusive. Much of the work done on the role and cycle
of organic matter in the ocean has been based on the
quantification of the TOC. In seawater, the salts have
hampered the estimation of the TOC but quantitative methods
have been developed (Duursma, 1961, Szekielda, 1967, and
Wangersky, 1972, 1975, 1976).

The principal sources of organic matter in seawater are
marine organisms, land, and the input by man. The particulate
fraction (POC) of the organic carbon is a small fraction
(seldom more than 10%) of the total. The role of the POC in
the cycle of organic matter has been discussed (Riley, 1970,

Menzel, 1974, Parsons, 1975, Eadie and Jeffrey, 1973, Meyers and Quinn, 1971, Khaylov and Finenko, 1968, Sharp, 1972, Agatova and Bogdanov, 1972, Sholkovitz, 1976) and studies of seasonal (Gordon, 1970, Banoub and Williams, 1976) and regional (Menzel, 1966, Chester and Stoner, 1974, Wangersky, 1974, 1975, 1976) distributions have been conducted.

The dissolved organic fraction (DOC) in seawater is derived from the extracellular production of plants and animals, the decomposition of organisms or particulate matter, the input from land, and man (Wangersky, 1976, Duursma, 1963, Riley, 1971 and Williams, 1975). The distribution of the dissolved organic materials has been determined in most areas of the oceans such as the Atlantic Ocean (Duursma, 1961, Menzel, 1970, Skopintsev, 1966, Sharp, 1973, Gordon and Sutcliffe, 1973), the Gulf of Mexico (Fredericks and Sackett, 1970), the Mediterranean Sea (Skopintsev, 1966, Banoub and Williams, 1972), the Black Sea (Starikova, 1971, Deuser, 1971), the Indian Ocean (Menzel, 1964), the Pacific Ocean (Starikava, 1971, Starikova and Yablokova, 1974, Ljutsarev et al., 1975, Holm-Hansen et al., 1966, Williams, 1971, Ogura, 1970), and the Arctic Ocean (Loder, 1971). In these studies, discrepancies in the DOC or TOC concentrations have been noted with different methods. Higher calculated concentrations were found with the dry oxidation than with the wet oxidation procedures. However

the broad distributions of the TOC concentrations by the different methods are similar; higher concentrations in the surface, decreasing to about 200-500 m, and relatively constant for the remainder of the depth profile. A decrease in TOC with depth is indicated in the study of Starikova, 1971 which contradicts the idea of refractivity of the organic material in deep water (Menzel, 1974).

Rates of production and utilization of organic matter in the surface zone have been postulated to explain the distribution of the TOC. The age of the organic material in the deep water has been estimated at 1000-3000 years (Williams et al., 1969, Skopintsev, 1971). If the organic matter in the oceans is at steady state, then the rate of removal or remineralization of the organic matter must equal the rate of production. From the calculated age and the estimated amount of productivity, about 0.3-1.0% of the yearly productivity has been calculated as entering the deep ocean each year.

This is a small fraction of the primary productivity but mechanisms for the loss of this material must be postulated. The pathways for removal include biological utilization and decomposition. Heterotrophic utilization of the organic matter by phytoplankton and animals and bacterial decomposition will occur mainly in the upper 200 m (Wangersky, 1976). The estimates of variations in heterotrophic

activity (Williams, 1970), and the rates and extent of the decomposition of the TOC have been determined (Ogura, 1970, 1972). The kinetics of the utilization of the DOC in interaction with the detritus was calculated by Khaylov et al., (1968, 1971, 1972). The organic matter had been considered to be refractive (Menzel, 1974) but Khaylov showed a potential pathway for the utilization of the organic matter in the ocean. Chemical and physical processes are also possible mechanisms for the removal of organic matter. Chemical remineralization by photochemical reactions has been proposed by Zafiriou (1976) for the potential decomposition of the biologically "refractive" component of the organic material while work by Zika (pers. comm.) has indicated that decomposition of labile organics will occur under the conditions found in nature. The formation of particles from the dissolved organic material in nature by mechanisms, such as flocculation (Sholkovitz, 1967) bubble breaking (Sharp, 1972), bubble dissolution or collapse (Johnson, 1976), adsorption to detritus (Meyers, and Quinn, 1971) and photochemistry (Zika, pers. comm.), may be important steps in the pathway for the the utilization by organisms or for removal by sedimentation of some of the organic material produced in the surface zone. Low molecular weight organics may be produced as byproducts in these processes of production or utilization of the organic

matter in nature. If these byproducts have a high enough vapour pressure, they will be volatile and may be lost from the natural system through physical methods (stripping or volatilization).

The removal processes (biological, chemical, physical) for the organic matter in seawater must balance the production processes (biological, terrestial input, man) so that the distribution of organic matter in the sea can be explained. Since no build up of organic materials is seen in the ocean or in the sediment (Eadie and Jeffrey, 1973) a steady state relationship must exist. Wangersky (1965, 1972, 1976), Parsons and Seki (1970), Menzel and Ryther (197), Williams (1971), and Skopintsev (1971) use this argument in their explanations of the cycle of the organic matter in natural waters.

The following study will attempt to answer some of the questions of the source, role, and distribution of the volatile fraction of the total organic matter in seawater. For the first time, a direct method for the quantification of the volatile fraction (VOC) in natural waters will be described. The distribution of the VOC, its variations (geographical, spatial, and temporal), and potential sources and pathways will be examined. The amount of VOC extracted from seawater samples will be normalized to the TOC (VOC/TOC).

Therefore a method for the determination of the TOC in seawater was developed. A precise and accurate dry oxidation method for TOC will be described and it will be compared to the standard wet oxidation procedure. The reasons for the differences found in the TOC by the two methods will be postulated. Explanations for the observed distributions of the VOC/TOC ratios will be presented and possible sources, pathways, and tentative identification for this volatile fraction will be developed and described.

DETERMINATION OF THE TOC IN SEAWATER: WET OXIDATION

A. Introduction

The procedures for the wet oxidation of organic matter in natural waters have undergone many changes over the years in both the conditions for the oxidation and the methods used for the detection of the resultant products. Methods are based on the oxidation of the organic material present in the water to CO_2, which is analyzed by volumetric, gravimetric, conductometric, titrimetric, or coulometric methods or the newer methods of non-dispersive infrared analysis, gas chromatography, or mass spectrometry. Since measurement is based on detection of the produced CO_2, interference from inorganic CO_2 must be eliminated. In seawater the inorganic carbon ($CO_3^=$ and HCO_3^-) is about 20 to 30 times the concentration of the organic carbon. To remove inorganic carbon, the pH is normally adjusted to below 4, so that the $CO_3^=$ and HCO_3^- are converted to CO_2, which is scrubbed from the sample. Questions concerning the completeness of oxidation, interference from other oxidation products, blank problems, loss of volatile organics during the purging of inorganic CO_2, incomplete removal of the inorganic CO_2 and many others have been raised.

The earliest method for the quantification of the dissolved organic matter in seawater was developed by Putter (1909), using chromic acid as an oxidant. Raben (1910) was

quick to point out that Putter's results were not without
fault and could be improved. In these early methods, Cl_2
produced during the oxidation step was an interference.
Krogh and Keys (1934) used a thallium sulfate trap to remove
the interfering Cl_2. Kay (1954), using chromic acid as an
oxidant in a closed system and silver dichromate to remove
the interfering halogens, was able to analyze organic matter
in seawater in areas of high concentration (range of 1-4
mg C/liter) with a detection system based on a titrimetric
determination.

Duursma (1960) used a modification of this procedure, in
which the CO_2 which was trapped in barium hydroxide was
estimated with a coulometric method. The oxidant was a
mixture of sulfuric acid, potassium dichromate and silver
dichromate which was added to a 50 ml. sample of seawater
and heated to 130°C for 2-2 1/2 hours. Duursma obtained a
high precision (±0.03 mg.C/liter) for samples in the 0.1-8
mg. C/liter range and he obtained a consistent and reliable
analysis of the organic matter in natural seawater samples.
These values for the organic carbon compare favourably with
results obtained by other methods since then but his method
was tedious, time consuming, and required scrupulous care.
In describing his method, Duursma carefully presents the
sources of error in his and other methods for the oxidation
of the organic matter in seawater. He discusses problems of

atmospheric contamination, reagent blank determination, preparation of "carbon-free" water, detector variation, completeness of the oxidation, loss of volatiles, interfering gases, and sampling and preservation procedures.

One of the main drawbacks to earlier methods was overcome by the introduction of the non-dispersive infrared analyzer and the gas chromatograph for the detection of the CO_2 produced during the oxidation. With time, the oxidants have been changed in the belief that the stronger the oxidant, the more complete the oxidation should be. Oppenheimer, Corcoran and Van Afman (1963) used a sulfuric acid and silver-potassium dichromate and detected the products with a gas chromatograph. They noted the increasing complexity of the organic matter led to incomplete oxidations, with up to 5% carbon monoxide being produced along with the carbon dioxide. With pure materials they reported quantitative oxidation. Szekielda (1967) used sulfuric acid and dichromate for analysis of seawater and with a conductometric detector measured organic carbon in 5 ml. samples with a precision of 5-6%.

Using potassium persulfate as his oxidant and an infrared detector, Wilson (1961) reported a precise method for determining the TOC in seawater. However, large samples (200 ml) and the long times were required for each analysis, so this method was not adopted until the simplified and more manageable procedure of Menzel and Vacarro (1964) was

introduced. The method of Menzel and Vacarro provided
speedy analysis of seawater samples with a reported precision
of +0.1 mg C/liter in a range of 0.1-20 mg C/liter.
Potassium persulfate was used for the oxidation of the
sample in a sealed glass ampoule which was autoclaved and the
resultant CO_2 was analyzed with an infrared analyzer. This
method has become a standard procedure (Strickland and
Parsons, 1968) for determining organic matter in natural
waters.

While the wet oxidation method has been accepted as a
standard method, many questions have been raised over the
accuracy of the results obtained by this procedure. The
loss of the volatile organic components during the purging
of the inorganic carbon from the sample, premature oxidation
of organic materials in the water by the persulfate before
sealing, and incomplete oxidation of more resistant organic
materials are possible problems with this method. Two camps
have formed; one believes that the oxidation is complete,
while the other questions the accuracy of the method because
of the discrepancies which exist between wet and dry
oxidation results. Williams (1969) used a C^{14}-labelled
glucose and amino acid mixture to determine the completeness
of the oxidation by persulfate and found that for these pure
compounds it was more than 95% effective. He concluded
that, for the organic compounds which he used, the method of
Menzel and Vacarro (1964) was complete.

However, he felt that the completeness of the oxidation for all the organic materials in seawater was still in question.

Sharp (1973) questioned the accuracy of the wet oxidation procedure of Menzel and Vacarro and showed that simple changes in operational procedure led to increases in the amount of organic carbon measured. He argued that the addition of persulfate during the purging of the inorganic carbon dioxide could possibly lead to premature oxidation of the very labile, easily oxidized organic compounds. An indirect comparison between the two procedures by Sharp (1972) showed that up to 30% more organic carbon was measured if the persulfate oxidant was added after the inorganic carbon dioxide had been scrubbed from the sample.

Russian workers (Ljutsarev et al., 1975; Starikova and Yablokova, 1975) have used a wet oxidation method with a mixture of sulfuric acid and silver and potassium bichromate as their oxidant. The values obtained by this method for waters of the equatorial Pacific (0.55-2.0 mg C/liter) are similar to those obtained by Sharp (1973) for the Northwestern Atlantic, which may indicate that the same kinds of organic matter are measured by their methods.

Another wet oxidation method for organic matter in seawater is photo-oxidation (Armstrong, Williams and Strickland, 1969 and Armstrong and Tibbitts, 1968). With irradiation from a U.V. lamp, the oxidation of the organic matter in

seawater was found to follow first order kinetics. Almost
complete oxidation was noted within 2-3 hours for most
compounds tested except urea. Problems with this method
include time of oxidation, temperature control, and doubt as
to completeness of oxidation, especially since urea is such a
problem. Williams (1969) found that the U.V. method yielded
about 10% higher results than the persulfate oxidation
method and he argued that the Menzel and Vacarro (1964)
method must be a complete oxidation since the two methods
give similar results. This conclusion is based on the
assumption that the U.V. method results in complete oxidation.

Mattson et al., (1974) described an in situ continuous
monitoring system in which the organic material in coastal
regions is quantified by a measurement of the U.V. absorbance
of the water. Problems with this lie in sensitivity and
interferences, but the method may have potential in areas of
high TOC with a similar matrix of organics. Work by Ragan
and Craigie (1976) shows that interferences from the polyphenolic
components exuded by algae may greatly affect the U.V.
absorbance of natural waters and lead to an overestimate of
the TOC concentration in areas where polyphenols are exuded
by brown macrophytes.

These are the principal wet oxidation methods which
have been developed over the years. There has been a
progression to use of stronger oxidants, from potassium

permanganate to later variations in which potassium
dichromate and potassium persulfate were used. Refinements
in sample handling, appartus, and detection have resulted in
better reproducibility and improved precision. But problems
and questions still remain. As Wangersky (1976a) summarizes,
there are major points of contention in the wet oxidation
methods:

1   The excessive handling of the sample with potential
        contamination during the removal of inorganic CO_2.

2.   The loss of volatile compounds during the purging of
        inorganic CO_2, and the potential premature oxidation of
        more labile forms of organic material if the persulfate
        is present during the purging.

3.   Most procedures require discrete sampling so that the
        analyst is prevented from immediate examination of results
        which would be provided by real time analyses.

4.   The problem of obtaining "carbon-free" water for the
        determination of reagent blanks.

5.   The discrepancy between wet-oxidation and dry combustion
        numbers. If these differences are real then the
        incompleteness of oxidation by wet oxidation is indicated,
        and future users of the wet oxidation procedure will have
        to accept that at least some fraction of the organic matrix
        is resistant to the oxidants used in solution. Whether
        this unoxidized material is a constant fraction with

locale and depth is a question which will have to be answered.

B. Development of My Wet Oxidation Method for TOC in Natural Waters

1. Determination of Reagent Blanks

In order to obtain absolute values of the organic carbon in seawater by wet oxidation reagent blanks must be determined. Included in this blank will be the carbon added by the phosphoric acid, the oxidant (potassium persulfate), and the oxidation ampoule. This value could be obtained by use of "carbon-free" water as the sample. If the exterior contamination was eliminated, then the organic carbon value found will be the reagent blank.

Treatment of double distilled water with potassium persulfate was assumed to give "carbon-free" water (Menzel and Vacarro, 1964) which could be used to calculate the blanks. Wangersky (1965, 1976 a) disputed this and recommended the use of a high temperature oxidation still. Sharp (1972) found that even this water had a concentration of 0.1-0.2 mg. C./liter. The amount of carbon was about the same as water from a Millipore Super-Q purification system operated under manufacturers specification. Analysis by my combustion techniques has showed that Super-Q water was indeed very low in measurable carbon and averaged about 0.04-0.06 mg C/liter.

Since "carbon-free" water is difficult to obtain, the

reagent blank was calculated indirectly. Menzel and Vacarro (1974) suggested that when the carbon values from a gradient of volumes (1,2,3,4 and 5 ml) of low carbon seawater were extrapolated to zero, an estimate of the reagent blank could be obtained. Loder (1972) calculated a reagent blank indirectly and found that the reagents added about 0.05 mg C/liter, but his total blank was about 0.3 mg C/liter, which he attributed mainly to the ampoule.

Using 5 ml samples of acidified Super-Q water, I calculated the reagent blank by the addition of 1, 2, and 3 times the normal amount of persulfate required (Table I). The reagent blank added from the persulfate was on the order of 0.05-0.1 mg C/liter, with carbon from the Super-Q water and the ampoule making up the rest. The high ampoule blank of Loder (1972) was not seen and the reason for his high blank was not obvious. Discrepancies in the values of reagent blanks determined by various workers is an obvious source of difference in the absolute values for organic carbon in seawater (Table II).

The quality of the persulfate is very important in the blank determination, and batch variations are to be expected. However, if in the blank determination the water in the sample was considered "carbon-free" (TOC = 0 mg C/liter), then the blank would be overestimated and there would be overcompensation in the calculation of the TOC concentration

TABLE 1

Reagent Blank Determination: Effect of the Amount of Potassium Persulfate Added

Sample	Amount of $K_2S_2O_8$ Added (mg.)	Concentration of Organic Carbon Measured (mg.C/liter)
1. 5 ml. Super-Q water + conc. H_3PO_4	200	$0.16\pm.03$
2. 5 ml. Super-Q water + conc. H_3PO_4	400	$0.21\pm.04$
3. 5 ml. Super-Q water + conc. H_3PO_4	600	$0.30\pm.01$

TABLE II

Reagent Blanks Calculated for the Wet Oxidation Procedure by Different Investigators

Investigator	Reagent Blank Calculated (mg.C/liter)
1. Duursma (1961)	0.30
2. Wilson (1961)	0.30
3. Menzel and Vacarro (1964)	0.52-0.54
4 Strickland and Parsons (1968)	0.15-0.30
5. Maurer and Parker (1972)	0.48-0.66
6. Loder (1972)	0.31
7. Sharp (1973)	no value given
8. MacKinnon (this study)	0.08-0.12

in the natural samples. This would tend to lead to an under-estimation of the natural carbon in the sample, and would explain some of the difficulties in the comparison of TOC values from various studies but would not grossly affect the qualitative interpretation.

2. Calibration of Infrared Detector

The detector was calibrated with standard solutions in low carbon water. I found that Millipore Super-Q water obtained under manufacturer's specifications was satisfactory for the preparation of standard solutions of dextrose. In the range of carbon values required, the response of the infrared detector was found to be linear. The amount of organic carbon in natural samples was calculated by subtracting the reagent blank from the detector response and dividing this by the slope of the calibration line obtained with the standard solution. Calibration lines were prepared daily so that a comparison of results from different runs could be done with confidence.

3. Acidification and Removal of Inorganic Carbon

1) Amount of Acid Added

The inorganic carbon in seawater is 20-30 times the concentration of the organic carbon present and must be removed completely in order to obtain accurate values of TOC in natural samples. Acidification of the sample to pH less than 4.5 results in the shift of the carbonate species to

CO_2, which is swept from the system with a flow of N_2. Strickland and Parsons (1968) used 0.25 ml of 3% phosphoric acid per 5 ml sample, but I used 0.05 ml concentrated phosphoric acid in 30 ml of sample since it seemed less prone to contamination (Sharp, 1973).

11) Time of Scrubbing

With 5 ml samples in the glass ampoules, Strickland and Parsons (1968) recommended 5 minutes of scrubbing at 200 ml/min. N_2 to purge the acidified sample of inorganic CO_2. Sharp (1973) states that 5 minutes of 100-200 ml/min. N_2 will remove CO_2 from his 30 ml samples. Sharp obtains higher numbers for his wet oxidation procedure than those reported by other workers in the literature. This difference may be the result of incomplete removal of the inorganic CO_2.

L. Gordon (personal communication) found that 5 minutes of purging at 100 ml/min. was not sufficient to remove all the inorganic CO_2, although at a rate of 200 ml/min. complete removal was noted. Using the standard Menzel and Vacarro (1964) method and Sharp (1973) method, he noted that at 5 minutes the Sharp method showed about 5% higher DOC, which diminished as the purging time was lengthened. This indicates that great care must be exercised in this scrubbing procedure. I examined the purging times required (Table III) by taking 35 ml seawater samples at varying temperatures

TABLE III

The Efficiency of the Inorganic CO_2 Purging in the Wet Oxidation Procedure

Sample	Flow Rate of N_2 (ml./min.)	Sample Temperature ($^{\circ}C$)	Scrubbing Time (min.)	Measured Conc. of Inorg. CO_2 in sample (mg. C/liter)
1. Tap Sea Water pH=2.5	250	15	2 5 7 10 15	1.00 0.20 0.03 0.05 0.00
2. Tap Sea Water pH=2.5	250	25-30	5 7 10	0.01 0.00 0.00
3. Tap Sea Water pH=2.5	250	0-1	5 7 9 11 15	0.26 0.04 0.01 0.00 0.00

and, after acidifying to pH 2.5, scrubbing them with a flow
of N (250 ml/min.).

After specific intervals (2, 5, 7, 10 and 15 min.) of
scrubbing, an acidified sample was placed in an ampoule,
sealed, and the amount of CO_2 still present was measured
with the usual procedure. Almost complete removal of
inorganic CO_2 was noted in the sample at room temperature
after 5 minutes but 5-10 minutes were required for the
samples at lower temperatures. With the conditions
described By Sharp (1973), complete removal is questionable.
This may explain his higher TOC numbers and some of the
"wild values" (Wangersky, 1975).

> iii) Loss of Volatiles during the Purging of Inorganic
> Carbon

The volatile fraction of the organic material present
in the seawater may be lost by prolonged purging and result
in an underestimation of the TOC concentration. Duursma
(1961) used a heat digestion to remove the inorganic CO_2 but,
by monitoring acetic acid, he concluded that the volatile
organic loss was small (about 10%). Using demineralized
water, Van Hall, Barth and Stenger (1965) concluded that
most of the hydrophilic compounds except acetone and acetaldehyde
were not readily removed, while hydrophobic forms were
rapidly lost.

I checked the fate of some volatile organic compounds

by the preparation of samples, spiked with volatile compounds, in acidified Super-Q water which had been purged of inorganic CO_2. These samples were scrubbed with N_2 at 225 ml/min. for 0.5, 5, and 10 minutes and then the oxidant was added, the ampoule sealed and the remaining volatile organic material was analyzed. As seen in Table IV, the hydrophobic materials were lost significantly, while the more hydrophillic materials were less easily removed. This indicates that although the lower weight materials are lost during the scrubbing step, it is not quantitative in the scrubbing time used. This effect on the measured TOC should be small (estimated at 1-3% of TOC).

4. Loss of TOC by Premature Oxidation

In the method of Menzel and Vacarro (1964), the oxidant $(K_2S_2O_8)$ and the phosphoric acid are added simultaneously to the sample, which is then purged of its inorganic CO_2. Sharp (1973) argues that dissolution of the potassium persulfate will begin during this 5 minutes period of purging and the more labile materials will begin to be oxidized. He advocates that the inorganic CO_2 should be purged before the oxidant is added and he claims that his 20-30% higher TOC values are the result of this modification. The Merck Index states that dissolution of the persulfate is very rapid at elevated temperatures but it proceeds slowly

TABLE IV

Fate of Volatile Organic Compounds During the Purging of the Inorganic CO_2

Sample	Time of scrubbing (min.)	Amount of Volatile Organics Added (mg.C/liter)	Amount of Volatile Organics Measured (mg.C/liter)	Amount of Volatile Organics Lost in Scrubbing (%)
1. Super-Q	0.5	0.66	0.66	0.0
+Dextrose	5.0	0.66	0.66	0.0
2. Super-Q	0.5	1.00	0.98	2.0
+Acetone	5.0	1.00	0.84	16.0
	10.0	1.00	0.79	21.0
3. Super-Q	0.5	1.85	1.83	1.0
+Iso-propanol	5.0	1.85	1.72	7.0
4. Super-Q	0.5	0.11	0.11	0.0
+Butyr-aldehyde	5.0	0.11	0.04	77.0
	0.5	0.55	0.53	4.0
	5.0	0.55	0.41	25.0
5. Super-Q	0.5	0.47	0.44	6.0
+2-Butanone	5.0	0.47	0.40	15.0
6. Super-Q	0.5	0.47	0.32	32.0
+Diethyl Ether	5.0	0.47	0.02	96.0
7. Super-Q	0.5	0.10	0.10	0.0
+Propionic Acid	5.0	0.10	0.10	0.0

even at room temperature.

Since premature oxidation would appear to be a potential problem in the wet oxidation procedure, I examined the effect of persulfate on the TOC values during the purging. Fresh samples from near surface coastal water and aged deep sea Sargasso Sea water were analyzed to see if organic material is oxidized during this scrubbing step (Table V). Samples were acidified with phosphoric acid and bubbled with nitrogen at 250-300 ml/min. for 10 minutes. Samples (5 ml) were withdrawn and placed in glass ampoules to which 200 mg of potassium persulfate had been added. These samples were further purged with N_2 for various times (0.5, 5, 10, 20 min.), at which point the ampoule was sealed, autoclaved, and analyzed. If premature oxidation were occurring, lower measured TOC concentrations would be seen with increased time of scrubbing (Table V). Even with 5 minutes of scrubbing in the presence of oxidant, a slight drop in the measured TOC (approx. 2-8%) was seen. In the surface water from the N. W. Arm, the largest drop (about 0.13 mg C/liter in 5 minutes) was found, while in the other samples TOC values were reduced by about 0.02-0.06 mg C/liter in a 5 minute period. Further reduction in measured TOC of about 2-6% was noted with extended scrubbing. The temperature of the sample was critical to the rate of dissolution of the oxidant, and at room temperature complete dissolution of

TABLE V

Premature Oxidation Caused by the Presence of $K_2S_2O_8$

During the Purging Step in the Wet Oxidation Method

Sample	Time of Scrubbing in Presence of $K_2S_2O_8$ (min)	Concentration of TOC (mg.C/liter)	Change in TOC from Initial (%)
1. Surface water from N.W.Arm, Halifax Harbour (20/8/75)	0.5	1.74±.05	---
	5.0	1.61±.02	-7.5
	10.0	1.55±.08	-11.0
	20.0	1.49±.03	-14.4
2. Aged Sargasso Seawater	0.5	0.87±.05	---
	5.0	0.81±.04	-6.9
	10.0	0.80±.02	-8.0
	20.0	0.82±.04	-5.8
3. Tap Seawater	0.5	1.08±.03	---
	5.0	1.06±.06	-1.9
	10.0	1.02±.03	-5.6
4. Tap Seawater	0.25	1.16±.04	---
	0.5	1.13±.05	-2.6
	5.0	1.13±.04	-2.6
	10.0	1.10±.01	-5.2
5. N.W.Arm (1m.) (13/1/76)	0.5	1.21±.07	---
	5.0	1.17±.03	-3.3
	10.0	1.15±.02	-5.0

the potassium persulfate was seen in 20 minutes. This modification to the wet oxidation procedure is minor but it should be used or a fraction of the sample may be lost by premature oxidation.

5.   Contamination Problems

In the analysis of TOC in seawater, the introduction of contamination must be prevented because the amount of organic material in 5 ml samples of seawater (TOC = 0.5-1.5 mg C/liter) will be very small (2.5-7.5 µg C). Scrupulous care in the analysis is required to prevent the introduction of foreign material into the sample. Since wet oxidation procedures require extensive sample handling in collection, storage, and analysis, the choice of sampling apparatus, sample bottle, and sample preservation are critical.

A further source of contamination in the wet oxidation procedure is in the acidification and purging of the inorganic CO_2. Blanks were run and the contamination from the purging process was considered negligible. Contamination from the atmosphere, the scrubber, and the system for sample transfer were all monitored and randomly high values in the triplicate analysis may be the result of contamination from these sources. The introduction of atmospheric CO_2 by leakage was minimized by the use of a small glass tube packed with ascarite (soda lime) that was fitted with a tygon tubing joint to the top of the ampoule during the transferring and

during the sealing step with the propane flame. Contamination
from the ampoule itself was minimized by preoxidation (450°)
of the ampoule and use of aluminium foil to cover the
ampoules during storage.

The accuracy and precision of the wet oxidation method
will suffer if the sample or the oxidation product is lost
during preparation and analysis. Sharp (1972) reports 15-
20% loss of samples because of contamination or leakage. In
my system the sample ampoule is enclosed in a large tygon
tube during the breaking of the ampoules. This method was
found to be effective and the oxidative product (CO_2) was
safely swept to the IR analyzer.

With these precautions, the threat of atmospheric
contamination and the loss of oxidation products can be
minimized but, by the nature of the wet oxidation procedure,
complete elimination of contamination cannot be assumed.

6.   Completeness of Oxidation

1)   Standards

Standard materials were added to samples and the
efficiency determined by the comparison of CO_2 measured and
the amount of compound added. The validity of this approach,
where up to 1000 times the concentration of the specific
component in natural waters is used, has been questioned
(Williams, 1969) since the completeness of oxidation for

standards does not guarantee similar efficiencies for the complex natural organic materials.

In the analysis of standards in seawater by wet oxidation (Table VII) the per cent recovery was good and complete oxidation was indicated. The efficiency of the oxidant for these materials seems high but extrapolation to the whole matrix of organic material in seawater may not be valid. A comparison of the method with one which is complete would provide the basis on which to calculate the completeness of the oxidation. Sharp (1973) indicates that the high temperature oxidation is more accurate than the wet oxidation. Later I will compare the results obtained from wet and dry methods and will argue that the accuracy or completeness of the dry oxidation is higher than that of the wet oxidation procedure. When the wet oxidation methods were compared (Williams, 1969) the TOC results by U.V. oxidation and wet oxidation were not significantly different. In my work, I found that after U.V. oxidation with a 1200 watt mecury arc lamp for 24 hours in the presence of hydrogen peroxide, up to 25% (5-25%) of the original material (TOC) was still measured. Thus the competeness of the TOC results obtained by UV oxidation, must be questioned.

11) Procedures

Changes in the standard procedures have been made by several workers in order to ensure completeness of oxidation.

TABLE VI

The Various Temperatures and Times of Heating Used

for the Persulfate Oxidation of the TOC in Seawater.

Study	Temperature of Heating (^{o}C)	Time of Heating
1. Wilson (1961)	100	60 min.
2. Menzel and Vacarro (1964)	130	30 min.
3. Strickland and Parsons (1968)	130	40 min.
4. Williams (1968)	100	25 hr.
5. Fredericks and Sackett (1970)	175	24 hr.
6. Maurer and Parker (1970)	125	60 min.
7. Loder (1972)	130	4 hr.
8. Sharp (1973)	121	60 min.
9. Kerr and Quinn (1974)	105	2 hr.
10. Gordon, L. (personal comm.)	Room temperature	extended
11. MacKinnon (this study)	121	60 min.

TABLE VII

Efficiency of the Persulfate Oxidation for Known

Compounds

Sample	Calculated Concentration of Standard Added (mg.C/liter)	Measured Concentration of Standard (mg.C/liter)	Theoretical Recovery (%)
1.Benzoic acid in Tap S.W.	1.47	1.38	94
	2.16	1.98	92
2.Urea in Tap S.W.	1.53	1.53	100
	2.35	2.22	95
3.Glycollic acid in Tap S.W.	1.40	1.37	98
4.Thiamine HCl in Tap S.W.	1.45	1.33	92
	2.24	1.87	84
5.Na Oleate a) in Tap S.W.	1.58	1.20	76
	2.44	1.59	65
b) in Super-Q	1.25	0.96	83
	2.30	2.00	87
6.Fulvic acid material a) in Tap S.W.	1.18	1.19	100
	1.35	1.27	94
b) in Super-Q	0.88	0.86	97
	1.76	1.64	94
7.Dextrose in Tap S.W. or Super-Q			95-100

In the persulfate method, the temperature (100-175°) and time (0.5-24 h) required for the autoclaving or heating of the sample with the oxidant has been varied considerably (Table VI). Workers have argued that these changes have resulted in maximum results even though the persulfate activity should not be affected by minor operational differences as long as temperatures are elevated to ensure complete dissolution of the persulfate. L. Gordon (personal communication) claims that the values for TOC that are obtained by room temperature dissolution of the persulfate are comparable to those obtained by dissolution at elevated temperatures.

iii) Effect of the Oxidant

The efficiency of the oxidant itself must be considered. There has been progression to stronger oxidants from permanganate to persulfate and increasing concentrations in measured TOC have been noted with each change. Earlier TOC values have been assumed to be the result of the measurement of the more labile, biologically important organic materials, but as the strength of the oxidant increased the more highly refractive materials were measured. Even after prolonged oxidations with nitric-sulfuric-perchloric acid mixtures at elevated temperatures (up to 320°C) some compounds, particularly those containing nitrogen, were not completely oxidized (Martinie and Schilt, 1976). This indicates that the oxidants which are used in the wet

oxidation procedures may not be as effective as workers would like to believe.

7.   Outline of the Wet Oxidation Method

The procedure described by Sharp (1973) was used for the wet oxidation of the organic matter in water, with the introduction of some further modifications in the handling of the samples.

The water samples which had been collected and frozen in the 50 ml serum bottles were thawed and well mixed. About 30 ml of the sample were acidified (pH 2-2.5), with about 0.05 ml concentration H_3PO_4 and scrubbed with N_2 at a flow rate of 200-250 ml/min. for a minimum of 7-10 minutes. Five ml aliquots were withdrawn with a glass syringe and placed in preoxidized (heated at 450-500°C for at least 2 hours just prior to use) 10 ml ampoules (Pierce Chemical Co. # 19806) into which 200 mg. of $K_2S_2O_8$ had been added. After a further 30 seconds of purging with N_2, the ampoule was capped with an Ascarite-packed tube to prevent atmospheric contamination until it was sealed with a propane torch. The sealed ampoule was then autoclaved at 121°C for 60 minutes.

The CO_2 produced during the oxidation was measured using a non-dispersive infrared analyzer (Beckman I.R. 15A). A Tygon tube (17 mm OD x 13 mm ID) was placed over the ampoule so that the neck and the top section of the ampoule

body was completely enclosed. The other end of the Tygon
tube was connected to a "T" joint so that the oxidative
products could be flushed from the ampoule, through the "T"
and carried to the IR analyzer. Before the ampoule was
attached to the Tygon tube, the neck was scored with a file
and a 1.5 cm polypropylene (10 mm ID x 14 mm OD) sleeve was
fitted over the neck of the ampoule. With pliers held at
this point around the Tygon tube, the neck of the ampoule
was crushed and leaks caused by sharp pieces of broken glass
piercing the Tygon tube were prevented. Flow meters were
placed in line before the ampoule and at the exhaust from
the analyzer, to permit easy monitoring of the system and
early detection of leaks.

A tube (1/16" stainless steel tubing), which passed
through the top of the "T" connection, was immersed into the
opened ampoule and N_2 was flushed through the sample to scrub
out the CO_2. A slow flow of O_2 (50-60 ml/min) was used for
the initial 60-90 seconds of scrubbing. This was followed
by a rapid flow of N_2 (300-350 ml/min), which swept the
produced CO_2 into the infrared analyzer (Beckman I.R. 15 A)
after passing through an acidified $FeCl_2$ trap (20% w/v), a
saturated silver sulfate solution (Ag_2SO_4), a condenser in ice
(0°C) and a drying column ($Mg(ClO_4)_2$). The dead space in the
system was sufficient so that the peak appeared as a sharp,
symmetrical signal about 60 seconds after the fast flow of

N₂ was started. This signal was recorded on a recorder
(Honeywell Electonik 194) and integrated (Royson Lectrocount
III). The response of the detection system was linear over
the range of concentrations expected for natural samples.
Total time for analysis was about 4-5 minutes.

C. Analysis of TOC in Natural Waters by Wet Oxidation
   Procedure

   1)ʼ Areas Studied

   I analyzed data from different areas (Gulf of St.
Lawrence, Scotian Shelf and Slope, and an area off the coast
of Senegal) with my wet oxidation procedure. The station
locations and data are presented in the Appendix. General
features and distribution are evident in Figs. 1, 2, and 3.

   2) Precision of TOC Analysis

   Samples were run in triplicate, and with my handling
methods only a few were lost by breakage in the study.
"Wild values", as described by Wangersky (1975), were found
in a number of samples (5-10%). Contamination or incomplete
removal of inorganic CO_2 were probably the cause of most of
these. A value is considered "wild" if it varies from the
mean by greater than 10% and unless explained was discarded.
In my analysis, precision was calculated as ± standard
error of the mean $(\sigma/\sqrt{n})$. The precision of the TOC
analysis by my wet oxidation method is presented (Table
VIII) as the relative standard errors (standard error /

TABLE VIII

Relative Standard Errors $\{(\sigma/\sqrt{n})/\bar{x}\}\cdot 100\}$ For

Persulfate Oxidation of Natural Samples

Sample Origin	n	Relative Standard Errors ± σ (%)	Range (%)
Gulf of St.Lawrence (5-6/75)	41	3.1±2.0	0.2-8.0
Scotian Shelf (8/75)	67	3.0±1.9	0.6-10.0
Off Coast of Senegal (2,3/76)	76	3.2±1.6	0.5-7.5

TABLE IX

Averaged Concentration of the TOC at 5 Depths (1,10,25,

50,and 75 m.) from Stations 1-7 on the Scotian Shelf

(8/75)

Station	Distance from the Coast (Km.)	Averaged TOC Concentration (mg.C/liter)
1	5-10	1.08
2	25	1.12
3	80	0.97
4	125	0.89
5	170	0.88
6	210	0.87
7	250	0.88

Fig. 1-1: Depth profile of TOC values (●) and depth averaged
          TOC values (Δ). Measured with a wet oxidation method.
          Samples collected in (Gulf of St. Lawrence (5-6/75).
          See Map #. pg. 73b.

Fig. 1-2: Depth profile of TOC values measured with a wet
          oxidation method (●). Samples collected on Scotian
          Shelf and Slópe (8/75). See Map #. pg. 75b.

Fig. 1-3: Depth profile of TOC value (●) and depth averaged
          TOC values (Δ) measured with a wet oxidation method.
          Samples collected in an area off the coast of Senegal
          (2,3,4/76). See Map #. pg. 79a.

28 c
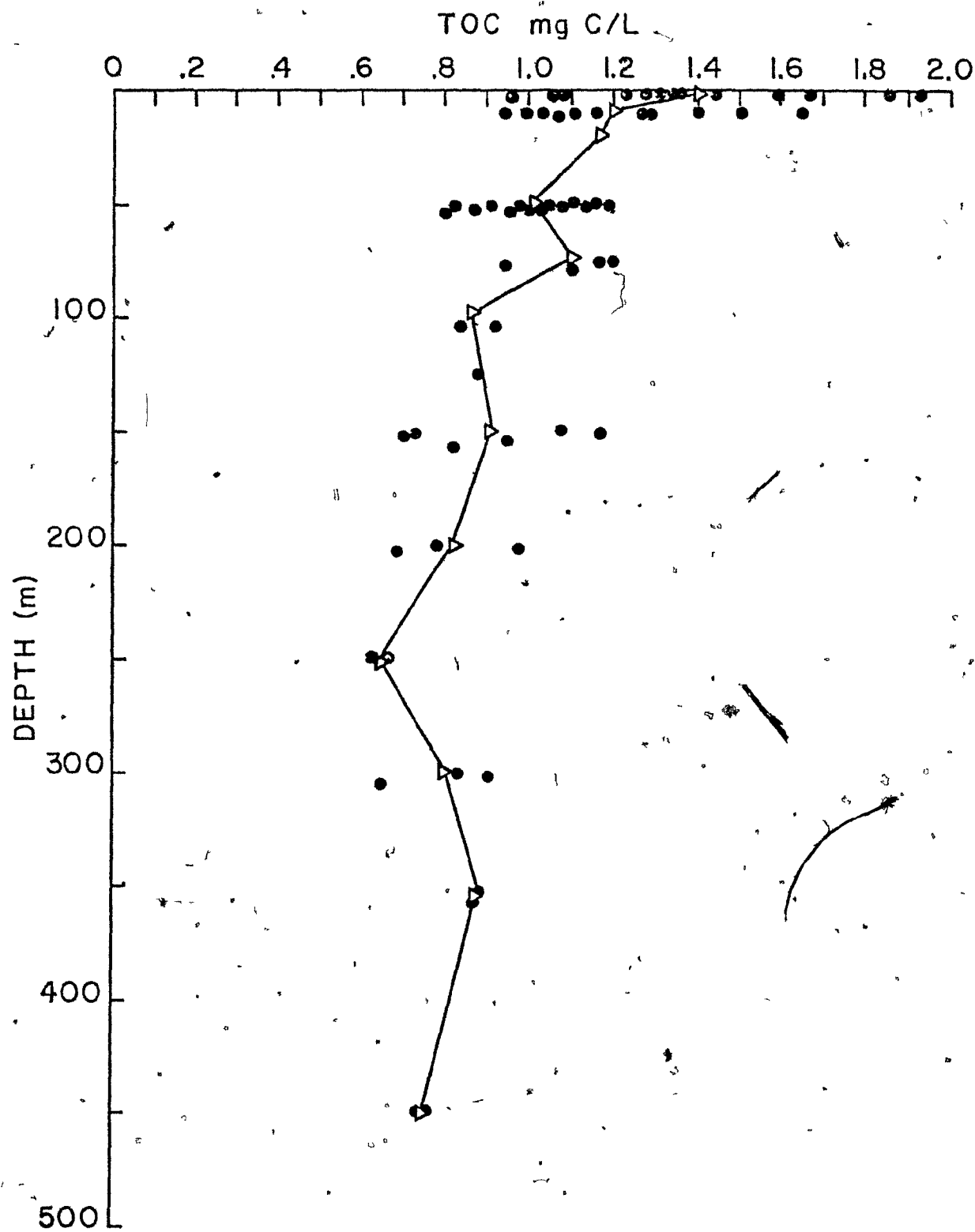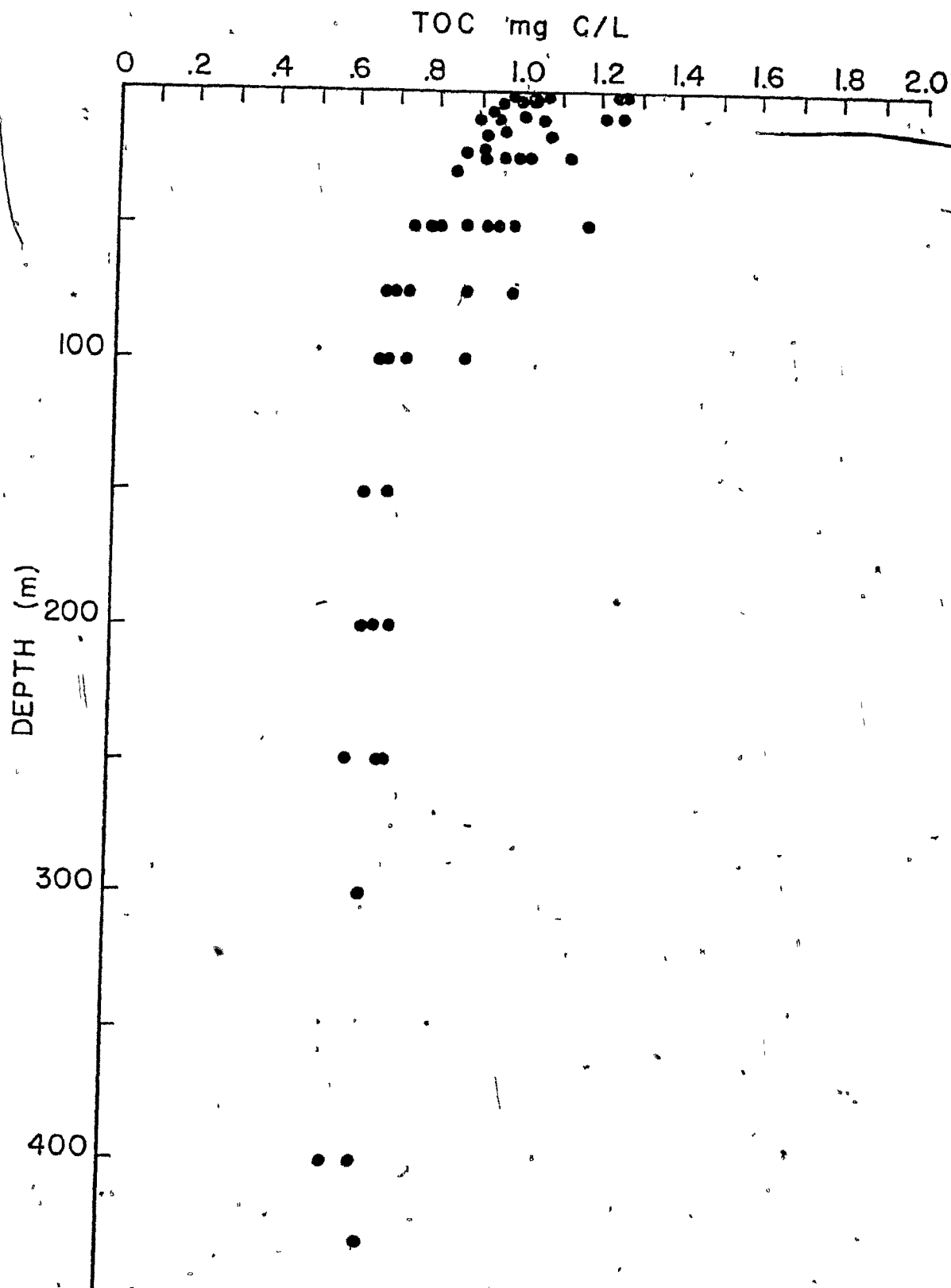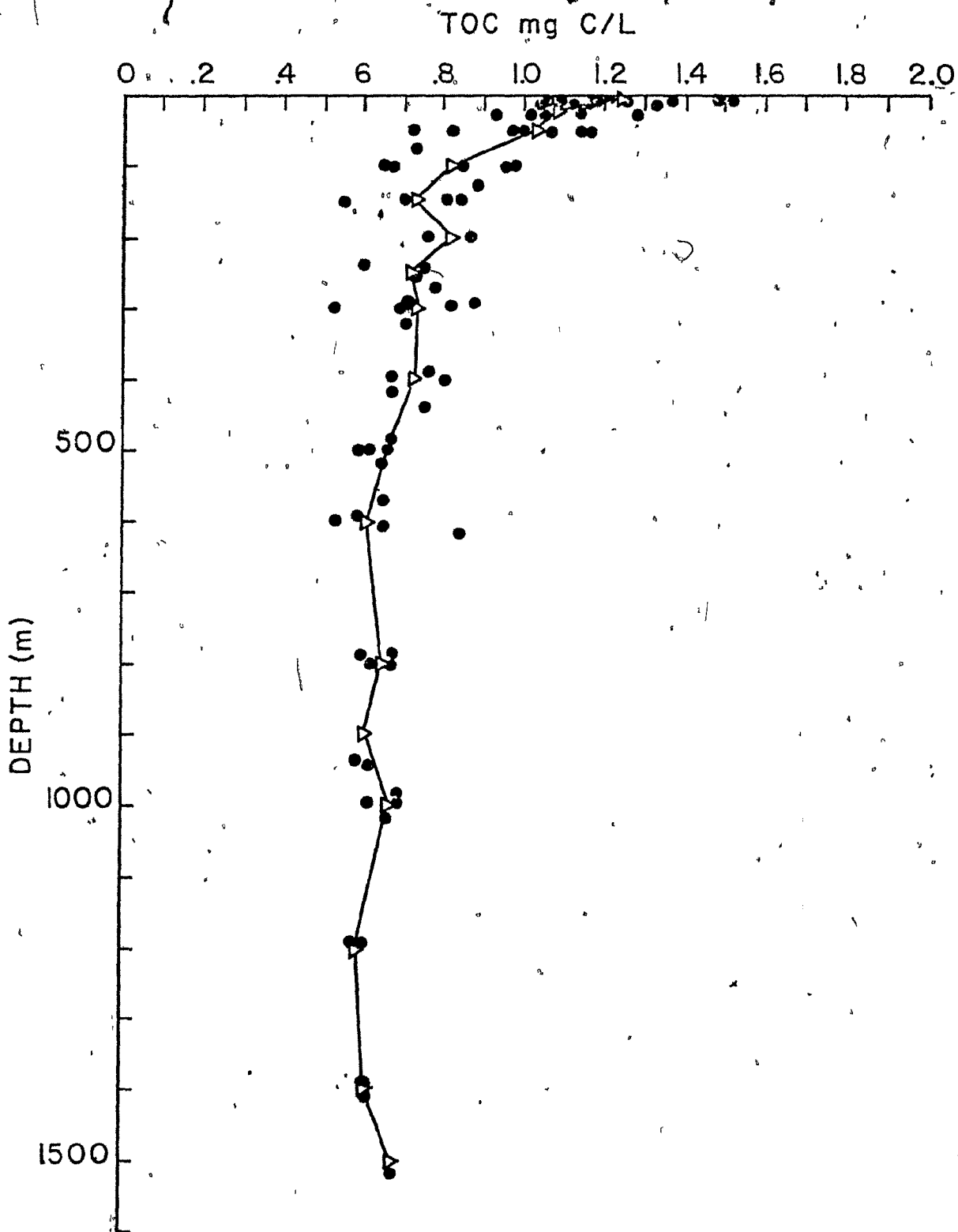
mean) x 100) Only samples which were done in triplicate
with no obvious "wild values" were included in this
calculation of error.

.The precision of individual sample analysis was high
with an average relative standard error of about 3.1%. The
calculated error was similar even though the place and time
of origin of the samples varied.

3)   Distributions of TOC values.

Because of variations from station to station, scatter
in the TOC results was to be expected.

In the Gulf of St. Lawrence (Figure 1) the TOC values were
highly scattered, particularily in the surface zone. Examination
of the origin of the samples led to a better understanding
of the distributions. In areas with high fresh water input,·
the highest TOC concentration were measured. A strong
negative correlation (r=0.87) exists between the TOC and
sigma-t (σ_t) values (Fig. 4). The surface or euphotic zone
and those areas with the greatest fresh water influence
(Corner Brook Bay and the mouth of the St. Lawrence) have
the lowest sigma-t values and the highest values of TOC.
These areas also have the highest calculated particulate
organic carbon (POC) values (Pocklington personal comm.,
1976). However, the POC only averaged about 3-9% of the TOC
in the surface zone and 2-5% in deeper water. This is not
enough to explain the high values and wide scatter of the

Fig. 1-4. The TOC values obtained by the wet oxidation method
from the Gulf of St. Lawrence plotted versus the
sigma-t values.

Fig. 1-5: Coastal effect on the TOC values. The averaged TOC
values (1, 10,25, 50,75m) obtained with the wet
oxidation method plotted with distance from the coast
of Nova Scotia on the Scotian Shelf (8/75). The bars
represent the range of measured TOC values.

FIGURE]-4
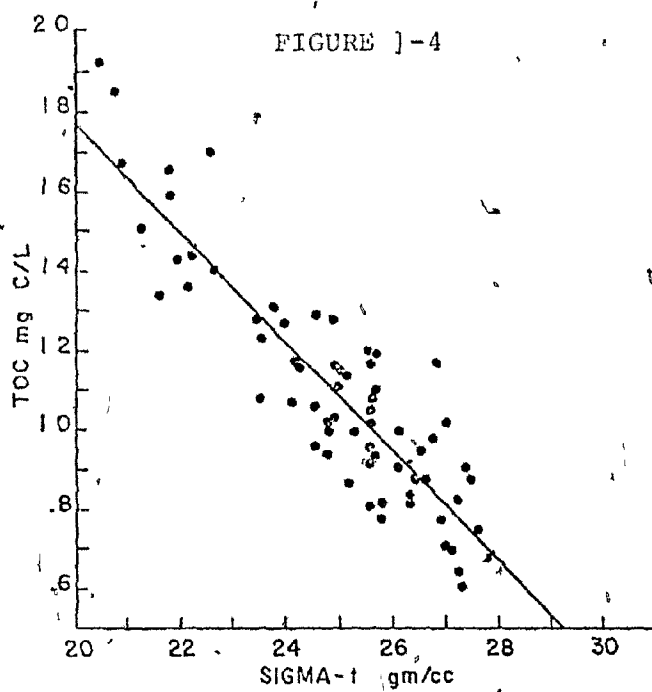
FIGURE I-5
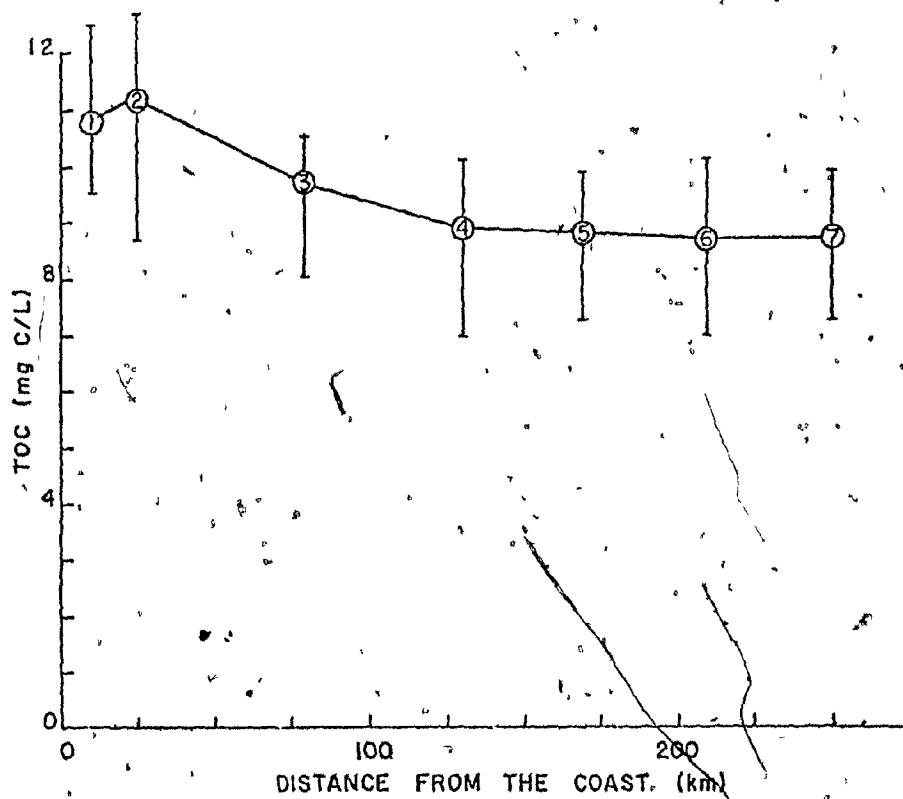
TOC. High values of TOC in the euphotic zone (area of high biological activity) are to be expected. Estuarine areas may be influenced by the TOC from the river (range of TOC about 2-20 mg C/liter depending on source and area) either directly or through flocculation of dissolved materials in the river-seawater mixing zone (Sholkovitz, 1976). A significant correlation between the TOC and POC was expected, but data collected by Pocklington in the Gulf cruise (May-June/75) does not show this. However, for specific high values of TOC, high values of POC were noted. The %, (POC/TOC) was never greater than 10%.

The data from the Scotian Shelf and Slope was collected in August 1975 during a transect from Halifax to the continental slope (Figure 2). The scatter is smaller than was seen in the Gulf of St. Lawrence (Figure 1). Smaller scale variations in the hydrographic parameters (salinity, O_2, nutrients, and the influence from fresh water) were exhibited on the Scotian Shelf so that less scatter in the TOC values would be predicted. However, when the averaged TOC concentrations (over 75 m) were plotted with distance from the coast (Fig. 5), an inverse relationship was noted between the TOC and the distance from the coast. Stations 1-7 were run as a transect from just off Halifax Harbour (5-10 km) to the slope of the continental shelf (250 Km). A definite coastal effect was evident, with the highest averaged TOC concentrations

being measured at Stations 1 and 2 (1.1 mg. C/liter),

dropping off at Station 3 (0.97 mg. C/liter) and levelling

to a constant value at Stations 4, 5, 6 and 7 (0.88 mg

C/liter) (Table IX). The scatter of TOC (Figure 2) was low

in deeper water (> 100 m), while the higher scatter was

found in the surface zone. Influence from coastal proximity

was a possible reason for this since high TOC values were

found close to the coast and low TOC values were noted as

the distance from the coast increased.

The third area of study (Figure 3) was a region off the

coast of Senegal which was sampled in early 1976. This is an

area of upwelling with high productivity and much of the

scatter in the top 200 m may be explained by this. Below

200 m the distribution of TOC was much less scattered and

the results were similar to the type of deep water distribution

of TOC proposed by Menzel (1967, 1970, 1974), who argued that

below 500 m the organic matter was refractive and DOC values

will show little variability.

4.   Comparison of Wet Oxidation Results with Other Studies

      1)   Comparison with Sharp (1973)

One purpose of this study was to compare methods used

for TOC determinations. Lack of access to data derived from

similar areas at the same time of year has hampered meaningful

comparison. Since I used basically the same wet oxidation

procedure as Sharp (1973), a comparison of results seemed
feasible if common areas of analysis could be found. There
appeared to be an overlap of my data from Stations 6 and 7
in the Scotian Slope area in August 1975 and with Sharp's
(1973) data from slope, Gulf Stream, and northern Sargasso
Sea of June 1971. In this comparison (Figure 6), it was
seen that Sharp measured higher TOC concentrations in his
wet oxidation method than I did. The small number of points
plus the differences in time and position of sampling will
explain some the discrepancy. The methodology was similar,
except for the modifications which have been discussed. If
Sharp was not completely removing the inorganic CO_2 during
his purging step as shown in Table V, his higher TOC values
and higher scatter, particularly at depth, may be explained.
The TOC results were compared as depth zones (Table X).
With a paired "t" test, the difference was found to be
significant at the 99% confidence level. Sharp's TOC values
are significantly higher (20%) than those obtained by my
work. Qualitatively the picture of the distribution with
depth is the same for both studies. A similar comparison
with the TOC data presented by Menzel (1967) for the same
region was attempted and Menzel's TOC values were found to
be about 10-15% lower than mine.

   ii) Comparison with Menzel (1970)

   The TOC data from Menzel (1970) for an area off the

TABLE X

Comparison of Wet Oxidation Results of Sharp (1973) and

MacKinnon (this study) from Similar Areas of the Atlantic

Depth Zone (m.)	n	TOC Measured by Sharp (1973) (mg.C/liter)	n	TOC Measured by MacKinnon (mg.C/liter)	Ratio of TOC(MacK.) / TOC(Sharp) (%)
0-25	6	1.29±.12	16	0.96±.06	74
26-75	5	1.18±.13	5	0.78±.11	66
100-400	6	0.92±.12	15	0.64±.04	70
500-900	5	0.79±.08	3	0.66±.01	84
1000-1400	6	0.80±.07	4	0.67±.04	84
1500-1700	6	0.79±.07	2	0.64	81
1800-2000	6	0.81±.11	3	0.64±.01	79

TABLE XI

Comparison of Wet Oxidation Results of Menzel (1970) and

MacKinnon (this study) from Off Coast of Africa

Depth Zone (m.)	n	TOC Measured by Menzel (1970) (mg.C/liter)	n	TOC Measured by MacKinnon (mg.C/liter)	Ratio of TOC(Menzel) / TOC(MacK.) (%)
1-50	20	0.99	24	1.13	88
50-150	20	0.87	10	0.78	112
150-250	20	0.75	7	0.77	97
250-500	50	0.59	15	0.73	81
500-900	80	0.53	10	0.63	84
1000-1500	50	0.51	9	0.64	80

TOC mg C/L

.6   .8   1.0   1.2   1.4

DEPTH (m)

500

1000

1500

2000
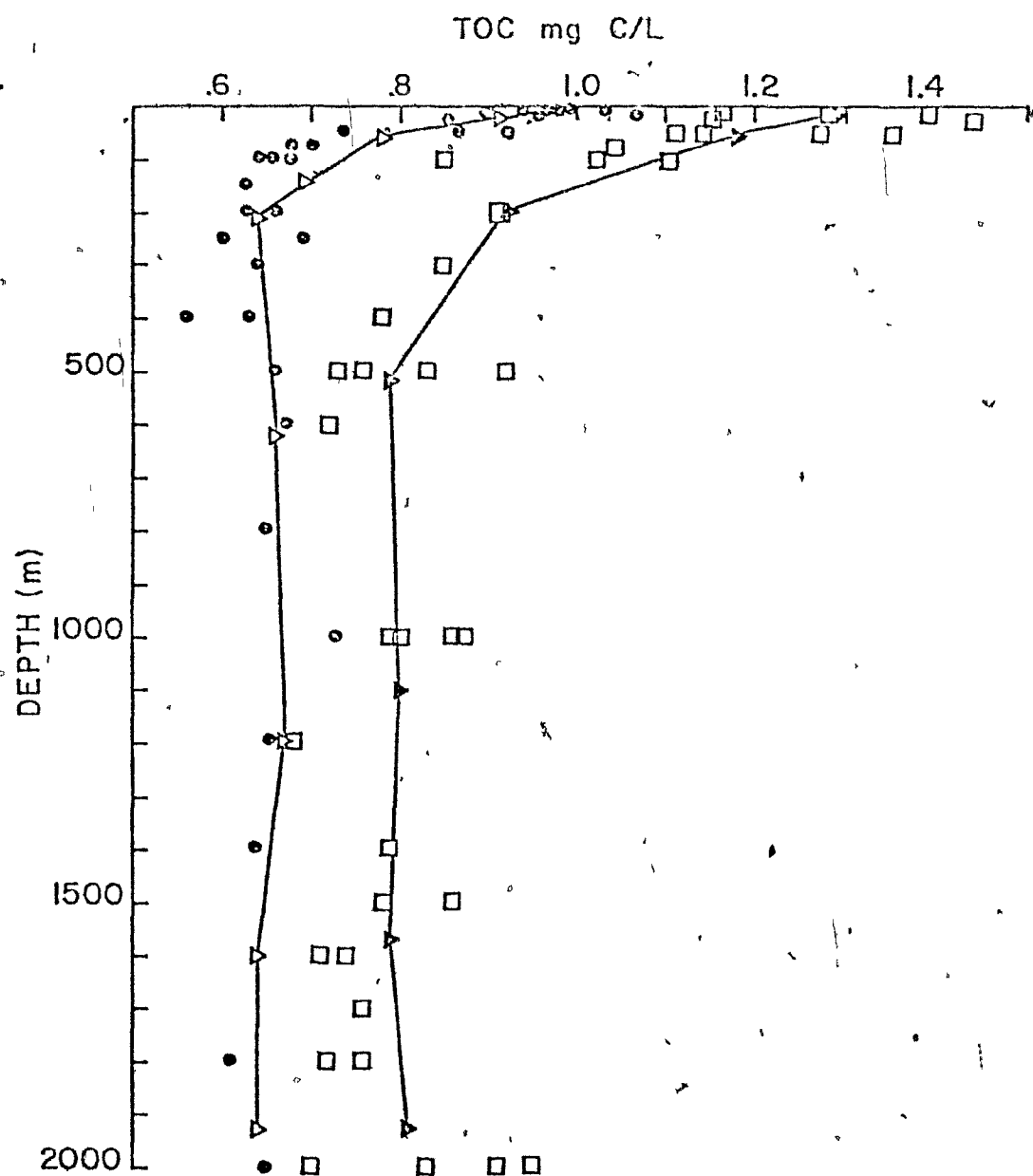
Fig. 1-6: Comparison of TOC values from Northwestern Atlantic
measured by wet oxidation methods of Sharp (1973) (□)
and MacKinnon (this study) (⊙).

▲ — averaged TOC values calculated from Sharp·(1973)

Δ — averaged TOC values calculated from MacKinnon
(this study).

coast of Africa and in the central Atlantic were compared with TOC values obtained by my wet oxidation in a similar area. The times and areas were not identical and values can be expected to be somewhat different. In Menzel's study, similar concentrations of TOC for several areas of the Atlantic were found below 500 m. Above 500 m, the values were more dependent on area. I compared his values for samples taken from an upwelling area off southwest Africa with those I obtained off Senegal (Table XI). In the top 250 meters, no significant difference in the TOC values from the two studies was found, but below 250 meters, my TOC results were significantly higher (about 20%) than those obtained by Menzel (1970). The surface zone is more susceptible to seasonal and spatial effects, so the comparison of the TOC values may not be truly significant unless simultaneous analysis had been carried out by both workers on the same samples. However, since smaller scale variations in TOC values are expected in deeper water samples, the comparison of TOC results from the two studies may be valid.

5. Conclusion

The TOC values which have been measured by my wet oxidation procedure in natural areas (Gulf of St. Lawrence, Scotian Shelf, and Sengal) have shown that the precision of my method is high for natural samples and that TOC values

similar to those reported by other workers can be obtained.
Also the variability and distributions that were found in
the TOC values were supported by other hydrographic data.
Comparison with previous studies has shown that TOC analyses by
my wet oxidation are lower than Sharp's (1973) but higher
than Menzel's (1967, 1970). These differences in the
calculated TOC values may be the result of different sampling
areas and times, but other explanations seem reasonable. If
Sharp did not completely remove the inorganic CO_2 or had
underestimated his reagent blanks, he would have obtained
higher TOC values than I found. If Menzel overestimated the
reagent blank or had encountered premature oxidation because
of his purging of the inorganic CO_2 in the presence of his
oxidant, his values for TOC would be lower than those
obtained in my study. These are obvious sources of difference,
which my study has pointed out, but not until simultaneous
analysis of natural samples are carried out will the difference
in TOC numbers by wet oxidation measured by different
workers be explained once and for all. In short, are the
differences we see the result of analytical problems or do
they really exist?

DETERMINATION OF TOC IN SEAWATER: DRY OXIDATION

A. Introduction

In wet oxidation methods, the organic matter is oxidized with an oxidant which is added to the water. In dry oxidation methods, the organic matter in dried samples is oxidized by chemical oxidants or high temperature oxidation. In seawater, the inorganic CO_2 is an interference which is removed, in the wet procedure by acidification and purging, while in dry methods the carbonate species are removed during the drying step. In both wet and dry methods the organic material is oxidized to CO_2, which is then analyzed. In the following work I hope to better define and quantify the relative efficiencies of the two approaches.

Krogh (1934) described a combustion method for dried fresh water samples but it was unsuccessful in seawater because of the salt interference. He tried a wet oxidation of the salt, and although superior to previous wet oxidation procedures, his TOC values were high and showed no vertical differentiation over a 5 Km vertical water column (TOC = 2.35 ± 0.09 mg C/liter).

Little work with the dry oxidation of TOC in seawater was reported until the Soviet workers presented their results in the 1960's (Skopintsev, 1960 and Skopintsev and Timofeyeva, 1962). Their dry combustion method was based on the evaporation of 30-40 ml of seawater at 50-60°C and the

high temperature oxidation (700°C) of the remaining salt.
The interfering substances produced by the high temperature
oxidation were removed and the CO_2 produced was analyzed by
a titrimetric determination. Values for TOC in the Atlantic
Ocean range from 0.99-2.71 mg C/liter with an average of
1.56 mg C/liter and a marked decrease in TOC concentration
with depth.

Skopintsev et al. (1968) compared TOC values from
similar ocean areas which had been analyzed by Duursma
(1961) and found that the TOC values by the wet oxidation
method of Duursma were about 50% of the dry oxidation
values. Skopintsev (1966, 1972) and Starikova (1970) have
analysed the TOC concentration in many areas and they noted
a consistency of the TOC results (between 1.00-2.50 mg
C/liter). Starikova suggested a common distribution of
organic carbon in seawater with highest values in the
surface zone and a steadily decreasing concentration with
depth, probably representative of the mineralization of
organic carbon occurring in the water column. This is a
direct contradiction of Menzel's (1967, 1968) idea of
refractory organic carbon.

The Skopintsev dry oxidation method is time consuming
(1-1.25 hours per analysis) and, although its precision
appears high, questions as to the accuracy have been raised
because of extensive handling and the types of detection

system (Sharp, 1973). With sample evaporation at 50-60°C, the loss of the volatile component of the TOC was complete. This loss was estimated at 15%.

A procedure in which the sample (10-50 ml) was distilled through a combustion furnace with subsequent combustion of the remaining residue was described by Montgomery and Thom (1962). Their high temperature combustion was complete with volatile determination by oxidation of the vapour during distillation. An infrared detector was used, but blanks were relatively high (0.7-3.0 mg C/liter), the time of analysis was also long (1.25-3 hours), and applicability to saline waters doubtful because of reduced sensitivity and interference.

Gordon and Sutcliffe (1973) developed a dry combustion method in which the seawater samples were prepared with a freeze drying procedure and aliquots of the resultant salt were oxidized in a Perkin-Elmer CHN analyzer. Distributions of TOC similar to those obtained by the Skopintsev (range of 1.00-2.8 mg C/liter) were found in the N. W. Atlantic. These values were about 2-3 times the TOC values reported by Duursma (1961) and Menzel (1967). Precision was high (about 8%) but problems with potential contamination by extensive handling and work up have been raised.

A long delay between sampling and analysis is required in all these dry methods. This may be overcome by a method

of direct sample injection into a combustion furnace. The sample size in direct injection is limited because of the water vapour production when the sample is introduced into the high temperature oxidation furnace (1 ml yields 5.6 liters of steam at 950°C). Since seawater has a low concentration of TOC and the amount of carbon that is introduced by these direct injection methods will be small, a very sensitive detection-system such as a non-dispersive IR or gas chromatograph is required.

Van Hall, Safranko and Stenger (1963) described a direct injection method in which 0.02 ml of samples purged of inorganic CO_2 was injected into a high temperature oxidation furnace and the produced CO_2 was measured with a non-dispersive IR. A detection limit of about 2 mg C/liter limited its use to fresh natural waters of high organic carbon concentration. Van Hall and Stenger (1967) modified this method by using a dual furnace unit which allowed determination of the total (high temperature combustion at 950°C) carbon and inorganic (low temperature acid treatment at 150°C) CO_2 in about 5 minutes. In this procedure the organic carbon content was determined by a different method. This method is less useful in seawater because the inorganic to organic carbon ratio is large. With a sensitivity of 2 mg C/liter, this method was limited to samples of high TOC concentrations. Jones and Dagefarde (1968) attempted to

improve the sensitivity by increasing sample size to 0.10 ml but it still had a lower limit of sensitivity of about 1 ppm, which is not enough for TOC analysis in seawater. This design was incorporated into the Beckman Total-Organic-Carbon-Analyzer, which works well for waste water (Busch, 1967).

West (1964) described a method which increased sensitivity in a direct injection method by the use of a gas chromatographic detection system. A sensitivity of 0.4 μg C with a precision of 8° was reported with fresh water, but the applicability of his procedure to saline waters appeared limited by interferences and by his combustion apparatus.

A commercial total carbon analyzer (Dohrmann DC-50) is a direct injection (Takahashi, Moore and Joyce, 1972) method in which the water (30 μl) is evaporated at 90°C. After the sample has been dried, the residue is oxidized to CO_2 and reduced to CH_4, which is analyzed by a flame ionization detector. With a system blank of 1-6 ppm, its application to saline waters is questionable. Pocklington (personal communication) has concluded that this instrument is not acceptable for seawater samples because of high blanks and large sample variability caused by interference from the salt or oxidative products.

All of these methods have been designed for waste or fresh water and their use in the analysis of TOC in seawater has been limited. Sharp (1973) developed a direct injection

method for the analysis of TOC in seawater. A 0.100 ml acidified sample, purged of inorganic CO_2, was injected into a combustion furnace at 1000°C, and the oxidized organic carbon was analyzed with a non-dispersive IR. A precision of about 5% with no measurable system blank or interference problems allowed determination of the TOC in seawater samples. Sample analysis required about 3 minutes and his system provided the possibility of shipboard analysis. However, maximum instrument sensitivity was required and the apparatus was a personalized piece of equipment. His precision was good but the scatter in his TOC results was high and the accuracy may have suffered. Of course, this variability might have been real, this will be discussed later. The TOC values in open ocean seawater samples varied from 0.75-1.8 mg C/liter and by direct comparison, he concluded that persulfate oxidation missed about 28% of TOC in natural samples. While Sharp's direct injection method yielded higher results than wet oxidation, his values were still only about 70-80% of the dry oxidation results of Gordon and Sutcliffe (1973) and the Soviet workers.

Controversies still exist in this field regarding the effectiveness of dry oxidation procedures. While individual workers have produced high precision in their analyses, the accuracy of these methods is still in question. The controversy between wet and dry oxidation values for TOC has

not been concluded and the development of real time analysis
of TOC from seawater samples has yet to become a reality
because of the problems of low organic carbon concentration,
high inorganic carbon concentration, chemical and physical
interferences, sample handling, and contamination. The
need for such an approach to TOC analysis has been discussed
by Wangersky (1975) but its introduction has been hampered
by the above problems.

I developed a dry oxidation method method in which the
sampling and handling procedure of Gordon and Sutcliffe
(1973) was used, the combustion method of Skopintsev (1960,
1966) was followed, and the TOC values could be compared to
the lower values of Sharp (1972). I will attempt to prove
that previous high temperature oxidation systems have led to
overestimations of the TOC in seawater because of systematic
errors and contamination. Also I will compare the TOC-
values obtained by the wet and dry oxidation methods from
simultaneous samples.

Two methods for dry oxidation will be described and the
advantages and disadvantages of both will be discussed.
Neither of these techniques solves the problem of real time
analysis of samples since both require a discrete sample,
work up, and analysis. One involves the evaporation of a
larger volume (15-20 ml) of acidified sample from which an
aliquot of the salt is removed and oxidized in a high

temperature oxidation furnace. Uncertainties pertaining to
the homogeneity of the salt and loss by absorption to
container were investigated by a second dry method in which
aliquots of acidified sample were evaporated in large tubes
and then oxidized. In this procedure the sample handling
was reduced but blank and contamination problems may have
offset this advantage. The TOC results from the two methods
will be compared. In the following pages, the method
development, evaluation of results, and applicability for TOC
analysis in natural seawater samples will be examined.

B.   Development of Dry Oxidation Methods

1.   Sample Preparation

a)   Contamination Problem

In the analysis of TOC in seawater, scrupulous care
with sampling procedures and preparation is required to
ensure that the organic carbon that one measures has not
been altered in the handling. At concentration
ranges of 0.5-1.5 mg C/liter, the seawater samples contain
0.5-1.5 µg C/ml. The TOC results will be invalidated by
minor contamination. Both discrete and systematic contaminations
must be prevented.

In most cases a "wild value" (2-3 times mean) in
homogeneous water can be eliminated unless explained by
other factors since they are usually the result of contamination.
This does not eliminate the possibility of inhomogeneity in

the TOC distribution in natural waters, but questions the acceptance of unexplained high TOC results as being "real" unless trends in other hydrographic parameters are noted.

Discrete "wild values" are easy to locate, but it is more difficult to identify systematic contamination which may have a small individual effect but will be uniform throughout a set of samples. This makes the control and quantification of this contamination difficult because it is not always obvious. In dry oxidation procedures, the accuracy and precision will be reduced by contaminants added during the collecting, storing, and transporting of the samples, in drying the samples, and in oxidizing the dried salt.

b)   Sample Collection

Most water samples were collected with Niskin bottles (General Oceanics) which were fitted with stainless steel springs instead of the usual surgical rubber tubing (no obvious source of contamination was observed from the rubber). The Niskins and the stopcocks for sample delivery were kept clean and sample contact was kept as short as possible.

After the sample was withdrawn from the Niskin, it was stored in a 50 ml ampoule, sealed, and frozen. The feasibility of filtration of the seawater samples has been questioned (Gordon and Sutcliffe, 1973, and Sharp, 1973) since the particulate organic carbon (POC) is seldom more than 10% of

TABLE I

Effect of the Addition of Concentrated H_3PO_4 on the TOC Values

Samples of Seawater (20 ml.)	Number of Drops of Acid Added From a #20 Gauge Needle	Measured TOC Concentration (mg C/liter)
1	1	0.92
2	2	0.96
3	3	0.89
4	3	0.92
5	4	0.93
6	4	0.94
7	5	1.01
8	6	0.97
	MEAN	0.94±.04

TABLE II

Effect of the Type of Septa on TOC Concentration in Seawater

Sample	Depth	T.O.C. Measured (mg.C/liter)		% Δ
		A Samples Sealed with Butyl Rubber Septa	B Samples Sealed with Hycar Septa	{(A-B)/B} x100
1. N.W.Arm	1	1.75±.15	1.60	+ 9.4
	15	1.40±.03	1.25±.06	+12.0
(10/7/75)				
2. N.W.Arm	1	1.44±.08	1.24±.04	+16.1
	10	1.40±.03	1.12±.01	+25.0
(10/7/75)				
3. N.W.Arm	1	1.58±.02	1.62±.01	- 2.5
	10	1.38±.01	1.42	- 2.8
(24/7/75)				
4. N.W.Arm	1	1.87±.01	1.58±.04	+18.4
	10	1.73±.06	1.52±.01	+13.8
(24/7/75)				
MEAN =		1.57	1.42	+10.5

the TOC in natural waters and only about 1-2° of the TOC in open ocean.' Contamination from the filtration could be potentially this high and only in areas with high particulate content did filtration seem necessary.

The seawater samples were immediately acidified to a pH of 2-3 with concentrated phosphoric acid (about 3-4 drops of reagent grade 85% ortho phosphoric acid from a #20 gauge needle to 20-30 ml of seawater) so that the inorganic carbonate species were converted to CO_2 and removed during the drying procedure. The potential contamination from the phosphoric acid was estimated by the addition of 1-6 drops of the phosphoric acid to a series of 15 ml samples of identical seawater which were then evaporated and analyzed. The effect of the acid on the measured TOC concentration was negligible, with the variation in TOC (0.94 ± 0.04 mg C/liter) within the precision of the method (Table 1). The pH effect also appeared to be negligible since in the pH range of 4-5 (1 drop of acid) to 1-2 (6 drops of acid), the measured TOC concentrations were about the same.

c) Storage of Samples

1) Effect of Sample Container

After the sample was collected and acidified, the serum bottle was capped with a septum, sealed with an aluminium seal and frozen. Since the septum is rubber, it is a source of contamination which must be considered. Gordon

and Sutcliffe (1973) reported that butyl rubber septa were inert, but I have found that they are not inert and are potentially a major source of contamination. The use of harder rubber such as Hycar septa (Pierce Chemical Co. #13230) after dilute acid washing and seawater aging is recommended, since Hycar septa are less susceptible to organic carbon bleed.

A strong rubber odor was noted when samples were stored with butyl rubber septa; this odor was not evident with samples sealed with the Hycar septa. The TOC contaminations for samples stored with the butyl septa were both higher and more variable than noted with the samples stored with the Hycar septa (Table II). Samples taken from the N. W. Arm, were treated identically except that half were stoppered with Hycar septa and the other half with butyl rubber. These samples were frozen and stored for 1-2 weeks before analysis. The difference between the pairs of TOC values was significant by a paired "t" test at the 95% confidence level. Higher TOC values (ave. difference = 11±3.5%) were obtained with the butyl rubber stoppers with a difference ranging from - 2.8% to +25%.

11) Septum Effects on TOC During Sample Storage

The rate and amount of contamination appeared to be dependent on how effectively the septa had been aged and

TABLE III

Effect on the TOC Values of Water Samples Stored With Various Septa

Depth	Station A 26°00'N, 62°45'W		T.O.C. Measured (mg.C/liter) Station B 32°50'N, 62°40'W		
	Samples stored with Hycar Septa for 3 months	Samples stored with Butyl Rubber Septa for 3 months	Samples stored with Hycar Septa for 3 months	Samples stored with Butyl Rubber Septa for 9 months (a.)	Samples stored with Butyl Rubber Septa for 9 months (b.)
10	0.99	1.02	1.02	1.54	
15		0.95		2.30	
20	0.93	0.90	0.99	1.56	
25		0.93		1.28	
MEAN =	0.96	0.95±.05	1.01	1.68±.43	
350	0.80	0.99	0.70,0.76	1.45	0.96
355		0.96		1.30	1.03
360		0.89		1.54	1.14
365		0.90	0.73	1.43	1.00
MEAN =	0.80	0.94±.05	0.73	1.43±.10	1.03±.08
985	0.80	0.98	0.66	1.05	0.98
990		0.97	0.64	0.82	1.17
995		0.89	0.70	1.05	1.54
1000	0.70	0.96	0.71,0.68	1.02	1.25
MEAN =	0.70	0.95±.04	0.68±.03	0.99±.11	1.24±.23

cleaned and by the time of storage of the frozen sample. A comparison of samples handled the same way but stored for different times (Table III) was performed on samples collected in the Sargasso Sea (2/75) by Dr. D. Gordon and myself. These seawater samples were acidified, frozen and stored for periods of 3 months and 9 months. Large and significant differences in the measured TOC values were evident with the samples sealed with the different septa for different periods of time.

While the samples were not collected from identical water, the discrepancies in TOC values cannot be explained by water mass differences nor solely from contamination by different Niskin samplers. The samples stored for 3 months with Hycar were found to yield lower and more consistent TOC concentrations (Table III) than samples stored for 3 months with the butyl rubber septa (TOC values were about 20-25% higher in the deeper water samples while they were comparable in the surface samples). However, the samples which had been sealed with the butyl rubber septa and stored for 9 months gave much higher and more variable TOC values between samples. In column (a) and (b) (Station B) of Table III, the TOC results from the different casts in the same water are shown. These samples had been stored for the same length of time (9 months) and yet the TOC values varied as much as 50% from each other. These TOC concentrations

were significantly higher than those calculated for the samples stored for 3 months with the Hycar septa (50-100% higher) and were also higher than those for samples stored for 3 months with the butyl rubber septa (5-70%).

The contamination from the septa is possibly a major source of the high TOC values found by Gordon and Sutcliffe (1973) in their analysis since they used the butyl rubber septa. The contamination was not constant and was dependent on factors such as the aging and cleaning of the butyl septa, length of storage, contact of water with the septa, and presence of septa during the freeze drying procedures. If samples are to be stored with a septa, the butyl rubber is a poor choice and is not recommended. Better accuracy and precision should be obtained in the TOC analysis if more inert materials like Hycar, silicone, teflon or viton are used for the septa after being carefully cleaned.

d)   Drying the Samples for the Dry Oxidation Methods

1)   Freeze Drying

Freeze drying was carried out in a Virtis (bench model 10-800) freeze drier in the early development of the method and the results were encouraging. However, when I was forced to use other freeze driers, contamination problems became unacceptable. A method for the determination of the contamination during the sample drying is described by Gordon and Sutcliffe (1973) in which identical samples were

run for different lengths of time in the freeze drier and any changes in the TOC results were measured. In their procedure contamination is assumed to be a function of the time in the drying chamber. I do not agree with this method because I feel that the dried salt is surface active and the salt should become saturated with the organic contaminants.

I determined the contamination of the drying system with freeze dried salts which had been cleaned for several hours at 450°C. These samples were handled identically to a natural sample and run through the drying procedure. The difference in the measured carbon before and after the drying step will be the amount of contamination picked up during the freeze drying step. The concentration of organic carbon added by this contamination in the freeze drier was estimated to be in the 0.5-2.0 mg C/liter range which for the analysis of TOC in seawater is unacceptably high. This can be assumed to be the maximum "potential" contamination (D. Cordon, personal communication) since the salt was freshly oxidized and the absorbance of contaminants by the salt should have been maximized. During sample drying, water is continually sublimating, and diffusion of contaminants into the sample container should be prevented because of the water vapor from the sample. If this "potential" contamination can be held to a minimum, the actual contamination of the samples during drying will be

small. In a freeze drier the condenser (-30 to -40°C)
should prevent contamination from the vacuum pump. If the
chamber was cleaned of all grease and of the potential
contaminants (rubber O-rings, septa, plasticizers) a
reduction in the contamination should be noted. Dr. D.
Cordon attempted this, and after much work lowered the
contamination. It still remained unacceptably high.
However, the freeze drier does not operate with a perfect
vacuum (5-50 μ of Hg), and if the laboratory air with
organic contaminants enters the chamber, the contaminants
may be adsorbed onto the fresh dried salt. Contamination
may be derived from the rubber O-ring required for a good
vacuum seal around the door of the chamber or other organic
materials which are used in the construction of the chamber.

11) Evaporation

I have designed a simple drying system in which there
are no organic materials and which is easy and inexpensive to
construct. However, it is slower than a freeze drier,
operates at a higher temperature, and the resulting salt
contains more water than in freeze drying so that a water
correction in analysis must be made. A cleaned vacuum
desiccator was used as the drying chamber and the vacuum
was provided by a water aspirator. The desiccator was
enclosed in a large glass battery jar into which purified
air (passed through CuO catalyst at 900°C) was introduced at

a rate of 1-2 liters/minute. The ground glass of the desiccator did not make a perfect seal and a vacuum of only about 7-15 mm Hg was obtained with a water aspirator. However, since only purified air, which filled the battery jar, would enter the desiccator, contamination was minimized.

The potential contamination observed with the freshly oxidized sea salts was in the range of 0-0.15 mg C/liter with an average of 0.05-0.1 mg C/liter. When the drying step was tried with freshly oxidized salts (450°C heating) which had been dissolved in 15 ml of Super-Q water, a blank approaching zero was obtained; the blank with no water addition showed a 0.15 mg C/liter carbon pick-up. With the presence of water during the drying step, the contamination will be reduced to negligible amounts. With this approach, very low blanks from my evaporation system were obtained, which for natural seawater samples seemed acceptable.

iii) Comparison of Freeze Drying and Evaporation for the Preparation of Samples

In Table V, a comparison between results obtained with the freeze drier and my evaporator is presented. Dr. D. Gordon collected replicate samples from Bedford Basin. Half were prepared in his freeze drier and half in my evaporator. Both sets were measured by my combustion procedure. The TOC values obtained by freeze drying the samples were significantly

TABLE V

Comparison of Freeze Dried and Evaporated Samples from

Bedford Basin Analyzed By Dry Oxidation Method (#1)

T.O.C. Concentration Measured for Samples Prepared in Freeze Drier (mg.C/l.)	T.O.C. Concentration Measured for Samples Prepared in the Evaporator (mg.C/l.)
2.80	2.18
2.78	2.11
2.70	2.04
2.73	1.89
2.56	2.27
2.68	1.95
2.51	
2.63	
2.61	

n=	9	6
MEAN=	2.67±.10	2.07±.14

higher by a "t" test at the 99° confidence level. About 29%
more organic carbon was measured in the freeze dried samples
(2.67 ± 0.10 mg C/liter) than in the evaporated samples
(2.07 ± 0.14 mg C/liter), indicating a major source of
contamination in the freeze drier.

Contamination from both the freeze drier and septa
(seal for the serum bottles) was examined (Table VI) in
samples from Petpeswick Inlet. Half were prepared by freeze
drying and half by my evaporation system. Those in the
freeze drying process were capped with either butyl rubber or
Hycar septa, while the evaporated samples used only the Hycar
septa. Dr. W. Sutcliffe prepared and analyzed the freeze
dried salts in a Perkin-Elmer CHN analyzer, obtaining C/N
ratios as well as the TOC. The evaporated samples were run
in my analyzer and the Perkin-Elmer CHN analyzer. The
results from both methods were not significantly different
(2.41 vs. 2.28 mg C/liter) by a paired "t" test at the 95%
confidence level. Thus the same fraction of organic carbon
was being measured by the two oxidation prodedures.

However, a significant difference by a paired "t" test
at 95% confidence level was found between the TOC values for the
freeze dried samples (3.21 ± 0.1 mg C/liter) and the
evaporated samples (2.42 ± 0.03 mg C/liter) in which the
Hycar septa were used. When seawater samples were prepared

TABLE VI

Effect of the Drying Procedure and the Type of Septa on the D.O.C. Concentrations and C/N Values For Samples From Petpeswick Inlet

Sample	Samples Dried by Evaporation		Samples Dried in Freeze Drier		
	D.O.C. Concentration (mg.C/l.) Measured by MacKinnon Dry Oxidation Method #1 Samples Sealed With Hycar Septa	C/N Ratio Measured by Sutcliffe CHN Analyzer Samples Sealed with Hycar Septa	D.O.C. Concentration (mg.C/l.) Measured by Sutcliffe CHN Analyzer Samples Sealed with Butyl Rubber Septa	Measured by Sutcliffe CHN Analyzer Samples Sealed with Hycar Septa	C/N Ratio Measured by Sutcliffe CHN Analyzer Samples Sealed with Hycar Septa
1.	2.45	2.37	3.79	3.30	5.96
2.	2.37	2.52	3.27	3.16	6.56
3.	2.36	1.90	3.27	3.18	2.67
4.	2.47	2.69	3.68	2.89	3.76
5.	2.42	1.94	3.29	3.50	3.43
MEAN =	2.41±.03	2.28±.16	3.60±.14	3.21±.10	4.48±.80

Note: C/N Ratio values under "Samples Dried by Evaporation" column (Measured by Sutcliffe CHN Analyzer Samples Sealed with Hycar Septa): 7.85, 8.34, 14.20, 9.80, 6.69, MEAN = 9.38±1.3

by the freeze drying method, a difference of about 12% was noted between the Hycar stoppered samples (3.21 mg C/liter) and the butyl rubber stoppered samples (3.60 mg C/liter). This difference in TOC was concluded to be the result of contamination from the butyl rubber septa.

The C/N ratios obtained for the samples which were stoppered with Hycar septa were compared. The samples prepared in the freeze drier were found to be significantly different, by a paired "t" test at the 95% confidence level, from the samples which were dried in the evaporator. The average C/N obtained for the evaporated samples (C/N = 9.38 ± 1.3) was twice the average C/N ratio obtained for the freeze dried samples (C/N = 4.48 ± 0.8). In natural waters a C/N ratio of less than 6 is difficult to explain unless the organic composition is mainly urea or other highly nitrogenous compounds. The C/N ratios for the evaporated samples appear to be more believable than those for the samples prepared in the freeze drier. These results seem to confirm the contamination problems with the freeze drier which I think are overcome by using my evaporator.

iv) Water Effects

The seawater samples dried in the evaporator are not as easy to work with as those prepared by the freeze drier and the salts are more difficult to scrape from the walls of the serum bottle. The water content (both absorbed water and

water of hydration) of the residual salt is higher in the evaporated salts. In my dry oxidation method #2, where 5 ml aliquots of the sample are dried in individual tubes, this water content is not a problem, but in dry oxidation method #1, where aliquots of the evaporated salt are weighed and analyzed, the water content becomes critical. In this method the concentration of TOC is calculated by measuring the ug C/mg salt. The seawater volume equivalent that is introduced into the combustion furnace, is calculated from the salinity. The concentration can be expressed as ug C/ml of mg C/liter. If the water content is high, the weighed salt aliquot will yield as overestimate of the volume equivalent of sample introduced into the furnace and thus the calculated estimate of the real concentration will be lower. A water correction is required and is easily computed. An aliquot of salt from the dried sample is weighed, heated to 350°C for 1 hour and the water loss is calculated. Strickland and Parsons (1968) define salinity as "weight in grams of the solids obtained from 1 Kg. of seawater when the solids have been dried to a constant weight at 480°C, the organic matter completely oxidized, the bromide and the iodide replaced by an equivalent amount of chloride and carbonates converted to oxides". The corrected TOC value of the sample is computed by the relationship

$$\text{water in salt aliquot} = \frac{\text{weight loss on heating at } 350°C}{\text{weight of salt aliquot}} \times 100$$

$$\text{volume equivalent of salt aliquot} = \frac{\text{grams of salt aliquot weighed (g)}}{\text{salinity (g/ml)}}$$

$$\begin{array}{l}\text{concentration of organic carbon C} = \dfrac{\mu g \text{ C measured}}{\text{volume equivalent}} = \mu g. \text{ C/ml} \\ \text{(uncorrected)}\end{array}$$

$$\begin{array}{l}\text{concentration of organic carbon C} = [C] \text{ uncorrected} \times \dfrac{1}{1 - \% \text{ water}} \\ \text{(corrected for water in salt)}\end{array}$$

The water content of a random group of samples (n=236) averaged $10.9 \pm 1.8\%$ with a range of $7.2 - 16.9\%$. This water correction is major but is relatively constant (about 11%).

Another drawback of the evaporator system is that the drying time for seawater samples is quite long (about 72 hours are required to dry 15-20 ml of seawater). Since the evaporation is done at slightly above room temperature there is the possibility of thermal degradation, while in the freeze drier, where the water sublimes from frozen samples, this degradation is minimized. In the evaporator system, the loss of volatile organic materials has been observed but thermal breakdown has not been noted during the drying.

2. High Temperature Oxidation of Seawater Samples

I developed a high temperature oxidation system based on that of Skopintsev (1960). The oxidation furnace consisted of a quartz combustion tube heated in a furnace at $800-900°C$ into which the sample was introduced. Oxidation

was carried out in an O_2 atmosphere at high temperature
(800-900°C) and the CO, produced by the organic carbon
oxidation was swept to a non-dispersive IR where it was
measured.

    1)   Interferences in High Temperature Oxidation Procedures

    In the initial work with the combustion system, the
interferences from products of high temperature oxidation of
the salt prevented any meaningful results. The CO_2 peak was
a sharp symmetrical peak followed by a long tailing peak
which took 10-20 minutes to be flushed from the system.
Interference from HCl formed during high temperature
combustion of the salts (Skopintsev, 1960) was expected.
Although interfering gases (Cl_2, I_2, HI, HCl, NO_2 and SO_2)
were reported during wet oxidation (Duursma, 1961), their
interference with the infrared detector should have been
small (Wilson, 1961). A KI and H_2SO_4 trap (Menzel, 1964) was
used to remove Cl_2 but in my system it was not effective
since the KI solution was very quickly oxidized. A
manganese dioxide trap was tried (Montgomery and Thom, 1962)
and was found to be partially successful but quickly
overloaded.

    Using the system of traps of Skopintsev (1960) the
interfering material was eliminated. This system consisted
of a ferrous chloride trap (25% in dilute H_2SO_4) in which the

interfering materials (probably Cl_2 and oxides of S and N_2) formed during high temperature oxidation of the salt residue were reduced but the produced CO_2 was not affected. A second trap of silver sulfate (saturated in dilute sulfuric acid) was used to precipitate chlorides produced by the reduction of Cl_2 in the first trap. The $FeCl_2$ (25%) trap was found to completely remove the interferences from the gas stream, to have a large capacity, and to be good for a regular day of analysis without overloading. This trap did not interfere with the CO_2 concentration from the oxidation of the organic matter and had only a minimal effect on the peak shape.

Interference from water in the sample and traps was overcome with a condenser in ice followed by two Anhydrone ($Mg(ClO_4)_2$) traps. The $Mg(ClO_4)_2$ has a large water capacity and, unlike Drierite ($CaSO_4$), exhibits no adsorption of CO_2.

Contamination from the O_2, that was used for the oxidation of the organic matter, was eliminated by oxidizing the contaminants at 850°C and removing any oxidative products (CO_2) before it was introduced to the combustion furnace. In some systems, the CO_2 from the oxidation of the sample is collected in a trap such as $Ba(OH)_2$ (Skopintsev, 1960) or liquid N_2 during the oxidation and the amount of CO_2 trapped is measured.

however, I noted that even with pure quartz, at the temperatures of oxidation (800-950°C) a small trace of CO_2 bleed was measured. Unless this is corrected for, it will lead to an overestimate of the organic carbon in the sample. Although their blanks would indicate this source of contamination, the higher TOC values of Skopintsev could be explained by this simple source of CO_2 contaminant from the oxidation of carbon impurities in the quartz combustion tubes.

ii) Conditions for the Oxidation

a) Temperature and Time

Since I had no interference problems with the salt from the sample melting and vapourizing (Gordon and Sutcliffe, 1973), a temperature of 800-900°C was found suitable for the oxidation. An oxidation time of 3 minutes at 800-900°C in an O_2 atmosphere was used, and complete oxidation was indicated since salts that had been oxidized could be rerun in the furnace with O_2 atmosphere and no further CO_2 production could be detected.

b) Flow Rates in the System

The flow rates for the oxidation were chosen so that time of analysis was reasonable and symmetrical peaks could be obtained. The flow rates were adjusted to give sharp symmetrical peaks in the linear response range of the detector. A slow (50-75 ml/min) flow of O_2 was used during the oxidation step, and was replaced by a fast (300-350

ml/min) flow of N₂ to sweep the oxidative products through the system and into the analyzer after the oxidation was completed. The system had sufficient dead space between the oxidation furnace and the IR detector to prevent premature measurement of the oxidative products before the fast flow of N_2 was initiated. A second combustion tube, packed with a platinized asbestos catalyst, followed the initial oxidation chamber to ensure complete oxidation.

c)   Calibration of Detector

To ensure reproducibility, the span of the IR analyzer was set each day with a standard gas (100 ppm CO_2 in N_2) before samples were run. Then a calibration curve was obtained with a standard solution of dextrose in Super-Q water (concentration 1-2 µg C/µl) which was quick, precise, and accurate to use. Over the expected concentration range of TOC in seawater, the analyzer was found to respond linearly so that the calculation of organic carbon in the natural samples was simplified.

iii) Dry Oxidation Method #1

In this method, an aliquot of the dried salt is placed in a quartz container that is then moved into the combustion zone of a furnace (quartz tubes 15 mm OD - heated at 850-900°C). The amount of organic carbon in the sample was measured and with the volume equivalent calculated from the salinity, water content of the salt, and weight of the salt

aliquot, the concentration of the carbon in the seawater was determined. The seawater sample (15-20 ml) was evaporated in my drying system and when the salt was dry and crystalline, aliquots of the salt were transferred to a cleaned (heated to 600°C for several hours) quartz container (2.5 cm x 9 mm OD). The quartz container was handled only with metal forceps or tongs and with proper precautions extremely good replication and minimal contamination was obtained.

The only contact with this quartz container was made during the salt weighing. The reagent blank from the phosphoric acid addition during acidification was found to be negligible (Table I). The system blank (amount of carbon introduced in the quartz container and its delivery system) was determined by the analysis of empty tubes which have been handled in the same manner as sample tubes. The variability of the blank, which is as important as its absolute value, was small. A normal blank of 0.05-0.2 ± 0.1 µg C was usual which, for an average sample of 4-5 ml (salt equivalent), represented about 0.01-0.04 mg C/liter. This was quite acceptable and within the method's precision. During regular analysis, a blank or standard was run every 2 or 3 samples to ensure instrumental reproducibility and to check for any gross contamination in the delivery system.

Samples were run at least in duplicate and if the values varied by more than 10%, a third replicate was run.

The precision of the method should not be worse than 5% and usually was in the order of .2 to 3%. Calibration curves were obtained (Figure 1) with a dextrose standard solution (1.45 µg C/µl). The slope of the calibration lines for standards prepared by direct injection into the quartz tubes (581 counts/µg C) was higher than the uncorrected slope for the standards that were added to 15 ml seawater samples (530 counts/µg C) and treated like a regular sample (dried in evaporator, salt scraped, a salt aliquot weighed, and oxidized in oxidation furnace). However, when these latter standards were corrected for their water content, the calculated slope (586 counts/µg C) was the same as that obtained for the standards prepared by direct injection into the quartz containers (581 counts/µg C). This indicated that with the water correction the method was accurate and precise.

The per cent recovery of standards with my dry oxidation method was calculated (Table VII). When the water correction was considered, the per cent recoveries were about 100%, which showed there was no significant loss of organic material during the drying step and no dramatic contamination in the oxidation procedure, although low level systematic errors may have been included. This method appeared to be feasible for the determination of TOC in seawater.

Fig. 2-1: Calibration lines for Dry Oxidation Method #1 prepared
with a Dextrose standard. a) direct addition ●
precleaned quartz tubes (slope 58 counts/μg C) b) added
to seawater sample (■) that was dried and analyzed
(slope 530 counts/μg C) with no water correction. c)
added to seawater sample (▲) where correction was made
for the water of resulting dried salt (slope 586 counts/μg C).

Fig. 2-2: Calibration lines for Dry Oxidation Method #2 prepared
with a Dextrose standard. 1. Direct addition (●)
precleaned quartz containers (slope = 546 counts/μg C)
versus addition into super Q water (▲) that was dried
in the quartz tube (slope = 548 count/μg C) 2. Direct
addition∧into precleaned quartz containers (slope =
461 counts/μg C) versus addition to seawater samples
(■) which were dried in the quartz container (slope
= 492 counts/μg C).

COUNTS / SAMPLE X 10³

DEXTROSE ADDED (µg)

FIGURE 2-2

COUNTS/SAMPLE

DEXTROSE ADDED (µg C/SAMPLE)
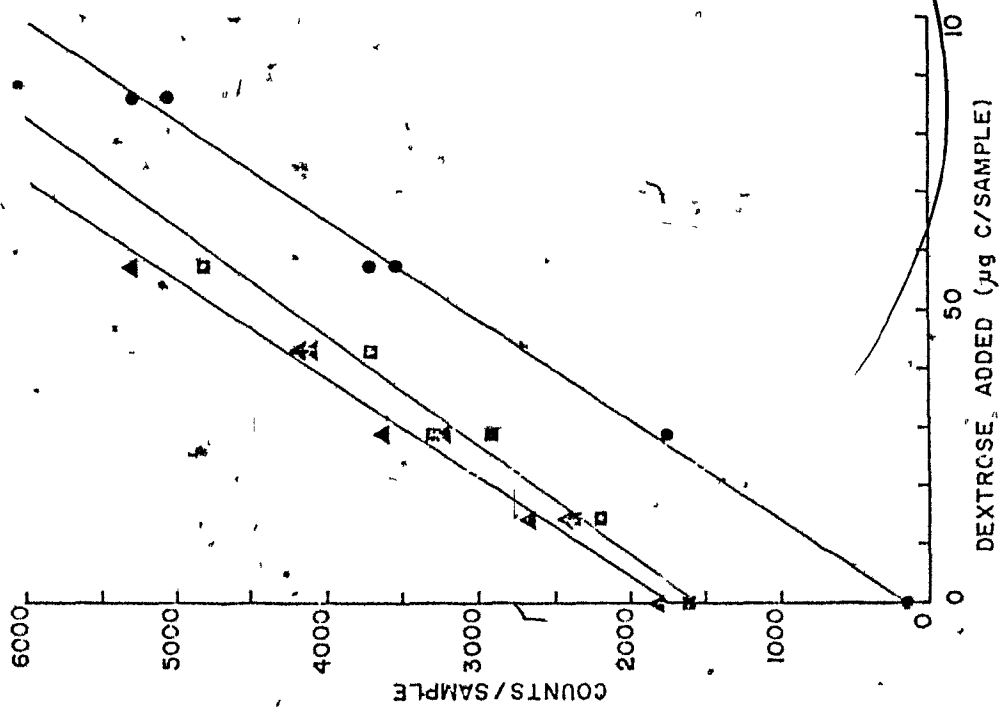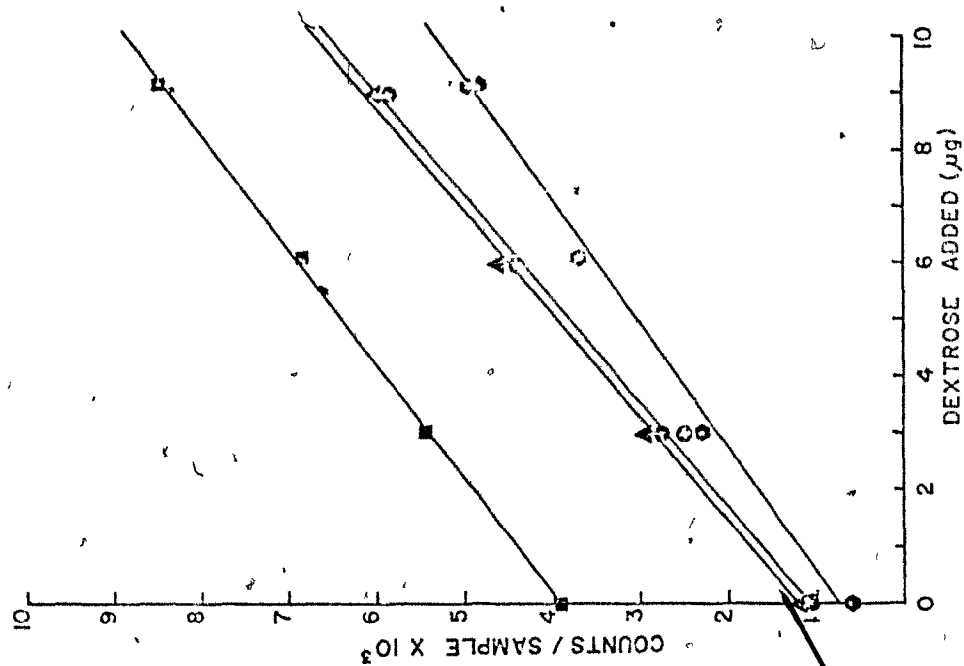
FIGURE 2-1

TABLE VII

Analysis of Standards Added to Seawater Samples
By Dry Oxidation Method #1

Standard Added	Calculated TOC Concentration Sample + Standard (mg C/liter)	Measured TOC Concentration (mg C/liter)	TOC Concentration Corrected for Water Content (mg C/liter)	% Recovery
1.Dextrose	1.51	1.31±.04	1.45±.05	96
(1.45	2.00	1.78±.07	1.93±.08	97
μg/μl)	2.48	2.13±.02	2.38±.02	96
	2.96	2.76±.06	3.04±.07	103
2.Dextrose	1.60	1.47±.01	1.65±.01	103
(1.48	1.89	1.68	1.89	100
μg/μl)	2.35	2.07±.10	2.33±.12	99
	2.88	2.54±.06	2.85±.07	99
3.Phenylalanine	1.56	1.37±.05	1.54±.06	99
(2.29	2.02	1.75±.06	1.97±.07	98
μg/μl)	2.78	2.49±.10	2.80±.11	101
	3.54	2.93±.01	3.29±.01	93
4.Dextrose	1.65	1.72±.09	1.93±.11	104
(1.48	2.22	1.90±.02	2.13±.02	96
μg/μl)	2.59	2.30±.09	2.58±.11	100
5.Phenylalanine	1.68	1.52±.03	1.70±.04	101
(2.29	2.25	1.91±.06	2.15±.07	96
μg/μl)	2.83	2.31±.03	2.59±.04	90

TABLE VIII

COMPARISON OF DRY OXIDATION METHOD #1 AND #2

Sample Area	n	Average TOC (mg C/liter) Method#1	Method#2	Difference by paired "t" test at 95% confidence level
1.Gulf of St.Lawrence May 1975	42	1.22±0.28	1.24±0.31	not signif.
2.Scotian Shelf August 1975	50	1.03±0.23	1.02±0.25	not signif.
3.Gulf of St.Lawrence Nov. 1975	29	1.11±0.14	1.09±0.19	not signif.
4.Coast Region	12	1.52±0.19	1.52±0.19	not. signif.

iv)   Outline of Dry Method #1

a)   Collection of Samples

About 30-35 ml of the sample were collected in precleaned (450°C) 50 ml. serum bottles (Pierce Chemical Co. # 12969) which were rinsed at least three times with the sample. About 0.05 ml of conc. H_3PO_4 (Reagent grade orthophosphoric acid) were added, the serum bottle was stoppered with a Hycar Septum (Pierce Chemical Co. # 13231), sealed with an aluminum seal (Pierce Chemical Co. # 13213) and immediately frozen until analysis.

b)   Preparation of Samples

The samples which had been collected and frozen were thawed. They were swirled to ensure that they were well mixed and a volume of 15-25 ml of the sample was dried. Sample drying was carried out in an evaporator from which all grease and organic materials were removed. The drying chamber consisted of an all glass vacuum desiccator (200 mm OD). A water aspirator was used for vacuum. The desiccator was placed in a large glass battery jar (300 mm OD) into which purified air (air passed through a furnace at 900°C to oxidize organic impurities) was introduced (1-2 liters /min.). After the Hycar septa was removed from the serum bottle, the samples were individually covered with pieces of perforated aluminum foil. These covered serum bottles were placed in the desiccator with some Drierite and

were dried for a period of 50-75 hours under 'vacuum' (7-15 mm) at room temperature" (25-30°C). After the samples had dried, they were removed and the salts on the walls of the serum bottle were scraped and well pulverized. If not run immediately, the samples were resealed with septa and frozen until analysis.

c) Analysis

Prior to analysis, the samples were placed in an oven at 60-70°C until the salt was powdery dry and well mixed. Subsamples of about 125-250 mg of sample salt were weighed into quartz sample containers (2.5 cm x 9 mm OD, 7 mm ID).

The quartz container with the sample was placed into the cool part of the combustion tube (3 ft. x 13 mm OD, 11 mm ID). A second combustion tube packed with a platinized asbestos catalyst was placed in line after the main combustion tube. After the sample was introduced into the combustion tube, the system was purged of atmospheric CO_2 with a fast flow (aprox. 300-350 ml/min.) of N_2. With flow meters placed in line before the reaction train and after the infrared analyzer (Beckman IR 15A), leaks were detected before the sample was run. A Tygon tube (13 mm ID) was fitted over the ends of the combustion tube and good seals at the connections were found.

When the analyzer returned to baseline after the

atmospheric CO_2 had been flushed from the system, the fast flow of N_2 was replaced with a slower flow (approx. 50-60 ml/min) of O_2. After 60 seconds the sample in the quartz container was introduced into the hot part of the furnace (approx. 800-850°C) by use of a system in which the sample was pushed with a glass rod which could be manipulated without atmosphere leakage into the system. The oxidation of the salt sample under the flow of O_2 was continued for 3 minutes. There was enough dead space in the combustion system so that no signal was recorded during this period. After the oxidation, a faster flow of N_2 (300-350 ml/min) was used to flush the oxidation products through the remainder of the system which included an acidified FeCl trap (25-40% w/v) a Ag_2SO_4 trap (saturated), an ice condenser (0°C) and two drying columns ($Mg(ClO_4)_2$). The CO_2 was measured with a non-dispersive infrared analyzer (Beckman IR 15A) whose signal was integrated (Royson Lectrocount 11½) and presented visually on a recorder (Honeywell Electronik 194) as a sharp and symmetrical peak with no tailing. When the signal had returned to baseline, the sample container was withdrawn from the furnace using a nichrome wire hook. The delivery system of the combustion tube was allowed to cool for a couple of minutes before the next sample was introduced. Total time for a sample analysis was about 10 minutes, and the response of the detector was linear.

v)   Dry Oxidation Method #2

In this method, a seawater sample (5 ml) was dried in a quartz tube (100 mm x 15 mm OD) which was introduced directly into the combustion tube (95-cm x 21 mm OD) where the sample was oxidized in an O_2 atmosphere at 900°C under the same flow conditions used in Method #1.

The advantage of this system is that minimum sample preparation and handling are required. After acidification of the sample, the only handling is in the transfer of the 5 ml aliquots of the sample to the quartz containers (100 mm x 15 mm OD) in which the drying is carried out. The scraping and weighing of the salt from the container, and the use of a water correction are not needed since the volume is known. Also with this system, low salinity or fresh water can be analysed by a dry oxidation procedure; this is difficult in Method #1.

The disadvantage of Method #2 was that high blanks were obtained from the large tubes (100 mm x 15 mm OD) required for the 5 ml of sample, even though they had been cleaned (heated at 600°C for several hours before use). In the beginning, blanks were determined by the analysis of these cleaned empty tubes which were run through the same drying and handling procedure as tubes containing sample. However the contamination from the blanks appeared to be overestimated. Contamination in these systems is dependent on surface. In

an empty tube, there will be more free surface than in one which contains the 5 ml sample. During the evaporation of the sample, water vapour is evolved. This seems to retard contamination of the quartz containers. Therefore 5 ml of carbon-free water (Millipore Super Q) was added to the cleaned quartz tubes for the drying step, so that the process of sample drying was duplicated in the blanks. With this approach, the carbon measured in the blank tubes which were dried in the evaporation was similar to that found for the freshly cleaned (600°C) quartz tubes after the carbon in the Super Q water had been corrected for. Even with extreme care in handling and preparation, the blanks (n=25) were high (about 0.7 ± 0.1 mg C/l). With new tubes and scrupulous care in the handling, the blanks were lowered to about 0.33 $\pm$ 0.05 mg C/liter (n=32) with a range of 0.15-0.45 mg C/liter. This was a lower blank value but was still high, and the precision and accuracy for the determination of TOC in most seawater samples was limited. In freshwater or seawater samples which contain high TOC, the procedure of Method #2 is acceptable and with the ease of sample preparation may be more desirable than Method #1.

The precision and accuracy of the oxidation of organic matter was estimated by the determination of the completeness of oxidation of standard materials. A dextrose standard was added to Super-Q water samples and analyzed by dry Method

#2: The calibration line (Figure 2) obtained from these standards (slope = 548) dried in the large tubes was compared to the results obtained by direct injection of the standard dextrose solution (slope =546) into the freshly cleaned (600°C) quartz tubes. The slopes and intercepts were essentially the same and negligible contamination problems were indicated. Standards were added to seawater and a similar slope (492 counts/µg C dextrose) to the slope (461 counts/µg C dextrose) obtained by standards run directly in the freshly cleaned (600°C) quartz tubes was obtained (Figure 2).

The efficiency of the dry oxidation Method #2 was high (Table X) for most of the materials, whether prepared in Super-Q or seawater medium, and very good recoveries (85-105%) were noted. An exception was benzoic acid, which after acidification showed poor recoveries (only 40-50%); when evaporated at neutral pH a recovery of 90-95% was found. Volatile materials should be lost during the evaporation procedure, but even some materials which should not be volatile under the drying conditions, such as benzoic acid (probably sublimes under acid conditions) can be lost.

vi)   Outline of Dry Method #2

a)   Preparation of Samples

Samples which had been collected, acidified, and frozen

TABLE X

Analysis of Standards By Dry Oxidation Method #2

Sample	Calculated TOC Concentration Sample + Standard (mg C/liter)	Measured TOC Concentration (mg C/liter)	% Recovery
1. Dextrose in Super Q	1.00	1.07±.01	107
	1.60	1.70±.06	106
	2.20	2.18±.05	99
	0.61	0.65±.01	107
	1.22	1.31±.10	107
	1.84	1.92±.07	104
2. Dextrose in Seawater	1.81	1.86±.06	103
	2.43	2.46±.07	101
	3.06	3.17±.07	104
	1.72	1.82±.03	106
	2.53	2.51±.14	99
	3.15	2.86±.05	91
3. Phenylalanine in Super Q Water	0.97	1.02	105
	1.94	2.05	106
	3.88	3.40	88
4. Phenylalanine in Seawater	1.93	2.14±.05	111
	2.62	2.72±.05	104
5. Urea in Seawater	1.70	1.70±.02	100
	2.52	2.34±.05	93
6. Thiamine HCl in Seawater	1.66	1.69±.06	102
	2.41	2.52±.06	105
7. Fulvic Acid a. in Super Q	0.44	0.41	83
	0.88	0.94	107
	1.76	1.61	91
b. in Seawater	1.61	1.53	95
	2.05	1.98	97
	2.39	2.22	93
8. Na Oleate a. in Super Q	1.15	1.33	116
	2.30	2.24	97
	2.30	2.19	95
	4.60	3.80	83
b. in Seawater	1.75	1.33	83
	2.61	1.99	76
9. Glycollic Acid a. in Super Q	0.24	0.26	108
	0.48	0.49	102
	0.96	0.99	103
b. in Seawater	1.57	1.43±.01	91

10. Benzoic Acid
   1. acid added
      a. in Super Q   0.93   0.83   46
                          1.66   0.97   52
                          3.72   1.79   48
      b. in Seawater   1.64   1.20   73
                          2.33   1.55   66
   2. no acid added
      a. in Super Q   1.86   1.79   96
                          3.72   3.31   89

were thawed and mixed. A 5 ml glass syringe, was used to withdraw 5 ml aliquots of the sample which were placed in quartz sample tubes (100 mm quartz test tubes, 15 mm OD, 13 mm ID). The samples were placed in a single container (bottle, Kimax, 150 ml) which was covered with aluminum foil and capped until dried. The drying was accomplished in the glass vacuum desiccator (200 mm OD) which had been thoroughly cleaned of all grease and was placed into a glass battery jar (300 mm OD) into which purified air (oxidized at 900°C over CuO catalyst) was introduced (1-2 liters/min). The bottles containing the quartz sample tubes were uncapped, the aluminum foil perforated and the bottles placed in a desiccator. After a period of 48-60 hours drying, the dried samples were removed and if not immediately analyzed, were capped and frozen.

b)   Analysis

The quartz sample container (100 mm quartz tubes, 15 mm OD x 13 mm ID)) was introduced into the cool part of the combustion tube (3 ft quartz x 21 mm OD) and the oxidation system was flushed of atmospheric CO_2 with a fast flow (300-350 ml/min) of N_2. When the signal from the analyzer returned to baseline, the gas flow was switched to a slow flow (25-35 ml/min) of O_2. After 60 seconds, the quartz sample container (100 mm x 15 mm) was pushed into the hot part of the furnace (950°C) using a quartz rod which could be manipulated without

introducing atmospheric CO_2. An oxidation time of 3 minutes was used. The main combustion tube was followed by a second combustion tube (3 ft quartz x 15 mm OD) packed with platinized asbestos. No premature signal was recorded on the IR detector while the oxidation was carried out. The gas flow was then switched back to a fast flow of N_2 (300-350 ml/min), which flushed the oxidative products through the trap system, which was described earlier, to the non-dispersive infrared analyzer (Beckman I.R. 15A) where the response was integrated (Royson Lectrocount 111) and shown graphically on a recorder (Honeywell Electronik 194) as a sharp and symmetrical peak. The detector response was linear over the range expected for natural samples. When the analyzer had returned to baseline, the sample tube was pushed to the far end of the combustion tube with a quartz rod and allowed to cool. This enabled immediate introduction of the next sample tube. Analysis time was about 10 minutes.

vii) Loss of Volatiles in Dry Oxidation Methods

During the evaporation the organic materials with a vapour pressure equal to or greater than that of water would be expected to be lost. The fate of some of the more volatile organic materials is presented in Table XI. Complete removal of acetone, isopropanol, butanol and propionic acid from seawater or Super-Q water is noted.

Each of these compounds has a high enough vapour pressure under the conditions used for the evaporation of the water that their loss was expected. This loss appears to be complete, which is unlike the wet oxidation results where the loss of the volatiles was more variable. This means that the determination of TOC by dry oxidation will not include the volatile component, but the actual percentage loss of caused by the removal of the volatile components, should be small (5%).

viii) Comparison of the Dry Oxidation Methods # 1 and 2
for TOC Results for Natural Samples

The results for TOC determination from natural samples by the two dry methods for identical or simultaneous samples from different regions are plotted against each other in Figures 3 and 4. The scatter of results was not great and a high linear coefficient (R = 0.9) was found for samples from the Gulf of St. Lawrence. Ideally the slope should be 1.00 but a slope of 0.78 was obtained with the lower values (<1.0 mg C/liter) being underestimated by Method #2 and the higher values (~ 1.5 mg C/liter) being underestimated by Method # 1 in relation to the other method. The TOC results by the two dry methods for simultaneous samples taken from the Scotian Shelf and the coastal zone were compared and less scatter (Fig. 4) and a higher linear correlation (r = 0.94) than in the Gulf samples were noted. The slope of 0.90 was close to ideal slope 1.00 which should be obtained if both methods gave identical results.

Fig. 2-3: Comparison of TOC results by Dry Oxidation Method #1 and Dry Oxidation Method #2 for identical samples collected in the Gulf of St. Lawrence in May 75 (0) and November (●). The dashed line represents the theoretical relationship.

Fig. 2-4: Comparison of TOC results by Dry Oxidation Method #1 and Dry Oxidation Method #2 for identical samples collected from the Scotian Shelf (●) and Coastal Regions (0).

FIGURE 2-3

Y-axis: TOC (mg C/L) DRY OXIDATION METHOD #1
X-axis: TOC (mg C/L) DRY OXIDATION METHOD #2

FIGURE 2-4

Y-axis: TOC (mg C/L) DRY OXIDATION METHOD (1)
X-axis: TOC (mg C/L) DRY OXIDATION METHOD (2)
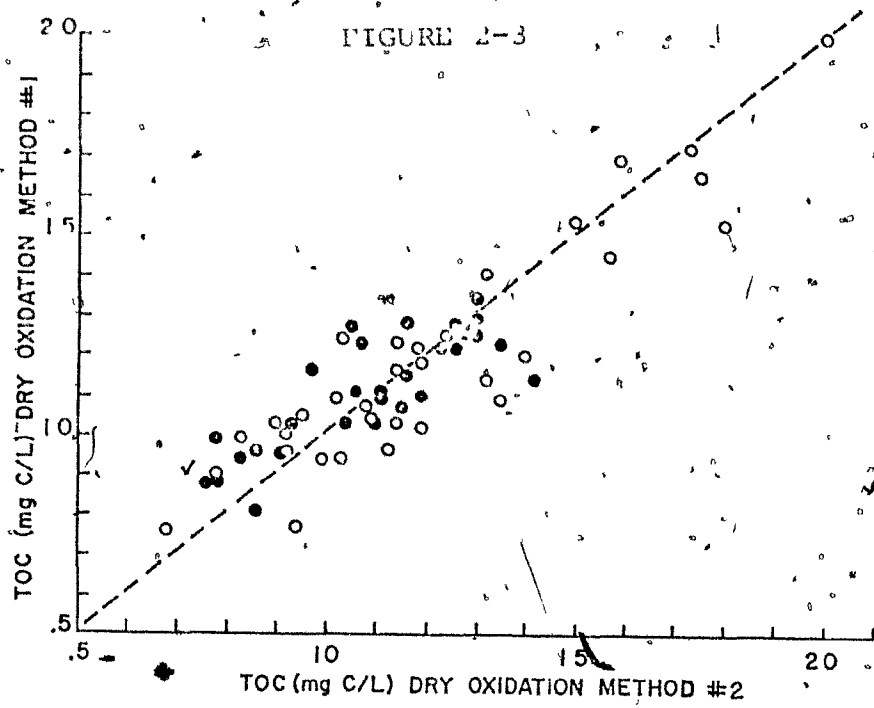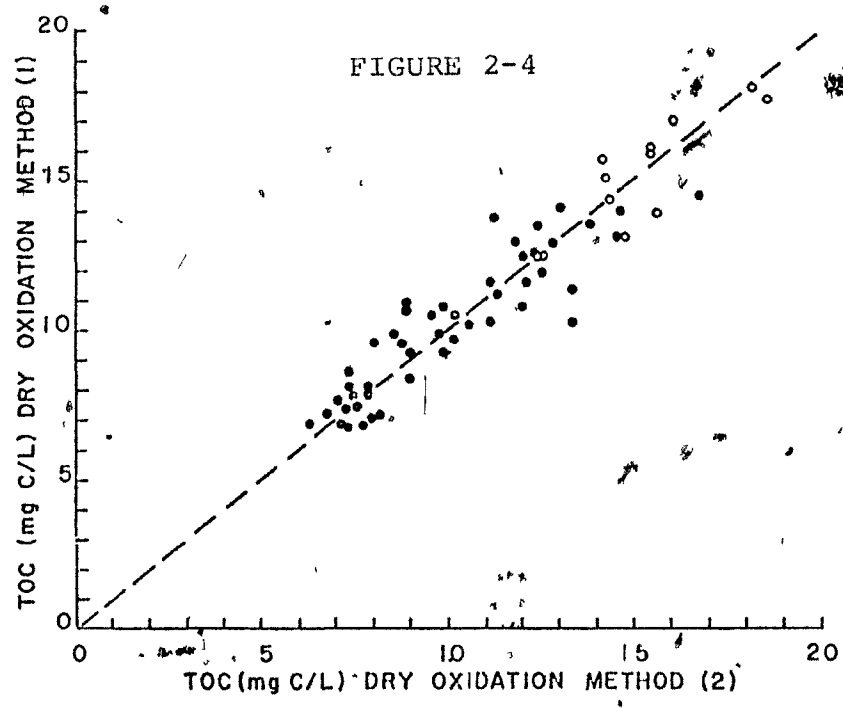
The results of the TOC analyses of natural samples with the two methods were compared (Table VIII). Paired "t" tests were run on 4 sets of duplicate data collected in the Gulf of St. Lawrence, Scotian Shelf and Coastal Region and no significant difference between the TOC results from Method #1 and Method #2 at the 90% confidence level was found. Different handling and workup procedures were followed in the two dry methods, but they appear to be measuring the same fraction of the organic carbon in the natural waters. The accuracy of the TOC results appeared to be acceptable for the TOC analysis in natural samples.

A comparison of the precision of the two methods was difficult. In Method #1, where samples were run in duplicate, the precision was estimated to be about 2-5%. In Method #2, samples were prepared and run in triplicate and the precision of the method for 3 sets of samples from different areas is given in Table IX as relative standard errors $(\sigma/\sqrt{n})/\bar{x}$ x 100). The precision of Method #2 was good and a relative standard error of about $2.8-3.5 \pm 1.5\%$ has been calculated. This is comparable to what was noted with the wet oxidation procedure.

IX) Contamination in Dry Oxidation Procedures.

In the dry oxidation methods, systematic contamination during the sample drying could adversely affect the accuracy of the method. If this source of contamination was a major

TABLE IX

RELATIVE STANDARD ERRORS ($\{(\sigma/\sqrt{n})/\bar{x}\} \times 100$) FOR DRY OXIDATION METHOD #2

Sample Origin	n	Relative Error(%)	Range (%)
Gulf of St.Lawrence (5-6/75)	27	3.5±1.8	0.5-7.1
Scotian Shelf (8/75)	71	2.8±1.5	0.2-6.2
Gulf of St.Lawrence	31	2.9±1.4	0.7-6.2

TABLE XI

Fate of Volatile Organics During Preparation For Dry Oxidation

Sample	Concentration of the Volatile Material (mg C/liter)	% Loss of the Volatile
1.Acetone in Super Q	1.00	100
in Seawater	1.00	100
2.Isopropanol in Super Q	1.00	100
in Seawater	1.00	100
3.Propionic Acid in Seawater	0.97	100
4.Butanol in Seawater	1.09	100

TABLE XII

Calculated TOC Concentrations of Seawater When Different Volumes of Sample Are Dried

Sample Volume (ml)	Calc. Conc. (mg C/liter)	%Variation from mean
1	1.15±0.05	+16
2	0.92±0.02	- 7
3	1.03±0.08	+ 4
4	0.94±0.07	- 5
5	0.91±0.03	- 8
mean =	0.99±0.04	

problem, different calculated TOC values for identical samples should be noted as the sample volumes, added to the large tube (100 mm x 15 mm) in dry oxidation Method #2 were varied Table (XII). If this contamination were small, the calculated TOC values should vary little with different sample volumes. However, with high and constant contamination the calculated TOC in the low volume samples, where a larger fraction of the TOC will be organic carbon from the contamination, will be much higher than the TOC in the larger volume samples. This was studied by the addition of 1-5 ml of a seawater sample to large quartz tubes. These samples were then evaporated and analyzed for TOC. The highest calculated concentration (1.15 ± 0.05 mg C/liter) was noted in the 1 ml sample but it was not significantly different (15%) from the mean of the other calculated concentrations (0.99 ± 0.04 mg C/liter). If contamination were a major problem, the calculated concentrations (ave. TOC = 1.03 mg C/liter) from the lower volumes (1-3 ml) should have been significantly higher than the TOC values calculated (ave. TOC = 0.93 mg C/liter) with the higher volumes (4-5 ml). A systematic contamination did not appear to be excessive, and the dry oxidation methods proved to be precise, accurate, and give a complete oxidation of the organic material in natural samples. My dry oxidation methods appeared to be acceptable for the TOC analysis in natural seawater samples if proper care in the handling,

work up, and analysis of the sample was taken.

C. Analysis of the TOC in Natural Waters

1. Comparison of TOC values for Natural Samples by Wet and Dry Oxidation

Both wet and dry oxidation procedures have been used in this study for the oxidation of TOC in seawater. The advantages and shortcomings of both approaches for TOC analysis have been discussed. A complete oxidation of the organic matter with the high temperature oxidation methods was shown with standards and samples and comparable efficiences in the per cent recoveries (90-100%) with the wet oxidation of standards was obtained. This might be an indication that the accuracy of the wet methods is similar to that of the dry methods, but only simple compounds were used as standards and the extrapolation to the matrix of organics present in a natural sample may not be valid. A direct comparison of the TOC results by the wet and dry oxidation procedures for natural samples (identical or simultaneous samples) was made; the wet TOC values were significantly lower than the dry TOC values (Figures 5, 6 and 7). The TOC values obtained by the dry methods and wet oxidation methods are plotted against depth and the averaged TOC values obtained for each depth zones are shown. The difference between the plotted averages is not great but is significant by a paired "t" test at the 95% confidence

level. In all cases, the averaged TOC values by the dry

methods were higher than those obtained with the wet oxidation.

2.   TOC Values in the Gulf of St. Lawrence

1)   Distribution

In the Gulf of St. Lawrence (5,6/75) data (Figure 5),

the scatter for the TOC values obtained by the dry oxidation

was high but the position of the stations may help to

explain this. In the surface zone, a large range of values

of TOC from 1.13 - 2.30 mg C/l were noted and the TOC values

were correlated to the sigma-t values; areas with the

greatest fresh water influence had the highest values for

TOC. The dry oxidation values and the sigma-t values were

plotted (Figure 8) and a high negative linear correlation (r

= 0.91) of the TOC with sigma-t was found. High POC values

were measured in the areas of low salinity and high fresh

water influence (40-170 µg C/liter) but these POC values

were not enough to explain the high and variable TOC values.

In the surface samples, the amount of POC averaged about 4.5

± 1.7% of TOC while deeper samples were only about 3.0

± 1.3% (POC/TOC) of TOC. Areas sampled were often shallow

and the amount of TOC in the water column could have been

influenced by input from the sediment. With fresh water and

sediment inputs of organic material, the high scatter of TOC

values would be expected.

Fig. 2-5: The TOC results from the Gulf of St. Lawrence (5 &
6/76) (Dry Method #1-0; Dry Method #2-●). □ - averaged
TOC values obtained by the Dry Oxidation methods
Δ - averaged TOC values obtained by the Wet Oxidation
method.

Fig. 2-8: The TOC values obtained by the Dry Oxidation methods
plotted against the sigma-t values for samples collected
in the Gulf of St. Lawrence (5 & 6/75). /

Map: Stations sampled in Gulf of St. Lawrence.
○ November, 1975
⊙ May, 1975
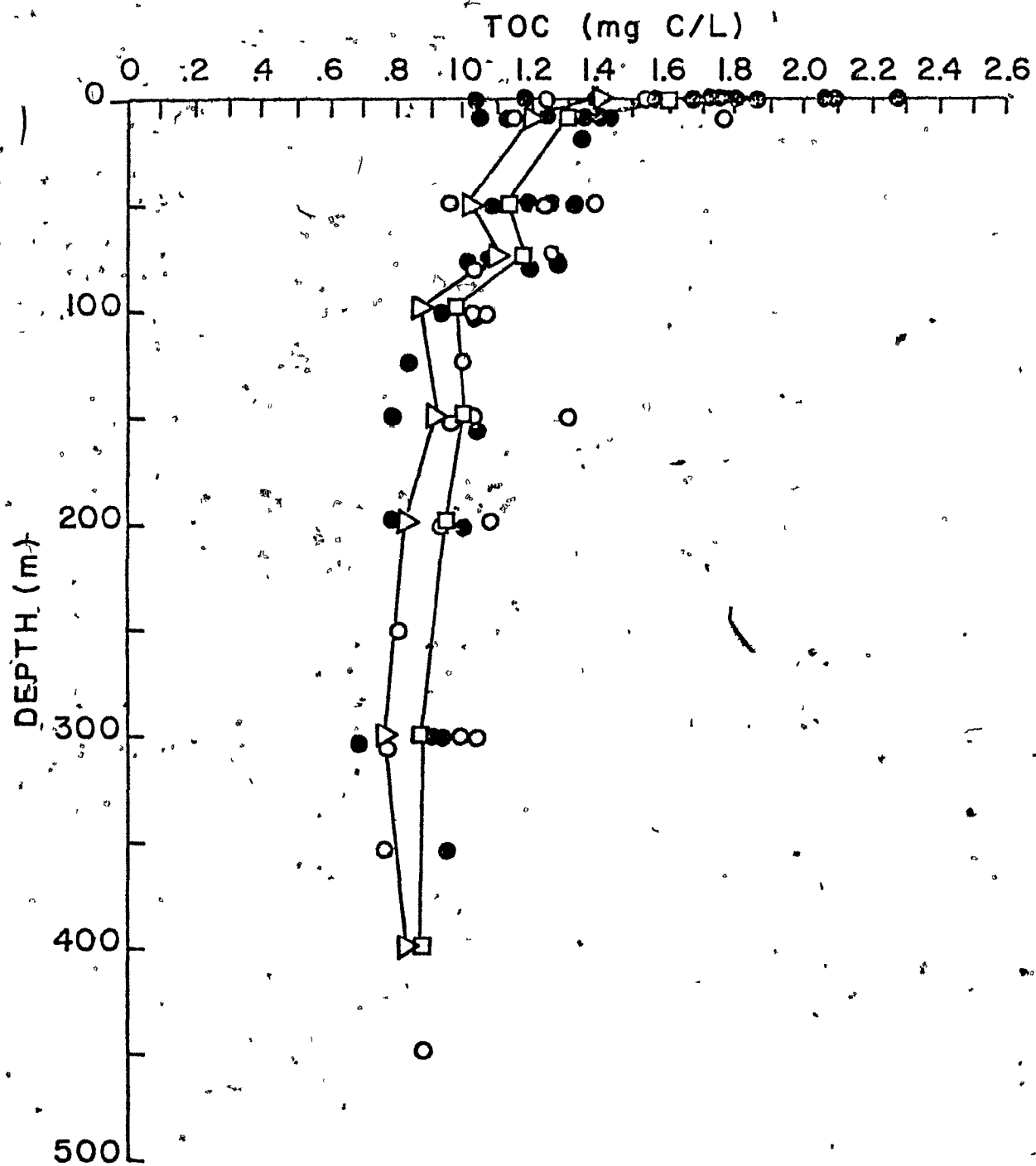
FIGURE 2-5
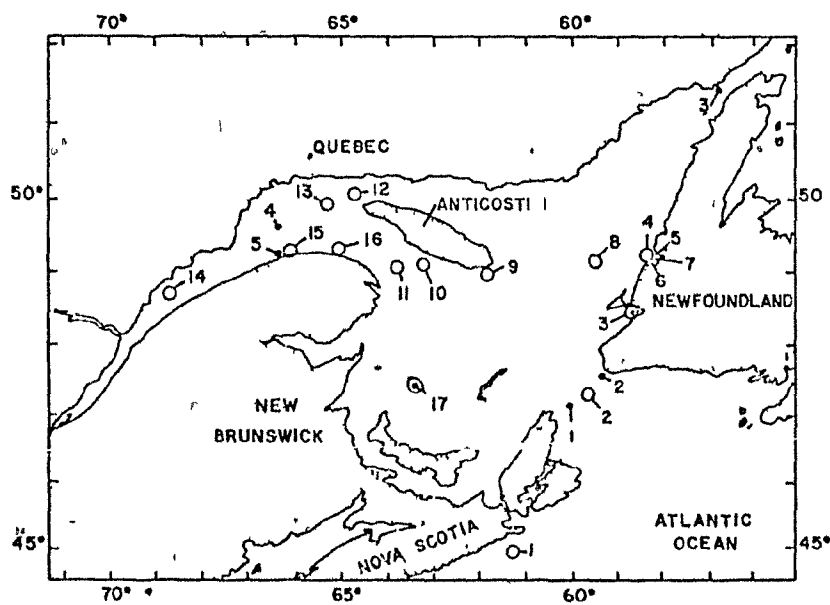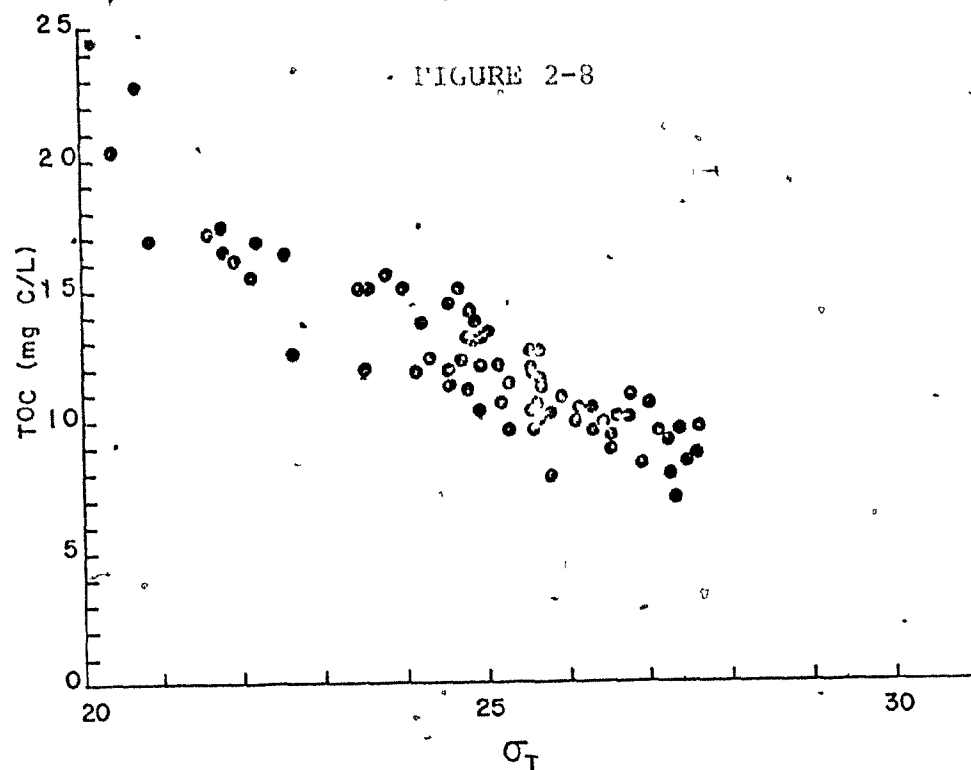
FIGURE 2-8

Gulf of St. Lawrence: Stations Sampled

11) Comparison of Wet and Dry Values of TOC

The averaged values of TOC for depth zones were higher when analyzed by the dry oxidation procedure than by wet oxidation procedure (Figure 5). In Table XIII, the actual calculated averages are presented along with the absolute differences obtained with the two methods. (average TOC_{dry} - average TOC_{wet}) and their % differences ($\% = \frac{TOC_{dry} - TOC_{wet}}{TOC_{wet}}$)

at each depth zone. The difference varied, with the largest absolute difference (diff. = 0.18 mg C/liter) in the TOC_{ox} values being found in the surface zone, while below 100 m a fairly constant difference is noted (diff. = 0.08 mg C/liter). Little change through the water column for the average % differences (9.8 ± 3.4%) was calculated. This difference between the wet and dry values was small but relatively constant. A paired "t" test was carried out on all the samples from the Gulf of St. Lawrence on which both a wet and dry analysis had been done and for these samples (n = 67), the difference between the TOC concentrations was significant at the 99.9% confidence level. The means of the TOC results were compared (Table XV); the dry oxidation values for TOC (ave. TOC = 1.23 ± .3 mg. C/liter) were about 13% higher than the wet oxidation numbers (ave. TOC = 1.09 ±.28 mg. C/liter). A difference in the absolute values for the TOC was observed, but with the high correlation

TABLE XV

DIFFERENCES BETWEEN WET AND DRY OXIDATIONS FOR IDENTICAL SAMPLES

Samples	n*	T.O.C. Concentration (mg.C/l)		% difference
		Wet	Dry	
1. Gulf of St. Lawrence (5,6/75)	67	1.09±0.28	1.23±0.30	13
2. Scotian Shelf (8.75)	69	0.84±0.19	1.01±0.23	20
3. Senegal Coast (2,3,4/76)	84	0.85±0.24	0.97±0.26	14
4. Coastal Areas (6/75 - 1/76)	20	1.50±0.12	1.81±0.13	20

mean % Δ $\approx$ 17.0

$$\frac{TOC_{dry} - TOC_{wet}}{TOC_{wet}} \times 100$$

* number of samples run by both methods

$(r = .93)$ between the TOC_{wet} and the TOC_{dry}, one would expect that the interpretations that could be extracted from the TOC concentrations and distributions from either method would be similar.

3. TOC Values on the Scotian Shelf and Slope Area

    1) Distribution

The TOC concentrations from the Scotian Shelf area are presented in Figure 6. Scatter in the TOC concentrations was noted in the surface zone and was correlated with the areas of higher productivity, of high load of particulate organics, and of influence from the coast. The higher TOC values were obtained in the stations closer to the coast. This coastal effect is shown in Table XIV. The average concentration of TOC from specific depths (0, 10, 25, 50 and 75 m) were calculated for 7 stations run on the Scotian Shelf (8/75). Both dry methods show the same trend of decreasing average TOC with distance from the coast (approx. 1.3 mg C/liter to 1.1 mg C/liter). A 10% drop in the averaged TOC was found in the first 3 stations (ave. TOC = 1.21 ± 05 mg C/liter) after which a relatively stable value of TOC (ave. TOC = 1.11 ± 04 mg C/liter) was found as the transect continued to the slope.

    ii) Comparison of Wet and Dry Values of TOC

The averaged TOC values at depth zones for the dry oxidation and wet oxidation results from Scotian Shelf and

Fig. 2-6: The TOC results from the Scotian Shelf and Slope
(8/75) (Dry Method #1-0; Dry Method #2-●). □ - averaged
TOC values obtained by the Dry Oxidation methods △
△- averaged TOC values obtained by the Wet Oxidation
method.

Map: Stations sampled on the Scotian Shelf region.
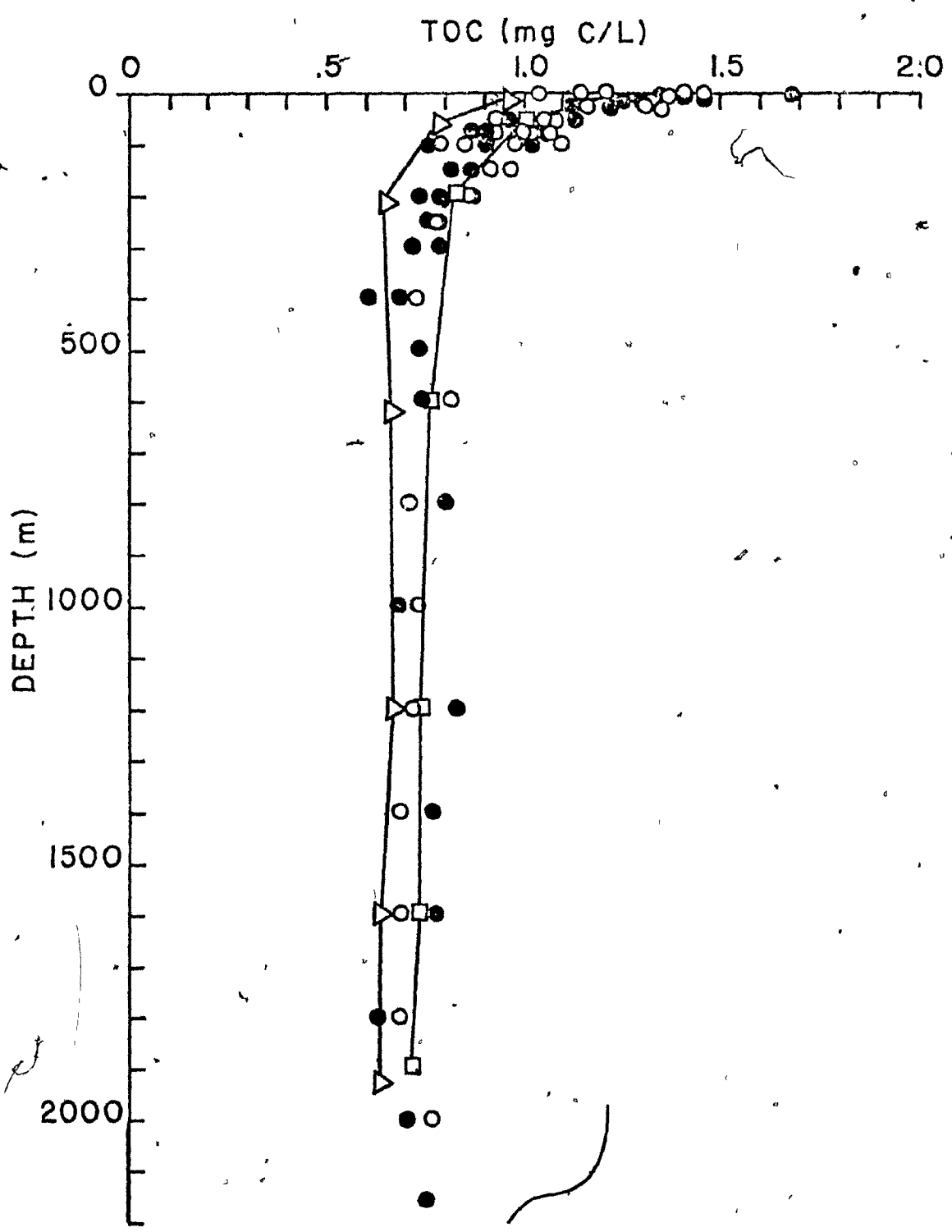
FIGURE 2-6

TABLE XIV

AVERAGED CONCENTRATION OF TOC OVER 1, 10, 25, 50 and 75 m DEPTH FROM STATIONS

1 - 7 ON SCOTIAN SHELF (8/75)

Station	Distance from coast (Km)	Average concentration (mg C/liter)	
		Dry Method #1	Dry Method #2
1	5 - 10	1.24	1.29
2.	25	1.22	1.19
3.	80	1.14	1.17
4.	125	1.06	1.10
5.	170	1.09	1.10
6.	210	1.18	1.14
7.	250	1.06	1.13

LOCATION OF SURVEY STATIONS
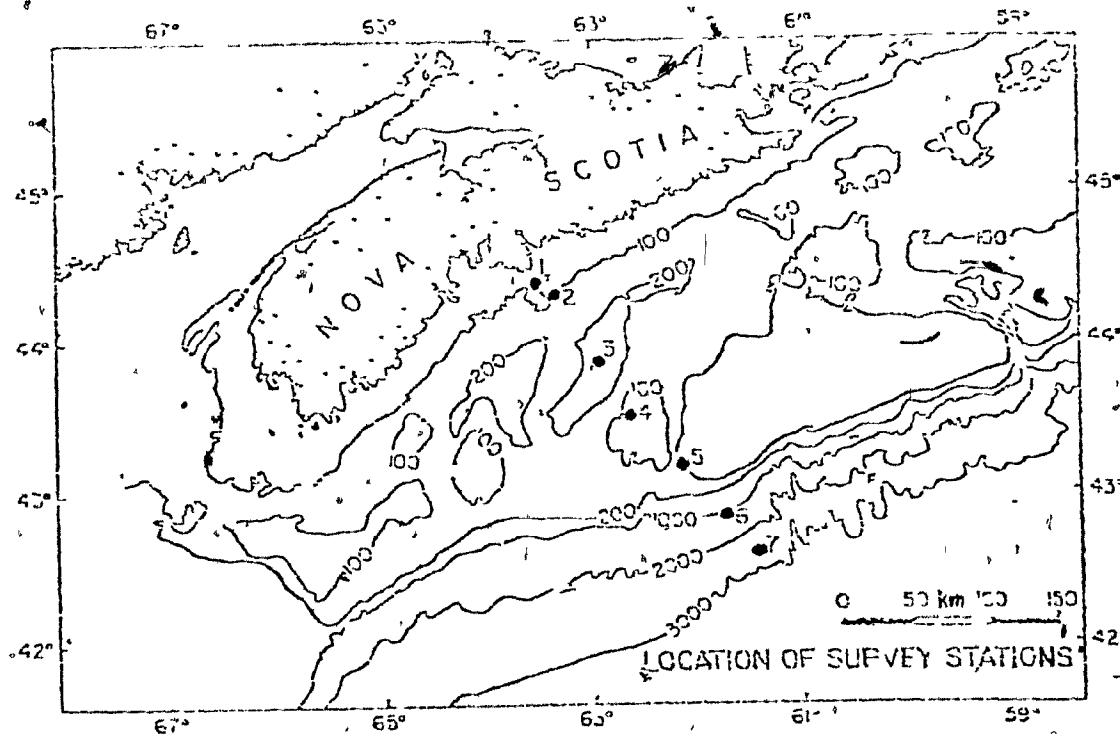
Slope are presented in Figure 6. The difference was not great but was significant (Table XIII). The absolute difference (diff. = $TOC_{dry} - TOC_{wet}$) was highest in the surface zone (Δ = 0.2-0.3 mg C/liter), while in deeper water the difference was relatively constant (Δ = 0.09 mg C/liter. However, the % difference (diff./TOC_{wet} x 100) was variable (10-30%) and higher % differences were observed in the surface zone (29%) compared to deep water (14%). If the source of the difference between the wet and dry oxidation methods was the incomplete oxidation of a fraction of the TOC in the sample by the wet oxidation procedure (Sharp, 1973), then this result was surprising. A larger % of the more easily oxidized labile organic material was postulated to exist in the surface zone and the TOC values by the wet and dry methods should be comparable. More refractory organic material (Menzel, 1964) which should be less effectively oxidized by the wet oxidation procedure should be found in deeper waters. Sharp (1973) used this argument to explain why the % difference in wet and dry TOC values increased with depth from the surface zone. This was an indication that a larger % of organic material in deeper water was resistant to persulfate oxidation in the wet method. This was not supported by my data from the Scotian Shelf, but not enough data has been examined from deep water to make any definite statements on the variations of %

differences of the TOC. However, a fairly constant %
difference between the oxidation methods has been suggested
by my results and only small variations throughout the water
column should be expected.

In samples (n = 69) from the Scotian Shelf (8/75), the
TOC values obtained by the wet and dry methods for identical
samples were compared by a paired "t" test and the difference
was found to be significant at the 99% confidence level
(Table XV). The mean of the dry oxidation values (ave. TOC =
1.01 ± 0.23 mg C/liter) averaged about 20% higher.

dry - wet x 100) than those obtained by wet oxidation (ave.
  wet

TOC = 0.84 ± 0.19 mg C/liter). A high correlation between
the two methods (r = 0.92) was noted and a similar qualitative
picture of TOC distributions could be extracted from either
wet or dry oxidation procedures.

4.   TOC Values From an Area Off Coast of Senegal.

      1)   Distribution

The TOC values (dry oxidation) from an area off the
coast of Senegal (2, 3/75) were not highly variable except
in the surface zone (Figure 7). Geographically, this is an
area of upwelling, and high biological activity would be
expected. The POC concentrations were determined (R. Pocklington,
personal communication) and were found to be a small
fraction of the TOC, with the highest percentage (POC/TOC)
about 8.5%. An average of 4% was found in the surface zone
(POC/TOC = (50/1250) ug C/liter) and about 1.5 % in deeper

Fig. 2-7: The TOC results from an area off the coast of Senegal
(2,3,4/75) (Dry Method #1-O) □ - averaged TOC values
obtained by the Dry Oxidation Method Δ - averaged TOC
values obtained by Oxidation Method.
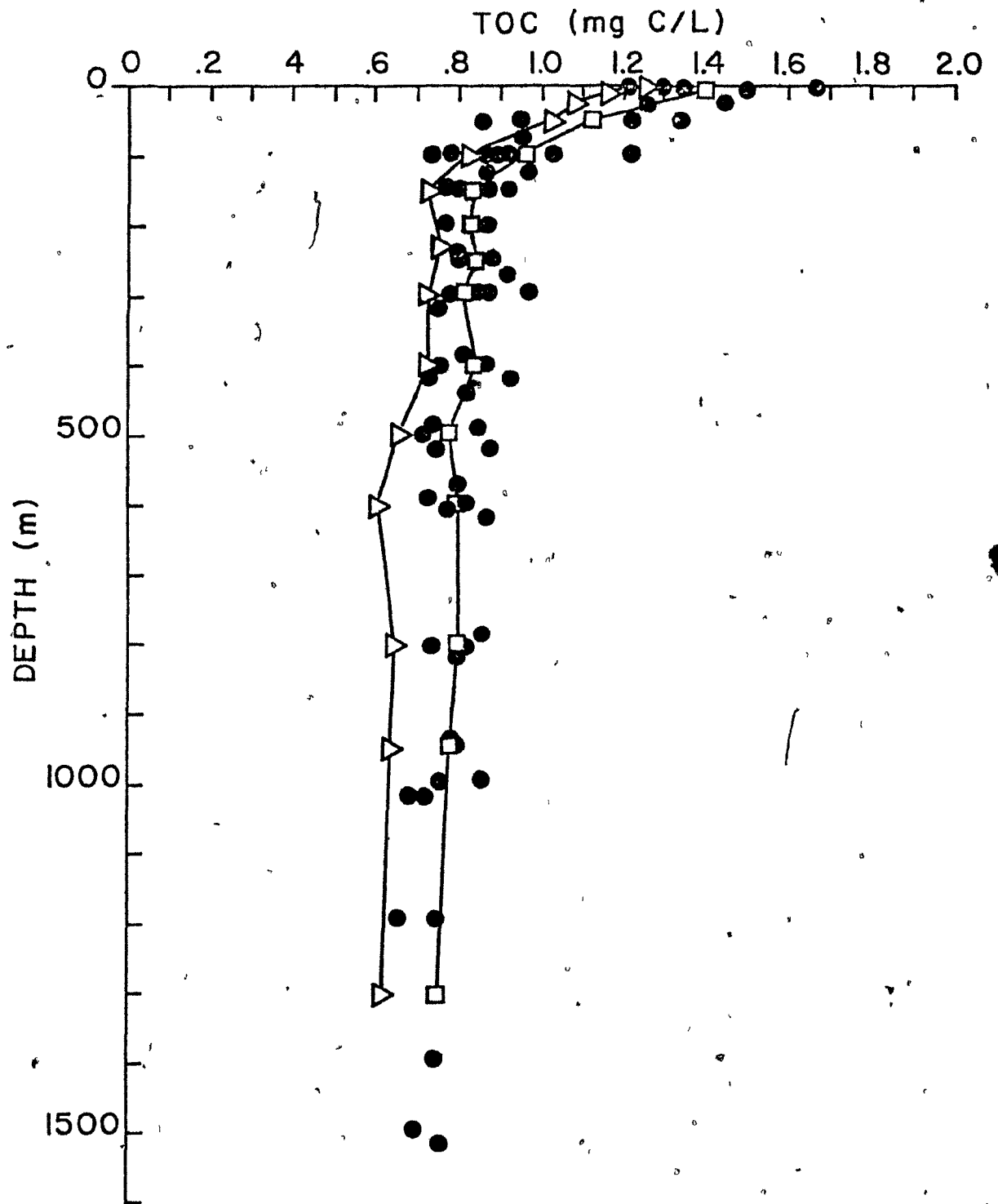
water (POC/TOC = (13/825) μg.C/liter). The TOC values were influenced by the POC, but the scatter in the TOC values could not be explained by the POC alone. The TOC values should have been affected by local factors, both hydrographic and biological, and scatter in TOC values would be influenced by the upwelling phenomenon in this area.

11) Effect of Hydrographic Properties on the TOC Distribution

The TOC values and sigma-t were negatively correlated (r = 0.90) and an increase in the scatter of the TOC was noted as the sigma-t values decreased. The TOC values were examined in a frequency diagram (Figure 9a) and the distribution was found not to fit the normal distribution. A bimodal distribution was obtained with a normal distribution for the TOC values >1.00 mg C/liter (ave. TOC = 1.33 ± 0.13 mg C/liter) and one for those <1.00 mg C/liter (ave. TOC = 0.83 ± 0.10 mg C/liter). The higher TOC values were found in the oxygenated surface zone (0-60 m) and appeared to be normally distributed (Figure 9b), while the lower TOC concentrations were found below the density discontinuity at the oxygen minimum, and also appeared to be normally distributed (Figure 9c).

A discontinuity in the density profile was observed at 50-75 m. The surface zone was well mixed, warm, highly oxygenated, and had low sigma-t values while the zone from

Fig. 2-9: Frequency distribution of TOC values obtained by
Dry Oxidation Method # 1 from an area off the Coast
of Senegal (2,3,4/75).

a) All the TOC values

b) TOC values in surface zone (0-60 m).

c) TOC values below pycnocline (>60 m).

Fig. 2-10: Depth profiles of O_2, TOC, temperature, and sigma-t
values for specific stations in the area off the coast
of Senegal. See Map # pg. 79(a)

a) Station 1:   14° 59'N, 20° 16'W

b) Station 3:   15° 21'N, 20° 41'W

c) Station 4:   15° 21'N, 17° 44'W

d) Station 11: 13° 41'N, 22° 11'W

e) Station 12: 14° 30'N, 18° 59'W

f) Station 6:   16° 23'N, 18° 30'W

FIGURE 2-9
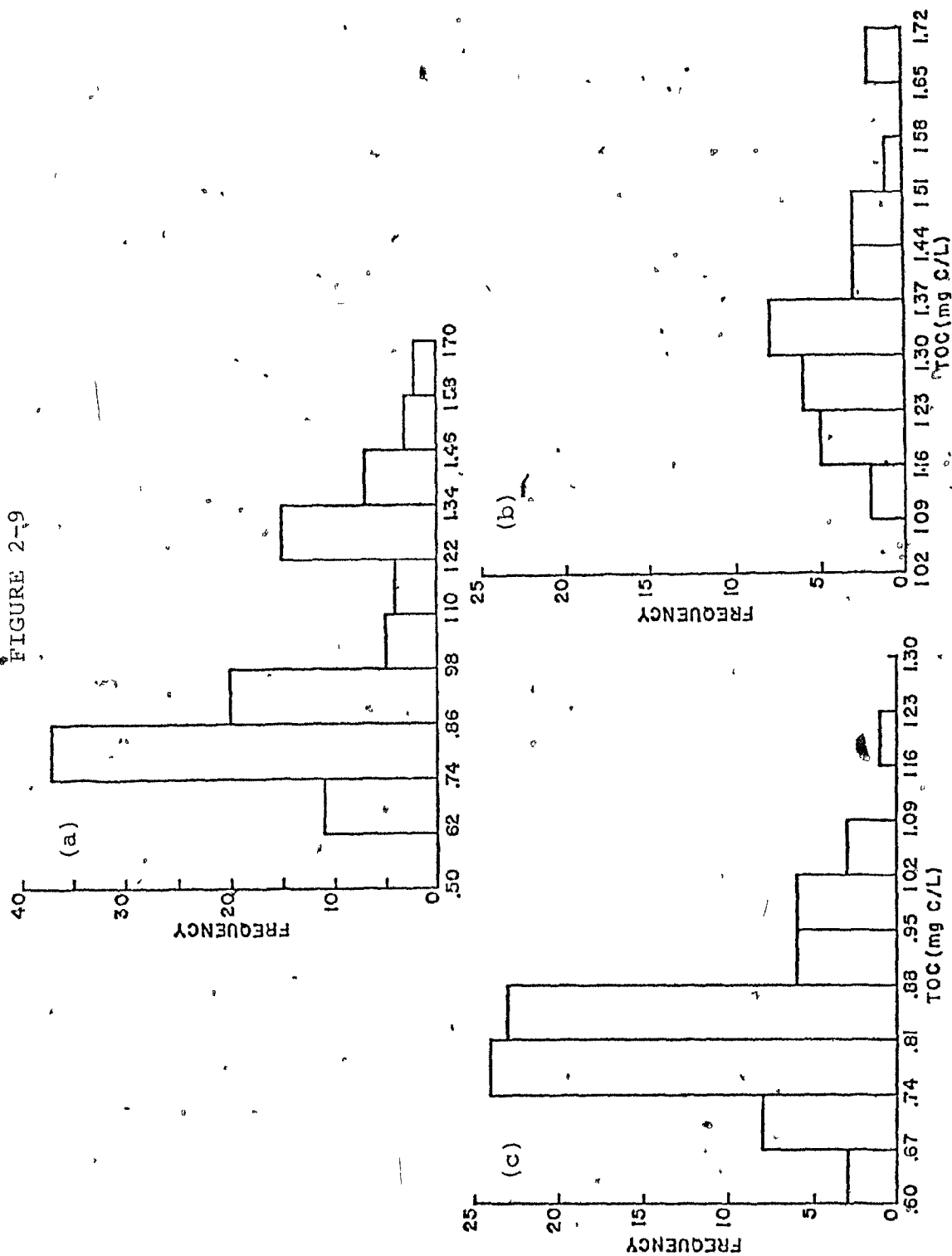
FIGURE 2-10
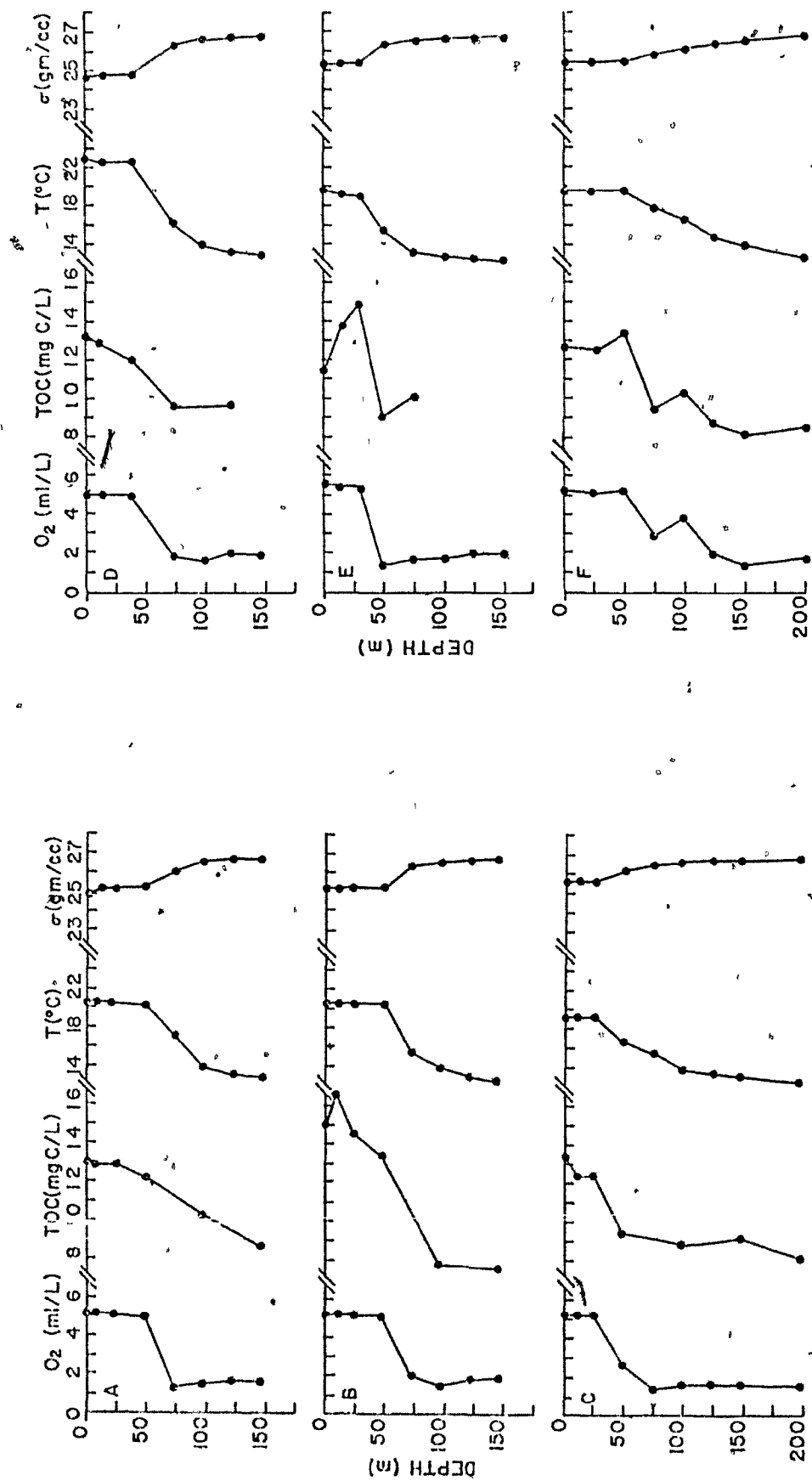
50-100 m was colder, lower in O_2, and more dense. The averaged values of TOC, O_2, temperature, and sigma-t for the surface zone (0-50 m) and the deeper zone (50-75 m) were tabulated (Table XVI) and the establishment of a strong pycnocline at about 50-75 m was indicated, with these two zones being separated by the density inhomogeneity. Since this is an upwelling area, the productivity in the surface zone should be high. If active mixing between the zones was prevented by this density layer, the organic material produced in the surface zone would be recycled or remineralized in the warmer, highly oxygenated zone. Oxygen will be utilized in the remineralization of organic material. If the mixing with the high oxygen water is reduced, water low in O_2 would be formed and an O_2 minimum would be expected. The profiles of both conservative and non-conservative properties (the O_2, TOC, temperature and sigma-t) were plotted over the upper 150-200 m (Figures 10a-10f) and a pycnocline at 30-60 m, was noted. At the pycnocline, a rapid decrease in temperature and TOC and an increase in sigma-t was observed, while the O_2 concentration droped dramatically from greater than 5.0 to less than 2.0 ml O_2/liter. The free mixing across the pycnocline was retarded by the presence of the strong pycnocline and a normal distribution of TOC in zones above and below the pycnocline was observed.

TABLE XVI

Water Properties Above and Below the Pycnocline

in Waters Off the Coast of Senegal

Depth Zone (m.)	Averaged Concentration of O_2 (ml.O_2/l.)	Averaged Sigma-t (g./cc)	Averaged Temperature ($^{\circ}$C)	Averaged Concentration of TOC (mg.C/l.)
0-50	5.12±.28	25.36±.41	19.61±2.7	1.33±.13
50-100	1.87±.50	26.35±.26	15.29±1.5	0.95±.11
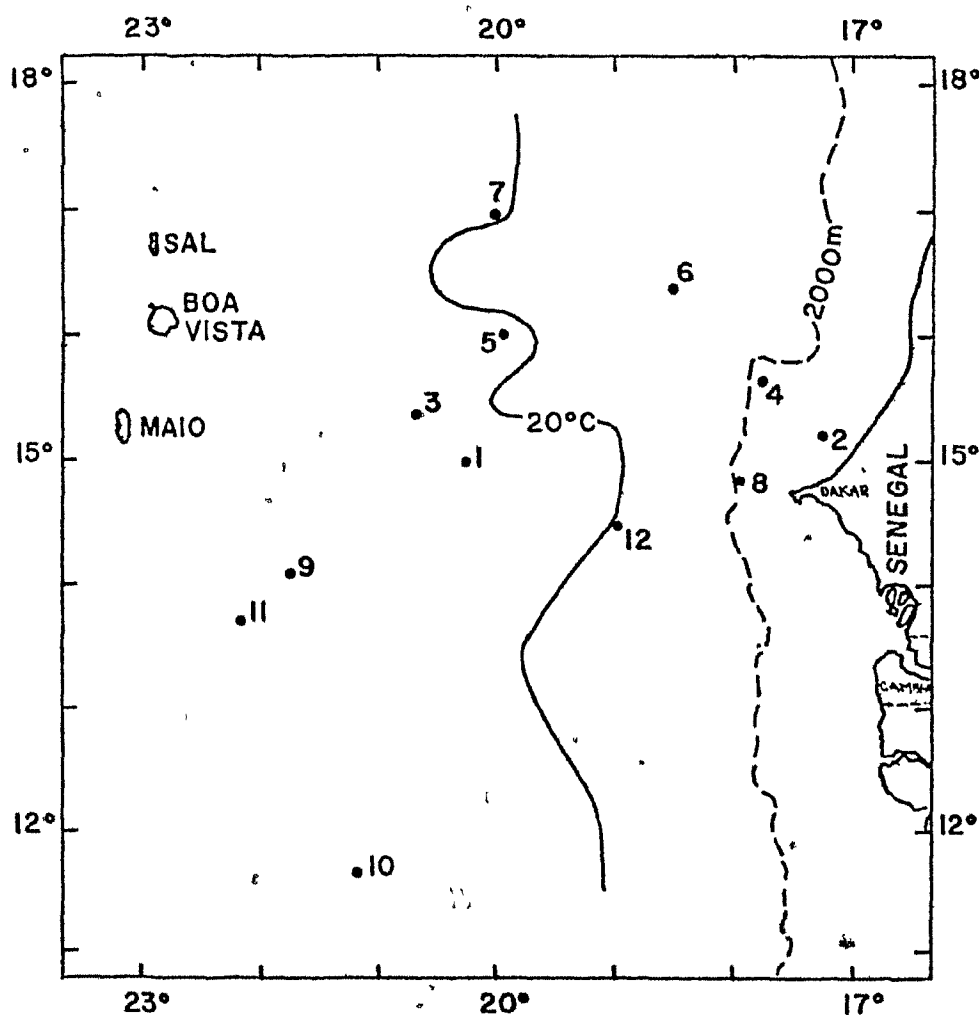
iii) Comparison of Wet and Dry Oxidation results

The TOC concentrations by dry method #1 for the area off the coast of Senegal were plotted (Figure 7) along with the averaged TOC values for specific depth zones. The averaged dry oxidation values for TOC were higher (9-31%) than the averaged wet oxidation values for identical samples from the same depth zones. The differences were small but consistent (Table XIII). The absolute difference ($\Delta = TOC_{dry}-TOC_{wet}$) in the TOC concentration was fairly constant below 100 m (0.13 ± 0.04 mg C/liter), while slightly higher in the surface zone (0.16 ± 0.05 mg C/liter). However, the % difference (Δ/TOC_{wet} x 100) was higher in the deeper water (18.5 ± 7%) than in the surface water (15.5 ± 4%). It has been predicted (Sharp, 1973) that this difference between wet and dry oxidation would increase with depth, since deeper waters should contain organic material more resistant to the persulfate oxidation of the wet procedure. The lack of comprehensive data make this argument tenuous.

When the values of TOC obtained by wet and dry oxidation methods for identical samples from the Senegal cruise were compared by a paired "t" test, they were found to be significantly different at the 99.9% confidence level. The average of the TOC values by the dry oxidation (0.97 ± 0.26 mg C/liter) was 14% higher (Table XV) than the average of the TOC values by

wet oxidation (0.85 ± 0.24 mg C/liter). The difference was small and the high linear correlation (r = 0.90) between the two oxidation methods was an indication that the qualitative picture developed from either set of TOC data should be similar.

5. TOC Values in Coastal Regions: Comparison of Wet and Dry Results

During this study, samples from coastal areas near Halifax were examined by both wet and dry oxidation procedures. Samples were taken from the North-west Arm (Table XIII) and the absolute calculated difference ($TOC_{dry} - TOC_{wet}$) for samples from the surface and 10 m was about 0.25 mg C/liter with a difference ((Δ/TOC_{wet}) x 100) of about 20%. This difference was shown to be significant at the 99.9% confidence level with a paired "t" test. The averaged TOC by the dry oxidation (1.54 ± 0.17 mg C/liter) for the samples (n = 14) from this close coastal area was 19% higher (Table XV) than that obtained by the wet oxidation procedure (1.29 · 0.14 mg C/liter).

A similar result was observed with samples taken from Petpeswick Inlet where an absolute difference of 0.44 mg C/liter was found (Table XIII). With a paired "t" test, the difference was significant at the 99.9% confidence level. The averaged TOC value obtained for these samples (n = 6) by the dry oxidation (2.44 ± 0.08 mg

TABLE XIII

DIFFERENT TOC VALUES BY WET AND DRY OXIDATION FOR DATA GROUPED INTO DEPTH ZONES

Cruise	Depth (m)	n	TOC Concentration ± σ (mg.C/liter) Wet oxid.	n	Dry oxid.	Absolute Difference $(TOC_{dry} - TOC_{wet})$	% Δ
1.Gulf of	1	16	1.41±0.28	29	1.59±0.27	0.18	13
St. Lawrence	10	14	1.20±0.21	22	1.30±0.21	0.10	8
(5,6/75)	50	16	1.01±0.12	28	1.12±0.11	0.11	11
	75	4	1.10±0.12	7	1.17±0.13	0.07	6
	100	2	0.86±0.02	7	0.97±0.08	0.11	13
	150	7	0.91±0.17	9	0.99±0.14	0.08	9
	200	3	0.82±0.14	4	0.94±0.12	0.08	10
	300	4	0.76±0.13	7	0.84±0.13	0.08	14
	400	2	0.82±0.04	3	0.86±0.07	0.04	5
2.Scotian Shelf	10	16	0.96±0.06	50	1.25±0.13	0.29	30
(8/75)	50	5	0.78±0.11	24	1.01±0.11	0.23	29
	200	15	0.64±0.04	23	0.82±0.11	0.18	28
	600	3	0.66±0.01	5	0.76±0.04	0.10	15
	1200	4	0.67±0.04	6	0.74±0.06	0.07	10
	1600	2	0.64±0	2	0.74±0.06	0.10	16
	1900	3	0.64±0	7	0.72±0.05	0.08	13
3 Senegal Coast	1	9	1.25±0.17	9	1.41±0.13	0.16	13
(2,3,4/76)	10	3	1.16±0.15	4	1.38±0.19	0.22	19
	25	6	1.08±0.12	6	1.29±0.09	0.21	19
	50	7	1.03±0.12	9	1.12±0.17	0.09	9
	100	5	0.82±0.15	8	0.96±0.13	0.14	17
	150	6	0.73±0.09	7	0.83±0.06	0.10	14
	225	7	0.76±0.09	8	0.84±0.06	0.08	11
	300	6	0.73±0.12	7	0.81±0.04	0.08	11
	400	4	0.73±0.07	5	0.84±0.07	0.11	15
	500	5	0.66±0.06	6	0.78±0.06	0.12	18
	600	4	0.61±0.05	5	0.80±0.05	0.19	31
	800	4	0.65±0.04	4	0.80±0.05	0.15	23
	950	7	0.64±0.04	5	0.78±0.06	0.14	22
	1300	4	0.62±0.04	4	0.75±0.06	0.13	21
4.N W. Arm	1	7	1.35±0.15	13	1.62±0.18	0.27	20
(6/75),(1/76)	10	7	1.22±0.10	13	1.45±0.14	0.23	19
5.Pctpeswick Inlet (10/75)	surface	6	2.00±0.10	6	2.44±0.08	0.44	22

C/liter) was 22% higher (Table XV) than that obtained with the wet oxidation (2.00 ± 0.10 mg C/liter).

6. Conclusion

In the areas of this study (Gulf of St. Lawrence, Scotian Shelf, Senegal, coastal regions) there were specific samples where TOC concentrations obtained by the wet oxidation procedure were greater than those obtained by the dry procedure. However in all the areas, the averaged TOC concentration by the dry oxidation procedure (Table XV) were about 15-20% higher than the wet oxidation results. These differences were significant at the 99.9% confidence level by paired "t" tests.

The differences between the TOC values measured by wet and dry oxidation were small but appeared to be significant whether the samples were taken from deep ocean water (low in organic carbon) or from coastal water (high in organic carbon). The consistency of the differences was maintained throughout the water column and in different areas. While the absolute differences varied, the % differences seemed relatively constant.

The consistency through the water column in the % difference of the TOC values by the different oxidation methods was not expected. A higher % difference for the TOC values in deep waters was predicted (Sharp, 1973) but was not evident in the areas I have sampled. It has been

assumed that the dry oxidation of the organic matter is
complete and the lower TOC values obtained by the wet
oxidation procedure should be the result of incomplete
combustion. If this difference between TOC values was the
result of a systematic contamination in the dry method, then
the absolute difference between the methods should have
remained constant. However, variations in the absolute
difference ($TOC_{dry}-TOC_{wet}$) were observed with the area and
with depth so that a fairly constant % difference was
calculated. There appeared to be a constant fraction of the
TOC which was not capable of being oxidized in the wet
oxidation method (refractive material or concentration
limit below which the oxidant was not capable of oxidizing).
The dry oxidation method should not be affected by these
problems.

A constancy of composition of the organic matter in
seawater was indicated with ultrafiltration (Ogura, 1974,
Baturina et al., 1975 and Smith, 1976) where only small
changes in the molecular weight fractions of the organic
matter in seawater were observed. A decrease of the % of
high molecular weight (> 10000) material with depth (surface
= 10-15% of TOC; depth = 1-4% of TOC) was shown in the open
ocean. If the high molecular weight organics were a more
refractive fraction of the TOC, then the argument that in
deeper water there should be a higher % difference in the

TOC concentration by the wet and dry methods would not be
supported. I think that the matrix of organic materials in
seawater will remain similar and a relatively constant
amount of this material will be difficult to oxidize under
the conditions of the wet oxidation. The amount of this
material will vary with respect to the TOC but the % will be
fairly constant. The depth and area of sampling may be
changed but only a small range in the % differences in the
TOC results in the dry and wet methods should be found.

A high correlation has been observed in the comparison
of the TOC results by wet and dry oxidation, and broad
oceanographic distributional interpretations which can be
extracted from the TOC data should not be greatly affected
by the method used. Precision in wet and dry methods was
comparable and care in sample manipulations in both methods
was critical for good TOC results. The time of preparation
and analysis was similar for the two approaches. However,
the dry method is more accurate and for work in which the
TOC values are used in an evaluation of fluxes or cycles of
organic materials, the dry oxidation method will probably be
more effective. In this study, I have developed methods
for dry oxidation of the TOC in seawater which are
accurate and precise when handled properly, and although
they are time comsuming and not a real time analysis, an
accurate picture of the distributions and variations of TOC

Fig. 2-11: Averaged TOC values ± standard deviation obtained
by Dry Oxidation method #1 for samples collected
in the Northwestern Atlantic (26° N to 43° 20'N).
The upper line - the TOC values from the surface zone
(0-200 m) are averaged; in the lower line the TOC
values from deeper water (>200 m) are averaged.
■ Sargasso Sea Cruise (2/75)
● Bermuda Cruise (10/74)
O Scotian Shelf and Slope Cruises (5/74, 8/75, and 3/76)

84 a
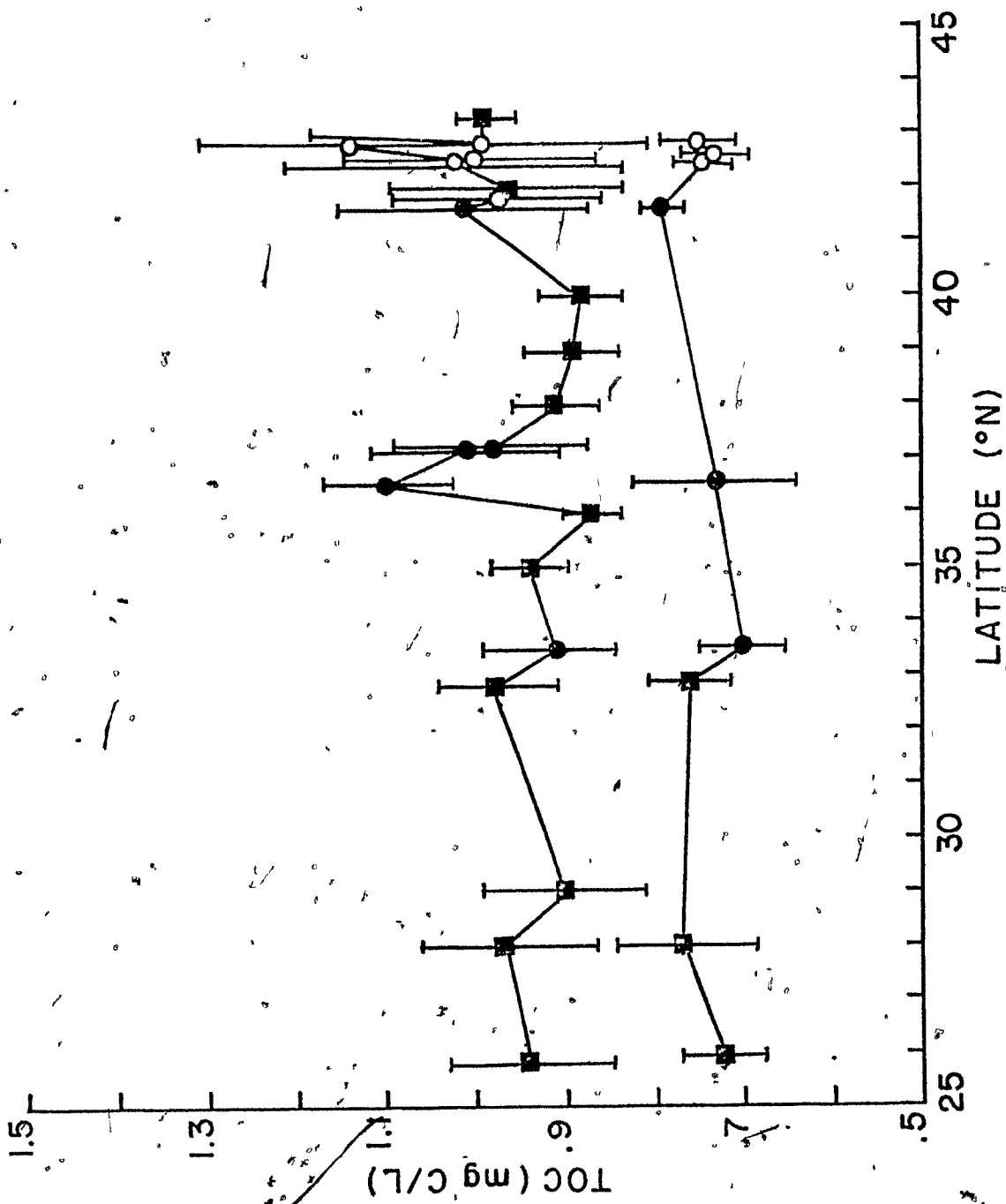
TABLE XVII

Averaged TOC Concentrations over Depth at Different Latitudes:

Comparison of the Surface Zone (0-200 m.) and Deep Water (>200 m.)

Date of Cruise	Position: Latitude	n	Averaged TOC (0-200 m.) (mg.C/liter)	n	Averaged TOC (>200 m.) (mg.C/liter)
2/75	26°00'N	7	0.94±.11	32	0.72±.05
2/75	27°50'N	6	0.97±.12	4	0.77±.08
2/75	29°00'N	6	0.90±.11		
2/75	32°50'N	6	0.98±.06	14	0.76±.05
10/74	33°30'N	4	0.91±.07	7	0.70±.05
2/75	35°00'N	5	0.94±.04		
2/75	36°00'N	6	0.87±.03		
10/74	36°35.2'N	7	1.10±.07	18	0.73±.10
10/74	37°09.8'N	6	1.01±.12		
10/74	37°10'N	7	0.98±.13		
2/75	38°00'N	7	0.91±.05		
2/75	39°00'N	6	0.89±.06		
2/75	40°00'N	6	0.88±.05		
10/74	41°37.8'N	6	1.01±.16	5	0.79±.02
3/76	41°56'N	4	0.97±.14		
2/75	42°00'N	6	0.96±.16		
5/74	42°31'N	7	1.02±.15	13	0.74±.04
8/75	42°32'N	6	1.00±.20	9	0.73±.04
8/75	42°52'N	6	1.14±.18		
5/74	42°51'N	5	0.99±.20	5	0.75±.05
2/75	43°20'N	4	0.99±.03		

in natural waters can be obtained.

D.   Comparison of TOC Concentration by Different Studies.

   1.   Comparison of Dry Oxidation Values from Different
        Cruises

Samples were collected in the Central and Northwestern
Atlantic during 5 cruises. The TOC concentrations were
determined with the dry oxidation method #1 and the detailed
results are presented in the Appendix. The TOC results were
found to be consistent for the different cruises. The TOC
values at each station were divided into two parts and
averaged (Table XVII). The TOC values in the 0-200 m depth,
which included the euphotic zone, should have been influenced
by variation in productivity and seasonal changes, while the
deep samples (>200 m) should have been more homogenous, with
only small regional or seasonal influences.

These averaged TOC values over the depth ranges
(surface zone = 0-200 m, deep = >200m) were plotted versus
latitude (Figure 11). In the February 1975 cruise relatively
constant TOC values were found in both the well mixed,
isothermal surface zone (0.93 ± 0.04 mg C/liter) and the
deep water zone (0.75 ± 0.03 mg C/liter). Higher concentrations
of TOC in the surface zone were obtained in the Fall 1974
cruise (1.00 ± 0.07 mg C/liter), but the TOC values for the
deep water samples (0.74 ± 0.05 mg C/liter) were found to be
similar to other cruises. Higher TOC values in the surface zone

(1.02 - 0.07 mg C/liter) but comparable deep water TOC
values (0.74 ± 0.01 mg C/liter) were found in samples from
the slope area during Scotian Shelf cruises (5/74, 8/75,
3/76). A range of 0.87-1.14 mg C/liter were noted in these
depth integrated TOC values from the surface zone, while only
a small range of 0.70-0.79 mg C/liter was measured in the
TOC values in the deep water. In these 5 cruises the TOC
concentrations in the deep water were very similar. Both
the accuracy of the dry method and the small variations in
deep water were shown. Larger variations in the TOC
concentrations were noted in the shallower samples, but
this was probably the result of regional or seasonal effects.

The results from these 5 cruises were presented as a
single profile (Figure 12), and while scatter of the TOC
concentration was noted in the surface zone (0-200m), the
TOC values in the deeper water were tightly distributed.
The integrity and accuracy of my dry oxidation method for
the analysis of TOC in natural seawater samples were high
and the comparison of TOC results from different cruises and
times seemed justified.

2. Comparison of My Dry Oxidation Results with TOC Values
    of Other Workers.

Since other studies have been conducted in this area, a
comparison of the results seemed feasible. Data was taken

Fig. 2-12: Depth profile of TOC values (●) collected in the
Northwestern Atlantic. The TOC values were measured
by the Dry Oxidation method #1. ▲ - averaged TOC
values.

Fig. 2-13: Comparison of averaged TOC results from Northwestern
Atlantic by authors using different methods.
● MacKinnon (this study) - Dry Oxidation Method
#1; ◆ Skopintsev et al. (1966) Dry Oxidation
after evaporation; ■ Gordon and Sutcliffe (1973) -
Dry Combination after freeze drying; Δ Sharp (1973) -
Direct Combination of sample; ▲ Menzel (1970) -
wet oxidation.
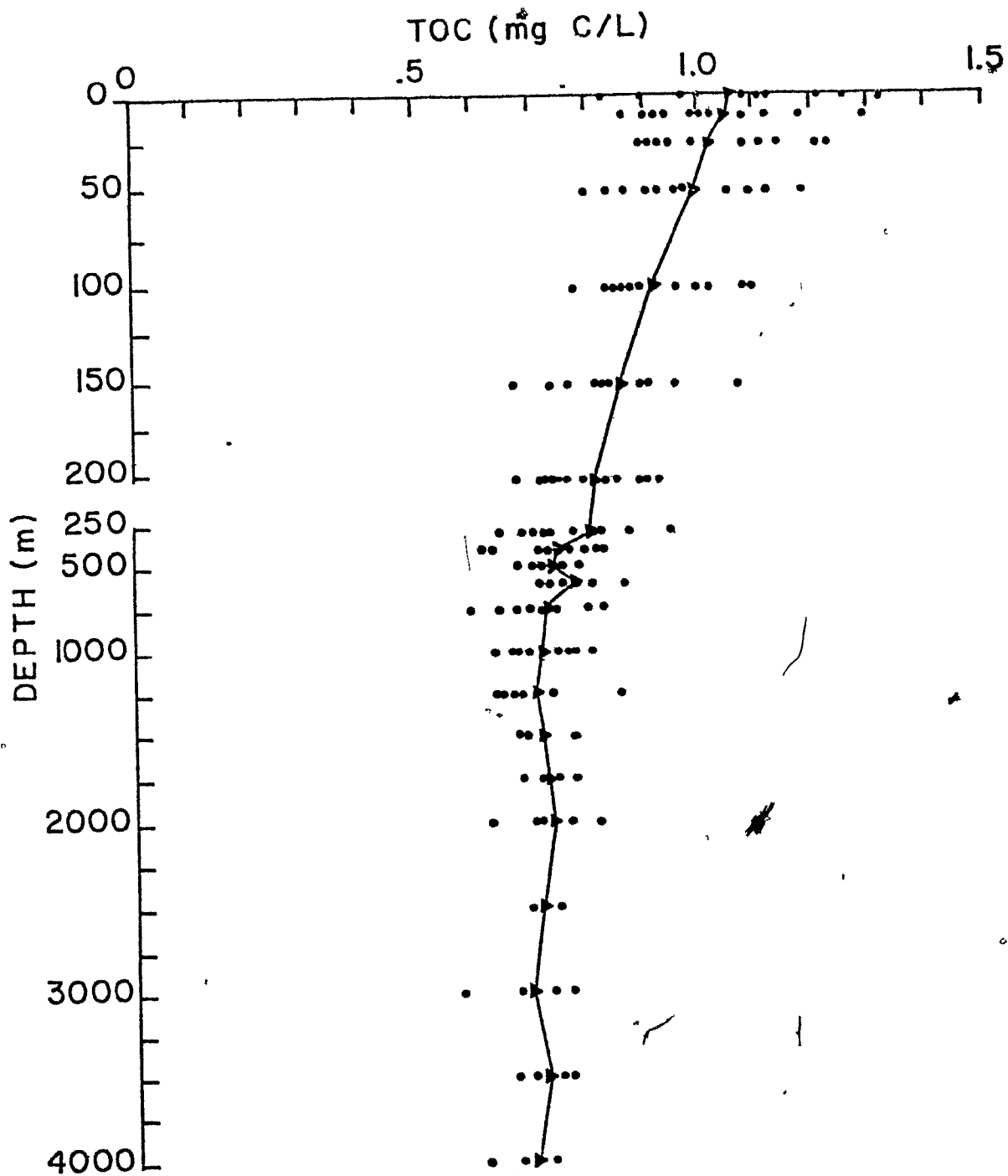
FIGURE 2-12
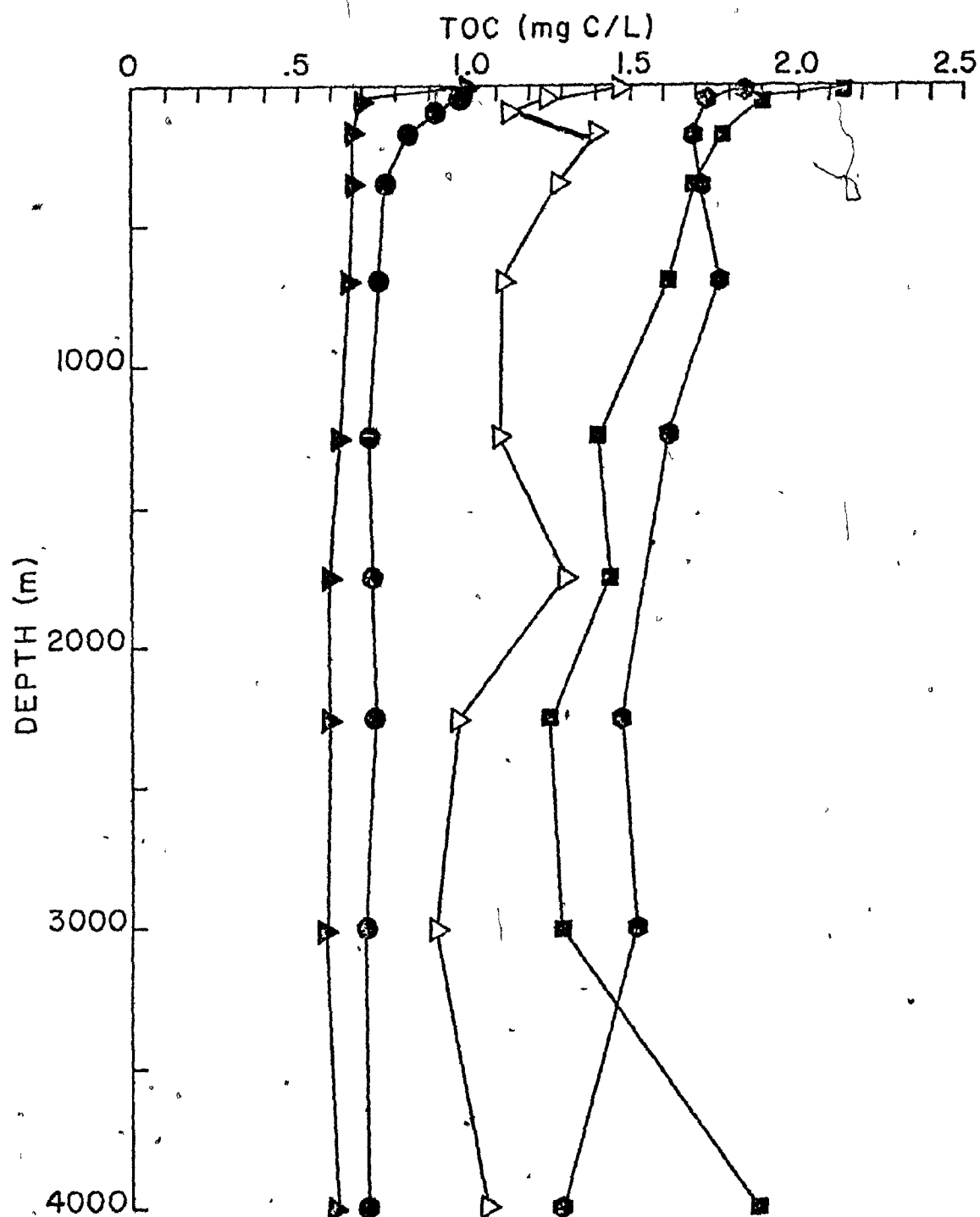
FIGURE 2-13

from Menzel (1970), Sharp (1973), Gordon and Sutcliffe (1973) and Skopintsev et al., (1966) and the TOC values were averaged into depth zones (Table XVIII) and were compared (Figure 13). All of the methods except Menzel's wet oxidation procedure were high temperature combustion methods (Sharp used a direct injection method, Gordon and Sutcliffe used a freeze drying method, while Skopintsev and this study used an evaporation procedure).

The results of Skopintsev and of Gordon and Sutcliffe were comparable, but were up to 4 times higher than those obtained by Menzel. Earlier discussions have argued that contamination from the storage and freeze drying procedure (unless blanks can be found to be acceptable for the equipment being used) could be used to explain the high and variable TOC concentrations which were observed by Gordon and Sutcliffe. However, the evaporation procedure which I used was similar to that of Skopintsev, but I obtained much lower TOC values than Skopintsev. The higher TOC values obtained by Skopintsev could be explained by a contamination or detector problem, which may be the cause of this large discrepancy. Later Soviet studies (Starikova and Yablokova, 1974, and Ljutsarev et al., 1975) have shown a tendence to a lower TOC values. Ljutsarev et al., (1975) used a wet oxidation procedure. The TOC values in deep water were very close to my values. Since the sample areas did not overlap, a direct comparison was not attempted. The values obtained by Sharp were higher

than those obtained in my study, but a large variability in
profiles of TOC values was shown and the fluctuations in TOC
concentrations of up to two times in adjacent samples in the
deep water of similar water types did not seem acceptable.
In Sharp's method, extreme instrument sensitivity was
required to allow detection of differences of 0.005-0.05 μg
C and very small interferences would have had drastic effects
on his results.

The vertical distributions of the TOC concentrations
obtained by Menzel and by this study were similar but my dry
oxidation values were about 20% higher (15-30%) than the wet
oxidation values of Menzel. This discrepancy between the
TOC concentration was very close to that noted in the
previous section, which compared wet and dry oxidation
procedures for the analysis of TOC in identical samples. A
similarity in the distribution of TOC results from wet and
dry procedures has been indicated by this study, and while
the two methods may not be measuring the same quantity of
organic carbon, the interpretations which can be extracted
from them should be similar (Table XIII).

Although the dry oxidation values of TOC that were
obtained with my analytical procedures cannot be assumed to
be the correct values, their closeness to the real value of
the TOC in natural waters is supported by the internal
consistency, the smoothness and predictability of
distribution, and the comparisons with other studies.

TABLE XVIII

Comparison of TOC Values From Different Studies in Similar Areas

Depth zone (m.)	n	Menzel (1970) (mg.C/l.)	n	Sharp (1973) (mg.C/l.)	n	Gordon and Sutcliffe (1973) (mg.C/l.)	n	Skopintsev et al.(1966) (mg.C/l.)	n	MacKinnon (this study) (mg.C/l.)
0-25 (10)	6	1.04	8	1.47±.14	8	2.14±.47		1.84	56	1.05±.12
25-50 (40)			6	1.26±.11					21	0.99±.10
50-100 (100)	6	0.70	3	1.14±.28	3	1.90±.33		1.74	18	0.92±.08
100-250 (175)	6	0.67	2	1.40	4	1.78±.62		1.70	29	0.84±.10
250-500 (350)	12	0.67	6	1.29±.28	4	1.70±.42		1.71	26	0.77±.08
500-1000 (700)	30	0.66	5	1.12±.24	10	1.62±.24		1.77	30	0.75±.06
1000-1500 (1250)	18	0.63	5	1.11±.21	4	1.41±.17		1.62	20	0.72±.06
1500-2000 (1750)	6	0.60	5	1.31±.20	4	1.44±.37			11	0.73±.03
2000-2500 (2250)	6	0.60	4	0.99±.17	3	1.27±.03		1.48	8	0.74±.06
2500-3500 (3000)	12	0.59	4	0.92±.16	2	1.30±.10		1.52	12	0.71±.05
3500-5000 (4000)	18	0.62	6	1.07±.24	2	1.68±.24		1.30	11	0.71±.04

VOLATILE ORGANIC CARBON IN NATURAL WATERS

A. Introduction

1. Definition:

The volatile organic matter (V.O.C.), is a fraction of the total organic matter (T.O.C.). In natural waters, the distribution and dynamics of this volatile organic matter are not fully understood largely because of analytical difficulties. Hypotheses have been postulated but reliable quantitative and qualitative data are sparse. The development of a better understanding of this fraction of the T.O.C. has been hindered by the lack of a precise definition for the volatile material. Instead, working definitions, based on the method of extraction and analysis, have been used and these vary according to the worker. A similar definition problem exists for the separation of the particulate and dissolved fractions of the T.O.C. in seawater (Sharp, 1973b).

The term volatile is ambiguous and can be defined in different ways:

1) Volatile material is usually defined as material which is "easily" vapourized, but the ease of vapourization is a relative term. In gas chromatography, organic compounds are considered volatile if they can be made to vapourize without any pretreatment. This sets an upper limit on the definition of volatile, and compounds in the C_{30} range are included. In the natural system, more interest should

be placed on those compounds with a vapour pressure equal to or greater than that of water (760 mm at 100°C and 24 mm at 25°C) since these are the materials which can be vapourized from the aqueous medium. Vapour pressure of organic compounds is inversely proportional to the carbon number, and volatile organics in natural waters should be mainly lower molecular weight compounds ($<C_8$).

ii) Volatile materials have been defined as the organic component which is stripped from a water sample with a gas under various conditions of heating and turbulence.

iii) Volatile materials can be defined as those compounds which will diffuse from the water under natural conditions of temperature and mixing.

Most classes of organic compounds (hydrocarbons, alcohols, aldehydes, acids, ethers, ketones, esters, amines, etc.) are included in these broad definitions for volatile material. The molecular weight cut off is dependent on the methods of extraction and analysis. Extraction methods for the volatile materials include distillation, liquid-liquid extraction, headspace analysis, and gaseous stripping. In this study the definition of the "volatile" component of the T.O.C. is based on a working definition which includes those organics which are stripped from heated seawater sample at natural pH with an inert gas and are concentrated on a solid support. However, not all materials which are

classed volatile by their vapour pressure will be analyzed.
Quantitative removal of hydrophilic polar compounds (acids,
amines) which fit the broad definition of volatile is not
found with the conditions used for the extraction. Similarly,
limitations in the trapping efficiences will lead to the
loss of very volatile components (C_1 - C_4 hydrocarbons).
These limits on the extraction and analysis procedures are
reflected in the working definition which is used in the
discussion of the volatile materials in this study.

The volatile organic carbon (VOC) has been discussed by
other workers as that fraction of the total organic carbon
(TOC) which is being lost (presumably during the acidification
and removal of the inorganic CO_2) with the present methods
for the analysis of the TOC. In wet oxidation procedures,
Wangersky (1972) argued that the purging step for the removal
of inorganic CO_2 will probably remove all the "volatile"
components, while Duursma (1961) observed only about a 5-10%
loss of low molecular weight acids during the purging.
Organic compounds of high vapour pressure and low solubility
are more likely to be lost (Van Hall, Barth, and Stenger,
1965) in the sample work up, but this should be only a small
and insignificant fraction of the TOC (Sharp, 1973). In the
dry oxidation procedures, the loss of the volatile components
of the TOC should be more than in the wet oxidation procedures
(Menzel and Vacarro, 1964, and Oppenheimer, Corcoran and Van

Arman, 1963) since organic compounds with a vapour pressure equal to or greater than that of water under the conditions used in the sample workup will be lost during the evaporation or freeze drying step in the TOC analysis (Montgomery and Tham, 1962, Skopintsev, 1966, Gordon and Sutcliffe, 1973). The importance of this volatile fraction of the TOC will be better understood by the quantification of the volatile organic material and the determination of its role in the cycle of organic matter in natural waters.

2.   Analysis of the V.O.C.

The existing TOC methods remove varying amounts of the "volatile" fraction. This loss is difficult to quantify. In order to develop a quantitative or qualitative picture of the volatile fraction of the TOC, methods of extraction and concentration are required which are gentle enough to prevent breakdown or alteration of the constituents yet complete enough to yield an accurate estimate of the "volatile" concentration. Both indirect and direct methods have been used.

i)   Indirect Methods

Skopintsev (1966) estimated that about 15% of the TOC was volatile by comparing the dry oxidation results for the TOC from identical samples evaporated at room temperature and elevated temperature (50-60°C). The difference in TOC values was assumed to be the result of the loss of volatiles

at the elevated temperature but, while the rate of evaporation would be affected by an increase in temperature, the increased loss of the volatile fraction during the evaporation is questionable. It is possible that the 15% difference reported by Skopintsev was the result of contamination during the extension of the evaporation period at the lower temperature and not the retention of the VOC. A direct injection method for TOC was described by Van Hall and Stenger (1967) in which the VOC was estimated by an indirect method ((TC-

TC)$_{(before purging)}$ - TOC$_{(after purging)}$ = VOC) but its use was limited to industrial wastes where up to 20% of the TOC was calculated to be volatile.

11) Direct methods

The direct determination of the volatiles has been attempted with distillation, liquid extraction, head-space analysis, gaseous stripping, and direct injection methods.

a) Distillation

Vacuum distillation of extracellular material from culture media was used by Armstrong and Boalch (1960) to extract and concentrate the volatile components which were considered to include acids, aldehydes, ketones, and amines. With this approach, concentrations of the VOC for culture media were found to be 10-110 µg C/liter and for seawater samples about 20-50 µg C/liter. Steam distillation was used by Lamer and Goerlitz (1963) for the examination of 20 carboxylic acids in lake waters, but the handling required

was extensive. Ryabov, Rabivanets, and Litvinenko (1972) described a wet oxidation procedure in which the distillate containing the volatile components was oxidized.' Only the organic compounds with a high volatility were measured by this technique and the application to seawater samples with low concentration of organic material seems questionable.

.Shortcomings of the distillation method include potential thermal decomposition of heat labile materials, incomplete removal of the volatile components, and the inefficiency of the trapping procedures.

b) Liquid - liquid extraction

Low molecular weight acids from surface and deep ocean waters were measured by Koyama (1962) and Koyama and Thompson (1964) using a continuous extraction for 3-5 weeks. Concentration in the 0-2.8 mg. C/liter range were found, but since excessive sample handling was required the results may be suspect. Using a distillation procedure, Creac'h (1955) found concentration of low molecular weight acids in seawater in the 4-5 μg C/liter range, while Kamata (1966) measured the volatile aldehydes and obtained concentrations of 0-10 μg C/liter over a 4000 meter profile in the Pacific. Shortcomings of this extraction approach to volatile analysis include the variation in the extraction efficiencies with various classes of compounds and the problems in the concentration of the volatile components which have been extracted.

c)   Head-space Analysis

Corwin (1970) used a head space method for the analysis
of low molecular weight ketones and aldehydes in seawater.
Samples were withdrawn from the headspace and injected into
a gas chromatograph and a sensitivity of 2 µg C/liter was
reported. The volatile organic distribution was found to be
irregular with depth and area. The volatile organic
concentrations were measured in the 8-40 µg C/liter range
with specific components, such as acetone, as high as 20 µg
C/liter in some ocean samples. Hurst (1974) modified the
head space method by using a liquid N_2 trap to collect and
concentrate the volatiles in the vapour phase above the
sample. Bassett and Ward (1969) discussed the quantitative
potential of the head space method. The method was found to
be 90% effective for high vapour pressure, low solubility
materials, like methyl sulfide, but as the volatility
decreased and solubility increased, the extraction efficiencies
were reduced so that only about 20% of acetone and 1-2% of
ethanol could be extracted from an aqueous medium. The
quantitative analysis of volatiles by this method is dependent
on the properties of the specific components, and standardization
or calibration to the matrix of organics is difficult.

d)   Gaseous stripping

The efficiency of the volatile extraction is increased
by the constant stripping of the head space over the sample

This procedure can be considered a dynamic headspace analysis. Diffusion of the volatiles from the water to the vapour above the sample is maximized by the constant removal of the head space, as discussed by MacKay and Cohen (1976) and Liss (1973, 1975). The rate of volatilization is expressed as a flux.

flux = mass transfer coefficient x concentration difference
of a component in sample
and head space
C (mass/volume)

F (mass/unit time x area) = K $\dfrac{\text{(unit of thickness)}}{\text{(unit time)}}$ x C

F = flux in moles per unit area per unit time

K = diffusion coefficient for a region of thickness between the two phases

The concentration difference (concentration of component in sample versus concentration in head space or vapour) is maximized by the constant flushing of the head space, and a maximum flux of material from the water into the vapour will be maintained. The flux for individual components is dependent on the mass transfer coefficient, or diffusion coefficient, concentration in the water, and concentration in the vapour phase.

$$F = K \, (C_{liquid} - C_{vapour}) = K \, (C_{liquid} - P/H)$$

since from Henry's Law

$$P = HC \text{ vapour}$$

Γ = mass flux

K = mass transfer coefficient in liquid

C_{liquid} = concentration of the component in liquid

C_{vapour} = concentration of component in vapour or head space

P = partial pressure in atmospheres

H = Henry's Law constant

The efficiency of the dynamic head space extraction is enhanced if the sample temperature is increased (20 fold increase in head space concentration of volatile organics for every 25°C increase of the sample) and the stripping gas is allowed to run through the sample (Mieure and Dietrich, 1973). The removal of specific components from seawater by purging the samples with gas was shown by chromatographic analysis before and after the stripping (Pueschel and Van Valin, 1974).

Different methods have been used for the concentration of the stripped volatile materials. Mieure and Dietrich (1973) used a porous polymer of 2,6-diphenyl-paraphenylene oxide (Tenax G.C.) to trap the volatiles from water samples. They reported a sensitivity of 1 ppb. The efficiency, properties, and application of the Tenax G.C. packing for the analysis of volatiles in seawater have been studied (Russel, 1975, Daemer et al., 1975). An automated system has been described (Dowty, Green and Laseter, 1976) in which the

volatiles were stripped from a heated sample, concentrated on a Tenax G.C. trap, desorbed into a G.C., and analyzed with a minimum of sample handling.

Zlatkis and his co-workers (Zlatkis et al., 1973, Zlatkis, Lichenstein, and Tishbee, 1973, Zlatkis et al., 1973, Bertsch, Zlatkis, Liebich and Schneider, 1974) developed the use of the Tenax G.C. polymer for the analysis of the volatile organics in air and biological fluids. This approach seemed feasible for the analysis of volatiles in natural waters. In their method, the volatiles in the head space from a heated sample (100°C) were concentrated on a solid support (Tenax G.C.) and were analyzed by GC-MS. A wide range of compounds of varying volatility and boiling points were shown to be extracted by this method.

A cold trap was used by Games and Hayes (1976) to concentrate the volatile organics stripped from a water sample. The volatiles were oxidized and quantified as CO_2, and while the method was 100%-efficient for heptane, it was only 1-2% efficient for acetone. The more soluble, less volatile organics were not extracted efficiently in this approach. Novak et al. (1973) stripped the volatile organics from sample, concentrated them in a cold trap, and identified them with GC-MS. At room temperature, they found that organic substances with boiling points up to 140°C were stripped from the water and an efficiency of extraction of

40-50°C was reported for the volatile components in the sample. Concentrations of individual volatile constituents. were determined to be of the order of 0.01 - 0.10 µg/liter.

'A charcoal trap was used by Grob (1973) for the qualitative analysis of the volatile components in natural waters. In an enclosed system, the purging gas was recycled through the water and the stripped volatiles were concentrated on a charcoal trap and analysed with G.C.-M.S. The effective removal of organic compounds up to C_{27}' from lake and drinking water with a ppt sensitivity was noted (Grob and Grob, 1974). The methods for the extraction of the volatile compounds from natural waters were examined (Grob, Grob, and Grob, 1975) and gaseous stripping was concluded to be more effective than liquid - liquid extraction for the volatile components.

Stripping methods were used in the analysis of lower molecular weight hydrocarbons (Swinnerton and Linnebom, 1967) in seawater samples. The results (Swinnerton and Linnebom, 1974 and Williams, 1975) were found to average about 0.01-0.10 µg/liter in the open ocean. Similar methods were used to study the halogenated hydrocarbons in fresh water (Lovelock, Maggs, and Wade, 1973).

The method of gaseous stripping and concentration for the volatile analysis seems to offer high extraction efficiency, good contamination control, and the choice of a

trapping system most suitable to the materials of interest.
However, methods of trapping and stripping must be optimized
for best results.

e) Direct injection methods

A direct analysis system in which the aqueous sample
was injected into a G.C.-M.S. system and analyzed directly
was described by Harris, Budde and Eichelberger (1974).
Many of the low molecular weight materials were identified,
but the application was limited to water of high organic
content such as waste waters and sewage. This approach,
if refined for natural waters, would eliminate the need for
the extraction and concentration steps of other procedures.

3. Sources of V.O.C. in Natural Waters

The volatile organic materials are a fraction of the
T.O.C. and their sources in nature should be similar.
The volatiles or low molecular weight organics are
introduced to natural waters by biological activity,
influence by man, input from terrestial systems and chemical
reactions.

a) Biological activity

The excretion and secretion of low molecular weight
organic materials from organisms (plant or animal) or the
decomposition of these materials should be a source of volatile
organic material in natural waters. Low molecular weight

byonic materials, which may be volatile under the conditions,
found in nature, have been reported as by-products of
primary productivity and extracellular production (Wangersky,
1972). An indication of the variety of organic compounds
that is to be expected was presented by Josefsson (1970).
Armstrong and Boalch (1960) estimated the actual quantity of
volatile material which can be produced in an algal culture
(about 10-100 g.C/liter). Many of the low molecular weight
organics have been linked to biological activity. Included
in this group are hydrocarbons (Lamontagne, Smith, and
Swinnerton, 1975), acids (Koyama, 1962, Shah and Wright,
1974, Drucker, 1970), aldehydes (Armstrong and Boalch, 1960,
Corwin, 1970, and Kanata, 1966) ketones (Corwin, 1970),
amines (Nemtseva et al., 1964, Armstrong and Boalch, 1960)
amino acids (Degens, 1970), and organic sulfur compounds
(Lovelock et al., 1972).

b) Influence by man

Low molecular organics are produced by man and are
introduced into the biosphere. An estimate of the rates of
the input of a number of synthetic volatile organics was
presented by Goldberg (1971). These synthetic materials
included aldehydes, amines, ketones, esters, hydrocarbons,
halogenated hydrocarbons, ethers, alcohols, nitriles, and
sulfides. These volatile materials may be introduced into
the ocean by wind or drainage systems. Low molecular weight

hydrocarbons were measured in oceanic waters by Swinnerton and Lamontagne (1974). The unsaturated hydrocarbons have biological sources, but the C_2-C_4 saturated hydrocarbons which did not appear to be the result of plankton activity may have been added by the activities of man. Many of the low molecular weight materials being added by man have toxic and carcinogenic properties; even at ppb concentrations these materials may be potentially harmful to biological systems in the natural environments (Pellizzari et al., 1976, Button, 1971). A review of these expected compounds has been presented by Duursma and Marchand (1974).

c)   Input from terrestial system

Freshwater systems are high in organic carbon (1-20 ppm), and higher inputs of low molecular weight materials are to be expected. However, effects should be localized, and little large scale effect on the oceans is to be expected. The input of volatile materials to the oceans would be further reduced if "salting out" effects occurred at the salt-fresh water mixing zone.

d)   Chemical reactions

Low molecular weight organics are possible products of chemical reaction in natural systems. The presence of halogenated hydrocarbons in drinking water (Dowty, Carlisle, and Laseter, 1975) could not be explained by biological or pollution sources only. Aerial and oceanic distributions of

the halogenated hydrocarbons (Lovelock, Maggs and Wade, 1973) were explained as a combination of all three sources of input (biological, synthetic, and chemical). Creac'h (1955) showed a photochemical production of acetone, aldehyde, acetic acid, formaldehyde, and formic acid when citric acid and malic-acid were irradiated in seawater with 3100 $\overset{o}{A}$ light. Production of C_2-C_4 hydrocarbons was considered to be the result of photochemical breakdown of the dissolved organic matter (Wilson, 1970). Zika (1977) reviewed photochemical reactions in seawater and showed that low molecular weight organics were produced by the photodecomposition under natural light conditions of amino acids at the concentrations found in nature.

4.   Distribution of VOC in natural waters.

The distribution of the volatile organic material in the aquatic environment has yet to be fully understood. With indirect methods, the molecular weight distributions of the organic matter have been examined and a rough idea of the geographic and depth profiles of the low molecular weight organics has been obtained. Ultrafiltration techniques were used to show the molecular weight variations in an estuary (Smith, 1976), and a large fractions was noted to have a molecular weight less than 1000 (30-40%). In ocean water, Ogura (1974) noted 24-42% (average 33%) of the organic material passed his Diaflo UM-05 filter, which had a 500 molecular

weight cut-off. The percentage of the low molecular weight material decreased with depth, although deep open ocean, samples were not examined. If these numbers from ultrafiltration were accurate, then the upper limit of the volatile fraction of the TOC would be set at about 30%, which was the fraction of TOC with molecular weight less than 500. Baturina et al. (1975) used ultrafiltration for surface and deep water in the equatorial Pacific and found that about 60% of the organic material passed through a 500 molecular weight membrane filter. With depth, the amount of material in this low molecular weight fraction was reduced to about 50% of the total. This higher estimate of the lower molecular weight fraction might mean that this fraction is more significant than the other workers had determined.

The shortcomings of this indirect approach are shown by the lack of agreement and differences in the interpretation obtained by a similar method. A direct quantification of the VOC is required to answer the questions pertaining to the distribution of the volatile component of the TOC.

The principal sources of the volatiles in the natural system have been presented. If the assumptions were valid, a prediction of the expected distributions in the ocean system can be made.

In areas of high biological productivity or activity with higher rates of secretion, excretion, or decomposition,

an increase in the VOC concentration should be observed.
During periods of biological blooms the VOC concentrations
should be influenced. The surface zone is the area where
photochemical reactions and biological productivity in the
oceans are occurring, so that higher values of VOC should be
measured in the surface zone, with the amounts of VOC
decreasing below the euphotic zone. The influence of man on
the VOC concentration in the oceans should be localized and
would be highest in areas of large population, heavy
industrialization, or shipping, and this influence may be
more important to the distribution and quantity of specific
constituents than to the total VOC concentration. The
input from fresh water systems should have little large
scale effect on the VOC concentrations in the ocean waters.
Geographically, higher values should be found in areas of
high biological activity, of input from coastal regions, or
under the influence of man. In vertical profiles, higher
values of VOC in the surface zone, decreasing concentrations
of VOC below the euphotic zone, and relatively constant
concentrations of VOC with depth except in anoxic areas should
be expected. The qualitative distribution of individual
volatile components should better reflect these influences, but
a quantitative change was also expected to be detectable.
However, if the volatile fraction is extremely labile and the
rate of consumption or decomposition balances the rate of production,

then little change with the different influences described
may be observed.

5.   Role of VOC in Natural Waters

The volatile fraction of the TOC may play an important
part in the cycle of organic carbon in the natural environment.
The low molecular weight "volatile" materials may be an
integral part of the pathways for the removal (physically-
vapourization into the atmosphere; chemically - breakdown to
more labile materials or complete remineralization; biologically -
more easily utilized by organisms) of a fraction of the TOC
from natural waters. These organic volatile materials may
be easily utilized, decomposed, and remineralized, so that
their role in nutrient regeneration may be very important.
Also, the influence by man on the natural system can be
monitored by the examination of the volatile components which
are known to be of anthropogenic origin. In situ production of
volatile organic materials by non-biological systems, such as
thermal reactions or photolytic oxidation or reduction, can be
followed. Insight into the importance and the extent of
these reactions in natural waters can be obtained.

6.   Study of VOC in Natural Waters

In this study, I have developed a direct method for the
precise and accurate quantification of the VOC in seawater.

I have examined the distribution of the VOC in various marine environments. The VOC results have been presented both as absolute concentrations and as a ratio of the volatile to the total organic carbons (VOC/TOC), which allowed for the normalization of the volatiles as a percentage of the TOC. I performed a series of experiments which were designed to provide information of the possible origin, role, and fate of the VOC. These studies are interpreted and discussed with respect to the total organic carbon pool and its dynamics.

B   Development of Method for VOC Analysis in Natural Waters

1.   Sampling

The accuracy of the analysis for the volatile fraction
was dependent upon the collection and analysis of a sample
that had not been changed from the time that it was in nature.
The loss of the VOC had to be minimized and introduction of
contaminants from the air or sampling apparatus had to be
prevented.

Niskin bottles (General Oceanics) were used for the
sampling and, when possible, they were fitted with stainless
steel springs instead of rubber tubing. The presence of
rubber in the sampler, however, was not observed to be a
problem. Another potential problem with the Niskins that
had to be considered was that they must pass through the
surface film open and the inner surfaces of the bottle may
become coated with organics which could contaminate the
deeper samples. This did not appear to be a major problem
in the quantification of the VOC, but if qualitative
analysis was required, this contamination of the bottle
passing through the surface zone might have been more
critical.

Care was also required in the transfer of the sample
from the Niskin to the sample bottles. The samples were
withdrawn from the Niskins as soon as possible after the
cast in order to minimize the contamination from the Niskin

or the atmosphere and to protect against vapourization of the more volatile materials in the sample. The procedure used for the withdrawing of samples for dissolved oxygen was followed (Strickland and Parsons, 1968). This prevented bubble formation and minimized the chances of loss of the volatile organics during the sample transfer. The samples were frozen during storage, so an air space was required above the sample to prevent breakage. The sample bottles were 650 ml amber bottles which had been cleaned and baked (150-200°C). Each bottle was filled to overflowing with the sample from the Niskin and then mercuric chloride (0.5 ml of 3%) was added to fix the sample. The use of $HgCl_2$ for the preservation of samples against biological alteration was recommended by Yoshinari (1973, 1976). After the sample was fixed, 50-75 ml were quickly poured out and the bottle was capped with an air tight plastic coated metal cap and then frozen. Microbial decomposition or production of volatiles during storage before analysis should be eliminated by the use of this procedure of fixing and freezing the sample. This sampling scheme seemed to minimize contamination and good reproducibility for VOC analysis was obtained.

2.   Conditions for the Extraction of the VOC from Water

In the preliminary development of an extraction procedure for the VOC, I tried a steady state stripping method from a

heated water column. The purging gas was split after passing through the water sample and half was carried directly to one side of a Lira Model 200 dual cell IR detector, while the other side of the Lira received the purging gas after being oxidized in an oxidation furnace. The difference in the measured CO_2 in the two streams was the result of the oxidation of the volatile fraction $(VOC_{(organic material removed by stripping)} + IC) - IC = VOC)$. This approach to VOC analysis was limited to high concentrations of non polar material (ether, heptane) and was not sensitive enough for the low concentrations found in natural waters.

The method that was accepted for the extraction of the volatiles from water was based on a head space stripping procedure in which the heated water sample was purged with N_2 (Mieure and Dietrich, 1973).

a)   Effect of Temperature on Extraction of Volatiles

Since the head space concentration of the volatile is increased (20 fold increase in concentration for 25°C increase) with sample heating, a higher temperature (80°C) was used to facilitate the removal of the VOC. However, care was required to ensure that thermal breakdown of larger organic materials was not a major source of measured volatiles. The problem of contamination of the VOC values from this source was not indicated in the results obtained.

Thermal decomposition would have been suspected if unusually large concentrations of VOC were found or if no decrease in the rate of extraction of the volatiles was observed with time. An upper limit was placed on the temperature of the sample during the extraction, in order to limit the amount of water evolved. Water was an interfering material, and if evolved in sufficiently large amounts, it reduced the efficiency of the traps and clogged the cold traps more quickly. At a temperature of 75-80°C, the extraction of the volatiles was increased but problems of excessive water vapour and thermal decomposition were not observed.

The amount of volatile material removed in a period of stripping is dependent on the water temperature (Figure 1). Using the same extraction procedure for identical samples, the amount of VOC measured in the same period of time was observed to increase as the sample temperatures were increased from 30-90°C (Table 1). The rate of extraction of the volatiles was found to be 2-3 times faster with the heated samples, and extraction times could be reduced. The complexity and range of the extracted volatiles should be expanded, since materials which would be missed or incompletely stripped (organic compounds with higher molecular weight and higher boiling points) at room temperature purging should be more efficiently extracted from the heated samples. I used this more efficient stripping procedure in this study, and

Fig. 3-1:   Effect of temperature on the amount of volatile
organic carbon extracted per unit time.
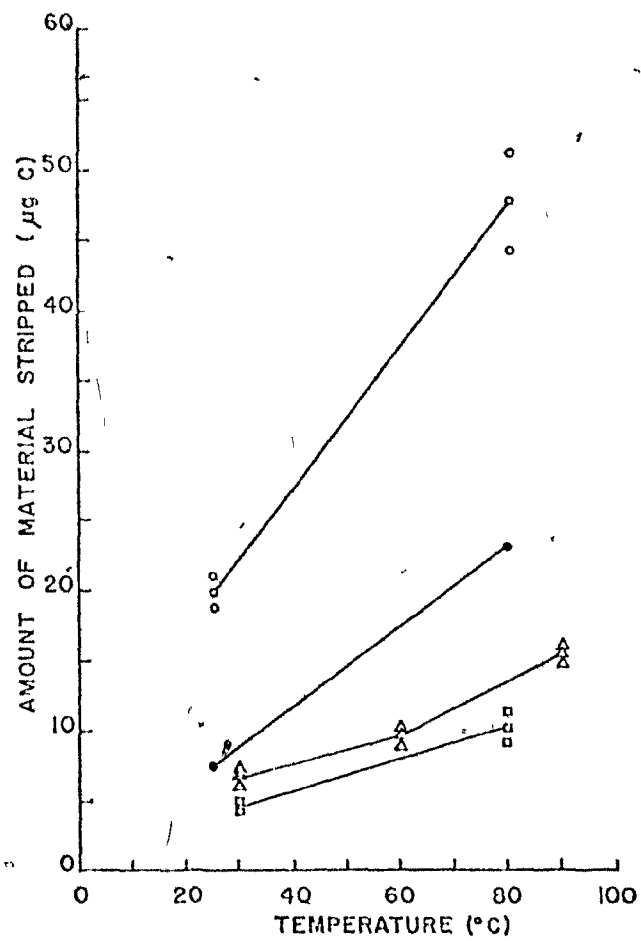
TABLE I

Temperature Effect on Rate of Stripping VOC From Seawater

Sample	Temperature $^{\circ}C$	Time of Stripping (hr.)	Organic Material Stripped per Liter (μg C)	Rate of Removal from the Water (μg C/liter)/hr.
1.	30	11.5	6.09 7.00	0.57
	60	11.5	10.10 8.90	0.86
	90	11.5	14.90 15.80	1.33
2.	30	9.0	4.3 4.7	0.50
	80	9.0	9.2 11.2	1.13
3.	25	9.0	7.39	0.87
	80	9.0	23.11	2.57
4.	25	9.0	18.74 20.91	2.20
	80	9.0	44.16 51.20	5.30

my working definition of "volatile" includes the organic materials extracted under these conditions.

b) Extraction Containers and the System Blank

The extraction of the VOC from the water was carried out either directly from the amber sampling bottle in which the sample had been stored or from a stripping chamber to which the sample was transferred under N_2 atmosphere. A sample size of 500-600 ml was found sufficient for a reliable and precise analysis of the VOC in natural waters.

Contamination from the sample bottle, sample handling, or the stripping procedure was estimated by examination of the calculated concentration of the VOC from different volumes of the same sample. The sample with smaller volumes would be expected to be more affected by the contamination, and to show higher VOC concentrations. The results from such an experiment with various sample volumes from identical water were analyzed and quantified (Table II). An increase in the calculated VOC concentrations for the smaller sample volumes was noted, but the volume effect on the calculated VOC was not excessive and a system blank of about 2.5 μg.C per analysis was estimated. For average samples of 500-600 ml this meant that blanks were about 4-5 μg.C/liter. When the calculated VOC concentrations in Table II were corrected for this system blank, the concentrations from the various

TABLE II

Effect of Sample Volume on the Calculated VOC Concentrations

Sample	Sample Volume (ml.)	VOC Measured in Sample (µg.C)	Calculated VOC Concentration (uncorrected for blank) (µg.C/liter)	Calculated VOC Concentration (corrected for blank) (µg.C/liter)
1. Tap Seawater	115	4.53	39.40	17.65
	165	5.91	35.81	20.67
	330	7.89	23.91	16.33
	385	8.44	21.92	15.42
	490	10.43	21.29	16.20
MEAN =				17.23±2.0
2. Tap Seawater	350	3.12	8.90	6.03
	400	4.06	10.16	7.65
	570	4.90	8.60	6.80
MEAN =				6.83±0.8
3. Tap Seawater	350	3.92	11.20	6.89
	550	5.06	9.20	6.45
MEAN =				6.67

TABLE III

Recovery of Acetone Added Directly to the Stripping Chamber Without Water

Amount of Acetone Added (µg C)	Amount of Acetone Measured (µg C)	% Recovered
5.0	5.42	108
12.5	12.61	101
12.5	10.03	80
25.0	25.71	103

sample volumes were in good agreement (·10%).

c) Effect of pH

The volatiles which were of the most interest in this study were those compounds which were potentially evolved in nature. Therefore, the pH of the system was left at the natural value (pH = 8.1-8.3). During the stripping of the seawater sample with the inert gas (N_2) a slight increase in the pH (pH = 8.5-8.8) was observed as the inorganic CO_2 was swept from the system, but the use of a buffer did not seem warranted. When seawater samples were extracted at a low pH (2.0) and at an elevated pH (9.0), no significant difference in the quantity of the volatile organic material extracted was found. However, as the pH is varied, the specific components that would be stripped from the sample would be expected to change. This is an area where future work with qualitative methods may provide some interesting answers.

3. Concentration of the VOC extracted from natural waters

After the VOC had been extracted from the water samples, a system was required which would quantitatively trap the material. This system should have a minimum of interference from the water or the CO_2 that are evolved during the extraction from seawater samples.

a)   'Choice of trapping system

A combination of a cold trap and a solid adsorbent trap was used to concentrate the volatiles. Ease in handling, storing, and desorbing is provided by the solid adsorbent trap, while a better trapping ability but less flexibility is found with the cold trap (dry ice or liquid N_2).

I tried several solid supports which had been recommended by other workers (Chromosorb 101, Chromosorb 105, Poropak Q and Tenax G.C.). Chromosorb 101 was eliminated since it was found to break down under the conditions used. Poropak Q was used (Takahashi et al., 1972) to trap volatile organics but the contamination problems (Hurst, 1974), such as thermal break down and column bleed, led to high blanks so its use was discontinued. Chromosorb 105 is an intermediate polar polyaromatic type porous polymer on which the organics were successfully trapped, but great care was required to prevent thermal breakdown and column bleed. Tenax G.C. (2,6-diphenyl-p-phenylene oxide) was found to fulfill most of the requirements expected for a packing material and had been used successfully in qualitative work (Zlatkis, 1973, 1974, Mieure and Dietrich, 1973). The adsorptive properties of Tenax G.C. for the concentration of organic components, expressed as breakthrough volume (Russell, 1975), are acceptable.

Tenax G.C. is a porous polymer which has a high maximum temperature (375°C) with no organic bleed noted below 250°C.

The Tenax traps were easy to handle and prepare and long column life was found. The columns were conditioned at 250-275°C and were desorbed at 160-200°C. No organic bleed was recorded in the analysis and column performance and efficiency were not adversely affected by the water contact (Janek et al., 1974) during the stripping procedure and by the repeated conditioning. A minimum of water and CO_2 are retained by the Tenax G.C. Initially the Chromosorb 105 was used in conjunction with the Tenax G.C., with the assumption that some of the material lost by the Tenax would be adsorbed by the Chromosorb. Any quantitative benefits were negated by problems in the contamination and care of handling required by the Chromosorb 105, so the use of the Chromosorb 105 was eliminated. The trap that was chosen for the concentration of the volatile organic material extracted from a water sample was a 25 cm long stainless steel (1/4" O.D.) tube packed with 2 cc of 35/60 mesh Tenax G.C. (Applied Science).

b)   Conditions for concentrating the VOC

Tenax G. C. has a low column efficiency, and at flow rates greater than 20-25 ml/min. the adsorbing efficiency is reduced rapidly. For the initial trapping period of my extraction, the stripping gas (N_2) was run at 30-40 ml./min. and the retention efficiency of the column should have been reduced. To compensate for this, I placed a dry ice trap

(-78°) in line after the Tenax trap to catch the organic materials which the Tenax was unable to retain under these flow conditions. This combination of traps proved quite effective. The initial extraction time could be increased if most of the water that was vapourized during the stripping step was condensed from the carrier gas before the traps. After the first stage of the extraction was completed and the traps removed, flow rates for the stripping gas were reduced to about 20 ml./min. and the Tenax trap was used alone for the concentration of the volatile organics.

With this extraction procedure, the more volatile materials should be removed from the water sample in the first stage of the extraction, and with continued stripping of the sample some of the more soluble and less volatile organic materials that are more difficult to extract should be removed. An even more efficient stripping of the water sample should be possible with a faster flow rate of the purging gas (greater than 50 ml./min.), but with the slower flow rates (20-40 ml./min.) the potential contamination of the traps with non-volatile organic material, carried in the aerosol rather than in the vapour phase, should be minimized.

   c)   Efficiency of the Extraction and Concentration of the VOC

An indication of the potential efficiency of the extraction

and trapping procedure for the VOC analysis can be obtained by the analysis of standard materials. In my extracting system, a scrubbing time of 4-6 hours under faster flow (30- 40 ml./min.) and 14-18 hours under slower flow (20-25 ml./min.) meant that the 600 ml. amber sample bottle was flushed an equivalent of about 50-60 times with the stripping gas (N_2) during the extraction. The efficiency to be expected from the stripping, extracting, and trapping system in my analysis was measured by the addition of acetone standard solutions to the large amber sample bottle with no water present (Table III). The volatile material was extracted with the same procedure used for a water sample. The efficiency of the removal, problems of absorption to the container or condenser, column efficiency, and completeness of the trapping for this acetone standard were tested and high per cent recoveries of the acetone (98%) were recorded. The feasibility and potential accuracy of my extraction procedure for the quantitative analysis of the small quantities of the VOC expected in natural samples seemed acceptable.

4. Analysis of the VOC

After the "volatile" (low molecular weight, high vapour pressure, low boiling point) organic material was stripped and concentrated under the conditions of my extraction procedure, either a quantitative or qualitative analysis

could be carried out. In this study the interest centered on the the quantification of this VOC.

a) Interferences in the Quantification of VOC

A detection system for the VOC was designed in which the extracted and concentrated organic matter was oxidized in a high temperature (900°C) oxidation furnace and the CO_2 produced was analyzed with a non-dispersive IR. The actual system will be described in more detail presently. In analyses that are based on the oxidation of the organic matter and the measurement of the CO_2, the interference from the inorganic CO_2 in the seawater samples must be overcome. While inorganic CO_2 was not adsorbed to any great extent by the Tenax G. C., enough CO_2 appeared to be absorbed so that the analysis of the small quantities of VOC was affected. The interference from the inorganic CO_2 was overcome with the use of a procedure where the material trapped on the Tenax column was desorbed (160-200°C) with a flow of N_2 (35-45 ml./min.) for 35-45 minutes into a stainless steel U-tube (50 cm. x 1/4" O.D.) which was placed in a Dewar flask packed with dry ice (-78°C). The organic materials which had been concentrated by the Tenax trap were trapped by the dry ice trap (-78°C), but the inorganic CO_2 was not. This inorganic CO_2 was monitored with the IR detector as it passed through the dry ice trap. In the preliminary work, liquid N_2 (-196°C) was used as the desorption cold trap, but at this temperature

the inorganic CO_2 was also trapped. The efficiency of the dry ice (-78°C) trap verus the liquid N_2(-196°C) trap for the trapping of a volatile material like acetone was found to be almost identical. In both cold traps, the vapour pressure of most of the volatile materials is extremely low (Games and Hayes, 1976). However, the dry ice was preferred as the cold trap since the interference from the inorganic CO_2 in the quantification of the VOC was eliminated.

The Tenax trap was desorbed at 160-200° C under a flow of N_2. The organic materials which are desorbed will be limited by their boiling point, and the interference from high boiling point nonvolatile organic materials, which might have been stripped from the water sample into the Tenax trap in an aerosol rather than in the vapour phase, should be minimized. Problems of oxidative breakdown of the larger molecular weight compounds or the columns packing (Tenax G.C.) were retarded by the desorption under a N_2 atmosphere.

b) Oxidation of the VOC

The volatile organic material from the Tenax trap was collected in the cold trap (-78°C). This was then quickly desorbed into the oxygenated zone of the high temperature oxidation furnace (850-950°C). The organic materials were carrried to the oxidation zone through a quartz tube (20 cm. x 15 cm.) which was maintained at 150°C. Since this tube was heated, water build up or volatile organic absorption to

the tube were prevented and the transfer of "nonvolatile",
high molecular weight organics was limited. Interference
from water was not found to be a problem, and after the
oxidation the water was removed with a condenser and a
drying column before the oxidative products reached the IR
detector.

c) Calibration of the detection system

An acetone standard (0.5%) was injected into the Tenax
column and then analyzed with my detection system. The
acetone was desorbed from the column into the cold trap (-78°C)
and then the acetone was flushed into the oxidation
furnace and the resulting CO_2 measured with the IR detector.
A simpler and faster procedure was the injection of this
acetone standard (2.5 µg.C/liter) into the stainless steel
U-tube which was used as the cold trap. This was then
heated and the material analyzed. Results from both procedures
were essentially the same, but the latter method was faster.
A linear response from the IR detector over the range of
concentrations expected in natural samples (0-25 µg.C) was
obtained. The peak shapes were very sharp and symmetrical,
and the calibration lines were linear in the desired concentration
range.

5. Accuracy and Precision of the Method for the Determination
   of the VOC in Natural Waters.

a)   Analysis of Standard Solutions

The evaluation of the effectiveness of the stripping, concentration, and analysis steps for the quantification of the volatile fraction of the organic matter in seawater was attempted by the analysis of standard materials. Standard solutions (classes of expected volatile materials) were injected into seawater samples which had been previously stripped of most of their "volatile" components. After the standards were added, the system used for the determination of VOC in natural samples was employed. Care was taken to prevent atmospheric contamination, and the effect of the system blank was monitored.

Acetone was used as a test material to check the effectiveness of the method, since acetone is water soluble, has a low molecular weight and a high vapour pressure (760 mm at 56.5°C). Acetone is a volatile material, but it is quite difficult to extract from aqueous medium because it is highly soluble (Games and Hayes, 1976, Ryabov et al., 1972, Bassette and Wade, 1969). With my extraction procedure, over the range of 0-100 µg.C (in sample of about 500 ml.), the extraction of the acetone was almost quantitative (Figure 2). The linearity of the calibration line appeared to breakdown for the higher acetone values (122.5 µg.C) which were probably beyond the linear range of the infrared detector. With these points omitted, a high linear

correlation was found (r=0.98) and the slope (0.97) was close to the theoretical value (1.00) for the quantitative removal and detection of the acetone (line in Figure 2). Over the concentration range of 0-200 μg.C/liter (Table IV), the extraction appeared to be complete and reproducible. An average % recovery of about 110±20% of the acetone added to the seawater samples was calculated. Thus, my method should be feasible for the extraction and analysis of organic materials of similar solubility and vapour pressure in an aqueous medium.

This same procedure for the analysis of VOC was used for other classes of volatile organic materials which would be expected to be present in natural waters. Some of the classes of compounds that were included in this study were hydrocarbons (heptane), aldehydes (butanal), ketones (acetone, methyl ethyl ketone), alcohols (methanol, iso-propanol), ethers (diethyl ether), acids (propionic acid), esters (ethyl acetate), amines (ethylene diamine), nitriles (acetonitrile), and aromatics (benzene). Not all of these organic compounds have equal solubilities or vapour pressures, and an indication of the limit of the extraction efficiency should be provided. The efficiency and rate of their stripping from the seawater, the completeness of their trapping, and the accuracy of their analysis was obtained and from this, an idea of the type of volatile components, that could be expected from the natural

Fig. 3-2: Efficiency of the extraction of acetone added to seawater samples (500 ml). The dashed line represents the ideal extraction.
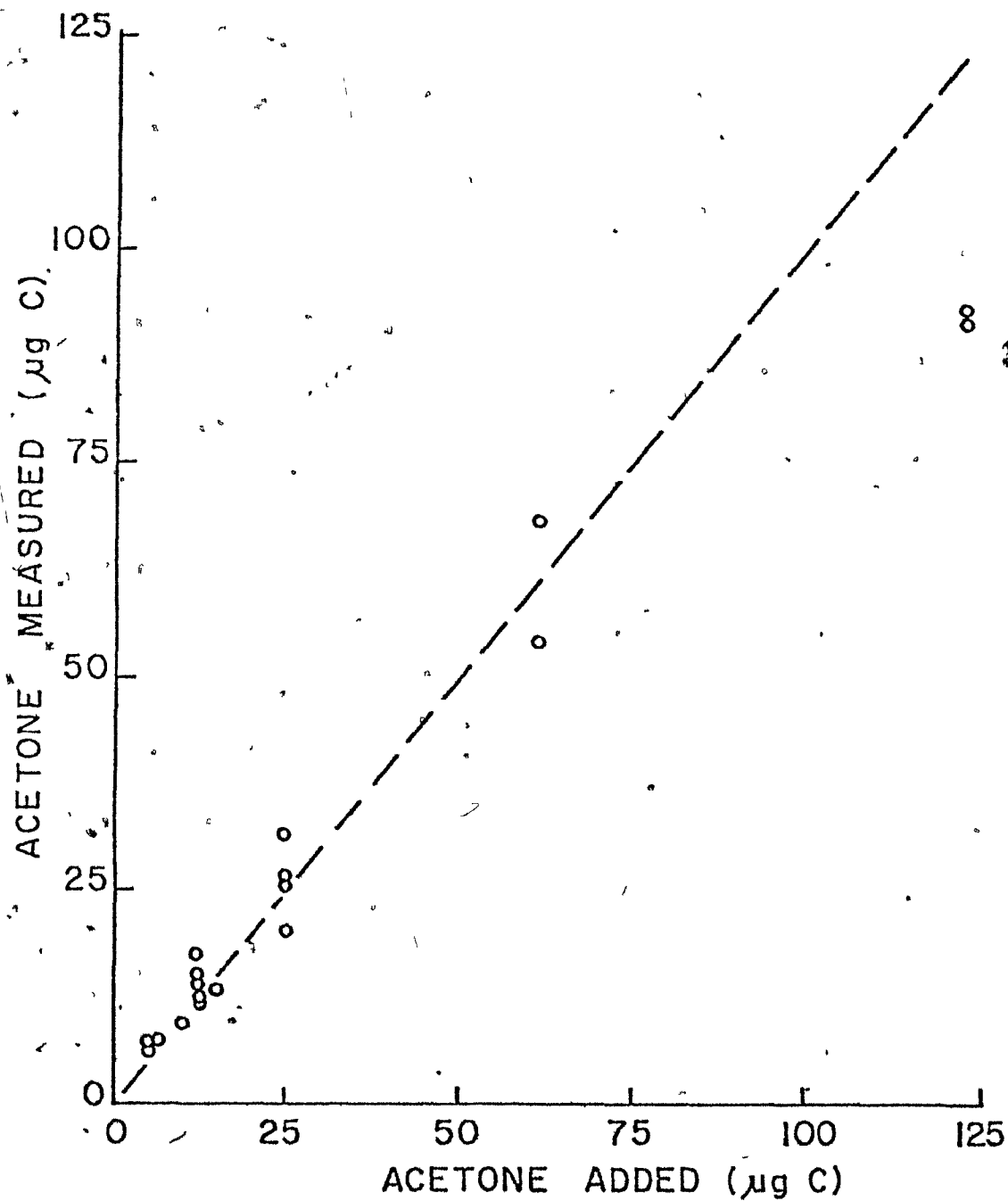
TABLE IV

Efficiency of the Extraction Method for the Analysis
of Acetone Standards Added to Seawater

Acetone Added (μg C)	Calculated Acetone Concentration (μg C/liter)	Measured Acetone Concentration (μg C/liter)	% Recovery
5.0	10.0	13.97	140
6.5	12.5	14.40	115
10.0	20.0	19.0	95
12.3	24.5	31.15	127
12.5	25.0	26.30	105
15.0	30.0	26.18	87
24.5	49.0	56.95	116
25.0	50.0	46.00	92
61.25	122.5	121.50	99
122.5	245.0	183.00	75

samples was obtained. For most of these standard compounds, the recovery of the added (Figures 3 and 4) material was high and a linear response was noted over a wide range (0-125 µg.). Poor recoveries were noted with the organic acid (propionic acid - 27% recovery) and amine (ethylene diamine- 44% recovery), which may be an indication that under the conditions used for the extraction, these organic materials were just too polar and soluble and not volatile enough to be stripped efficiently from the seawater. The calculated and measured concentrations of the standard solutions of the volatile compounds were compared (Table V), and for most of the materials a high average per cent recovery (104±20%) was noted; with a range of 55-145% for all materials except the acid and amine. The wide range of % recoveries (55-145%) in this work will probably be reduced by better control of the standard preparation, standard addition, and blank correction. Since a high recovery of the standards with my extraction procedure was found, similar results for the VOC in natural samples were expected, and my analytical procedure for the quantification of the VOC in seawater appeared to be acceptable as a routine method for the determination of the volatiles in natural samples.

b) Accuracy of the VOC analysis

Since the exact matrix of the volatile components and their concentrations in the real system are not known, the

Fig. 3-3:   Efficiency of my extraction procedure for volatile
             compounds added to seawater samples (500 ml).

             A - Acetone
             B - 2 - Butanone
             C - Diethyl ether
             D - Ethyl acetate
             E - Ethylene diamine
             F - Benzene

Fig. 3-4:   Efficiency of my extraction procedure for volatile
             compounds added to seawater samples (500 ml).

             1 - Heptane
             2 - Butanal
             3 - Methanol
             4 - Iso-propanol
             5 - Propionic acid
             6 - Acetonitrile

FIGURE 3-3
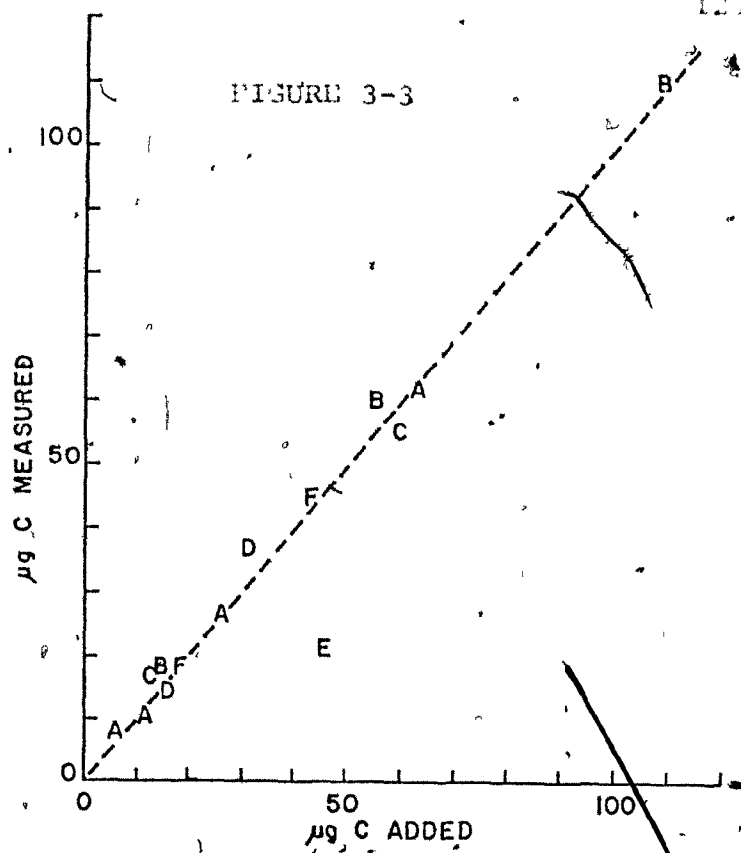
FIGURE 3-4
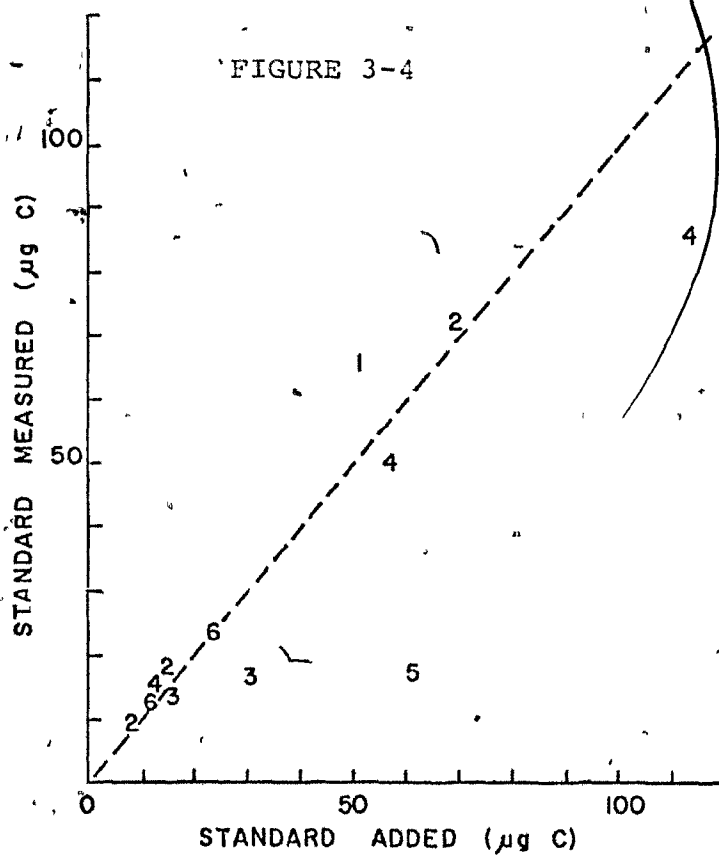
TABLE V

Efficiency of Extraction From Seawater of Various Compounds

Compound Added to Seawater	Amount Added (µg C)	Calculated Concentration (µg C/liter)	Measured Concentration (µg C/liter)	% Recovery
1. Heptane	50.0	100.0	129.3	129
	100.0	200.0	248.4	124
2. Butanal	6.8	13.6	16.8	124
	13.6	27.2	33.6	104
3. Methanol	14.8	29.6	25.0	84
	29.7	59.4	32.0	54
4. Iso-Propanol	11.2	22.4	27.4	122
	56.0	112.0	98.0	88
	112.0	224.0	169.0	75
5. Propionic Acid	60.5	121.0	33.0	27
6. Aceto-nitrile	11.0	22.0	24.2	110
	22.1	44.2	45.4	103
A. Acetone	5.0	10.0	14.4	144
	10.0	20.0	19.6	95
	15.0	30.0	26.2	87
	25.0	50.0	51.0	102
	61.5	123.0	121.6	99
B. 2-Butanone	16.2	32.4	34.3	106
	53.5	107.0	118.1	110
	107.0	214.0	218.7	102
C. Diethyl Ether	11.6	23.2	32.4	138
	58.0	116.0	108.4	93
D. Ethyl Acetate	15.0	30.0	26.6	89
	30.0	60.0	71.0	118
E. Ethylene Diamine	45.0	90.0	40.0	44
F. Benzene	16.9	33.8	33.4	99
	42.3	84.6	88.2	104

completeness or efficiency of the extraction and analysis
was based on the ability to analyze standard materials added
to seawater samples. In this study, the extraction efficiency
was tested by an indirect method. After a water sample had
been stripped and the VOC analysis was completed, the
extraction and analysis procedure were repeated. Little
further volatile material should have been observed during a
repetition of the analysis if the initial extraction procedure
was complete for the "volatile" materials. The extraction
was repeated for a random set (n=16) of samples (both surface
and deep water). The rate of the extraction (μg.C/hour)
of the volatiles from seawater in the repeated extraction
after the initial analysis procedure (18-24 hours) was only
about 40% of the original rate. Only a small amount of
organic material was trapped in the dry ice trap that was in
series with the Tenax trap during the repeated extraction.
In absolute terms (μg.C) most of the easily removed "volatile"
material (60-75%) was removed in the initial stripping
procedure (18-24 hr.), and continued extraction for extended
periods did not seem warranted since the chances of contamination
of the sample and breakdown of the larger molecular weight
non-volatile material in the water would be increased.

In several samples, the stripping procedure was continued
for an extended time beyond the regular extraction time.

A steady drop in the rate of removal of the VOC was noted. After 35-40 hours, the rate of extraction was only about 10-20° of the initial rate (Table VIa). The more volatile materials that are easier to extract (hydrophobic, low molecular weight, low boiling point, and high vapour-pressure) should be stripped in the early extraction, while the less volatile materials (more polar, lower vapour pressure, high molecular weight and boiling point) should be removed with extended extractions. If the components which were stripped from the seawater samples were examined qualitatively, a change in the compounds with time of extraction should be noted.

All the organic compounds which are classed as volatile by their volatility as pure compounds will not be stripped from the aqueous medium with my extraction procedure, but in the time for the extraction, most of the easily extracted materials and a major portion of the more resistent materials should be analyzed. However, the quantitative removal of the polar (fatty acids, amines) materials of lower volatility should not be expected in the time and under the conditions of the purging system that were used in this study.

c) Precision of the VOC analysis

In order to calculate the precision of my method for VOC analysis the samples must be identical, treated the same, extracted, and quantified under the same conditions.

The precision of my method was obtained for several sets of
samples which were sampled in different areas (Table VIb).
The precision of the calculated VOC concentrations was good
and a coefficient of variation (100 x Standard Deviation/mean)
ranging from 4.1-16% was calculated. The precision
of the VOC/TOC ratio was also high and a coefficient of
variation ranging from 5-14% was calculated. In terms of
the relative standard errors (100 x $(\sigma/\sqrt{n})/\bar{x}$) for the VOC
values, a range of 0.9-2.5% with an average relative standard
error of about 1.8% was calculated. If the high precision
from these sets of samples were indicative of that to be
expected in natural samples, then the interpretation of the
variations or trends in the distributions of the VOC values
that have been observed should be valid.

d)   Validity of results of VOC analysis

The accuracy and precision of my method for the extraction
and analysis of the VOC in natural samples have been found
to be reasonable with the procedures which I have used to
test these parameters. The absolute accuracy of the extraction
procedure has not been determined but only estimated. Some
materials which fit the broad definition of volatiles (low
molecular weight organic compounds with high vapour pressure)
will not be measured by my method since they are too polar
to be extracted under the conditions used for the stripping

TABLE VIa

Effect of Extended Extraction on Rate of Volatile Removal

Sample	Number of the Extraction in the Series	Time of Each Extraction (Hours)	Amount of VOC Removed With Each Extraction (µg C/liter)	Calculated Rate of Extraction (µg C/hour)
1.Tower Tank Seawater	1	4.7	32.35	6.88
	2	4.3	9.70	2.26
	3	12.7	10.04	0.79
	4	8.3	7.60	0.92
	5	16.0	8.88	0.56
	6	8.0	10.11	1.26
	7	18.5	7.07	0.38
2.Tower Tank Seawater	1	4.8	41.42	8.63
	2	5.3	13.35	2.52
	3	11.0	19.29	1.75
	4	13.3	13.45	1.01
	5	11.0	12.00	1.09
	6	13.0	14.42	1.11
	7	11.0	8.33	0.76
3.Tap Seawater	1	6.0	27.81	4.64
	2	1.7	5.23	3.08
	3	15.0	11.89	0.79
	4	10.0	7.85	0.79
	5	12.0	10.04	0.84
	6	7.0	8.90	1.27
4.Tap Seawater	1	5.3	23.83	4.50
	2	4.7	9.53	2.03
	3	12.0	11.30	0.94
	4	12.0	11.15	0.93
	5	12.0	4.17	0.35
	6	5.2	4.14	0.80

TABLE VIb

Precision of the Method For Extraction and Analysis of VOC

Sample	n	Average Concentration of VOC±σ (µg C/liter)	Average Concentration of TOC±σ (mg C/liter)	Average Ratio of VOC/TOC (%)
1.Petpeswick Inlet	5	50.72±1.0	2.41±.03	2.1±.02
2.North West Arm	7	30.96±1.5	1.68±.03	1.8±.08
3.St.Margaret's Bay	6	33.43±2.0	1.73±.04	2.0±.12
4.Tap Seawater	6	33.50±1.8	1.26±.02	2.7±.15
5.North West Arm	4	30.40±1.1	1.42±.03	2.2±.10

Effect of Extended Extraction on Rate of Volatile Removal

Sample	Number of the Extraction in the Series	Time of Each Extraction (Hours)	Amount of VOC Removed With Each Extraction (µg C/liter)	Calculated Rate of Extraction (µg C/hour)
1. Tower Tank Seawater	1	4.7	32.35	6.88
	2	4.3	9.70	2.26
	3	12.7	10.04	0.79
	4	8.3	7.60	0.92
	5	16.0	8.88	0.56
	6	8.0	10.11	1.26
	7	18.5	7.07	0.38
2. Tower Tank Seawater	1	4.8	41.42	8.63
	2	5.3	13.35	2.52
	3	11.0	19.29	1.75
	4	13.3	13.45	1.01
	5	11.0	12.00	1.09
	6	13.0	14.42	1.11
	7	11.0	8.33	0.76
3. Tap Seawater	1	6.0	27.81	4.64
	2	1.7	5.23	3.08
	3	15.0	11.89	0.79
	4	10.0	7.85	0.79
	5	12.0	10.04	0.84
	6	7.0	8.90	1.27
4. Tap Seawater	1	5.3	23.83	4.50
	2	4.7	9.53	2.03
	3	12.0	11.30	0.94
	4	12.0	11.15	0.93
	5	12.0	4.17	0.35
	6	5.2	4.14	0.80

<u>TABLE VIb</u>

Precision of the Method For Extraction and Analysis of VOC

Sample	n	Average Concentration of VOC±σ (μg C/liter)	Average Concentration of TOC±σ (mg C/liter)	Average Ratio of VOC/TOC (%)
1. Petpeswick Inlet	5	50.72±1.0	2.41±.03	2.1±.02
2. North West Arm	7	30.96±1.5	1.68±.03	1.8±.08
3. St. Margaret's Bay	6	33.43±2.0	1.73±.04	2.0±.12
4. Tap Seawater	6	33.50±1.8	1.26±.02	2.7±.15
5. North West Arm	4	30.40±1.1	1.42±.03	2.2±.10

procedure. A high precision for the measured VOC in the natural samples and standards was found with the described procedure.

The definition of the volatiles was set by the conditions of the extraction (working definition); this will set the limits on the materials which will be classed as volatiles in the discussion of the results from natural samples. I will not claim that the material which I measured included all the volatile components of seawater, but only the volatile components that could be extracted with the conditions of the described procedure.

6. Outline of the Method for the Analysis of VOC in Natural Waters

a) Sample collection

Samples of about 550 ml were transferred into precleaned 650 ml amber bottles from Niskin bottles as soon as they were brought aboard the ship. The Niskins were fitted with springs for the closing mechanisms instead of a rubber system. The sample was withdrawn from the Niskin with a glass delivery tube (11 mm OD) that was connected to the Niskin with an aged Tygon connector and extended to the bottom of the amber bottle. After rinsing 3 times, the amber bottle was filled to overflowing. During the transfer of sample, care was taken to prevent bubble formation. About 50-75 ml were removed from the bottle, and then the

sample was fixed with 0.5 ml of 3% mercuric chloride (HgCl₂) solution, the bottle was sealed with a plastic coated metal cap, and the sample frozen until analysis. If the air space was not left in the bottle, breakage was likely to occur during the freezing and storage.

b) Extraction of VOC

1) Conditions for Extraction

The extractor was placed in a water bath at about 80°C with a flow rate of 20-40 ml/min of.N₂ (purified by passage through a charcoal column) for the scrubbing of the volatile organics from the water sample. The scrubbed organics were flushed through a condenser (either air condenser or Dewar type condenser which could be packed with ice) and into the trapping system, which consisted of a 25-30 cm stainless steel column (1/4" OD) packed with Tenax GC (2 cc) and a U-shaped stainless steel 50 cm x 1/4") cold trap (-78°C). After 5 hours, the flow rate (35-40 ml) was reduced to 20-25 ml/min and the cold trap in the dry ice (-78°C) was removed and analyzed immediately. The Tenax trap was replaced and the extraction continued for 5-7 more hours at 80°C but with the reduced flow rate (20-25 ml/min). This trap was replaced and the temperature of the water bath reduced to 60-65°C as the extraction was continued for a further 10-12 hours. Total analysis time required about 24 hours with 3 Tenax columns and at least one cold trap used

for the collection of the purged organic matter.

11) Traps

The VOC stripped from the water was trapped for later analysis. Two traps were used in series. The first trap consisted of a 25-30 cm stainless steel tube (1/4" OD) packed with 2 cc Tenax GC 35/60 mesh (Applied Science Lab. Inc. #04901). Columns were conditioned for 40 minutes under N_2 at 250-300°C before use. The second trap in series consisted of a 40-50 cm stainless steel (1/4" OD) U-shaped column packed with quartz wool and placed in a Dewar with dry ice (-78°C). A flow meter was attached to the exit from the traps to monitor the flow rate and to detect any leaks or clogging before the extraction was hampered. Connections between the extractor system and the trap system were made with 1 cm tygon tubes (9 mm OD x 7 mm ID).

11) Extraction vessels

Two types of extractors were used; the VOC results from both systems were comparable.

1. The amber sample bottle, after thawing, was decapped and connected to a condenser (25 cm air condenser that could be cooled with ice if required). A glass "T" was fitted to the top of the condenser. Through one arm the scrubbing gas was introduced into the sample while through the other arm, the stripped material was flushed to the trapping system. The scrubber (1/16" teflon tubing) passed through the "T" and

the condenser and was immersed below the surface of the sample. Flow rates of between 20-50 ml/min N_2 were used at various stages of the extraction.

2. The second extractor was a 500 ml vacuum flask with a glass frit (coarse) scrubber which was held in place by a silicon rubber stopper. The side arm of the vacuum flask was joined to a Dewar condenser (Kontes 14/20) by means of a tygon tube (1" long x 13mm ID). A glass tube was used to deliver the sample to the flask from the amber sample bottle under an atmosphere of N_2. Care was taken to prevent contamination from the lab air. Flow rates of between 20-50 ml/min N were used. The sample was scrubbed and the stripped organics were flushed through the condenser (efficiency of the condenser could be improved by use of ice) to the traps.

c) Quantification of the Volatile Organic Carbon

The column (10" x 0.25" stainless steel) packed with 2 cc Tenax GC (35/60 mesh) that was used to adsorb the stripped organic volatiles was inserted into a 25 cm tube oven (15 cm OD quartz tube wrapped with 4 ohm nichrome ribbon for heating), and connected by means of a 1 cm tygon tube to a cold trap (U-shaped stainless steel column, 20" x 0.25", packed with quartz beads). The cold trap was placed in a Dewar flask and then packed with dry ice (-78°C). Into this cold trap, the volatile organic contents of the Tenax

column were desorbed as the column was heated (175°C) for 35-45 minutes with a slow flow of N_2 (35-45 ml/min). When the desorption was completed, the dry ice and the Dewar were removed, and the U-shaped column was heated quickly with a Bunsen burner. The desorbed organics that were concentrated in the cold trap were driven into the combustion tube (95 cm x 15 mm quartz tube) through a side arm (20 cm x 15 mm quartz tube) heated to 140°C. The organic material was carried into the oxidation zone of the combustion tube packed with a catalyst (cupric oxide) and was oxidized at 950°C with a combustion furnace (Lindberg Mini-mite). The combustion tube was Y-shaped. Through the side arm the desorbed volatile organic material was introduced by a slow stream of N_2, while through the other arm a constant flow of O_2 was introduced to ensure complete oxidation of the organic materials in the oxidation zone of the furnace. During the desorption of the organics from the Tenax column into the cold trap (35-45 minutes), and while these desorbed organics were driven from the cold trap (2-6 min), a slow flow of O_2 (20-25 ml/min, purified by passage through an Ascarite and Molecular Sieve 5A column after oxidation in a high temperature oxidation furnace) was maintained in the main combustion tube until the sample had been completely flushed from the cold trap (3-6 min). The O_2 flow rate was increased with a switching valve from a slow rate

(20-25 ml/min) to a fast flow (350 ml/min). The oxidative products (CO_2) from the oxidation of the VOC were forced by this fast flow of O_2 through a water condenser (ice 0°C) and a drying column ($Mg(ClO_4)_2$), and then the products were measured with a non-dispersive infrared analyzer (Lira IR 200). The signal was graphically displayed on a recorder (Honeywell Electronik 194) and was integrated (Infotronics CRS-108). Each sample required 40 minutes for the initial desorption from the Tenax column, a further 6 minutes for desorption from the dry ice trap and 2 minutes to flush the oxidative products through the system. With the large amounts of dead space in the system, the detection of the oxidative products was delayed and a premature signal was prevented from reaching the detector during the period of desorption before the O_2 was switched to the fast flow (350 ml/min). Sharp and symmetrical peaks were produced. With standard solutions, the response of the system was found to be linear over the range of values that were expected for natural samples.

C.   Analysis of the VOC in Natural Samples

In this study both coastal areas (Scotian Shelf, Gulf
of St. Lawrence, near coastal regions) and open ocean areas
(Sargasso Sea) have been analyzed and the results of the VOC
concentration, its importance to the TOC (VOC/TOC), and
trends will be discussed.

1.   Scotian Shelf and Slope Area

a)   Distribution

Samples were collected on cruises which were run on a
transect from Halifax to the edge of the continental slope
region in May, 1974, in August 1975, and in March, 1976.
The data for the VOC and TOC concentration, depths, salinities,
and locations are presented in the Appendix.

The vertical distribution of the measured VOC was
relatively uniform with depth and in most cases only small
absolute changes were measured between the surface and the
deeper water. The VOC concentration along with the fraction
of the TOC which was VOC (VOC/TOC) are plotted in Figure 5.
The average and range of values are tabulated in Table XI.
The average VOC concentrations (35-40 µg.C/liter) were
highest in the surface zone (0-25 m). These values decreased
slowly (average VOC = 25-35 µg C/liter) with depth. Averaged
surface values of VOC were higher than the values found at
depth. Scatter in the VOC values also decreased with depth;
range of 24-69 µg C/liter in the euphotic zone versus

Fig. 3-5: Depth profiles of the VOC concentration (●) and
VOC/TOC values (0) which were collected on the
Scotian Shelf and Slope (5/74, 8/75, and 3/76).
▲ = averaged VOC values
Δ = averaged VOC/TOC values.

Fig. 3-6: Depth profiles of the VOC, TOC and VOC/TOC values
for specific stations on the Scotian Shelf and
Slope.   See map # pg. 75b
   a) Station 1 (3/76)
   b) Station 2 (3/76)
   c) Station 3 (3/76)
   d) Station 4 (3/76)
   e) Station 6 (8/75)
   f) Station 7 (6/74)
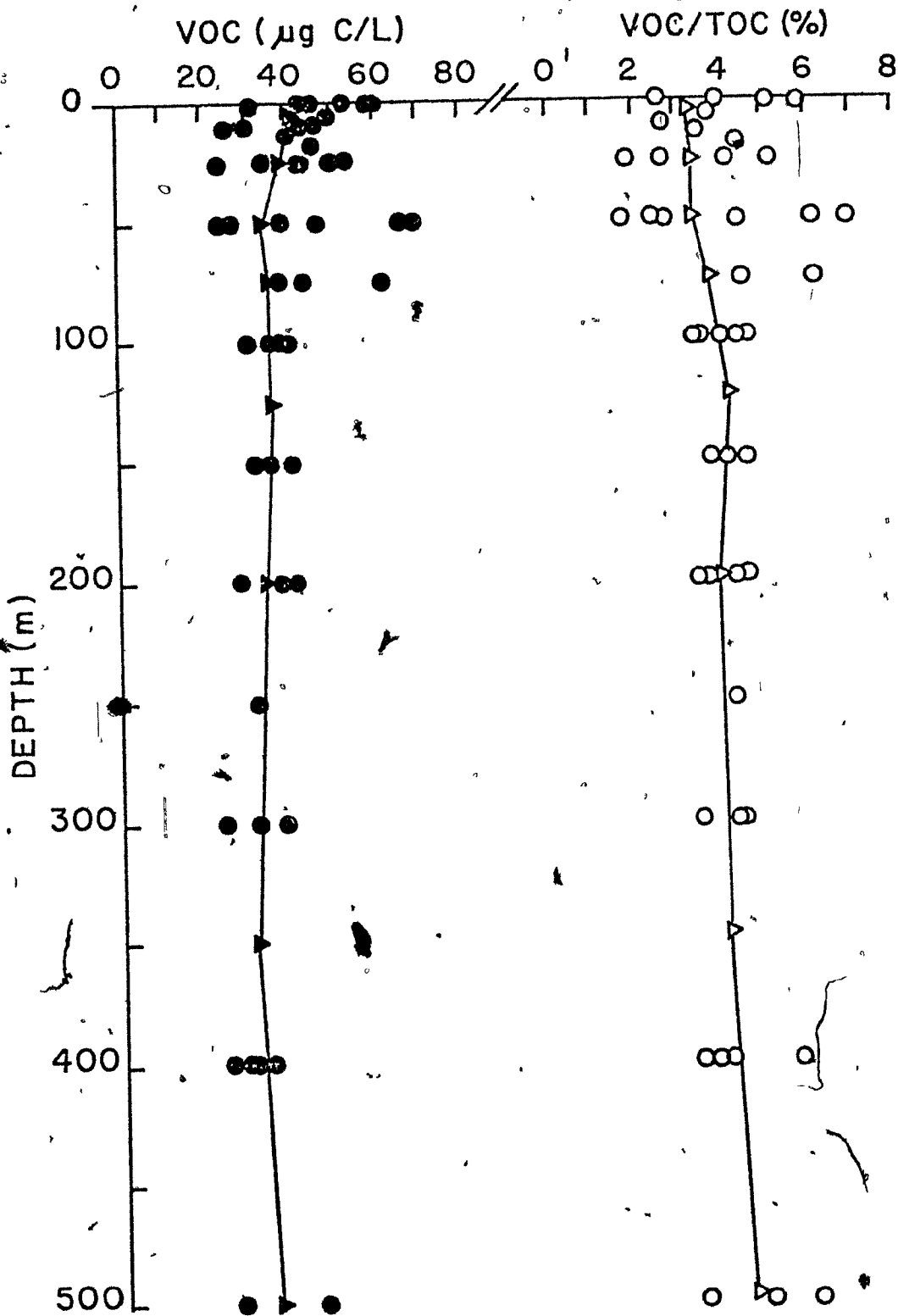
FIGURE 3-5
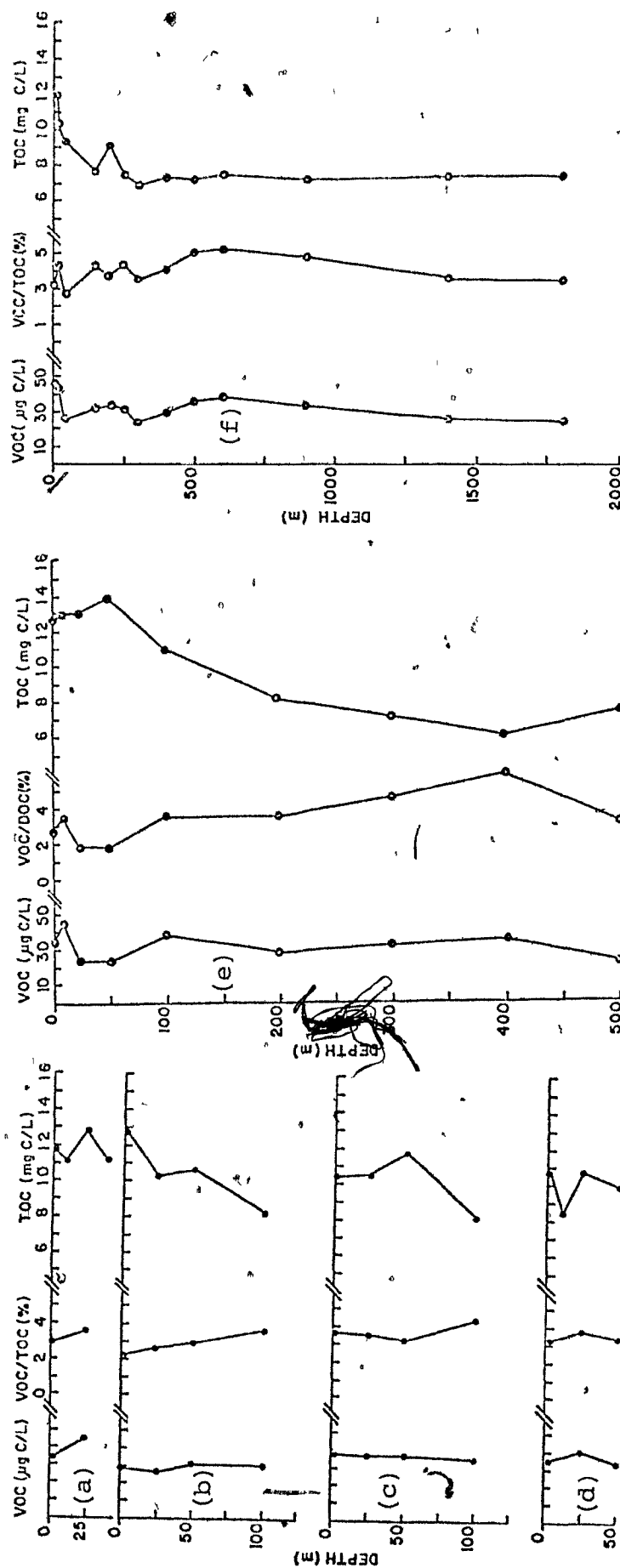
FIGURE 3-6

22-46 µg C/liter in deeper water. Trends were not as evident in the vertical distribution of the VOC/TOC ratio, which appeared to remain relatively constant (3.9 ± 0.5%) with depth and to vary within a narrow range (3.3 - 5.0%). In deeper water, a slight increase in the VOC/TOC ratio was observed. The significance of this is difficult to ascertain.

.In Figure 6, the distribution of the VOC, VOC/TOC, and TOC values with depth are shown graphically for specific stations. The precision and accuracy of the analytical methods has been shown to be high, so that the variations with depth should be real, although variations from contamination in the sampling, handling, and analysis procedure must not be overlooked.

b)   Coastal Effects

An attempt was made (Table VII) to correlate the VOC concentrations averaged over a depth of 75 meters (1, 10, 25, 50 and 75 m) with distance from the coast. It was assumed that proximity to the coast should lead to higher VOC values because of higher input and production. A decrease in the averaged VOC (ave. over 75 m) values with distance from the coast was observed; less than 100 Km. from the coast, ave. VOC= 41±6 µg.C/liter, greater than 100 Km. from the coast, ave. VOC = 35.95±3.7 µgC/liter. The highest averaged VOC values were found at Station #1 (45.97±10.5

TABLE VII

Coastal Effect on VOC Concentrations on Scotian Shelf

Station	Distance from Coast (km)	n	Averaged VOC Concentration (µg C/liter)	Relative % with Respect To Station #1
1	5-10	7	45.97±10.5	100
2	25	12	33.74±7.7	73
3	80	10	43.38±7.4	94
4	125	10	41.15±9.7	90
5	170	8	32.40±4.0	70
6	210	7	35.10±8.6	76
7	250	8	35.14±9.7	76

TABLE VIII

Seasonal Effect on VOC Concentrations on Scotian Shelf

Station	Distance from Coast (Km)	n	Averaged VOC Concentration (µg C/liter). Values in Spring	n	Values in Summer	% Difference
1	5-10	5	39.7±5.0	11	48.5±11.0	+18
2	25	8	28.3±2.8	6	41.6± 2.5	+32
3	80	11	38.3±4.7	5	45.5± 9.3	+16
4	125	7	36.1±4.8	5	57.7± 8.9	+37
5	170	5	36.7±3.9	5	30.7± 3.1	-20
6	210	5	41.4±4.6	9	31.4± 7.3	-32
MEAN			36.8±4.6		42.6±10.4	+14

µg.C/liter) just 5-10 km. off the coast, while lower, more constant values were found at the farthest stations from the coast. A strong correlation was not apparent, but a trend towards an increase of the VOC in coastal region was indicated.

c) Seasonal Effects

Samples were collected on the Scotian Shelf at different times and in different seasons (Spring, 6/74 and 3/76, Fall, 8/76). The spring data was collected just before (3/76) and shortly after (6/74) the spring bloom period, while the summer cruise (8/75) was well after the bloom period and algal productivity relative to the other times of the year was low (chlorophyll a less than 0.4 mg/(liter)^3).

Temporal variations are examined in Table VIII. The mean of the VOC for the summer (42.6 µg C/liter) was about 16% higher than the spring mean (36.8 µg C/liter), but when the individual stations were compared by a paired "t" test this difference was not significant at the 95% confidence level.

While hints of coastal effects and seasonal variations on the VOC concentrations have been indicated in this study, more data will be required to determine whether these variations are real and predictions can be made.

2. Gulf of St. Lawrence

a) Distributions

Samples were collected from the Gulf of St. Lawrence in

Fig. 3-7:. . Depth profiles of the VOC concentrations (●) and
the VOC/TOC (0) values which were collected in
the Gulf of St. Lawrence (11/75).
▲ - averaged VOC values
Δ - averaged VOC/TOC values
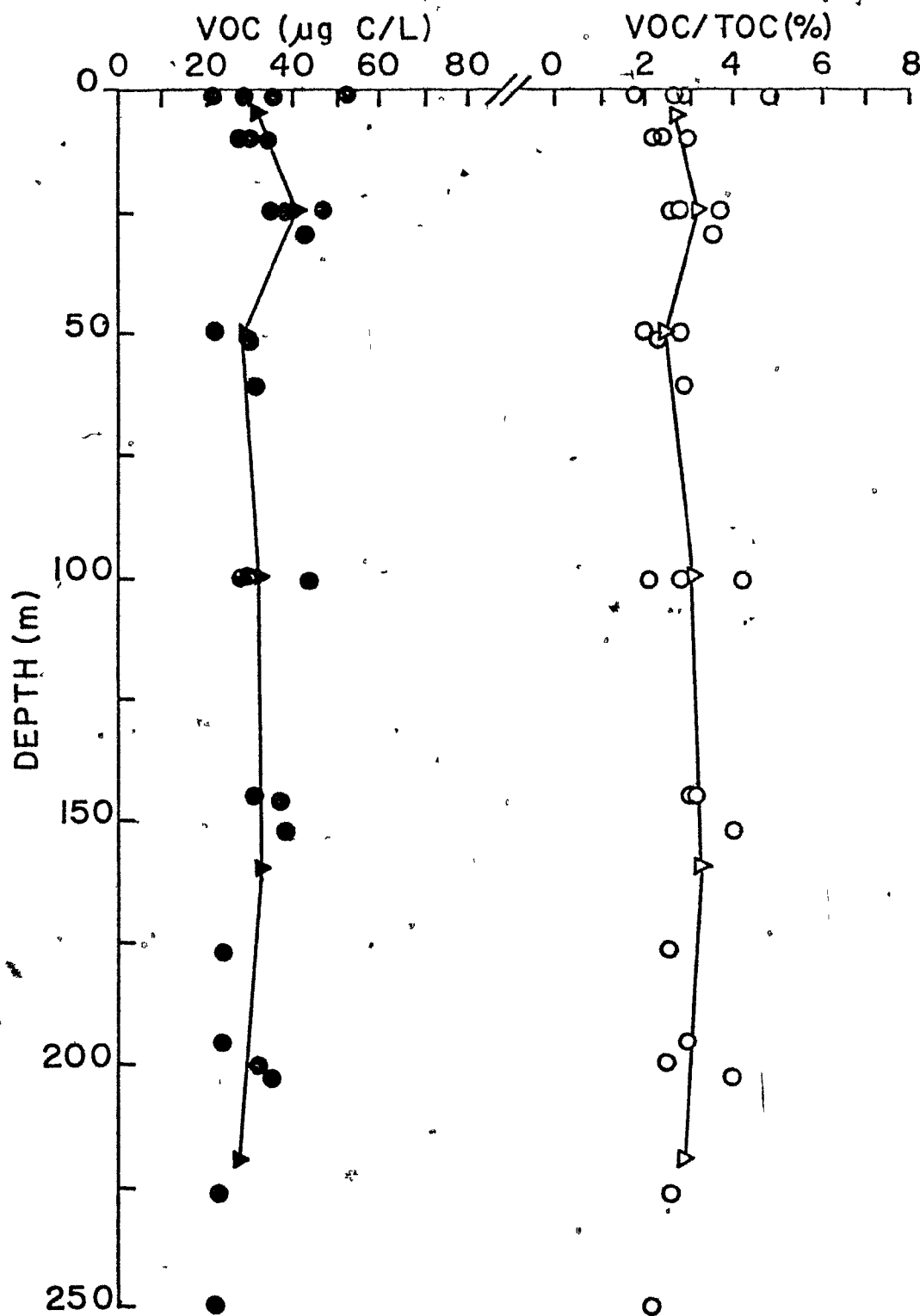
November, 1975. The VOC and TOC concentrations, VOC/TOC values, salinities, and station locations are tabulated in the Appendix. A depth profile of the VOC and VOC/TOC values was plotted (Fig. 7) and little vertical structure was shown. These results were averaged over depth (Table XI); the values of the VOC in the surface zone (30-40 µg.C/liter) were found to be only 10-20% higher than the VOC concentrations found in the deeper water (27-33 µg.C/liter). The calculated ratio of VOC/TOC was found to average about 2.95±.3% over the depth profile with a range of only 1.8-4.5%. The volatile content of the TOC was small even in this area where the influences from man, land, and biological systems would be expected to be significant.

b) Coastal influence

Samples were collected in the Cabot Strait and in the estuary of the St. Lawrence River. The Cabot Strait samples were affected by oceanic influences, but the water was derived mainly from the Gulf (Pocklington, personal comm.)., If fresh water run off and drainage from the land by fluvial systems were a major source of volatiles, then the VOC values for the stations in the St. Lawrence estuary which had the lowest salinity would be expected to be higher than in the Cabot St., which had less direct input from the land, as shown by the higher salinity. However, this was not observed (Table IX). Higher averaged VOC concentrations from the surface

TABLE IX

VOC CONCENTRATIONS IN GULF OF ST. LAWRENCE

Station	n	[VOC] ug C/liter surface zone (0-25 m)	n	deep water (25 m)	n	total (0-200 m)	average % VOC/TCC
Cabot Strait Fig.9(a)	3	42.95	4	31.30	7	36.30 ± 9.7	3.20 ± 0.84
Fig.9(b)	3	35.98	4	31.90	7	33.67 ± 7.7	3.05 ± 0.65
St Lawrence Estuary Fig.9(c)	3	30.80	4	29.00	7	29.76 ± 4.5	2.65 ± 0.67
Fig 9(d)	3	30.90	4	31.20	7	31.08 ± 7.5	2.88 ± 0.76

-zone (0-25 m) in the Cabot St. samples (35-40 µg.C/liter) were found than in the samples collected closer to the mouth of the St. Lawrence River (30 µg.C/liter). The averaged VOC values for the deeper samples were similar for all the stations (29-32 µg.C/liter). Similarily, a small increase in the averaged VOC/TOC ration was noted in the Cabot St. stations (3.2%) versus the ratio in the river stations (2.7%).

In the analysis of other coastal rivers, VOC concentrations were found to be high (50 - 75 µg.C/liter) and should have an influence on the VOC values in the estuary. However, samples were not taken directly from the St. Lawrence River, so an estimate of its input was difficult. The lower VOC values found in the estuary may mean that the river was low in VOC at the time of sampling.

c) Seasonal influences

The low values for VOC found in the Gulf may be accounted for by the time of year (November), when the productivity was low, water temperature was dropping (1-4°C), and the surface zone was well mixed. A natural stripping of the volatile materials may have occurred during this period of autumn storms with mixing and turbulence.

An indication of the effect of natural stripping of the water was obtained in an experiment which was run to compare the rate of removal of the volatile organics from seawater

under calm (simple diffusion) and turbulent (vigorous shaking or stirring) conditions. The rate of VOC loss was enchanced by the turbulent conditions, but a good estimate of the importance that this mechanism of natural stripping may have in the natural environment was not determined.

3. Open Ocean Areas

   a)   Area of Study

Samples were collected in the Central and North-West Sargasso Sea in October 1974 and February 1975. These sampling areas were far removed from the direct influence of land, so that coastal effects were minimized. The algal productivity in the areas and times of sampling were relatively low (chlorophyll a = 0.5 µg/liter).

   b) Distribution

   1)   With depth

The VOC and TOC concentrations and the VOC/TOC ratios for the stations from this area are presented in the Appendix. The VOC and VOC/TOC values are plotted as a depth profile in Figure 8.

These values were averaged into depth zones and these are tabulated (Table XI). In the surface zone (0-200 m), the averaged VOC concentrations (30 µg.C/liter) were only about 10-15% higher than the VOC values measured for the deeper water (greater than 200 m) samples (26.5 µg.C.liter).

Fig. 3-8: Depth profiles of the VOC concentration (●) and VOC/TOC
           values (o) which were collected in the Sargasso Sea
           (10/74 and 2/75).
           ▲ - averaged VOC values
   Δ - averaged VOC/TOC values
Fig. 3-9: Depth profiles of VOC, TOC, and VOC/TOC values for
   specific stations in the Sargasso Sea (10/74 and 2/75).
   See Map # pg. 140b.
           a) 26° 00'N, 62° 45'W (2/75)
           b) 32° 50'N, 62° 40'W (2/75)
           c) 36° 35.2'N, 63° 17.6'W (10/74)
           d) 42° 16'N, 61° 30.5'W (10/74)
           e) 33° 30'N, 64° 00'W (10/74)
           f) 38° 59'N, 62° 46'W (2/75)
   g) 42° 01'N, 63° 05'W (2/75)
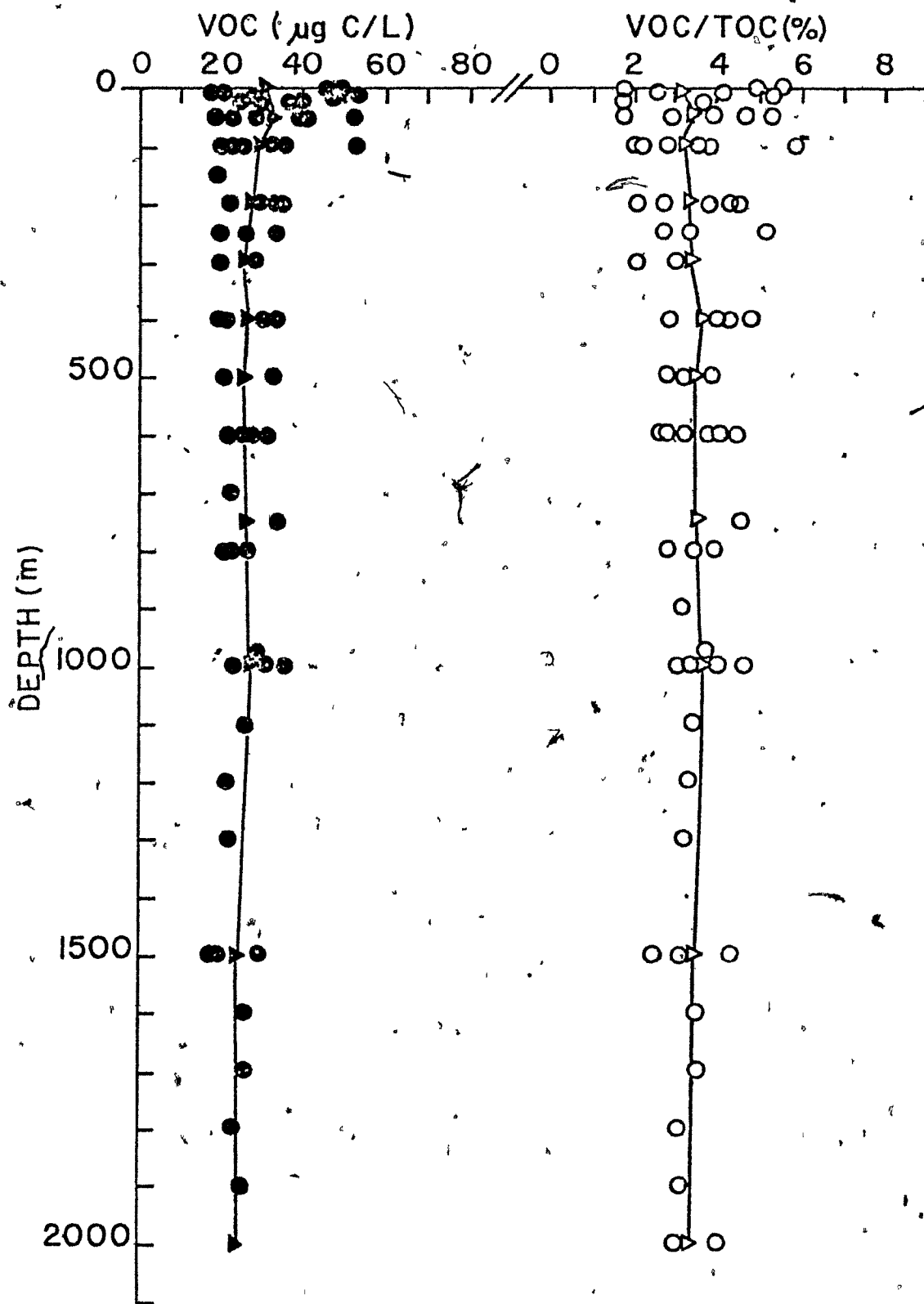
FIGURE 3-8

FIGURE 3-9

(d)

(c)

138 c

(f)

(e)

(g)
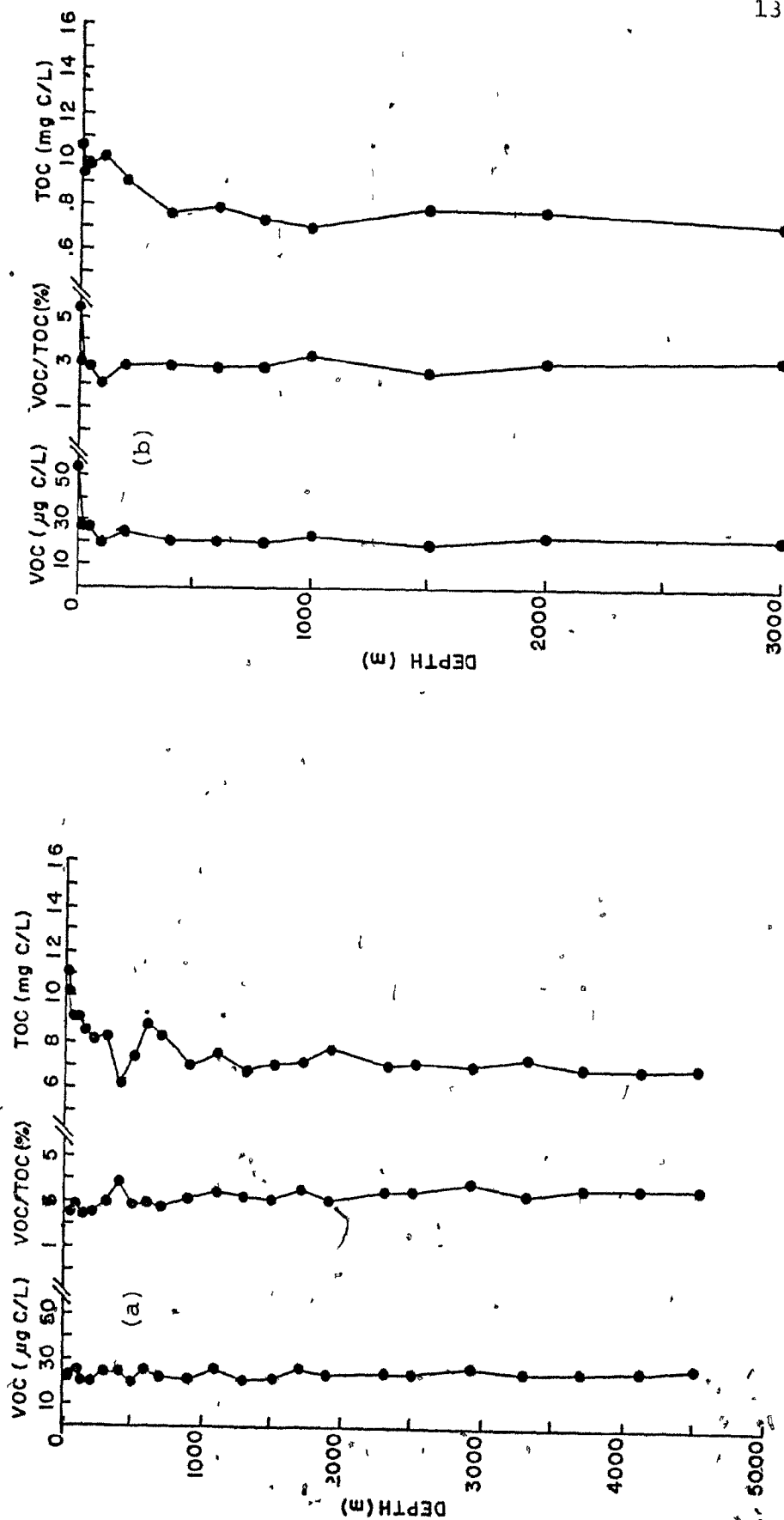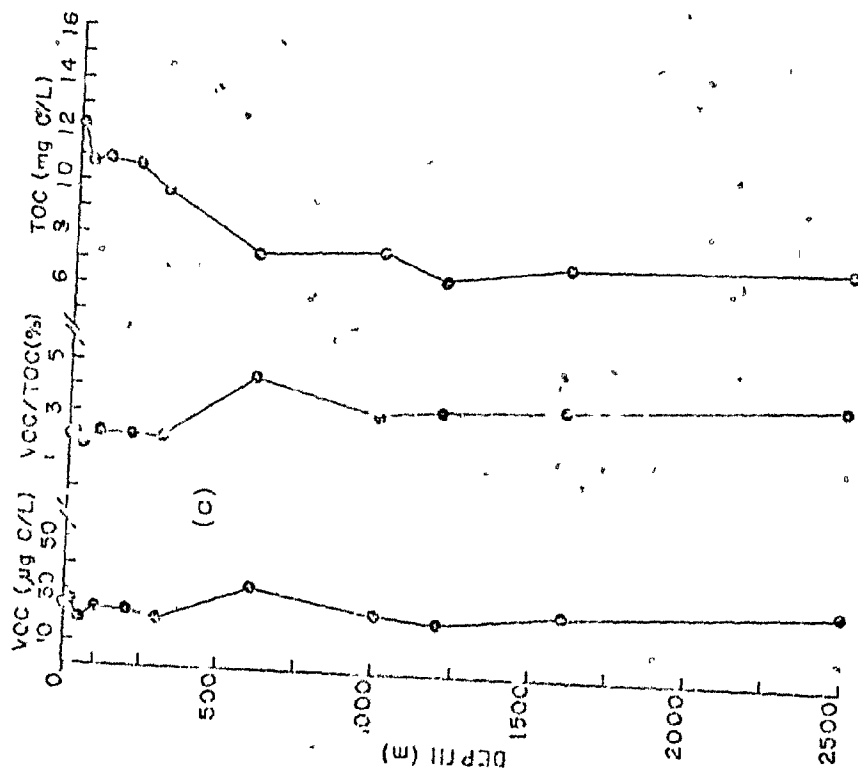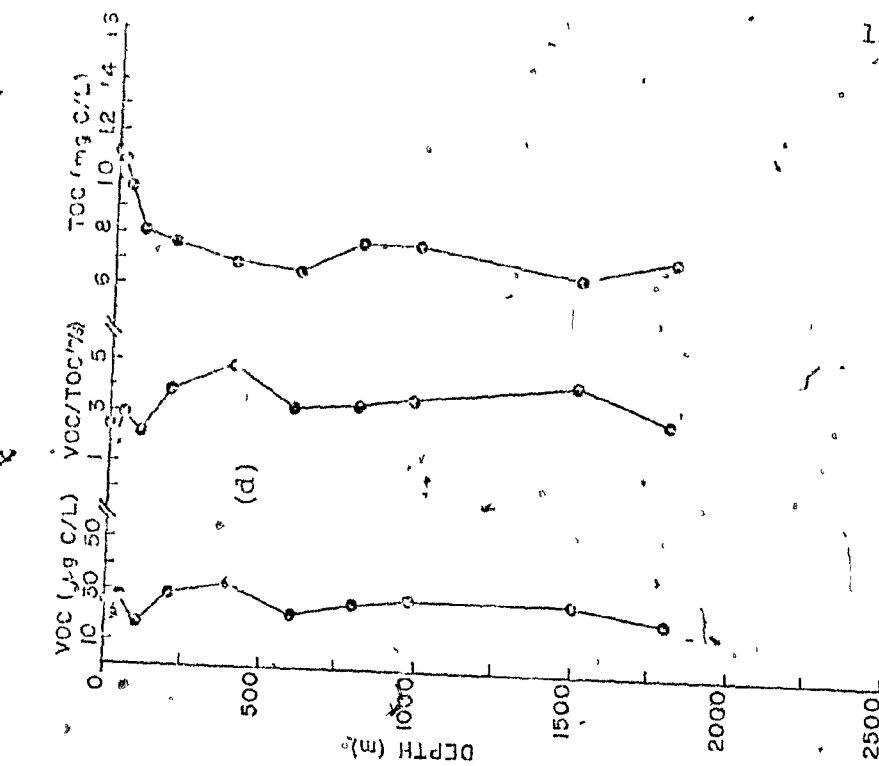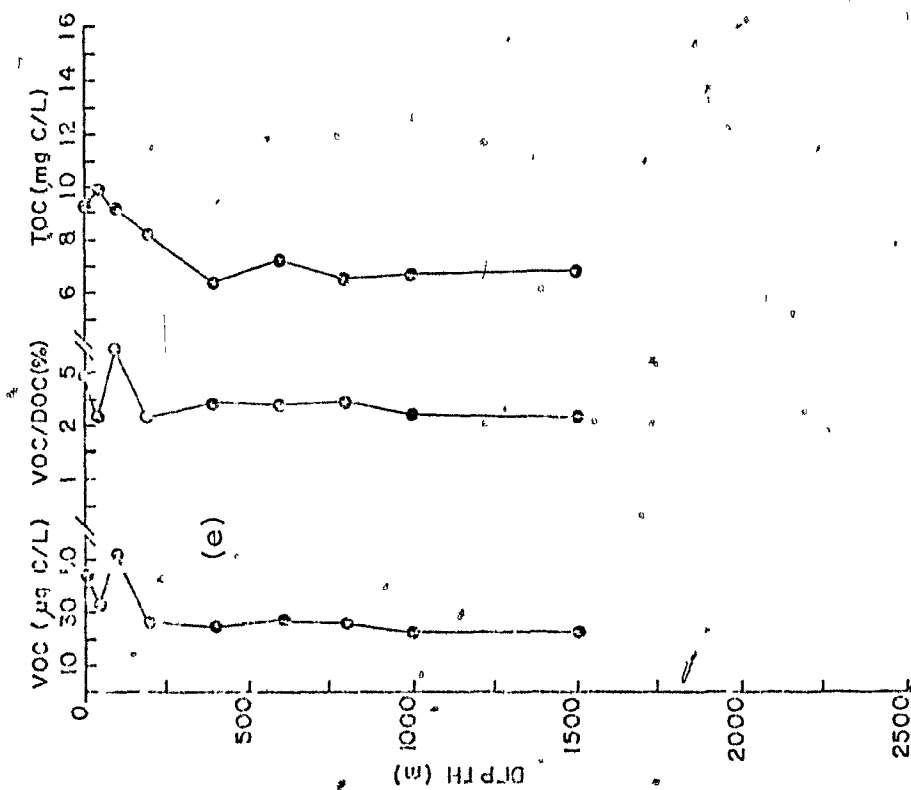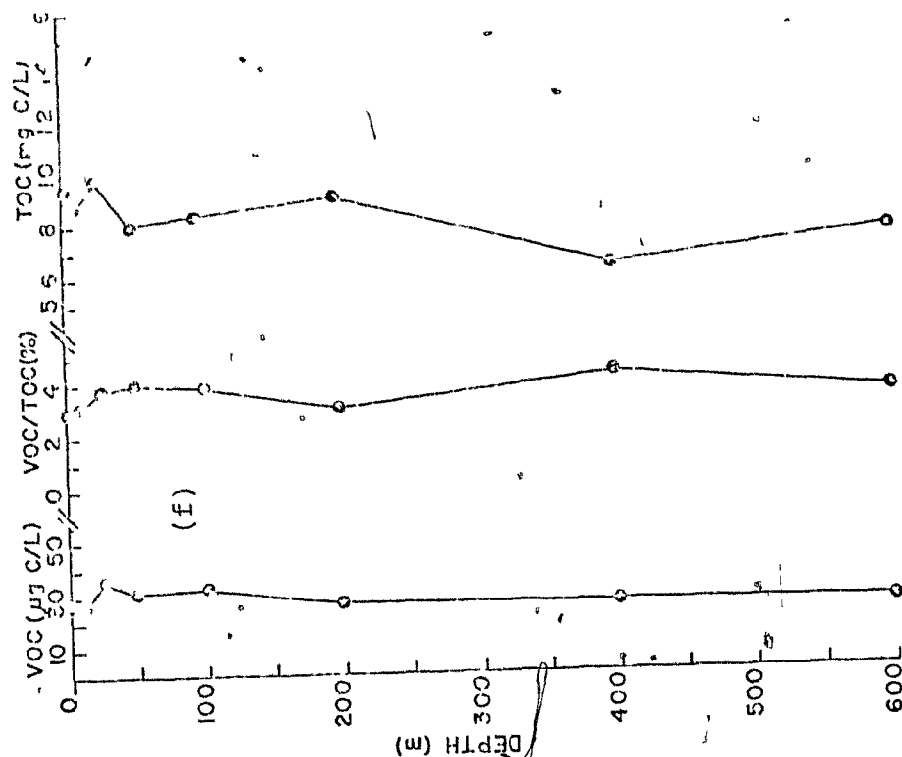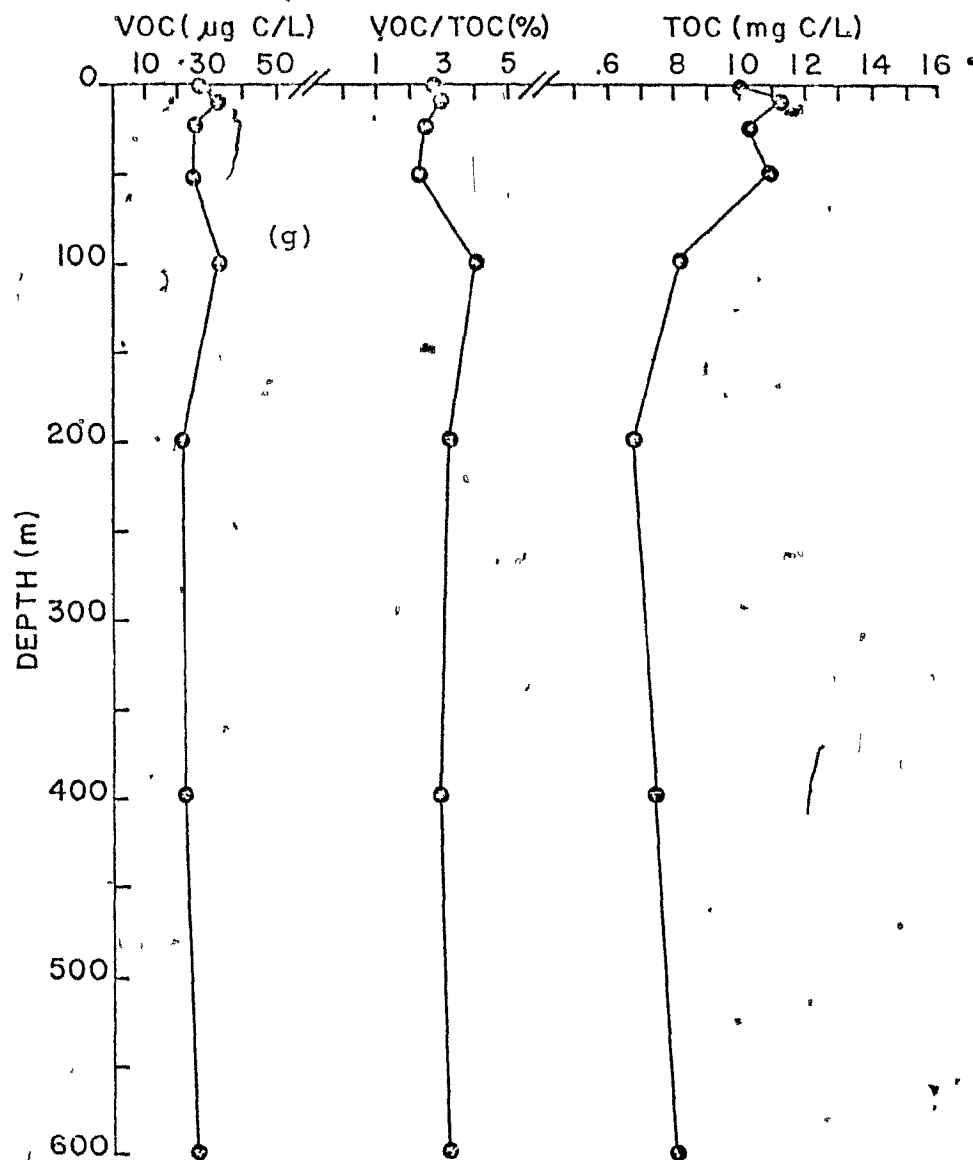
Similar results for the depth profile of the averaged ratio
of the VOC/TOC were obtained. The ratio was about 3.3±.7%
for all samples, with a slight increase from the surface
values (3.1%) to the deeper water (3.5%) values.

However, no obvious correlation with depth was evident.
The uniformity of the vertical profiles of the VOC was not
surprising, since homogeneity was also noted in other
parameters. During the February '75 cruise, little density
structure was noted in the surface zone (0-200 m) and
isothermal profiles were evident in the Sargasso Sea
stations. This surface layer was well mixed by winter
storms, so that little vertical structure was expected and
even the TOC values were fairly uniform in the top 200
meters (0.85-1.10 mg C/liter).

In Figure 9, several stations from this open ocean area
are presented. The VOC and TOC concentrations and VOC/TOC
ratios are plotted and small changes with depth are seen.

The actual interpretation of the VOC data from the open
ocean area (Sargasso Sea) was difficult because only small
scale variability was observed. The absolute differences in
the VOC concentrations were small and systematic errors in
the handling and analysis of the samples could not be
eliminated as the source of these small variations. A
uniform distribution of the VOC/TOC with depth was revealed.
In absolute terms, the amount of volatile material was

found to be a small fraction of the TOC (Table XI).

11) Geographic

The effect of large scale horizontal changes on the variability of the quantity of VOC measured is shown graphically in Figure 10. The stations that were sampled in these cruises ranged from the central Sargasso Sea to across the Gulf Stream (26°N to 43.3°N). The water in the Sargasso Sea, Gulf Stream, and slope regions would be expected to have different origins and history, and changes in the temperature, age, productivity and light influences should be expected. The averaged values of the VOC concentrations and the ratio of the VOC/TOC at each station are plotted versus the station position (Figure 10). The data from the two cruises were very similar, with no strong correlation of the VOC concentration with location. The small differences that were noted in the VOC values from these two cruises might be explained by variations in the handling and extraction procedures in the different studies. A range of 21-36 µg.C/liter for the averaged VOC concentrations and 2.1-4.3% for the averaged VOC/TOC ratios was observed in the areas studied (Table X). A slight drop in the VOC and VOC/TOC values was noted in the Gulf Stream (about 40-41°N), but the correlation was not significant. The values of the VOC on the north side of the Gulf Stream (21-27 µg.C/liter) appeared to be slightly lower than

Fig. 3-10: The effect of geographical position (transect in the
          Atlantic Ocean from 26°N to 43.3°N) on the averaged
          VOC and VOC/TOC values. The bars represent the
   standard deviation of the values. See Map # pg. 140b
          ● - Samples collected 2/75
          0 - Samples collected 10/74
Map: Stations sampled in the Sargasso Sea.
          ▲ - October 1974
   ◆ - February 1975

FIGURE 3-10

HALIFAX

1800 m

BERMUDA

△ OCT '74
○ FEB '75
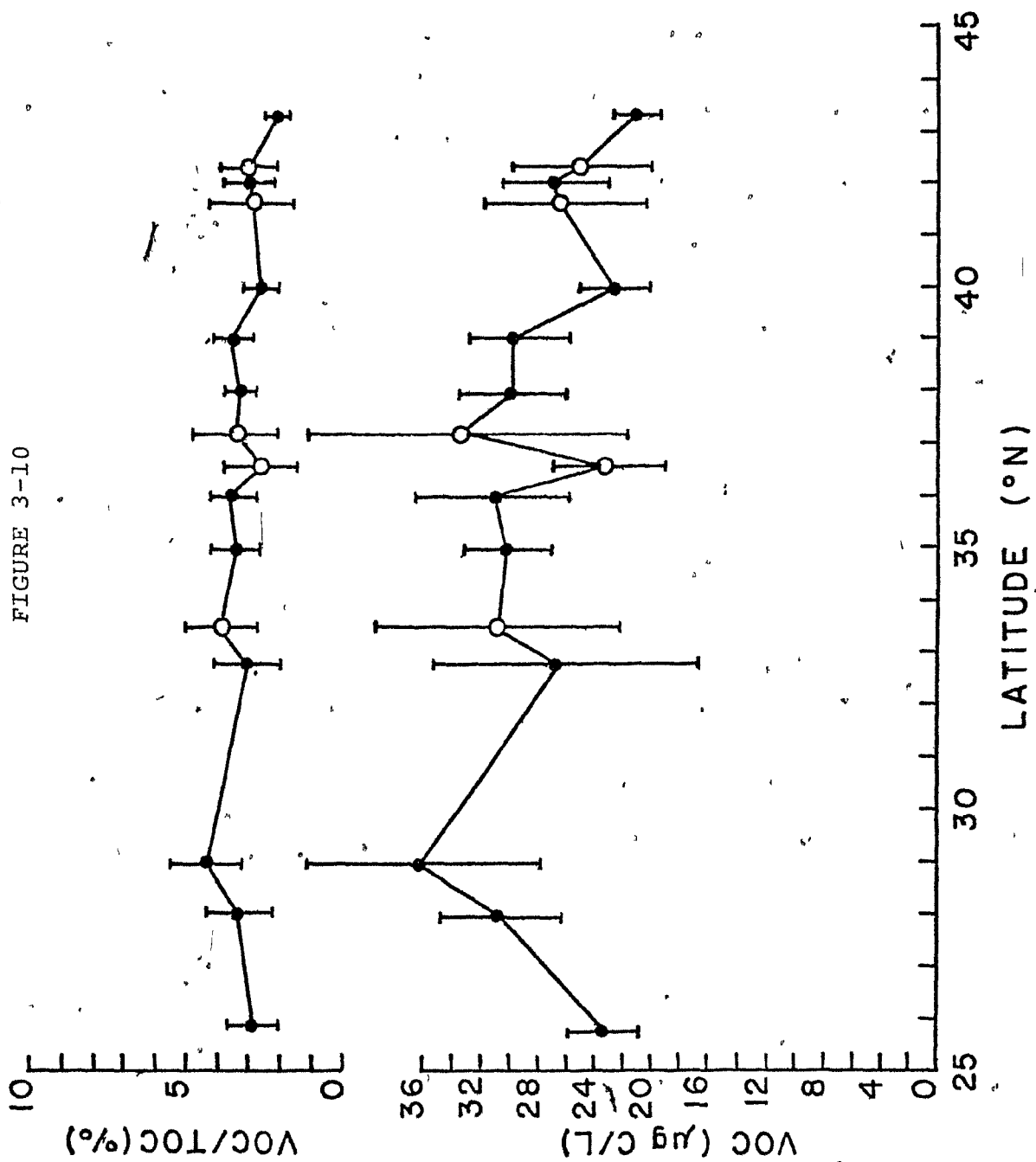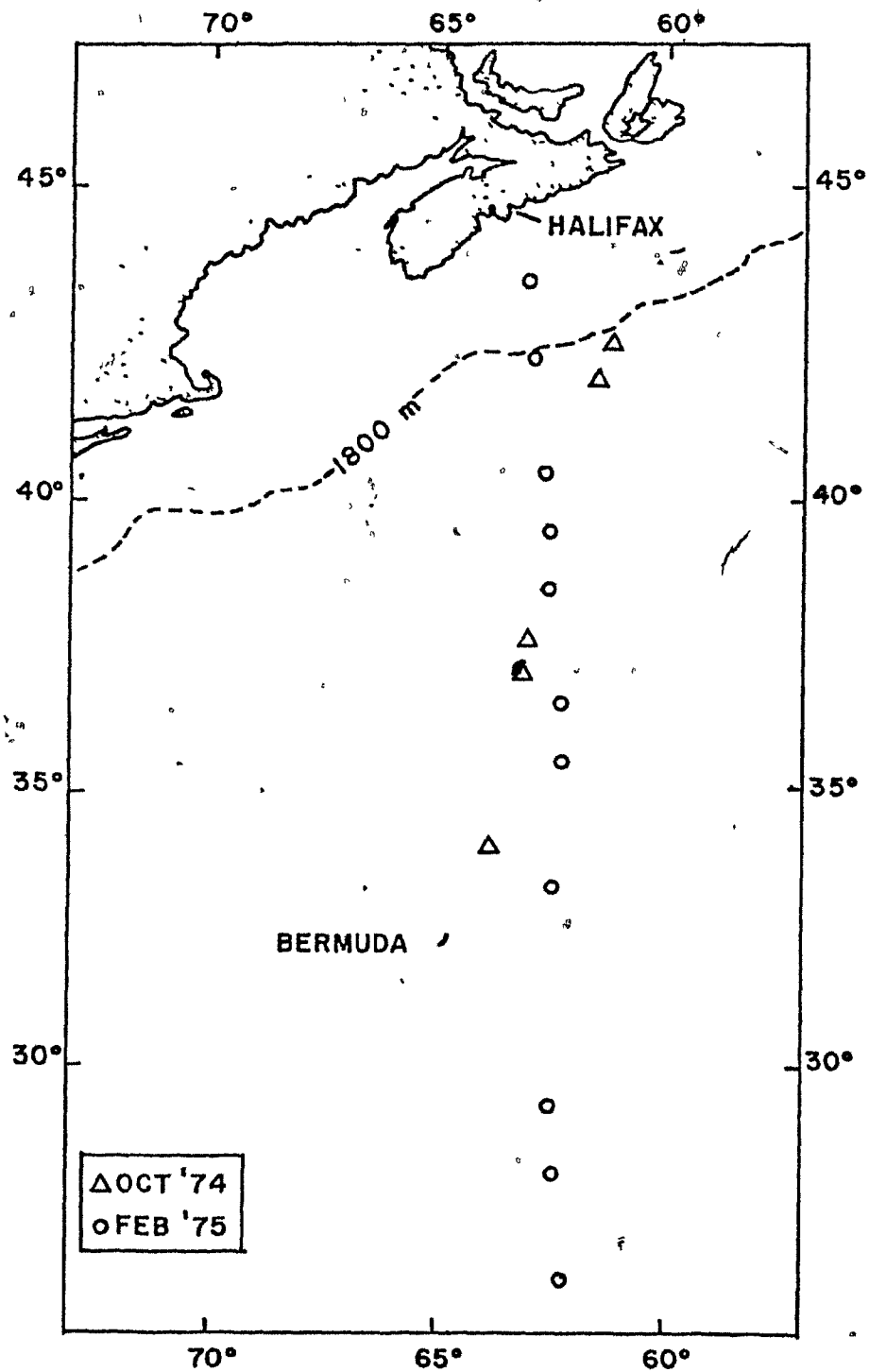
TABLE X

Variation of VOC Values (Averaged over Depth) with Position in the Atlantic Ocean

Station and Date	n	V.O.C. Concentration (μg.C/liter)		VOC/TOC Ratio (%)	
		Range of Values	Average of Values	Range of Values	Average of Values
1. 26°00'N, 62°45'W (2/75)	21	20.0-27.7	23.65±2.2	2.4-3.9	2.98±0.48
2. 27°50'N, 62°40'W (2/75)	8	19.8-36.4	30.85±5.6	1.9-4.5	3.37±0.89
3. 29°00'N, 62°45'W (2/75)	8	25.1-49.3	36.37±8.6	3.3-5.5	4.37±0.90
4. 32°50'N, 62°40'W (2/75)	13	19.3-52.4	26.78±10.5	2.0-5.3	3.70±0.86
5. 33°30'N, 64°00'W (10/74)	9	22.6-52.3	30.77±10.5	3.3-5.8	3.95±0.86
6. 35°00'N, 62°28'W (2/75)	9	29.0-34.7	30.34±3.2	2.6-4.7	3.44±0.63
7. 36°00'N, 62°34'W (2/75)	7	19.6-32.4	31.1±6.0	2.7-3.7	3.65±0.58
8. 36°35'N, 63°18'W (10/74)	12	17.6-32.4	23.30±4.3	1.7-4.0	2.67±0.95
9. 37°10'N, 63°16'W (10/74)	7	18.8-52.2	33.51±11.8	2.0-5.2	3.44±1.21
10. 38°00'N, 62°45'W (2/75)	8	24.5-37.9	29.88±4.29	2.8-3.6	3.33±0.33

11. 39°00'N, 62°46'W (2/75)	8	28.2–36.2	29.84±3.46	3.0–4.3	3.59±0.48
12. 40°00'N, 62°52'W (2/75)	8	19.3–25.8	22.75±2.22	2.2–3.3	2.69±0.34
13. 41°38'N, 61°48'W (10/74)	7	18.0–33.5	26.49±5.99	1.6–4.5	2.89±1.16
14. 42°01'N, 63°05'W (2/75)	9	21.9–32.9	27.03±4.04	2.3–4.0	3.10±0.61
15. 42°16'N, 61°31'W (10/75)	12	17.0–32.9	25.15±4.61	1.7–4.2	3.10±0.79
16. 43°20'N, 63°13'W (2/75)	4	20.8–22.3	21.19±0.77	2.0–2.3	2.14±0.14

the values of the VOC that were found in the Sargasso Sea
(23-36 µg C/liter), but the difference was small. The low
values in the Slope area might be explained by the time of
year in which the samples were taken, when the algal
productivity was relatively low. The water temperatures for
the stations on the Scotian Shelf were higher in Oct. '74
(15-20°C) than in Feb. '75 (2-6°C). The lower values of
VOC found in the Feb. samples (21-22 µg.C/liter) than in
Oct. (25-27 µg.C/liter) might be expected since in the
colder water the biological activity would be greatly
reduced.

4. Discussion and Interpretation of VOC Analysis in
   Natural Samples

In the main areas sampled (Scotian Shelf, Gulf of St.
Lawrence, Sargasso Sea, and coastal regions) in this study
(Table XI), the volatile component of the TOC was small (2-
6%). Although indications of coastal and seasonal influences
were seen in the Scotian Shelf data (Table VII) and some
small scale variations with depth and water mass were seen,
the observed distributions of the VOC concentrations might
have been steady-state or background values. This volatile
fraction of the TOC may be important in the cycle of carbon
in natural waters even though it is a minor (2-6%) component
of the TOC. If volatiles are produced in situ, this production

TABLE XI

Distribution of Averaged VOC Concetrations With Depth From Different Areas

Sampling Area and Time of Sampling	Depth (m.)	n	VOC Concentrations		VOC/TOC Ratio	
			Range of VOC Values (µg.C/l.)	Averaged VOC Values (µg.C/l.)	Range of Values (%)	Average Values (%)
A.Gulf of St. Lawrence (11/75)	5	9	21.7-51.7	31.84±8.4	1.86-4.8	2.7±.9
	25	4	35.2-47.0	40.92±5.1	2.80-3.7	3.2±.4
	50	4	22.3-32.2	28.67±4.4	2.00-2.9	2.5±.4
	100	4	27.5-43.6	32.64±7.4	2.20-4.2	3.1±.9
	160	4	24.7-38.6	33.23±6.4	2.60-4.0	3.3±.6
	220	5	22.8-35.6	27.60±5.9	2.20-4.1	2.9±.7
B.Scotiaん Shelf (5/74) (8/75) (3/76)	5	26	23.9-60.6	40.95±9.1	1.8-5.9	3.3±.9
	25	16	24.0-53.0	37.63±8.1	1.9-5.2	3.4±.8
	50	12	24.0-68.5	33.47±11.4	1.8-6.2	3.4±1.1
	75	5	26.0-42.5	35.24±7.9	2.8-6.2	3.8±.6
	125	12	30.6-41.2	36.06±3.6	3.5-4.9	4.2±.5
	200	5	28.3-38.1	34.22±3.8	3.7-4.4	4.0±.5
	350	7	25.0-38.3	31.26±4.4	3.5-5.8	4.2±.8
	700	5	22.4-46.4	35.45±8.6	3.0-6.1	5.0±.9
	1500	5	23.2-29.7	26.17±2.4	3.4-4.0	3.7±.3

Location		n	Range	Mean ± SD	Range	Mean ± SD
C. Central and Northwest Atlantic (10/74) (2/75)	1	16	17.6-49.3	29.70±9.5	1.7-5.5	3.1±1.1
	10	15	19.8-52.4	31.10±9.9	1.8-5.3	3.1±1.1
	25	14	18.8-36.7	27.03±6.2	1.7-3.2	2.8±0.7
	50	15	22.6-52.2	31.86±9.8	2.3-5.8	3.4±1.1
	100	15	17.0-52.3	28.71±8.6	2.0-5.8	3.2±1.0
	200	20	18.8-34.0	26.81±5.0	2.1±5.2	3.3±0.8
	300	6	19.6-26.4	24.85±4.9	2.5-5.1	3.3±1.0
	400	7	21.1-32.9	26.02±4.2	2.8-4.3	3.6±0.5
	500	9	20.4-32.4	25.68±4.3	2.8-4.4	3.4±0.6
	750	5	20.2-26.1	25.54±5.0	2.7-4.5	3.5±0.8
	1000	10	21.5-34.7	26.39±4.3	3.1-4.7	3.6±0.5
	1500	7	19.2-28.6	23.50±3.1	2.5-4.3	3.4±0.6
	2000	4	22.4-24.9	23.68±1.2	3.0-3.5	3.2±0.2
	2500	4	22.0-29.3	25.90±3.2	3.1-4.0	3.6±0.4
D. North West Arm	1-10	37	20.4-49.4	32.60±7.8	1.2-2.9	1.9±0.4
E. St. Margaret's Bay	1-40	28	10.8-45.5	30.90±6.2	1.4-3.4	2.3±0.5

must be very slow, since no build up in the VOC concentration is observed, or the rate of loss of the volatiles (consumption, decomposition, or evolution) from the water must balance its rate of production. The low VOC values can be explained if the volatiles are maintained at a threshold concentration at which the utilization by organisms will occur.

The importance of the volatile materials in the egeneration and utilization processes of the organic matter in seawater is supported by the concept of a steady state relationship of the VOC. An essential step in the cycle of organic matter in seawater may be played by the volatiles, but if this cycling is dynamic, dramatic spatial or temporal changes in the VOC concentration will not be evident in the quantification of the volatile component. The integrity of my extraction and analysis system was shown in the work with standards; the "volatile" fraction of the TOC should be removed and analyzed by the extraction procedure used in my work.

If we accept the assumption that the volatile components were removed from the seawater with my method of extraction, then reasons for the type of distribution observed must be sought. The volatile material extracted from the seawater was a small but relatively constant fraction of the TOC. Little structure was shown in the depth profile of the VOC/TOC ratio, and while the specific components of the TOC may

have changed, a constant per cent of the matrix of the TOC
was analyzed as VOC by my extraction procedure.

This uniformity in the ratio of the VOC component was
shown indirectly by work with ultrafiltration (Baturina
et al., 1975 and Ogura, 1974) where drastic changes in the
moelcular weight fractionation with depth were not observed.
In the Pacific, a consistancy of distribution in the low
molecular weight fraction (less than 500) was indicated, and
a drop from 65% of the TOC in the surface to about 50% in
the deep water was observed.

If volatiles are formed by one of the predicted mechanisms
(productivity, biological activity, chemical reactions,
input by man), an increase of the VOC should be observed in
the areas where these sources have the most influence. The
surface zone would be expected to be the most influenced
area. In the depth profiles, the amount of VOC extracted
from the seawater samples was usually higher (up to 50-100%
higher) in the surface zone than in the deeper water, but
this enhancement was not reflected in the ratio of the
VOC/TOC, since the rates of decrease of VOC/TOC with depth
were about the same. If the volatiles were being produced
in the surface zone, then the VOC/TOC ratio should have been
highest in this area. This was not always observed.

The volatile organic material would be maintained as a
steady state concentration if the rate of production of the

volatile material was equal to or slower than the rate of
its consumption or removal from the natural system. If
utilization or removal processes were only biological, then
the organic material which was removed from this region of
formation (surface zone) should be eventually consumed by
organisms. The age of the DOC in the deep water has been
estimated at 1000-3000 years (Williams, Oeschger, and
Kinney, 1969, Skopintsev, 1972). Even if the biological
utilization was slow, the volatile material should eventually
be consumed and remineralized. This argument must assume
that the production of low molecular weight material in the
deeper water is negligible (however, some low molecular
weight organics could be produced by biological decomposition
and utilization of larger molecular weight organics at depth,
but the effect should be small).

In the analysis of natural samples in this study, the
absolute amount of the volatile material was shown to
undergo a small decrease in concentration with depth, but the
VOC concentration was never found to be zero. Complete
utilization of the volatile material was not observed. This
suggests a threshold concentration below which utilization
of the volatile organic material cannot take place. The
VOC concentration would be maintained at this threshold
concentration if the volatile material were produced
at a rate that was equal to or less than the rate

of utilization or removal. Relatively constant distributions with depth would be expected if this steady-state relationship existed. More variable distributions would be expected in the surface zone. This type of distribution was evident in many of the profiles that were obtained.

The input of VOC from contamination would be expected to influence the VOC distribution. The low VOC values expected in deeper water would be enhanced by a system blank in the extraction procedure. However, the VOC values at depth can not be explained entirely from the system blank, which was estimated at 2-5 µg C/liter. The VOC concentrations from deeper water may be affected by the introduction of contaminants during the sampling, handling, and analysis of the samples, so that the measured VOC values could have been higher than the true value. The accuracy of the extraction system would have been affected by the introduction of these small scale systematic contaminants, and a smoothing of vertical gradients in the VOC could be expected.

Even though the VOC concentrations have been found to be low and little structure was seen in their distribution, I feel that this volatile fraction is important in the cycling of the organic matter in natural waters. However, if the volatiles are important, it is required that these volatile materials be produced in the natural system. If this produced material can be monitored, the role of this volatile fraction in the carbon cycle can be better understood.

D.   Sources of VOC in Natural Waters

1.   Introduction

A series of experiments were designed in an effort to discover and understand the sources and potential pathways for the volatile organic matter in seawater. Attempts were made to discover, understand, and quantify the mechanisms most likely to contribute to the volatile material in the natural systems. A better understanding of the sources of the "volatile" material may help to answer the questions regarding the role and significance of the VOC in the natural system. Volatile compounds would be expected to be produced directly by organisms, by breakdown of larger organic materials, or by input to the natural system.

Biological production of VOC is expected from metabolic by-products during primary productivity, respiration, or utilization and during the microbial decomposition and fragmentation of the larger molecular weight organics. Some of these biological sources of the volatile materials were studied in experiments which will be described. An experiment was also designed to examine the production of the volatiles by photochemical decompostion of the TOC.

2.   Production of VOC in Biological Systems

a)   Effect of Primary Productivity on the VOC

High biological activity was expected to lead to an

input of volatile matter. It was difficult to reproduce the natural system in the laboratory since culture systems are grown in populations that are too high and in media which could interfere with the determination of the VOC produced. Therefore, I decided to monitor the VOC and TOC in a natural population during periods of intense biological activity. The VOC and TOC concentrations were measured at various times before, during, and after the intense biological activity of a spring bloom. Coastal areas (North West Arm, St. Margaret's Bay) were used for this study (Fig. 11). The results obtained will be discussed presently.

1)   The North West Arm Study

Samples were collected in the North West Arm (an arm of Halifax Harbour) at two stations during the period January 1976 to June 1976. Station A was within the N.W. Arm, while station B was just outside the Arm. The volatile organic carbon (VOC), total and dissolved organic carbon (TOC and DOC), and the ratio of the volatile fraction of the total (VOC/TOC) were measured. An accurate estimation of the stage and condition of the bloom was monitored by chlorophyll a (determined by K. Sellner and J. Dunbrack) and a rough estimate of the bloom was obtained with a Secchi depth, which correlated well with the chlorophyll a data for the prediction of the bloom. The samples for TOC and VOC analysis were collected at 1 and 5-10 m. A summary of the

averaged data from both stations is presented in Table XII.

The start of the spring bloom was noted in the early part of March and the bloom appeared to continue until May. The lowest value of VOC for both station A and B was found on March 9 (20-24 µg.C/liter), which was just as the bloom was beginning. The averaged VOC concentrations before March 9 and after May 4 (30.5±4.2 µg.C/liter) were about 85% of the averaged VOC values during the blooom period of March 16 - April 20 (35.71±6.4 µg.C/liter) The significance of this difference was questionable, but a trend to higher VOC values during the bloom was noted and a correlation of the bloom and the VOC values was evident.

A more dramatic and better indicator of the bloom period was seen with the TOC values, which increased from 1.4-1.65 mg.C/liter (ave. 1.45±.05 mg.C/liter) before the bloom to 1.5-2.3 mg.C/liter (ave. 1.92±.2 mg.C/liter) during the bloom, and dropped to f 1.7-2.1 mg.C/liter (ave. 1.80±.15 mg.C/liter) after this bloom period. Values of TOC were obtained in the summer (7 and 8/75). The concentrations were found to range from 1.3-1.9 mg.C/liter (ave. 1.56±.2 mg.C/liter), which were about the same as the pre-bloom values. The DOC values were calculated on samples which had been filtered through a 0.8 µ filter. The increase in the dissolved fraction (DOC) seemed to start 1-2 weeks after the

TABLE XII

Effect of Biological Activity on the Organic Carbon in the N.W.West Arm

Date	Station	Depth	Chlorophyll a (μg.C/l.)	Secchi Depth (m.)	V.O.C. (μg.C/l.)	T.O.C. (mg.C/l.)	D.O.C. (mg.C/l.)	VOC/TOC (%)
7/7/75	A	1				1.30		
		10				1.12		
	B	0				1.60		
		15				1.25		
24/7/75	A	1				1.58		
		10				1.52		
	B	1				1.62		
		10				1.40		
13/1/76	A	1		5.5	27.65	1.31		2.11
		10			41.16	1.44		2.86
	B	1			26.65	1.57		1.68
		10			33.54	1.51		2.22
24/2/76	A	1	1.24	4.0	32.95	1.42		2.32
		5			32.35	1.46		2.22
	B	1				1.41		
		10			32.95	1.43		2.30
9/3/76	A	1	8.80	4.5	24.06	1.53	1.40	1.57
		5			20.38	1.42	1.40	1.44
	B	1			22.86	1.65		1.39

Date	Group							
16/3/76	A	1	11.6	2.5	28.75	1.84	1.36	1.56
		5			27.35	1.82	1.39	1.50
	B	1	7.1	2.5	30.87	1.59	1.48	2.00
		10			25.69	1.47	1.37	1.75
23/3/76	A	1		2.4	47.78	2.04	1.59	2.34
		5			34.94	1.95	1.59	1.79
	B	1		2.0	46.62	1.94	1.65	2.40
		10			42.41	2.40	1.56	1.77
1/4/76	A	1	7.6	2.5	33.49	1.84	1.61	1.82
		5			40.98	1.98	1.69	2.07
	B	1	10.8	2.7	31.09	1.89	1.64	1.64
		10			42.33	1.79	1.47	2.36
13/4/76	A	1	6.8	2.5	24.27	2.06	1.56	1.18
		5			32.30	1.89	1.70	1.71
	B	1	6.2	2.7	31.21	1.82	1.38	1.71
		10				1.79	1.35	
20/9/76	A	1	4.0	3.0	47.38	2.10	1.65	2.26
		5			28.29	2.32	1.56	1.22
	B	1	3.8	3.8	49.41	1.90	1.62	2.60
		10			37.86	1.95	1.61	1.94
4/5/76	A	1	2.5	2.5	25.27	1.98	1.82	1.28
		5			29.09	1.62	1.37	1.74
	B	1	2.0	2.0	40.56	1.85	1.63	2.19
		10			31.30	1.51	1.45	2.10
8/6/76	A	1	2.2	3.0	26.68	1.87	1.62	1.43
		5			25.50	2.11	1.79	1.21
	B	1	1.9	2.5	24.98	1.75	1.69	1.43
		10			23.87	1.62	1.22	1.47

increase in the TOC values was noted. The TOC values
increased rapidly as the bloom started, but the
increase in the DOC values was delayed until the TOC values
had built up. The increase in the DOC was probably the
result of the excretion of organics by organisms during
growth as well the decomposition of the POC. However, the
delay in the DOC increase was shorter than the lag time of
greater than a month suggested by Banoub and Williams
(1973). The DOC values at the beginning of the bloom period
(1.40±.02 mg C/liter) were found to increase (1.58±.09
mg.C/liter) as the bloom was followed. The DOC values
remained high after the bloom had peaked and begun to slow
down (greater than 1.5 mg.C/liter).

While significant changes in the TOC and DOC were
observed during this period of intense biological activity,
only a slight increase in the VOC concentration was noted.
This meant that the change in the VOC/TOC was small and at
the height of the bloom a slight drop in the ratio was
found. The VOC/TOC variations during the sampling period
(1.3-2.4%) were not great and remained relatively constant.
These results for the TOC, DOC, VOC, and VOC/TOC (averaged
over the 2 sampling depths) for station A (Figures 12a) and
station B (Figure 12b) are plotted against time.

While the samples were collected from stations under
slightly different conditions (input from surrounding areas),

Fig. 3-12: Effect of biological activity during the spring bloom
(1/76 - 6/76) on the organic carbon in the North West
Arm.

☐ - TOC

⊂⊃ - DOC

○ - VOC/TOC

△ - VOC

12-A - Averaged results from 1 and 5 m at Station A -
see Figure 11.

12-B - Averaged results from 1 and 10 m at Station B -
see Figure 11.

A.

TOC & DOC mg C/L

VOC μg C/L   VOC/TOC(%)

7   21 13   27 3   17   2   10   30 6   20   4   18   1   15
July   Jan   Feb   March   April   May   June
1975   1976
TIME

B.

TOC&DOC, mg C/L

VOC μg C/L   VOC/TOC(%)

7   21 13   27 3   17   2   10   30 6   20   4   18   1   15
Jul,   Jan   Feb   March   April   May   June
1975   1976
TIME
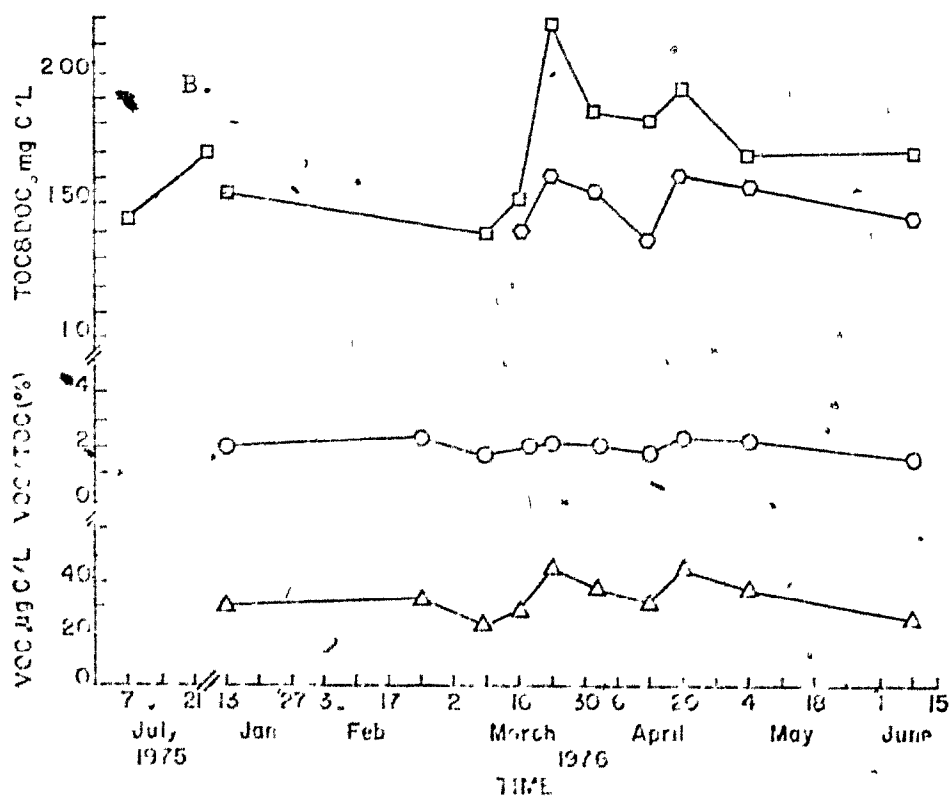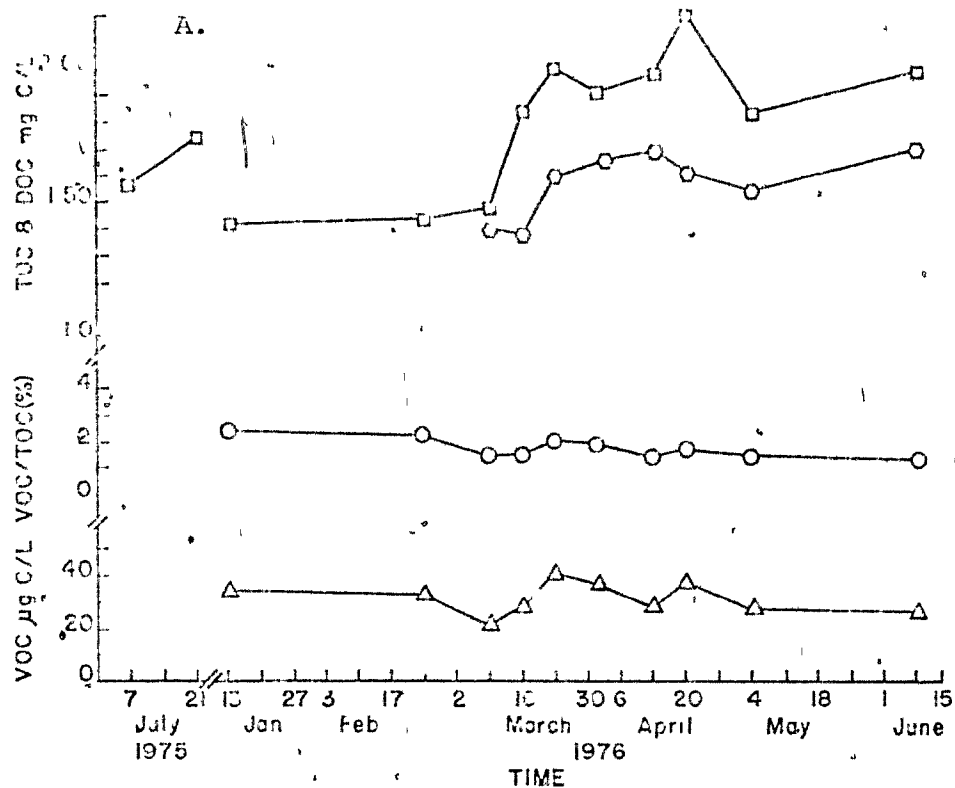
the bloom period was found to have almost identical effects at both Station A and B. During the period of March 16 to April 4, the highest TOC and DOC values at both stations were measured and small increases in the VOC were noted. The uniformity of the VOC/TOC ratio during this period was reflected at both stations. This was a period of intense biological activity and the highest POC (TOC-DOC) concentrations were calculated during the bloom. The concentrations of POC, which should have been mainly the result of the algal bloom, were calculated to be in the 0.5-0.8 mg.C/liter range. The DOC values (DOC increase by .2-.4 mg.C/liter) were influenced by this high concentration of organisms during this period of high productivity, but the VOC values were affected only in a small way (VOC increase of 5-15 μg C/liter).

This small increase in the VOC concentration might have been an indication that only a small amount of the organic material produced during this period of high productivity will be included in my working definition for the "volatiles", so that only a small change in the measured VOC fraction will be noted. If the VOC components were highly labile and the low molecular weight materials were biologically, chemically, or physically unstable in the natural system, their lifetime under natural conditions would be short (rate of removal exceeds rate of production). The area of this study was a rich system where microbial

activity might have been large; the bacterial utilization might be a significant scavenger of the produced low molecular weight materials.

During the bloom period, the relatively constant and, low (about 2%) values of the VOC/TOC ratio with time were difficult to justify. This result was an indication that only a small but relatively constant fraction of the matrix of the total organic matter in natural waters will be classed as "volatile" under my working definition, If the changes in the DOC concentrations during and after the bloom compared to the concentration before the bloom were assumed to be the result of biological activity, and if the difference in the VOC concentration before and during the bloom were also the result of biological activity, then the ratio of the differences (ΔVOC/ΔDOC) may be indicative of the per cent of the biologically produced DOC which was measured in my system as "volatile".

$$\frac{\text{Ave. VOC } (36.66\pm7.9 \text{ µg.C/l}) - \text{Ave. VOC } (29.07\pm5.4\text{µg.C/l})}{\text{Ave. DOC } (1.58\pm.12 \text{ mg.C/l}) - \text{Ave. DOC. } (1.40\pm.04 \text{ mg.C/l})} = \frac{\Delta\text{VOC}}{\Delta\text{DOC}} = 4.22\%$$

(during the bloom) (before the bloom)

(during the bloom) (before the bloom)

This ratio of the difference in the VOC to the difference in the DOC (VOC/DOC) was calculated and a value of about 4% was obtained, which is about twice the average VOC/DOC value found for samples during this study in the bloom period.

The validity of the assumptions in this calculation are questionable since the analytical methods only allow for the measurement of standing crop values. With these obvious shortcomings in the calculations, the amount of the VOC added to the water from the biologically derived DOC was estimated and was found to be a small fraction of the organic matter added by biological systems (about 4%). However, this calculated value may not be significant in the overall value, since many factors of volatile utilization and loss from the system were difficult to estimate for this calculation. Nevertheless it was interesting that the calculated ratio of $\Delta VOC/\Delta DOC$ (4%) was not much different than the VOC/TOC ratio (2%) that was measured in the natural samples.

11) St. Margaret's Bay Study

Samples were collected from a station in the central part of St. Margaret's Bay (Fig. 11) from March 2 to May 10, 1976, which was the period before, during and after the spring bloom. The results are shown in Table XIII. The VOC and VOC/TOC ratio were measured at 3 depths (1, 5, and 25 m), while the TOC values were determined at 5 depths (1, 5, 10, 25, and 40 m).

The bloom period in St. Margaret's Bay was very short compared to the bloom that was observed in the N. W. Arm, but the results were similar. The distributions of the averaged VOC and TOC concentrations, the VOC/TOC ratios, and

TABLE XIII

Effect of Biological Activity on the Organic

Carbon in St. Margaret's Bay

Date	Depth (m.)	Chloro-phyll a (μg.C/l.)	V.O.C. (μg.C/l.)	T.O.C. (mg.C/l.)	D.O.C. (mg.C/l.)	VOC/TOC (%)
2/3/76	1	< 0.5	25.09	1.22		2.05
	5	< 0.5	34.50	1.21		2.85
	10	< 0.5	19.80	1.39		1.42
	25	< 0.5		1.08		
	40	< 0.5		1.08		
9/3/76	1	0.5	22.04	1.17		1.88
	5	0.5	21.81	1.27		1.72
	10	0.5		1.39		
	25	0.5	27.02	1.23		2.20
	40	0.2		1.09		
16/3/76	1	0.5	32.27	1.34	1.17	2.41
	5	0.6	39.44	1.16	1.20	3.40
	10	0.5		1.18		
	25	0.5	23.46	1.36	1.40	1.73
	40	0.5		0.92		
23/3/76	1	0.5	30.86	1.36	1.29	2.27
	5	0.8	40.82	1.15	1.10	3.55
	10	0.6		1.16		
	25	0.5	28.09	1.14		2.45
	40	0.5		1.24		
26/3/76	1	0.9	30.39	1.19		2.55
	5	1.0	39.34	1.35		2.91
	10	0.7		1.15		
	25	0.4	26.58	1.08		2.46
	40	0.3		1.10		
2/4/76	1	0.8	33.19	1.43	1.40	2.32
	5	0.9	36.22	1.41	1.36	2.57
	10	0.5		1.42		
	25	0.5	27.64	1.21		2.28
	40	0.4		1.13		
12/4/76	1	0.8	26.20	1.70	1.65	1.54
	5	0.8	33.87	2.12	1.71	1.60
	10	1.5		1.63		
	25	2.0	26.17	1.37	1.16	1.91
	40	0.2		1.22		

15/4/76	1	3.8	32.28	1.71	1.44	1.89
	5	7.3	45.53	1.99	1.28	2.29
	10	8.1		2.03		
	25	2.5	30.96	1.33	1.24	2.33
	40	1.3		1.55		
26/4/76	1	0.6		1.37	1.35	
	5	0.5	36.87	1.33	1.24	2.77
	10	0.6		1.33		
	25	0.8	32.20	1.14	1.14	2.80
	40	0.8		1.14		
10/5/76	1	0.6	31.44	1.41	1.26	2.23
	5	0.6		1.37	1.35	
	10	0.6		1.33		
	25	0.5	30.01	1.11	1.10	2.70
	40	0.5		1.20		

FIGURE 11
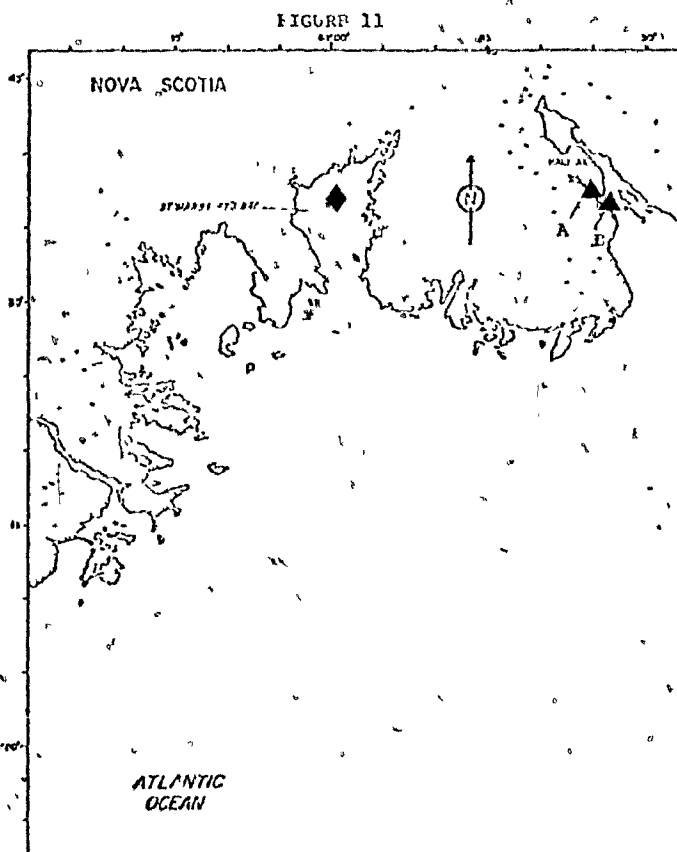
Fig. 3-11: Map of coastal areas used in this study.

▲ – North West Arm Stations

◆ – St. Margaret's Bay Station

the chlorophyll a values over the 3 depths (1, 5 and 25 m) that were collected during this study in the St. Margaret's Bay were plotted against time in Figure 13. Little variation in the VOC and VOC/TOC values were noted, but a rapid increase in the TOC concentration was seen.

The variations in the averaged VOC concentrations were very small, with a range of 23-36 µg.C/liter and an average of 30.98±3.8 µg.C/liter during the study. There did not appear to be any noticeable increase in the VOC concentrations with the onset of the bloom, which from chlorophyll a data (measured by K. Sellner) was between April 2 and April 12. A dramatic increase in the averaged TOC values (from ave. TOC= 1.25 before to ave. TOC= 1.65 mg.C/liter during the bloom) was observed during the early part of April. A peak in the TOC values was found on April 15 (ave. TOC= 1.72 mg.C/liter), but by April 26 the averaged TOC values were reduced to approximately prebloom values (ave. TOC= 1.2-1.3 mg.C/l). The DOC values closely followed the TOC values, but when there was little POC, it was difficult to obtain good values for the DOC fraction because I had a contamination problem during the filtering step (estimated about 0.1 mg C/liter). Only on April 12 and April 15 did there appear to be a large fraction of the TOC present as POC. The POC was calculated by an indirect method, (TOC-DOC), and from this the POC values before and after the bloom were found to

Fig. 3-13: Effect of biological activity during the spring
bloom (2/76 - 6/76) on the organic carbon at station
in St. Margaret's Bay. Values are averaged over 3
depths (1, 5, 25 m). See Figure 11.

☐ - TOC

○ - VOC/TOC

△ - VOC

⬡ - Chlorophyll a

Fig. 3-14: Plot of the averaged TOC and Chlorophyll a values
during the period of the spring bloom in St. Margaret's
Bay (2/76 - 6/76).

☐ - TOC averaged over 5 depths (1, 5, 10, 25, 40 m)

⬡ - Chlorophyll a averaged over 5 depths (1, 5, 10, 25,
40 m).

FIGURE 3-13
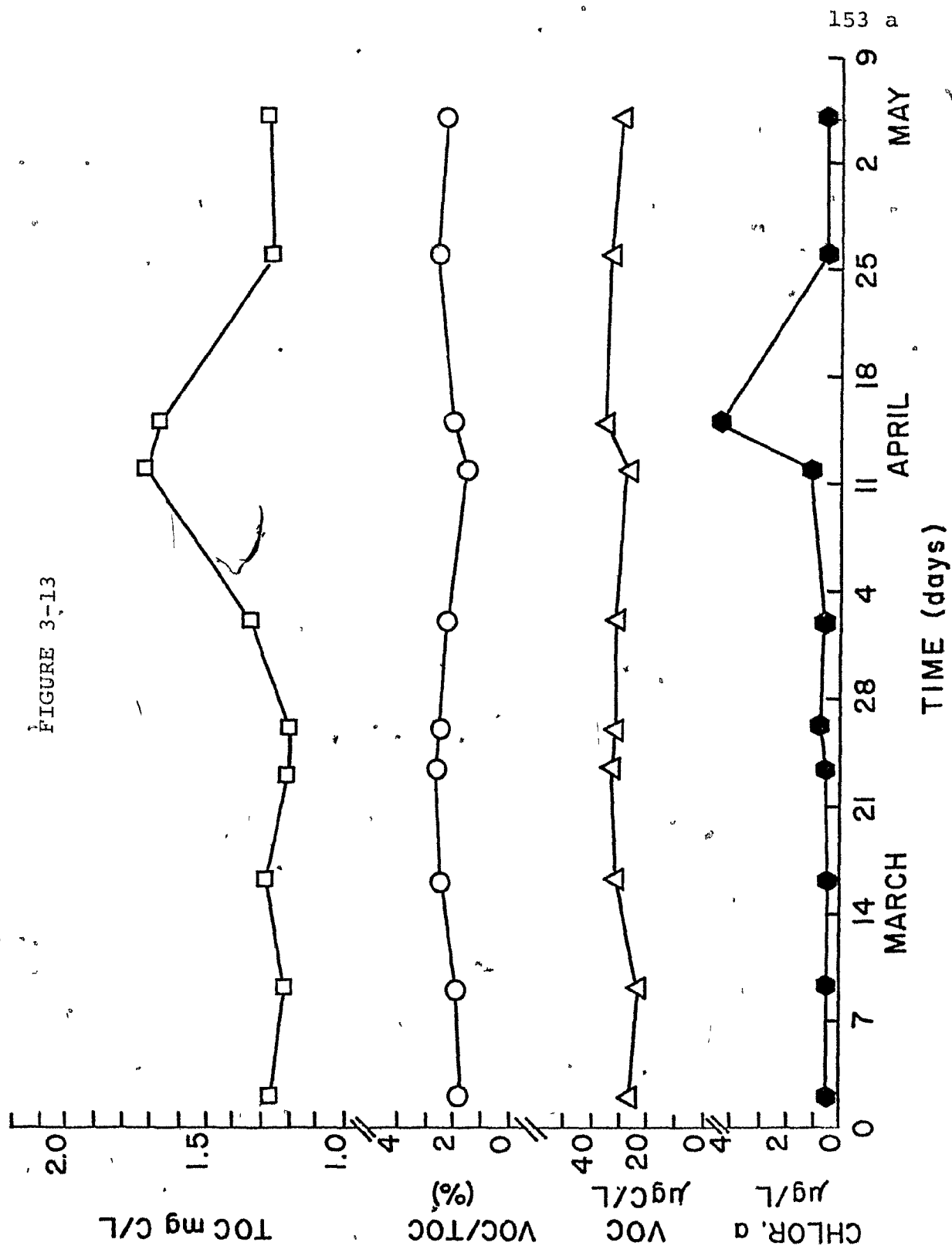
TABLE XIV .

Averaged TOC and Chlorophyll a Values Over 1,5,10,25,and 40m.

From St. Margaret's Bay (Spring 1976)

Date	Average Chlorophyll a Concentration (µg/liter)	Average TOC Concentration (mg C/liter)
March 2	0.5	1.20±.13
March 9	0.5	1.23±.11
March 16	0.5	1.29±.18
March 23	0.6	1.21±.09
March 26	0.7	1.17±.11
April 2	0.6	1.32±.14
April 12	1.1	1.61±.35
April 15	4.6	1.72±.30
April 26	0.7	1.26±.11
May 10	0.7	1.28±.13

FIGURE 3-14
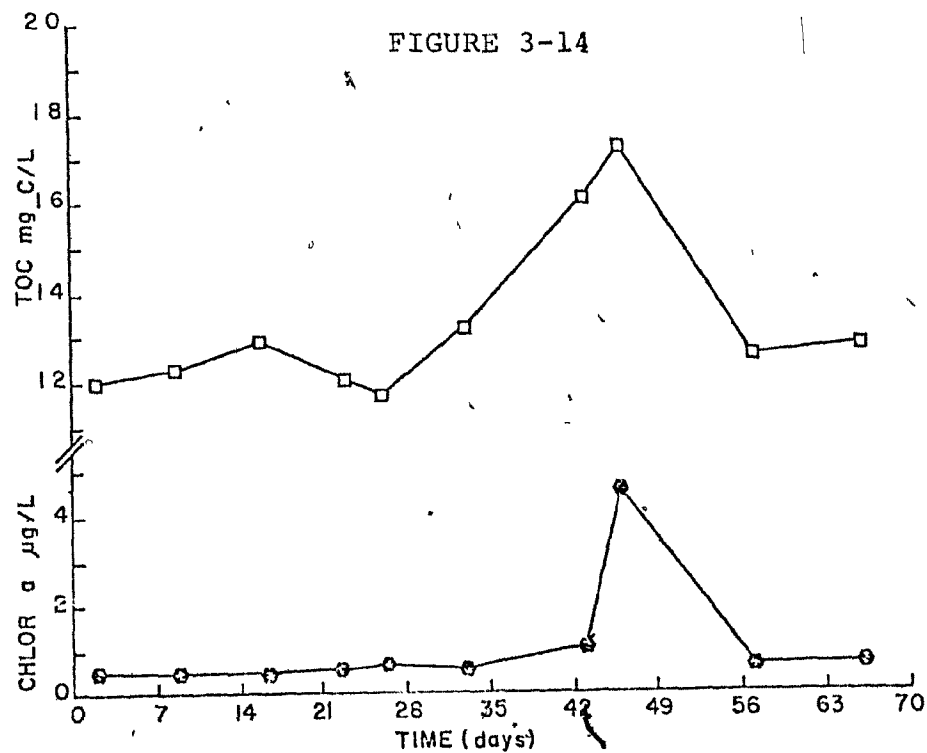
average about 40 µg C/liter, while during the bloom (April 12 and April 15) POC values were found to be greatly increased (290 µg.C/l) to as much as .5-.7 mg.C/liter. The shortness of the bloom was evident in the POC values, as they were high only during this peak period, after which the POC values rapidly dropped to pre-bloom values (10-125 µg.C/l). This rapid collapse of the bloom might have been a hydrographic effect caused by the periodic flushing of the Bay, so that the extension or continuation of the bloom was terminated by the intrusion of offshore water (Platt et al., 1972).

The averaged TOC and chlorophyll a values over the 5 depths were plotted (Figure 14) with respect to time. At the time of high chlorophyll a (April 15) values, the TOC concentrations were the highest (ave. TOC = 1.72 mg. C/l). After the bloom period the chlorophyll a values quickly dropped off, as did the TOC values (ave. TOC = 1.3 mg. C/l). This period of high chlorophyll a values and TOC values was also the period of the largest DOC concentrations (ave. DOC = 1.5 mg. C/l) (Table XIII). The averaged DOC values (from 1,5, and 25 m) for April 12 (1.51 mg. C/l) were about 15-25% higher than the DOC values before and after the bloom (ave. DOC= 1.2-1.3 mg. C/l). The very rapid return of the DOC values to the pre-bloom values after the bloom had subsided was surprising. Since a rapid decrease in the POC values was also observed, the assumption of removal of the produced

organic materials by a general flushing of the Bay was supported. If the POC material had not been removed from the system, then increased DOC values would have been expected as this particulate material was utilized and decomposed. The decomposition of this produced material should have resulted in an increase of the VOC concentration, but this was not observed. If the Bay had been flushed, the products of such decomposition would have been removed before they had a chance to build up, and low values of VOC would be explicable.

iii) Conclusions

Previous workers argued that the highest DOC values would be expected to follow the bloom period by a long lag time (greater than a month), in which time the produced particulate matter would be decomposed (Duursma, 1961, Morris and Foster, 1971 and Banoub and Williams, 1973). In both the St. Margaret's Bay and North West Arm studies, the lag time between particulate build-up and DOC build-up was quite short. In the N. W. Arm, the DOC increase appeared to follow the TOC increase by only 1-2 weeks, while in S.M.B., the increase in the TOC and DOC were about a week apart. This rapid increase in the DOC values may be an indication that the POC is a more labile fraction than previous workers might have expected. This result must bring into question the methods used for the analysis of the

TOC and DOC concentrations which were discussed earlier.

No large increase in the concentration of the VOC has been indicated in the natural systems in this study during a period of intense biological activity. Different regions and depths under varying influences were examined, and while large TOC changes were evident, VOC changes were minimal. This may mean that in periods of high biological productivity only a small fraction of the produced materials can be classed as "volatile" by my detection system. However, byproducts of photosynthesis are known to include low molecular weight organics which may be volatile under the natural conditions and should be measured by my extraction method.

If the rate of production of these "volatile" materials were balanced by their rate of removal (consumption or decomposition by biological of chemical processes, physical stripping, or vapourization), the material that was extracted and measured by my system may have been the background or steady-state concentration. A steady-state situation would result in the measurement of only a fraction of the VOC material produced in the natural system and only small variations in the VOC and VOC/TOC values would be expected in natural samples. A much better correlation of the productivity was evident with the TOC and DOC values than was obtained with the VOC fraction. Unless the basic assumption, that low molecular weight organics are produced by biological

activity, is not valid, mechanisms such as described earlier
for the formation and maintainance of a steady-state or
threshold concentration must be used to explain the low and
consistent values for the VOC and VOC/TOC that were obtained
during the spring bloom period.

b) Effect of Biological Decomposition of the TOC on
the VOC.

The production of volatile organic compounds was
expected from the decomposition of larger organic compounds
by microbial action or breakdown and utilization by larger
organisms. An experiment was designed in which these two
effects (bacterial and larger organisms utilization) on the
VOC values were estimated. The result was extrapolated to
the natural system.

1) Description of experiment

Water from three areas (North West Arm - N.W.A., St.
Margaret's Bay - S.M.B., tapped sea water - T.S.W.) was used
in this study. Water from the N.W.A. and S.M.B. was collected
with 5 liter Niskin bottles (General Oceanics) at about 2-5
meters depth during the height of the spring bloom period,
when the TOC values were high (1.7-1.8 mg.C/l). Samples for
the VOC analysis were not filtered and were transferred into
pre-cleaned 650 ml. amber bottles using the standard procedure.
Half of the bottles were fixed with 0.5 ml. of 3% $HgCl_2$
while the other half were not fixed. The samples were

stored at room temperature in the dark. Simultaneously, 25
ml. samples from the same water were collected for TOC
analysis in pre-oxidized (450°C) 50 ml. ampoules which were
sealed and kept at room temperature in the dark until ready
for analysis by the dry oxidation method #1. Half of these
samples were fixed with 50 µl. of 3% $HgCl_2$. A similar
series of samples were collected from the tap seawater
(T.S.W.) system, in which the water from the N.W.A. was piped
into the lab after filtration through a sand filter.

A blank value for the VOC was obtained by analysis of a
sample as quickly as possible after collection. Samples
were run at random times over a period of about 60-65 days.
At each of these times, VOC samples (fixed and unfixed with
the $HgCl_2$) were analyzed and TOC samples (fixed and unfixed
with the $HgCl_2$) were unsealed, pH adjusted to about 2-2.5
with the addition of concentrated H_3PO_4, resealed and then
frozen. When the experiment was completed, the samples were
analyzed for TOC by dry oxidation. With this approach, three
sets of data from the three experiments were obtained and the
change with time of the VOC and TOC concentration of the
samples (fixed and unfixed with the $HgCl_2$) was monitored.

    ii)   Results

The results of these three experiments are tabulated in
Table XV and are presented graphically in Figures 15
(N.W.A.), 16 (S.M.B.), and 17 (T.S.W.), where the TOC, VOC,

Fig. 3-15: Effect of biological decomposition on the organic carbon in seawater from the Northwest Arm.

Fig. 3-16: Effect of biological decomposition on the organic carbon in seawater from St. Margaret's Bay.

Fig. 3-17: Effect of biological decomposition on the organic carbon in seawater which was pumped into the lab from N.W. Arm.

□ TOC - Sample fixed with Hg.Cl₂

■ TOC - Sample not fixed with Hg Cl.

○ VOC/TOC - Sample fixed with HgCl

● VOC/TOC - Sample not fixed with HgCl.

△ VOC - Sample fixed with HgCl₂

▲ VOC - Sample not fixed with HgCl₂

FIGURE 3-15
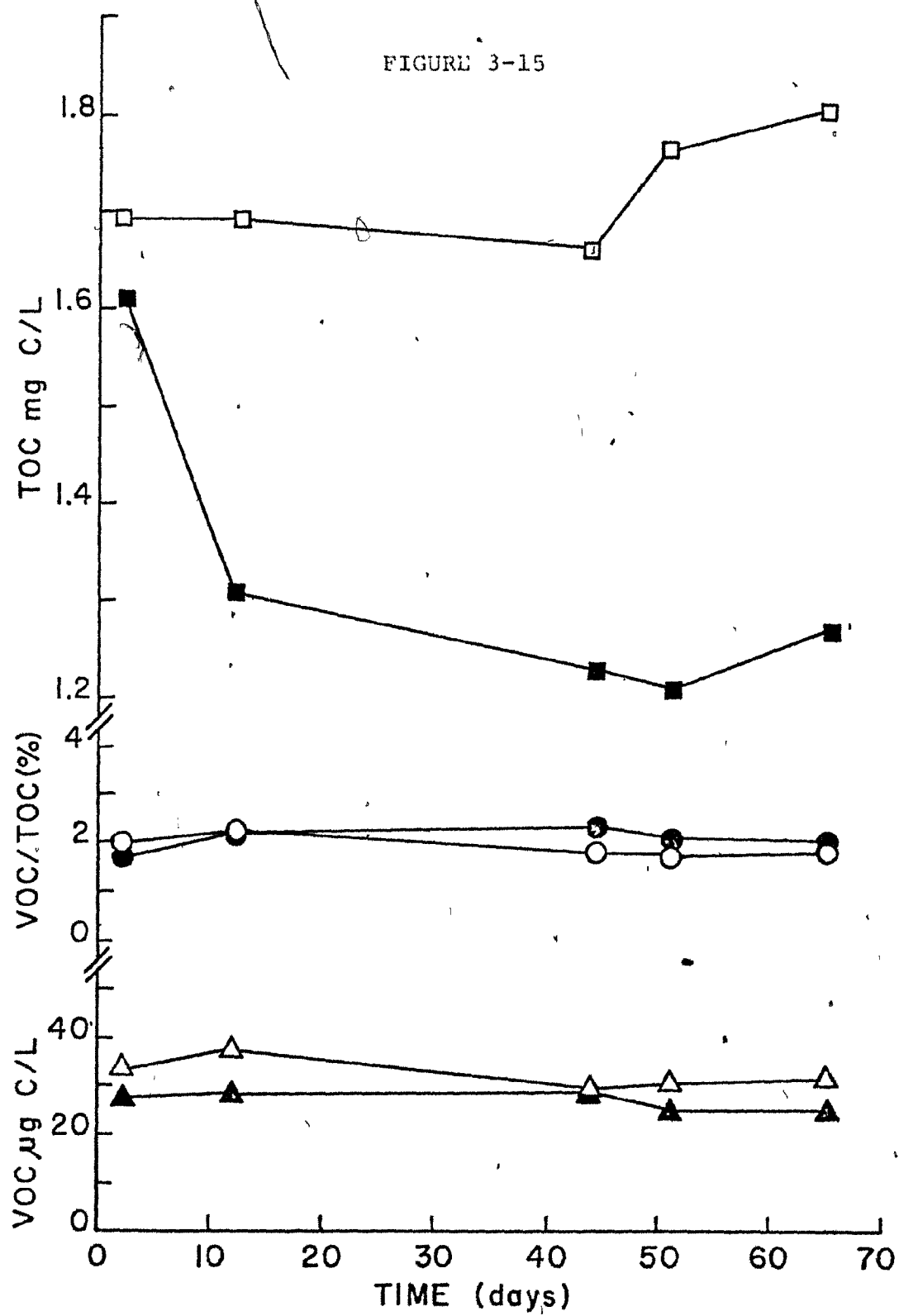
FIGURE 3-16

FIGURE 3-17

158 c
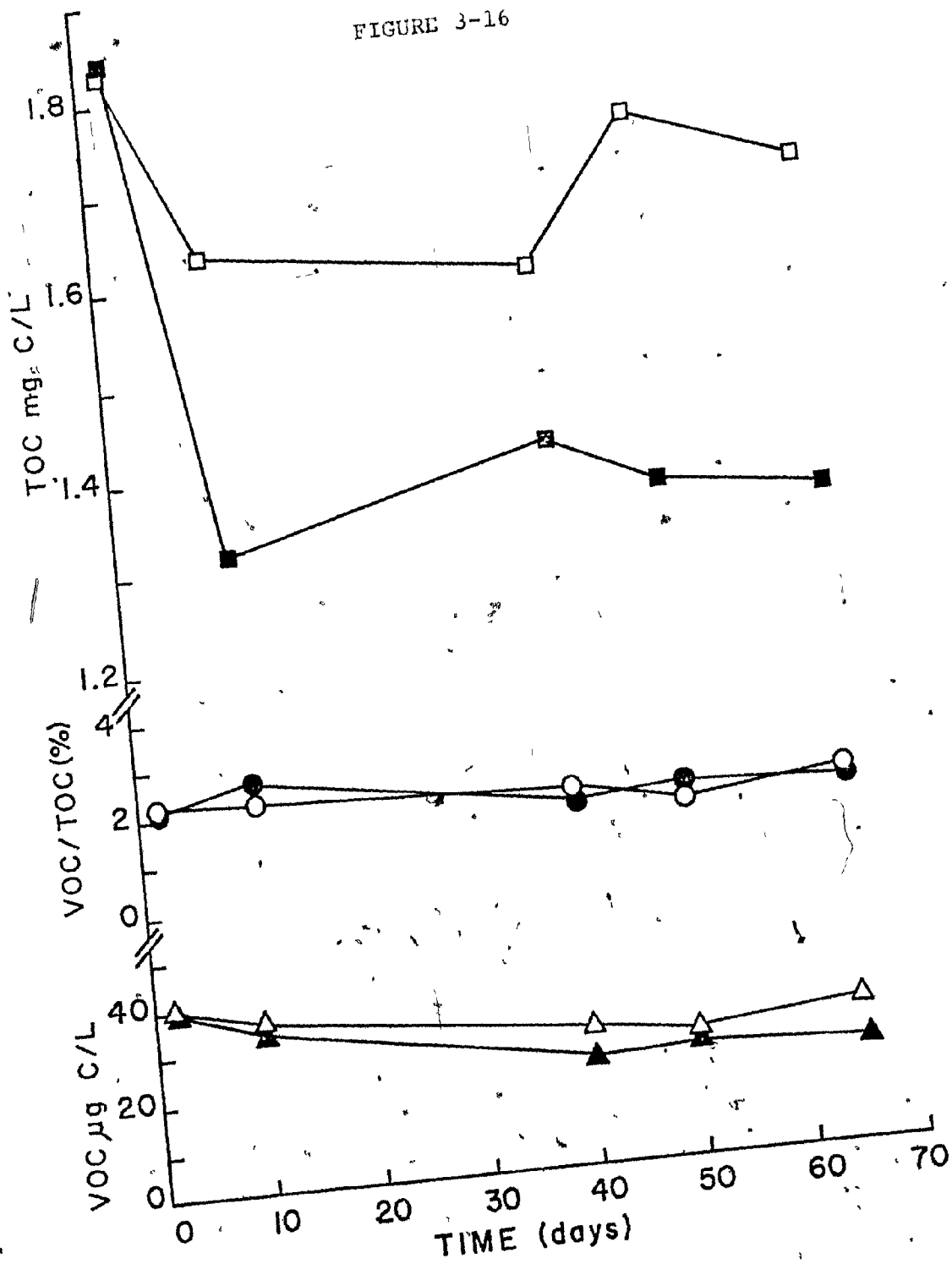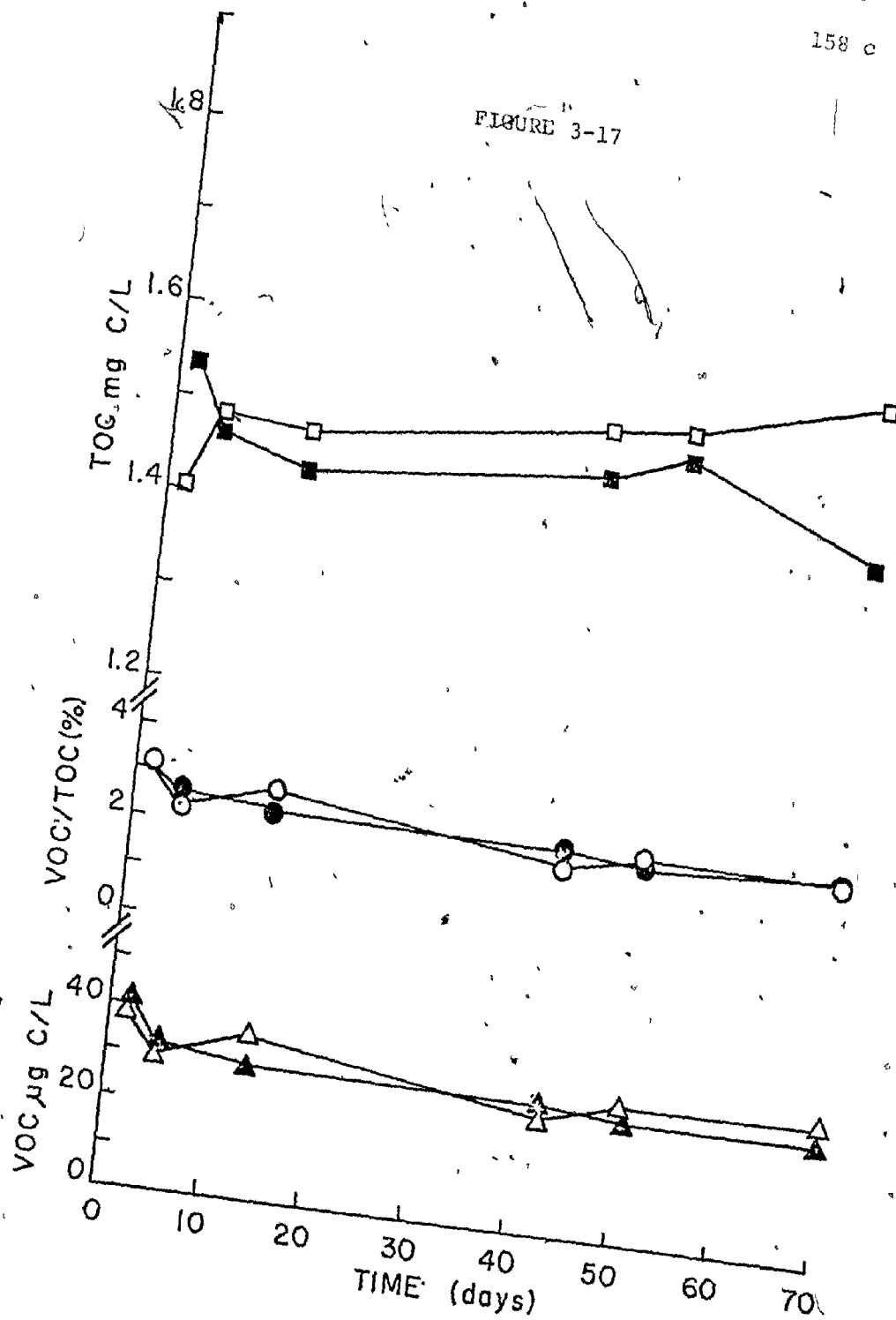
and VOC/TOC are plotted against time. A decrease with time
in the TOC concentrations in the unfixed samples from the
N.W.A. and S.M.B. was noted, but no significant decrease in
the TOC concentration in the unfixed sample from the T.S.W.
sample was seen. The TOC concentrations for the unfixed
samples from the N.W.A. were reduced by about 25% from the
start (1.70 mg.C/l) to the end (1.25 mg.C/l) of the experiment,
and in the S.M.B. samples were reduced by 27% from the start
(1.85 mg.C/l) to the end (1.35 mg.C/l), while in the T.S.W.
samples, the TOC concentrations were not significantly reduced
from the beginning (1.30 mg C/l.) to the end (1.25 mg C/l.) of
the experiment. At the same time the fixed samples ($HgCl_2$)
were analyzed for the TOC content. Little change in the
TOC concentrations was measured during the period of the
experiment. At the conclusion of the experiment, the TOC
values in the fixed samples from N.W.A. and S.M.B. were
about 25-40% higher than the unfixed samples, while the
T.S.W. samples showed little change (Table XV).

Interpretation of the changes in the VOC was not as
straightforward. The amount of change in the VOC concentration
with time in both the fixed and unfixed samples was small
(Table XV). With time, there appeared to be a slight
decrease of the VOC values in the unfixed samples, as
compared to the VOC concentrations in the fixed samples. In
the N.W.A., the averaged VOC concentration over the time of

TABLE XV

Effect of Biological Decomposition on the
Organic Matter in Natural Waters

Sample	Date	Treatment with $HgCl_2$ (3%)	V.O.C. (μg.C/l.)	T.O.C. (mg.C/l.)	VOC/TOC (%)
A.North West Arm	14/4	+	33.13	1.69	1.96
		−	27.76	1.61	1.72
	24/4	+	37.29	1.69	2.21
		−	28.77	1.31	2.20
	26/5	+	29.33	1.66	1.77
		−	29.00	1.23	2.36
	2/6	+	30.31	1.76	1.72
		−	25.51	1.21	2.11
	16/6	+	31.17	1.80	1.73
		−	25.54	1.27	2.01
	MEAN	+	32.3±3.2	1.72±.06	1.88±.21
		−	27.3±1.7	1.33±.16	2.08±.24
B.St. Margaret's Bay	13/4	+	39.83	1.83	2.18
		−	38.61	1.84	2.10
	21/4	+	35.78	1.63	2.20
		−	33.37	1.32	2.53
	21/5	+	29.20	1.59	1.84
		−	22.63	1.41	1.60
	31/5	+	26.70	1.74	1.53
		−	23.80	1.36	1.75
	15/6	+	30.50	1.68	1.82
		−	21.61	1.34	1.61
	MEAN	+	32.4±5.3	1.69±.09	1.91±.28
		−	28.0±7.6	1.45±.22	1.92±.40

C.Tap	8/4	+	37.03	1.20	3.09
Seawater		–	39.97	1.33	3.00
	11/4	+	29.17	1.28	2.28
		–	31.26	1.26	2.48
	20/4	+	34.94	1.27	2.75
		–	28.65	1.23	2.33
	19/5	+	24.98	1.31	1.91
		–	27.88	1.26	2.21
	27/5	+	29.44	1.32	2.23
		–	26.31	1.29	2.04
	14/6	+	29.90	1.37	2.18
		–	26.00	1.20	2.17
MEAN		+	30.9±4.4	1.29±.06	2.41±.4
		–	30.0±5.2	1.26±.05	2.37±.3

the experiment for the fixed samples (32.25+3.2 μg. C/l)
was 18% higher than for the unfixed samples (27.32+1.7 μg.C/l);
in the S.M.B., the fixed samples (32.4±5.3 μg.C/l) were
about 16% higher than the average for the unfixed samples
(28.0±7.6 μg.C/l), and in the ·T.S.W., the averaged VOC for
the fixed (30.91±4.4 μg.C/l) and the unfixed (30.01±5.2
μg.C/l) samples were essentially the same.

The decrease in the TOC concentration that was observed
in the S.M.B. and N.W.A. samples was rapid; most of this loss
occurred in the first 10 days, after which relatively
constant TOC values were obtained. The differences between
the absolute VOC values found during this study were not
great. The unfixed samples from the N.W.A. and S.M.B.
appeared to be 15-35% lower than the fixed samples. The
VOC/TOC ratio for the fixed and unfixed samples from the
three areas showed little change in the course of these
experiments (1.5-3.1%) and no trends were evident.

iii) Discussion and Interpretation of Results.

In the samples fixed with $HgCl_2$, biological activity
should have been prevented (Yoshinari, 1973) while biological
activity should have continued in the unfixed samples.
Since the samples were stored in the dark, primary productivity
or photochemical reactions should have been eliminated, and
the utilization of the organic material in the sample should
have been the result of bacteria and other organisms. A

drop in the TOC concentration in the unfixed samples with time was expected. If volatile compounds were produced by the utilization or decomposition of this TOC, then the VOC concentration should increase with time in the unfixed samples, while in the fixed samples, where biological activity had been retarded, only minimal variations in the VOC and TOC concentrations should be observed.

The results from this study indicated that about 25% of the organic matter in the N.W.A. and S.M.B. samples had been utilized during the 60 days, while little or no utilization of the organic matter in the T.S.W. samples was indicated. The low utilization of the TOC in the T.S.W. samples was explicable if the organic material was refractive; this would be hard to accept since the water was derived from an area rich in labile organic material. However, the water might have been sterilized during the filtration step by the removal of most of the bacteria and other organisms or by the addition of some inhibiting substance to the water. This retardation of the biological activity was a possible explanation for the small differences in the TOC concentrations observed during the duration of the experiment (1.29±.06 mg.C/l) for the fixed and unfixed samples of T.S.W. In the samples from the other areas, significant differences between the fixed and unfixed samples were measured.

In these experiments the utilization of the TOC was

shown by the loss of the TOC with time, but no build up in the VOC concentration was observed. The production of low molecular weight organics during the decomposition of the labile material in the TOC was assumed to be a major source of volatiles. However, no increase in the VOC or VOC/TOC was found, and the reasons for this must be postulated.

The extent of the biological activity was indicated by the TOC loss. If the "volatiles" were also labile, their utilization and remineralization by organisms should be expected. If the larger organic components were utilized, the low molecular weight materials should also be utilized; this would explain why the loss of the TOC but no absolute change in the VOC was observed. No buildup of VOC would be measured if the rate of production of the volatiles were balanced by its rate of utilization, so that what was measured in the analysis was the steady state or threshold concentration (below which concentration the organisms are unable to use the volatile material). Small VOC changes would be expected if the low molecular weight products of the decomposition of the TOC were not measureable by the stripping method employed in this study (either too soluble or polar, like acids or amines, to be extracted, or too volatile, like C_1-C_4 hydrocarbons, to be trapped by the traps used).

From these experiments on the decomposition of the TOC,

it was evident that the utilization and decomposition of the
TOC during storage was prevented by the use of the $HgCl_2$ to
fix the samples, since relatively little change in the TOC
with time was measured (Table-XV). Similarly, the VOC
values in the samples that were fixed with the $HgCl_2$ were
little changed with time. Therefore, the method that was
used in this study for the preservation of samples during
storage (0.5 ml. of 3% $HgCl_2$ per 500 ml. of sample which
was then frozen during storage) for the VOC analysis appeared
to be quite acceptable, and utilization and decomposition of
the organic material was minimized.

3.   Production of VOC by Photochemical Reactions
     i)   Photochemical Production of VOC in Natural Waters
     Previous workers (Creac'h, 1955, Wilson, 1970) have
indicated that photochemical reactions with organic matter
present in natural waters were capable of producing volatile
organic matter. Discussions with R. Zika (personal comm.)
led to the conclusion that low molecular weight organics
were likely products of the photochemical decomposition of
the organic matter in seawater. Whether the yield of VOC
from photochemical reactions under natural conditions was
detectable by my method was not known.
     ii)   Description of Experiments
     Several experiments were run to see if the TOC from
natural waters underwent photochemical decomposition which

led to the production of measureable "volatiles". The integrity and homogeneity of the sample were ensured and sample variations were minimized by the use of a precleaned and sterilized 5 liter Pyrex flask with a glass stopcock as the reactor. Both artificial (sunlamp) and natural light (bright sunny day on the top of the building) were used as light sources. Tap sea water and North West Arm water which had been filtered through a .22 μ Millipore filter to remove the organisms and had been buffered with a borate buffer to pH of about 8.3-8.5 (pH is critical in the photochemical reactions, Zika, 1977) were irradiated. Experiments under artificial light were run for up to 26 hours, while the natural light experiment was run for 8 hours.

Samples for VOC were collected and analyzed using the standard method. At the same time, TOC samples were collected in precleaned (450°C) 50 ml. ampoules, the pH adjusted to 2-2.5, the bottle sealed, and frozen until analyzed. A blank was obtained for the TOC and VOC by the removal of a sample aliquot before the irradiation, and after being fixed with the $HgCl_2$ it was stored until analyzed. At the beginning of an experiment a dark sample for the TOC and VOC was withdrawn, capped, and stored at room temperature in the dark for the duration of the experiment. At the end of the experiment, this dark sample

was fixed with the $HgCl_2$ and recapped until analyzed. The changes in the TOC and VOC in the dark sample were assumed to be the result of microbial action during the duration of the experiment.

iii) Results of Photochemical Reactions

In the experiments (A-D) shown in Table XVI, the changes in the VOC concentration during the irradiation were small, while larger changes were noted in the TOC concentration. The TOC values were reduced by 1-12% during the irradiation. The differences between the VOC and VOC/TOC values for the irradiated and blank samples were calculated. While the absolute differences were small, the per cent differences in the VOC and VOC/TOC were large and variable, but accounted for only a very small amount of the TOC loss. For example, when the tap sea water was irradiated with the sunlamp (Experiment #B) for 18 hours, a loss of about 0.10 mg.C./liter was noted, but the change in the VOC from the blank value was negligible. The samples in the dark bottles were examined, and little loss of TOC during the experiment was noted.

iv) Discussion and Interpretation of Results

Since the changes in the dark samples were negligible during the experiment, it was concluded that microbial action had been retarded by the filtration (.22 μ) and that the loss of TOC in the light samples during the irradiation was a photochemical rather than biological decomposition.

TABLE XVI

Photochemical Effect on the Organic Matter in Seawater

Sample	Light Source	Time of Irradiation (hr.)	V.O.C. (µg.C/l.)	% Difference From the Blank	T.O.C. (mg.C/l.)	% Difference From Blank	VOC/TOC (%)	% Difference From Blank
A. Tap Seawater	Sun Lamp	0 (Blank)	25.27		1.03		2.45	
		3.0	37.25	+47	0.96	−6.8	3.88	+56
		14.5	26.51	+5	1.06	+3.0	2.50	+2
		26.5	30.32	+20	0.93	−9.7	3.26	+33
		0 (Dark)	25.48	+1	0.99	−3.9	2.57	+5
B. Tap Seawater	Sun Lamp	0 (blank)	25.45		1.20		2.12	
		1.0	31.67	+24	1.09	−9.2	2.91	+37
		8.0	22.84	−10	1.06	−11.7	2.15	+1.4
		18.0	23.84	−6	1.10	−8.3	2.17	+2.4
		0 (Dark)	25.63	+1	1.17	−2.5	2.19	+3.3
C. Tap Seawater +0.3mgC./l. Methionine	Hg Arc Lamp	0 (Blank)	22.18		1.41		1.57	
		2.0	33.62	+52	1.40	−1.0	2.40	+53
		3.0	29.98	+35	1.41		2.12	+35
		10.0	29.19	+32	1.38	−2.0	2.12	+35
		14.0	28.85	+30	1.40	−1.0	2.06	+31
		0 (Dark)	26.29	+19	1.41	0	1.86	+18
D. North West Arm (5 m.) (8/6/76)	Natural Sun Light	0 (Blank)	19.16		1.72		1.11	
		1.0	22.23	+16	1.65	−4.0	1.35	+22
		3.5	23.56	+23	1.50	−13.0	1.57	+41
		8.0	17.71	−8	1.51	−12.0	1.12	+1
		0 (Dark)	25.60	+34	1.67	−3.0	1.53	+38

The production of low molecular weight organic materials was
expected during the photochemical decomposition of the TOC,
but their production was not measured. The products of this
decomposition did not fit my working definition of "volatile".
Some of the expected volatile products may have volatilized
or escaped from the reaction vessel during the irradiation,
but since the water temperature was controlled (reactor was
cooled in a water bath) and turbulence was prevented (no
bubble formation or shaking), the loss of the volatiles
would have to be explained by diffusion, I do not think
this was sufficient to account for the low VOC values.

In the experiments which were run no significant
increase in the VOC (except possibly in the samples with the
shortest irradiation) concentrations was found. Possible
explanations for these results include the complete remineralizati
of the TOC to CO_2 (the volatile materials may be photolabile)
or the production of non-measureable low molecular weight
materials that are not detected by my method (too volatile
or too polar). If the breakdown products of the photochemical
reaction of the TOC were not extracted by my stripping
procedure, but were lost during the evaporation step in the
dry oxidation procedure (loss of organic materials with
vapour pressure equal to or greater than that of water

during evaporation) then low TOC concentrations after irradiation with little change in the VOC would be expected.

The rate of the decomposition of the organic matter during the irradiation was rapid. Even under natural conditions of temperature and light, the TOC was reduced significantly (13% in 3 hours) to about 10-15% below the initial TOC concentration. A fraction of the TOC (10-20%) appears to be very labile to photochemical decomposition (Table XVI) and a decrease of 5-13% was noted in the TOC concentrations for the samples which had been irradiated with either the natural or artificial light. The decrease in the TOC by photochemical decomposition was calculated as the difference between the dark (microbial action) and the irradiated (photochemical and microbial action) samples. This photochemical decomposition of TOC might be important in the remineralization of the organic matter to nutrients in the euphotic zone and may provide an essential pathway in the cycling of organic matter in natural waters.

4. Qualitative Analysis of the Volatile Organic Material in Natural Waters

i) Introduction

The analysis of the specific components of the volatile organic material has become more feasible with the advent of the gas chromatography-mass spectrometer (G.C.-M.S.)

systems. For the trace organics in natural waters, the organic materials are preconcentrated by extraction or by traps and are analyzed by the GC-MS system. Most work in this area has centered on fresh or waste water systems and biological fluids (Zlatkis et al., 1972, 1973, 1974, Grob et al., 1973, 1974, 1975, Dowty et al., 1976, Hites, 1975 and Harris et al., 1974).

ii) Conditions for Analysis

Since I did not have access to a GC-MS system, the qualitative analysis was difficult to pursue. However, some preliminary analysis by GC-MS for samples from the North West Arm (August 1975) were run by P. Gschwend at W.H.O.I.

Samples were collected in Tenax G. C. traps, which were desorbed into the GC-MS system. Problems with relatively large amounts of water in the traps were overcome by a one hour desorption at room temperature with a flow of 50 ml/min. N_2 before analysis for the adsorbed organics. Since time was limited, the column used in the G. C. (6 ft. glass column, 1/4" O.D. packed with 0.4 % Carbowax 1500 on Carbosieve) was not optimized for the classes of materials that were expected, and a bias in the type of materials detected was to be expected.

iii) Results of Analysis

A separation of the organic materials adsorbed on the Tenax trap was obtained and 36 peaks were observed. The

tentative identification (P. Gschwend) on the numbered peaks from Figure 18 is shown in Table XVII. The compounds identified included aldehydes, ketones, aromatic hydrocarbons, halogenated hydrocarbons, and perhaps alcohols. Boiling points as high as 160°C were noted for the identified materials. The harsh handling of the Tenax traps required to remove the water interferences probably also led to the loss of some of the more volatile and polar materials. The choice of column packing for the separation was not optimum since the packing was designed for the separation of halogenated and aromatic compounds. The compounds detected were of intermediate polarity, and complete separation of the volatiles trapped on the Tenax was not obtained.

iv) Interpretation of Results

With this rough approach to the qualitative analysis of volatile components, an indication of the type and range of the materials from a natural system under large influence from land and urban pollution was obtained. The potential for the qualitative analysis of the organic constituents present in the volatile fraction of the organic material in seawater has been shown and future work in this area is required. Many questions of the source, role, fate, and distribution of the volatile materials in natural samples should be better answered by their qualitative analysis.

Fig. 3-18: Reconstructed G.C. chromatogram of VOC sample
collected on Tenax G.C. and desorbed. Sample was
analyzed by P. Gschwend, W.H.O.I.

G.C. conditions 0.4% Carbowax 1500 on Carbosieve
1/4" O.D. glass column, 6 ft.
Temp. program 1 min. @ 80°C
80° - 170° @ 4°C/min.

TABLE XVII

Qualitative Analysis of the Volatile Components in Samples

From the North West Arm

Peak Number	Tentative Identification	Boiling Point Of Compound (^{o}C)
4	methyl isopropyl ketone	94
7	benzene	80.1
	trichlorethylene	87
8	dibromoethylene	112.5
14	bromoform	149.5
15	4-methyl-2-pentanone	116.9
20	tetrachlorethylene	121
	2-hexanone	128
21	n-hexanal	128
22	toluene	110.6
24	mesityl oxide	129.8
31 & 32	xylene isomer	138-144
34	n-propyl benzene	159.2
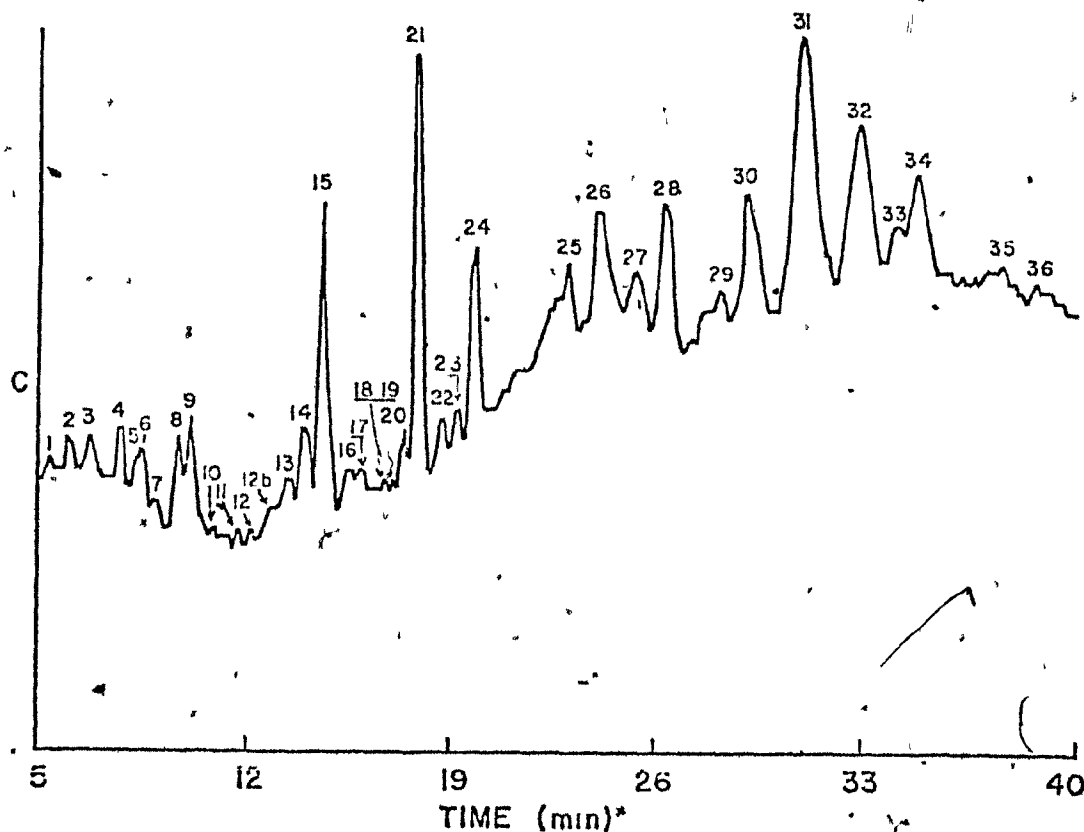
E.   Conclusion

Volatile organic compounds are defined as low molecular weight materials which are easily vapourized. They usually contain no more than 8-10 carbons and at most two functional groups. Included in this definition are the lower aliphatic and aromatic hydrocarbons, alcohols, ethers, thiols, aldehydes, ketones, acids, esters, amines, halogenated hydrocarbons, etc. In this study, the volatile organic material has been defined with a working definition as that material which is stripped from a seawater sample at an elevated temperature (80°C) and natural pH (8.1-8.3) with a flow of N_2. This extracted material is concentrated on a solid support (Tenax G.C.) and a cold trap (-78°C), which are desorbed into a high temperature oxidation furnace where the organic matter is oxidized to CO_2 and quantified with a non-dispersive infrared detector. Using standard materials, the efficiency of the method was obtained. For low molecular weight compounds with high vapour pressure and low solubility in water, the method appears to be quantitative. For organic materials of decreasing vapour pressure and increasing molecular weight, boiling point, and solubility, the extraction from natural samples becomes more difficult, is less than complete, and longer periods of extraction are required.

With my extraction procedure for VOC from natural samples, different classes of materials are removed at

different stages of the extraction. During the first stage
of extraction, the easily removed lower weight materials,
which are more volatile and less water soluble, are stripped
from the sample, while the less volatile and more water
soluble will be purged from the sample during extended
extractions. Since the more polar materials are difficult
to extract, their complete removal with the conditions used
in this study is not expected. However, a large fraction of
the material which fits the working definition for "volatile"
has been shown to be extracted in the time and under the
conditions of the described procedure. The completeness
of their removal is shown by a decrease in the rate of
extraction with extended purging.

In this study, the direct measurement and quantification
of the volatile component of the total organic matter in
seawater has been shown and a method is described for the
extraction, concentration, and analysis of the VOC. The
efficiency, precision, and accuracy of the method have been
studied and contamination problems in the analysis of the
natural samples have been minimized. Evidence of thermal or
biological decomposition of the TOC during the analysis of
VOC has not been observed. The method of extraction is long
and time consuming, but, for the first time, an estimate of
the absolute concentration of the volatile organic matter in
natural seawater samples has been calculated.

Coastal and open ocean areas have been analyzed and the ratio (VOC/TOC) of the total which is volatile was found to range between 1.5-6.5% (average about 3.5%) for all the areas and depths studied. The variations with location, depth, and biological activity are not as dramatic as expected. Only small influences and trends from coastal input or from areas of higher productivity are noted. Minor enrichment of the VOC in the surface zone is revealed in the depth profiles. Trends are even less obvious when the ratio of VOC/TOC (%) is examined. Very uniform, almost random results are obtained and a constancy of the volatile fraction is indicated. In the areas studied, little effect on the VOC concentration is evident from the impact or input by man. Better correlations with these influences (geographic, spatial, depth, time, biological activity) are found with the TOC values than are obtained from the VOC fraction.

The uniformity of the distribution of the volatile material in the different sampling areas is difficult to explain. The sources of this volatile organic matter in natural waters are biological(secretion, excretion and decomposition), chemical (photolytic, thermal), terrestial (aerosol, fluvial), and anthropogenic (shipping, urban and industrial pollution). Surface or coastal areas should have been the most influenced by these processes. While a positive correlation between the measured VOC and these

areas has been found, no significant correlation of the
ratio of VOC/TOC with these areas is shown. This constancy
of per cent (VOC/TOC) is an indication that a fairly
constant fraction of the matrix of the TOC is measured by my
extraction procedure. The composition of the organic matter
in natural waters must be fairly constant. This assumption
is supported by work which has been done with ultrafiltration
for the study of the molecular weight distribution of the
organic matter in seawater.

If the rate of consumption or removal of the volatiles
is equal to or greater than the rate of production, a
relatively constant value of VOC will be maintained. If the
low volatile concentration is maintained at a threshold
concentration at which organisms are capable of utilizing
this organic material, the absence of zero concentrations
of volatile materials in areas of expected complete utilization
can be explained. Since the formation of the volatile
matter should be mainly in the surface zone, a decrease of
VOC concentration with time of removal from the surface zone
would be expected, with the measured volatile concentrations
approaching zero if removed long enough from the areas of
main input. Complete utilization of the VOC in deep water
was not observed and the idea of a threshold concentration
is supported by this result.

The sources of this volatile material are examined in

this study and through these experiments a better under-
standing of the distributions observed in natural samples
is provided. The volatile fraction was found to vary little
during the periods of intense biological activity (spring
bloom), even though at the same time the TOC was found to be
increased by up to 50%. During microbial decomposition of
organic matter only a small change of VOC was noted, while
the TOC values were reduced by 25-30%. These experiments
were an indication that while total organic matter undergoes
dramatic changes from biological processes (primary
production, biological utilization), no large scale changes
are observed in the amount of volatile material present in
the water. This low standing value of VOC may be a steady
state or threshold concentration and the low molecular weight
organics, which are produced by organisms or by decomposition
of larger organics (biological or chemical), may have a
short lifetime in the natural system. While the production
of VOC in the photochemical decomposition of the organic
matter in seawater is predicted (R. Zika, personal comm.),
the photochemical experiments were not conclusive. While
decomposition of the TOC is indicated, a small increase
followed by decrease in the VOC fraction is observed. These
decomposition products from the photochemical decomposition
of the TOC are likely to be a complex mixture and these
materials may be unstable under conditions in which they are

produced. The products may be photolabile, non-detectable by my extraction procedure (too volatile to be trapped or too polar to be extracted), or lost by diffusion during the irradiation.

In this study, the results obtained from examination of distributions and possible sources of the volatile fraction of the total organic matter have been used to postulate the role that the volatiles play in the cycling of organic matter in seawater. Since no build up in the volatile fraction was found, a balance must exist between the rate of production and the rate of loss of this material. If this balance relationship is valid, the VOC concentration should be maintained at a steady state or threshold concentration.

Rate of Production of VOC $\leq$ Rate of Loss of VOC

VOC measured
(steady state or
threshold concentration)
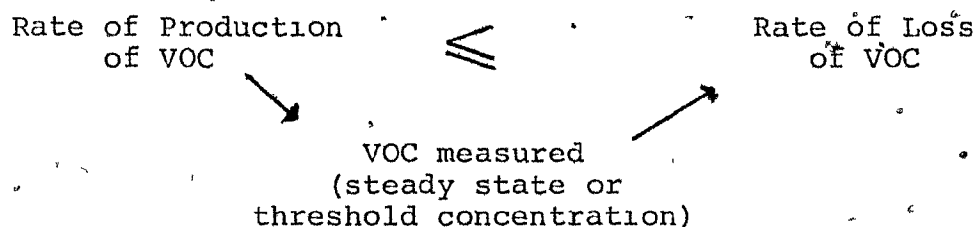
This relationship between the pools of organic matter in natural waters is shown in Figure 19. The volatiles as defined in this study (low molecular weight compounds of high vapour pressure and low solubility which are extracted by the stripping procedure) can be produced in situ or can be added to the system.

a)   Production of VOC

1)   In Situ

The production of VOC in natural waters is expected from several sources:

1.   Biological production would be expected from by-products of photosynthesis, from the excretion or secretion of volatile materials by marine plants or animals, and by the biological decomposition or utilization of particulate or larger molecular weight organic matter by bacteria, plants, or animals during heterotrophy.

2.   Chemical production would be expected from the photochemical or chemical decomposition of larger molecular weight organics.

ii)   Input from external sources.

Biological or chemical processes can lead to the production of breakdown products of the terrestial organics and these may enter the ocean through the atmosphere or through river or drainage systems. Similar pathways can be used for the introduction of urban, industrial, or agricultural wastes and man-made pollutants.

b)   Removal of VOC from Natural Waters

1.   Biological utilization or decomposition of VOC by heterotrophic utilization or remineralization.

2.   Photochemical or chemical decomposition of the volatile materials in the water. Photolability of VOC was

indicated in this study. Photochemical condensation and polymerization reactions of the volatile materials might be a mechanism for loss of volatiles by the formation of less volatile and larger molecular weight materials (DOC and POC). This type of reaction would not be expected in the bulk solution because the concentrations of the components are very low, but could possibly occur in the surface film, which is high in organic materials.

3. Physical removal of the VOC. Volatilization of materials with high vapour pressure and low solubility should occur in the seawater system by diffusion, which will be enhanced by turbulence and bubble formation. Volatiles from freshwater inputs may undergo a "salting out" effect, which would decrease the solubility of the incoming organic materials and increase their rate of vapourization. Some of the VOC should be lost by the physical or chemical adsorption of volatile compounds into particles which sink to the sediment or to an area where it can be utilized.

The cycle (Fig. 19) of volatile production and removal has been postulated to explain the results obtained in this study. Definitive answers are not possible by only quantitative methods. Qualitative analysis and tracing of specific components from the various sources should provide an idea of the cycle that these "volatile" materials follow

FIGURE 19

The Cycle of the Volatile Organic Carbon in Natural Waters

Sources
for
Production
of V.O.C.

Biological
a.) by-product of photosynthesis
b.) secretion
c.) excretion
d.) decomposition

Chemical
a.) photochemical
b.) thermal

Input from External Sources
a.) fluvial
b.) atmosphere
c.) urban, industrial, and agricutural wastes

V.O.C. Measured

Pathways
for
Loss of
V.O.C.

Biological
a.) heterotrophic utilization
b.) bacterial decomposition and remineralization

Chemical
a.) photochemical decomposition

Physical
a.) condensation or adsorption
b.) diffusion
a.) vapourization
b.) absorption on to particles
c.) bubble stripping
d.) "salting out" effects

In Situ

in the natural system. A radiocarbon tracer experiment might be used to answer some of the questions on the cycle, role, and ultimate fate of the volatile material. A culture could be grown on $C^{14}O_3=$, $HC^{14}O_3^-$, or C^{14}-labelled organic nutrients. During primary production, the amount of VOC^{14} produced as the by-products of the photosynthesis, or produced by secretion or excretion by organisms could be monitored. Decomposition experiments (biological or chemical) could be run. The organic-C^{14} could be traced and the fate of the label examined to see if the label remained in the TOC fraction or in the breakdown products of the TOC, (volatile material measured as VOC^{14}, non volatile material measured as TOC^{14} or complete remineralization to $C^{14}O_2$). The ultimate fate of the VOC^{14} could also be followed. The incorporation or utilization of the VOC by heterotrophic organisms could be studied, and the rate of remineralization by biological or chemical processes could be estimated. With an understanding of the rates of production and of loss of the volatile fraction of the TOC in natural waters, an idea of the importance which the volatile material plays in the complete cycle of organic matter in natural waters may be obtained.

While, little variability has been found in the VOC in natural seawater samples, and the source and role of the volatile fraction are still in question, the VOC may be a

very important pathway to the cycling and remineralization of the organic matter in the sea. The answer to these questions by quantification has proven inconclusive and until this fraction has been analyzed qualitatively these questions will remain unsolved. While small scale changes are noted in the absolute amount of VOC, the individual components may be much better indicators of what is happening in the real system. Changes in the specific organic compounds may correlate with areas of different productivity, light influence or local changes in the hydrographic properties. Future work should be directed to the qualitative analysis of this volatile fraction. I am sure that a better understanding of the sources and roles of the volatile organic material in natural waters will be obtained.

F.   Summary

In this study, wet and dry methods have been developed
and used for the determination of the total organic carbon
(TOC) in natural waters. The precision of both methods
was high. However, when identical or simultaneous samples
were analyzed, significantly higher TOC results were measured
with the dry oxidation method. The TOC distributions from
various areas (open ocean, coastal, and estuarine) were
obtained. Correlations of the TOC values with other hydrographic
parameters were attempted and in certain areas high correlations
were noted. While higher TOC values were measured with both
of the dry oxidation methods developed in this work, the
characteristics of the profiles were similar for both the
wet and dry methods (high in surface, decreasing to below
the euphotic zone, and relatively uniform in deep water).
The percentage differences between the methods remained
relatively constant (15-20%) with depth and area. The dry
method was considered to be a complete oxidation, so that the
lower wet oxidation results were assumed to be the result of
incomplete oxidation. The difference in TOC results from
the two oxidation procedures was small but consistent.
Thus, a fraction of the organic matrix in natural waters
appeared to be missed by the wet methods, but the profiles of
TOC distributions were comparable to dry oxidation results.

The TOC results obtained in this study were compared

with the results of other workers. The differences that were noted in various studies could be explained by problems in the handling, workup, and analysis used in different methods. I was able to overcome many of these problems and feel that my TOC results are close to the true TOC values for natural waters.

In most methods for TOC analysis, the volatile fraction (low molecular weight and boiling points, high vapour pressure) of the TOC is partially or completely lost during the removal of the inorganic carbon. Therefore, a method based on extraction, concentration, and analysis was developed for the direct measurement of the volatile organic carbon (VOC). In this study, the VOC was defined by a working definition (organic material stripped with N_2 from a heated sample at natural pH and concentrated in a trap). The extraction was effective for the more hydrophobic volatile compounds (80-100%), but was less effective for hydrophilic and polar materials (30-60%). The systems used for the concentration and detection of the volatiles were important factors in setting the limits of materials included in this working definition. For the first time, the VOC in seawater has been quantified by a direct method. Variations in VOC concentrations with geographic area, depth, seasons, and productivity in natural waters were examined. The VOC

values obtained by my method were found to be a small and relatively constant fraction of the TOC (2-6%). The VOC appeared to be maintained at a steady state or threshold concentration where the rate of production was balanced by a rate of loss. Biological, chemical, and physical processes have been postulated as controlling mechanisms in the natural system. A steady state relationship has been used by other workers to explain the TOC distribution in natural waters. A similar mechanism may help to explain the low and constant VOC values. However, for TOC a time scale on the order of weeks (surface zone) to years (deep water) is evident, while for the VOC a much faster rate of removal is required to support the observations.

It was difficult to obtain the actual dynamics of the VOC in real systems because the analytical methods involve discrete rather than real time sampling. Until a real time analysis system is developed, the rates of the processes operating in the natural cycling of organics will be difficult to quantify and understand. In this work, the TOC values correlated well with areas of high productivity, biological decomposition, geographic area, or season, while no dramatic or significant relationship with these parameters was found for the VOC values. Previous workers have shown that volatile compounds are likely products of biological production and chemical or biological decomposition. The enhancement of

the VOC fraction during experiments designed to show this was not obvious. This observation could be explained if the these low molecular weight materials are unstable (chemically, physically, or biologically) under natural conditions, so that they are lost from the system as quickly as they are produced. However, zero concentrations of the VOC in natural samples were not found. This indicated that the VOC material may be maintained at a threshold concentration below which utilization was not possible.

The fraction of the TOC that was measured as VOC was small (20-60 μg C/liter), but if a steady state relationship were maintained, the role of the VOC in the cycling of organic matter in seawater may be important. However, until analytical methods of VOC analysis have been refined, the significance of this material in the real system will not be completely understood.

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CRUISE Bar. o...
DATE 1/2/75 - 11/2/75
STATION 1, 27°47.?'N, 62°41.8'W

Depth (m)	Salinity (o/oo)	D O Diff.method #1 (mg C/liter)	V O C (mg C/liter)	VOC 100
1	36 5	1 1?	2? 04	2 37
10	36 5?	1 ?2	1? 82	1 ?4
25	36 5?	1 0?	3? 10	? ?0
5?	3? ?	0 ??		
100	3? 5	0 ?6	32 96	3.43
200	36 2?	0.75	31 82	4 24
300	36 2	0 88	2? 38	3 00
500	36 0	0 ??		
? 0	35 7	0 74	33 28	4 50
1000	35 5	0 78+ 03	2? 10	3 6?

STATION 2, 26°0?'?, 62°45'W

1	36 ?	1 ?12	27 66	2 47
10	36 6	1 ?	24 ?4	2 44
25	36 5	0 99	?4 22	? 45
5?	3? 5	0 91	22 36	2 4?
100	36 5	0 ?1	21 50	? 69
110	36 5	0 ?2		
1?0	?6 5	0 83		
150	36 4	0 79	20 18	? 40
17?	?6 4	0 88		
1?0	36 3	0 ?3		
200	36 0	0 81	21 54	2 66
?00	35 8	0 82	23 ?8	2 92
?10	35 8	0 ?8		
330	35 7	0 ?0		
350	35 7	0 ?6		
370	35 5	0 73		
390	35 4	0 8?		
400	35 5	0 ?2	23 82	3 84
500	35 5	0 74	20 42	2 76
600	35 4	0.87	24 82	2.85
700	35 4	0 83	22 16	2 67
710	35 4	0 71		
730	35 4	0 67		
750	35 4	0 ?0		
770	35 3	0 ?5		
790	35 3	0 76		
8?0	35 4	0 74		
900	35 4	0 ?0	21 48	3 07
985	35 3	0 ?6		
990	35 3	0 64		
995	35 3	0 ??		
1000	35 3	0 70		
11?0	35 2?	0 7?	25 44	3 39
1?00	35 1	0 ?4		
13?0	35 1	0 6?	21 44	3.15
14??	35 1	0 6?		
14?0	35 1?	0 ??		
14 0	35 1?	0 ??		
1500	3? 0	0.70	?2 06	3 11
1?20	35 0	0 6?		
1?10	35 0	0 ?4		
1600	35 0	0 74		
17?0	35 0	0 ?	25 52	3 54
1??0	35 0	0 74		
1?? 0	3? 0	0 7?	?? ?	? ?
20?0	35 0	0 7?+ 04		
21?0	3? 0	0?1		
2200	35 0	0 71		
2?00	3? 0	0 71	24 ?4	3 51
2400	35 0	0 7?		
2?00	35 0	0 72	24 82	3 45
2?00	35 ?	0 ??		
2??0	35 0	0 71	27 ?4	3 8?

3100	35 0	0 68		
3300	3 0	0 74	25 00	3 38
3500 0	35 0	0 74		
3700	35 0	0 70	25.10	3 66
3900	35 0	0 72		
4100	35 0	0 70	25 76	3.68
4300	35 0	0 f		
4500	35 0	0 72 01	27 00	3 75

STATIC   3, 29°30'N, 62 15'N

1	36 0	0 10	4 26	5.48
10	6 0	05	11	4 11
25	26 0	95	29 81	3 11
50	36 03	0 17	31 86	4 63
100	36 55	0 84	31 08	3 70
150	36 47	0 87	4 84	5 20
200	8 14	0 76	23 14	3 30
250	6 42	0 65	3 20	5 11

STATION   4, 32°50'N, 6 30'N

1	36 43	1 06	46 98	4 43
10	36 5	0 93	52 41	5 30
25	36 44	0 93	27 04	2 90
50	36 46	0 97	27 06	2 80
100	36 49	1.00	19 82	1 86
200	36 43	0 76	25 28	2 81
300	36 49	0 83		
400 P	36 43	0 76	21 10	2 80
500	36 34	0 73		
600	36 10	0 78	21 08	2 70
800	35 35	0 73	20 22	2 80
1000	35 04	0 70	23.20	3 30
1250	35 20	0 86		
1500	35 19	0 78	19.18	2 46
1750	35 20	0 73		
2000	34 95	0 77	23 00	2 99
2500	34 97	0 71		
3000	34 97	0 71	21.98	3 10
3500	34 95	0 75		
4000	34 89	0.74		

STATION   5, 35°00'N, 62°28'N

1	36 47	1.00	30 10	3 01
10	36 47	0 92	23 86	2 60
25	36 47	0 91	28 96	3.20
50	36 44	0 94	32 24	3 43
100	36 45	0 82	28 58	3 48
200	36 44	0 87	34 04	3 92
400	36 43	0 76	29 80	3 92
600	36 40	0 75	30 72	4 10
1000	35 05	0 74	34 72	4 60

STATIO   6, 36°00'N, 62°30'W

1	36 45	0 83	32 58	3 93
10	36 46	0 87	37 40	4 30
25	36 47	0 90	34 02	3 80
50	36 47	0 84	31 90	3 80
100	36 48	0 87	5 08	4 03
150	36 46	0 99	27 08	3 01
250	36 44	0 73	19 60	2 70

STATION   7, 38°00'N, 62°45'W

1	36 41	0 82	24 54	2.80
15	36 40	0 34	23 20	3 50
25	36 44	0 92	27 16	2 98
50	36 49	0 99	37 88	3 83
100	36 41	0 87	30 50	3 51
150	36 41	0 91	29 24	3 21
200	36 45	0.86	30 60	3 56
250	36 50	0 76	25 62	3 28

```
STATION  8, 38°59'N, 62°46'W

    1      35 92      0 74           28 24           3 00
   10      35 89      0 87           27.34           3 14
   25      35 7       0 94           3t 18           3 80
   50      35 77      0  0           32 04           4.00
  100      35 74      0 64           32 98           3 90
  200      35 39      0 90           27 90           3 10
  400      35 40      0 64           27 36           4 30
  600      35 66      0 76           26 66           3 50
 1000      31 97      0 61

STATION  9, 40 00'N, 47°52'W

    1      35 68      0 90           23 20           2 60
   10      35 88      0 91           25 84           2 84
   25      35 97      0 90           19 32           2 15
   50      35 67      0 91           24 62           2 73
  100      35 66      0 30           22 78           2 48
  150      35 70      0 74           24 14           3 30
  200      35 53      0 77           22 68           2 87
  250      35 50      0 61           20 30           2 51

STATION  10, 43°01'N, 49°05'W

    1      32 67      0 97           26 32           2.71
   10      32 67      1 12           32 76           2 93
   25      32 67      1 03           25 30           2 46
   50      33 20      1 09           25 00           2 29
  100      33 90      0 82           32 88           4 01
  200      35 24      0 68           21 94           3 23
  400      35 94      0 75           22 56           3 01
  600      34 91      0 61           26 44           3 26
 1000      34 95      0 75           30 10           4 01

STATION  11, 43°20'N, 63°13 3'W

    1      32 07      0 97           20 80           2 14
   10      32 04      1 00           20 90           2 09
   25      32 04      1 03           20 72           3 01
   50      32.34      0.96           22 34           2 33
```

LIST I Station Hole ...
DATE 6/74
STATION 6, 42°51'N, 61°44'W

Depth (m)	Salinity o/oo	TOC (ug C/liter) Dry Method #1	Dry Method #2	Wet Oxidation	VTOC (ug C/liter)	TOC (%)
1	35 05	1 32				
23	35 75	0 95				
50	35 05	0 97± 05				
75	35 25	0 93± 02				
150	35 43	0 82				
200	35 57	0				
300	35 33	0 71				
400	35 20	0 90				
600	35 20	0 74				
800	35 15	0 60± 07				
900	35 15	0.68				

STATION 7, 42°33'N, 61°24'W

Depth	Salinity	#1	#2	Ox	VTOC	TOC %
1	34 50	1 21			40 14	3 30
6	34 55	1 24± 08			41 10	3 81
14	34 58	1 15			39 86	3 47
18	34 93	1 04			45 80	4 40
25	35 15	1 02			42 72	4 19
50	35 3	0 93			25 30	2.72
75	35 36	0 93± 04				
100	35 38	0 58± 05				
150	35,52	0 77			32 16	4 18
200	35 43	0 91			33 68	3 70
250	35 45	0 74			31·96	4 32
300	35 40	0 69			24 36	3 53
400	35 40	0 73			30 02	4.11
500	35 30	0 72± 04			35.86	4 98
600	35 30	0 73			38.30	5 18
700	35 25	0 74				
900	35 20	0 72± 04			34 30	4 76
1000	35 15	0 84				
1200	35 15	0 74				
1400	35 15	0 73± 05				
1600	35 10	0 73				
1800	35 10	0 73				
2000	35 10	0 82				

CRUISE Scotian Shelf # IV
DATE 8/75
STATION 1, 44°24'N, 63°28'W

Depth	Salinity	#1	#2	Ox	VTOC	TOC %
1	31 22	1 45	1 68± 08	1 24± 01	41 80	2 88
10	31 24	1 31	1 46± 05	1 21± 04	46 36	3 54
25	31 22	1 35	1 25± 03	1,02± 02	49 96	3,71
50	31,73	1 08	0 99± 08	0 95± 08	66 60	6 17
75	32 21	1 02	1 06± 11	0 99± 04	37,70	3 70

STATION 2, 44°16'N, 63°19'W

Depth	Salinity	#1	#2	Ox	VTOC	TOC %
1	30 92	1 40	1 47± 05	1 25± 03	44 14	3 15
10	30 97	1 41	1 31± 02	1 20± 04	43 26	3 07
25	31 04	1 16	1.12	1 12± 08	42 26	3 64
50	31 84	1 05		1 17± 01	37 08	3 59
75	32 06	1 07	0 89	0 87±.03	42 48	3.97
100	33 05	0 97	1 02± 04	0 97	39 56	4 07

STATION 3, 44°57'N, 62°53'W

Depth	Salinity	#1	#2	Ox	VTOC	TOC %
1	31 59	1.14	1 34± 10	1 06	58 40	5.12
5	31 55	1 21				
11	31 52	1 36	1 39± 08	1 05± 04	49 62	3 65
15	31 78	1 17				
25	32 72	1 16	1 22± 02	1 60		
50	34 26	1 05	0 96± 07	0 99± 11	46 64	4 43
100	34 78	0 84	0 90± 03	0 73± 01		

150 34 97	0 91				5 04	3 85
200 34 95	0 86	0 74+ 10	0 73± 01	38.08		4.43
250 35 04	0 78	0 79± 08	0 70			

STATION 4, 43°29'N, 65°27'W

1 31 78	1 03	1 34± 03	0 94+ 03	60 60	5 88
10 31 78	1 95	1 21+ 04	1 02 1	45 00	3 40
25 31 91	1 03	1 1	0 04+ 03	53 00	5 15
50 33 18	0 99	0 94± 12	0 7 ± 01	48 52	6 92
75 33 62	1 00	0 86± 08	0 7 + 04	61 94	6.19

STATION 5, 48°11'N, 62°06"

1 31 43	1 20	1 26 0	0 97+ 03	31 54	2 60
10 32 00	1 12	1 11 ± 08	0 9 + 04	30 44	2 72
25 32 47	1 26	1 24± 06	0 96± 01	34 44	2 73
50 32 93	0 93	0 99± 07	0 81± 04	34 46	3.38
75 33 57	0 96	0 88± 11	0 71±03	43 28	4 51

STATION 6, 42°50'N, 61°44'W

1 31 57	1 26	1 25± 06	0 59+ 02	33 50	2 70
4 31 65		1 25+ 0	1 07+ 06		
10 31 3	1 29	1 9± 06	1 01± 06	44 34	3 44
17 32.20	1 15		1 0		
25 32 84	1 30	1 19± 11	0 91± 02	24 04	1 85
50 33.77	1 36	1 06± 00	0 7 86	24 34	1 76
75 33 76	0 93	0 90± 01	0 68+ 07		
100 34 36	1 09	0 86+ 07	0 67± 08	37 78	3.47
150 34 71	0 96	0 81	0 03± 04		
200 3 81	0 81	0 79± 03	0 6 ± 01	28 30	3.49
250 34.81		0 75	0 60± 02		
300 34 86		0.71±.08	0 64± 05	31 98	4.50
400 34.96		0 60±.09	0 56± 02	34.66	5 78
500 34 88		0 73±.10	0 66	27 00	3 50

STATION 7, 42°32'N, 61°24'W

1 34 16	1 26	1 25±.08	0 98± 02	52 72	4.18
4 34 19	1 07		0.95± 07		
11 35 33	1 08	1.24± 12	0 90± 03	25 34	2.35
15 35 40	1 20		0 96± 05		
23 35 38	1 02	1.22± 03	0 86± 01	31 56	3 09
30 35 40			0 84± 01		
50 35 40	1.05	1 13± 07	0 92± 04	26 24	2 50
75 35 86					
100 35 77	0 78	0 89± 10	0 68± 04	34 76	4 46
150 35 52		0 86			
200 35 35	0 74	0 87+ 04	0 66± 04	34 38	4 65
250 35 19					
300 35 12		0 78± 08			
400 35 10	0 72	0 68± 04	0 63± 06	24 98	3 47
600 35 10	0 61	0 73	0 67± 02		
800 35 05	0 71	0 80± 01	0 65+ 04		
1000 35 05	0 68	0 73± 10	0 73± 02	26 98	3 97
1200 35 02	0 72	0 83± 04	0 66± 07		
1400 34 99	0 69	0 77± 06	0 64± 03		
1600 35 00	0 63	0 78± 08	0 64± 01		
1800 35 02	0 69	0 63± 12	0 61± 01	23 16	3 36
2000 35 00	0 77	0 71+ 01	0 65± 08		
2200 35 01	0 75	0 76± 06	0 67	29 68	3 96

CRUISE Scotian Shelf V

DATE 3/76

STATION 1, 44°24'N, 63°28'W

1 31 34	1 17			34 38	2 94
10 31 33	1 11				
25 31.35	1.27			44 98	3 54
40 31 70	1 11				

STATION 2, 44°16'N, 63°19'W

1	31 14	1 28		28 60	2 23
25	31 98	1 03		27 18	2 64
50	32 16	1 06		30 80	2 91
100	33 74	0 93		30 56	3.68

STATION 3, 43°53'N, 62°53'W

1	31 88	1 16		37 56	3 25
10	31 90	1 12			
25	31 03	1 04		35 00	3 46
50	33 14	1 15		36 00	3 13
100	34 56	0 87		41 00	4 70
200	34 99	0 69			

STATION 4, 43°29'N, 62°27'W

1	32 12	1 07		35 22	3 29
10	32 12	0 85			
25	32 12	1 07		39 98	3 74
50	32 40	0.99		33 78	3 41

STATION 5, 43°11'N, 62°06'W

1	31 96	1 01		40 22	3 98
25	33 11	1 10		32 08	2 92
50	34 95	1 00		33 00	3 30
150	34 99	0 66		40 00	4 65
300	35 06	0 87		38 28	4 40
400	35 07	0 81		31 10	3 84

STATION 6, 42°51'N, 61°44'W

1	31 96	1 11		45 64	4 11
50	34 95	1,07		38 06	3 59
100	35 00	0 86		40 32	4 69
200	35 10	0 84		36 68	4.37
500	35 10	0 76		46.38	6 10

CRUISE Gulf of St Lawrence
DATE 27/5/75- 8/6/75
STATION 1, 45°04 6'N, 61°10 5'W

Depth (m)	Salinity o/oo	Sigma-t g /cc	T O C (mg C/liter)		
			Wet Oxidation	Dry Method #1	Dry Method #2
1	30 07	23 77	1 31	1 73	1 39
10	30.05	23 97	1 27±.03	1 51	1 34
20	30 32	24 20	1 17	1 42	
50	31 22	25 10	1 14± 13	1 23	
76	31 81	25 54	1 20	1.33	1 08

STATION 2, 47°23 2'N, 59°50 2'W

1	31 26	24 26	1 28± 09	1 38	
50	31 92	25 86	1 19	1.16	
150	33 44	26 75	0 98± 11	1 02	
200	34 01	27 00	1 02± 08	1 07	
450	34 86	27 59	0 75	0 87	

STATION 3, 48°27 4'N, 58°35 5'W

1	29 84	23 56	1 23	1 33	1 68
10	30 98	24 79	1 02		1 32
50	31 78	25 56	1 02	1 18	1 19
75	31 83	25 60	1 17	1 26	

STATION 4, 49°10 3'N, 58°16 2'W

1	27 31	21 60	1 34	1 70	1 73± 05
10	30 41	24 70	1.16±.08	1 24	
50	31 74	25 55	1 05± 12	1 27	1 26
200	32 09	25 79	0 78± 01		0 79± 05

STATION 5, 49°11 9'', 58°06 8'W

1	27 87	22 13	1 38±.01	1.56± 02
10	30 90	24 73	0 94± 01	1 12± 15
52	31 83	25 54	0 91± 01	1 03± 12
156	32 06	25 7	0 62± 05	1 03± 12

STATION 6, 49°00'., 58°05 1'W

1	26 32	20 72	I 85± 11	2 20± 10
10	30 91	24 80	1 00± 07	1 42± 14
51	31 80	25 56	0 92± 0	0 97± 10
77	31 90	25 64	0.94± 04	1.01± 08

STATION 7, 48°58 1'N, 57°57 5'W

1	28 11	22 21	1 44	1 69
10	31 00	24 91	1 03	1 04
52	31.80	25 56	0 96	1 04± 07
78	31 91	25.66	1 10	1 27± 12

STATION 8, 49°10'N, 59°58 3'W

1	31 15	24 54	1 06± 03	1 45	1 19± 11
10	31 15	24 85	1 10± 06	1 43	
50	31 91	25 67		1 13	
151	33 51	26 78		1 30	0 97
252	34 51	27 26	0 65± 06	0 80	

STATION 9, 48°58 6'N, 62°04'W

1	31 13	24 66	1 54	1 50
11	31 47	25 14	1 14	1 32± 16
54	31 85	25 17	1 03	1 14±.10
81	32 22	25 92	1.02	1 19

STATION 10, 49°04 9't, 63°29 9'W

1	28.67	22 54	1 70	1 46	1 86
10	30 86	24 55	1 28	1 23	1 24
51	32 52	26 14	1 00	1 07	1 02
102	33 22	26 62	0 88± 11	1 02	
203	34 12	27 11	0 70	0 92	0 99
355	34 77	27 47	0 88	0 76	0 94

STATION 11, 49°02 1'N, 63°56'W

1	29 09	23 46	1 28± 02	1 45	1 57± 18
10	31 18	24 96	1 11± 03	1 34	1 30
59	32 47	26 10	0 91± 02	1 05	0 95±.10
151	33 72	26 94	0 73± 02	0 96	0 78
302	34 59	27 38	0 91	1 03	0 90± 10

STATION 12, 49°59 8'N, 61°42'W

1	27 75	21 79	1 59	1 51	1 80
10	31 32	24 93	1 16	1 07	1 35
51	31 85	25 61	1 08	1 03	1 09
154	33 07	26 52	0 95	0 95	0 92

STATION 13, 43°59 8'N, 65°36 0'W

1	31 17	24 55	0.96± 09	1 24	1 03
51	31 29	26 31	0 92	0 96	1 13
152	33 9₂	27 02	0 71± 03	0 98	
305	34 49	27 32	0 66± 04	0 76	0 68

STATION 14, 48°40 5'N, 68°42 2'W

1	26 11	20 41	1 92	2 04	2 06
10	27 54	21 77	1 65± 06	1 76	
50	31 16	25 03	1 15	1 38	1 32
151	33 55	26 82	1 17± 16		
301	34 31	27 23	0 83	0 98	0 92

STATION 15, 49°13 8'N, 66°09'W

1	26 59	20 67	1 67	1 65	1 75
10	26 71	21 26	1 51		
51	31 00		0 98	1 23	1 14± 04
103	32.95	26 44	0 88	1 06	0 93

STATION 16, 49°16 1'N, 65°06 8'W

1	27 89	21 92	1 43± 08	1 65	1 59± 15
10	28 30	22 64	1 40± 08	1 14	1 40
52	31 49	25 29	1 00± 05	1 16	1 14± 03
104	32 77	26 32	0 84± 09	0 95	1 01
125	33 08	26 53	0 88± 08	0 99	0 63± 11

STATION 17, 47°21 8'N, 63°19 5'W

1	30 27	23 52	1 08± 10	1 22	1 18
10	30 56	24 14	1 07± 06	1 19	
52	31.29	25 18	0 87± 05	1 07	1 08± 10

CRUISE Gulf of St Lawrence
DATE 17/11/75- 28/11/75
STATION 1, 47°07'N, 60°09'W

Depth (m)	Salinity o/oo	Sigma-t g /cc	TOC (mg C /liter) Dry Method #1	TOC (mg C /liter) Dry Method #2	V O C. (ug C/liter)	VOC TOC (%)
1	31 03	24.66	1 07	1 15± 16	51 74	4 84
10	31 03		1 28	1 26± 10	36 08	2 35
25	31 08		1 28	1 29±.02	47 02	3 67
50	32 04		1 09	1 11± 06	30 16	2 77
100	32 79	26 31	1 03	1 04± 08	30 36	2 95
145	33 21	26 59	0 65	0 78± 10	32 04	3 24
200	33 95	26 97	1 27	1 05± 08	32 60	2 57

STATION 2, 47°34 8'N, 59°20 3'W

1	32 28	25 72	1 22	1 26± 09	35 40	2 90
10	32 28	25 73	1 11	1 42± 09	34 02	2 98
25	32 28	25 74	1 29	1 30± 08	38 57	2 99
50	32 52	26 01	1 13		27 26	2 02
101	33 03	26 85	1 03	1 10± 07	43 58	4 23
146	34 34	27 14		0 97± 10	37 40	3 22
196	34 50	27 19	0 61	0 86± 10	24 50	3 02
227	34 39	27 39	0 68	0 76± 08	24 42	2 66

STATION 3, 51°28'N, 56°48'W

1	31.64	25 37	1 10	1 19±.10	28 30	2.57

STATION 4, 49°34.1'N, 66°18 2'W

1	31 49	25 22	1 11	1 11± 04	29 64	2.67
10	31 48	25 21	1 26	1 28± 10	27 50	2 18
25	31 51	25 25	1 26	0 96±°04	35 24	2 80
51	32 59	26 18	1 22	1 73± 06	30 06	2 46
101	33 39	26 73	1 28	1 16± 07	27 54	2 15
152	33 78	26 91	1 15	1 16± 13		
203	34 13	27 12	0 f8	0 78± 10	35 12	4 05
253	34 43	27 26	1 03	0 93± 10	22 76	2 21

STATION 5, 49°11 '' ,66°18 1'W

1	28 75	23 04	1 23	1 35	21 70	1 76
10	28 76	23 05	1 25	1 30± 02	28 22	2 26
30	31 10	24 85	1 23	1 07± 05	42 90	2 49
61	32 36	25 98	1 11	1 07± 08	32 70	2 90
101	32 91	26 43	0 95	0 91± 4	29 06	3 06
152	33 65	26 87	0 96	0 86± 07	38 78	4 04
177	33 88	27 00	0 94	0 63± 03	24 70	2.63

CRUISE Cff\Coast of Senegal

DATE 2/76-3/76

STATION 1, 14°59'' ,20°16'W

Depth (m.)	Salinity o/oo	Sigma-t g /cc	TOC (mg C/liter)		Dissolved Oxygen (ml /liter)
			Wet Oxidation	Dry Method #1	
1	35 29	24 89	1 16± 02	1.30	5 20
10	35 59	25 08	1 12± 02	1 29	5 20
24	35 63	25 12	1 05± 04	1 29	5 16
49	35 74	25 29	1 05± 07	1 22	5 02
97	35.43	26 75	0 97± 02	1 03	1.54
146	35 36	26 70	0 73± 07	0 87	1 64
244	35 32	26 81	0 75± 02	0.82	1 79
292	35 30	26 90		0 81	1 72
418	35 19	27 01	0 67± 03	0 73	1 48
518	35 13	27 14		0 88	1 25
618	35 02	27 24	0 84± 02	0 87	1 45
1016	34.91	27 48	0 66± 01	0 69	2 96

STATION 2, 15°11'N, 17°13'W

1	35 67	26 04	1 24± 08	1 40	4 55
25	35 59	26 17	1 06± 04	1 32	4 19
49	35 54	26 30	0 97± 04	1 01	3 09
148	35 35	26 71	0 73	0 80	1 59

STATION 3, 15°21'N, 20°41'W

1	35 73	25 19	1 15± 11	1 51	5 17
10	35 74	25 20	1 33± 01	1 66	5 17
24	35 74	25 20	1 14± 04	1 45	5 15
48	35 74	25 21	1 00	1 34	5 14
96	35 41	26 54	0 65± 03	0 78	1 54
144	35 35	26 75	0 70± 05	0 76	1 89
191	35 35	26 84	0 8 ± 04		1 80
239	35 30	26 90	0 60± 03	0 80	1 78
300	35 26	26 97	0 53± 03	0 78	1 51
500	35 11	27 16	0 60	0 72	1 28
592	35 03	27 23	0 59± 04	0 73	1 32
789	34 90	27 37	0		2 02
986	34 89	27 50	0 69± 03		2 84

STATION· 4, 15°37'N, 17°44'W

1	35 82	25.02	1 17± 01	1.34	5 28
12	35 82	25 02		1 24	5 26
25	35 82	25 63	1 02± 04	1 24	5 28
49	35 72	26 16	0 72± 05	0 95	2 70
98	35 51	26 61	0 84±.10	0 69	1 64
147	35 41	26 72	− 0 84	0 92	1 66
196	35 39	26 80		0 82	1 62
295	35 30	26 92	0 82± 08	0 84	1 59

STATION· 5, 18°00'N, 19°59'W

1	35 85	25 24	1 09± 04	1.33	5 10
12	35 85	25 24	1 01± 02	1 32	5 10
25	35 85	25 24	1 28	1.19	5 14
50	35 89	25 37	1 16± 10	1 22	5 06
99	35 84	26 61	1 26± 3	1.22	1 78
138	35 64	26 83	0 76± 01	0 77	1 72
297	35 38	26 96	0 72	0 87	1 38
396	35 23	27 07	0 67± 01	0 87	1 16
441	35 10	27 15	0 76± 02	0 82	1 39
786	34 94	27 40	0 68	0.86	2 19
942	34 94	27 52	0 62±.05	0 79	2 97

STATION· 6, 16°23'N, 18°30'W

1	35 78	25 48	1 05± 03	1 27	5 25
26	35.78	25 48	0 94± 05	1 26	5 24
50	35 78	25 48	1 07± 03	1 34	5 28
75	35 67	25 81	0 75± 05	0.95	3 00
100	35 64	26 10	0 78± 03	1 03	3 79
125	35 53	26 42	0 89± 05	0 87	1 93
150	35 46	26 57	0 57± 02	0 82	1 37
200	35 45	26 81	0 87± 09	0 85	1 69
250	35 43	26 82	0 74± 03	0 81	1 37
300	35 39	26 92	0 71± 06	0 79	1 28
399	35 23	27 03	0.81	0 87	1 17
499	35 15	27 14	0 61± 03	0 78	1 09
600	35 06	27 22	0 56± 03	0 82	1 32
797	35 28	27 39	0 63± 06	0 86	1 50
995	34 90	27 50	0 62± 04	0 86	2 77
1192	34 98	27 64	0 60± 03	0 75	3 56

STATION· 7, 16°59'N, 20°02'W

1	35 92	25 44	1 38± 10	1.41	5 28
49	36 16	25 66	1 16± 09	1 10	5 05
97	36 09	26 43	0 97± 02	0 92	2 32
146	35 88	26.70	0 81	0 77	2 21
291	35 47	26.94	0 88± 02	0 82	1 50
388	35 25	27 06	0 77± 01	0 82	1 16
486	35 11	27 16	0 67± 08	0 74	1 26
569	35 04	27 23	0 65	0 60	1.52
936	34 95	27 51	0 59± 01	0 78	2 76
1395	35 01	27 75	0 61± 03	0 70	4 28

STATION 8, 14°50'N, 17°55'W

1	35 55	25 78	1 52± 08	1.67	
50	35 51	26 49	0.82	0.85	
100	35 40	26 58	0 84± 05	0 87	1 52
220	35 35	26.80		0 86	1 49
270	35 34	26 87	0 78± 03	0.92	1 37
320	35 32	26 94	0 71± 03	0 75	1 29
419	35 19	27 06	0 87± 02	0 93	1 11
519	35 12	27 17	0 65± 06	0 75	1 12
606	35.03	27 24	0 65± 03	0 78	1 31
801	34 83	27 39	0 67± 05	0 74	2 13
997	34 84	27 50	0 69± 07	0 76	2.79
1192	34 91	27 63	0.58	0 66	3 56

STATION 9, 14°04'N, 21°45'W

1	35 86	24 98	1 48± 28	1 50	5 04
49	35 80	25 52	1 17± 15	1.02	3 04
618	34 06	27 9		0.69	2 16
1017	34 81	27 53		0.72	2 97
1516	35 00	27 5	0 68± 05	0 4	4 70

STATION 10, 11°39'N, 21°10'W

1	35 55	24 64		1 27	5 00
50	35 61	26 17		0 86	2 23
99	35 2	26 51		0 74	1 94
298	35 10	26 81		0 81	2 16
400	34 97	26 97		0 76	1 46
496	35 10	27 10		0 65	1 05
802	34 79	27 38		0 83	2 06
1496	34 95	27 77		0 70	4 76
1991	34 37	27 82		0 70	5 44
2479	34 95	27 88		0.66	5 57

STATION 11, 13°41'N, 22°11'

1	35 83	24 64		1 32	5 13
25	35 84	24 74		1 20	4 31
74	35 70	26 26		0 96	1 82
123	35 42	26 69		0 97	1.87
245	35 11	26 89		0 88	1 75
294	35 11	26 94		0 84	1 53
499	35 06	27 15		0.85	1 22

CPUISE Sarg.. o Sea

DATE 15/10/74- 23/10/74

STATION 1, 42°16'N, 61°30 5'W

Depth (m)	Salinity o/oo	T O C (mg C/liter) Dry Method # 1	V O C (ug C/liter)	VOC/TOC (%)
1	33 84	1 03	26 04	2 53
10	33 89	1 10	24 24	2 20
25	34 07	1 08	18 76	1 74
50	34 44	0.97	27 68	2 85
100	35 67	0 80	17 00	2 13
200	35 64	0 76± 08	28 56	3 76
400	35 12	0 69	32.90	4 77
600	34 95	0 66	21 16	3 21
800	34 96	0 77	26.14	3 39
975	34 97	0 77	28 34	3 68
1500	34 95	0 66	28.56	4 33
1800	34 98	0.74	22 38	3 02

STATION 2, 37°10'N,63°15 5'W

1	35 53	1 03	31.62	3 06
10	35 57	1 04	42 92	4 13
25	35 16	1 14	36 06	3 16
50	35 66	1 00	52 16	5 22
100	35 95	1 02	20 54	2 01
150	35 91	0 91	18 84	2 07
200	35 91	0 73	32 56	4 46

STATION 3, 36°35 2'N, 63°17

1	36 16	1 02± 02	17 64	1 73
10	36 19	1 17	23 16	2 04
25	36 16	1.21± 05	24 78	2 05
50	36 21	1 07	18 32	1 71
100	36 43	1 08	22 56	2 09

150	36.50	1 07± 07		
200	36 .7	1 06	21 76	2 05
250	36 45	0 94		
300	36 11	0 96± 06	19 36	2 02
400	36 27	0 73		
500	36 10	0 71± 06		
600	35 98	0 73	32 86	4 40
700	35 81	0 75		
800	35 20	0 75		
900	35 09	0 60		
1000	35 05	0 67	23 18	3 10
1100	35 01	0 67		
1200	35 00	0 65	21 16	3 30
1400	35 04	0 67		
1600	35 01	0 71	25 06	3.53
1800	34 99	0 74		
2000	35 01	0 77		
2500	34 99	0 73	29 26	4 01
3000	35 11	0 58		
3500	34 96	0 67		
4000	34 89	0 62	29 14	4 70
4300	34 91	0 71		

STATION 4, 33°30'N, 61°00'W

1	36 14	0 91± 04	44 61	4 90
50	36 31	0 98±.08	32 16	3 30
100	36 55	0 91± 10	52 32	5 80
200	36 48	-0 82	26 66	3 30
400	36 42	0 64	24.60	3 80
600	35 99	0 72	27 14	3 80
800	35 37	0 65	25 92	3 90
1000	35 08	0 67	22 76	3.40
1500	35 22	0 68	22 56	3 30
2000	35 21	0 73		
3000	35 13	0 77		

STATION 5, 37°09 8'N, 63°08'W

1	36 13	1 06		
10	36 13	1 13± 14		
25	36 13	1 03		
50	36 15	1 11		
100	36 34	0 90		
150	36 56	0 83		
250	36 48	0 81		

STATION 6, 41°37 8'N, 61°48 3'W

1	35 74	1 03	19 76	1 92
10	35 75	1 18	29 44	1 80
25	35 89	1 08		
50	35 74	1 12	18 02	1 61
100	36 32	0.91	27 72	3 10
200	35 97	0 75	33 50	4 50
300	35 59	0 81		
400	35 24	0 77	32 40	4 21
500	35 70	0 79	24 56	3 19

STATION 7a, b, c

a) 43°33 5'N, 63°11'W

1	30 92	1 58	37.88	2 40
10	31 23	1 44	26 40	1 83
25	31 38	1 15	31 42	2 73

b) 43°28 5'N, 63°13'W

1	30 63	1 66	48 30	2 91
10	30 97	1 44	44 44	2 44
25	31 32	1 23	51 38	4 18

c) 43°12 5'N, 63°10 5'W

1	31 23	1 42	37 58	2 65
8	31.28	1 13	25 99	2 18
18	31 28	1 21	26 38	2 18