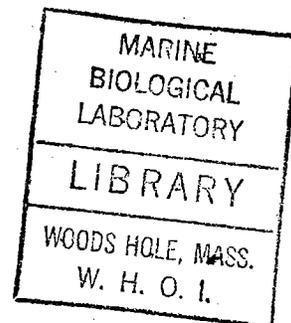


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VOLATILE ORGANIC COMPOUNDS IN SEAWATER

By

Philip M. Gschwend
B.S., California Institute of Technology
1973



Submitted in Partial Fulfillment
of the Requirements for the
Degree of

Doctor of Philosophy

at the

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PHILIP M. GSCHWEND

Submitted to the Woods Hole Oceanographic Institution on January 26, 1979, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Vapor phase stripping and solid adsorbent trapping were applied to seawater and related samples to concentrate volatile organic compounds. The concentrates were subsequently analyzed by glass capillary gas chromatography and combined gas chromatography-mass spectrometry. The compound identities and the spatial and temporal distributions of their concentrations were used to determine some sources, transformations, and transport mechanisms of organic matter in the sea.

Volatile organic compounds were determined in seawater samples from the Sargasso Sea, the western Equatorial Atlantic, and the upwelling region off Peru. Pentadecane was present in all three areas in surface samples at 10-40 ng/kg and decreased to 1-2 ng/kg in the deep water. A source related to the transformation of the algal fatty acid, hexadecanoic acid, by zooplankton is proposed since anthropogenic and direct phytoplankton sources are unlikely. C₂-alkylated benzenes were found in the upwelled water off Peru at about 4 ng/kg in the surface (5 and 20m), 3 ng/kg below the thermocline (100m), and 2 ng/kg or less in deeper water. A surface or atmospheric source is required to produce this distribution. C₆-C₁₀ aldehydes were also found in seawater from off Peru. The direct correlation of their concentrations with chlorophyll a and with oxygen indicated that they are derived from chemical oxidation of algal metabolites, for example, unsaturated fatty acids. Total volatiles in the oligotrophic Sargasso Sea were about 10-30 ng/kg while the biologically productive upwelling region off Peru contained up to 100 ng/kg.

The temporal variations of volatile organic compound concentrations were investigated in coastal seawater from Vineyard Sound, Massachusetts. Pentadecane and heptadecane showed large summertime concentration increases which were ascribed to benthic algal sources. Laboratory incubations of benthic algal samples supported this conclusion. The saturated hydrocarbons, from C₁₃-C₁₇, and alkylated benzenes and naphthalenes were all abundant after an oil spill several miles from the sampling site. C₂- and C₃-benzenes were the most persistently abundant volatile compounds and their

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concentrations were observed to be 2-10 times higher than average immediately after summer weekends, peak periods of tourist and recreational activities on Cape Cod. Naphthalene and its homologues were more abundant in the winter than in the summer. C₆-C₁₀ aldehydes were observed year-round, but showed a concentration maximum at the time of the late-winter phytoplankton bloom. C₁₂-C₁₅ aldehydes were also found in abundance at that time. Oxidation of algal matter by zooplankton or photochemically-produced oxidizing agents may produce the aldehydes, since laboratory cultures of phytoplankton did not produce these oxygenated volatiles. An alkene, structurally similar to the known benthic algal gamone, fucoseraten, was also found in Vineyard Sound seawater and in the upwelling region off Peru. Its appearance in Vineyard Sound samples coincided with the period of expected algal reproductive activity in February and March. Dimethyl polysulfides were found in coastal seawater. They may be produced within the water from precursors such as methyl mercaptan or other known polysulfide metabolites. Total volatile concentrations in Vineyard Sound seawater varied between 200 and 500 ng/kg for the period from January to June. Maximum concentrations occurred during the late-winter phytoplankton bloom and again in the spring from anthropogenic inputs of hydrocarbons.

The highest concentrations of C₂- and C₃-benzenes found in Vineyard Sound seawater coincided with motorboat use in the immediate vicinity of the sampling station. The average year-round isomer distribution most closely resembled distributions from gasoline and auto exhaust dissolved in seawater, consistent with an inboard or inboard/outboard motorboat source. Atmospheric and runoff delivery of C₂- and C₃-benzenes to Vineyard Sound seawater during the period from spring through fall was concluded to be of lesser importance. The atmosphere may serve as a buffer for seawater concentrations of the aromatic compounds, supporting low concentrations in the winter and limiting high concentrations in the summer.

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I would like to thank all the people who have contributed information and supplies for my work. Drs. Nelson Frew and René Schwarzenbach trained me in the arts of glass capillary gas chromatography and combined gas chromatography-mass spectrometry. Bruce Tripp, Mary True, Gale Nigrelli and Richard Sawdo have provided most of the supplies used in this work from the labs which they administer. Mary True and Jane Alford collected the seawater samples from the upwelling region off Peru. Dr. John Hobbie and Breck Bowden carried these samples from Lima, Peru to Woods Hole as personal baggage. Dr. Zophia Mlodzinska performed my nutrient analyses. Dr. Robert Guillard grew phytoplankton cultures for my use.

Neil Swanberg assisted in chlorophyll a determinations. Dr. Mac Hulburt identified and counted phytoplankton samples. Dr. Dietrich Müller provided authentic algal gamone compounds. Dick Edwards, Robert Anderson, and Tom Duncan supplied fuel and exhaust samples for aromatic hydrocarbon

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BIOGRAPHICAL NOTE

The author was born in Pomona, California on May 22, 1951 and was raised in Antioch, California. His father is a chemist and technical superintendent working for Fibreboard Corporation and his mother is a housewife and secretary at Crown Zellerbach Corporation. He has four younger brothers.

The author attended Antioch High School where he was first introduced to research by Mr. J. J. Olenchak, teacher of biology and physiology. Later he majored in Biology at the California Institute of Technology. In June, 1973, after an ill-fated cross-country drive, in which he ventured east of Nevada for the first time (and spent a week pumping gasoline in Illinois to raise enough money to fix his car), the author arrived at Woods Hole and began his tenure as one of the first two WHOI Ph.D. program candidates in chemistry.

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Farrington, J.W., N.M. Frew, P.M. Gschwend, and B.W. Tripp. (1977) Hydrocarbons in cores in northwestern Atlantic coastal and continental margin sediments. *Estuarine and Coastal Marine Science*, 5, 793-808.

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CHAPTER 1. INTRODUCTION

"No specific organic substances, defined as to their structures and molecular formulas, have been identified with absolute certainty in seawater...."

E. K. Duursma, 1961

In order to understand the origins, interactions, transport, and fates of organic matter in the sea, it is useful to identify the specific organic compounds involved (Anderson, 1977). Moreover, it is important to measure the spatio-temporal variations of the concentrations of these compounds.

Less than twenty years ago, leaders in the field of marine chemistry lamented at our inability to study specific organic compounds in seawater. Now, due to tremendous technological advances, this can be done. This has allowed three important advantages. First, by focusing on defined organic substances, our knowledge of the basic organic chemistry and biochemistry of these compounds may be utilized to understand their roles in the environment. Second, the accuracy and precision of the analyses of specific compounds may be investigated. This provides a necessary background on which to interpret the data. Finally, laboratory simulations of environmental processes may be studied for their effects on specific organic compounds.

This thesis describes studies concerning a group of volatile organic compounds in seawater. This introductory chapter defines the fraction of the total volatiles to be discussed, provides background information from other volatile-compound studies in seawater, describes what is known about various sources of specific volatile compounds, and offers historical perspective on the analytical methods. The next chapter reports the results of investigations on the spatial distributions of volatile organic compounds in three different open-ocean regions. Then, a seasonal study of volatile organic compounds in coastal seawater is described. Having this temporal study as

background, the next two chapters report investigations into the sources of some anthropogenic and some natural volatile compounds.

These studies have provided insight into several aspects of marine organic chemistry. First, organic compounds and their concentrations in seawater have been determined, allowing speculations concerning their chemical, biochemical, and photochemical transformations. Next, additional insight into the quantity and lability of the volatile fraction has been obtained and can be put into the context of the larger carbon cycle. Also, information pertinent to the feasibility of proposed transport mechanisms, for example, from land via the atmosphere to the sea, has been acquired. Evidence for chemical signals from marine organisms has been obtained and suggests the strength and timing of these signals. Finally, data describing "Man's infringement" on the sea have been procured and reveal not only the presence of anthropogenic volatile compounds, but have also suggested their mode of introduction, their longevity, and their potential for biological interference.

Definition of Volatiles

The volatile fraction which is the subject of this thesis is described by an operational definition. Three criteria are used to limit this fraction. First, a compound must be "stripable", that is, it must be of sufficiently low water solubility and high vapor pressure to be purged from the seawater sample by bubbling with an inert gas. Next, the component must be retained at room temperature by a solid adsorbent such as charcoal or Tenax. Lastly, the volatile must be amenable to gas chromatographic analysis. It must be separable from interfering low-boiling compounds, it must be thermally stable within the gas chromatograph, and it must be detectable with the flame ionization detector.

Potentially, this fraction includes many normal, branched, and cyclic alkanes, alkenes, aromatics, aldehydes, ketones, esters, ethers, halogenated hydrocarbons, and thioethers. Consequently, one would expect a diverse group of organic compounds to be included. This diversity holds substantial information concerning sources, transformations, and sinks of the specific compounds, as well as of the more general organic fraction. This fraction does not include organic compounds of boiling point lower than about 100°C or of water solubility greater than about 1 gm/kg (\approx 0.01 M). Therefore, this fraction is a subset of the total volatile fraction.

Estimates of the Size of the Total Volatile Fraction

Motivated by the desire to measure accurately the dissolved organic carbon (DOC) in seawater, a few workers have attempted to estimate the size of the total volatile fraction. Duursma (1961) reported that less than 10% of the DOC, or about 0.1 mg/kg, was volatile. This conclusion was based on an experiment in which he used acetic acid as a model volatile compound.

Vityuk (reported in Skopintsev, 1966) also attempted to measure the total volatile fraction. He dried one set of seawater samples at 60°C for routine dry-combustion analysis and a parallel set at room temperature with a desiccant. He found an average 18% lower value for the 60°C dried samples, indicating that the volatiles make up 15% of the DOC (or about 0.3 mg/kg)*. However, if some of the organic matter autoxidizes during evaporation of the seawater, more oxidation will certainly occur at the elevated temperature. This would also reduce the DOC values of samples dried at 60°C relative to

* Russian workers, using dry-combustion methods, typically find 2 mgC/kg seawater, about twice the value found by Canadian and American investigators, who rely chiefly on wet-combustion analyses.

those at room temperature. On the other hand, many volatiles will be lost even with evaporation at room temperature, and, therefore, comparison to this sample may underestimate the volatile fraction of the DOC. Thus, it is difficult to judge the accuracy of Vityuk's result.

Armstrong and Boalch (1960) measured the UV absorption of several seawater distillates. They found an absorbance maximum (10 cm cell) of 0.17 at 210 nm^{-1} . Assuming a fairly high extinction coefficient of 10,000, a concentration of distilled absorbing material of $2 \times 10^{-6} \text{ M}$ or approximately $200 \text{ } \mu\text{g/kg}$ (for MW 100) can be calculated. Returning this to the original seawater (1/10 distilled over), the figure reduces to $20 \text{ } \mu\text{g/kg}$. The authors made DOC determinations on the distillates obtained from seawater with excess NaOH added and found $20\text{--}50 \text{ } \mu\text{gC/kg}$ seawater. They also reported the presence of sulfur in the distillates at approximately $1\text{--}4 \text{ } \mu\text{gS/kg}$ seawater. These data tell us little about volatiles undetected by UV absorbance (must be less than ca. $50 \text{ } \mu\text{gC/kg}$ seawater), and unfortunately the UV method will include those compounds which codistill with water but are not "stripable."

Recent work by MacKinnon (pers. comm.) has shown that on the order of $1\text{--}10 \text{ } \mu\text{gC/kg}$ seawater may be purged with prolonged bubbling from seawater (at 60°C) and trapped on Tenax. This volatile fraction estimate is based on procedures most closely resembling those of this thesis. Therefore, this is the most relevant estimate of the volatile fraction which is the subject of this thesis.

Qualitative Information on the Volatile Fraction in Seawater

There is very little information available concerning the structures of volatile compounds occurring in seawater.

Giger (1977) has recently reviewed "the inventory of organic gases and volatiles" in the marine environment. He notes that methane is the only

volatile which has been studied in sufficient detail for us to have determined the major aspects of its marine geochemistry.

Numerous reports have been made concerning the occurrence of C_1 to C_4 hydrocarbons in seawater (Linnenbom and Swinnerton, 1970; Frank et al., 1970; Lamontagne et al., 1971; Brooks et al., 1973; Brooks and Sackett, 1973; Swinnerton and Lamontagne, 1974; Lamontagne et al., 1974; Lamontagne et al., 1976; Scranton, 1977). Methane typically occurs at about 30 ng/kg seawater (2.2 nM), ethane at 0.6 ng/kg (0.02 nM), and propane at 0.6 ng/kg (0.014 nM). Even lower levels of ethene, propene, butane, isobutane, butene and pentane are found. Methane and ethene have biological sources; all of the saturated lower hydrocarbons have petroleum-related sources; and the unsaturated compounds may arise from photochemical processes.

Some effort has been made to study the volatile halogenated hydrocarbons in seawater due to interest in their anthropogenic origin. Volatile chlorinated and fluorinated hydrocarbons are produced industrially at about 35,000 MT/yr, and about 4000 MT/yr are used in directly dispersed manners (NAS, 1975a). Table 1-1 lists the compounds reported, the concentrations found, the suspected source(s) and the location of the samples. Only tetrachloroethylene ($Cl_2C=CCl_2$) and hexachlorobutadiene ($Cl_2C=CCl-CCl=CCl_2$) would be amenable to detection by the methods used in this thesis (but not particularly so since a flame ionization detector is used).

Volatile organic sulfur compounds such as carbon disulfide (Lovelock, 1974) and dimethyl sulfide (Lovelock et al., 1972) have also been isolated from seawater samples. Carbon disulfide occurred at about 0.5 ng/kg while dimethyl sulfide was found at about 12 ng/kg. Biological sources for these materials are suspected.

Most recently, Sauer et al. (1978) have reported the concentrations of the volatile liquid hydrocarbons in seawater from the Gulf of Mexico.

Table 1-1. Halogenated volatile organic compounds, their concentrations (ng/kg) in seawater samples, and their suspected sources.

<u>compound</u>	<u>seawater concentration (ng/kg)</u>	<u>sample location</u>	<u>suspected source</u>
CH ₃ Cl	20	coastal	industrial or rxn from CH ₃ I
CH ₃ Br	8	coastal	rxn from CH ₃ I
CH ₃ I	12	coastal	benthic algae
CHCl ₃	8	NE Atlantic	industrial sewage treatment
CCl ₂ F ₂	traces		aerosol dispensers, refrigerant
CCl ₃ F	0.05	N & S Atlantic	aerosol dispensers, refrigerant
CCl ₄	0.14	NE Atlantic	biological or industrial
	250	Liverpool Bay	
	0.4	N & S Atlantic	
CHCl=CCl ₂	7	NE Atlantic	industrial solvent, dry cleaning paint stripping
	300	Liverpool Bay	
CCl ₂ =CCl ₂	0.5	NE Atlantic	industrial solvent, dry cleaning paint stripping, fumigant
	120	Liverpool Bay	
CCl ₃ CH ₃	250	Liverpool Bay	industrial solvent or fumigant
CCl ₂ =CCl-CCl=CCl ₂	4	Liverpool Bay	industrial (PVC)

references: Lovelock et al., 1973; Lovelock, 1975; Pearson and McConnell, 1975;
Su, 1976; Giger, 1977.

They found total n-alkanes (C_6-C_{14}) at 9-50 ng/kg and total aromatics (C_6-C_8) at 20-450 ng/kg. Petroleum related sources were suggested for these compounds as they correlate with the anthropogenic C_1 and C_2 hydrocarbons.

We can derive some lessons from the little that is known regarding volatile organic compounds in seawater. First, we now know that many volatiles which are found in seawater have terrestrial sources and must arrive at the ocean via the atmosphere. Next, society's use and handling of fossil fuels is responsible for large inputs of volatiles to the sea. Biological and photochemical processes are thought to produce some volatiles in seawater. Finally, individual concentration levels are typically in the ng/kg range for the open ocean and higher in coastal zones.

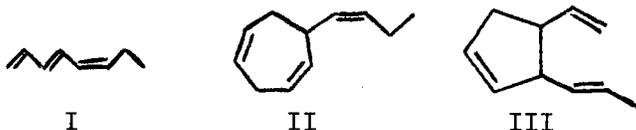
However, most of the above insight has been acquired for volatiles which are not the subject of this thesis. Most of the volatile fraction discussed in this thesis has not been reported in seawater due to the absence of suitable techniques and equipment. This technology became available only recently (e.g., Zlatkis et al., 1973; Grob, 1973).

Sources for Volatile Organic Compounds Amenable to Study in this Work

Marine Algae

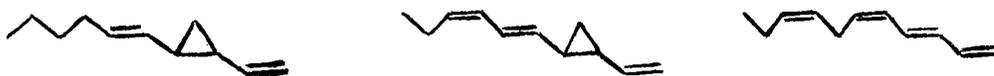
Ever since Haas (1935) demonstrated the presence of methyl mercaptan (CH_3SH) in Polysiphonia spp., workers have found other volatile organic compounds in numerous marine algae. Armstrong and Boalch (1960) demonstrated the liberation of large quantities of volatile materials into culture media by algae. In another early study, Cook et al. (1951) found that a volatile compound was responsible for sperm attraction to the eggs of Fucus spp.

However, it has been only recently that specific compound characterizations have been accomplished (Fenical, 1975; Crews, 1977; Moore, 1977). Müller and Jaenicke (1973) identified the Fucus attractant as trans, cis-1,3,5-octatriene. (I, fucoserraten). These workers have also found similar agents from Ectocarpus sp. (II, ectocarpen) (Müller et al., 1971) and from Cutleria multifida (III, multifiden) (Jaenicke et al., 1974). In the process, several other unsaturated cyclic compounds were also found.



Ectocarpen was found to make up 0.06% of the dry weight of the algal gametophyte material.

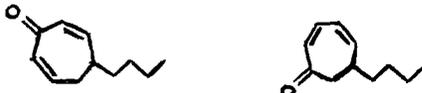
Moore and his coworkers (1974) have discovered a new group of C_{11} compounds which they have termed the "dictyopterenes." These include unsaturated straight chain and cyclopropyl compounds.

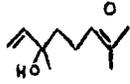


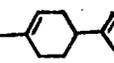
Fenical et al. (1972) have found a cadinene-type sesquiterpene in the brown seaweed, Dictyopterus zonarioides. This compound made up 0.04% of the dry weight of the alga.



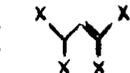
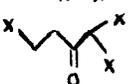
Moore and Yost (1973) have also found dihydrotropones in the Dictyopterus algae.



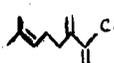
Thus, it can be expected that oxygenated volatiles occur in marine plants. Katayama (1958, 1961, 1962) using harsh steam-distillation techniques has reported the occurrence of oxygenated volatiles in a variety of seaweeds. His inventory includes furfural (), methyl furfural (), valeraldehyde (), benzaldehyde (), 1,8-cineol (), linalool (), geraniol () and p-cresol (). He reports the presence of p-cymene (),

alpha-pinene (, and limonene () in Ulva pertusa and Laminaria sp. Work was also done to demonstrate the antimicrobial activity of the carbonyl and terpene fractions isolated (Katayama, 1962). Some effects on annelids and nematodes were also demonstrated (Katayama, 1962).

Ulitzur and Hastings (1978) have shown that straight-chain aldehydes (C_9-C_{16}) are utilized in bioluminescent reactions of marine bacteria.

Many workers have shown the occurrence of halogenated volatiles in algae. Burrenson et al. (1975) found numerous haloforms in Asparagopsis taxiformis, the dominant one being bromoform ($CHBr_3$). These compounds accounted for 0.4% of the dry weight of the alga. Tetrabromomethane (CBr_4), tetrahalopropenes (, monohaloacetones (, polyhalobut-3-en-2-ones (, and 3,3-dihaloacroleins () were also found.

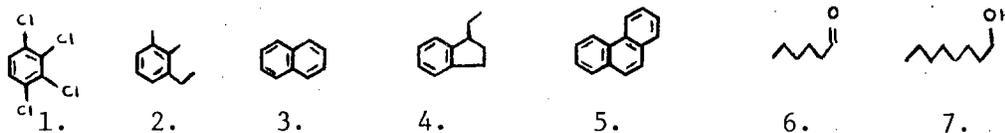
Lovelock (1975) has interpreted high levels of methyl iodide (CH_3I) in Laminaria beds as production and release of this volatile by these algae. Zafirion (1975) noted that this compound will react in seawater yielding methyl chloride (CH_3Cl) among other products.

Numerous volatile halogenated monoterpenes have been found in red algae. These include mono- and di-halo myrcenes ( ) (Burrenson et al., 1975; Ichikawa et al., 1974).

Volatiles from Marsh Grass

Miles et al. (1973) have analyzed Juncus roemerianus (a marsh grass) for its volatile content by steam distillation. Numerous compounds were found and included $C_{11}-C_{20}$ hydrocarbons, several C_7-C_9 aldehydes, nine C_5-C_{18} ketones and some $C_{12}-C_{15}$ ethers. The volatile

fraction represented 0.01% of the initial plant starting material. One may infer from these data that many of these compounds were accumulated from the environment (#'s 1-5), while others were synthesized de novo (6 and 7).

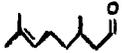
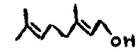


Other Sources

Volatiles are also important for marine animal life. Hasler and Wisby (1951) determined that a volatile material acts as a stream marker for salmon. Thus, rivers add volatiles to the sea.

Land organisms are an important source of volatile organic compounds. Several workers have shown that land plants produce and release tremendous quantities of terpenes (ten carbon branched and cyclic unsaturated hydrocarbons) (Went, 1960; Rasmussen and Went, 1965; Rasmussen, 1972; Tyson et al., 1974; Whitby and Coffey, 1977). It has been estimated that $2-4 \times 10^8$ metric tons of terpenes are released annually (Rasmussen and Went, 1965; Rasmussen, 1972) to the atmosphere. The major compounds are alpha and beta pinene and limonene (Rasmussen, 1972). Air measurements within forests have shown total terpene levels of 50 ng/liter-air (Whitby and Coffey, 1977). Downwind from the forest, levels between 4 and 11 ng/liter were observed. Still other workers have shown seasonal variations in these emissions (Zavarin et al., 1971; Powell et al., 1973; among others).

Land microorganisms also evolve large quantities of volatiles. Stotzky et al. (1976) have reviewed the subject and have demonstrated that terpenes, aldehydes, ketones, and sulfides affect the growth of various microorganisms.

Land animals also utilize volatiles as chemical messengers. For example, Wilson (1977) notes that the ant, Acanthomyops claviger, utilizes several compounds for its interspecific communications including 2, 6-dimethyl-5-heptenal, citronellal (), nerol (), geranial (), undecane, tridecane, pentadecane, 2-tridecanone, and 2-pentadecanone.

Another important source of volatiles derives from the activities of man. Industrial processes, as indicated earlier, release large quantities of volatile organic compounds to the environment (NAS, 1975). Anthropogenic inputs also come from our use of fossil fuels. Numerous workers (Altshuller et al., 1971; Grob and Grob, 1971; Bertsch et al., 1974; Ciccioli et al., 1976; Lonneman et al., 1974). have measured the hydrocarbon concentrations in urban air samples. They find individual compound concentrations on the order of ngs/liter-air. The fate of these materials and of the natural emissions, especially as regards potential transport to the sea, is unknown (Duce et al., 1974; Duce, 1977; Garrett and Smagin, 1976).

RECENT ADVANCES IN METHODOLOGY

As noted earlier, tremendous advances in the methodology available for the determination of the volatiles in aqueous samples have been made within the last five or six years. This progress was motivated by the biomedical profession's desire to utilize metabolic profiles to assess patients' health (Horning and Horning, 1971; Zlatkis et al., 1973, Teranishi et al., 1972) and the desire to monitor drinking waters and other natural freshwaters for volatile pollutants (Grob, 1973; Bellar et al., 1974;

Novotny et al., 1974; Dowty et al., 1975; Bertsch et al., 1975; Hites, 1977). These advances were primarily of two kinds. First, solid adsorbents were investigated for their ability to collect and retain volatile organic materials from air streams. Tenax, a polymer of 2,6-diphenyl-phenylene oxide, is found to adsorb volatiles and is thermally stable. Thus, a Tenax trap may be used to collect a volatile concentrate and can be directly inserted into the injection port of a gas chromatograph for thermal desorption of the volatiles. Charcoal has also been used in traps by Grob and his coworkers (Grob and Zürcher, 1976). This trap can be extracted with a small amount of solvent providing a concentrated volatile sample.

The second important advance was the availability of glass capillary gas chromatography. This facilitates the separation of hundreds of compounds per analysis and enables the efficient analysis of complex natural mixtures. These together allowed rapid and routine recovery, separation, identification, and quantification of a chemically diverse group of volatile organic compounds.

SUMMARY

This thesis reports the application of current technology to the study of an "analytical window" of volatile organic compounds in seawater.

The literature suggests that the total volatiles in this analytical window are present in seawater in concentrations of about 1-10 $\mu\text{g}/\text{kg}$. Also there is ample evidence for both natural and anthropogenic sources of volatile organic compounds to seawater.

Work in this field has added to our knowledge of the identity of some organic reactants occurring in seawater, the size of the volatile fraction and its relation to the larger organic carbon pool, the

importance of transport mechanisms in controlling volatile distributions in the sea, the importance of chemical communication processes between the organisms of the sea, and the pathways and levels of anthropogenically produced volatile organic compounds into the sea and the nature of their fate.

CHAPTER 2. VOLATILE ORGANIC COMPOUNDS IN OPEN OCEAN SEAWATER

INTRODUCTION

In the past, many efforts to learn about the marine organic carbon cycle have utilized measurements of bulk parameters such as dissolved organic carbon (DOC) in seawater samples collected from vertical and horizontal profiles (e.g. Menzel and Ryther, 1970). It now appears that most of the DOC is made and recycled in the surface waters of the sea, that the deep water organic matter is, for the most part, biologically inert, and that the DOC has a mean residence time of about 3000 years (Williams et al., 1969; Williams, 1971; Skopintsev, 1972; Menzel, 1975). The investigators have also suggested that two cycles are operating simultaneously in the sea, one which is fast for labile compounds and the other which is slow for more refractory organic matter.

More recently, studies concerning the spatial distributions of specific organic compounds such as the low-molecular-weight hydrocarbons (Swinnerton and Lamontagne, 1974), sterols (Gagosian, 1975; Gagosian, 1976), sugars (Handa, 1970; Hitchcock, 1977), amino acids (Lee and Bada, 1975; Pocklington, 1971, 1972), lipids (Jeffrey, 1966), and hydrocarbons (Barbier et al., 1973; Iliffe and Calder, 1974) have added to our understanding of the internal workings of the larger carbon cycle. Concentrations of individual compounds vary widely and are usually highest in surface seawater. These groups of compounds, and to some extent, the individual compounds within them, have been shown to have their own unique cycles.

Recently, methods have been developed for the semiquantitative analysis of volatile organic compounds in aqueous samples (Zlatkis et al., 1973; Grob, 1973; Bellar and Lichtenberg, 1974; May et al., 1975; Grob and Zürcher, 1976). Study of this fraction of the organic matter in seawater has been neglected in the past due to a lack of suitable methods.

It was the intention of this work to apply gas-phase stripping and solid-adsorbent trapping methods to the analysis of open-ocean seawater samples in order to assess the importance of this volatile organic fraction. Moreover, because the method is based only on the criterion of "stripability" (see Methods), many diverse organic compounds containing alkyl-, alkenyl-, aryl-, carbonyl-, alkoxy-, acyl-, and/or halo-functional groups could be represented and be used to study the chemistry of compounds containing these moieties in the environment.

Three markedly different open-ocean regions were investigated: the Sargasso Sea near Bermuda, the western Equatorial Atlantic, and the Peru upwelling region. The first two have low primary productivity while the third is known for its extremely high production. The western Equatorial Atlantic is influenced by a riverine input (Amazon) (Ryther et al., 1967). Different atmospheric transport patterns would be expected for these regions as the Sargasso Sea receives volatile inputs, including industrial materials, from the North American continent (Harvey and Steinhauer, 1976), but the western Equatorial Atlantic and the region off Peru should show the effect of dust and organic vapor transport from arid lands (Zuta et al., 1975; Simoneit et al., 1977). The Peru upwelling region is oxygen deficient in midwater and is underlain by anoxic sediments.

This situation allows the investigation of the influence of different redox conditions on the volatiles. This chapter reports the observations made on volatile organic compounds in these three widely differing oceanic regions.

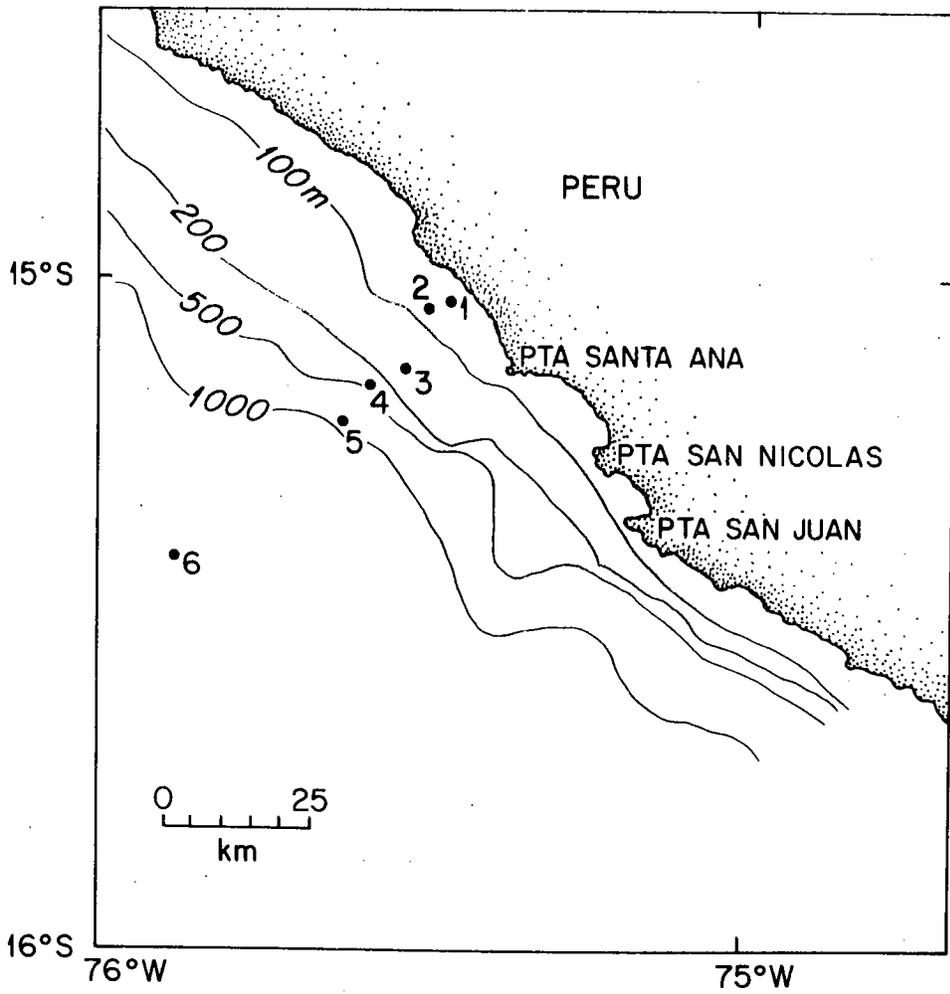
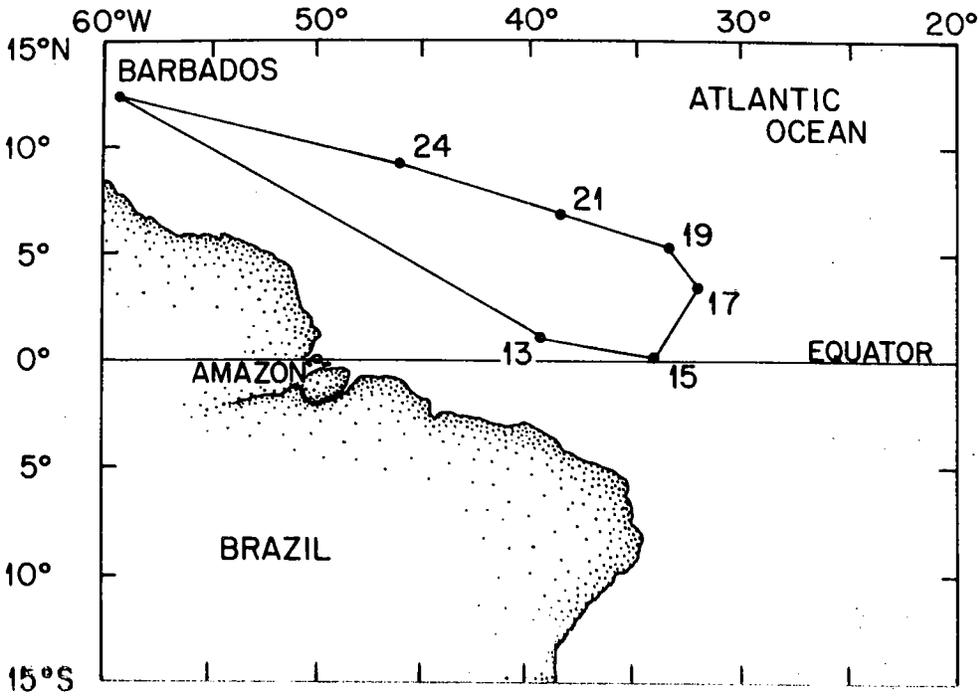
METHODS

Sampling

In February, 1977, seawater samples were collected in the Sargasso Sea near Bermuda from the R/V Panulirus II ($32^{\circ}10'N$ x $64^{\circ}30'W$, about 3000 m depth). The weather was marked by strong winds and approximately 3-m swells. Water was collected with a single 30-liter Niskin (Teflon coated spring) and transferred into 2-liter round bottom flasks on the deck. Upon our return to the dock, water was transferred to the stripper, spiked with an internal standard, and stripped. Traps, stored in screw-cap vials, were returned to Woods Hole for gas chromatography analysis. Hydrographic data were provided by Dr. B. Morris and Ms. E. Schroeder from the regular Panulirus station visited within a week of our sample collection.

Seawater samples were also collected from 6 hydrocasts made from the R/V Oceanus (cruise 22) in the western Equatorial Atlantic in March, 1977 (Figure 2-1). Sampling occurred between 10:00 and 14:00 local time. PVC Niskins (5- or 30-liter with Teflon coated stainless steel springs) were used. Sample depths were computed from reversing thermometer data. Water was transferred in a closed system from the Niskins through glass to 2-liter round bottom flasks. Samples for salinity, nutrients, and chlorophyll a were also drawn from the same Niskins.

Figure 2-1. Station locations on cruise 22 of the R/V Oceanus to the western Equatorial Atlantic ocean (March, 1977) and on cruise 73 of the R/V Knorr to the Peru upwelling region (March, 1978).



A third set of seawater samples was collected at 6 stations in March, 1978 on cruise 73 of the R/V Knorr to the upwelling region off the coast of Peru (figure 2-1). A single 30-liter Niskin was used. Water was drawn from the bottle through a polypropylene tube and an in-line filter (precombusted 142 mm glass fiber filter in a stainless steel holder) which were rinsed with a portion of the sample. Reagent bottles (2-liter) with ground-glass stoppers were filled with seawater, poisoned with 0.5 ml HgCl_2 solution (40 mg HgCl_2 per ml water), and then tightly stoppered. Filtering and poisoning were done to prevent biological activity from altering the volatile organic compound content of the samples during storage. Samples were stored at 4°C in the dark for 3 to 6 weeks until being returned to the lab at Woods Hole.

In order to check for the effects of filtering and poisoning treatments, some replicate samples were left untreated while others were only poisoned. Untreated samples were always drawn first, then unfiltered samples, and finally those that were filtered.

Samples for salinity, oxygen, nutrients, chlorophyll a, and phaeophytin were drawn from the same Niskin bottle and analyzed on board.

Analysis of Volatile Organic Compounds

The seawater samples from the Sargasso Sea and the western Equatorial Atlantic were analyzed for volatile organic compounds using the "Tenax method." Details of this method are provided in Appendix I. It is chiefly adapted from methods reported in the literature (Zlatkis et al., 1973; Bellar and Lichtenberg, 1974; May et al., 1975).

Briefly, the method involves bubbling a warmed seawater sample with helium and passing the effluent gas stream through a trap loaded with a solid adsorbent, Tenax. The volatiles, which are concentrated on this trap, are transferred by thermal desorption within a gas chromatograph injection port into a cryogenic loop which was made by reshaping the front end of the glass capillary gas chromatography column. After this transfer, the loop is warmed and chromatography is performed.

The method determined those compounds of sufficient volatility and low solubility to be stripped (hence the term "stripability") and not interfered with by the variable contamination (presumably atmospheric) by compounds boiling below 100°C. The lower limit of detection for nonpolar compounds was about 1 ng/kg seawater. Precision, as determined by the recovery of 1-chloro-n-decane added to the seawater at 10 ng/kg, was $\pm 20\%$. Compound recoveries varied, but were better than 80% for nonpolar volatile compounds, about 50% for slightly polar compounds such as alkylated benzenes, and less than 20% for more polar compounds such as the aldehydes.

The Peru seawater samples were analyzed using the "Grob" method (Grob, 1973; Grob and Zürcher, 1976; Schwarzenbach et al., 1978; Appendix I). Just before analysis, 200 ml of water was poured off at a nearby beach to provide a clean-air headspace. At the lab, samples were stripped for 2 hours at 35°C using the recycled headspace air. Volatile compounds were collected on a charcoal trap placed in the recycling vapor path. After the water was stripped, the trap was extracted with 15 μ l CS₂. GC and GCMS analyses were performed on aliquots of this extract.

These analyses provided a lower limit of detection of about 1 ng/kg. Reproducibility based on previous work (Schwarzenbach et al., 1978) was about $\pm 10\%$. Greater stripping efficiency was obtained using the Grob method, such that nonpolar and slightly polar compounds were recovered with an efficiency exceeding 80%. Relatively polar volatile compounds such as the aldehydes were recovered at about 30%. Only samples which were both filtered and poisoned are discussed. Comparison to untreated samples showed that these procedures did not contaminate the samples (Appendix I). Surface samples which were filtered sometimes showed lower concentrations (about 50%) for aldehydes and n-pentadecane than unfiltered replicates (Appendix I, Table I-3).

RESULTS

The winter Sargasso Sea station had a well-mixed surface layer to 400 meters as evidenced by the temperature, salinity, and oxygen data (figure 2-2). Pentadecane was the only volatile organic compound found at greater than trace (≈ 2 ng/kg) concentrations (Table 2-1). Three samples from 10 m and one from 100 m contained between 10 and 25 ng pentadecane/kg. The 1200-m sample had less than 1 ng/kg.

The hydrographic data from the western Equatorial Atlantic cruise reveal the presence of a seasonal thermocline at about 100 m for the 6 stations studied (figure 2-3, Appendix II). No anomalously low surface salinity samples were found; thus the influence of the Amazon was not important for any of these surface samples. Nutrients were depleted in the surface mixed layer and increased in the deeper waters to a maximum at several hundred meters. Chlorophyll a showed low values (0.1 - 0.6 $\mu\text{g}/\text{kg}$ above 50 m

Figure 2-2. Temperature ($^{\circ}\text{C}$), salinity ($^{\circ}/\text{oo}$) and oxygen concentrations (ml/l) of seawater samples taken at a station southeast of Bermuda in February, 1977.

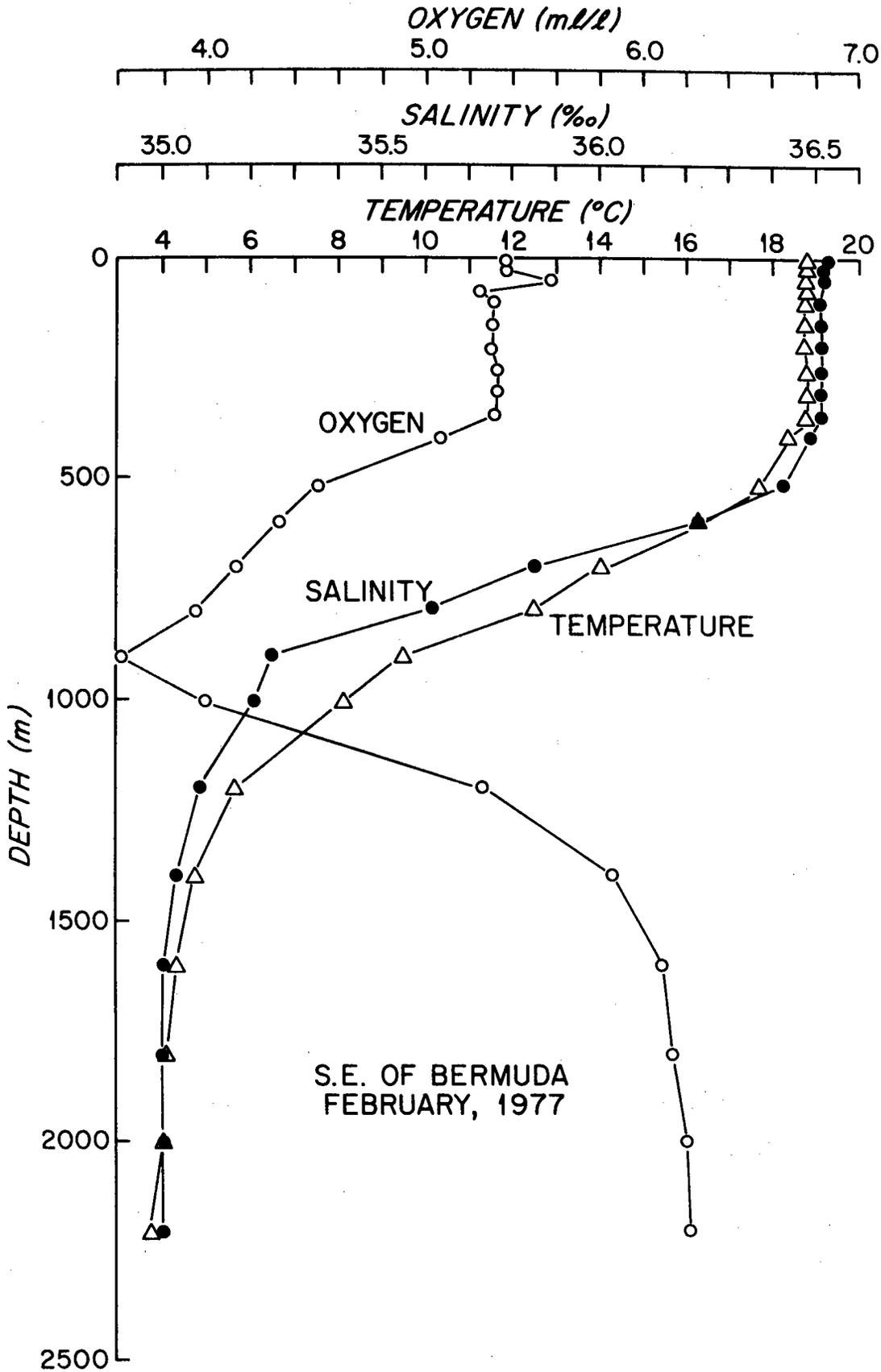
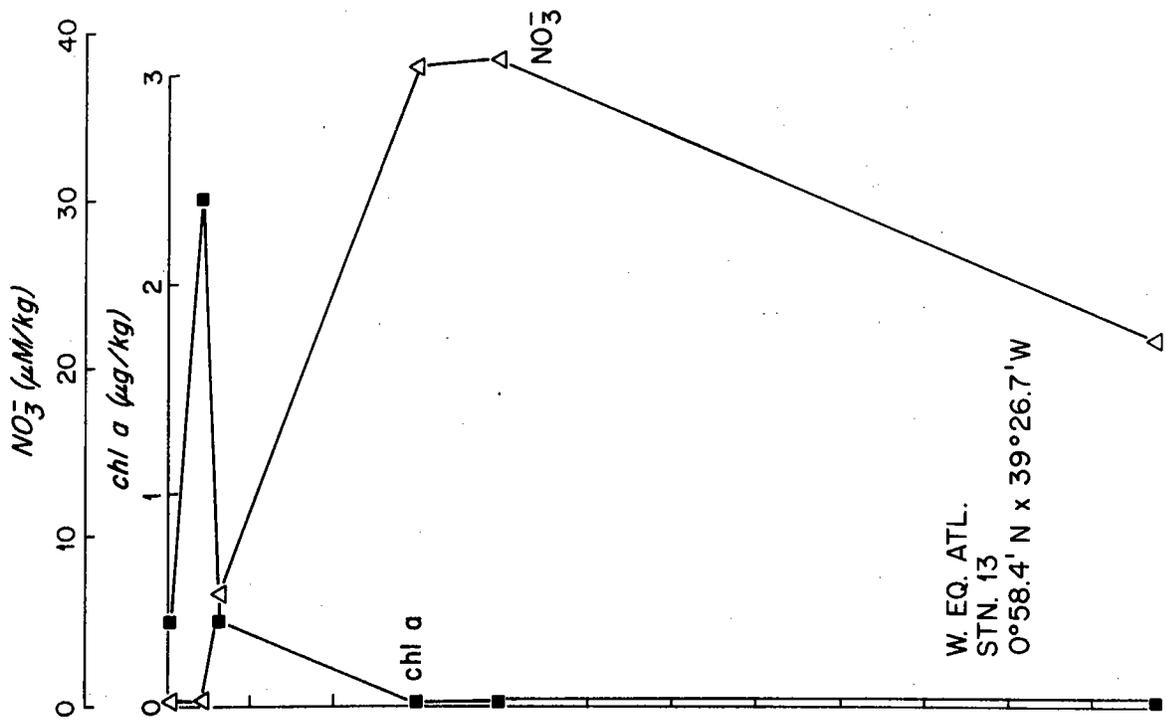
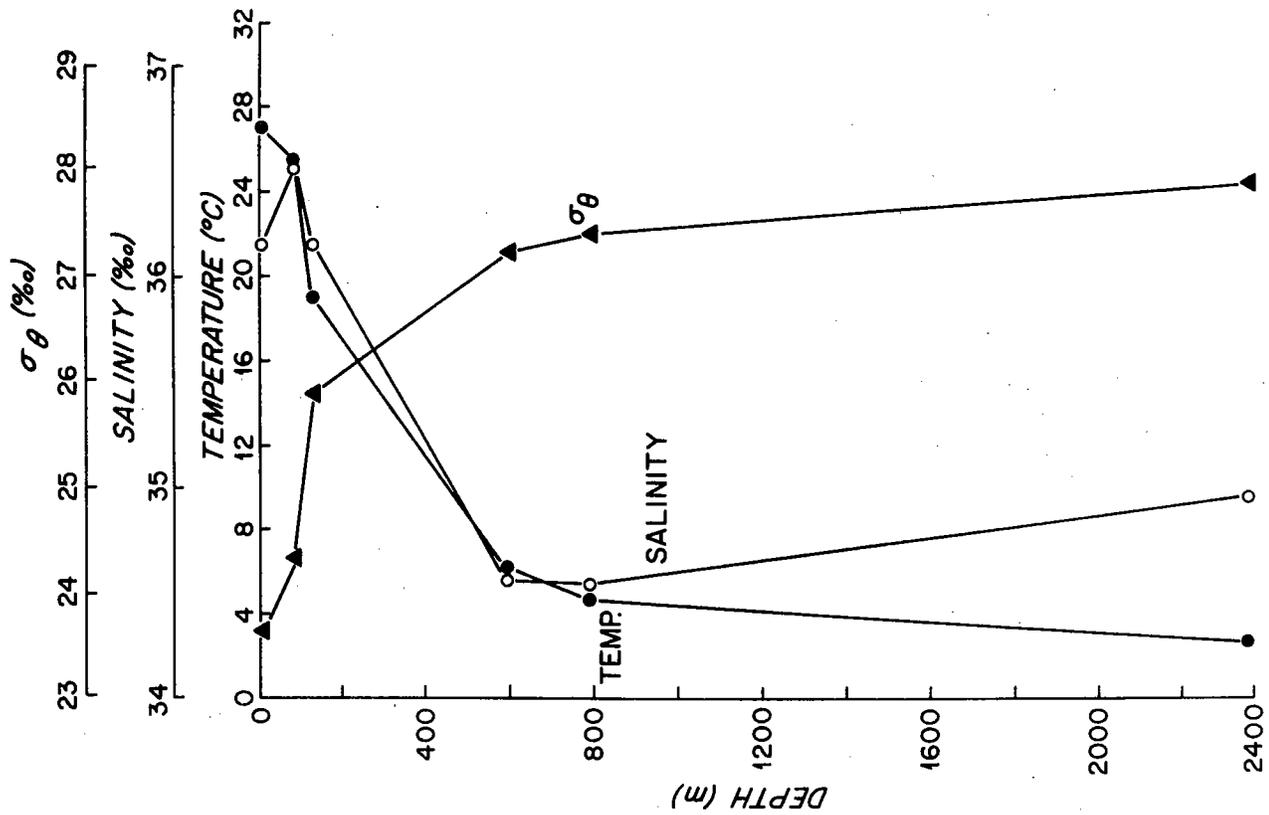


Table 2-1. Pentadecane concentrations (ng/kg) in seawater samples from southeast of Bermuda and the western Equatorial Atlantic ocean.

<u>Sample station/depth(m)</u>	<u>approximate pentadecane concentration (ng/kg)</u>
Sargasso Sea/10	10
Sargasso Sea/10	12
Sargasso Sea/10	25
Sargasso Sea/100	15
Sargasso Sea/1200	<1
Equatorial Atlantic	
13/5	24
13/87	4
13/131	26
13/594	<1
13/792	1
13/2376	9
15/7	9,37 (both from same 30 l Niskin)
15/116	1
15/146	4
15/176	2
15/750	1
15/2255	<1
17/5	3
17/83	15
17/133	1
17/173	1
17/631	<1
17/641	1
17/1896	14
19/6	10
19/108	1
19/147	<1
19/188	<1
19/680	2
19/690	1
24/7	10,38 (each from a separate sampler)
24/35	26
24/83	7
24/180	2
24/700	3
24/1923	29

Figure 2-3. Temperature ($^{\circ}\text{C}$), salinity ($^{\circ}/\text{oo}$), sigma θ ($^{\circ}/\text{oo}$), nitrate ($\mu\text{M}/\text{kg}$) and chlorophyll a ($\mu\text{g}/\text{kg}$) versus depth in seawater from station 13 ($0^{\circ}58.4' \text{ N} \times 39^{\circ}26.7' \text{ W}$) in the western Equatorial Atlantic ocean.



W. EQ. ATL.
 STN. 13
 0°58.4' N x 39°26.7' W

and a subsurface maximum of about 2 $\mu\text{g}/\text{kg}$ at 70 - 90 m. Hence fairly low phytoplankton productivity was encountered. Due to variable sample contamination of the volatiles on the western Equatorial Atlantic cruise, only pentadecane provided useful data (Table 2-1). Surface values varied considerably and were as high as 40 ng/kg. Some thermocline samples contained 20 to 30 ng/kg, while most of the samples between 100 and 1000 m had less than 3 ng/kg. Curiously, 3 of the 4 deep water samples showed elevated concentrations of pentadecane between 10 and 30 ng/kg.

The hydrographic data (figure 2-4) from the Peru upwelling region demonstrated the presence of active upwelling inshore of station 3 during the sampling. The nutrients were relatively high at station 1 and then reduced in the offshore stations to relative minima at stations 4 and 6 (figure 2-5). An oxygen deficient subsurface layer was encountered at all stations at about 100 m (figure 2-6). Chlorophyll a was very high (greater than 10 $\mu\text{g}/\text{kg}$) in the surface waters offshore of station 2 (figure 2-6). Phaeophytin did not reveal any marked trends beyond being higher in surface seawater than in deeper samples (figure 2-6).

The seawater samples from the upwelling region near Peru contained detectable levels of several groups of volatile organic compounds. The individual C_2 -alkylated benzenes were found at less than 10 ng/kg; surface seawater samples contained 2 to 3 times more of these aromatic hydrocarbons than did samples from 1000 m (figure 2-7).

An unknown compound was found to be coeluting with ethyl benzene in several surface seawater samples. Mass spectral evidence suggested that this was an octatriene. A molecular weight of 108 was determined for this compound based on the presence of m/e 109 (M+1), 137 (M+29),

Figure 2-4. Sections showing potential temperature ($^{\circ}\text{C}$), salinity ($^{\circ}/\text{oo}$) and sigma θ ($^{\circ}/\text{oo}$) in seawater from the Peru upwelling region. Note that depth is shown on a log scale.

Figure 2-5. Sections showing nutrient concentrations ($\mu\text{M}/\text{kg}$) in seawater from the Peru upwelling region. Note that depth is shown on a log scale.

Figure 2-6. Sections showing oxygen concentrations (ml/kg), chlorophyll a concentrations ($\mu\text{g}/\text{kg}$) and phaeophytin concentrations ($\mu\text{g}/\text{kg}$) in seawater from the Peru upwelling region. Note that depth is shown on a log scale.

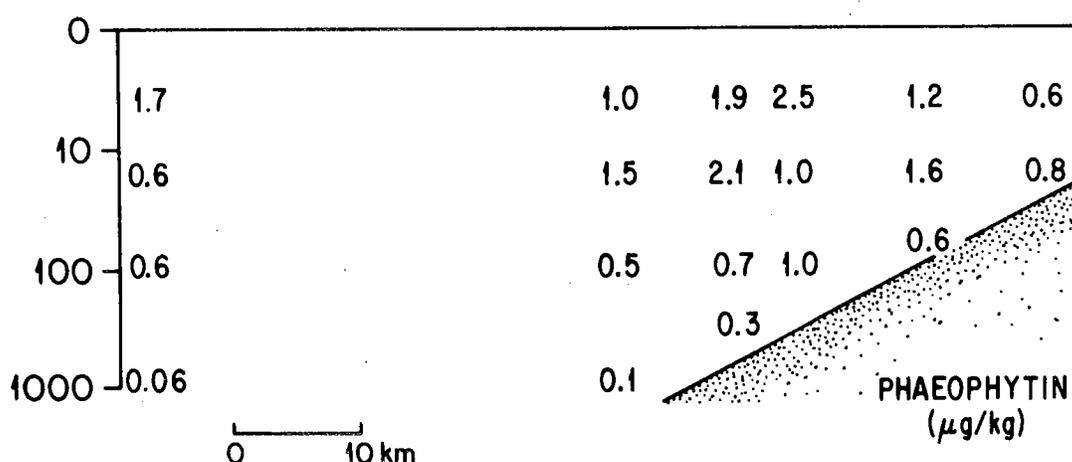
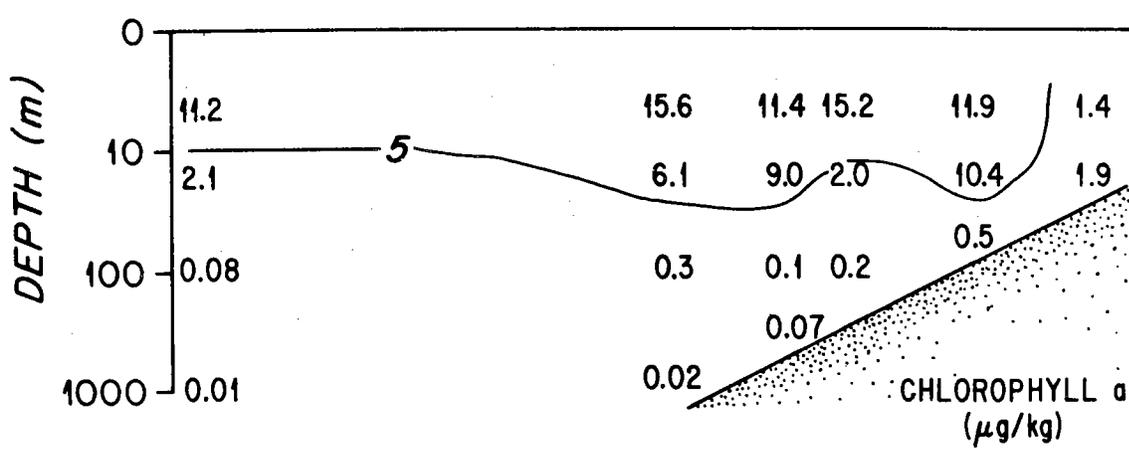
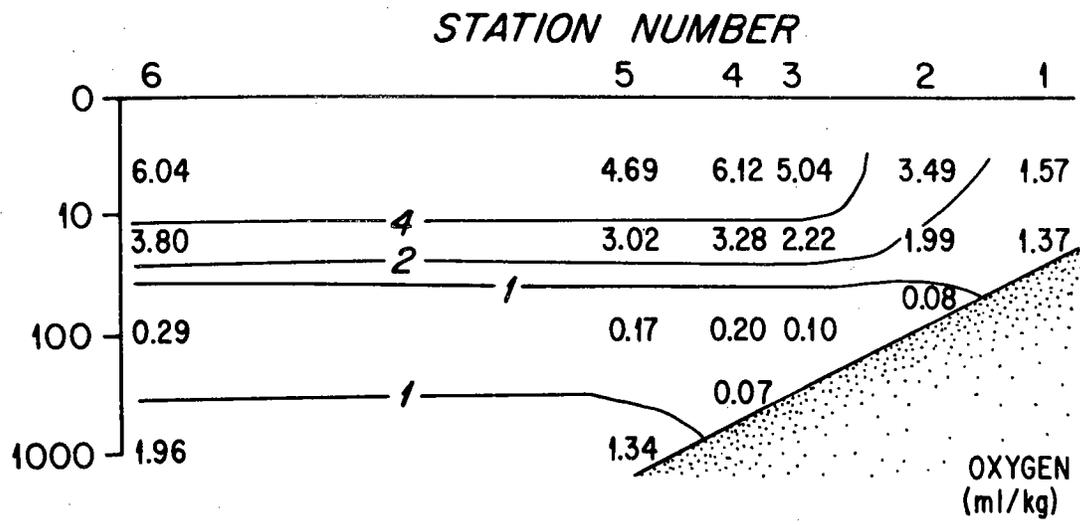
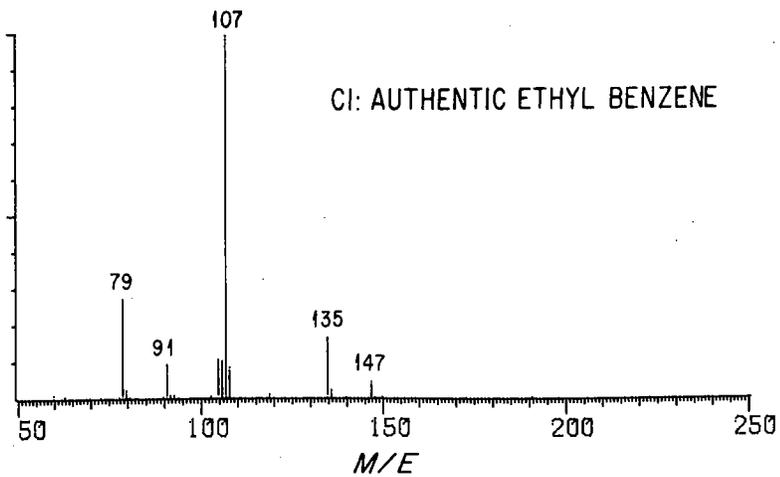
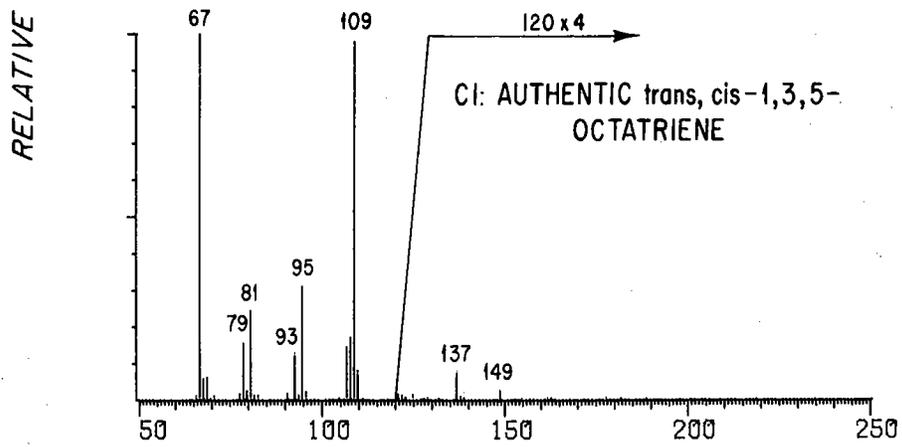
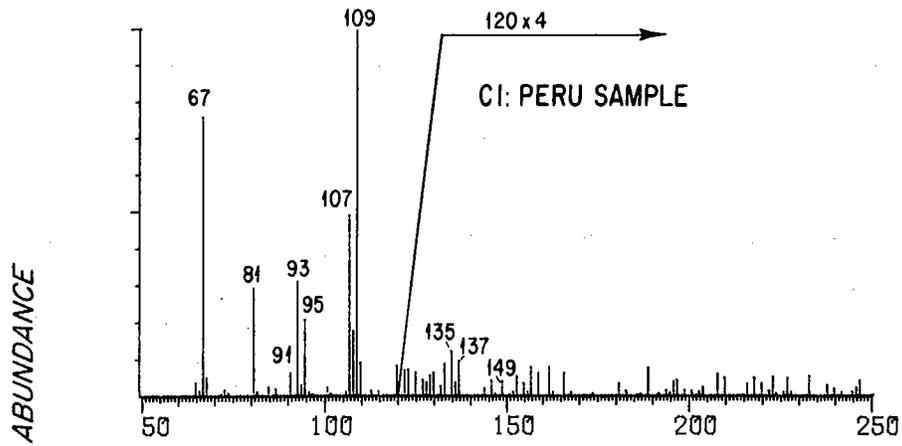
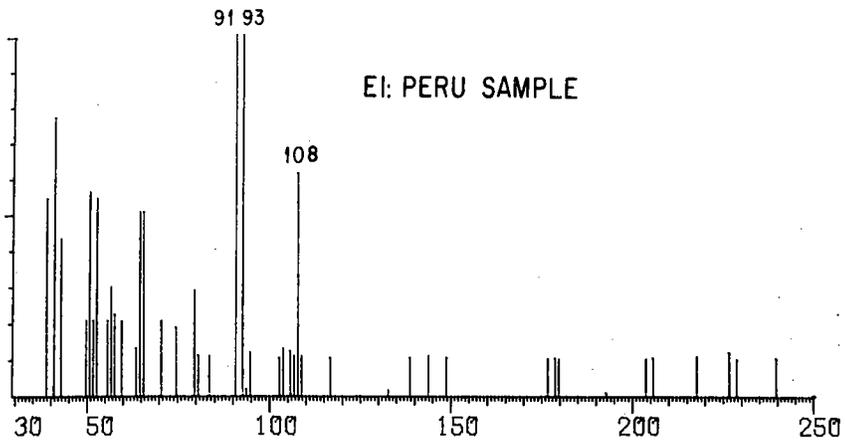


Figure 2-7. Sections showing 1,4-dimethyl benzene + 1,3-dimethyl benzene (para + meta xylene), unknown (mw 108), and pentadecane concentrations (ng/kg) in seawater from the Peru upwelling region. Note that depth is shown on a log scale.

and 149 (M+41) ions in the CH₄ chemical ionization (CI) spectrum and m/e 108 in the electron impact (EI) spectrum (figure 2-8). Loss of 13 and 27 mass units (giving m/e 95 and 81) in the CI spectrum indicates the presence of a terminal ethenyl group (Field, 1968), while loss of 15 mass units (giving m/e 93) in both the EI and CI spectra suggests that there is a terminal methyl substituent also. Due to insufficient sample size, the remainder of the EI spectrum was largely uninterpretable. Authentic trans,cis-1,3,5-octatriene and ethyl benzene CI spectra are also shown in figure 2-8. These spectra have all the same major fragment peaks as the unknown and ethyl benzene mixture in the sample. However, since this octatriene does not coelute with ethyl benzene, the unknown cannot be this particular isomer. Although not all cyclic and branched structures can be ruled out, these data are consistent with a structure such as a straight chain octatriene.

The GC peak heights of this unknown compound (mw 108) were estimated by subtracting assumed ethyl benzene peak heights from that of the mixed GC peak. The ethyl benzene peak heights were obtained by assuming that they were proportional to the peak heights of the other C₂-benzene isomers. This was reasonable because ethyl benzene levels covary with the other C₂-benzene isomer concentrations in most fossil fuels and environmental samples tested (chapter 4). These difference estimates agree well with predicted peak heights based on GCMS where data were available. The resultant spatial distribution of the concentration of this unknown compound (mw 108) is shown in figure 2-7. Maximum values were always found near the surface. Station 3 showed the highest level of all surface samples and the concentrations decreased in the offshore direction.

Figure 2-8. Electron impact (EI) and methane chemical ionization (CI) mass spectra of unknown compound (mixed with ethyl benzene) isolated from seawater samples collected in the Peru upwelling region. Also shown are CI spectra from authentic trans, cis-1,3,5-octatriene and ethyl benzene. Fragments from m/e 76 to 79 were not collected in the sample spectra because of solvent (CS₂) interference. M/E values greater than 120 are amplified 4 times in the CI spectra of the Peru sample and trans, cis-1,3,5-octatriene.



Mass plots for m/e 109 in the CI-CH₄ GCMS analyses showed that, while only one "octatriene" was found at station 3, additional isomers had appeared in the surface seawater at station 6. Mass spectra showed that these compounds were very closely related.

Pentadecane was also found in the upwelling region near Peru (figure 2-7). Surface samples contained the highest concentrations except at the most nearshore station. The 20-m and 100-m samples at the most offshore station showed atypically high pentadecane concentrations.

A comparison of filtered and unfiltered 5- and 20-m samples from the Peru upwelling region showed 2 samples with 50-60% losses of pentadecane and 1 sample with no significant difference on filtering (Appendix I, Table I-3). A filtering experiment done on coastal seawater from Vineyard Sound also showed about one-half removal of pentadecane on filtering. These losses may be due to a particle association of a significant fraction of this hydrocarbon.

A particle association of pentadecane may also explain the high variability observed for this compound in the Atlantic surface seawater samples (Table 2-1). Replicate samples from the same depth (e.g., Sargasso Sea/ 10 m and w. Eq. Atl. 24/7 m) showed very poor reproducibility. Gardner (1977) has found that a large fraction of the particulate matter in a seawater sample will settle below the outlet of a 30-liter Niskin. Particle concentrations may be 2-20 times higher in the dregs of the 30 liter Niskin than in the remainder of the water. Thus, factors such as the time of standing of the sampler after retrieval and the sequence of subsampling may have affected the particle distributions in the subsamples of this work, and as a result, the pentadecane concentrations may have also varied.

A family of straight chain aldehydes from hexanal to decanal were observed in seawater from off Peru at 1 to 10 ng/kg. As was the case for the other volatiles, concentrations were highest in offshore surface samples (figure 2-9).

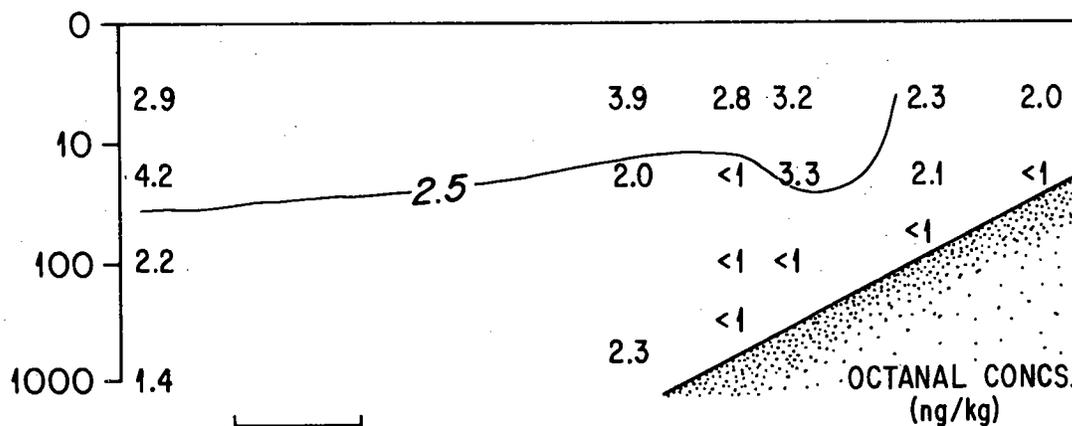
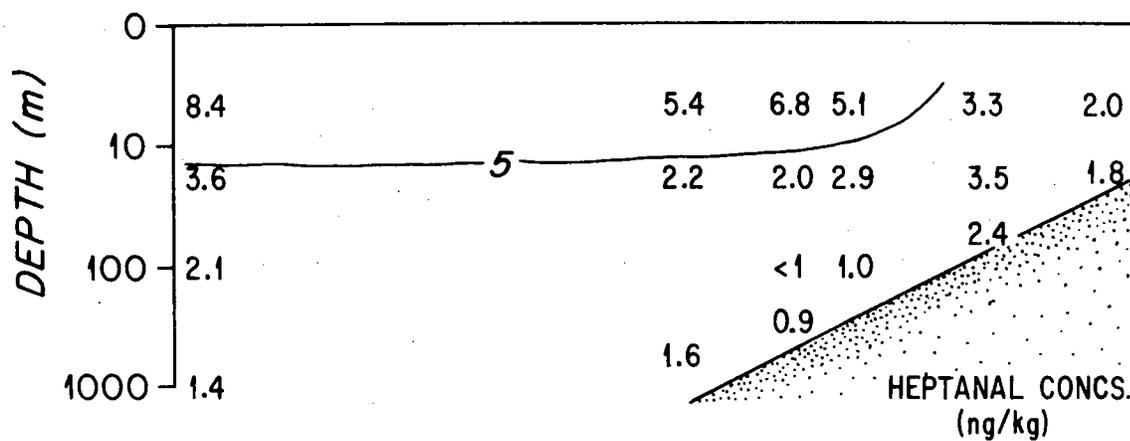
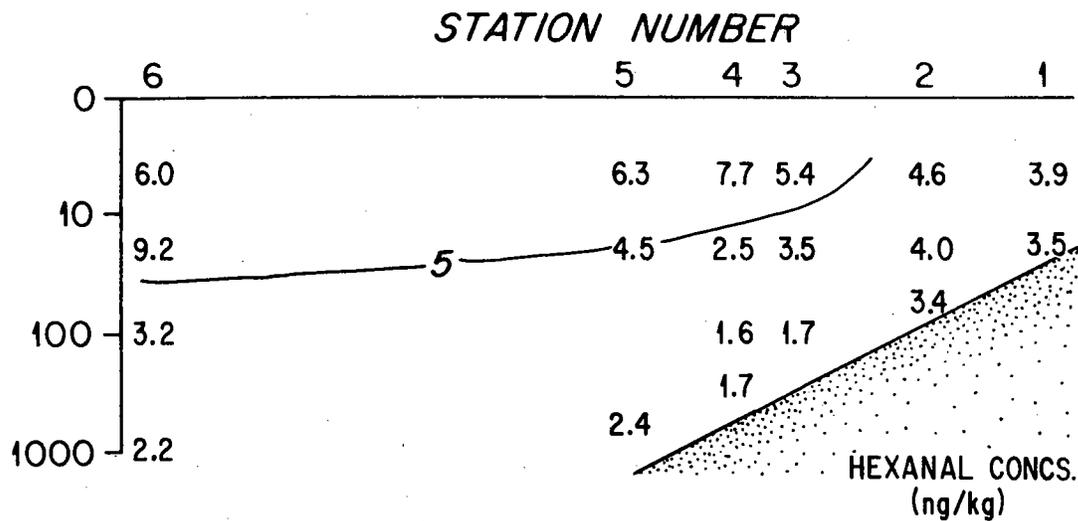
DISCUSSION

Total Volatiles

For all three regions, 40 ng/kg was the maximum concentration observed for an individual compound. Total levels in surface samples were on the order of 10-30 ng/kg in the Sargasso Sea and about 100 ng/kg near Peru. Deep samples contained 10 ng/kg or less. Three general explanations for this scarcity of volatiles may be offered. First, there may be a lack of sources. In areas such as the Sargasso Sea and the western Equatorial Atlantic, primary production of organic matter is low and consequently might not be expected to be an important source for the volatiles. Also, remoteness from land for these Atlantic regions may have precluded transport from natural or industrial terrestrial sources. The coastal region of Peru is a sparsely populated coastal desert near the area where the samples were acquired. Thus, terrestrial sources to these nearshore samples are unlikely to be strong, in spite of offshore winds. However, primary production in this upwelling region was very high at the time of sampling, and although elevated total volatile concentrations were seen, it seems likely that some other mechanism limits these organic constituents dissolved in seawater to only trace levels.

The levels of the volatile organic compounds may also be limited by a dynamic remineralization system. Investigators using several

Figure 2-9. Sections showing hexanal, heptanal and octanal concentrations (ng/kg) in seawater from the Peru upwelling region. Note that depth is shown on a log scale.



0 10 km

approaches to the study of organic matter in the sea have previously suggested the importance of this phenomenon. Menzel (1975), in his review of organic matter in the sea, has speculated that DOC is rapidly decomposed after pulse inputs since only poor correlation with measured primary productivity and DOC values could be found. Observations on specific organic metabolites such as amino acids (Lee and Bada, 1975) have also led investigators to conclude that these compounds are quickly removed after release into seawater. Thus, it appears that the concentrations of some biochemically labile materials may be controlled in seawater by heterotrophic activity.

Volatile compounds, whose principal source is production in surface seawater, have an additional sink from seawater in transport into the atmosphere. The mixed layer of the open ocean is degassed with a residence time of about 1 month (Broecker and Peng, 1974). Therefore, unless sources in the mixed layer continually produce a volatile organic compound, this atmospheric sink will rapidly deplete the individual volatile organic compound concentrations to values in equilibrium with the atmosphere.

The total volatile fraction found in the Sargasso Sea and the Peru upwelling region samples comprises less than 0.01% of the DOC.

Specific Volatiles: Pentadecane

Pentadecane was the best-studied volatile compound. It was ubiquitous in surface seawater samples at a concentration near its calculated thermodynamic solubility (Schwarzenbach et al., 1978). The lack of other homologues (e.g., tetradecane and hexadecane) indicates that this compound was not derived from a fossil fuel source. Land derived dust, for example, from the region of the

Equatorial Atlantic, does not contain detectable amounts of pentadecane (Simoneit et al., 1977). Other workers have confirmed this finding by noting that all of the pentadecane in their atmospheric samples was in the vapor phase (Cautreels and van Cauwenberghe, 1978). The partition coefficient (Schwarzenbach et al., 1978) for this saturated hydrocarbon is such that it is unlikely that a gaseous source of pentadecane to the open ocean could maintain the tens of nanograms per liter observed. Chemical reduction of oxygenated analogues such as pentadecanoic acid to pentadecane is not likely in oxygenated surface seawater.

In situ biological production is another potential source. Some phytoplankton have been shown to produce pentadecane (Clark and Blumer, 1967; Blumer et al., 1971). Clark and Blumer (1967) reported 100 ng nC₁₅/gm dry algae for three phytoplankters. Blumer et al. (1971) also found that an older dinoflagellate culture (i.e. in stationary phase) contained proportionately more pentadecane. Thus it is possible that the "age" of the bloom and the species involved are important factors controlling the pentadecane concentration in seawater.

A brief calculation suggests the magnitude of this phytoplankton source of pentadecane. Assume that the average phytoplankton have 100 ng nC₁₅/gm and that surface POC values represent an upper limit to phytoplankton biomass. In a region with 100 µg POC/kg, this would correspond to only 0.02 ng nC₁₅/kg. Even for the Peru upwelling region where up to 1000 µg POC/kg may be found, this only suggests that 0.2 ng nC₁₅/kg was present in the phytoplankton. These particulate stocks would have to turn over 100 to 1000 times and release all of their pentadecane to the seawater to provide the observed levels.

This seems unlikely to occur fast enough to build up sufficient pentadecane against the atmospheric sink. Possibly, unexamined species of phytoplankton contain much more pentadecane than those studied by Clark and Blumer (1967), and these algae may be the source of this volatile compound.

Another potential mechanism for pentadecane production is decarboxylation of hexadecanoic acid by zooplankton, analogous to the pathway proposed for the formation of pristane (Blumer et al., 1964). Phytoplankton are rich in this fatty acid (Ackman et al., 1968; Chuecas and Riley, 1969; Fisher and Schwarzenbach, 1978) and may contain about 10 mg/gm dry weight. Thus a potential standing stock of this starting material would be between 2 and 20 $\mu\text{g}/\text{kg}$ seawater. Should only a fraction of a percent of this fatty acid be metabolized in a fashion similar to that proposed for phytol to phytanic acid to pristane (Avigan and Blumer, 1968), tens of nanograms of pentadecane/kg could result. Tetradecane and hexadecane would not be found in similar abundance because phytoplankton do not contain much of the appropriate fatty acid precursors. In support of this proposed source, biogenic pentadecane and pristane appeared together in seawater collected in the fall during a seasonal study on Georges Bank (Energy Resources Company, Inc., 1978).

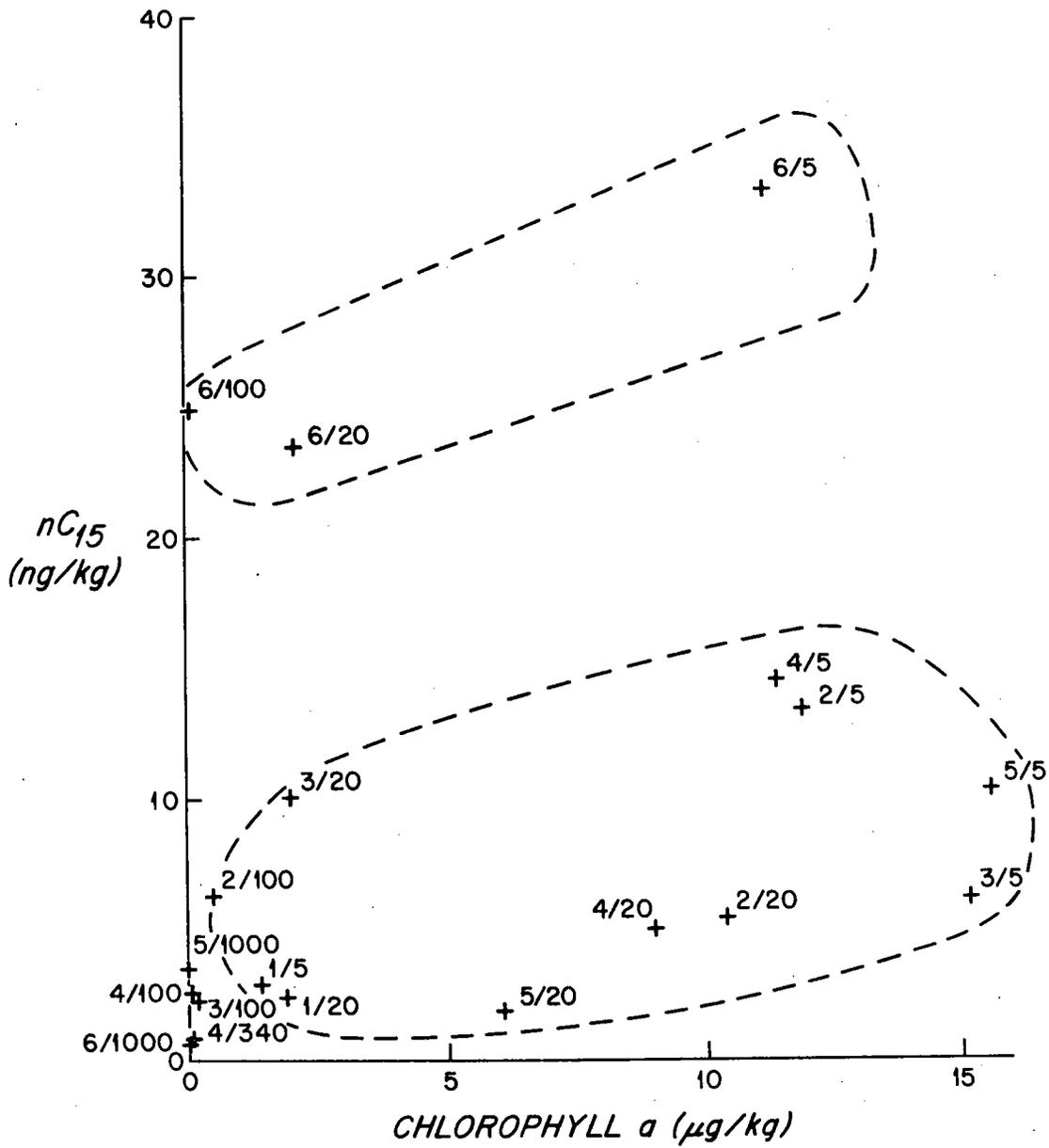
Station 6 off Peru was found to have a dinoflagellate bloom while the more inshore stations were dominated by diatoms. Dinoflagellates may contain greater amounts of hexadecanoic acid than diatoms (2-3x) (Ackman et al., 1968). Thus, the correspondence of relatively high pentadecane concentrations with the occurrence of dinoflagellates may be the result of higher precursor availability.

Zsolnay (1973, 1976) has reported the correlation of chlorophyll a and nonaromatic hydrocarbon concentrations in seawater samples from the upwelling region off Northwest Africa and in the slope waters between the Gulf Stream and Nova Scotia. This has been taken as evidence for a phytoplanktonic source of these hydrocarbons. Plots of pentadecane concentration versus chlorophyll a for the western Equatorial Atlantic and the Peru cruises are shown in figures 2-10 and 11. If one considers all samples from a region, the correspondence in these parameters is very poor. However, if the sample locations are noted, additional insight may be found. In the western Equatorial Atlantic, 4 of the 5 high-pentadecane observations were from shallow samples of the two westernmost stations (13 and 24). Possibly these sites were populated with a biological community capable of greater pentadecane production than the stations to the east. Similarly, if the Peru upwelling region samples are divided by sample locations, the station 6 samples fall into one region while the other surface samples are found in another. Thus, the relationship of pentadecane and chlorophyll a seems to be dependent on site specific parameters.

The station 3 surface samples from the Peru upwelling region were collected at different times of day relative to the other shallow samples (about 18:00 instead of 10:00 for the 5-m sample and vice versa for the 20-m sample). Time of day appears to affect the chlorophyll a and phaeophytin values. These pigments always built up during the day (Gagosian, pers. comm.) and consequently show uncharacteristically high values at station 3/5 m and low values at 3/20 m. Pentadecane seems to vary in the opposite fashion (i.e., diminishing during the day). Sample 3/5 m had quite low pentadecane concentration relative to other neighboring samples while the 3/20 m

Figure 2-10. Pentadecane concentrations (ng/kg) versus chlorophyll a concentrations ($\mu\text{g}/\text{kg}$) in seawater samples taken in the western Equatorial Atlantic ocean. Points are identified with the station number followed by the sample depths in meters.

Figure 2-11. Pentadecane concentrations (ng/kg) versus chlorophyll a concentrations (μ g/kg) in seawater samples taken in the Peru upwelling region. Points are identified with station number followed by the sample depth in meters.



sample was enriched relative to adjacent samples of the same depth. This atypical result may be caused by organisms which are particularly rich in pentadecane (or somehow capable of producing pentadecane) and which migrate vertically during the day. This interpretation also suggests the involvement of zooplankton in the formation of pentadecane.

Three deep samples from the western Equatorial Atlantic (13/2376 m, 17/1896 m, and 24/1923 m) showed unexpectedly high values of pentadecane. Other workers (Illiffe and Calder, 1974; Barbier et al., 1973) have reported increased total hydrocarbon concentrations with depth after an initial subsurface concentration decrease. These higher concentrations may represent relic hydrocarbons produced by organisms in surface seawater at the site of deep-water formation. Blumer et al. (1971) noted the relative stability of the saturated hydrocarbons, and these compounds have been proposed as water mass tracers (Illiffe and Calder, 1974). It seems unlikely that in situ production or remineralization of materials transported from the surface could generate the pentadecane found at these depths.

Specific Volatiles; C₂-benzenes

The individual C₂-benzenes were found at less than 10 ng/kg. The mean value for the meta + para xylenes in 5- and 50-m samples from off Peru was 4 ng/kg. Values declined to less than 3 ng/kg at 100 m. Less than 2 ng/kg were found in the deepest samples. This pattern suggests a surface or atmospheric source. Biological sources of these compounds are unknown. Since the recently upwelled waters at station 1 also have 4-5 ng/kg of these compounds, the transfer from the source must be very rapid. If the atmosphere were the

source, air concentrations in this region would have to be about 1-2 ng/l air ($K \approx 0,34$). This value may be compared with the 3-5 ng/l air measured near Cape Cod (chapter 4) and in rural areas of Florida (Lonneman et al., 1978).

Station 4 in the Peru upwelling region demonstrated two unusual features. The sum of the 5-m, 20-m, and 100-m concentrations for the meta + para xylenes was much lower than that for any other station. Also, the deep sample from this station revealed an anomalously high concentration. The fact that surface water at this station also shows a nutrient minimum suggests that the production of large numbers of phytoplankton cells may have caused additional removal from seawater of these aromatics either via adsorption or absorption. Subsequent sedimentation and remineralization of this biogenic material on the bottom may have caused the unusually high concentration of meta + para xylene in the 4/340 m sample. This injection of aromatic hydrocarbons to deep water may also explain the background levels (< 2 ng/kg) found in the other deep water samples from this region.

Specific Volatiles: Unknown (mw 108)

The section showing the concentrations of the "octatriene" suggests a phytoplankton source for this compound (figure 2-7). However, it is known that Fucus, a sublittoral benthic alga, releases an octatriene (trans,cis-1,3,5-octatriene) into seawater (Müller and Jaenicke, 1973). Possibly this Fucus octatriene was transported via longshore and offshore currents to the sampling stations and was isomerized (e.g. cis to trans) during transit to yield the unknown compound (mw 108). Additionally, the precursor may have undergone further rearrangements to yield the other "octatrienes" found at station 6.

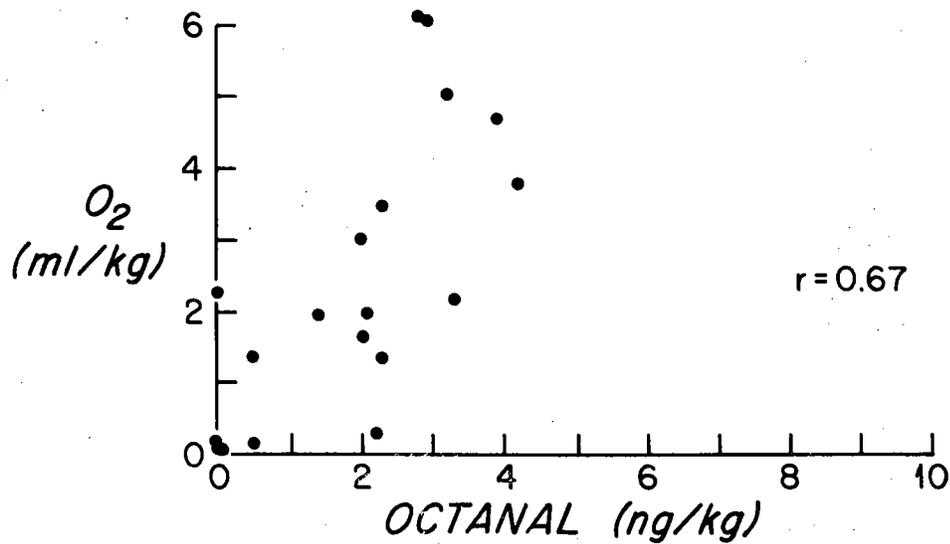
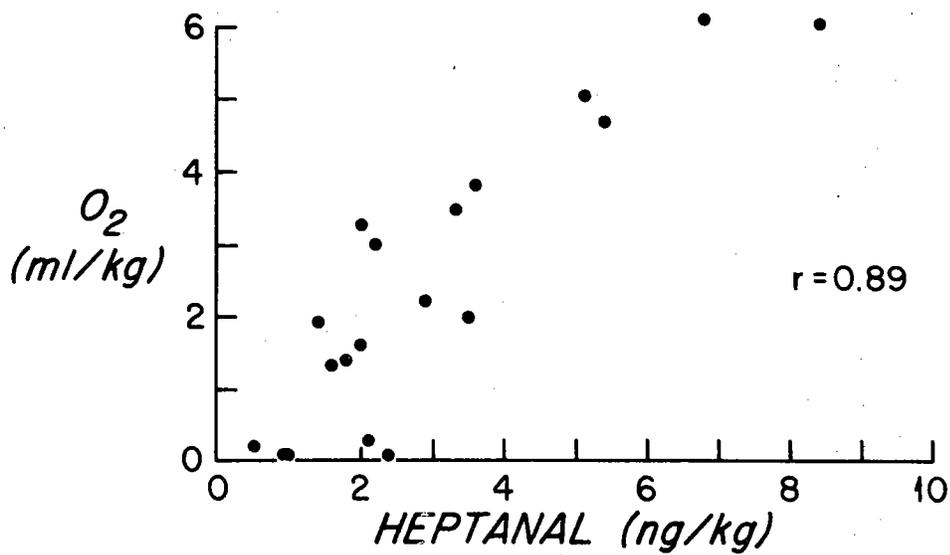
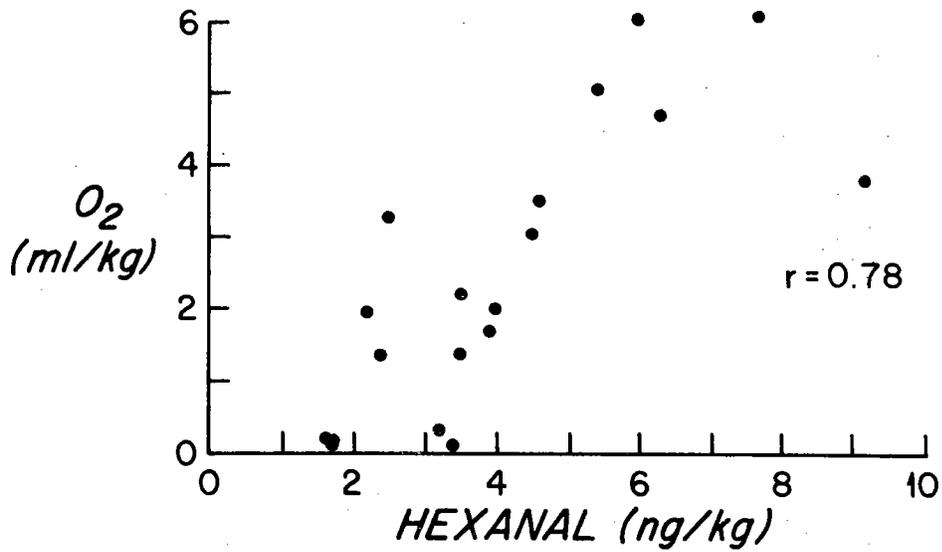
On the other hand, a phytoplankton source cannot be ruled out. Little work has been done to isolate volatile compounds from phytoplankton.

Specific Volatiles: C₆-C₁₀ Aldehydes

The C₆-C₁₀ straight chain aldehydes were observed in the Peru upwelling region samples predominantly in surface waters (figure 2-9). These aldehydes may be produced by phytoplankton. The linear correlation coefficients for hexanal and heptanal with chlorophyll a were 0.55 and 0.76 respectively. Other workers have found aldehydes as constituents of freshwater diatoms (Kikuchi et al., 1974) and fresh water yellow-green algae (Collins and Kalnins, 1965).

Alternatively, these aldehydes may be intermediate oxidation products of algal organic matter by heterotrophs. For example, hexanal has been obtained from the metabolism of linoleic and linolenic acids (Jadhav et al., 1972). In order to see if these aldehydes might be produced by remineralization processes in the seawater off Peru, the aldehyde concentrations were plotted against oxygen (figure 2-12). Rather than the expected inverse correlation, a strong direct correlation was observed for hexanal and heptanal (linear correlation coefficients of 0.78 and 0.89). Octanal showed a weaker correspondence ($r = 0.67$), whereas the trace levels of nonanal and decanal precluded useful testing. The direct correlation of aldehyde concentrations with oxygen suggests that these compounds were not produced by heterotrophs during remineralization. Instead, the observed correlation suggests another source for the C₆-C₁₀ aldehydes, chemical oxidation. Possibly higher oxygen concentrations cause this reaction to proceed more quickly and therefore result in higher aldehyde levels.

Figure 2-12. Hexanal, heptanal, and octanal concentrations (ng/kg) versus oxygen (ml/kg) in seawater samples taken in the Peru upwelling region. Linear regression coefficients (r) are also shown.



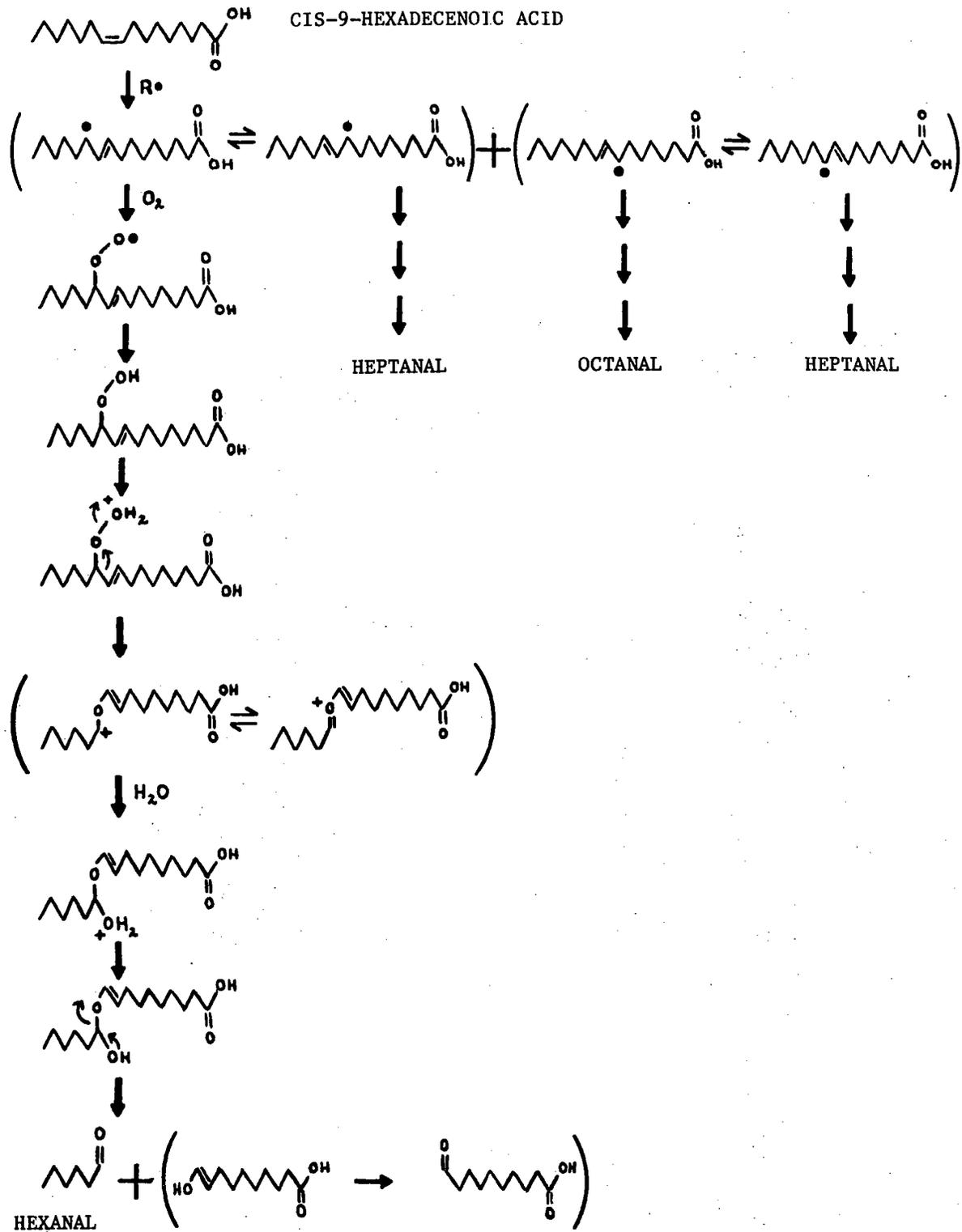
Potential precursors for chemical oxidation to aldehydes are the unsaturated fatty acids. Two of the most common fatty acids found in phytoplankton are cis-9-hexadecenoic acid and cis-9-octadecenoic acid (Ackman et al., 1968; Chuecas and Riley, 1969). Oxidation by reactants such as ozone which add to the double bond would yield only heptanal and nonanal from these compounds. It is difficult to produce octanal and decanal from such reactions, given that the appropriate fatty acids are uncommon. A second mechanism which produces all the C₆-C₁₀ aldehydes is shown in figure 2-13. This mechanism does not have to be the dominant pathway of decomposition of the fatty acids, as these acids are found in µg/kg quantities (Jeffrey, 1966; Kattner and Brockman, 1978) while the aldehydes are found at only ng/kg levels. Side products in this reaction are omega-carboxy-aldehydes which are not volatile. The 2 fatty acids mentioned above are also found at µgs/kg in surface slicks (Kattner and Brockman, 1978), which may be the site of (photo?) oxidation.

SUMMARY

Individual volatile organic compounds appear at less than 40 ng/kg in open-ocean samples from diverse areas such as the Sargasso Sea, the western Equatorial Atlantic, and the Peru upwelling region. Total volatiles for the analytical window investigated range between 10 and 100 ng/kg. These low levels may indicate: (1) insignificant sources were present, (2) rapid turnover of these organic compounds occurred, or (3) degassing to the atmosphere was important.

Pentadecane is present in most surface seawater samples at about 10-40 ng/kg, which is very near the calculated thermodynamic solubility (Schwarzenbach et al., 1978). This hydrocarbon may be produced from an abundant phytoplankton

Figure 2-13. Mechanism for production of hexanal, heptanal, and octanal from cis-9-hexadecenoic acid. The steps are drawn out for only 1 of the 4 possible free radicals created by abstraction of an allylic hydrogen.



fatty acid, hexadecanoic acid, in a manner analogous to that of pristane from phytanic acid, or may be produced directly by phytoplankton. The concentration of pentadecane does not correlate well with chlorophyll a, as site-specific factors appear to affect this relationship. Other alkanes were observed at trace levels.

C₂-benzenes occurred in surface waters off Peru at about 1-10 ng/kg. The Peru samples showed higher values (2-3x) in surface waters than in deep ones, suggesting an atmospheric or surface source. Sedimentation of biogenic particles may transfer these aromatic hydrocarbons to deeper water.

A group of compounds suggested to be octatrienes was found in the Peru upwelling region. A single isomer of this group may be produced in near-shore waters by phytoplankton or benthic algae and may rearrange in the environment to yield several new conformers.

Aldehydes (C₆-C₁₀) were found in samples from near Peru. The direct correlation of their concentration with O₂ has led to the suggestion that they are oxidation products of unsaturated fatty acids from algae.

CHAPTER 3. TEMPORAL VARIATIONS OF VOLATILE ORGANIC COMPOUNDS AT A COASTAL STATION

INTRODUCTION

In the past, oceanographers have observed the relationship of dissolved organic carbon (DOC) to primary productivity. For example, Duursma (1961) carried out a time series study in the Baltic region and observed that DOC increased during the spring phytoplankton bloom. Other workers have monitored specific organic compounds such as amino acids (Riley and Segar, 1970) and hydrocarbons and fatty acids (Schultz and Quinn, 1977) in coastal regions and also noted the coincidence of specific compound level increases with phytoplankton blooms. Consequently, it would be expected that certain volatiles would increase in concentration during local spring (and fall) algal blooms (Fish, 1911; Lillick, 1937; Yentsch and Ryther, 1959).

In the coastal region studied, seasonal cycles in abundance and physiology occur for the various benthic marine algae (Conover, 1958; Sears and Wilce, 1975; Ragan and Jensen, 1978) and for the seagrasses (Sand-Jensen, 1975). The intensive primary productivity of these plants (which may be as high as 1 to 10 gmC/m²/day (Kanwisher, 1966; Sand-Jensen, 1975; Phillips, 1978) may also control the levels of specific volatiles. It has recently been shown that various volatile unsaturated hydrocarbons are chemical messengers for benthic marine algae (Müller, 1977). These signals may demonstrate seasonal variation, and their study may discern both the periods and intensity at which they occur.

The region of Cape Cod also shows a seasonal influx of residents and tourists. Thus, one may reasonably expect to see changes in anthropogenic volatile introduction to the coastal zone on a seasonal basis.

In addition, the Cape, and the Northeast U.S. in general, are heavily forested. Seasonal variations in the outputs of volatile organic compounds such as the terpenes (Whitby and Coffey, 1977) and their subsequent transport into coastal seawater may be expected.

All of these seasonal processes, and many others, occur and involve changes in the introduction of volatile organic compounds to the environment. It is the intention of this work to attempt to interpret the variations in volatile compound concentrations of the coastal seawater in terms of the effects of such processes.

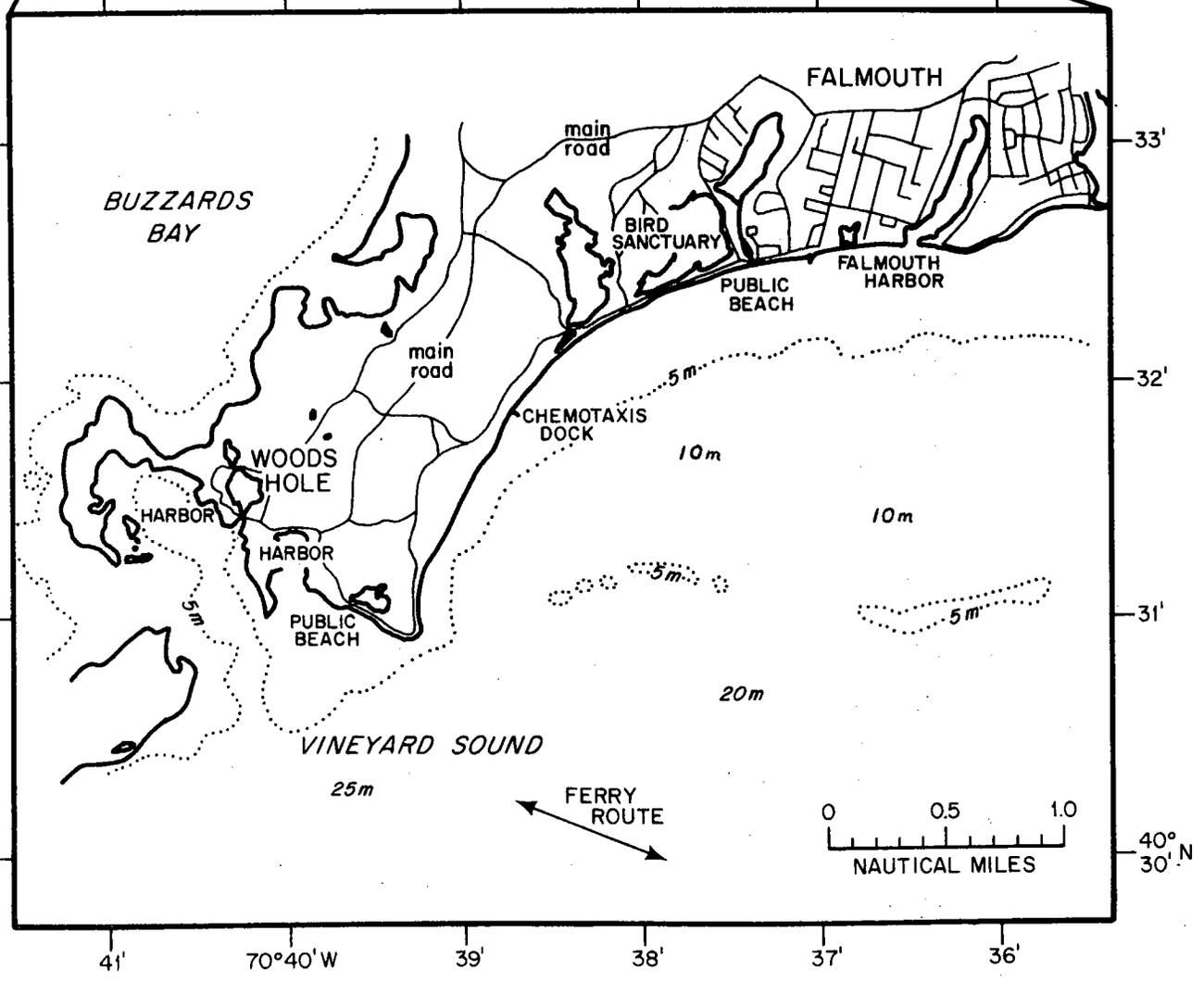
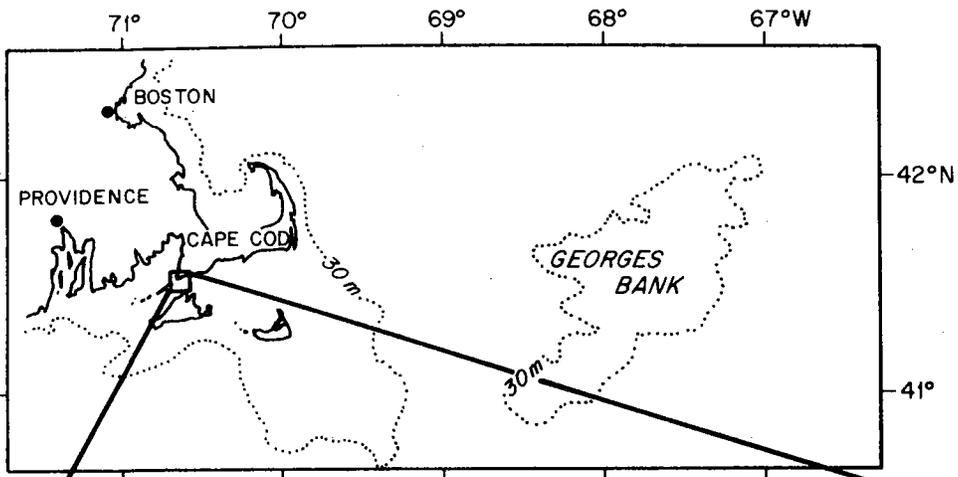
Accordingly, the temporal variations of a diverse group of specific organic compounds have been studied in coastal seawater. The preliminary results have been reported by Schwarzenbach et al. (1978; Appendix III). In these studies, an inventory of specific organic compounds and their concentrations was acquired. The changes in the specific compound levels were compared with variations of other processes (such as algal blooms). It was then possible to speculate concerning the manner in which environmental processes affect the cycling of these organic compounds. Moreover, opportunities arose (such as pollution events) to observe the manner and rate at which the natural system responded to perturbations. These results have allowed consideration of the environmental chemistry of these organic materials, and by extension, the more complex organic matter to which they bear structural resemblance.

METHODS

Sampling

Samples were obtained biweekly at Chemotaxis Dock (CD) (figure 3-1), a wooden pier which extends about 10 meters into Vineyard Sound. The water depth off the end of the dock is between 1.5 and 2.5 meters and

Figure 3-1. Map showing region near Chemotaxis dock (CD).



varies with about a 0.6 meter tide. The bottom is sandy and covered seasonally with an extensive algal and seagrass growth. The shore is cobbled and backed by a mixed oak and pine forest band. The main road in the region is greater than 0.5 km away and is separated from the beach by this vegetation. Public beaches are located about 1 km to either side, and Woods Hole and Falmouth harbors are beyond these. Ferries to Martha's Vineyard and Nantucket pass several times per day several kilometers offshore. A series of brackish water ponds discharge into the Sound to the east of the sampling site. Groins are placed along the shore and inhibit the longshore drift which is in the net eastward direction (Bumpus et al., 1971).

Seawater was collected 20 cm below the surface with a 1-liter round bottom flask fastened to the end of an aluminum rod by a PVC bracket. The flask was filled and emptied three times, and then three separate additional aliquots were used to rinse a 5-liter round bottom flask. Finally this larger flask was filled with 4 liters of seawater, spiked with an internal standard solution (2 μ l of 20 ng each 1-chloro-n-decane, -dodecane, -tetradecane/ μ l acetone), and swirled. The 1-liter flask was then used to acquire samples for salinity, nutrients, chlorophyll a and phytoplankton counts.

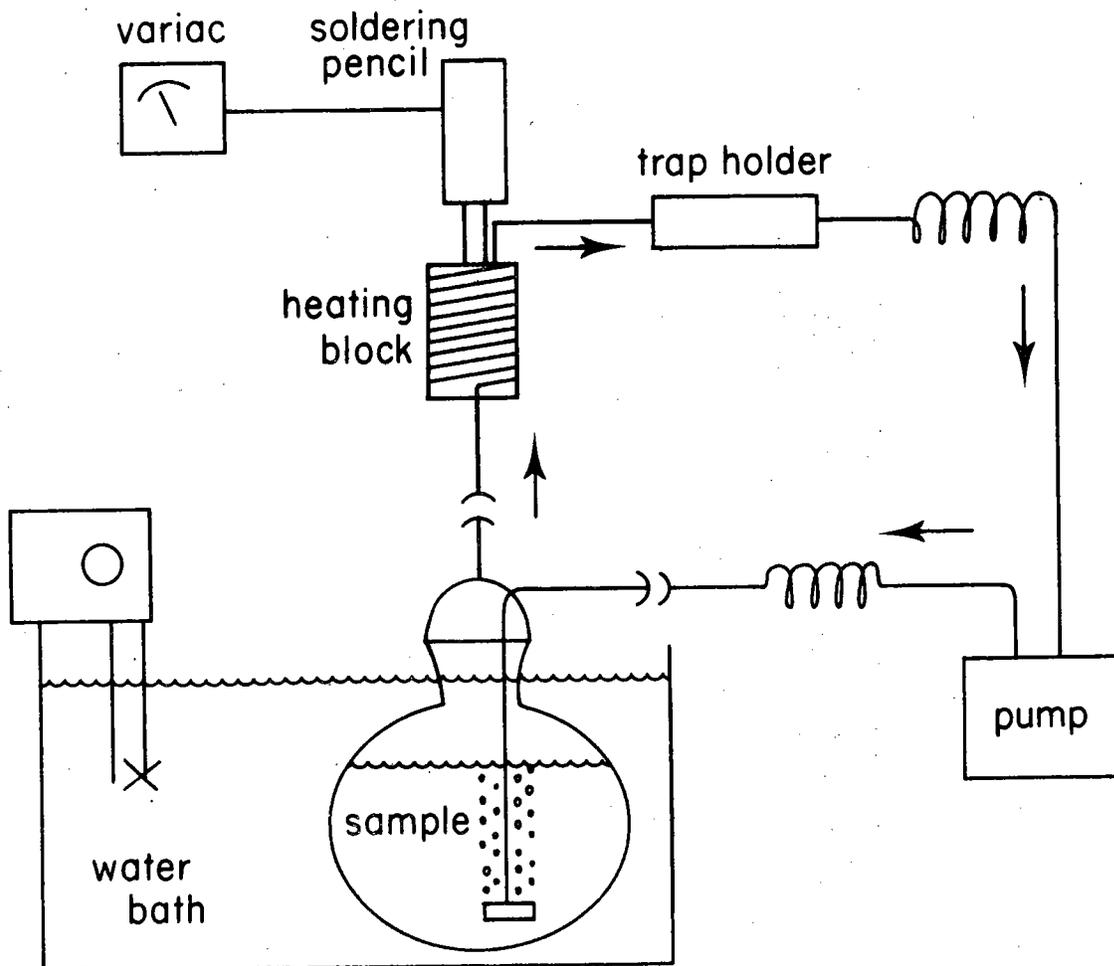
Stripping

Samples were immediately returned to the lab and analyzed. The 4-liter seawater sample was stripped according to the methods of Grob and Zürcher (1976). Briefly, a metal bellows pump forces air through a frit into the bottom of the water sample (figure 3-2). The resultant column of bubbles sweeps the sample of its volatile compounds, and the effluent air carries this organic load through glass and stainless steel tubing

Figure 3-2. Recirculating stripper configuration from Grob and Zürcher (1976).

RECIRCULATING STRIPPER

ref. Grob and Zürcher, 1976



(heated to 60°C to reduce the relative humidity), before reaching a charcoal trap. The microcharcoal trap consists of a glass tube in which about 1 mg of charcoal has been fixed between two stainless steel screens glass-blown into the tube. After passing through the trap, the air returns to the pump for recirculation through the system. The sample was stripped for 2 hours at a flow rate of about 1.5 liter/min. The water sample was heated to 35°C by a water bath. All water samples were restripped onto a fresh trap for an additional 2 hours immediately after the first strip (henceforth referred to as a restrip),

After stripping, the trap was removed from its holder and extracted with 15 µl CS₂ (figure 3-3). This was done by adding another internal standard (2 µl of 20 ng 1-chloro-n-octane/µl CS₂) onto the trap and then adding 6 µl CS₂. Cooling the vial of the assembled extraction apparatus drew the solvent plug down through the charcoal. Warming the vial pushed the solvent back up through the charcoal. After several such passes, the solvent was drawn down and away from the charcoal by prolonged cooling, and with a quick flick was shaken down into the bottom of the vial. Repeating the extraction with an additional 6 µl CS₂ efficiently completed the removal of the volatiles from the trap and provided a concentrated solution for further analysis.

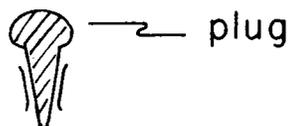
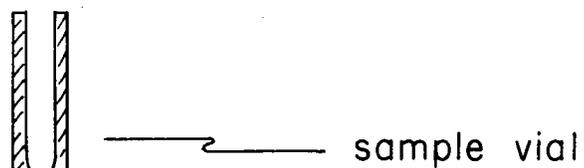
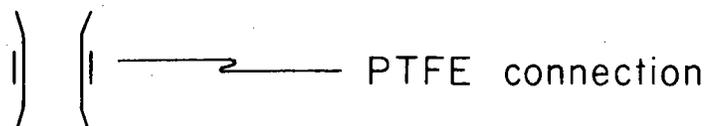
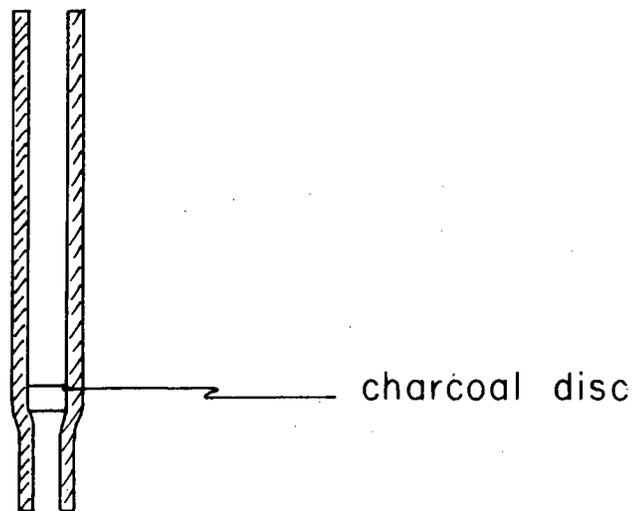
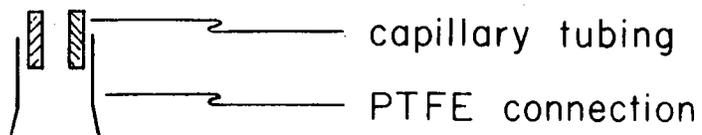
Gas Chromatography and Gas Chromatography - Mass Spectrometry

The volatiles were analyzed using gas chromatography (GC) and combined gas chromatography-mass spectrometry (GCMS). A single SE54 glass capillary column (0.3 mm i.d. x 20 m long; purchased from Jaeggi, 9043 Trogen, Switzerland) was used. A Carlo Erba Model 2151 AC gas chromatograph equipped with a flame ionization detector (FID) and a special Grob injector was used. Injections were made with the split

Figure 3-3. Microcharcoal trap extraction apparatus from Grob and Zürcher (1976).

VOLATILE EXTRACTION

ref. Grob and Zürcher, 1976



closed. The split was opened (10:1) after 30 seconds. Helium was used as the carrier gas at 0.6 atm pressure at the column front (ca. 3 ml/min). The oven was operated at room temperature for 8 min. and then programmed from 20 to 200°C at 3°C/min. The data were displayed on a strip chart recorder (1 mv full scale). In January, 1978 a CSI Supergrator II was added to facilitate the measurement of peak heights. Peak height measurements are more precise than area measurements for chromatograms containing unresolved compounds.

Compound concentrations were calculated by comparison of GC peak heights to that of the internal standard, 1-chloro-n-octane. A correction was made for peak width differences based on results obtained from resolved standard mixtures. However, the reported concentrations do not take into account FID response differences nor stripping efficiency differences.

GCMS was performed on a Finnigan 3200 system. A single SE52 column (0.3 mm i.d. x 20 m long) was used. EI spectra were obtained at 70 eV. CI spectra were acquired with methane as the reactant gas at 950 microns and using an ionization potential of 130 eV.

Ancillary Data

Seawater temperatures were obtained from daily readings made at the Woods Hole Oceanographic Institution dock. Salinity samples were measured at the WHOI facility. Nutrients were determined using a Technicon autoanalyzer. Chlorophyll a and phaeophytin were measured using the fluorescence technique of Strickland and Parsons (1972). Dr. M. Hulburt (WHOI-biology) counted and identified the phytoplankton from CD samples.

Blanks, Recoveries and Reproducibility

A detailed discussion of the quality characteristics of the methods

used by our laboratory has been reported previously (Schwarzenbach et al., 1978). Blank levels were far below the concentrations of volatile compounds which we observed in samples. Most hydrocarbons were recovered at greater than 85% efficiency. Slightly polar substances, e.g., aldehydes, were recovered at reduced efficiency (about 20-30%). Since the initial report, additional recovery experiments have been performed on compounds which were routinely found in coastal waters. Tetrachloroethylene and dimethyltrisulfide were recovered at high yields (90% and 75% respectively). However, bromoform (40%) and dimethyldisulfide (20%) exhibited poor recovery. These compounds were recovered in the same proportion at all levels tested (10-200 ng/kg).

Replicate samples indicated that the concentrations of the volatile compounds were determined with a precision of about $\pm 10\%$.

RESULTS AND DISCUSSION

Hydrographic and Nutrient Data

Temperature of the water showed a sinusoidal cycle with a maximum of about 23°C in August and a minimum of about -1°C in February (figure 3-4). Salinity showed a general decline throughout the study period (figure 3-4). The $33^{\circ}/\text{oo}$ at the outset of the work was an uncharacteristically high value and may be erroneous. Chase (1972) found that salinity never exceeded $32.5^{\circ}/\text{oo}$ between 1956 and 1969. The salinity variations for samples taken twice a day for a late summer week are exhibited in figure 3-5. The tidal flow brings in saltier water from the west, and the ebb allows fresh water outflow from the neighboring ponds (e.g., Oyster Pond: $1-3^{\circ}/\text{oo}$). This tidal exchange, in conjunction with a period of rain near the beginning of this series, was probably responsible for the daily fluctuations observed over the several days of this example. Data

Figure 3-4. Seawater temperature ($^{\circ}\text{C}$) and salinity ($^{\circ}/\text{oo}$) of biweekly seawater samples from CD and cumulative rainfall (inches) between biweekly sample collections.

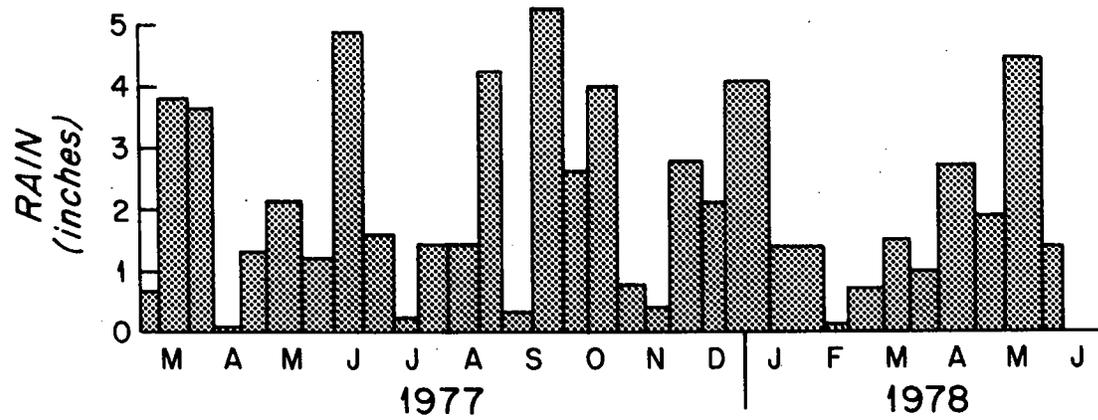
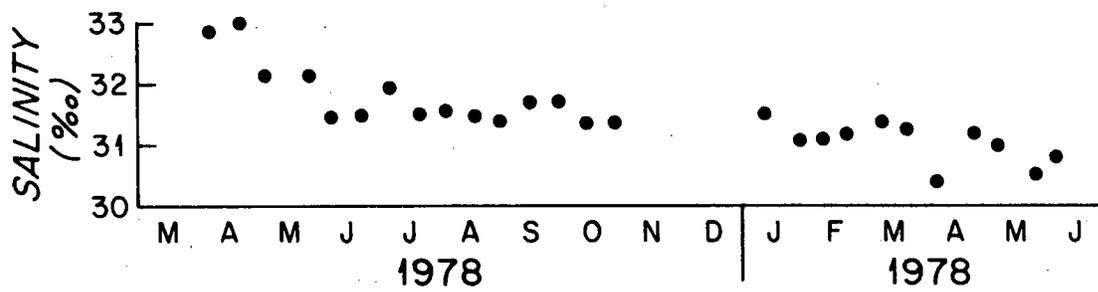
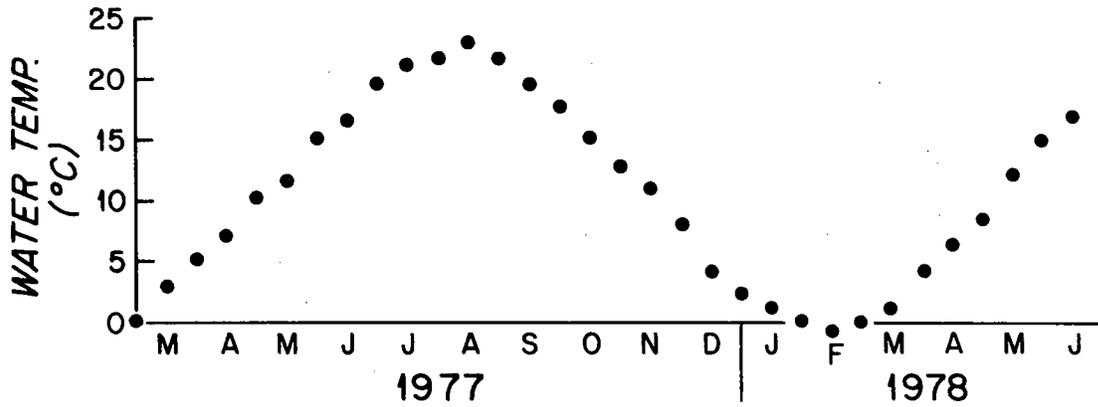
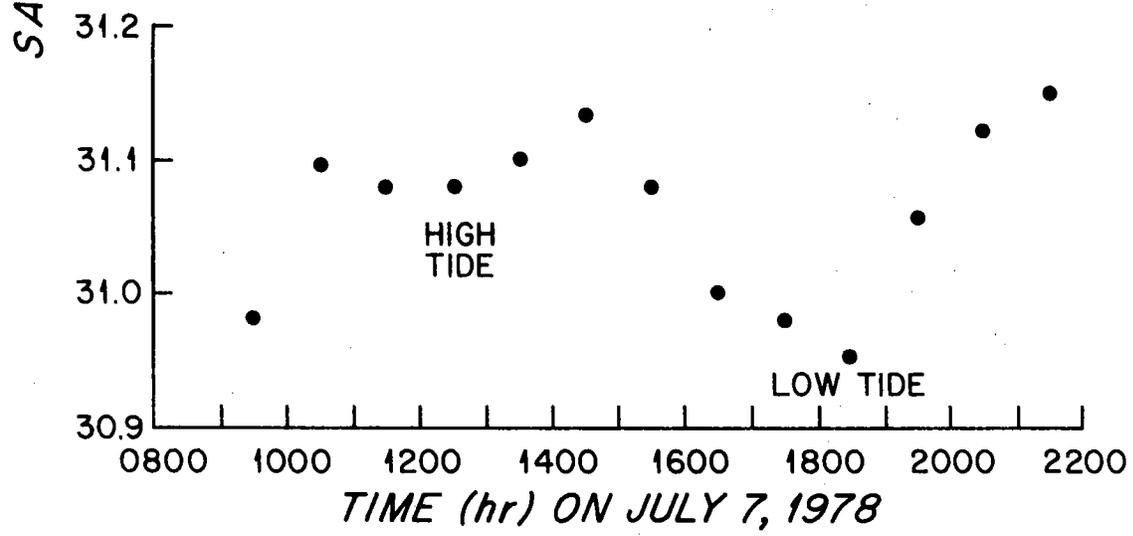
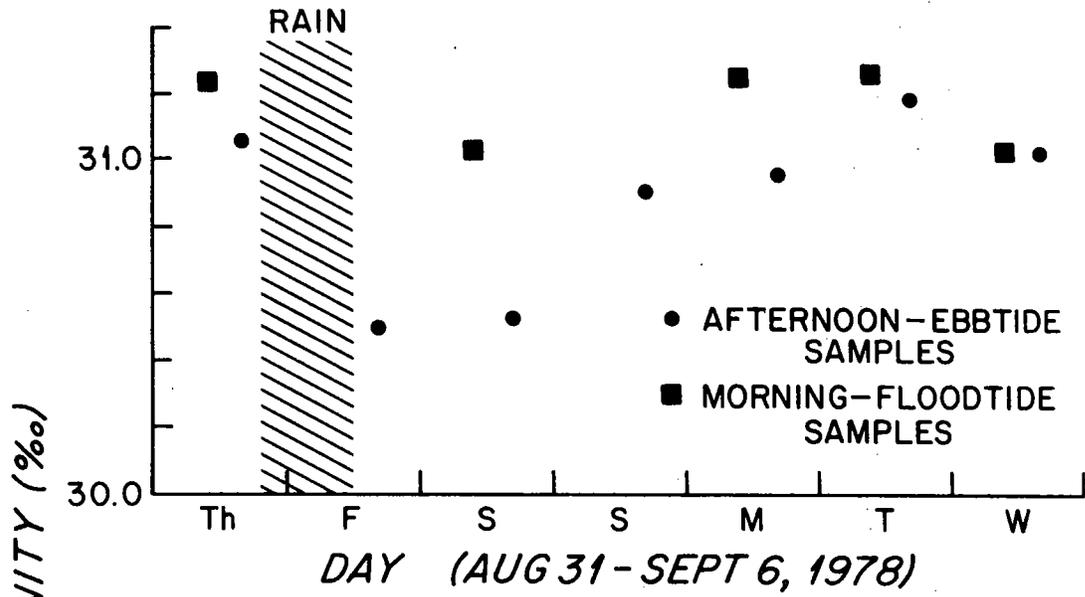


Figure 3-5. Salinity ($^{\circ}/\text{oo}$) versus time in seawater samples from CD.



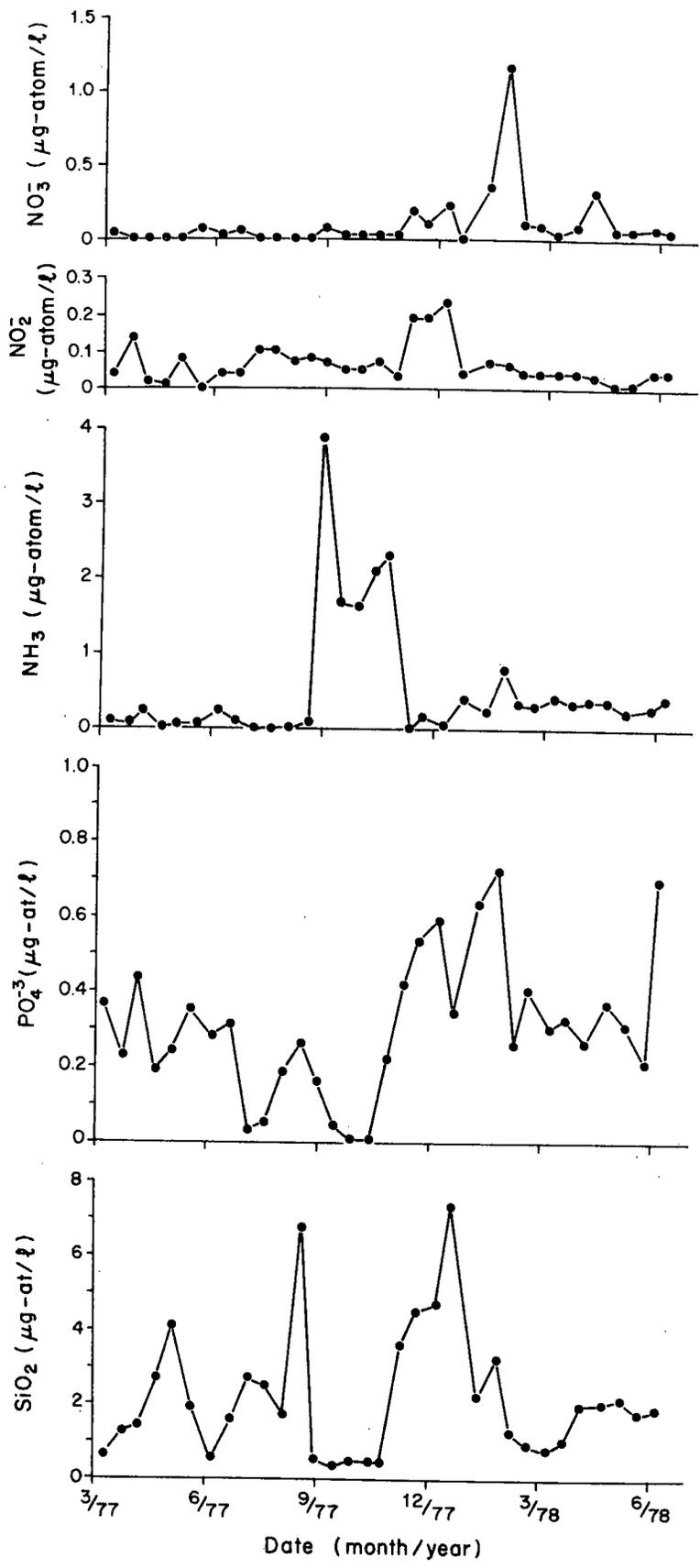
revealing the variation of salinity at CD on an hourly timescale show a range of salinities of about $0.2^{\circ}/\text{oo}$. These salinity data suggest that pond water exiting to the Sound was diluted about 150 times with coastal seawater by the time it reached CD.

During the period of this study, precipitation was spread quite evenly throughout the year (figure 3-4).

The distributions of the nutrients in the waters off CD are shown in figure 3-6. Nitrate, nitrite and ammonia showed an interesting succession with the most reduced form, NH_4^+ , appearing at the end of August and remaining until October. The NO_2^- became important in November and the beginning of December. Finally, NO_3^- grew in while NO_2^- was still present and peaked in concentration in January. NH_4^+ may be introduced after the breakdown of the seasonal thermocline in the nearby Oyster Pond in the late summer with mixing of its anoxic bottom waters and spillage into the Sound (see Emery, 1972). However, samples taken along an offshore transect on October 3 showed similar levels of NH_4^+ in all samples, although salinity increased offshore. Thus it is unlikely that mixing of pond water into the Sound was the source of this NH_4^+ . Rather this ammonia was probably part of the classical picture of fall-winter remineralization of organic matter. The virtual absence of these nutrients throughout the remainder of the year is indicative of the activity of marine plants.

Phosphate demonstrated a more scattered distribution, as did silicate. The simultaneous minima of these two nutrients in October may reflect a fall bloom triggered by the sudden abundance of nitrogen in the form of NH_4^+ . This was not indicated by the chlorophyll a measurements although a fall diatom bloom is common in this region (Fish, 1925;

Figure 3-6. Nutrient concentrations ($\mu\text{g-atom/l}$) in biweekly seawater samples from CD.



Lillick, 1937). Possibly, the benthic algae were responsible for these autumn nutrient depletions.

Phytoplankton

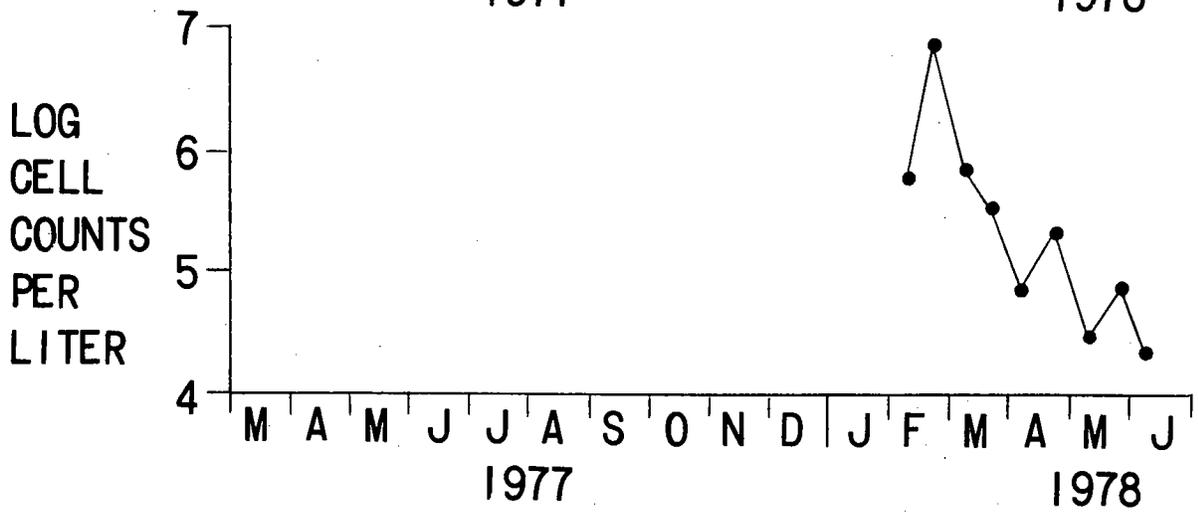
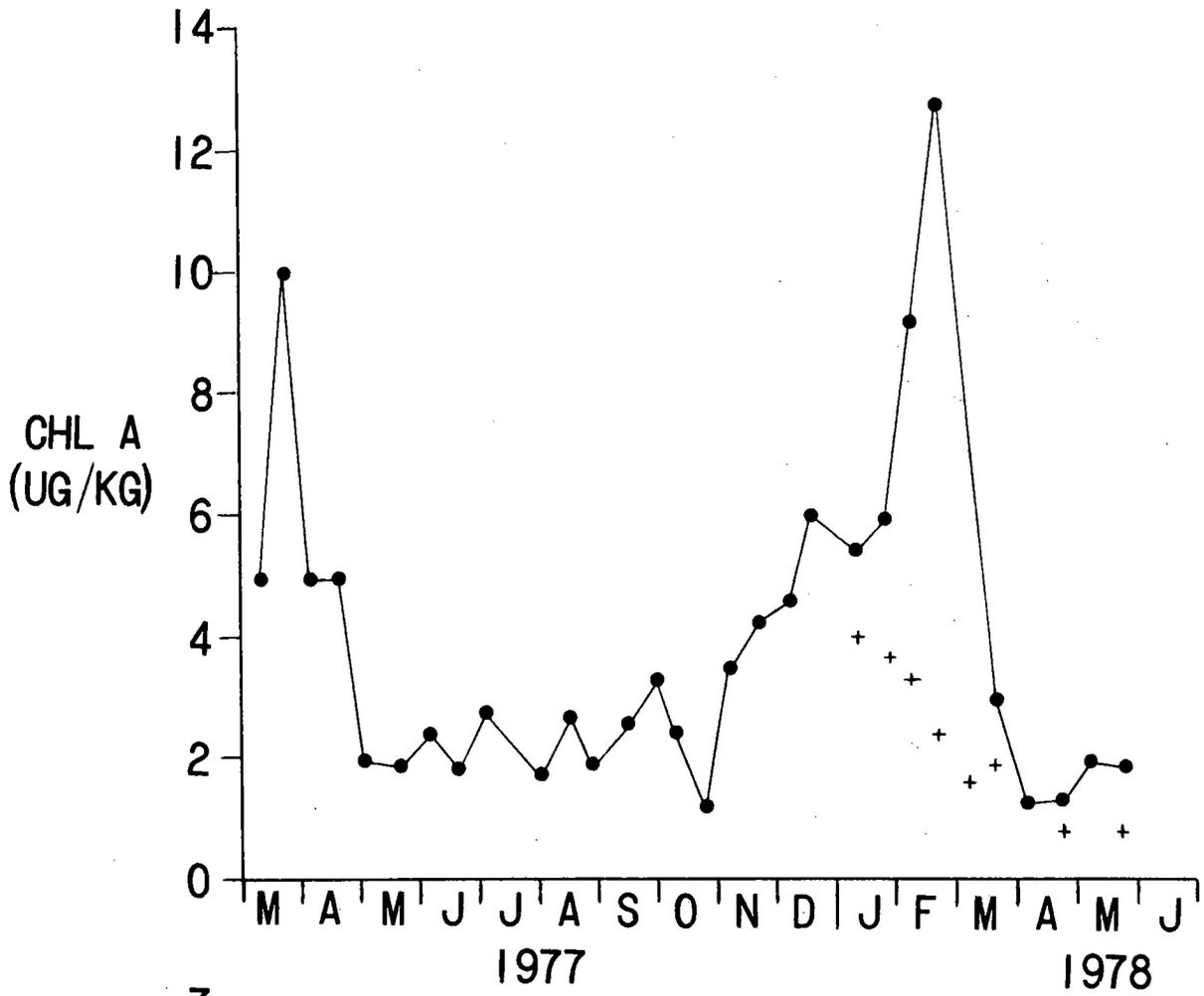
Chlorophyll a concentration peaked in late winter in both years (figure 3-7). Beginning in December, 1977 phaeophytin was determined and showed increased importance suggesting either the active degradation of chlorophyll a or the return of degradation products to the water column as winter storms stirred up the sediment.

Phytoplankton counts revealed a tremendous late-winter bloom of Thalassiosira nordenskiöldii. Several million cells per liter were found at the peak of this bloom. The appearance of this diatom bloom coincided with the February, 1978 chlorophyll a maximum and the disappearance of NO_3^- , PO_4^{-3} , and SiO_2 . More than 85% of the bloom population (by cell numbers) consisted of this species.

Other Observations

In the fall (end of September and again at the beginning of November) large beach washups of the seagrass, Zostera marina, and associated macroalgae occurred with the incidence of strong storm activity. These washups may not be solely attributable to stormy weather, but also to a weakening of the plants by physiological changes generally thought to occur at this time of year (Sand-Jensen, 1975; Ragen and Jensen, 1978). These plant materials could be seen to be pulverized in the surf zone and were responsible for greatly increasing the turbidity of the shallow water.

Figure 3-7. Chlorophyll a ($\mu\text{g}/\text{kg}$) and log phytoplankton counts (cells/liter) in biweekly seawater samples from CD. Crosses indicate phaeophytin concentrations ($\mu\text{g}/\text{kg}$).



Three known incidents of hydrocarbon spills occurred in the region during the study period. In January, 1977 a barge carrying Bouchard no. 2 fuel oil spilled part of its cargo at the head of Buzzards Bay (ca. 16 km. from CD). Sometime later, ice, laden with some of this oil, was observed in the waters near CD. Also, in March, 1978 a large gasoline spill occurred near Block Island in Long Island Sound (ca. 80 km. from CD). Finally, in April of 1978, a second barge spilled oil near the west end of the Cape Cod Canal (ca. 16 km. from CD). Only the first of these accidents could be clearly related to the level of volatile organic compounds at CD (see below and Schwarzenbach et al., 1978).

Variations of Volatile Organic Compounds

Alkylated Benzenes. The seasonal changes in the concentrations of the C₂- and C₃-alkylated benzenes are shown in figures 3-8 and 3-9. All of these compounds, except ethyl benzene (see later discussion), closely covary. The C₂-benzenes usually appear at an isomer ratio of ethyl benzene: m + p-xylenes: o-xylene = 1:2:1. These isomers were always more abundant than the C₃-benzenes. Still more highly substituted benzenes were also observed at lower concentrations and their temporal distributions parallel those of the lower homologues.

In order to demonstrate the nature of a source of the alkylated benzenes, one of them, o-xylene (or more properly, 1,2-dimethyl benzene) has been replotted including three samples taken the three days immediately following the Memorial Day weekend (May 27-29, 1978) (figure 3-10). One can see a tremendous fluctuation in the concentration of this compound at this time over a very short time interval. Indeed, the sample following the weekend shows the highest concentration found all year.

Figure 3-8. C₂-benzenes (ng/kg) in biweekly seawater samples from CD. Question marks indicate samples in which ethyl benzene coeluted with an unknown compound. The open circle shows ethyl benzene concentration found when volatiles were chromatographed on a column which resolved these compounds.

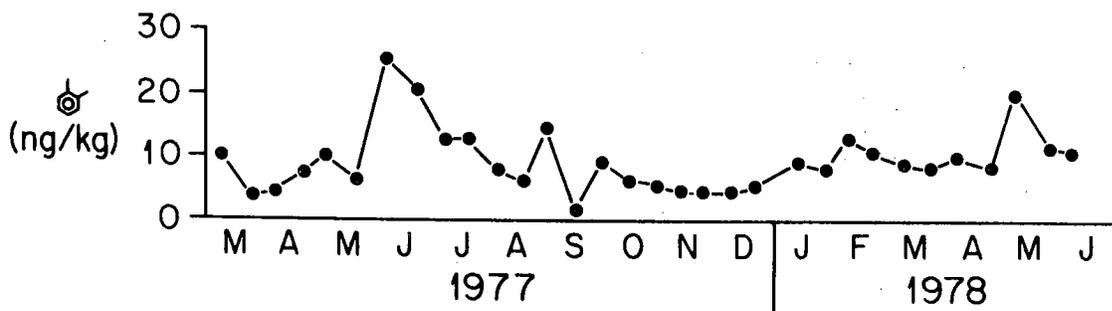
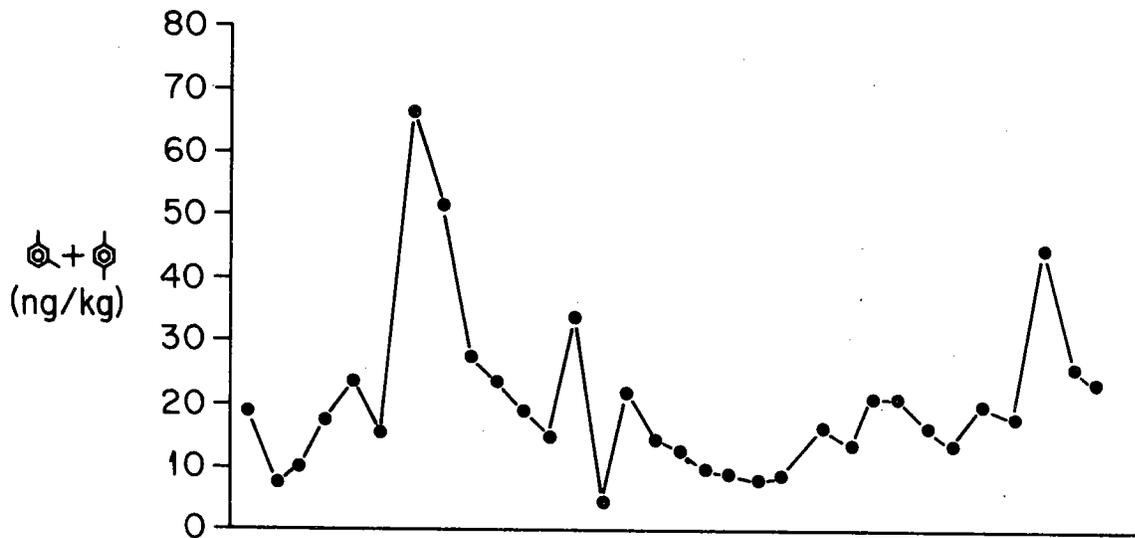
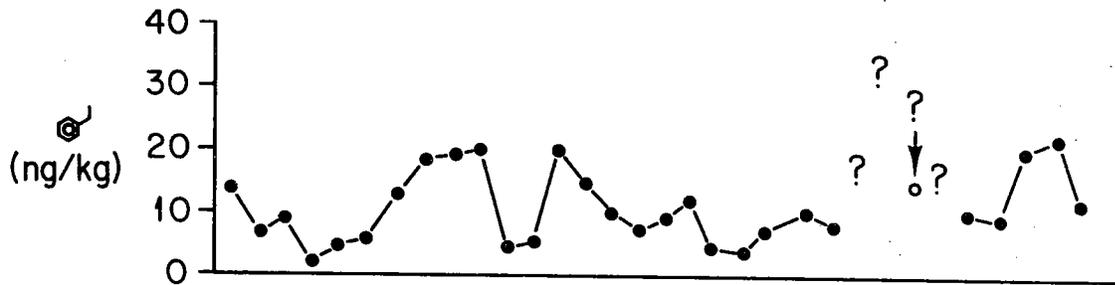


Figure 3-9. C₃-benzenes (ng/kg) in biweekly seawater samples from CD.

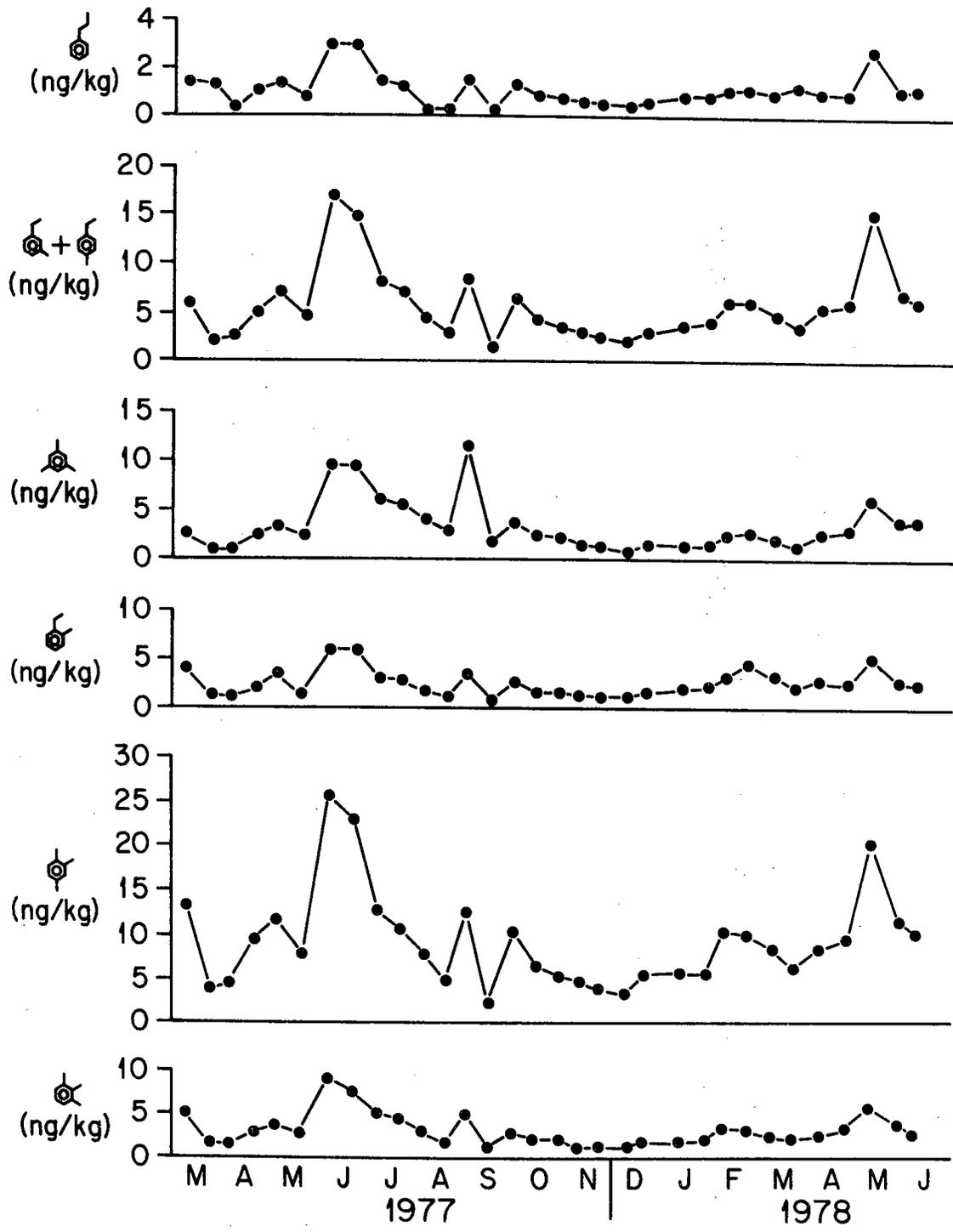
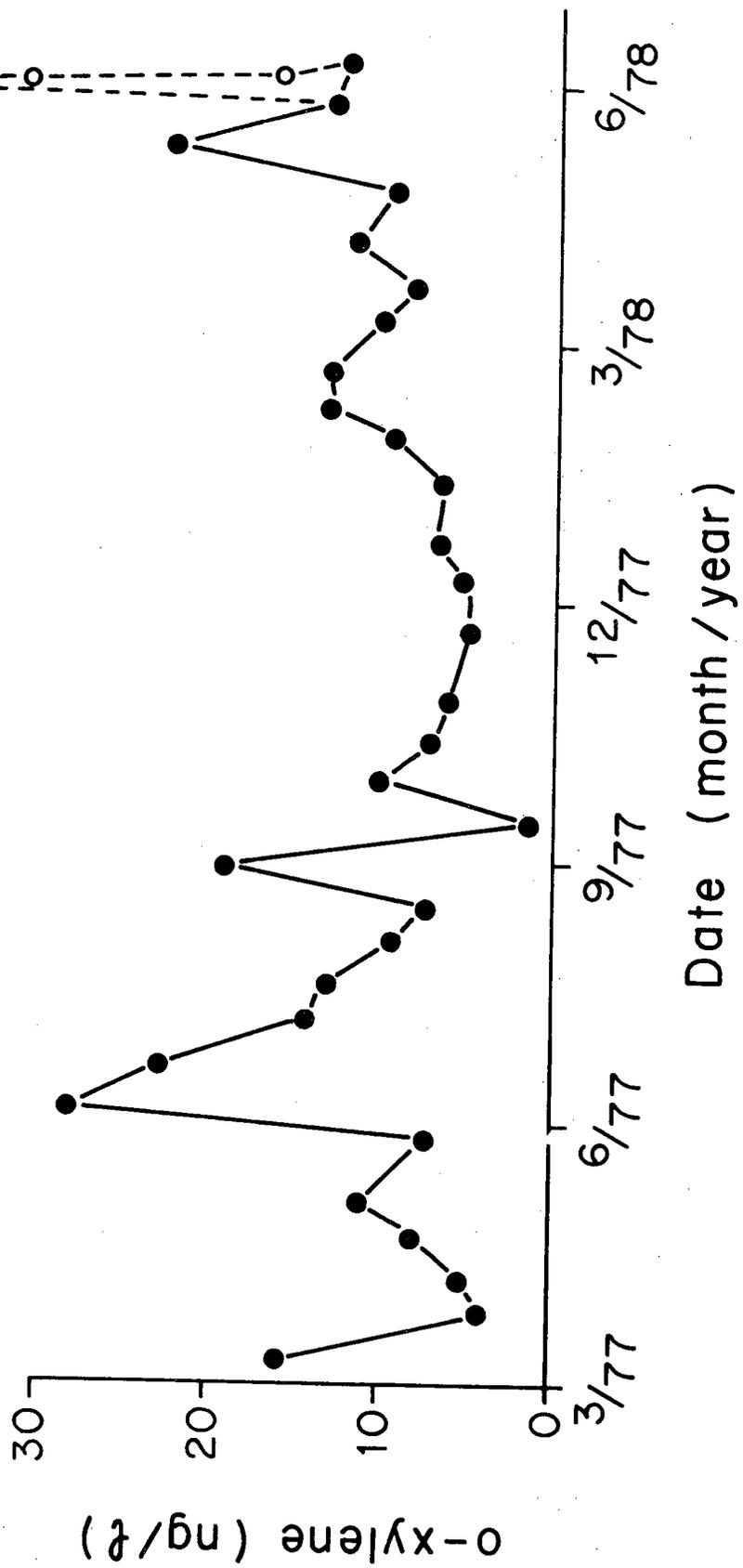


Figure 3-10. O-xylene concentrations (ng/l) in biweekly seawater samples from CD (closed circles) and in 3 seawater samples taken during the week after the Memorial Day holiday weekend, May 27-29, 1978 (open circles).



These data suggest the source of these alkylated benzenes may be related to the activities of tourists and summer residents on Cape Cod. A plot of the o-xylene data according to the day of the week in which the samples were taken clearly shows higher levels earlier in the week (figure 3-11). Separating the summer data from those of the "off season" further emphasizes this trend in the summer. Thus one may reasonably hypothesize that gasoline use by automobiles or motorboats has introduced these pollutant hydrocarbons into coastal seawater, especially during periods of intense tourism. Levels climb to about 3 times those seen during the rest of the year. Based on the plot of o-xylene concentration versus day of the week, it appears that this anthropogenic input is removed from the coastal seawater with a half-life of about 1-2 days. This is consistent with the observed decline of the o-xylene levels after the Memorial Day weekend, 1978. A combination of air-sea exchange and tidal flushing may be sufficient to lower the o-xylene levels this quickly. It is also apparent from this information that the time scale of interest for these volatiles is on the order of days and not weeks.

Ethyl benzene concentrations do not always appear to covary with the other alkylated benzene isomers because ethyl benzene was unresolved from another compound in the chromatograms. CI-CH₄ mass spectral examination of this mixed peak in a sample acquired in February, 1978 revealed the simultaneous presence of a compound of molecular weight 108 (figure 3-12). This molecular weight assignment is assured due to presence of M + 1, M + 29, and M + 41 peaks in the CI-CH₄ spectrum. The m/e 95 fragment suggests that the compound contains a terminal ethenyl group (Field, 1968), while the m/e 93 fragment indicates the presence of a terminal methyl substituent. It is known that the brown alga, Fucus spp., utilizes trans, cis-1,3,5-octatriene (mw 108) as its sexual chemotactic agent

Figure 3-11. O-xylene concentrations (ng/l) in biweekly seawater samples from CD grouped according to the day of the week on which they were collected.

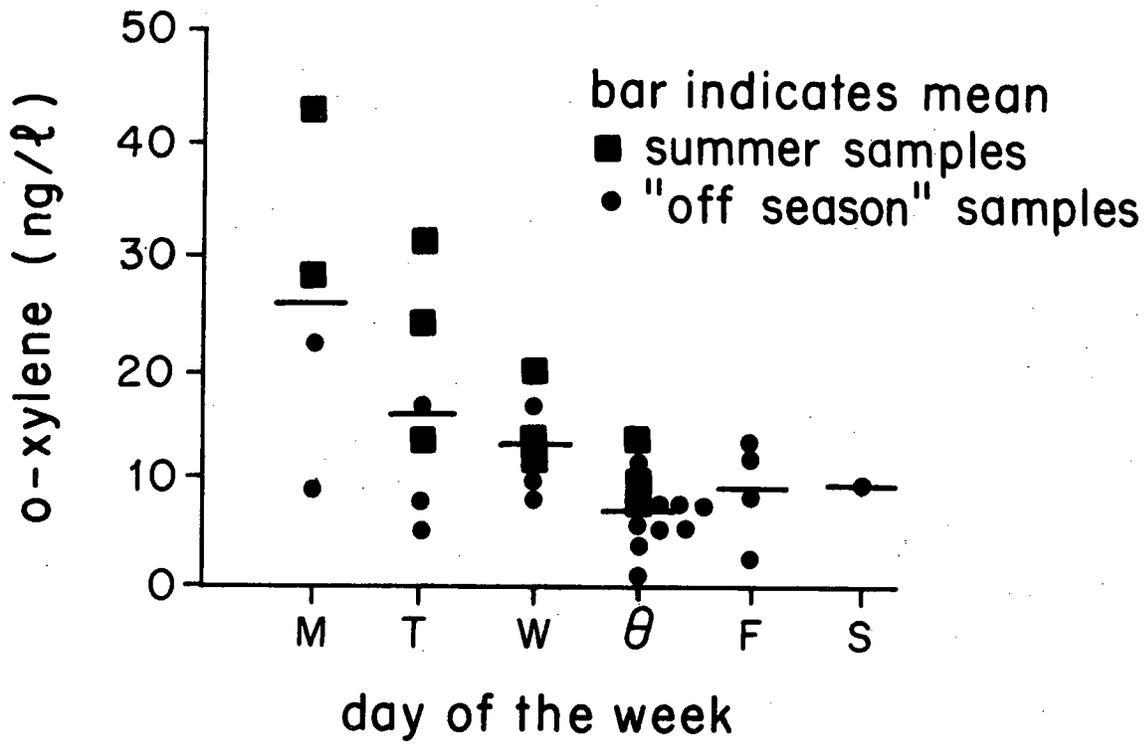
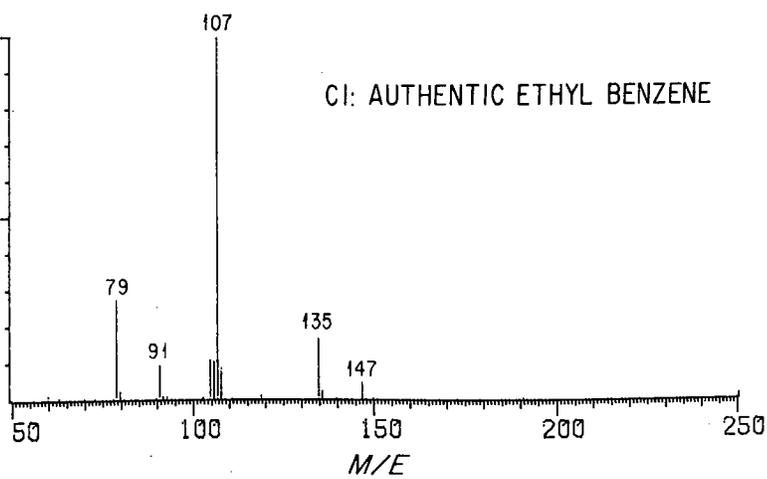
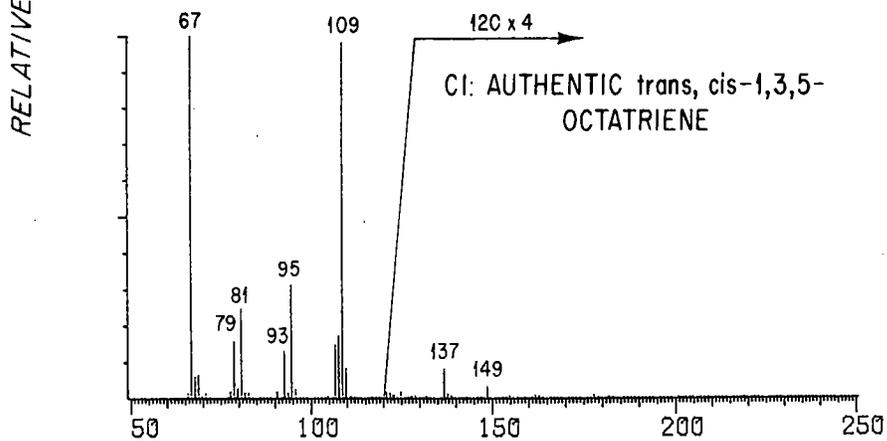
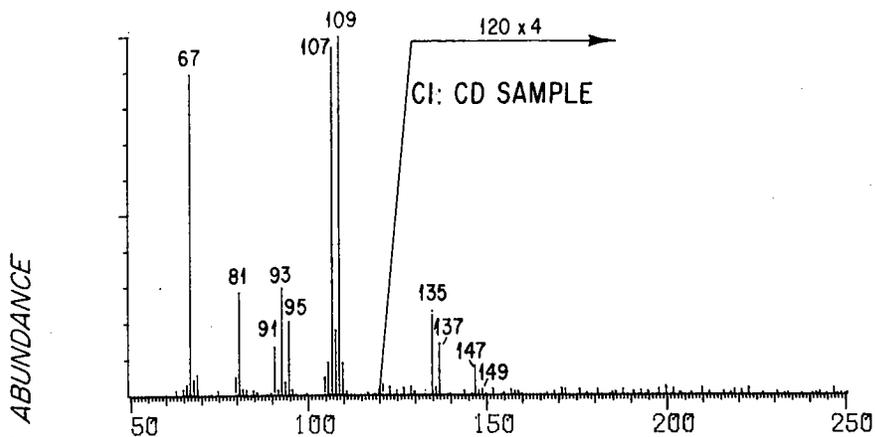
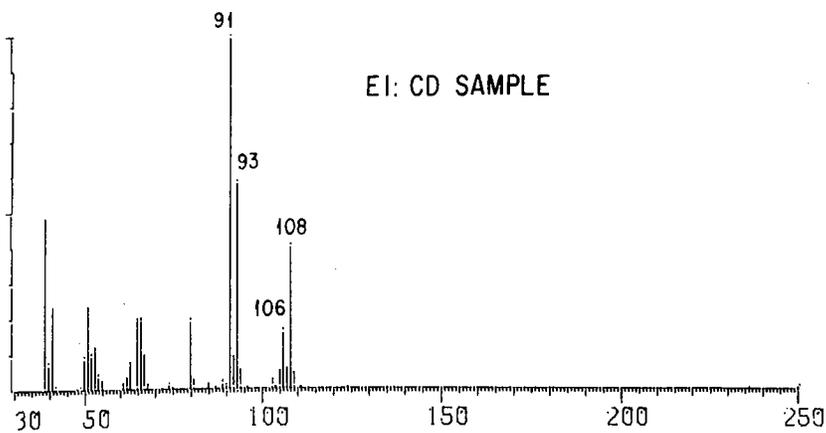


Figure 3-12. Electron impact (EI) and methane chemical ionization (CI) mass spectra of unknown compound (mixed with ethyl benzene) isolated from seawater samples collected from CD in February and March 1978. Also shown are CI spectra from authentic trans, cis-1,3,5-octatriene and ethyl benzene. Fragments from m/e 76-79 were not collected in the sample spectra because of solvent (CS₂) interference. M/E values greater than 120 are amplified 4 times in the CI spectra of the CD sample and trans, cis-1,3,5-octatriene.



(Müller and Jaenicke, 1973). Fucoserraten, as this structure is called, was obtained from Dr. Müller and its GC and spectral properties ascertained. The authentic compound elutes later than ethyl benzene (RICA* = 101) on the SE54 column (RICA* = 110) but its CI-CH₄ spectrum is very similar to that of the unknown (figure 3-12). The only difference is that the authentic fucoserraten has m/e 95 about 2 times m/e 93, while the compound found in this study showed the reverse. This suggests that the unknown compound is a closely related isomer of fucoserraten, e.g., trans, trans-1,3,5-octatriene.

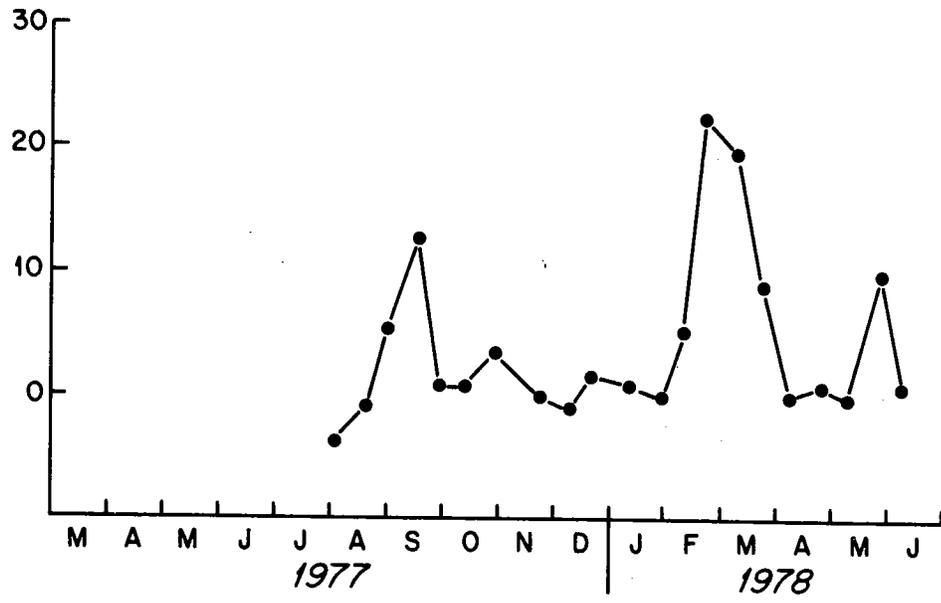
By GCMS analysis, one may estimate that the February 22, 1978 sample contained a 60:40 mixture of the unknown and ethyl benzene. This estimate of the concentration of ethyl benzene corresponds to that which one might expect from the typical isomer ratio of this compound and the xylenes. This suggests that one may obtain an idea of the temporal variation of the "octatriene" by plotting the deviation of ethyl benzene from that expected from the other C₂-benzenes versus time (figure 3-13). A peak in concentration of this material occurred in late February and March.

Mathieson et al. (1976) have reported that sunlight may be the key environmental variable controlling the release of gametes by Fucus spp. The solar irradiance level, which they found to be critical, occurred at the beginning of February at CD. Thus it is possible that this unknown was related to the algal sexual activity. Isomerization of fucoserraten (especially in sunlight) may have quickly produced the unknown observed in this year-round study. This compound was also observed in surface seawater from the upwelling region off Peru (chapter 2).

* RICA: retention index relative to the 1-chloro-n-alkane standards, e.g., 110 means that the compound eluted 10% of the way between the 1st i.s. (1-cl-n-hexane) and the 2nd (1-cl-n-octane).

Figure 3-13. Estimated unknown compound concentrations (ng/kg) in biweekly seawater samples from CD.

UNKNOWN
m.w. 108
(ng/kg)

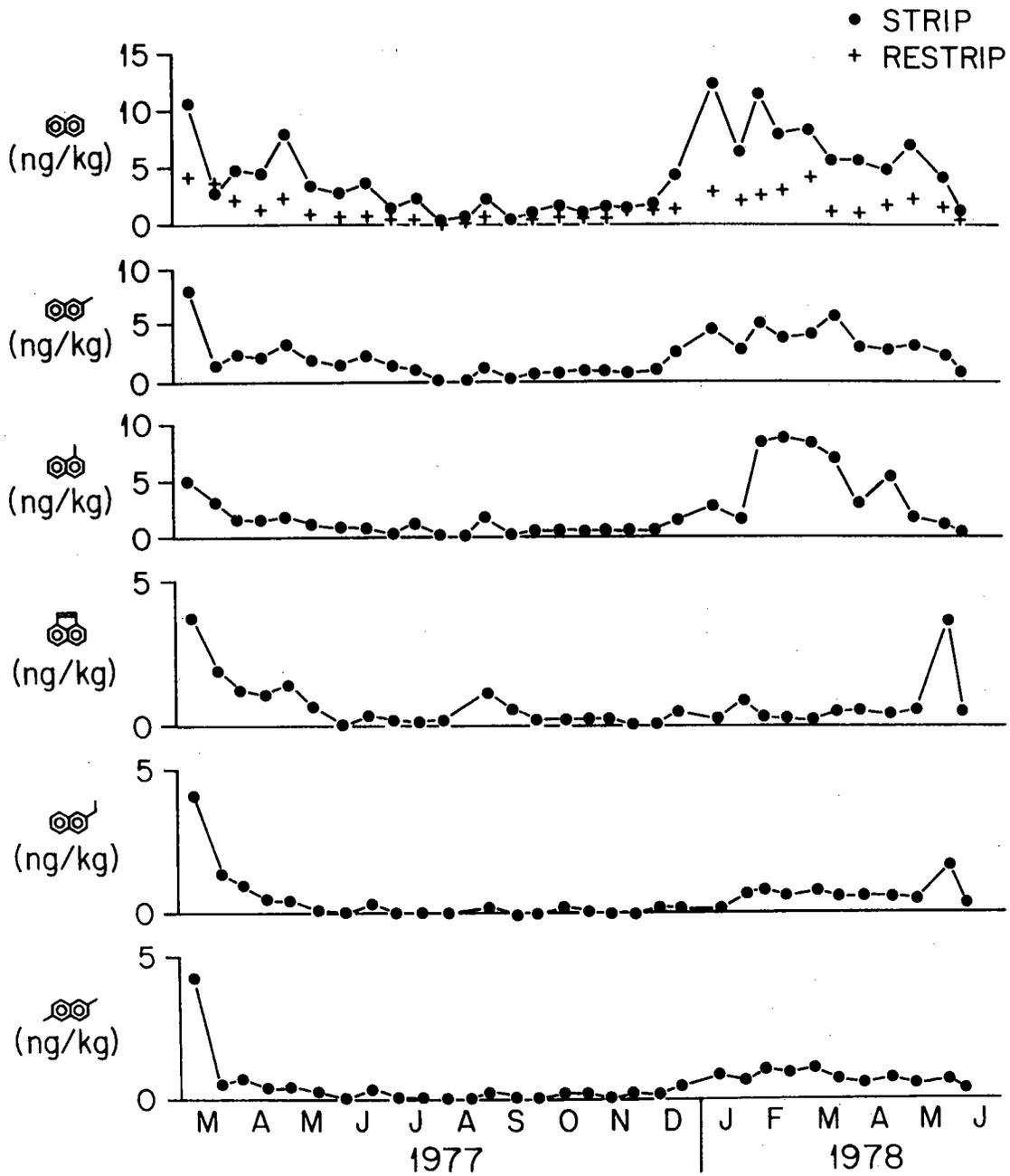


Naphthalenes. The naphthalenes showed a different temporal function in their concentrations (figure 3-14). The March 8, 1977 sample was rich in these compounds (as it was for alkylated benzenes). Examination of the isomer relations at CD and those from a sample of no. 2 fuel oil reveal identical patterns (Schwarzenbach et al., 1978). Thus direct input of oil was the most likely source of these compounds at that time. However, two weeks after the next sample was taken, the seawater concentration of these compounds had decreased dramatically. As noted in Schwarzenbach et al. (1978) a period of intense storm activity between these two samples may have been responsible for this thorough flushing. It is difficult to identify either the atmosphere or the sediments as the ultimate sink, as transfer to either reservoir would be enhanced during storm-induced introduction of bubbles or particles into the water.

Naphthalenes also showed relatively high levels in the winter of 1977-1978. Possibly this may be attributed to the use of home heating oil at this time of year.

The homologue ratios may add some insight into the source of naphthalenes throughout the year. By analogy to the higher polycyclic aromatic hydrocarbons, the ratio of naphthalene to the sum of the C₁-naphthalenes may reflect the temperature of formation of the source material (Blumer and Youngblood, 1975a, 1975b, and 1976) as well as the environmental transport processes which brought them to CD (Laflamme and Hites, 1978). For example, if a high temperature source was responsible, naphthalene concentration should be greater than that of the methyl substituted compounds. If atmospheric transport of the compounds to CD has occurred, the ratio may increase as the lighter naphthalene exhibits a higher vapor pressure and therefore is more easily volatilized. Obviously, the possible combinations of source ratios and their environmental transformations are numerous and complex.

Figure 3-14. Naphthalene and substituted naphthalenes (ng/kg) in biweekly seawater samples from CD. Closed circles show concentrations recovered in first 2 hours of stripping, while crosses show concentrations recovered in an additional 2 hours of stripping.



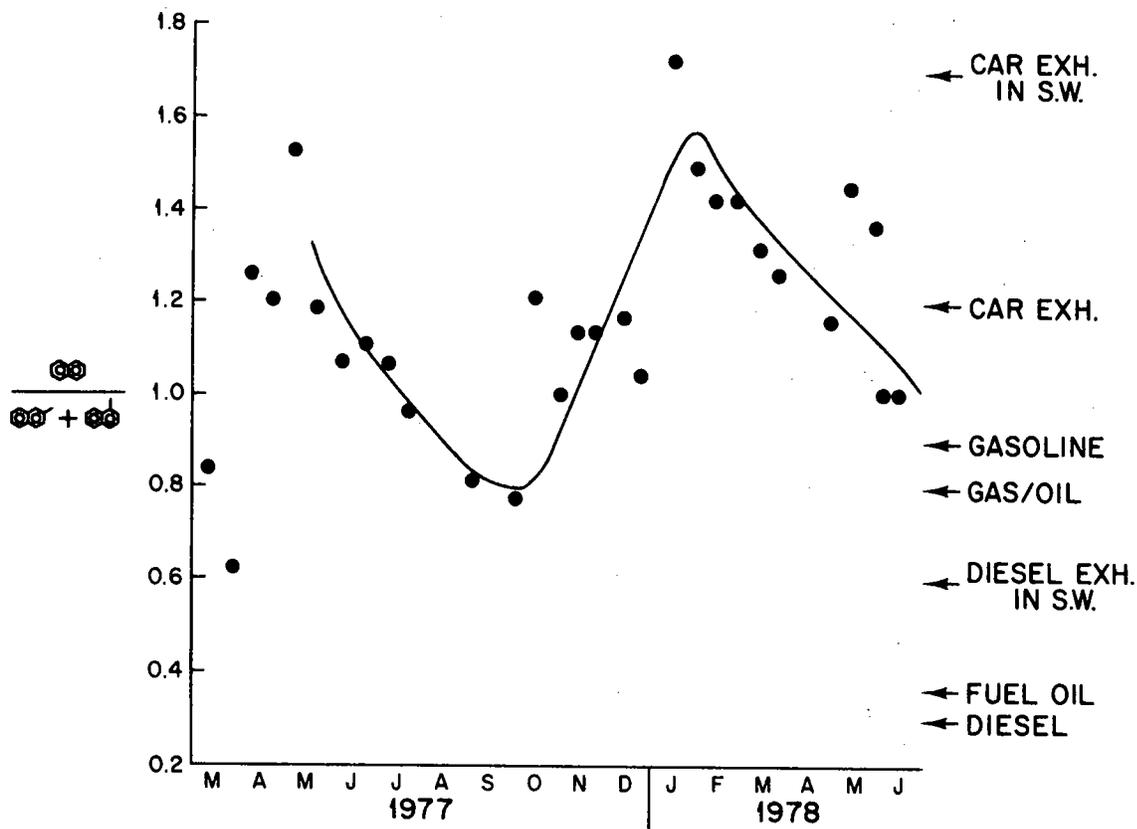
The naphthalene-to-methyl naphthalenes ratios are plotted for all the year-round samples in figure 3-15. A sinusoidal pattern is apparent with low ratios in the summer and high ones in the winter. The March, 1977 sample was contaminated by the oil spill and consequently had a very low ratio.

Also shown (figure 3-15) are the ratios found in laboratory studies of various possible sources of these aromatic compounds. Gasoline, gasoline and oil for outboards, diesel fuel, and API standard no. 2 fuel oil were diluted and analyzed directly by GC. Car exhaust and diesel exhaust were collected in glass flasks, stripped onto charcoal traps, extracted with CH_2Cl_2 , and analyzed by GC. These exhausts were also connected to flasks containing exhaustively prestripped seawater (gently stirred) and allowed to exchange the volatiles between the vapors in one flask and the water in the other. After one day, the water was stripped and chromatography was performed on the volatile concentrate.

These source data, in conjunction with the year-round pattern, suggest that more direct inputs to coastal seawater occurred in the summer than in the winter. The ratios seen in the winter samples indicate that a good deal of fractionation must have taken place to produce such high values from any of the known sources. The general trend in the experimental data was to increase the ratio by burning a fuel and to increase it still further by atmospheric transport. Therefore, these data may indicate that atmospheric sources become more important in the winter (e.g., from the burning of home heating oil).

A significant concentration of naphthalene was also found in the restrips (figure 3-14). This suggests that this compound was somehow unavailable for exchange into the vapor phase of the purging bubbles. The relatively low air-water partition coefficient (0.016 as compared

Figure 3-15. Naphthalene to C₁-naphthalenes ratios in biweekly seawater samples from CD. Arrows on the right margin indicate the naphthalene to C₁-naphthalenes ratios found in laboratory studies.



with 0.29 for o-xylene and 0.076 for heptanal) of this compound indicates that it might not be stripped effectively; filtering experiments suggest that about half of the naphthalene can be removed by a glass fiber filter from seawater. Consequently, it is likely that the naphthalenes occur as both dissolved and particulate species in seawater, and neither of these forms are readily purged from water samples.

Alkanes. The temporal variations of the C_{13} to C_{17} n-alkanes and of pristane (2,6,10,14-tetramethyl-pentadecane) are shown in figure 3-16. The levels were high in March, 1977 as a result of the oil spill. This interpretation is supported by an odd-even carbon preference index ("CPI") calculated as $nC_{15} + nC_{17}/nC_{14} + nC_{16}$ which at this time was 1.2 (figure 3-17). Pentadecane showed two maxima in the summer of 1977 and another beginning in the summer of 1978. Schwarzenbach et al. (1978) attributed this to production by the extensive benthic algal growth in the area. A biological source was also suggested by the high "CPI". Heptadecane also showed two concentration peaks in the summer of 1977, the second of which corresponds to the second pentadecane spike. Again, the high "CPI" suggests a biological source of this hydrocarbon for both of these concentration spikes. Benthic algae in this region are known to be rich in these compounds (Clark and Blumer, 1967; Youngblood et al., 1971; Youngblood and Blumer, 1973). The July peak demonstrated a nC_{17} /pristane ratio of about 120 suggesting a green algal source (Clark and Blumer, 1969). The late summer peak in the concentrations of nC_{15} and nC_{17} may reflect the onset of senescence in some of the seaweeds, or be due to other physiological changes. As mentioned earlier, large washups of seagrass and macroalgae were observed soon after these peak levels were observed.

Figure 3-16. Alkane concentrations (ng/kg) in biweekly seawater samples from CD. Closed circles show concentrations recovered in first 2 hours of stripping, while crosses show concentrations recovered in an additional 2 hours of stripping. The concentrations of hexadecane in March and April, 1978 include an unresolved substance as determined by GCMS.

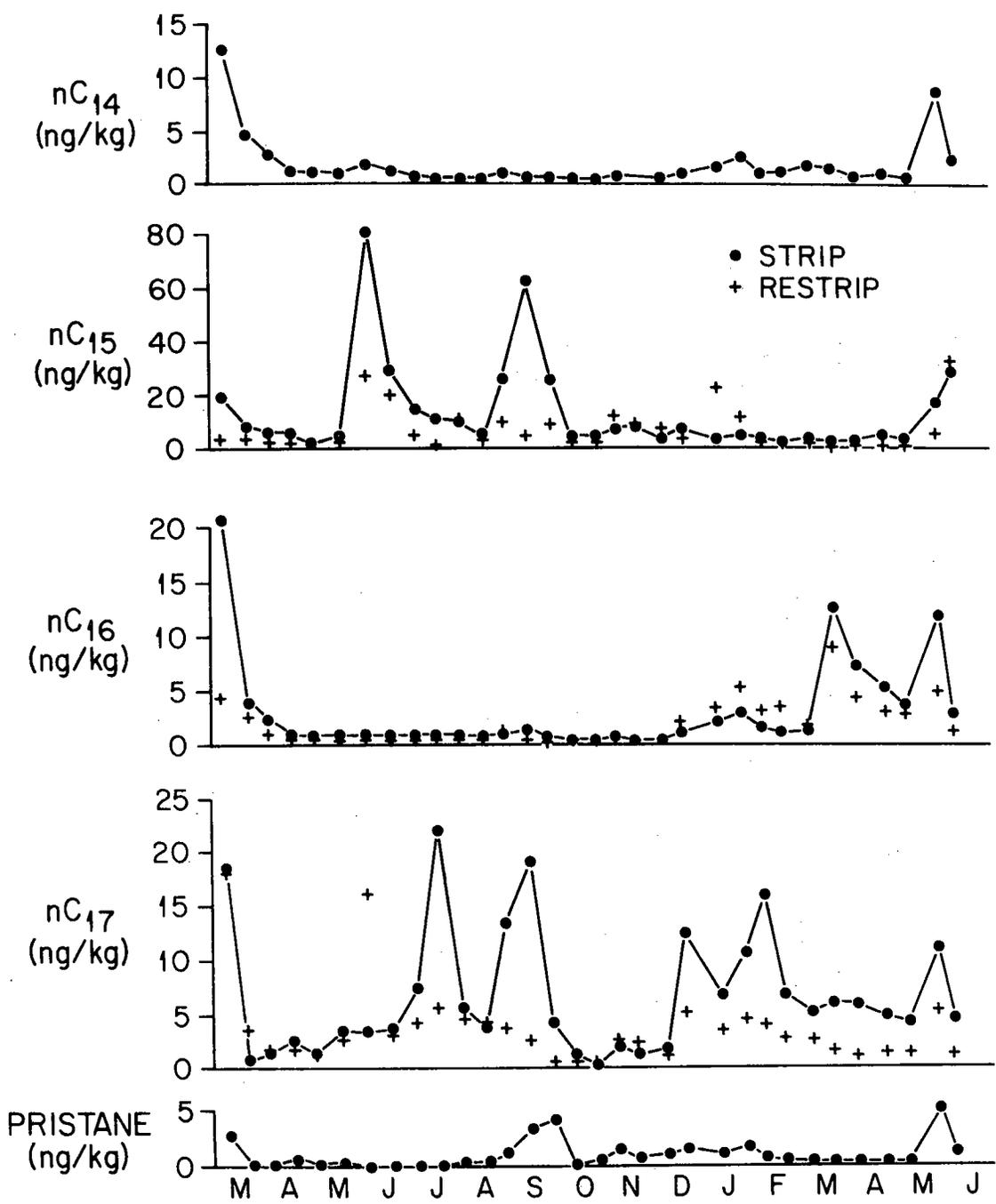
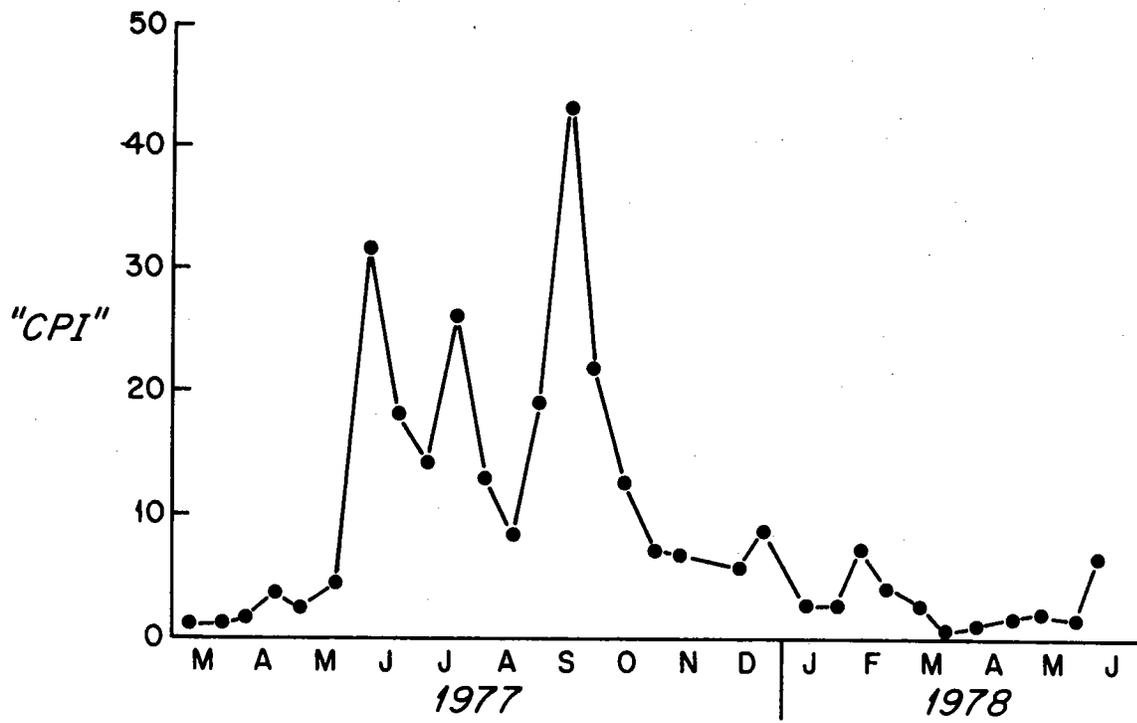


Figure 3-17. "Carbon preference index" (defined as $nC_{15} + nC_{17} / nC_{14} + nC_{16}$) in biweekly seawater samples from CD.



The winter peaks of heptadecane are of unknown origin. Possibly, they reflect the return to the water from the sediments of previously deposited material.

The increased concentrations of all the n-alkanes in late May, 1978 with "CPI" of 1.4 indicate a pollution event. However, only acenaphthalene and 2-ethyl naphthalene covary with the n-alkanes among the various naphthalene isomers investigated. Possibly the source was of a higher boiling or weathered petroleum fraction.

As was the case for naphthalene, the n-alkanes were also found in abundance in the restrips (figure 3-16). The filtering experiments also demonstrated that about half the concentrations of these compounds could be retained by a glass fiber filter. One concludes that these compounds occur in seawater either adsorbed to particles or associated with microorganisms.

(The hexadecane peak in March and April was due to the occurrence of another compound coeluting (figure 3-16); this is supported by GCMS.)

Aldehydes. A group of straight chain aldehydes (C_6-C_{10}) were recovered throughout the year from the seawater at CD (figure 3-18). These compounds represent a highly reactive, both biochemically and chemically, group of volatiles. The temporal variation of the aldehydes in restrips is similar to that seen in the initial (figure 3-18) strips and would be expected to be so from the known poor recoveries of these compounds. The most important feature of the year-round patterns for these aldehydes was the concentration maxima in the spring and fall corresponding to periods of algal blooms (see discussion of nutrients and chlorophyll a). This was most pronounced in the spring when the phytoplankton bloom was most intense (figure 3-19). These compounds may be the result of direct

Figure 3-18. C₆-C₁₀ aldehyde concentrations (ng/kg) in biweekly seawater samples from CD. Closed circles show concentrations recovered in first 2 hours of stripping, while crosses show concentrations recovered in an additional 2 hours of stripping.

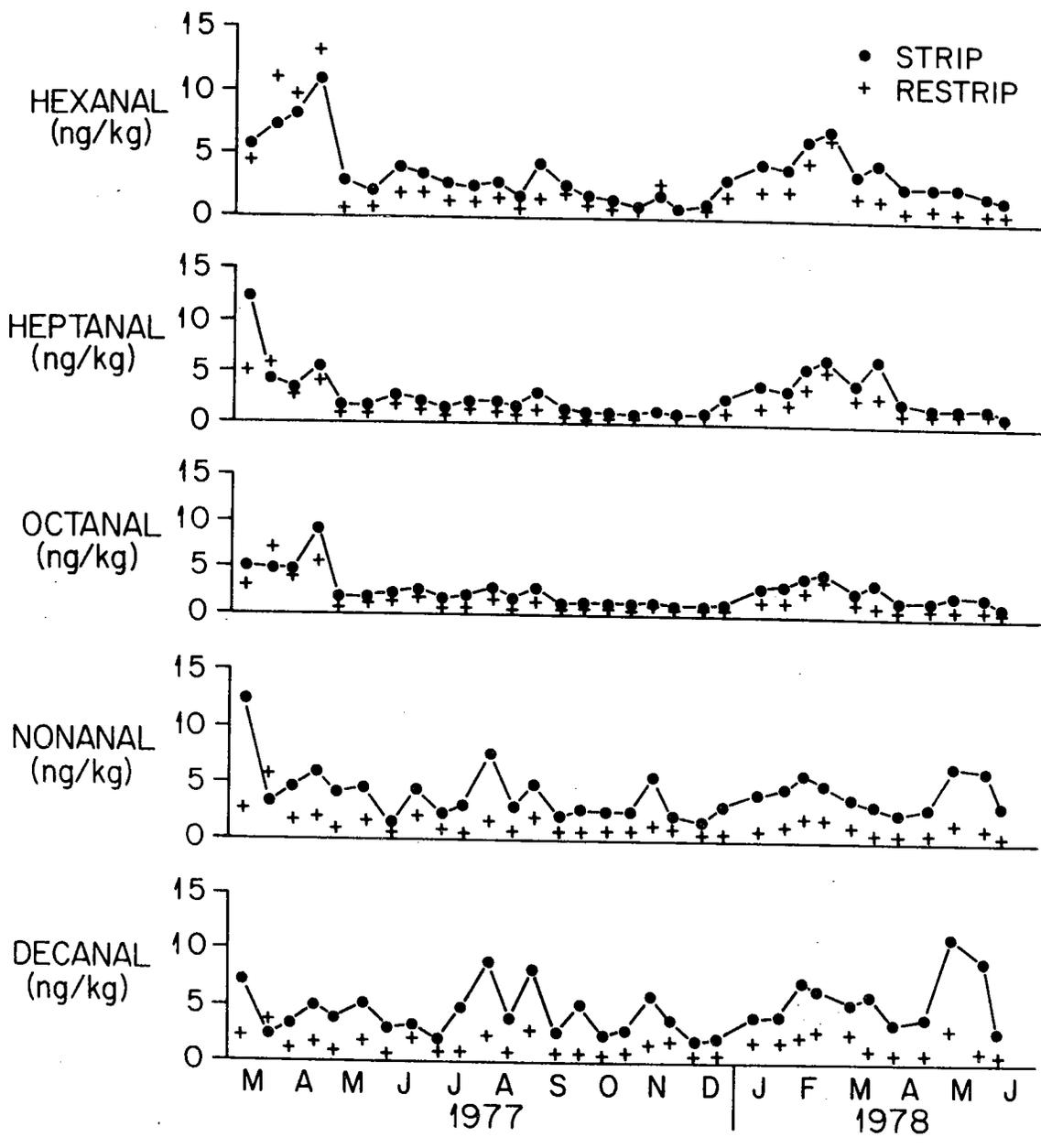
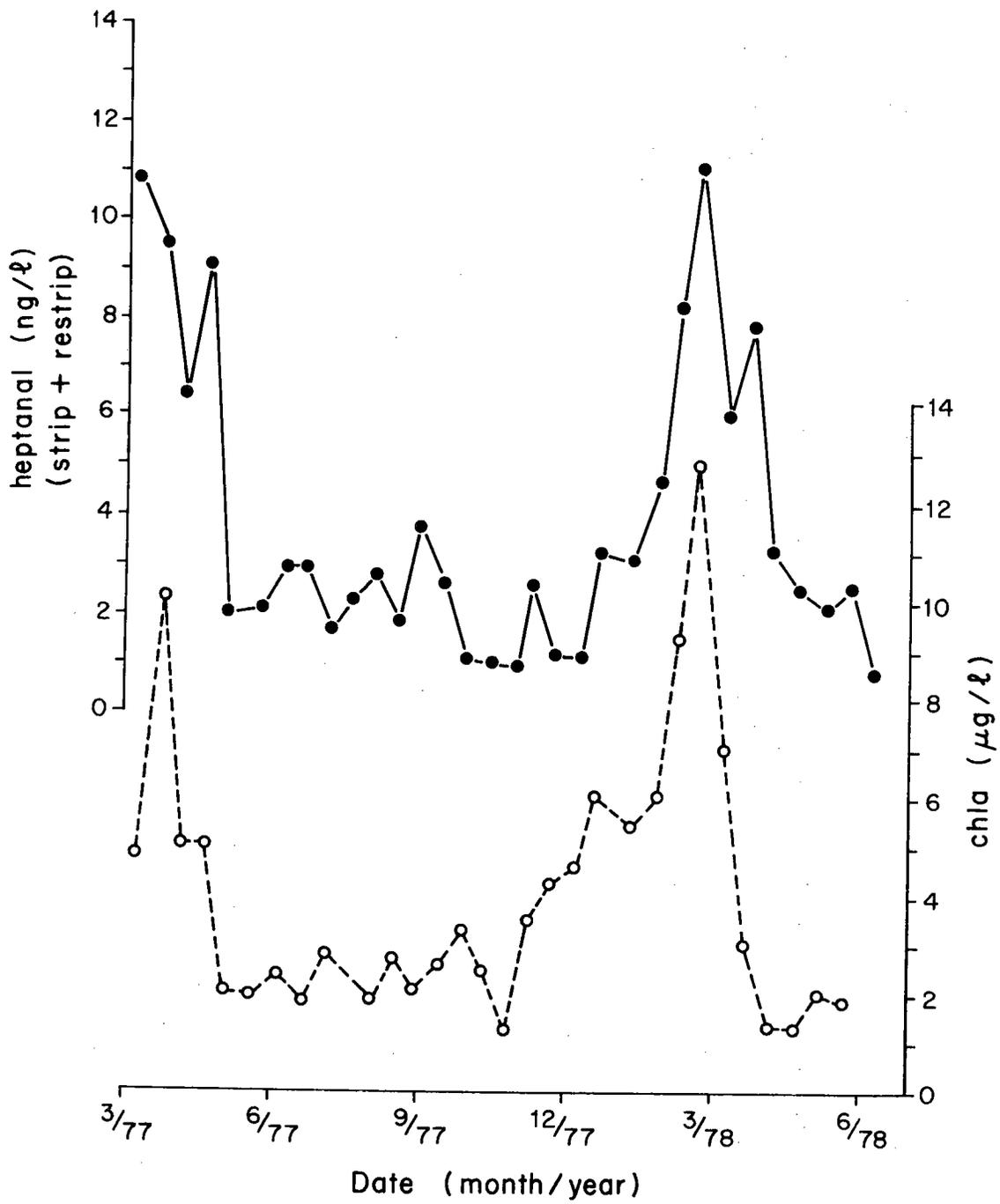


Figure 3-19. Heptanal concentrations (ng/l) and chlorophyll a concentrations ($\mu\text{g}/\text{kg}$) in biweekly seawater samples from CD. Heptanal concentrations were obtained by summing the recoveries from both the first 2 hours and the additional 2 hours of stripping.



production by the plankton or may represent oxidation products of algal lipids. Potential precursors and a viable mechanism for chemical oxidation of algal fatty acids to C₆-C₁₀ aldehydes are described in detail in chapter 2 (figure 2-12).

A group of longer-chain aldehydes became particularly abundant during the phytoplankton bloom of February, 1978. These included C₁₂ to C₁₅ saturated and unsaturated aldehydes (figure 3-20). The bloom was more than 85% Thalassiosira nordenskiöldii as mentioned previously; thus it seemed likely that this diatom was the ultimate source of this material. Figure 3-21 demonstrates the correlation of these compounds with cell numbers of this diatom.

Accordingly, pure cultures of this diatom were grown in the laboratory. Cultures (1600 ml of $\sim 3 \times 10^4$ cells/ml in log phase growth) were extracted with CH₂Cl₂ after collection on a glass fiber filter, and the extract chromatographed. No evidence for the presence of any aldehydes could be found. Another culture was stripped directly as normal volatile analysis of water samples is performed, but no aldehydes were found by this approach. Finally, approximately 100 ml of CD seawater were added to a culture and incubated for two additional weeks (stationary phase). Stripping this culture did not provide any aldehydes either. Thus, it seems that the diatom does not produce the aldehydes directly.

Possibly, zooplankton plays a role in aldehyde production. Another possibility is that photochemical oxidation (which cannot occur with the lights used to incubate algae) of algal metabolites produced the aldehydes. Also, a less abundant phytoplankton species may have released these compounds during the bloom.

Dimethyl Polysulfides. Another group of compounds (figure 3-22) observed

Figure 3-20. C₁₂-C₁₅ aldehyde concentrations (ng/l) in some biweekly seawater samples from CD.

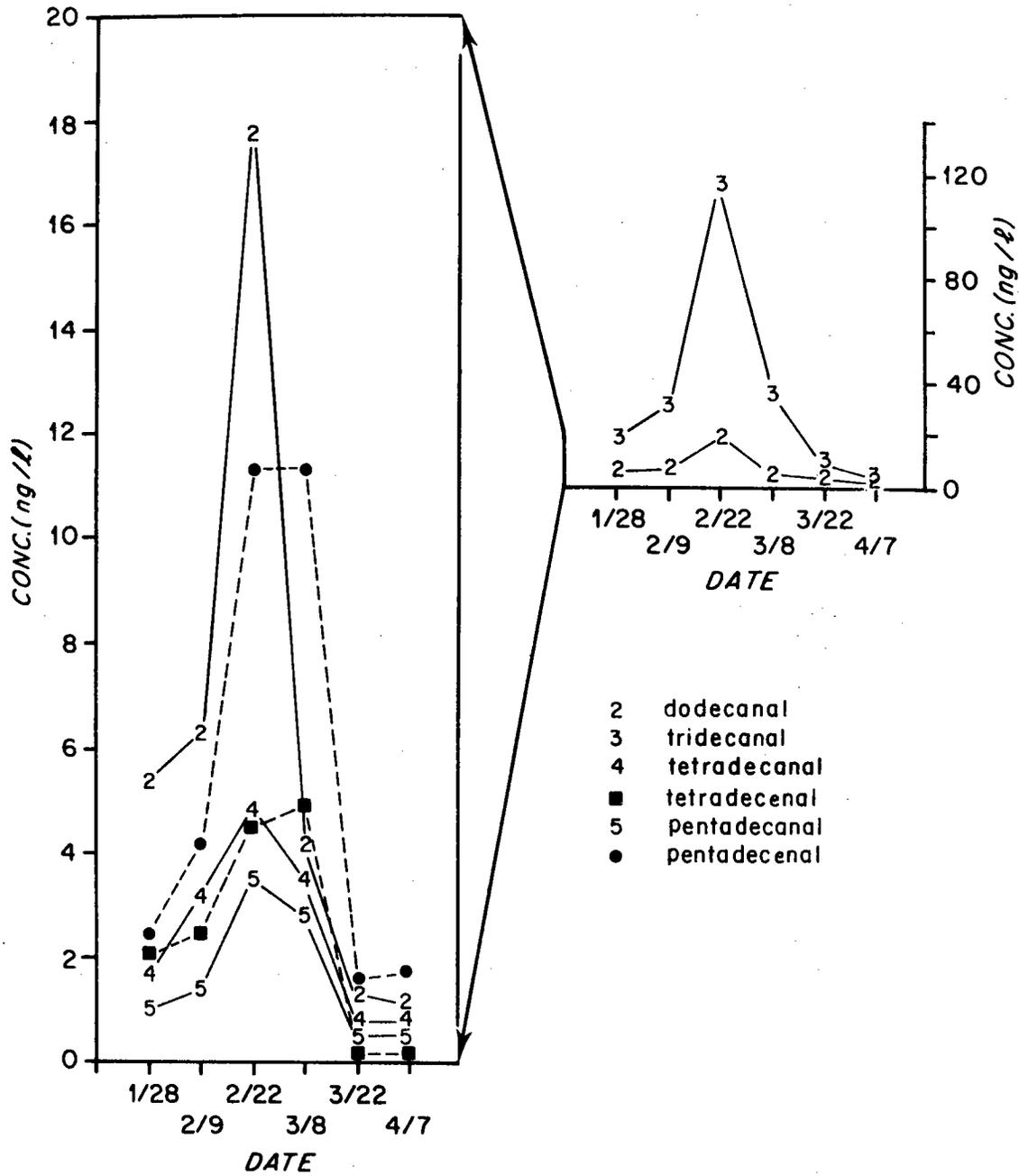


Figure 3-21. Diatom cell numbers ($\times 10^6/\text{kg}$), pigment concentrations ($\mu\text{g}/\text{l}$) and aldehyde concentrations (ng/l) in biweekly seawater samples from CD.

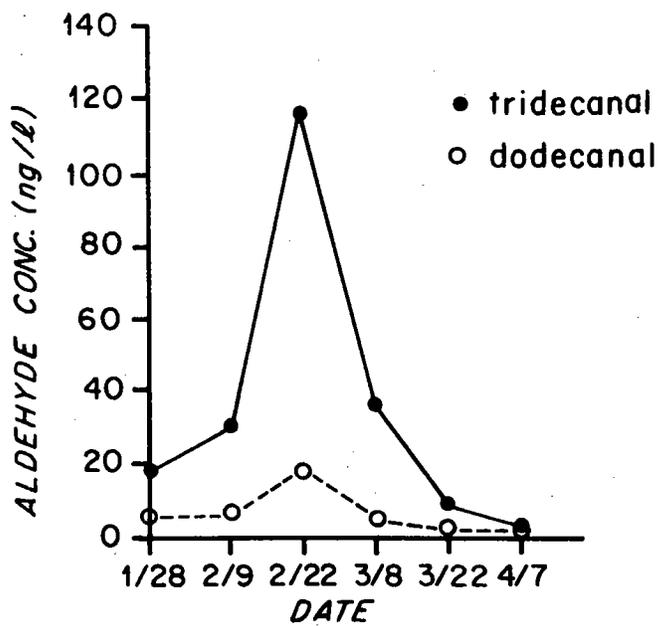
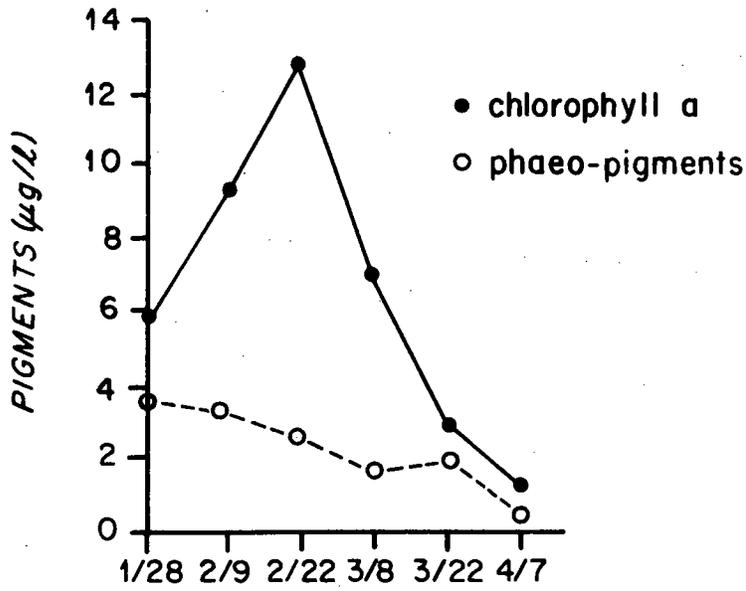
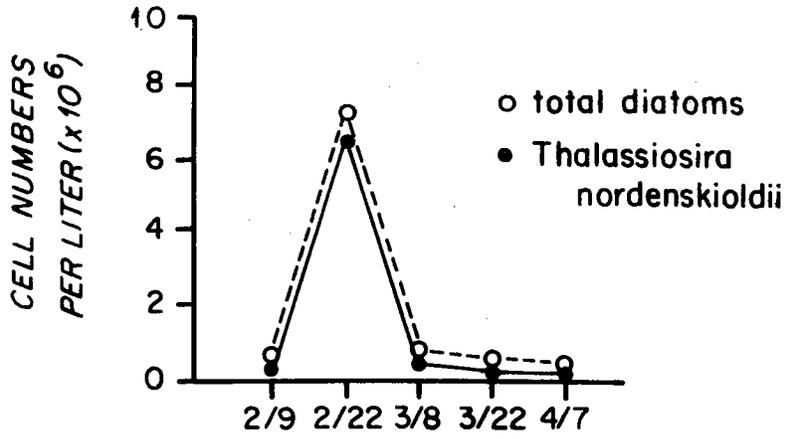
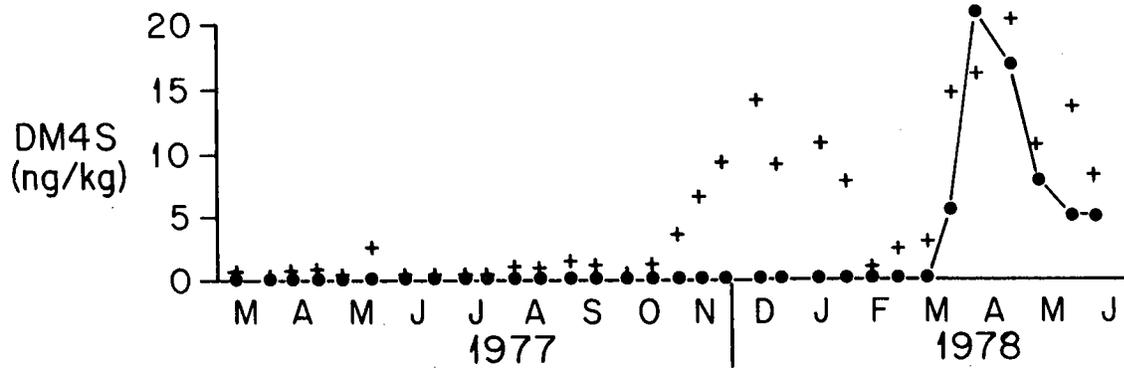
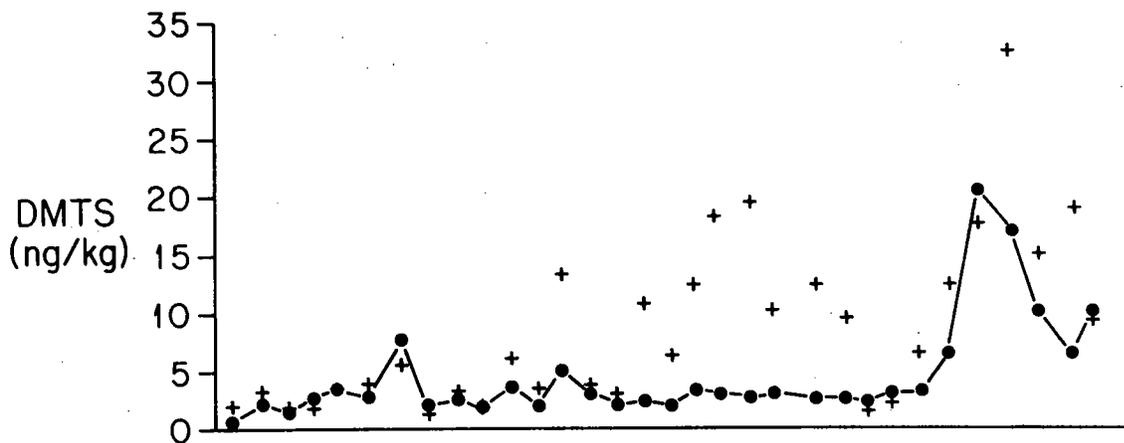
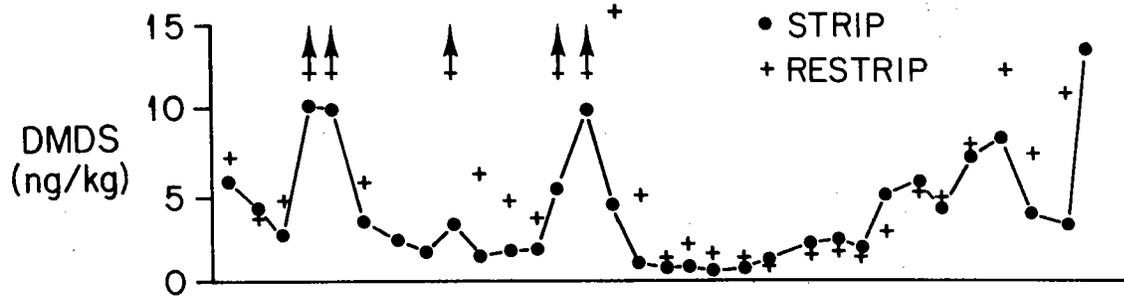


Figure 3-22. Dimethyl polysulfide concentrations (ng/kg) in biweekly seawater samples from CD. Closed circles show concentrations recovered in first 2 hours of stripping, while crosses show concentrations recovered in an additional 2 hours of stripping. Arrows indicate undetermined large quantities.



were the dimethyl polysulfides, CH_3SSCH_3 (DMDS), $\text{CH}_3\text{SSSCH}_3$ (DMTS), $\text{CH}_3\text{SSSSCH}_3$ (DM4S). DMDS appeared in the spring and summer. DMTS and DM4S were found in the restrips of winter samples and in both the strips and restrips of the spring samples of 1978.

These compounds are frequently recovered in greater amounts in the second 2 hours of stripping than in the original strips (figure 3-22). As discussed in Schwarzenbach et al. (1978), a capacity for the formation of these polysulfides must be contained within the samples.

DMDS may be formed by the oxidation of methyl mercaptan (Reid, 1958), a common product from marine algae (Haas, 1935; Challenger, 1959) and microorganisms (Kadota and Ishida, 1972). DMDS, DMTS, and DM4S may all be produced by the reaction of methyl mercaptan and elemental sulfur at room temperature (McMillan and King, 1948; Vineyard, 1966). Possibly, the analytical conditions increase the release of methyl mercaptan by microorganisms into seawater, allowing the concentration of this thiol to build up. As a result, the rate of production of polysulfides would also increase in time, and restrips would contain higher yields than the original 2 hours of stripping.

Elemental sulfur may also add to DMDS to yield DMTS and DM4S. The ratio of sulfur to starting disulfide (Murdock and Angier, 1970) or mercaptan (Vineyard, 1966) has been shown to control the distribution of polysulfide products. Excess elemental sulfur levels favor the production of compounds with longer sulfide chains. Thus the different distributions of polysulfides seen in the year-round study may reflect the concentration of elemental sulfur in the seawater throughout the year.

Also these compounds may be derived from other metabolites. Cyclic polysulfides (Wratten and Faulkner, 1971) and acyclic forms (Moore, 1971) have been reported and their degradation may be the source of these

polysulfide volatiles. Particularly attractive candidates are compounds like the bis-(3-oxoundecyl) di-, tri- and tetra sulfides or bis-(3-acetoxyundec-5-enyl) disulfide found in the red alga, Dictyopteris spp. (Roller et al., 1971; Moore, 1971; Moore et al., 1972).

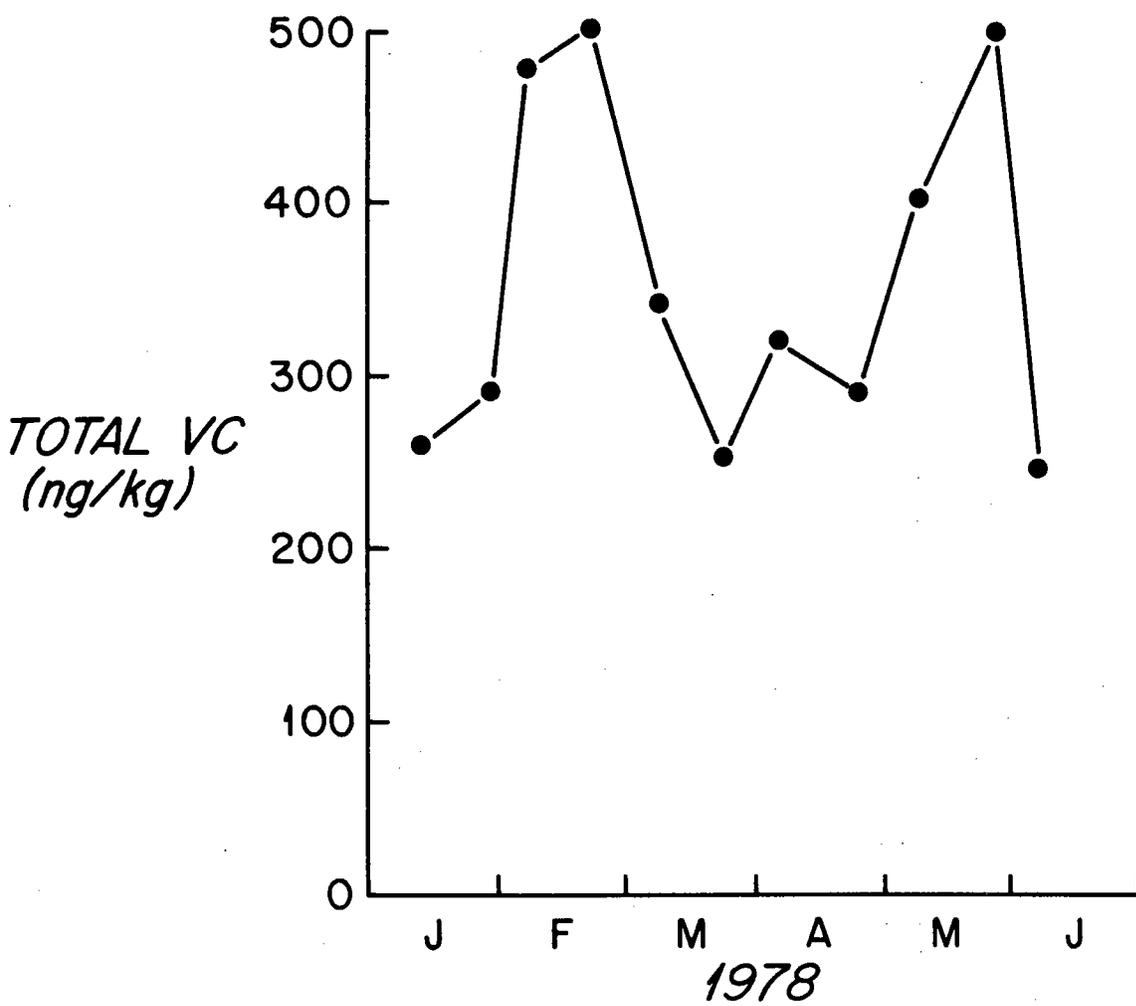
A simple calculation suggests the importance of these polysulfides to the sulfur cycle. The seawater at CD contained about 10 ng-S/kg in the form of these polysulfides; this represented a standing stock of 20 $\mu\text{g-S/m}^2$. If this material was swept into the atmosphere in about 3-4 days (Schwarzenbach et al., 1978), this amounts to the local introduction of about 2 $\text{mg-S/m}^2/\text{yr}$ to the air. This figure is similar to the 2 $\text{mg/m}^2/\text{yr}$ calculated for H_2S and the 6-10 $\text{mg/m}^2/\text{yr}$ for dimethyl sulfide found in the coastal region of Chesapeake Bay (Maroulis and Bandy, 1977). However, a global biological source of about 130 $\text{mg-S/m}^2/\text{yr}$ is needed to balance the sulfur cycle (Friend, 1973).

Other Volatile Organic Compounds. Two halogenated volatiles were observed in seawater at CD. The first was tetrachloroethylene at about 1 ng/kg. This value is similar to that reported for the Northeast Atlantic of 0.5 ng/kg, but much lower than the concentration in Liverpool Bay (120 ng/kg) (Murray and Riley, 1973). The source of this compound was most likely anthropogenic as it is heavily used in a direct dispersal manner (McConnell et al., 1975).

Bromoform (CHBr_3) was also found, particularly in the summer. The source of this compound was probably the benthic algae (chapter 5 and Burreson et al., 1975).

Total Volatile Organic Compounds. Figure 3-23 shows the total volatile organic compound concentrations over a six-month period as measured by

Figure 3-23. Total volatile compound concentrations (ng/kg) in biweekly seawater samples from CD.



the CSI Supergrator II.

First, it can be seen that the total levels approximately doubled during, and presumably in response to, the phytoplankton bloom. Also, a second peak occurred in May. The nutrient data do not support the contention that this second maximum could be remineralization of the earlier produced phytoplankton organic matter. The chlorophyll a values do not show that another bloom occurred at this time. The individual volatiles provide insight to the source of this second increase.

The alkylated benzenes demonstrated a doubling in the early part of the month. Based on previous discussion, this may be attributed to pollution associated with weekend recreational activities; this sample was acquired on a Monday. Therefore, the value of 400 ng/kg total volatiles may be only a few-day transient level.

The alkanes and some of the naphthalenes show a concentration spike at the end of the month. This was earlier ascribed to a pollution event involving a heavy petroleum fraction.

The total volatile organic carbon investigated in this study comprised about 0.02 - 0.05% of the DOC (assumed 1 mg/kg) pool. This is much less than the 1-10 µg/kg total volatiles found by MacKinnon (pers. comm., 1978) who utilized similar methods.

SUMMARY

The temporal variations in the concentrations of several groups of volatile organic compounds in coastal seawater have been studied. Correlations with other known processes were sought to provide insight into the cycling of these compounds.

The C₂- and C₃-alkylated benzenes covaried. Large concentration increases were observed in the summer, immediately following weekends.

This suggested an anthropogenic source related to summer recreational activities for these large inputs.

An unknown compound, probably an octatriene, was found in late February and March. This material may be related to the chemical attractant utilized by Fucus spp. (Phaeophyta) and may represent a biological signal.

Naphthalenes were most abundant after an oil spill and in winter samples. Winter samples contained a greater abundance of naphthalene, relative to the methyl naphthalenes, than did summer samples; this suggests that more indirect sources are important in the winter and thereby allow fractionation during transport of these homologues.

Pentadecane and heptadecane were the dominant n-alkanes observed. Separate large concentration increases for these compounds were found in the summer and the high "CPI" strongly suggests a biological source of these compounds. Benthic algae are abundant at this time of year, have been shown to contain these hydrocarbons (Youngblood et al., 1971; Youngblood and Blumer, 1973), and consequently have been identified as the probable sources.

C₆-C₁₀ straight chain aldehydes were found in all samples year-round. These aldehydes, and longer chain homologs from C₁₂-C₁₅, were greatly increased in abundance in the late winter. The coincidence with the Thalassiosira nordenskiöldii bloom indicated that this phytoplankton, or oxidation of the organic matter produced by this diatom, was the source of these oxygenated volatiles.

Dimethyl di-, tri-, and tetrasulfides were found in the coastal seawater. These polysulfides may be formed by reaction of methyl mercaptan and elemental sulfur, or from polysulfide metabolites of marine organisms.

The total volatile organic compounds accounted for only about 0.02 - 0.05% of the DOC (assuming 1 mg/kg). This was about an order of magnitude less than that found by MacKinnon (pers. comm., 1978) utilizing similar methods. Similarly intense peak levels of total volatiles seem to occur in response to either natural or anthropogenic activities.

"Also, short range transport and deposition should be measured in field studies performed in coastal regions relatively close to major urban sources. A prime site for such a study is the area off the northeast coast of the United States."

NAS, 1978

Chapter 4. SOURCE OF C₂- and C₃-ALKYLATED BENZENES TO COASTAL SEAWATER

INTRODUCTION

Recently there has been a great deal of discussion concerning the tropospheric transport of petroleum-derived hydrocarbons to the oceans (Duce et al., 1974; NAS, 1975b; Garrett and Smagin, 1976; NAS, 1978). Approximately 6×10^5 metric tons of petroleum hydrocarbons per year are estimated to be delivered to the sea by the atmosphere (NAS, 1975b). This amounts to 10% of the estimated total petroleum hydrocarbon input to the marine environment.

The gaseous hydrocarbons in urban air are chiefly benzene homologues (NAS, 1978). Several investigators have reported between 1 and 40 ng individual C₂- and C₃-benzenes/l-urban-air (Grob and Grob, 1971; Altshuller et al., 1971; Bertsch et al., 1974; Ciccioli et al., 1976). Lonneman et al. (1978) have found 0.2-4 ng/l-air in regions of Florida, including the Everglades. If air parcels with these concentrations were equilibrated with coastal seawater, water levels of 0.3-120 ng/kg-seawater would result. This includes the range of values found for the C₂- and C₃-benzenes in a year-round study of coastal seawater (Chapter 3; Schwarzenbach et al., 1978).

Many workers have attributed aromatic hydrocarbons in air to automobile exhaust, based on the composition similarity of air and exhaust samples, and on the spatial and temporal covariations of high compound concentrations and dense traffic (Grob and Grob, 1971, 1974; Altshuller et al., 1971; Bertsch et al., 1974; Lonneman et al., 1978).

Very little work has been done concerning the C₂- and C₃-benzenes in coastal seawater. Sauer et al. (1978) found levels of 0.3-24.4 ng/kg of individual C₂-benzenes in seawater from 8 coastal stations in the Gulf of Mexico. They identified oil production and transport sources for the aromatic hydrocarbons.

Clark et al. (1974) have suggested that outboard engine exhaust may be an important source of petroleum hydrocarbons to coastal seawater. They indicated that about 10% of the fuel used by these engines may be put directly into seawater.

In this chapter, efforts to ascertain the importance of atmospheric delivery versus direct inputs of C₂- and C₃-alkylated benzenes are described. Since my ability to assess air samples directly was limited by my analytical capabilities, several independent approaches utilizing water sample analyses were taken to provide insight to this problem. First, the long-term variations of these compounds found in the year-round study were investigated for seasonal, tidal, and rain effects. Short-term temporal studies were conducted to identify the timing and magnitude of effect of inputs associated with intensified tourist and recreational activities on summer weekends (Chapter 3). Also, the isomer distributions of the C₂- and C₃-benzenes in some fuel samples and the fractionation of these isomers in laboratory simulations of transport into seawater were investigated. Four studies of the concentrations of the aromatics in seawater samples from other nearby stations on the Sound

were conducted. Rain samples were analyzed to indicate the potential of the atmosphere as a source. Fresh and brackish water samples from inland sites were investigated to test the importance of runoff. Finally, a brief effort was made to determine the concentrations of the C₂- and C₃-benzenes in air.

METHODS

Water samples were analyzed for volatile organic compounds by the methods of Grob and Zürcher (1976) and Schwarzenbach et al. (1978).

RESULTS AND DISCUSSION

In order to simplify discussion, only o-xylene (1,2-dimethyl benzene) concentrations will be considered except in the isomer distribution studies. This is reasonable since all the C₂- and C₃-benzenes covary to a first approximation, and since o-xylene is cleanly resolved in the chromatograms.

Year-round Chemotaxis Dock Seawater Data.

As noted in Chapter 3, the concentrations of o-xylene in samples from the year-round study were higher immediately after summer weekends (figure 3-10). This suggested an anthropogenic source related to recreational activities at that time of year.

If the C₂- and C₃-benzenes were delivered to Chemotaxis Dock (CD) from one dominant source (e.g. Woods Hole harbor), one should observe an influence of the tide on these aromatic compound concentrations. Accordingly, the concentrations of these aromatic compounds in the biweekly samples from CD in the year-round study were considered as a function of the tide at the

time of collection. Five samples in the year-round group were taken within 1 hour of low tide, and these showed an o-xylene concentration of 8 ± 3 ng/kg. Six other samples, acquired within 1 hour of high tide, had 16 ± 5 ng o-xylene/kg. All of the remaining samples (21) contained 9 ± 5 ng o-xylene/kg. Thus, there is some indication of a source related to high tide (i.e. located to the west of Chemotaxis Dock). However, all of the high-tide samples were obtained in the months of May, June and July. Consequently, the relatively high o-xylene average found in this group might also be caused by a seasonal factor.

Another possibility is that rain delivers C_2 - and C_3 -benzenes to coastal seawater. This may occur by two mechanisms. First, if the atmosphere contains high levels in excess of equilibrium with seawater of these aromatic compounds, rain may acquire this hydrocarbon burden and deposit it on the sea. Grob and Grob (1974) favored this explanation for the increase of the alkylated benzene concentrations in Lake Zurich after rain. The other mechanism entails increased runoff from streets and sewers due to rain. Urban runoff has been cited for delivery of 0.3×10^6 metric tons petroleum hydrocarbons per year to the sea (NAS, 1975b).

To test for the effects of rain, samples from the Chemotaxis Dock year-round study were grouped into those (7 samples) taken within 1 day of greater than 0.1" rain and those (16 samples) acquired at least 4 days after the last rain. The samples taken shortly after rain contained 12 ± 6 ng o-xylene/kg, while those obtained more than 4 days since the last rain showed 9 ± 4 ng o-xylene/kg. Thus, there is no significant difference.

Short-term Temporal Studies.

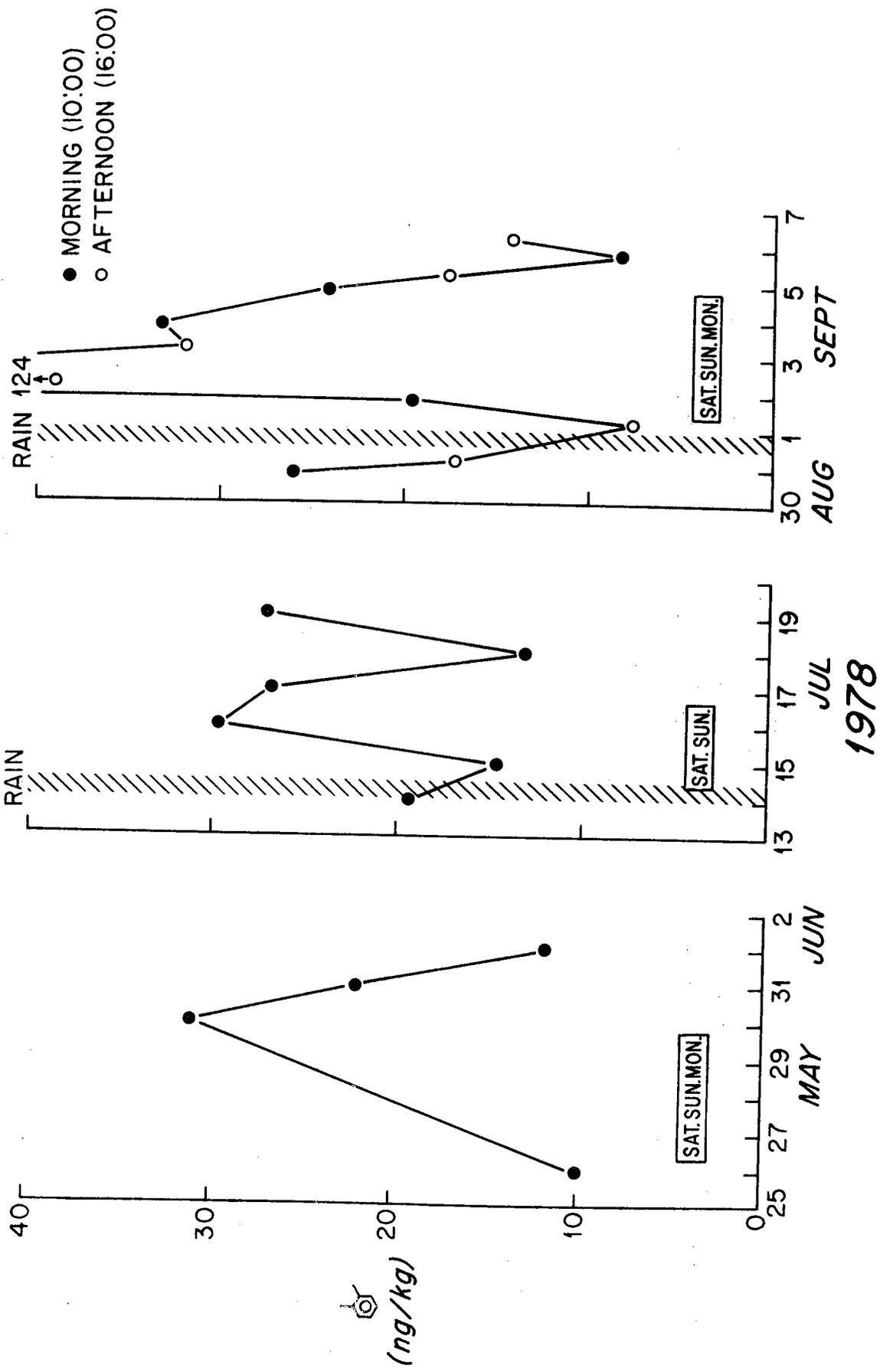
The o-xylene concentration in samples from CD acquired before, during, and after summer weekends is shown in figure 4-1. In the first study (May 26 - June 1, 1978), the concentration of o-xylene was greatly increased after the weekend, relative to before the weekend. In the other 2 cases (July 14-19, 1978; August 31 - September 6, 1978) samples were taken during the weekend and showed that the concentration of o-xylene increased during that time. Notably, the early part of these weekends did not have peak concentrations; in July the highest concentration was found on Sunday while in September this maximum occurred on Saturday afternoon. This indicates either a delay in the water response to heightened atmospheric levels or that recreational activities on Saturday afternoon provide these aromatic compounds. The Saturday afternoon sample on September 2 was taken while two power boats were towing water skiers in the vicinity of CD. This was the highest concentration ever observed and undoubtedly derived chiefly from these motorboats.

Isomer Distributions

Isomer distributions were studied in an effort to "fingerprint" the sources of the C₂- and C₃-benzenes. Interpretation of isomer distributions in seawater is difficult due to differential effects of environmental processes which operate on an isomer distribution. However, "young" dominant sources should leave revealing "fingerprints,"

Gasoline, gasoline/oil for outboard engines, and fuel oil were diluted and analyzed directly by gas chromatography (GC). Auto exhaust was collected

Figure 4-1. O-xylene concentrations (ng/kg) in seawater samples collected before, during and after summer weekends. May 27-29, 1978 was the Memorial Day holiday weekend. September 2-4, 1978 was the Labor Day holiday weekend. Periods of rain are indicated by crosshatch. Closed circles indicate concentrations in samples collected in the morning; open circles indicate concentrations in samples collected in the afternoon.

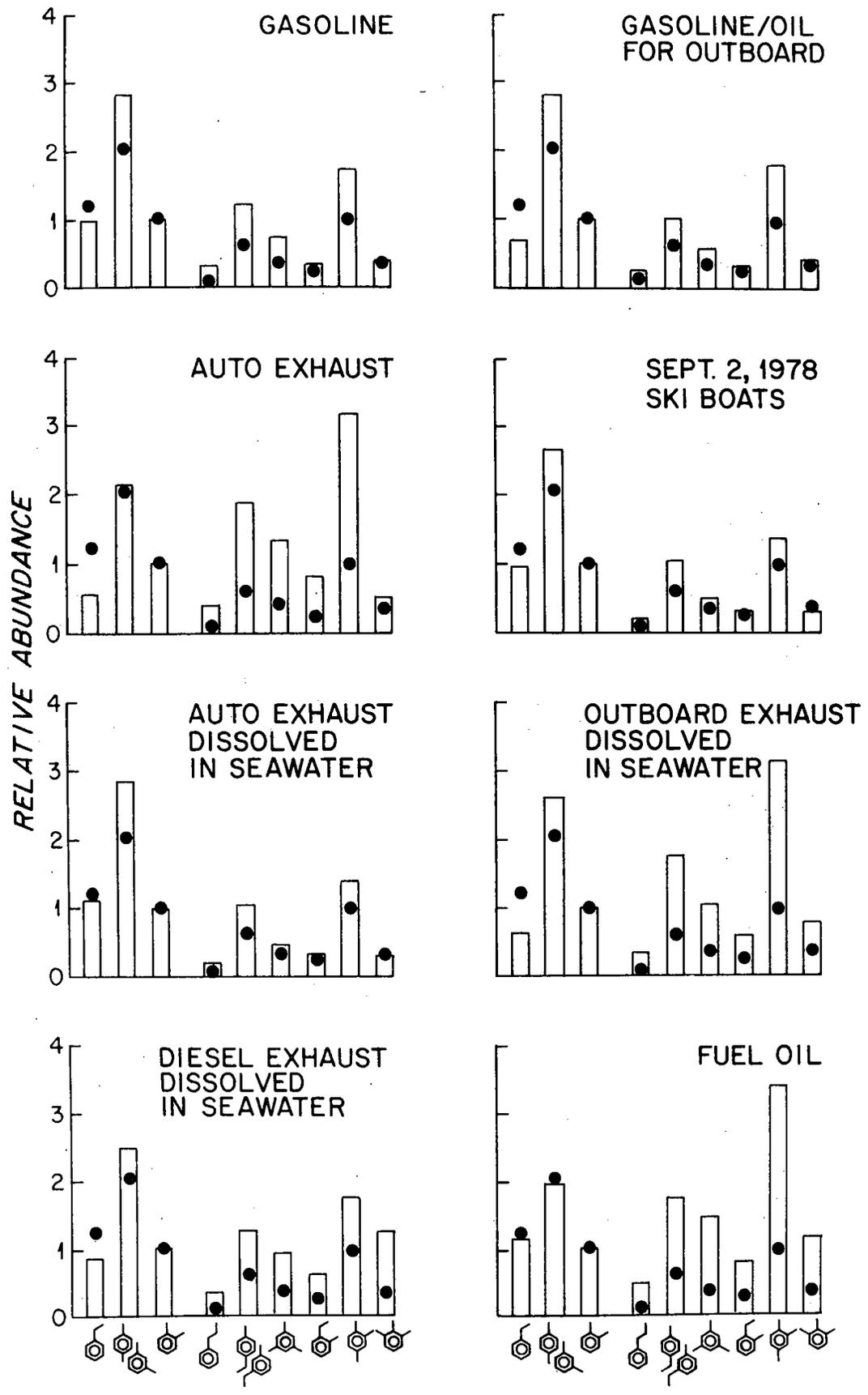


in a glass flask, stripped onto a charcoal trap, extracted into methylene chloride, and analyzed by GC. In another experiment, auto and diesel exhaust were collected in empty glass flasks. Each was connected by a U-shaped neck to an identical flask containing thoroughly prestripped seawater (gently stirred). The vapors were then allowed to exchange between the air and the seawater for 1 day. The water was then analyzed for C_2 - and C_3 -benzenes. In order to study the effects of outboard engines, water was collected near the underwater exhaust of an outboard engine, and this was analyzed for its isomer distribution. Also, a seawater sample was collected at CD on September 2 during an afternoon of continual motorboat activity in the immediate vicinity of CD. The resultant isomer distributions are shown in figure 4-2.

Although all of the patterns are similar, some important differences exist. Gasoline and gasoline/oil for motorboats contain less C_3 -benzenes than the heavier fuel oil. Auto exhaust and outboard-exhaust-dissolved-in-seawater have similar isomer distributions. This may be explained if both engines produced like exhaust patterns, and this pattern is not changed on transfer into seawater by underwater exhaust systems of outboard engines.

The isomer distribution obtained from exchange of auto exhaust vapor with seawater differs from that of the original exhaust by an enrichment in the lower-boiling compounds. The pattern of auto-exhaust-dissolved-in-seawater resembles that observed in CD sample of September 2. This may be due to boats operating near the dock that had either inboard or inboard/outboard engines. These powerboat types exhaust directly into the atmosphere, a situation simulated in the lab by placing exhaust gases in close proximity to seawater and allowing them to dissolve.

Figure 4-2. Relative C₂- and C₃-benzene isomer abundances from several fuels, auto exhaust, and some exhausts dissolved in seawater. Abundances are normalized so that o-xylene (1,2-dimethyl benzene) equals 1. Closed circles show average relative abundances from biweekly seawater samples from CD.



Finally, the diesel-exhaust-dissolved-in-seawater pattern differs from the gasoline-exhaust-dissolved-in-seawater pattern in that the former showed C₂- and C₃-benzenes at similar levels while the latter had relatively more C₂- than C₃-benzenes. This is probably due to the relatively facile transfer of C₂-benzenes on the one hand, and to the original enrichment of C₃-benzenes in the heavier diesel on the other hand. This C₃-benzene enrichment is particularly evident for 1,2,3-trimethyl benzene relative to the other lower-boiling isomers.

The average year-round isomer distribution is indicated by the dots in figure 4-2 and most resembles the patterns for auto-exhaust-dissolved-in-seawater and September 2 boat exhaust at CD. The linear correlation coefficients for the isomer distributions found in the lab studies versus the average year-round distribution values were: gasoline, 0.91; auto exhaust, 0.46; auto exhaust dissolved in seawater, 0.95; gasoline/oil for outboards, 0.88; outboard exhaust dissolved in seawater, 0.61; Sept. 2, 1978 ski boats, 0.94; diesel exhaust dissolved in seawater, 0.80; and #2 fuel oil, 0.44. The most notable discrepancies in these distributions are found for the peaks containing para substituents (para-xylene, p-ethyl methyl benzene, and 1,2,4-trimethyl benzene; the first 2 were not resolved from the meta isomers by GC and appear as a single peak in the isomer distributions). These compounds were found to be the most rapidly degraded of the alkylated benzenes by Kappeler (1976) in his studies of the microbial degradation of the alkylated benzenes in groundwater. Thus, the discrepancies may reveal the importance of a similar biochemical degradation in these coastal seawaters.

Utilizing o-xylene as an internal standard, the other C₂- and C₃-benzenes may be studied for their relative variations during the year

(figure 4-3). Propyl benzene showed a strong negative deviation (-80%) from its mean ratio to o-xylene in August. Ethyl benzene also showed this effect, although less pronounced (-50%). Grob and Grob (1974) also saw strong relative removal of these compounds in Lake Zurich when water temperatures were above 20°C. They suggested that biological degradation was occurring by a microorganism suited to these warm temperatures and capable of metabolizing the elongated sidechains. A warm-weather metabolic degradation of these compounds may also occur in the coastal zone near CD.

Mesitylene (1,3,5-trimethyl benzene) showed a 3-fold relative maximum in September at CD. This compound was also found in relative abundance in marsh samples (Schwarzenbach et al., 1978). Possibly an unknown biological source of this compound exists.

O-xylene in Seawater from Other Vineyard Sound Stations.

Four investigations of the concentrations of the C₂- and C₃-alkylated benzenes in surface water from Vineyard - Nantucket Sound were conducted. Samples were obtained within 3 km of CD. Salinity data are available from 3 of these studies (figure 4-4) and, along with knowledge of the tide at the time of sampling, have been used to draw the lines of flow shown. Salinity always increased offshore from CD. It appears that the shoals, about 2 km off CD, do not provide a major barrier to mixing of surface waters.

The concentrations of o-xylene in seawater from these stations are shown in figure 4-5. No trends were consistently observed. Although there were always significant concentration differences, e.g, between samples from stations at CD and 0.8 km. offshore, sometimes offshore levels were lower

Figure 4-3. Ratios of C₂- and C₃-benzene to o-xylene in biweekly seawater samples from CD. Year-round mean ratio has been set equal to 1. March - July, 1977 and February - March, 1978 ratios of ethyl benzenes to o-xylene are unknown due to coelution of ethyl benzene and other compounds in samples from these periods.

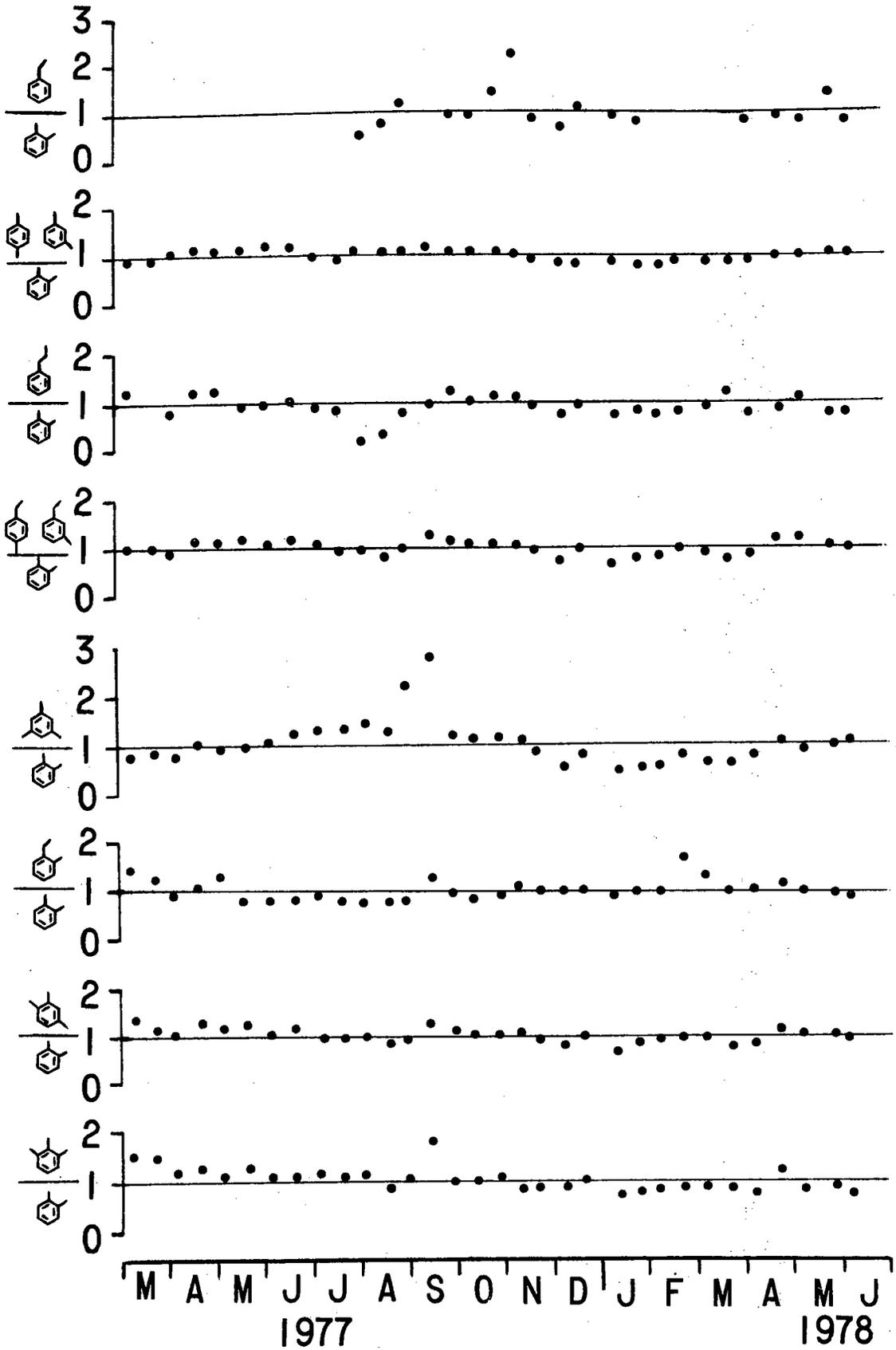


Figure 4-4. Salinity ($^{\circ}/_{oo}$) in seawater samples from the region near CD taken at different times of year. Arrows indicate the velocity of tidal currents at the time of sampling.

SALINITY (‰)

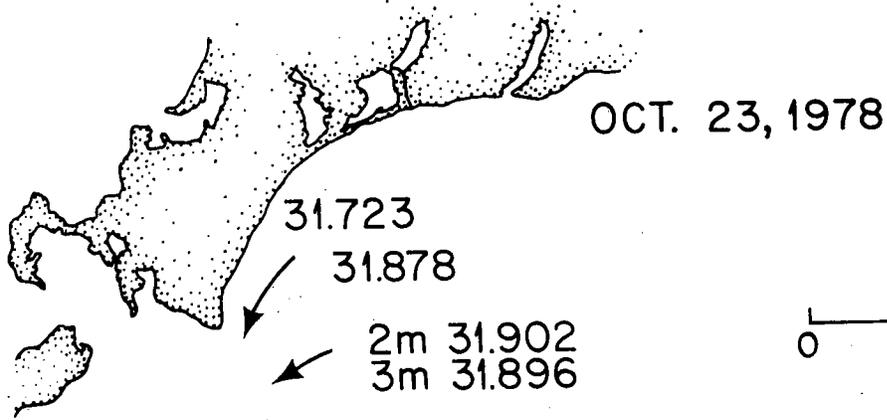
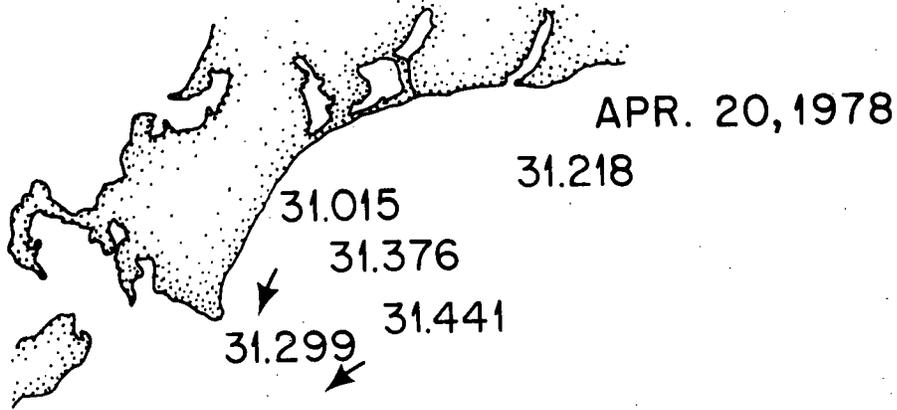
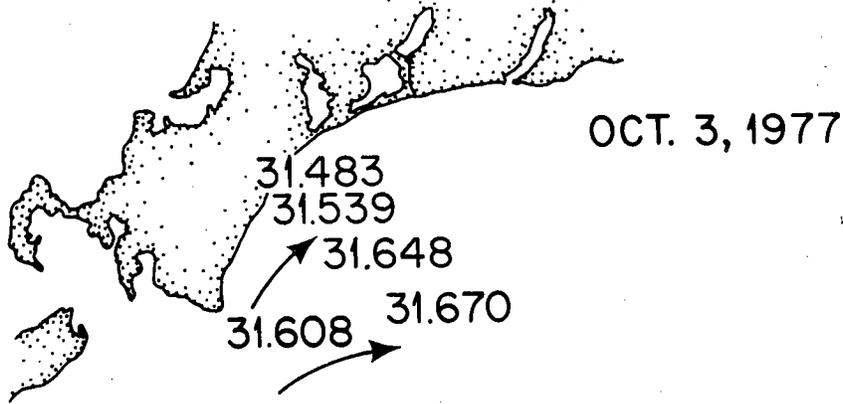
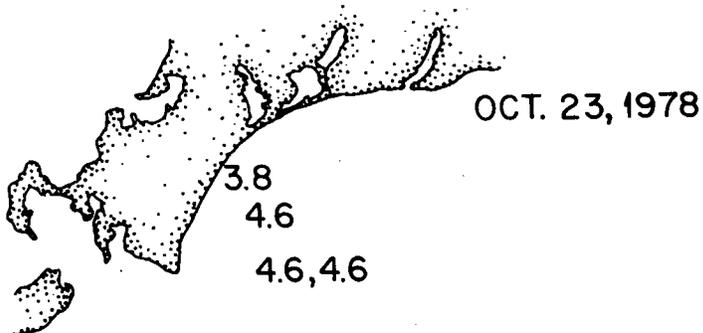
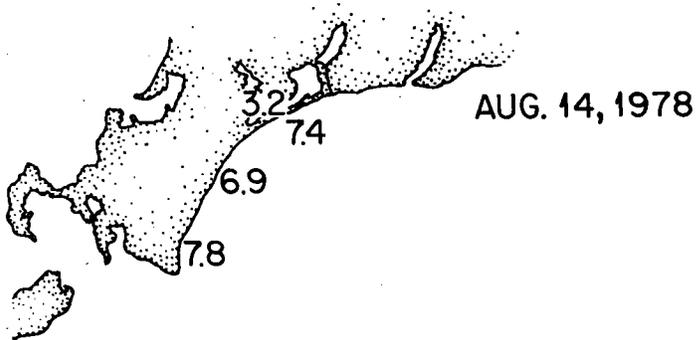
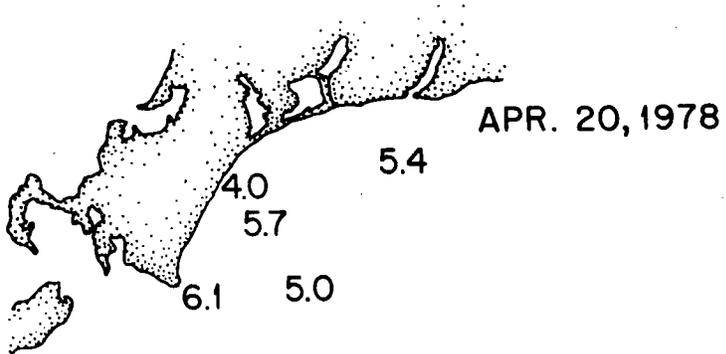
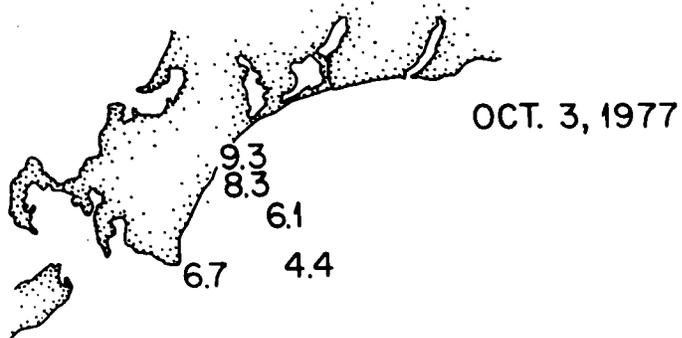


Figure 4-5. O-xylene concentrations (ng/kg) in seawater samples from the region near CD taken at different times of year. O-xylene concentration (ng/kg) in Oyster Pond water is also shown for August 14, 1978.

**o-XYLENE CONCENTRATIONS
(ng/kg)**



0 1 NAUT.
MILE

while at other times they were higher. Similarly, concentrations did not always increase in the samples taken closer to Woods Hole harbor. The inhomogeneity of o-xylene levels was much greater than can be explained by the analytical error ($\pm 10\%$). This variability is unexpected for a dominantly atmospheric source, assuming that the rate of removal of o-xylene from surface seawater was similar at these stations.

Rain

Two rain samples were analyzed for the C_2 - and C_3 -benzenes (Table 4-1). The C_3 -benzenes were present at very low concentrations, and consequently, only the most abundant isomer, 1,2,4-trimethyl benzene, is reported. The 2 samples contained very similar levels of C_2 -benzenes. The spring sample had very much lower levels of C_2 -benzenes than seawater at that time, while the fall rain sample had concentrations comparable to those of seawater. If the rain was near equilibrium with respect to air concentrations of these C_2 - and C_3 -benzenes, an estimate of the atmospheric concentrations of these aromatic compounds may be calculated from the rain results. These air concentrations may then be used to infer the direction of air-sea exchange for the C_2 - and C_3 -benzenes at the time of rain collection. From this approach, it appears that seawater was degassing the C_2 - and C_3 -benzenes in June, but was near equilibrium in November.

These estimates of the atmospheric concentrations of the C_2 - and C_3 -benzenes probably reflect the levels in air present during the entire rain period. If these compounds occur as vapors, rainfall cannot efficiently scrub the atmosphere of them since the partition coefficients (0.1-0.4) are so low. Thus comparison of these estimated aromatic

Table 4-1. C₂-benzenes and 1,2,4-trimethyl benzene concentrations (ng/kg) in rain. For comparison, concentrations (ng/kg) are also shown for seawater taken at CD in the biweekly sampling series.

Compound	Rain 6/14/77	CDsw 6/6/77	CDsw 6/21/77	Rain 11/9/77	CDsw 10/27/77	CDsw 11/10/77	CDsw 11/22/77
ethyl benzene	6	14	20	4	10	13	5
m & p-xylene	12	73	57	10	14	11	10
o-xylene	6	28	23	5	6	5	5
1,2,4-trimethyl benzene	3	23	21	2	5	4	4

compound concentrations in air to seawater concentrations of the C₂- and C₃-benzenes may be a valid indicator for the longer-term direction of flux.

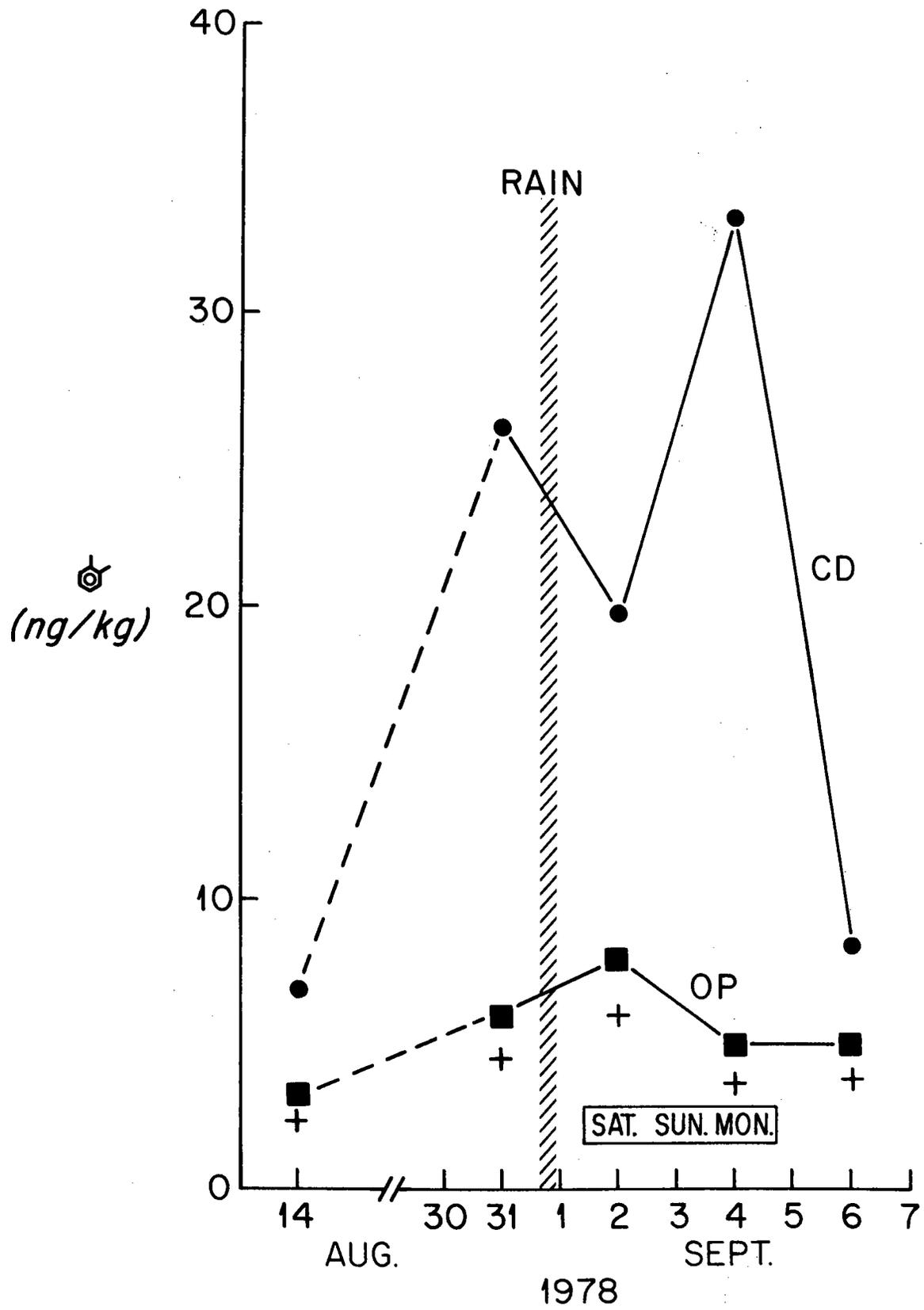
Oyster Pond, Quashnet River, and Sippewissett Marsh.

Inland water samples were analyzed for their volatile content. Five samples of Oyster Pond water were acquired in August and September, 1978. This pond is located very near CD and is separated from the coastal seawater by a narrow stretch of land (figure 3-1). The pond is a collecting basin for groundwater and runoff, and releases about 3×10^6 liters of water to the Sound near CD per day (Emery, 1972). Motorboats are not allowed on Oyster Pond.

The concentrations of o-xylene in Oyster Pond were consistently found to be lower than those in CD (figure 4-6). Assuming that sinks such as biodegradation or loss to the sediments are no more important in the pond than they are at CD, these data suggest that the atmosphere was not an important source of C₂- and C₃-benzenes to CD at this time. Since o-xylene is more soluble in freshwater than in seawater, the concentrations in freshwater should be higher than in seawater given an atmospheric source at equilibrium with both (Sutton and Calder, 1975; Appendix IV).

After rain, the Oyster Pond concentration of o-xylene increased (30%), while at CD the concentration decreased (25%). This observation indicates that the atmosphere is the source of this aromatic compound to Oyster Pond but not to CD. It also supports the conclusion from the year-round data that rain does not lead to delivery of aromatic hydrocarbons to CD.

Figure 4-6. O-xylene concentrations (ng/kg) in water samples, collected concurrently from CD (solid circles) and Oyster Pond (solid squares) in August and September, 1978. A period of rain is indicated by the crosshatch. The Labor Day holiday weekend (September 2-4, 1978) is indicated. Crosses indicate concentrations expected for seawater in equilibrium with the atmosphere, if Oyster Pond samples accurately reflect atmospheric concentrations.



The Quashnet River and Sippewissett Marsh (low tide) were sampled in August, 1977 and July, 1977, respectively. Both samples showed lower levels of C₂- and C₃-benzenes than seawater collected on the same day (Table 4-2). These observations, together with those on the Oyster Pond samples, suggest that runoff in the summer dilutes seawater with respect to these aromatic hydrocarbons.

Air Measurements.

Air samples in August and September, 1978 were analyzed for C₂- and C₃-benzenes. Air at CD was pumped through a 5-liter round bottom flask for 15 minutes at a rate of about 2 liter/min. After this flushing, the air was rerouted through a charcoal trap for 15 min. Repeating this sequence 4 more times allowed the analysis of 25 liters of air.

Figure 4-7 shows the result of a midweek air analysis. Standards (added to the charcoal trap just prior to extraction and indicated in the figure by dots) indicate the 1.6 ng/l-air concentration level. First, one can see that the concentrations of the alkylated benzenes were quite low. Moreover, a restrip of the same air onto a fresh charcoal trap showed significant levels of these compounds relative to the first strip. This suggests that 15 min. for the first strip was insufficient for complete recovery from 5 liters; and therefore, the concentrations of these compounds in air may be underestimated by these analyses. Finally, an analysis of exhaustively prestripped air is shown and reveals that the procedural blank was very good.

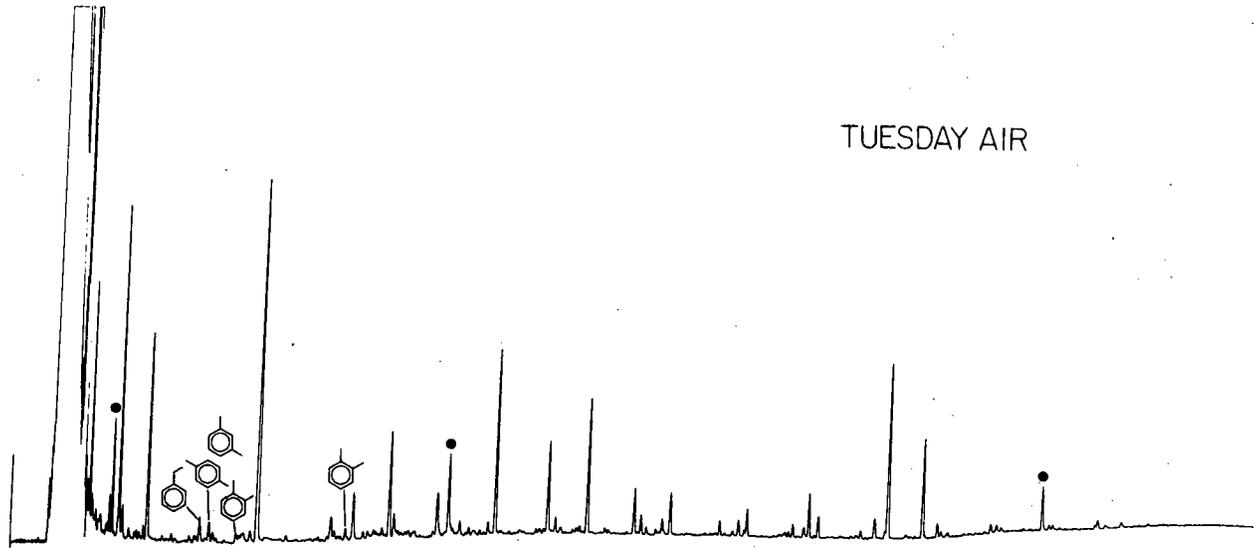
Table 4-3 shows the observed levels for o-xylene in air. Highest values were found on Saturday and Monday of the Labor Day holiday weekend.

Table 4-2. C₂-and C₃-benzenes concentrations (ng/kg) in water samples from the Quashnet River and Sippewissett Marsh (low water). For comparison, C₂-and C₃-benzenes concentrations (ng/kg) in seawater from CD collected on the same dates are shown. Most of the C₃-benzenes were present in Quashnet River water at too low water concentrations to be measured.

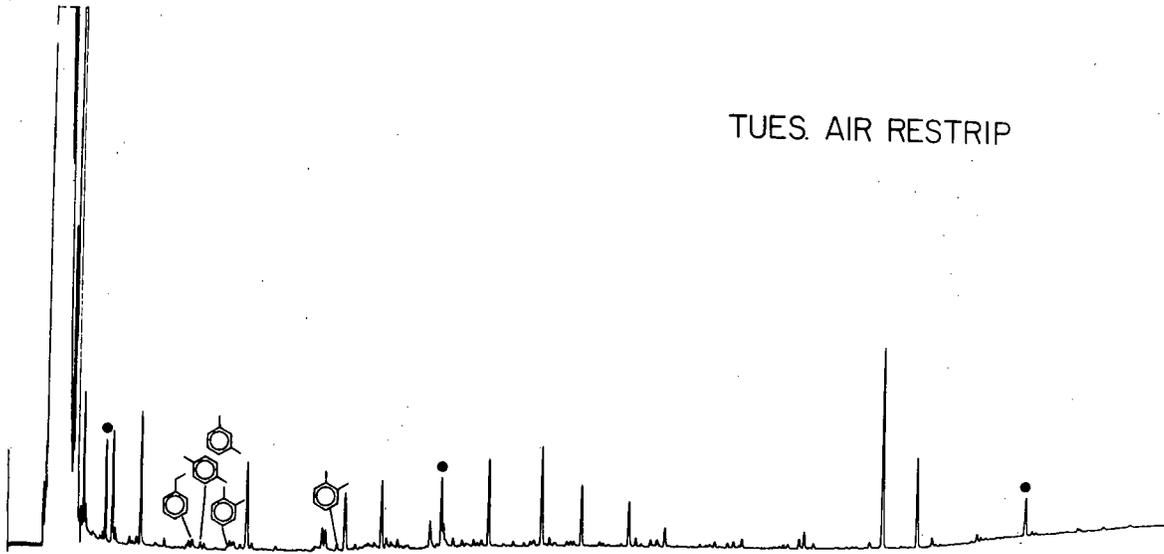
Compound	Sippewissett	
	Quashnet River 8/22/77	Marsh low water 7/19/77
ethyl benzene	3.3	8.1
m & p xylene	3.1	17.9
o-xylene	3.0	9.3
1,2,4-trimethyl benzene	0.6	5.8
propyl benzene		0.4
m & p ethyl methyl benzene		3.3
1,3,5-trimethyl benzene		4.0
o-ethyl methyl benzene		1.6
1,2,3-trimethyl benzene		1.9
	5.4	
	>12	
	6.2	
	4.4	
		11.2
		1.5
		8.5
		11.4
		3.4
		4.6
	22	
	37	
	16	
		CD Seawater 7/19/77

Figure 4-7. Gas chromatograms showing volatile compounds collected from air, from a restrip of that air, and from exhaustively prestripped "blank" air. Closed circles indicate the 1-chloro-n-alkane internal standards (5,8,16) which are added at 1.6 ng/l-air. C₂-benzenes and 1,2,4-trimethyl benzene peaks are also indicated. The GC column was a 0.3 mm x 20 m SE54 glass capillary column operated at room temperature for 8 min. and then programmed from 20-200°C at 3°C/min.

TUESDAY AIR



TUES. AIR RESTRIP



BLANK

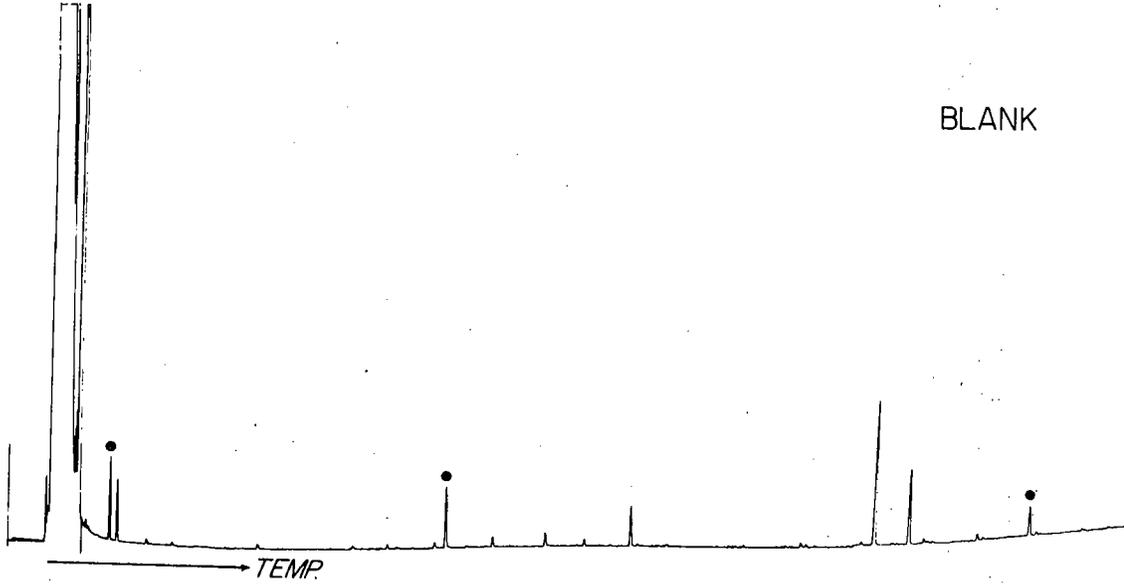


Table 4-3. O-xylene concentrations (ng/ℓ) in air from direct measurements and calculated from rain and Oyster Pond o-xylene concentrations assuming equilibrium with the atmosphere.

(September 2-4, 1978). Also shown are the concentrations calculated from the levels found in rain and Oyster Pond samples assuming that these were at equilibrium with the atmosphere (physical data in Appendix IV). The general range of these calculated values agrees well with the levels measured. Seawater, at equilibrium with the air values found, would contain 0.4 to 6.6 ng o-xylene/kg. Seawater samples always contained greater levels of o-xylene than this, and therefore the atmosphere appears to have been a sink, rather than a source, for C₂- and C₃-benzenes at this time.

Aromatic hydrocarbons introduced into the atmosphere are degraded largely by reaction with OH[•] (Darnall et al., 1976). Reaction rates indicate that this removal process from polluted air occurs with a half life of only a few hours in daylight even for the slowest reacting alkylated benzene. If the metropolitan area of New York were the source of a large plume of aromatic hydrocarbon-rich air, by the time it reached Cape Cod, (ca. 8 hours, Cleveland et al., 1976), it would have been largely diluted and cleansed by OH radical reactions. The 5-10 ng o-xylene/l-air found in urban areas (Grob and Grob, 1971; Altshuller et al., 1971; Bertsch et al., 1974; Ciccioli et al., 1976) may be reduced to the 0.1 to 1.5 ng o-xylene/l-air found in this study.

It is difficult to know the nature of the source of C₂- and C₃-benzenes in the winter since the samples in this study were taken in the late spring through early fall. Levels almost never fell below 5 ng o-xylene/kg, even in the winter; hence possibly the atmosphere serves as a buffer and maintains this "background" level. This would require the atmosphere to contain about 1.1 ng o-xylene/l-air, possibly a reasonable level for the metropolitan Northeast U.S. In the summer, it seems that the atmosphere is not a source,

but that direct inputs (e.g. from boating activities) dominate. However, even at this time, the atmosphere may operate as a buffer and act as a sink until the return of concentrations to background levels after summer weekends. A brief calculation, utilizing the stagnant boundary layer model of the air-sea interface (Broecker and Peng, 1974; Liss and Slater, 1974) can show that exchange to the atmosphere may diminish a suddenly increased concentration of a volatile compound in seawater to less than 20% of the size of the spike within a week:

$$\text{flux after spike input} = \frac{dC}{dt} = -\frac{D}{z} \times \frac{A}{V} (C_{\text{excess}})$$

where C = concentration of the organic compound,

t = time

D = diffusion coefficient

z = stagnant boundary layer thickness

A = cross sectional area of diffusion

V = volume of water column under A

C_{excess} = spike concentration over and above concentration in equilibrium

rearranging and integrating

$$\ln C/C_0 = -\frac{DA}{zV} \times t$$
$$C = C_0 \exp\left(-\frac{DA}{zV} \times t\right)$$

for the region of CD,

$D = 0.6 \times 10^{-5} \text{ cm}^2/\text{sec}$ based on diffusion coefficient of methane and the proportion of the square roots of molecular weights (Witherspoon and Bonoli, 1969; Liss and Slater, 1974).

$$A = 1 \text{ cm}^2$$

$$z = 10^{-2} \text{ cm}$$

$$V = 200 \text{ cm}^3$$

corresponding to a wind velocity of 4.5 m/sec
(Kanwisher, 1963)

depth at CD ca. 2 meters.

$$\text{then } DA/zV = 3 \times 10^{-6} / \text{sec}$$

$$\text{and after 1 hour } C_o \exp (-DA/zV) \times (t) = 0.99C_o$$

$$\text{after 1 day} = 0.78C_o$$

$$\text{after 3 day} = 0.46C_o$$

$$\text{after 1 week} = 0.16C_o$$

Thus, if 30 ng o-xylene/kg were added to a 5 ng o-xylene/kg background, degassing would reduce an observed concentration of 35 ng o-xylene/kg to 10 ng o-xylene/kg within 1 week. This reduction would be even faster if wind speeds were greater or if other sinks such as mixing with cleaner water also were available.

SUMMARY

Several independent approaches have been taken in an effort to assess the transport of C₂- and C₃-benzenes to coastal seawater.

The data suggest that the atmosphere was not an important route of delivery of these aromatic compounds to the seawater in the summer. The highest concentrations of C₂- and C₃-benzenes ever observed at CD were associated with motorboat traffic on a summer weekend. Two other lines of evidence suggest that the air was not a source of these compounds to coastal seawater in the period from late spring through fall. First, the inhomogeneity of concentrations in surface seawater from Vineyard Sound indicated that

an atmospheric source did not control these levels. Also air concentrations of o-xylene (measured directly, calculated from rain data, and calculated from Oyster Pond data) were below values expected for equilibrium with observed seawater levels.

Analyses of inland freshwater samples from Oyster Pond, the Quashnet River, and Sippewissett Marsh also revealed that runoff, through these relatively undeveloped areas, diluted the coastal seawater with respect to the aromatic hydrocarbons. This is not to say that runoff entering the Sound through, for example, Falmouth Harbor, does not contain high concentrations of these pollutants.

The relative constancy of concentrations and isomer ratios of the C₂- and C₃-benzenes in coastal seawater may indicate that a "buffer" controlled the background levels of these materials. The metropolitan northeastern U.S. may provide a continuous background of aromatic hydrocarbons and this, in conjunction with the prevailing south westerly wind pattern, may maintain the background levels observed at CD. This was supported by the November rain sample which indicated that the atmosphere was near equilibrium with seawater with respect to the C₂- and C₃-benzenes at that time.

Superimposed on this background, there may have been short-term effects related to tourist and recreational activities on Cape Cod.

Additional work is required to study the "off season" effects. Also, many assumptions concerning the sinks of these relatively refractory hydrocarbons have been made and need to be investigated. Finally, the development of dependable analytical methods for air samples is needed to complement the reliable procedures already available for water samples.

CHAPTER 5. VOLATILE ORGANIC COMPOUNDS FROM BENTHIC ALGAE AND SEAGRASS

INTRODUCTION

Marine benthic algae are known to produce a variety of volatile organic compounds (chapter 1) which may be secreted, excreted, or released to the surrounding seawater on death, senescence, or structural deterioration. In a year-round study of the volatile organic compounds in the coastal region of Vineyard and Nantucket Sounds, several compounds were suspected to have been derived from benthic algal sources (Schwarzenbach et al., 1978; chapter 3). These included hydrocarbons such as pentadecane and halogenated compounds such as bromoform. This chapter details efforts to assess the input of these volatiles to seawater from benthic algae and seagrass.

METHODS

Algae and seagrass were collected in the vicinity of Chemotaxis Dock (CD). Table 5-1 gives relevant information. Efforts were made to avoid epiphytized plants, that is, plants on which other species of algae are attached and living. However, it was impossible to exclude all other organisms. The algae were placed in 2-liter reagent flasks filled with seawater and stoppered. The flasks were then anchored on the bottom at CD or stored in outdoor running-seawater tanks at a nearby laboratory. The algae were exposed to ambient sunlight and temperature conditions during incubation. After 24 hours, the flasks were purged for 1 hour (with the algae still in place) with recycled air at 20°C (except the May samples at 35°C). The effluent volatile organic compounds were trapped on a charcoal trap which was subsequently extracted with 15 μ l of CS₂ or CH₂Cl₂.

Gas chromatographic analyses were made using a Carlo Erba model 2551

Table 5-1. Date of collection and dry weight of benthic algal samples collected near CD. Also shown are the seawater temperature and the insolation (average for month) at the time of collection.

<u>Sample</u>	<u>Date</u>	<u>Dry Weight (gm)</u>	<u>Seawater Temperature (°C)</u>	<u>Insolation (cal/cm²)</u>
<u>Phaeophyta</u>				
Fucus vesiculosus	May 11, 1978	~10	12	600
Fucus vesiculosus	Aug 22, 1978	~ 5	22	600
Fucus vesiculosus	Oct 2, 1978	9.6	17	400
Fucus vesiculosus, juveniles	Oct 18, 1978	10.0	14	300
Petalonia fascia/Scytosiphon lomentaria	May 11, 1978	~5	12	600
Sargassum filipendula	Oct 2, 1978	6.6	17	400
Ascophyllum nodosum	Oct 18, 1978	21.8	14	300
<u>Chlorophyta</u>				
Codium fragile	Oct 2, 1978	5.5	17	400
Enteromorpha spp.	Oct 2, 1978	3.4	17	400
<u>Rhodophyta</u>				
Polysiphonia spp.	Oct 2, 1978	3.8	17	400
Porphyra umbilicalis	Oct 2, 1978	4.1	17	400
Chondrus crispus	Oct 18, 1978	8.3	14	300
Ceramium spp.	Oct 18, 1978	1.3	14	300
<u>Seagrass</u>				
Zostera marina	Aug 22, 1978	~2	22	600

gas chromatograph equipped with a flame ionization detector (FID) and splitless injector. Samples were chromatographed on an SE 54 glass capillary column (0.32 mm i.d. x 20 m long) purchased from Jaeggi (9043 Trogen, Switzerland) and on a UCON HB 5100 glass capillary column (0.3 mm i.d. x 20 m long) supplied by Dr. K. Grob (EAWAG, Dubendorf, Switzerland). The columns were held at room temperature for 8 min. and then programmed from 20 to 200°C at 3°C/min. for the SE54 or 20 to 180°C at 3°C/min. for the UCON. Helium was the carrier gas (ca. 1 ml/min.) Compound concentrations were calculated based on peak height relative to the 1-cl-nC₈ standard and were not corrected for stripping efficiency and FID response (e.g. the FID is about 4 times more sensitive to 1-cl-nC₈ than to bromoform on a weight basis).

Gas chromatography-mass spectrometry was performed on a Finnigan 3200 GC-MS system using an SE52 glass capillary column (0.3 mm i.d. x 20 m long). Electron impact spectra were acquired with an electron potential of 70 eV. Chemical ionization spectra were obtained with methane as the reagent gas at 950 μ and with electron energy of 130 eV.

RESULTS

Table 5-2 lists the major components identified, the GC retention times on the two columns, and whether EI or CI spectra were acquired. Sample spectra are shown in Appendix V. Retention indices were calculated relative to the even 1-chloro-n-alkanes.

Algal production and release of individual volatile organic compounds has been estimated by subtracting the seawater control concentration from that observed with the algae, and then dividing by the weight of the sample. These results are shown in Table 5-3 for the hydrocarbons and Table 5-4 for the halogenated methanes. Most of the discussion will be restricted to samples which showed more than 5 times the concentration of a given compound relative to the control seawater. Increases of only 2 - 5 times over control levels

Table 5-2. Retention indices (RI) on SE54 and UCON HB5100 glass capillary columns for hydrocarbons and halomethanes released to seawater by marine benthic algae. Crosses indicate mass spectra (shown in Appendix V) available from samples.

<u>Compound</u>	<u>SE54 RI</u>	<u>UCON RI HB5100</u>	<u>EI spec</u>	<u>CI spec</u>
pentadecane	415	388	x	x
heptadecane	512	485		
17:1	507	480	x	x
17:1	500	480	x	x
CHBr ₂ Cl	075	140	x	x
CH ₂ BrI	081	075	x	
CHBr ₃	123.5	189	x	x
CH ₂ I ₂	139	149	x	x

RI defined with respect to 1-chloro-n-alkanes

50-100: 1clnC₅ - 1clnC₆

100-200: 1clnC₆ - 1clnC₈

200-300: 1clnC₈ - 1clnC₁₀

300-400: 1clnC₁₀ - 1clnC₁₂

400-500: 1clnC₁₂ - 1clnC₁₄

500-600: 1clnC₁₄ - 1 clnC₁₆

Table 5-3. Hydrocarbon release rates (ng/gm dry weight/day) from algae into seawater. Values in parentheses indicate that seawater concentrations of hydrocarbons after algal incubation were 2-5 times greater than concentrations found in the control seawater. Other values represent increases in seawater concentrations of hydrocarbons of more than 5 times over the concentrations in the control seawater.

Table 5-4. Halomethane release rates (ng/gm dry weight/day) from algae into seawater. Values in parenthesis indicate that seawater concentrations of halomethanes after algal incubation were 2-5 times greater than concentrations found in the control seawater. Other values represent increases in seawater concentrations of halomethanes of more than 5 times over the concentrations in the control seawater.

Sample	Date	Release rates (ng/gm dry weight/day)				
		CHBr ₂ Cl	CH ₂ BrI	CHBr ₃	CH ₂ I ₂	CH ₂ I ₂
<u>Phaeophyta</u>						
Fucus vesiculosus	May 11, 1978			10		1
"	Aug 22, 1978		(0.2)	20		1
"	Oct 2, 1978		2	20		
"	Oct 18, 1978		(0.1)	4		(0.3)
" , juveniles						
Petalonia fascia/Scytosiphon lomentaria	May 11, 1978	1	(0.2)	30		
Sargassum filipendula	Oct 2, 1978			(1)		
Ascophyllum nodosum	Oct 18, 1978	(0.5)		8		
<u>Chlorophyta</u>						
Codium fragile	Oct 2, 1978			(1)		9
Enteromorpha spp.	Oct 2, 1978	(0.6)		20		
<u>Rhodophyta</u>						
Polysiphonia spp.	Oct 2, 1978					
Porphyra umbilicalis	Oct 2, 1978					
Chondrus crispus	Oct 18, 1978	(0.2)				4
Ceramium spp.	Oct 18, 1978					
<u>Seagrass</u>						
Zostera marina	Aug 22, 1978			2		(0.1)

are shown in parentheses. The lower limits allow assurance that observed concentration increases cannot be due to analytical imprecision.

DISCUSSION

Pentadecane was observed to be produced and released in large quantities in three samples: (1) Fucus, brown alga, May 11, (2) Petalonia/Scytosiphon, browns, May 11, and (3) Enteromorpha, green, October 2. All of the other samples of brown algae showed small (less than 5 times the control seawater) releases of this compound. The other Fucus samples may not have demonstrated the strong pentadecane release capacity for reasons of method or physiology. While the May Fucus sample was stripped at 35°C, all of the other Fucus samples were stripped at 20°C and for this reason may not have large pentadecane enrichments. This interpretation was not supported by finding only 6 ng nC₁₅/gm juvenile Fucus stripped at 50°C as compared with 20 ng nC₁₅/gm Fucus (May 11) stripped at only 35°C. Thus, while there may have been some effect of the temperature of stripping, it seems that other factors must also have been involved.

Seasonal differences in the physiology of Fucus at different times of year may have been important. Conover (1958) found that Fucus was "dormant" locally in the months of July and August, but had maximum growth in the months before and after this time. Mathieson et al. (1976) have shown that spring and early summer is the period of maximum growth and reproduction of Fucus vesiculosus in a New Hampshire estuary. Consequently, the May sample of Fucus may represent a physiological condition different from later samples.

Blumer and his coworkers (Clark and Blumer, 1967; Youngblood et al., 1971; and Youngblood and Blumer, 1973) have showed the predominance of pentadecane in brown algae. They have reported 10-100 µg nC₁₅/gm dry weight algae. Even the largest release rates, calculated for the brown

algal samples from the present work, would take many months to empty the reservoir of pentadecane in these algae. Therefore, these release rates appear reasonable.

These investigators have also reported somewhat lower levels of pentadecane in the green alga, Enteromorpha, of 1 $\mu\text{g}/\text{gm}$. The higher rate of release of pentadecane from the sample of Enteromorpha examined in this study may indicate a greater "leakiness" of this alga. This plant shows a high surface-to-volume ratio relative to its brown counterpart, Fucus. Even if handling of this fragile form caused the observed production, similar damage is to be expected in the environment. This alga lives in the shallowest waters and suffers breaking waves and occasional exposure.

Simple calculations may be made to see if the release rates indicated by these experiments may be responsible for the observed levels of pentadecane in CD seawater. A typical benthic algal biomass for this region is given by Conover (1958) as ranging between 1.5 and 4 kg wet weight/ m^2 . Assuming these plants are 80% water, this converts to 300 to 800 gm dry weight algae/ m^2 . At a production and release rate of 30 ng/gm dry weight/day and assuming the average residence time of water at CD is 2 days (ch 3&4), a standing stock of pentadecane as much as 18 to 48 $\mu\text{g}/\text{m}^2$ may be expected. For a 2-meter water column, this corresponds to 10 to 20 ng nC_{15} /liter seawater. Nearly all of the seawater samples assessed in the year-round study at CD were in this concentration range (figure 3-16). On three occasions (June and September, 1977 and May-June, 1978) pentadecane levels in seawater rose dramatically. These incidents may reflect particularly strong storm activity destroying algal structural integrity and releasing pentadecane to the seawater. On the other hand, algal physiology, which is closely aligned with environmental parameters such as light and temperature, may be responsible. Since these parameters are changing rapidly in

June and September, it may be more reasonable to expect algal physiology changes to cause the observed pentadecane seasonal increases. Algal incubations conducted precisely at these times of year are necessary to confirm this hypothesis.

Surprisingly, heptadecane was not produced and released at high rates in these incubation experiments. This lack of release is in strong contrast to the case of pentadecane. Previous workers (Clark and Blumer, 1967; Youngblood et al., 1971; and Youngblood and Blumer, 1973) have reported the importance of this hydrocarbon in red algae. They found between 100 and 1000 $\mu\text{g/gm}$ dry weight of red algae. At most, only a few ng/gm dry weight/day were found in the present experiments. A standing crop calculation similar to that performed for pentadecane indicates that this rate would support about 0.5 to 2 ng/liter seawater. Many of the CD year-round values are only slightly above this concentration range. Peak heptadecane concentrations at CD may be derived from algal species or physiological stages of algae not included in these studies.

The two green algae studied revealed very high production rates for some unsaturated 17-carbon compounds. The retention time and GCMS data, along with the work of Youngblood et al. (1971), suggest that the compound from Enteromorpha is *cis*-3-heptadecene. Since this compound shows such a high release rate, one would expect to observe it along with pentadecane in seawater. This compound was not seen in CD seawater and reaffirms the suggestion made by Schwarzenbach et al. (1978) that brown benthic algae were the major source of pentadecane. Codium also demonstrated production and release of another unsaturated heptadecene.

Production of halogenated methanes was found in these incubations. All of these compounds have been previously reported from a red alga, Asparagopsis taxiformis (Moore, 1976). Halogenation in the Rhodophyta has been extensively documented (see Fenical, 1975 for review), but little work has been done on other algal classes.

Members of every algal class showed production of bromoform (tribromomethane). The low levels of apparent production by the vascular plant, Zostera, were quite startling, however. Epiphytic algae or attached microorganisms may have been responsible. Also Zostera may have accumulated this compound from the surrounding seawater only to release it upon stripping. These sorts of "production" mechanisms may also be operating for some of the algae examined and explain the prevalence of this production.

An examination of the Fucus data suggests that maximum release of bromoform occurs in the middle of the summer, at a time when the algae may have been dormant (Conover, 1958). If a tribromo-2-keto-compound were present in the essential oil of this brown alga and were released during this period into the seawater, decomposition to produce bromoform would occur (Burreson et al., 1976, quoted in Moore, 1977).

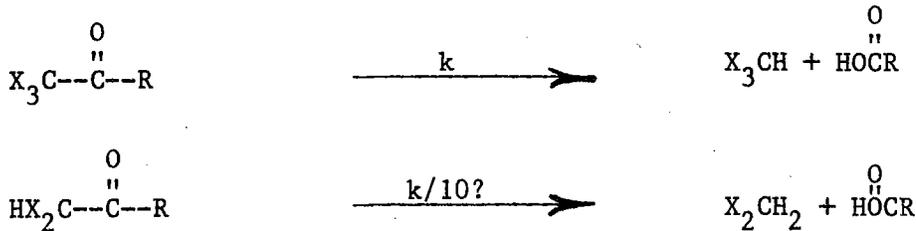
Lesser amounts of chlorodibromomethane were also frequently produced with bromoform; however strong production of this compound was confined to the brown algae samples.

Release rates of 20-40 ng haloform*/gm dry weight/day suggest that standing stocks of 1-2 ng*/liter seawater would result in coastal seawater. Such levels of bromoform were observed in the year-round

*Note that these weight values underestimate the true haloform levels due to insensitivity of an FID relative to the 1-cl-nC₈ internal standard.

study in some summer samples (Schwarzenbach et al., 1978; chapter 3) and in the August and October control seawater samples of this study.

Two dihalomethanes were also found. These were produced at about 0.1 times the rate of the trihalomethanes. This may reflect the greater difficulty of cleavage of the dihalo-2-keto-compounds relative to that of the trihalo analogues. The presence of iodine in both of these dihalocompounds would serve to enhance this cleavage.



Release rates on the order of several ng/gm dry weight/day suggest that standing stocks of less than 1 ng/liter seawater would result. Thus detection by the FID would not be expected and indeed the CD year-round samples did not reveal the presence of these compounds. However, future work utilizing an electron capture detector may be fruitful, since this detector is particularly sensitive to halogenated compounds.

Undoubtedly, many other compounds substituting halogens for one another were present in the algae of this investigation, but were not seen due to limitations of the methodology (e.g., iodoform may be too soluble and have too high a boiling point to be stripped).

One potential problem with this study is that algae may be artificially induced to release the volatiles to seawater by the experimental conditions. However, since algae do not have root systems, they do not die upon disengagement from the seafloor.

Also, wave action is frequently very strong in the shallow near-shore region and may be expected to break up algal structures. It was hoped that by restricting the period of incubation to only one day and by controlling the flask temperature at that of the ambient environment, the chemistry of the enclosed seawater would not drastically change and cause unnatural release of organic compounds.

The stripping process may also alter algal production and release of the volatiles. Warming the samples and agitating the algae with vigorous bubbling may influence the release of these substances. The efficiency of stripping a water sample with a large algal surface area included is unknown, but might be expected to be lower than that containing only water due to competition between the surface and the compound in solution (i.e., a "strippable" state).

Despite these reservations, the data do indicate that hydrocarbons and halocarbons are released at significant rates by various marine algae into seawater.

The purpose behind the biochemical synthesis of the halo-compounds is unknown. Fenical (1975) suggests that they may be utilized as anti-microbial or anti-herbivore agents. Thus a topical location of these materials would be most useful and their consequent release to the seawater would be expected to be easier than for hydrocarbons. If competitive advantages exist, it would also be useful for a higher marine plant such as Zostera to accumulate these compounds from seawater. Also it may be particularly advantageous to maximize production in the summer to protect plants during this period of intense grazing by animals.

Surprisingly, the Rhodophyta showed the least ability to release these halogenated compounds. These algae are well known for the halogenation of terpenes and other metabolites (Fenical, 1975; Crews, 1977). The studies of the red algae have typically involved destruction of the plant structure and therefore may not pertain to the introduction of compounds into seawater. It is possible that the physiological status of the red algae samples in these studies was such that the release of halocompounds was low.

Study of more algal classes with nondestructive conditions is necessary. Work to determine possible communication mechanisms using these chemicals in seawater may also be useful. Study of the degradation of these natural products may lend insight into the processes degrading more complex industrial halogenated materials (Fenical, 1975).

SUMMARY

Evidence for the production and release of several hydrocarbons and halomethanes by benthic marine algae was obtained.

The observed rates of release to seawater were consistent with the levels found in most CD seawater samples obtained in a year-round study of the region.

Seasonal physiological changes of the algae may be the most important factor controlling large inputs of volatile organic compounds to seawater.

CHAPTER 6. SUMMARY AND CONCLUDING REMARKS

The major objectives of this thesis were to identify and quantify volatile organic compounds in seawater, and to deduce their sources, transformations, and transport mechanisms. Two approaches have been taken to accomplish these goals. First, samples from 3 open-ocean regions, the Sargasso Sea, the western Equatorial Atlantic, and the upwelling region off Peru, were analyzed for volatiles, and correlations with ancillary data were sought. In the second approach, temporal variations of the concentrations of volatile organic compounds in coastal seawater were investigated and interpreted by comparison with those of known coastal processes.

Open-Ocean Seawater

Total volatile concentrations found in oligotrophic surface Sargasso Sea samples were only 10-30 ng/kg, while total concentrations in samples from the biologically productive upwelling region off Peru were about 100 ng/kg.

Pentadecane was found in surface seawater samples from all 3 regions, typically at 10-40 ng/kg. This compound was not derived from fossil fuel inputs as other homologues (e.g. nC_{14} and nC_{16}) were present at only trace levels. Based on a calculation, it appeared that a phytoplankton source was improbable, as the literature suggest that these organisms do not contain sufficient amounts of pentadecane. A transformation of the abundant fatty acid, hexadecanoic acid, to pentadecane by zooplankton, in a manner analogous to the production of pristane from phytanic acid, may have been the source of open-ocean pentadecane.

Three deep samples (ca. 2000m) contained high concentrations of pentadecane. In situ production or vertical transport and release at depth do not seem likely to be the source of this hydrocarbon occurrence. Advective transport of North Atlantic Deep water may have carried this fairly stable organic compound from the biologically productive surface formation sites to the deep ocean.

C₂-benzenes were found in the recently upwelled surface water off Peru. Concentrations of meta + para xylene were about 4 ng/kg at 5 and 20m, about 3 ng/kg at 100m, and about 2 ng/kg or less in the deeper samples. This distribution indicates a surface or atmospheric source. The air concentration necessary for the atmosphere to have been a source was 1-2 ng/l-air.

Vertical transport of m + p xylenes was indicated by the anomalously low concentrations of these aromatic hydrocarbons in 5- and 20-m samples at stations 4 and 5 off Peru and by an unusually high concentration of these compounds in seawater collected near the bottom at station 4. Low nutrient concentrations in these surface seawaters revealed that intense phytoplankton production had occurred, and if the m + p xylenes became associated with biogenic particulate matter, subsequent sedimentation and remineralization near the bottom may have introduced these compounds to deep water.

An unidentified alkene (mw 108) was recovered at up to 30 ng/kg from surface seawater samples from the upwelling region off Peru. The GC retention index and mass spectra of this compound showed that it is probably structurally related to fucoserraten, an unsaturated hydrocarbon used by the benthic alga, Fucus, as a sexual chemotactic signal. The unknown compound may be formed by isomerization of fucoserraten (trans,

cis-1,3,5-octatriene) to a more stable isomer (trans, trans-1,3,5-octatriene), and therefore Fucus may be the ultimate source of this material. However, planktonic sources cannot be ruled out.

C₆-C₁₀ aldehydes were found at 1-10 ng/kg in seawater off Peru. The correlation of their concentrations with chlorophyll a levels indicates a phytoplankton source. An even closer direct correlation of their concentrations with oxygen was found and led to the hypothesis that these aldehydes resulted from chemical oxidation of algal-produced metabolites, for example, unsaturated fatty acids. If unsaturated fatty acids were the precursors of aldehydes, the mechanism of this postulated reaction must have involved the intermediates free to rearrange rapidly (e.g. a vinylic free radical) so that similar abundances of these C₆-C₁₀ aldehydes would be produced.

Coastal Seawater

Total volatile concentrations found in a study of coastal seawater were between 200 and 500 ng/kg. Higher total concentrations coincided with the late-winter phytoplankton bloom. Anthropogenic inputs of hydrocarbons caused similarly high total concentrations.

All of the C₁₃-C₁₇ alkanes and pristane were found at relatively higher concentrations after a nearby oil spill. The "carbon preference index" was near 1 at that time and corroborated the assignment of these compounds to a fossil fuel source.

Pentadecane and heptadecane showed separate large concentration increases up to 80 and 20 ng/kg, respectively, in the summer. The high "carbon preference index" associated with these concentration maxima

indicated that these hydrocarbons resulted from biological inputs. It is known that benthic algae contain pentadecane and heptadecane, and a calculation demonstrated that it was reasonable to propose that these algae were the source of these saturated hydrocarbons.

The C₂- and C₃-benzenes concentrations covaried temporally in coastal seawater. They were most concentrated after the oil spill and after summer weekends. Summer weekends are peak periods of tourist and recreational activities in this coastal region, and strong inputs of C₂- and C₃-benzenes were attributed to the uses of fossil fuels during these activities.

An unknown compound (mw 108) was found at about 20 ng/kg in coastal seawater of Vineyard Sound in February and March, 1978. GC retention data and mass spectra showed that it was identical to the unknown compound recovered from off Peru and was similar to fucoserraten, the sexual chemotactic agent utilized by benthic algae, Fucus. The appearance of this unsaturated hydrocarbon compound coincided with the time of year in which Fucus were expected to be reproductively active. As was the case for the region off Peru, rapid isomerization of fucoserraten may have yielded the observed unknown compound.

Naphthalenes were found in coastal seawater at about 1 ng/kg in the summer, and as high as 5-10 ng/kg in the winter. The naphthalene to methyl naphthalenes ratios of the temporal study samples oscillated sinusoidally such that maximum ratios near 1.6 were found in the winter while minimum values of 0.8 appeared in the summer. This may be due to more indirect inputs (e.g. via the atmosphere) of naphthalenes to coastal seawater in the winter allowing more fractionation of these homologues.

C₆-C₁₀ aldehydes were also found in all the biweekly seawater samples from Vineyard Sound. The concentrations of these compounds increased

markedly during the late-winter phytoplankton blooms of 1977 and 1978. Oxidation of algal unsaturated fatty acids may also produce these aldehydes in coastal seawater as suggested for open-ocean seawater.

In addition, C₁₂-C₁₅ aldehydes occurred at very high concentrations in February, 1978. Tridecanal was recovered at more than 100 ng/kg. Cultures in log and stationary growth phase of Thalassiosira nordenskioeldii, the predominant diatom found in the late-winter bloom, did not produce these aldehydes. Oxidation by zooplankton or photochemically-produced free radicals may be necessary to produce these aldehydes from algal metabolites.

Dimethyl di-, tri-, and tetrasulfides were found at up to 20 ng/kg in coastal seawater. The observation that the first 2 hours of stripping frequently recovered less of these polysulfides than an additional 2 hours of stripping led to the conclusion that formation of these volatile sulfur compounds must occur within the sample. Marine microorganisms are known to produce methyl mercaptan, which may be oxidized to dimethyldisulfide. Reaction of methyl mercaptan or dimethyldisulfide with elemental sulfur will yield other polysulfides. These polysulfides may also be derived from degradation of other polysulfide metabolites.

C₂- and C₃-benzenes in Coastal Seawater

Additional work was performed to describe the sources of the C₂- and C₃-benzenes to coastal seawater. Short-term studies carried out over summer weekends showed that large inputs of these pollutants occurred at these times (2-10 fold concentration increases). The highest concentrations ever found coincided with ski boat activity in the immediate vicinity of the sampling site. The C₂- and C₃-benzene isomer distribution of the

average year-round sample data most closely resembled the distribution found in gasoline and auto-exhaust -dissolved-in-seawater. The largest deviations of the average year-round isomer distribution from these laboratory-determined distributions was for peaks containing para-substituted benzenes. These particular isomers may be preferentially degraded, for example by microorganisms,

C₂- and C₃-benzenes were not homogeneously distributed in surface seawater collected near CD in the fall, spring, or summer. Rain samples from June and November contained lower or equal concentrations of these aromatic hydrocarbons than seawater. Oyster Pond, a nearby freshwater pond on which motor boats are not allowed, had lower concentrations of C₂- and C₃-benzenes than seawater samples from CD collected at the same time in August and September. Atmospheric levels of these compounds measured at CD in August and September were also below those expected for equilibrium with coastal seawater. All of these results are consistent with the hypothesis that the atmosphere was not a source of C₂- and C₃-benzenes at CD from the spring through the fall.

Low concentrations of C₂- and C₃-benzenes in samples from inland sites showed that runoff through these relatively undeveloped regions dilutes seawater with respect to these compounds.

Hydrocarbons and Halomethanes from Benthic Algae and Seagrass

Algae released hydrocarbons and halomethanes to seawater during day long incubations. Pentadecane, heptadecane, and bromoform were produced at rates which may support the observed coastal seawater levels. The other compounds were not identified in the year-round study and release rates suggest that they would appear at only trace levels.

Pentadecane and the halomethanes were found especially in brown algae. Two green algae produced 2 different 17-carbon mono-unsaturated hydrocarbons.

Zostera marina, a higher vascular plant, also released bromoform to seawater. This observation suggests that Zostera, and other algae, may concentrate it from seawater.

Volatile Organic Compounds Not Detected in Seawater.

Volatile ketones, esters, and ethers were not detected in seawater. The methodology used was capable of the analysis of suitable representatives of these compound classes. Esters are known to have biological sources, but they were also found to be rapidly degraded chemically in seawater (half life of a few days with respect to hydrolysis in seawater). Ketones and ethers are at least as stable chemically as aldehydes, therefore their observed absence may be attributed to insufficient sources.

Several other volatile compound groups were not detected, and therefore upper limits for their occurrence in Vineyard Sound seawater of less than 1 ng/kg have been established. Lower n-alkanes (nC_8 - nC_{12}), prominent constituents of petroleum products; chlorinated benzenes, produced by chlorination of sewage and drinking water; and halogenated terpenes, known from red algae of shallow Pacific coast regions, were not detected.

Terpenes were also undetectable. This result is consistent with the following scenario for delivery of C_2 - and C_3 -benzenes and terpenes from land to the sea. The terrestrial sources of both generate atmospheric concentrations of individual compounds of 1-40 n/l-air near the site of input. The tertiary and allylic hydrogens of the terpenes and the benzylic

hydrogens of the C₂- and C₃-benzenes, are very reactive with atmospheric free radicals (e.g. OH·). Darnall et al. (1976) report that terpenes (limonene and beta-pinene) are attacked by OH· 1-3 times faster than the most reactive C₃-benzene. Therefore, decomposition of individual terpenes is faster than that for C₂- and C₃-benzenes during atmospheric transport. Relative transfer into seawater may be described by consideration of the relative partition coefficients. Solubility data for terpenes are not available, but an estimate of these values may be made using an empirical relationship of molar volume and log solubility (McAuliffe, 1966). Utilizing this approach, one finds that terpenes are about an order of magnitude less soluble than C₂- and C₃-benzenes. Thus since vapor pressures for terpenes are similar to those of C₂- and C₃-benzenes, one may conclude that the terpenes will partition between air and seawater such that the proportion of a terpene compound dissolved in seawater will be about an order of magnitude less than that for C₂- and C₃-benzenes. If atmospheric contributions to the C₂- and C₃-benzenes in coastal seawater at CD support the observed background levels of 1-10 ng/kg (chapter 4), then terpenes could well be present at less than 0.1-1 ng/kg, hence escaping detection.

Future Work

While this thesis adds to our knowledge of the spectrum of low-polarity organic compounds in the analytical window from n-octane to n-pentadecane, additional work is still required to determine the volatile organic fraction boiling between n-pentane and n-octane. This unstudied fraction contains many of the compounds used as solvents and consequently may reveal strong

anthropogenic inputs. Work in this area must include extra precautions to avoid spurious results derived from laboratory contamination. This problem has made the results on toluene from the analyses reported in this thesis difficult to evaluate.

Benzenes and naphthalenes are persistent constituents of coastal seawater. The transport of volatile aromatic hydrocarbons to seawater is incompletely understood. The elucidation of the role of the atmosphere as a source or a sink of these alkylated benzenes and naphthalenes to coastal seawater awaits the simultaneous application of more detailed air and water measurements. Also, little is known about the affinity of these aromatic hydrocarbons for particles, their transport into sediments, or their microbial degradation rates.

Additional work to confirm transformations, proposed in this thesis, is necessary. Also work to ascertain the roles of catalysts, light, and special reactants, such as elemental sulfur, is needed so that these reactions may be extended to predict effects on more complex organic matter in the sea.

Additional work is necessary to confirm the identification of the unknown alkene and its source. Since this compound, which may be a chemical signal related to the sexual reproduction of a benthic alga, and volatile hydrocarbon pollutants are found simultaneously in coastal waters in Vineyard Sound and off Peru, the question arises: do these pollutants interfere with the natural communication process?

Throughout these studies on the cycling of both natural and anthropogenic compounds, it was apparent that much additional work on acquiring basic physical chemical data, e.g. solubilities of compounds such as aldehydes, is needed.

Application of sensitive selective detectors (e.g. electron capture detector) may reveal many additional natural (e.g. haloterpenes) and anthropogenic (e.g. chlorobenzenes) compounds in seawater.

APPENDIX I ANALYTICAL METHODS USED FOR THE DETERMINATION OF
VOLATILE ORGANIC COMPOUNDS IN SEAWATER

Introduction

This appendix describes the methods used for the analysis of volatile organic compounds in seawater. These stripping methods have been adapted from others reported in the literature ("Tenax": Zlatkis et al., 1973; Novotny et al., 1974; Bellar and Lichtenberg, 1974; Bertsch et al., 1975; May et al., 1975; "Grob": Grob, 1973; Grob and Zürcher, 1976). Experiments performed to evaluate the methods will also be described. Finally, a brief discussion of the relative merits of these methodological approaches will be provided.

Sampling

PVC Niskins (5- and 30-liter) with stainless steel or Teflon-coated springs were used to collect seawater samples. The bottles were flushed with tapwater and then extensively rinsed at sea before use. Bottles were stored closed on deck.

A comparison of the volatile organic compounds in surface seawater samples collected with a 5-liter glass round bottom flask and a PVC Niskin did not reveal any differences. This was also seen for coastal seawater samples (Schwarzenbach et al., 1978).

Sampling was always performed with the winds blowing off the sea and onto the side of the ship with the hydroplatform.

On the Sargasso Sea cruise, water samples were transferred through the air into round bottom flasks. For the western Equatorial Atlantic samples, water was transferred from the Niskin samplers through glass

tubing into round bottom flasks. Finally, on the Peru cruise, the seawater was passed through polypropylene tubing, precombusted glass fiber filters, and a stainless steel filter holder before entering the glass flasks. No indication of contamination by these transfers was found. It seems that the limited contact with open ocean air during transfers does not add volatile organic compounds at the ng/kg level. This was also found by Schwarzenbach et al. (1978) for samples transferred at coastal sampling sites.

Tenax Methodology

The first method chosen to investigate open ocean volatiles sought to provide rapid and routine semiquantitative analysis of this fraction. Based on the literature, methods utilizing Tenax as a solid adsorbent of volatiles purged from aqueous samples by dynamic headspace stripping seemed most suitable. The following is a description of the details of this methodology as it was applied to the analysis of seawater samples.

Tenax traps

The Tenax traps were made from 0.125" o.d. x 1.5" long Pyrex glass tubing. One end was firepolished until the opening constricted to less than 1 mm. A glass wool plug was inserted and packed into this constricted end. Then 6 mg 60/80 mesh Tenax beads (approximately 0.1 m² surface area) followed by a second plug of silanized glass wool were added. Individual traps were stored in Teflon-lined screw-cap vials which were previously washed with soap and water and baked dry. The traps were cleaned just before use by heating to 250°C under helium flow (2 ml/min) for 1 hour.

Tenax (Applied Science Laboratories, Inc., State College, Pennsylvania) is a polymer of 2,6-diphenyl-para-phenylene oxide that has been shown to serve as a useful adsorbent for low-to-medium polarity organic compounds (Zlatkis et al., 1973; Bellar and Lichtenberg, 1974; Novotny et al., 1974; Bertsch et al., 1975; Dowty et al., 1975; May et al., 1975). It has no affinity for water. Furthermore, samples may be stored on Tenax for several weeks (Zlatkis et al., 1973). This polymer is thermally stable (up to 400°C; van Wijk, 1970; Sakodynskii et al., 1974) and hence is suitable for thermal desorption of a sample load in the hot injection port of a gas chromatograph.

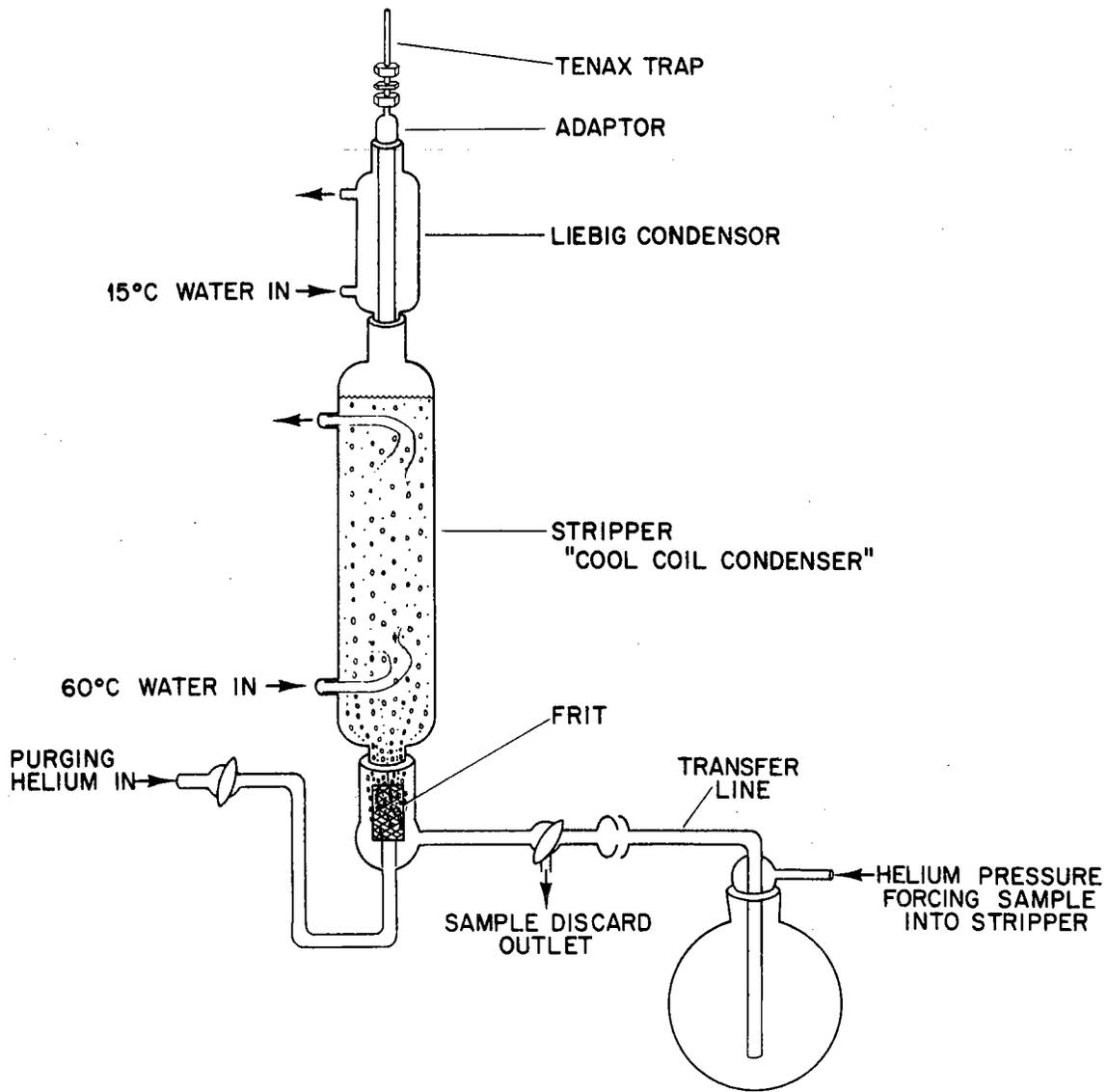
Stripper

The stripper (figure I-1) reservoir consisted of a 2 liter "cool coil" condenser with 24/40 ground glass joints. Below this was a glass-blown piece including the frit (pencil shaped, fine porosity) for introduction of the purging gas and a sidearm tube with a stopcock and ball joint for sample input. Above the stripper was a Liebig condenser operated at 15°C to minimize water transport to the trap (Zlatkis et al., 1973; Novotny et al., 1974). An adapter on the Liebig condenser reduced the 24/40 exit to 0.25" glass tube. This, in turn, was reduced with a 0.25" male to 0.125" male swagelok union with Teflon ferrules. When not in use, an 0.125" glass rod was inserted into this union to keep the stripper clean. A Tenax trap was substituted for this rod just prior to seawater sample introduction into the stripper.

Stripping

A precleaned trap was inserted in place on the stripper. The "cool coil" condenser had 60°C water running through it to rapidly heat the

Figure I-1. Stripper used with Tenax traps.



sample. Sample water was forced into the stripper reservoir by connecting a 2-liter round bottom flask containing the sample to the sidearm piece for sample introduction and pressurizing this flask with helium. Midway through sample transfer, the stopcock was closed, the pressure was released, the joint in the transfer line was parted, and an internal standard (20 ng each 1-chloro-hexane, -decane, -dodecane in 2 μ l acetone) was injected into the water in the transfer line. Connections were rapidly remade and the stripper filling was completed. This transfer took about 10 minutes during which time a 1700 ml sample initially at 15°C was heated to 20°C at the stripper bottom and 40°C at the top. Immediately upon bubbling, temperatures equilibrated, and at the end of a 5 minute strip, the water was at 50°C.

Once the sample was introduced, purging with helium was begun. High-purity charcoal-filtered helium was used for stripping at 150 ml/min. After 5 minutes of stripping, the gas flow was stopped, and the trap was replaced by the glass plug. The trap was returned to the small vial and stored in a freezer. The seawater was then forced out the sample inlet tube by continued bubbling with helium into the plugged stripper; once the stripper was empty, the helium flow was continued for an additional 5 to 10 minutes to flush the stripper and leave it full of helium for the next sample.

Gas chromatography and combined gas chromatography-mass spectrometry

The volatile organic compounds were detected and identified using glass capillary gas chromatography (GC) and combined gas chromatography-mass spectrometry (GC-MS). GC was performed with an HP5700 chromatograph equipped with a flame ionization detector and subambient attachment (CO₂). An 0.125" injector was used and filled halfway with 0.125" o.d. glass

tubing to hold the short Tenax trap near the injection port opening and to reduce the dead volume of the injection port. The column extended into the injection port for the length of this glass insert. The other end of the column extended into the detector just below the bottom of the flame jet. The front of the column was made into a small loop for cryogenic trapping. Both ends of the column were deactivated with PG20,000 (0.5% in CH_2Cl_2).

Sargasso Sea samples were chromatographed on an 0.3 mm o.d. x 20 m long SE30 glass capillary column purchased from J & W Scientific (Sacramento, CA). This column was programmed at room temperature for 2 min and then 30-200°C at 4°C/min. The carrier was helium at 1 ml/min.

The western Equatorial Atlantic samples were analyzed using a 0.3 mm o.d. x 20 m long UCON LB550 glass capillary column. This phase was chosen to work in conjunction with the reduced temperatures made possible by the subambient attachment. The column was programmed at 10°C to 120°C at 2°C/min. Helium was again used as the carrier at 1 ml/min.

For analysis, the GC oven was cooled to its starting temperature, and then the oven control was turned to "off". A liquid nitrogen (LN) bath was placed around the cryogenic loop. Next, the septum cap was removed, the Tenax trap dropped into the injection port, and the cap quickly reinstalled. Desorption was then carried out at 250°C for 5 minutes with helium flow carrying the volatiles into the cryogenic loop at the front of the GC column. Finally, the LN was removed and with the trap still in place, the temperature program was begun.

For GC/MS analysis, the UCON LB550 column was transferred to a Finnigan 3200 quadrupole GCMS. Tenax traps were analyzed as with the GC. Electron impact spectra were obtained with 70 eV ionization voltage. Chemical

ionization spectra were acquired using CH_4 as the reactant gas at 950 μ pressure, with the ionization chamber at about 180°C and 130 eV ionization potential.

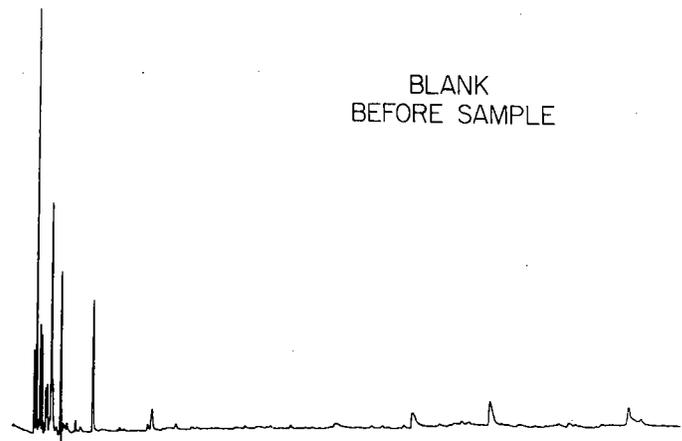
Evaluation of the Method

Blanks were determined throughout the cruises. Precleaned Tenax traps were placed on the helium-flushed empty stripper. Helium purging was begun, as if the seawater sample were in place, and continued for 5 minutes. At the end of this time the trap was removed to a screw-cap vial and stored in the freezer along with other sample traps until GC analysis. Typical gas chromatograms for blanks (no standards added) and open ocean seawater samples are shown in figure I-2. The blank chromatogram was very similar to that shown previously by May et al. (1975). Contamination peaks were present in the "solvent region" (pentane, acetone, methylene chloride) and for this reason, and because the resolution in this region of the chromatogram was poor, this part of the gas chromatograms was subsequently ignored. Peaks were also present near the high-boiling end of the chromatogram, but these elute beyond the volatile compounds concentrated by stripping.

A large and variable blank was found for the western Equatorial Atlantic samples. Identification of the compounds found in this contamination showed the presence of several unusual compounds which were stored in the same refrigerator as the Tenax traps. Traps stored in more than one refrigerator before GC analysis showed contamination from compounds unique to each refrigerator. Thus, Tenax trap storage in the screw-cap vials was not always adequate for the prevention of large blanks.

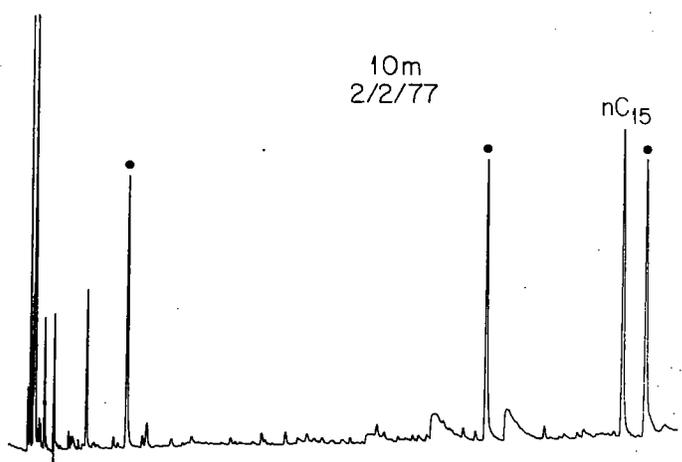
Figure I-2. Gas chromatograms showing volatile compounds collected with Tenax method from 10 m and 100 m seawater samples at a station southeast of Bermuda in February, 1977. Gas chromatograms from blank analyses run before and after the samples are also shown. Closed circles indicate the 1-chloro-n-alkane internal standards (6, 10,12) which were added to the water at 10 ng/kg. For gas chromatography conditions see text.

BLANK
BEFORE SAMPLE



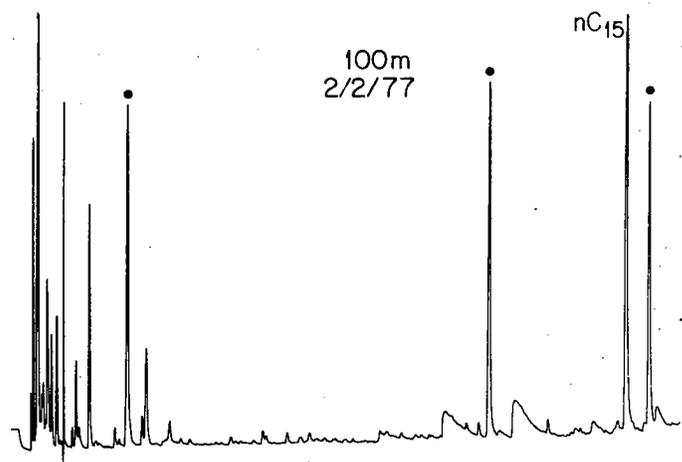
10m
2/2/77

nC₁₅

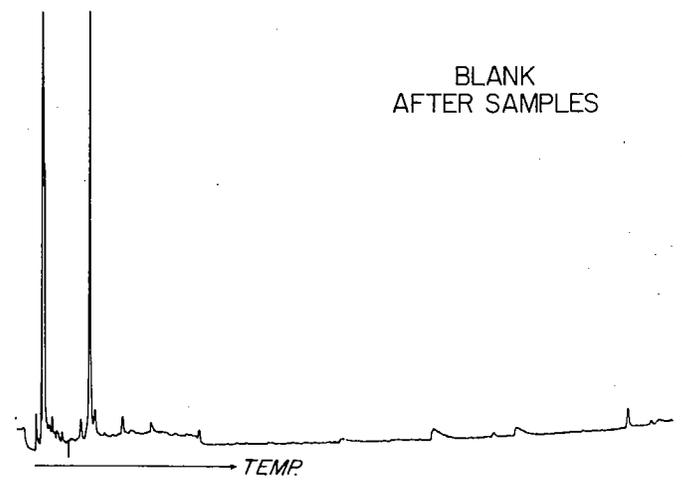


100m
2/2/77

nC₁₅



BLANK
AFTER SAMPLES



For traps analyzed soon after loading, compounds boiling higher than about 100°C and lower than about 300°C, could be measured at the ng/kg level and be seen well above background in the chromatograms.

The efficiency of stripping was assessed in a series of experiments in which coastal seawater samples were spiked with known quantities of a variety of compounds. For recovery experiments at less than 50 ng/kg, the water was prestripped, removed from the stripper, allowed to cool, spiked and then analyzed. Table I-1 shows the recoveries of these compounds as compared to direct spikes of solvent containing the same compounds on the traps. Nonpolar and highly volatile compounds were recovered at greater than 80% efficiency. Slightly polar materials, such as the aromatics, were stripped at lower efficiency. Relatively polar substances such as the aldehydes were recovered poorly or not at all. Higher-boiling compounds such as heptadecane were found at reduced efficiency. Pentadecane recoveries at low spike levels appear enhanced and this was probably due to relatively large concentrations still in the seawater despite prestripping. A 50% recovery figure was probably appropriate for pentadecane. No other evidence for nonlinearity of recovery was seen within the 10-300 ng/kg range tested. Relative variability of these recovery determinations was calculated to be approximately 20%.

The standard deviation of the analysis of 21 samples from the western Equatorial Atlantic for the 1-chloro-n-decane internal standard was $\pm 20\%$. Other work on seawater samples collected in the coastal region near Woods Hole shows similar levels of reproducibility for other compounds. Table I-2 shows this result for an aromatic and an aldehyde, as well as for two internal standard chloro-alkanes.

Table I-1. Recoveries (%) of standard compounds from seawater using Tenax method relative to direct spikes of compounds in solvent onto Tenax traps. Standard compounds were added to seawater at concentrations from 12-290 $\mu\text{g}/\text{kg}$. Also shown are the mean recoveries (%) the standard deviations (%) of the 8 samples about the mean (unless noted in parentheses) and the deviation relative to the mean.

Spike Concentrations
(ng/kg)

compound	Spike Concentrations (ng/kg)										mean (%)	std. dev. (%)	std. dev. mean
	12	12	12	22	39	48	125	290	290	290			
n-octane	85	121	96	94	121	108	63	66	66	94	22	23%	
1-octene	85	113	96	91	125	117	63	68	68	95	23	24%	
n-pentadecane	119	79	68	90	58	42	49	52	52	70 (8) 54 (5)	26 (8) 10 (5)	37% 19%	
n-heptadecane	27	---	---	25	8	5	4	3	3	12 (8) 5 (4)	11 (8) 2 (4)	92% 40% (4)	
1-cl-n-decane	84	72	95	82	103	92	57	71	71	82	15	18%	
ethyl benzene	38	55	51	49	46	53	39	40	40	46	7	15%	
1,3,5-trimethyl benzene	36	41	51	50	62	61	44	43	43	49	9	18%	
n-butyl benzene	62	64	65	87	79	79	66	74	74	72	9	13%	
naphthalene	4	5	6	5	4	4	5	5	5	5	1	20%	
methyl naphthalene	4	6	5	4	?	5	5	5	5	5	1	20%	
heptanal	10	6	15	12	8	9	5	6	6	9	3	33%	
decanal	33	50	46	53	34	28	32	28	28	38	10	26%	
2-octanone	3	2	3	5	3	4	4	5	5	4	1	25%	
methyl octanoate	12	20	19	22	19	19	22	22	22	19	3	16%	
1-octanol	3	0	2	1	1	2	1	1	1	1	1	100%	

Table I-2. Standard deviations of replicate analyses of seawater samples by Tenax method. 1-cl-n-hexane and -decane were added to 3 of 4 replicate samples, while o-xylene and decanal were already present.

RUN NO.	1-cl-nC ₆	1-cl-nC ₁₀	A(o-xylene)	B(decanal)
1	---	---	2.3	0.94
2	2.8	2.7	3.3	0.81
3	2.9	2.6	3.3	0.94
4	3.4	3.2	3.8	0.88
	-----	-----	-----	-----
\bar{x}	3.0	2.8	3.2	0.89
σ	0.33	0.31	0.63	0.06
σ/\bar{x}	11%	11%	20%	7%

Grob Methodology

The methods of Grob (1973), Grob and Zürcher (1976) and Schwarzenbach et al. (1978) were used to analyze seawater samples from the Peru upwelling region. Briefly, this involved stripping a 2-liter seawater sample in a recirculating fashion for 2 hours at 35°C and 1.5 liters/minute flow. Purged volatiles were trapped on a charcoal trap consisting of 1 mg charcoal sandwiched between 2 stainless steel screens. After stripping, 20 ng 1-chloro-n-octane in 2 μ l CS₂ was added to the trap and then the trap was extracted with 15 μ l CS₂. Further analysis was by GC or GCMS.

Method Tests

In order to investigate the effects of filtering and poisoning on the Peru upwelling region samples, 6 samples were drawn in replicate and subjected to different combinations of these treatments (Table I-3). The two deepest samples (6/1000 m and 5/900 m) suggest that the treatments do not add significant volatile compound concentrations (i.e., less than about 2 ng/kg).

Shallow control samples suggest that filtering may remove some volatiles. This was particularly evident for the aldehydes in the 5-meter samples. Filtered samples contained 40 to 70% lower aldehyde concentrations than did unfiltered ones. Filtering experiments on coastal seawater samples conducted before the cruise, indicated that only high-boiling nonpolar compounds such as pentadecane and naphthalene were removed by filtration (about 50% removal). Therefore, some volatiles may be associated with particles in seawater, and caution must be exercised in comparing filtered and nonfiltered samples.

In an experiment to assess the effects of seawater storage on the volatiles, 30 liters of coastal seawater were collected in a Niskin sampler,

Table I-3. Volatile compound concentrations (ng/kg) in Peru upwelling region seawater samples subjected different treatments (i.e. none, poisoning, or filtering and poisoning).

compound	m & p xylenes	mw 108	nC ₁₅	hexanal	heptanal	octanal
sample (stn/depth) treatment						
6/1000	tr	tr	tr	1.7	tr	tr
6/1000P	tr	tr	tr	1.8	tr	tr
6/1000FP	tr	tr	tr	2.2	tr	2.2
5/900	tr	tr	tr	tr	tr	tr
5/900P	tr	tr	tr	tr	tr	tr
5/900FP	tr	tr	3.5	2.4	tr	2.3
2/5P	4.5	9.3	21.8	10.0	9.9	4.5
2/5FP	4.3	4.7	13.4	4.6	3.3	2.3
3/20P	2.9	2.5	14.9	3.9	3.2	2.0
3/20FP	2.7	2.7	10.1	3.5	2.9	3.3
4/340P	tr	tr	tr	tr	tr	tr
4/340FP	6.8	tr	tr	tr	tr	tr
5/5P	3.0	22.2	8.3	9.9	9.5	6.2
5/5FP	2.8	18.4	10.3	6.3	5.4	3.9

tr: trace (less than 2 ng/kg or 10% of the I.S.)
 F: filtered
 P: poisoned

glass fiber filtered by gravity into six 2-liter reagent flasks, poisoned with mercuric chloride, and spiked with compounds exhibiting the same functionality as those found in the Peru samples but with carbon skeletons not seen in coastal seawater. Three of these samples were analyzed immediately, while the other 3 were sealed in styrofoam chests and stored at 4°C for 1 month (as were the cruise samples). At the end of that time, the samples were analyzed and the resultant recoveries for the spiked compounds compared to those exhibited by the unstored samples (Table I-4). The three hydrocarbons, an alkane, an olefin, and an aromatic, all showed approximately 60% relative recovery at 1.5 times greater efficiency than a month earlier. Each triplicate set showed less than 20% variation of these results.

The decreased recoveries of the hydrocarbons after storage may be due to their removal from solution, i.e., a stripable state. Possibly these compounds were adsorbed onto the walls of the glass flask (Kaiser, 1971) or were incorporated into newly formed particulate matter (Riley, 1970). In keeping with this, the more soluble the hydrocarbon, the greater was its relative recovery after storage.

On the other hand, 2-ethyl hexanal is relatively very soluble and may be unaffected by these processes. In fact, these changes may have increased the proportion of this compound in a stripable state and thus accounted for the improved recovery after storage.

Comparison of Tenax and Grob Methods

The Tenax method offers several advantages. First, it is much faster and is the only one capable of handling numerous samples as they are returned from hydrocasts. Next, the traps are easy to prepare. It is difficult to construct the charcoal traps of Grob, and we have always

Table I-4. Recoveries (ng/kg) of standard compounds added to 6 filtered and poisoned replicates after no sample storage and after one month sample storage. Also shown are the relative recoveries (%) after one month as compared to no storage.

	<u>Compounds</u>			
	2,6-dimethyl- 3-heptene	2-ethyl- hexanal	1-ethyl- 2-methyl- benzene	tridecane
<u>Analysis</u>				
at time zero				
1.	33.3	16.6	20.9	20.2
2.	29.1	12.0	19.5	19.3
3.	30.5	11.9	18.7	18.1
$\bar{x} \pm \sigma$	31.0 \pm 2.1	13.5 \pm 2.7	19.7 \pm 1.1	19.2 \pm 1.1
at time one month				
1.	17.1	20.3	12.6	10.4
2.	18.9	19.6	11.9	11.5
3.	20.2	20.6	13.9	11.4
$\bar{x} \pm \sigma$	18.7 \pm 1.6	20.2 \pm 0.5	13.3 \pm 0.7	11.1 \pm 0.6
$\frac{\bar{x}(\text{one month})}{\bar{x}(\text{zero})} \times 100\%$	60%	150%	68%	58%

purchased them. Tenax may be more inert than charcoal in terms of degrading the volatiles. Thermal desorption of Tenax is efficient. On the other hand, charcoal traps desorb only about 35% of naphthalene and about 60% of 1-octanol. The Tenax method may allow for greater sensitivity as the entire sample is introduced into the GC, while the Grob technique limits this to about 10-20% of the sample. If good storage methods are devised, Tenax may allow the analysis of very low-boiling compounds. This is impossible with the Grob method due to solvent interference.

On the other hand, the Grob procedures offer certain advantages. Relatively involatile compounds are recovered more efficiently. This, in turn, facilitates greater reproducibility (1 sigma about 10% compared to 20% observed for Tenax). The gas recirculation method tends to maintain the chemical character of the seawater sample (e.g., oxygen content). This may help preserve the organisms in unfiltered samples. Helium, on the other hand, would strip oxygen, which may be useful for inhibiting oxidation reactions during stripping. Methods for the introduction of internal standards are easier for Grob techniques and enable monitoring of two separate steps in the procedure. Probably the most important advantage of the Grob system is that multiple GC or GCMS analyses of the volatile concentrate are possible. This allows analysis on more than one type of column. Stream splitting of the purging gas onto several Tenax traps could potentially provide similar multiple-analysis capability, but this has proved to be an irreproducible procedure.

Both methods allow for good sample storage. In this work, Tenax traps have retained their volatiles for many months; the problem we have experienced with these traps is that, unless they are adequately isolated, they will acquire high contamination levels. Grob microvials can retain

a solvent extract for many months, but occasionally poor fitting plugs allow sample loss.

Neither method introduced water into the glass capillary columns at a level which resulted in the rapid deterioration of the columns.

Appendix II. Hydrographic data from stations in the western Equatorial Atlantic Ocean, March 1978.

Station	Depth (M)	Potential Temperature (°C)	Salinity (‰)	Sigma _θ (‰)	chl a (µg/kg)	PO ₄ (µM/kg)	NO ₃ (µM/kg)	SiO ₂ (µM/kg)
0°58.4'N x 39°26.7'W								
13	5	26.993	36.140	23.618	0.4	0.11 0.12	0.08	1.42
	87	25.574 25.378	36.510	24.330 24.389	2.4	0.16 0.15	0.19	1.28
	131	19.043 19.029	36.145	25.900 25.904	0.4	0.53	6.48	3.26
	594	6.200 6.212	34.566	27.217 27.216	0.02	2.10	37.74	23.33
	792	4.707 4.687	34.544	27.379 27.381	0.02	2.23	38.23	30.94
	2376	2.900 2.922	34.988	27.902 27.900	0.02	1.19	21.88	22.60
0°1.8'N x 34°0.0'W								
15	7		35.962 35.956		0.2 0.2	0.06 0.05	0.08 0.00	1.23 1.66
	116	14.775	35.536	26.467	0.2	0.90	14.16	5.78
	146	13.557	35.402	26.620	0.1	1.03		6.75
	176	12.518	35.291	26.747	0.08	1.15	19.77	8.06
	750	4.729 4.731	34.498	27.340 27.340	0.05	2.18	38.94	30.16
	2255	3.038 3.031	34.965	27.872 27.872	0.01	1.18	22.57	21.44
3°30'N x 32°02'W								
17	5	27.358	35.876	23.305	0.03	0.09 0.12	0.08	2.25
	83	20.113 20.088	35.974	25.491 25.498	1.8	0.18	2.24	2.15
	133		35.347		0.3	1.21	21.69	7.87
	173	12.551 12.548	35.244	26.703 26.703	0.1	1.28	23.28	8.60
	631		34.579		0.03	2.23	38.98	26.63 26.67
	641	5.495 5.516	34.559	27.300 27.297	0.04	2.12	37.88	26.09 26.09
	1896	3.528 3.505	36.104	28.733 28.735	0.03	1.17	23.31	18.68

5°11.2'N x 33°29.5'W
19 6

	26.434	35.983	23.674	0.3	0.05	0.04	1.23
	26.440		23.672				
108	17.819	35.824	25.965	0.5	0.86	15.19	5.64
147		35.326		0.1	1.18	19.22	8.69
188	10.947	35.079	26.881	0.05	1.46	24.17	11.07
	10.945		26.881		1.49		
680		34.590		0.03	2.23	33.60	28.42
690	5.187	34.556	27.334	0.03	2.16	34.69	28.66
	5.165		27.337				
1623	3.277	34.966	27.856	0.02	1.19	20.21	22.17
	3.288		27.854				

6°42'N x 38°24'W
21 14

	26.166	35.985	23.758	0.4	0.00	0.00	1.23
	26.119		23.772				1.23
34	26.130	36.010	23.786	0.3	0.00	0.10	1.28
70		36.193		1.5	0.02	0.01	1.42
114	15.655	35.669	26.365	0.4	1.01	17.38	7.19
154	12.992	35.347	26.694	0.2	1.24	21.46	9.13
	13.030		26.868				
164	13.317	35.373	26.647	0.2	0.97	20.98	9.23
341	8.933	36.821	28.587	0.05	1.70	27.60	15.14
706	5.887	34.584	27.270	0.02	2.13	33.54	25.90
	5.807		27.280				
ca450	7.515	34.730	27.166	0.03	2.00	33.32	20.03
517		34.709		0.04	2.21	35.78	21.10
		34.724		0.03	1.50	52.80	19.84

9°03'N x 45°55'W
24 7

		36.120		0.3	0.05	0.00	1.62
ca35		36.154		0.5	0.07	0.00	1.71
							1.71
35	25.900	36.155	23.966	0.6	0.08	0.02	1.62
	25.894		23.969				
83	22.029	36.173	25.116	1.8	0.65	10.27	3.85
180	12.098	35.294	26.830	0.1	1.50	23.58	10.39
ca700		34.648		0.04	2.30	34.59	25.32
1923	3.441	34.989	27.855	0.02	1.28	21.08	18.24
	3.466		27.852				

Appendix III. Volatile organic compounds in coastal seawater.
Schwarzenbach, R.P., R.H. Bromund, P.M. Gschwend,
and O.C. Zafiriou. *Organic Geochemistry*, 1, 93-107.

Volatile organic compounds in coastal seawater*

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Abstract—The occurrence and temporal variations of a variety of low to medium polarity organic compounds in the volatility range bracketed by *n*-heptane and *n*-octadecane have been studied in seawater from a station in Vineyard Sound, Massachusetts, and from a tidal creek in Sippewissett Marsh, Massachusetts. The closed-loop vapor phase stripping method of Grob and Zürcher (*J. Chromatogr.*, v. 117, p. 285–294), high resolution glass capillary gas chromatography, and gas chromatography–mass spectrometry were used. Approximately 50 compounds were found at ≥ 2 ng/kg; most were recovered at less than 10 ng/kg, while the 20 ng/kg level was only rarely exceeded by a few components. The total material recovered was 0.2–1.0 μ g organic carbon equivalent/kg seawater. The major compound classes found were normal alkanes, alkenes, aromatic and alkylaromatic hydrocarbons, *n*-aldehydes, dimethyldisulfide and dimethyltrisulfide, and a few halogenated hydrocarbons. The preliminary results suggest that both biogenic and anthropogenic sources were represented. Also, air–sea gas exchange and other physical processes may be important non-biological sinks.

INTRODUCTION

SEAWATER contains an extremely complex, diverse, and largely unidentified mixture of organic compounds. Historically most studies of seawater organic matter have focused on such properties of the mixture as its concentration and distribution (Skopintsev, 1966, 1971; Menzel and Ryther, 1970; Menzel, 1974; Williams, 1971; Riley, 1970; Wangersky, 1972, 1976; among others), its size distribution (Sheldon *et al.*, 1972; Sharp, 1973; Ogura, 1974), or qualitative properties such as $\delta^{13}\text{C}$ (Williams, 1968; Williams and Gordon, 1970), absorption spectrum (Mattson *et al.*, 1974), or biodegradability (Barber, 1968; Ogura, 1970, 1972; Zsolnay, 1975). Only a minor portion of the organic matter in seawater has been characterized structurally, principally as amino acids and sugars and their biopolymers, urea, fatty acids and alcohols and their esters, sterols, hydrocarbons, partially characterized pigments, and vitamins (Wagner, 1969).

Recently, efforts have been made to obtain the molecular composition of some compound classes in seawater for numerous individual samples in order to characterize the marine environment in terms of the individual organic structures present and their spatio-temporal variability (e.g. Brooks and Sackett, 1973; Lee and Bada, 1975; Gagosian, 1976). These studies have obtained information regarding the sources, transport, transformations, and sinks of organic matter in the water column.

Thus far methodological difficulties have prevented the application of this molecular approach to seawater organic compounds over a structural range broader than individual compound classes. The analytical task of determining these compound groups routinely has been arduous enough to make wider coverage by simultaneous use of several methods prohibitively difficult.

In this paper we report the preliminary results of analyses of volatile organic compounds (VC) in coastal seawater samples. The compounds falling into the VC class constitute a little-investigated group of compounds in seawater, which are too volatile to be handled by conventional extraction techniques, yet not volatile enough to be determined by procedures designed for the determination of very light organic compounds, such as C_1 – C_4 hydrocarbons (Swinnerton and Linnenbom, 1967; Brooks and Sackett, 1973).

We used the closed-loop vapor phase stripping method of Grob and Zürcher (1976), in conjunction with glass capillary gas chromatography (GC) and combined gas chromatography–mass spectrometry (GC–MS), for the rapid and routine recovery, separation, identification, and quantification of this chemically diverse group of marine organic compounds. The method consists of removing those compounds with appreciable vapor pressure over seawater from a sample by purging it with a large volume of gas as finely divided bubbles, followed by adsorbing the compounds in the gas stream onto a charcoal trap. Subsequent extraction from charcoal and high performance GC and GC–MS analyses characterize and quantify the volatile compounds. The method was originally developed for drinking water quality assessment and the study of pollutants in lakes and rivers (K. Grob and G. Grob, 1974). We have applied the method to studying volatile compounds at the ng/kg level.

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Dr. Max Blumer proposed and initiated the application of the methods used here to seawater samples as one approach to unravelling the complexities of marine organic chemistry (Blumer, 1975). He recognized during his tragic illness that he would be unable to complete this effort, and requested not to be listed as an author of this paper. While respecting this wish, we emphasize that he made very substantial contributions to the underpinnings of this study.

METHODS

Sampling

Water samples were taken from sites near Woods Hole, MA. Nearshore samples were taken approximately every two weeks beginning March 1977 at high tide in fair weather from "Chemotaxis Dock" (CD). This unused wooden pier extends about 10 meters into Vineyard Sound in 1.5–2.5 m water. The salinity is roughly 32‰. The area has weak to moderate longshore currents, a sandy, rocky bottom, and extensive seasonal benthic algal cover. No boats are moored within 0.5 km and most ferry and recreational boating is greater than 2 km away. The adjacent shoreline is pebbly and only lightly used recreationally. A 50 m band of forest vegetation separates the beach from the nearest road.

During winter, 1976–1977 considerable ice formed along the shores of Vineyard Sound and Buzzards Bay. In late December, 1976 a sizeable spill of No. 2 fuel oil occurred at the head of Buzzards Bay. In January, 1977 during partial breakup of the ice, oiled ice was seen passing from Buzzards Bay through Woods Hole and into Vineyard Sound (J. Farrington, personal communication) a few km from our sampling site.

A few samples were taken in Great Sippewissett marsh on Buzzards Bay, Massachusetts at the confluence of two small tidal creeks. One creek drains an area of high blue-green algal mat density while the other empties an area with high concentrations of inorganic sulfur compounds and detectable sulfide at times in the water (R. Howarth, personal communication).

Water samples at these shore sites were taken at 20 cm (5 cm for low tide marsh) depth by dipping a 1 l round bottom flask attached to a 2 m aluminum pole by a PVC bracket. The water was poured into a 5 l glass round bottom flask that was rinsed three times before adding 4 l of water. Repouring samples between 5 l flasks did not greatly affect the volatiles found. The sample was spiked with internal standards (40 ng each 1-chloro-hexane (No. 100), 1-chlorodecane (No. 300), and 1-chlorododecane (No. 400) in 2 μ l acetone (compounds are numbered for identification on chromatograms). The sample flask was stoppered, swirled, and returned to the laboratory for stripping within 1–4 hr after collection.

Offshore coastal waters were sampled from the *R/V*

Asterias by lowering a stoppered empty 5 l round bottom flask in a PVC frame to 5–10 m. The stopper was pulled from the flask by a line. After the flask filled, the sample was retrieved and stoppered immediately. Once ashore, 1 l of water was poured out and discarded at CD, the sample was spiked, and was then brought to the laboratory for stripping. This procedure entrapped CD air rather than ship or lab air in the flask headspace, reducing erratic airborne contamination. CD air and PVC do not add significant volatile contamination to our samples. Chlorophyll *a* was measured using the fluorescence technique of Strickland and Parsons (1972). Nutrients were measured using a Technicon Autoanalyzer.

Stripping and collecting VC

We term the organic compounds potentially recoverable from natural waters by stripping methods 'volatile compounds' (VC). VC were recovered from seawater by stripping the samples using a slight modification of the closed-loop method of Grob and Zürcher (1976). A larger sample flask and frit and a different pump were used. In this technique, the Teflon and stainless steel pump forces air through a frit near the bottom of the water. The VC partition between the bubbles and the water. The effluent air is warmed to 60°C to drop its relative humidity and then passed through a micro charcoal adsorptive trap (Bender-Holbein AG, Reidistr. 15, 8006 Zurich, Switzerland) before pump intake for recycling. We maintained the water temperature at 35°C, and the air flow rate at 1.5–2 l/min for 2 hr through a 20 mm diameter coarse porosity frit. Samples with 1.5 l headspace were stripped in the same five liter flask in which they were collected. A stainless steel and Teflon bellows pump, Model MB 118 purchased from Metal Bellows (1075 Providence Highway, Sharon, MA 02067), was used.

Immediately after stripping, the VC were extracted from the trap with a total of 15 μ l of purified carbon disulfide. Just prior to this extraction, 40 ng 1-chlorooctane (No. 200) in 2 μ l CS₂ were added onto the filter surface as an extraction recovery standard. The samples were stored in microtubes in a refrigerator. With the exception of increasing the sample and pump size, the methods of Grob and Zürcher required no modification to deal with seawater samples. However, the generally low levels of VC in seawater relative to the waters previously investigated by stripping necessitated numerous blank and control analyses.

Analysis

GC was performed on a Carlo Erba Model 2551 AC gas chromatograph equipped with FID and a special splitless injector designed by Grob (personal communication, 1976). Separations were performed on a 20 m \times 0.35 mm i.d. SE 54 glass capillary column (Jaeggi, 9043 Trogen, Switzerland) of separation number 34. An aliquot (usually 1 μ l) of the VC in

CS₂ was injected with the split closed (K. Grob and K. Grob, Jr., 1974). The split was opened (10:1 ratio) after 30 sec. The helium carrier gas flow rate was 3 ml/min at 20°C. The injector and detector were operated at 250°C. The temperature program was: 20–22°C isothermal for 8 min, then 3°C/min to 250°C.

GC-MS analyses and structural identifications were performed on a Finnigan Model 3200 equipped with a Data System 6000 computer. A Finnigan Model 9500 gas chromatograph equipped with a Finnigan splitless injector and a 25 m × 0.32 mm i.d. glass capillary SE 52 column was interfaced to the MS with an all-glass transfer line, held at 250°C, allowing coaxial introduction of reagent gases for chemical ionization (CI-MS) (Blum and Richter, 1975, 1977). Mass spectra were recorded at the rate of one per 1.5 sec from 35 to 350 amu at 70 eV and 90°C source temperature for EI; and at one per 1.5 sec over a range of 60–350 amu at 130 eV and 90°C source temperature for CI. Methane was used as the chemical ionization reagent gas. Compounds were identified by comparison of GC and GC-MS properties with those of authentic standards or library spectra as indicated in Table 2.

Method characteristics

Blanks. Since most VC in seawater were present below the 10 ng/kg level, much below the levels previously reported for other samples (K. Grob and G. Grob, 1974), a premium was placed on achieving sensitivity and low, reproducible blanks. Figure 1A shows a representative gas chromatogram of the trap extract from stripping a moist 51 flask containing prestripped air. As usual, 40 ng 1-chloro-octane (No. 200) were added to the trap before extraction and its peak height corresponded to 10 ng/kg in water usually processed. This typical instrument blank shows quantitative recovery of the standard and the presence of very few peaks, corresponding to less than 1 ng each VC/kg seawater introduced by the stripping procedure from the apparatus and by subsequent manipulations. Contamination from laboratory air can erratically be a serious problem. Pouring pre-stripped water from one flask to another in the laboratory introduced numerous contaminants at the 10 ng/kg level. However, stripping five liters of 'CD air' (sampled by emptying a flask filled with pre-stripped water at CD) does not give these laboratory contamination problems.

Recovery. The recovery of internal standards relative to 1-chloro-octane (No. 200) was always above 85%. We restrip all samples immediately after the first strip and again after 24 hr to monitor recovery and compound generation. The internal standards are never detectable in these restrips. Figure 1B is typical of additional recovery of VC on restripping a relatively non-turbid water sample after initial strip (Fig. 2C). For most compounds little material above the blank occurs in the restrip. However, substantial

quantities of *n*-pentadecane (No. 417) and *n*-heptadecane (No. 515) frequently occur in the second strip, and the yield of dimethyldisulfide (No. 37) and dimethyltrisulfide (No. 149) typically increases, especially after 24 hr (Fig. 1C). A few samples that were especially turbid or contained high total levels of volatiles yielded substantial recoveries on restripping. This is illustrated in Fig. 1D, the restrip of the turbid sample shown in Fig. 2B. The VC concentrations reported in this paper are those recovered in the first 2 hr stripping only.

Recovery experiments were also conducted in duplicate using two different strippers, traps and analysts. Different seawater samples were spiked with a test mixture of compounds encompassing a variety of chemical functionalities and volatilities within the expected range of the technique. Samples were spiked at 5, 10, 50, and 100 ng of each compound/kg seawater. Acetone solutions of the mixture were used to introduce the spike. The two lower level experiments utilized exhaustively prestripped low-turbidity CD water, whereas the two higher level experiments used untreated CD water of low turbidity. The recovery for each compound was determined by comparing GC peak areas (normalized to 1-chloro-octane, No. 200) determined by a Columbia Scientific Instruments "Supergrator 3" electronic integrator for the sample with peak areas from GC analysis of the test mixture. The test mixture composition and the average recoveries are given in Table 1. For each compound, the fraction recovered was independent of the level added, suggesting the absence of 'threshold effects' at these levels. The poor recovery of the naphthalenes is entirely due to poor extraction recovery from the charcoal traps (35%) as shown by trap spiking experiments. Although 1-octanol is also lost to some extent on the traps (58% recovery), its extremely poor total recovery is probably primarily due to its high water solubility.

Reproducibility. In order to assess the reproducibility of sampling, stripping, and analysis as applied to environmental samples, duplicate seawater samples were obtained on five separate occasions and processed concurrently on two different strippers by two different analysts. Precision was estimated by measuring the heights of twenty of the larger peaks relative to the 1-chloro-octane (No. 200) peak height. With the few exceptions listed below, these peak height ratios did not vary between duplicates by more than 15%. Peak height ratio differences of up to 30% were shown by dimethyldisulfide (DMDS, No. 37), demethyltrisulfide (DMTS, No. 149), nonanal (No. 225), decanal (No. 275), and *n*-heptadecane (No. 515).

We find that removing salt and other deposits from seawater samples from the charcoal traps by the procedure of Grob and Zürcher (1976) after every few samples maintains good reproducibility. The moderately large headspace over our samples was adopted to minimize the salt spray transport onto the traps. We have experienced irreversible trap clogging from

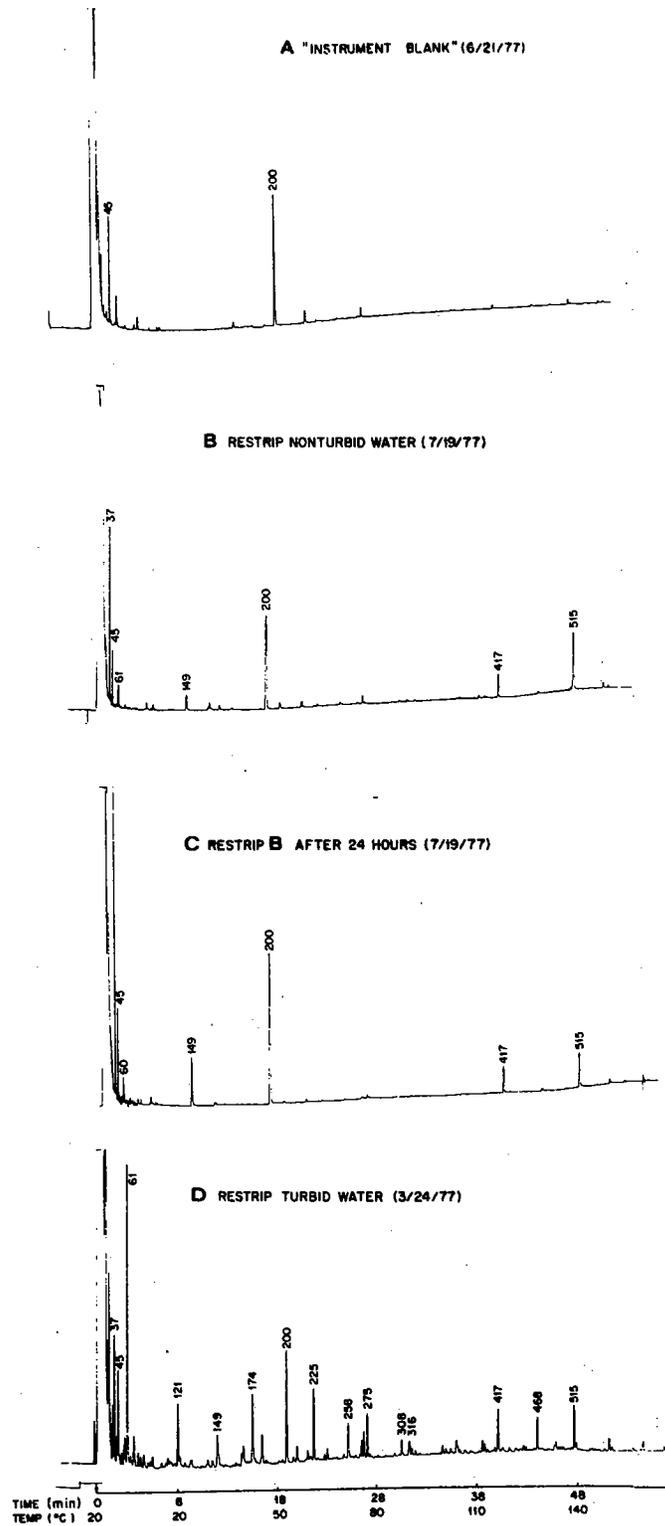


Fig. 1. Characteristics of the procedure. Peak No. 200 is the internal standard applied to the trap at the time of extraction and corresponds to 10 ng/kg of seawater sample. For peak number identifications refer to Table 2.

Table 1. Recoveries of standard compounds spiked into seawater

Compound	Recovery (%)
1-octene	> 85
<i>n</i> -octane	> 85
<i>n</i> -pentadecane	> 85
<i>n</i> -heptadecane	> 85
1-chloro- <i>n</i> -decane	> 85
ethylbenzene	> 85
1,3,5-trimethylbenzene	> 85
<i>n</i> -butylbenzene	> 85
naphthalene	35
1-methylnaphthalene	35
<i>n</i> -hexanal	20
<i>n</i> -decanal	25
2-octanone	35
methyl octanoate	60
1-octanol	< 5

accidental transport of large amounts of material to the trap, as, for example, when samples foam.

RESULTS

Figure 2A-C shows chromatograms selected from an on-going year-round study of VC at the CD site. Sample A was taken just after the melting and breakup of ice cover (March 1977), sample B was taken at the height of the spring buildup of chlorophyll *a*, and sample C was taken on 19 July 1977, a few weeks after the Memorial Day increase in recreational activity on Cape Cod. Figure 2D shows VC sampled several km from shore in Buzzards Bay on 21 June 1977. The chronological variation in selected peak height ratios and chlorophyll *a* for the period March-August 1977, is shown in Fig. 3. Figure 4 shows VC from the marsh creek sampled at low and high tides.

We have identified most peaks with height equivalent to ≥ 2 ng/kg of 1-chloro-octane (No. 200) by glass capillary GC and by GS-MS (EI and CI) characterization and comparison with authentic materials or EI library spectra. The compounds identified are listed in Table 2, which also lists estimates of the concentration ranges found at CD. Concentration estimates were corrected according to the recoveries given in Table 1 for those compounds and close analogs to them. Other compounds are reported as the chloro-octane (No. 200) peak height equivalent and are thus not corrected with recovery and FID response factors.

Examination of the GC-MS data revealed that most of the peaks seen by GC are predominantly or entirely single compounds; the larger peaks are almost totally resolved on the glass capillary column. Furthermore, specific ion-series searches did not reveal the presence of additional compound types.

DISCUSSION

The stripping method enabled us to recover a variety of compounds from seawater in a volatility range that has heretofore been little investigated. Several major features stand out. About fifty compounds are routinely detected, belonging to several major structural classes. These are primarily: alkanes, alkenes, aromatic hydrocarbons, aldehydes, methyl sulfur compounds, and some halogenated compounds. Most of the individual compounds are recovered in the concentration range trace-10 ng/kg. Only toluene (No. 45) routinely occurs at > 10 ng/kg; other peaks very rarely exceed 20 ng/kg. By summing the estimated recoveries or by planimetry of chromatograms, we estimate that the typical total detector response is equivalent to 300-1500 ng/kg of VC, or approximately 0.2-1.0 μ g/kg volatile organic carbon (VOC), as discussed later.

Although the VC are operationally defined and their levels are low, their behavior is relatively consistent. Duplicate samples from CD and the marsh creeks were quantitatively similar for a wide variety of compounds at high and low concentration levels. Restrips of most samples yielded very little additional material. Furthermore, in other experiments (R. M. Bromund and P. M. Gschwend, unpublished) in which CD samples were stripped at 25 or 60°C with inert gas, and the VC trapped on and thermally desorbed from Tenax (Applied Sci. Tech. Bull. No. 24; Novotny *et al.*, 1974; Bertsch *et al.*, 1975; Zlatkis *et al.*, 1973; Bellar and Lichtenberg, 1974), a similar picture of VC was obtained. Thus, major changes in technique result in only moderate, rather than drastic changes in the observed VC distributions. The recovery of spikes (5-100 ng/kg) from seawater is reproducible, level-independent, and generally fair to excellent, even for labile compounds such as aldehydes.

Thus, by the criteria of reproducibility, level-independence, insensitivity to minor changes in methodology, and spike recovery, the VC are a relatively well-behaved subclass of material. However, the components of VC recovered do not necessarily represent the total quantity of those structures in the sample, since these compounds may also be present in forms that do not exert significant vapor pressure. For example, we know nothing about the stripability of potentially volatile compounds within living and dead biological structures, which spiking cannot simulate. With further work, the behavior of compounds on restripping may yield useful indications concerning sources and speciation of VC in natural waters.

Non-aromatic hydrocarbons

Aside from samples with a major oil-derived component, the predominant aliphatic hydrocarbons were *n*-pentadecane (No. 417) and *n*-heptadecane (No. 515). During the period of oil contamination, other hydrocarbon peaks and an "unresolved complex mixture" of compounds were also present (Fig. 2A).

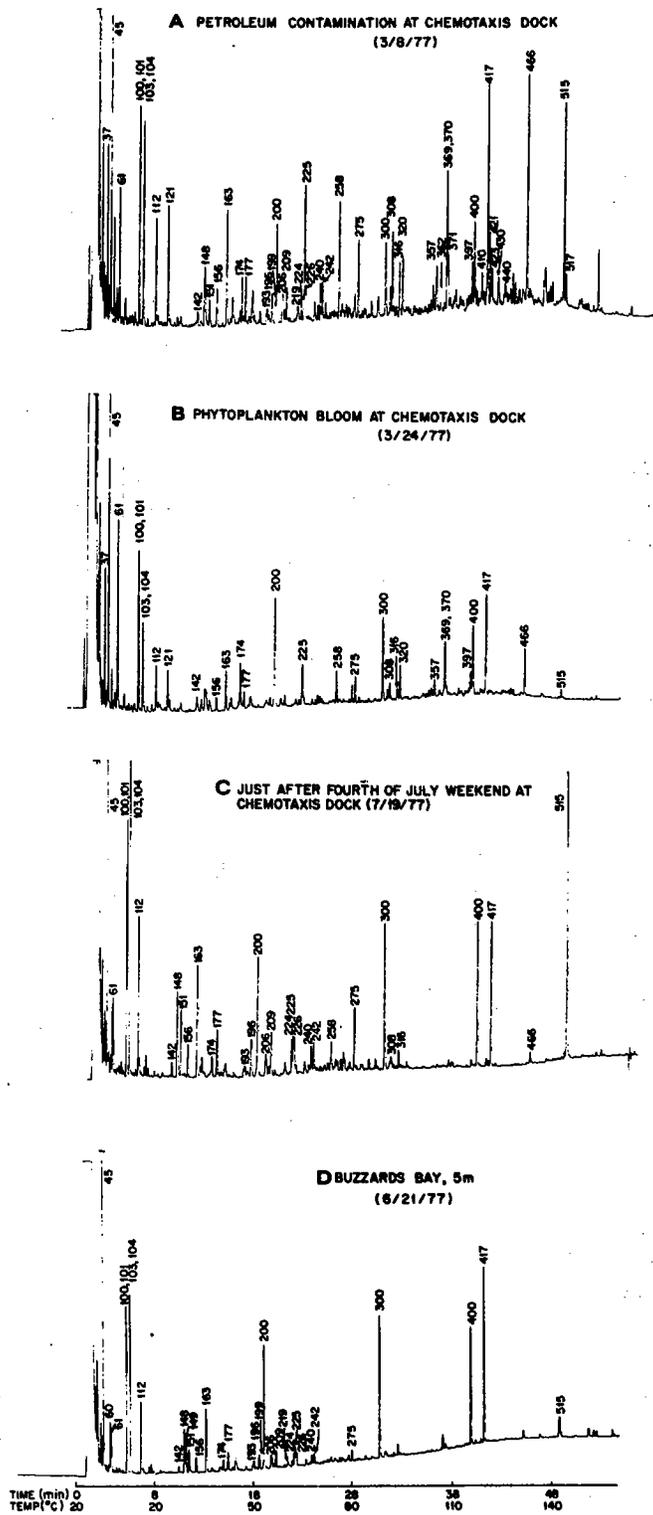


Fig. 2. Variations in VC found in some coastal seawater samples. Peak Nos. 100, 300, and 400 are internal standards added to the seawater sample at 10 ng/kg, while peak No. 200 is the internal standard applied to the trap at the time of extraction. For peak number identifications refer to Table 2.

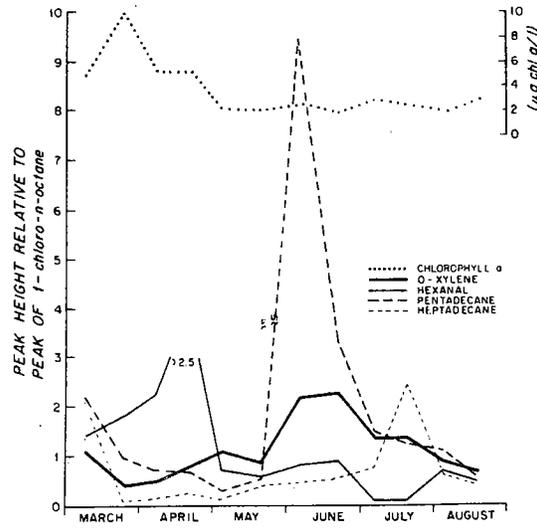


Fig. 3. Temporal variations at CD (March-August 1977).

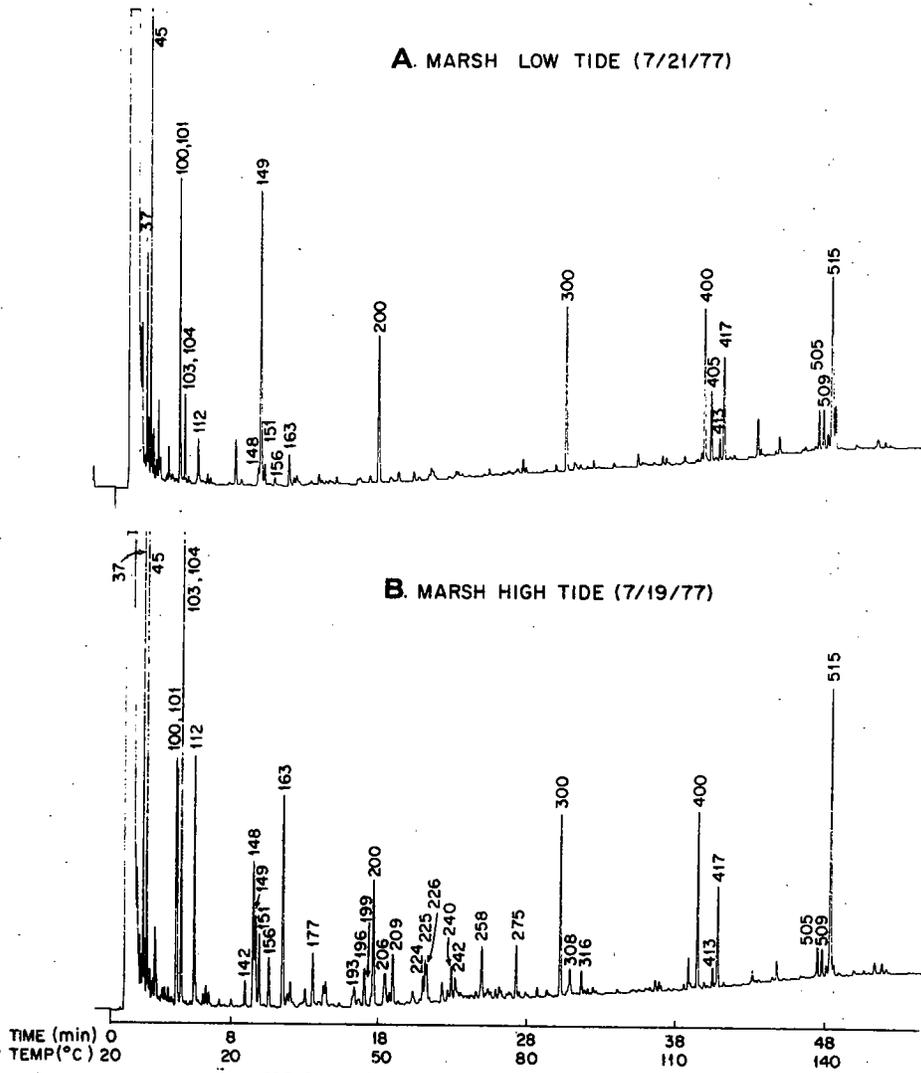


Fig. 4. Gas chromatograms showing VC found in marsh waters. Peak Nos. 100, 300, and 400 are internal standards, added to the seawater sample at 10 ng/kg, while peak No. 200 is the internal standard applied to the trap at the time of extraction. For peak number identifications refer to Table 2.

Table 2. Volatile compounds in coastal seawater samples

Compound number	Structure	Concentration range* (ng/kg)		Identification§ method
		CD	Marsh†	
37	dimethyldisulfide (DMDS)	?	?	2
45	toluene	>10	>10	1
60	tetrachloroethylene	5	5	2
61	<i>n</i> -hexanal	5-100	tr-10	1
100	1-chloro- <i>n</i> -hexane	(10)	(10)	standard
101	ethylbenzene	5-25	2-20	1
103	1,3-dimethylbenzene	15-50	6-40	1
104	1,4-dimethylbenzene			1
109	bromoform	?	?	2
112	1,2-dimethylbenzene	5-25	2-20	1
121	<i>n</i> -heptanal	5-40	tr-10	1
142	<i>n</i> -propylbenzene	tr-3	0-2	1
148	C ₃ -benzene	4-20	1-12	2
149	dimethyltrisulfide (DMTS)	?	?	2
151	1,3,5-trimethylbenzene	3-15	1-8	1
156	C ₃ -benzene	2-10	1-6	2
163	C ₃ -benzene	5-25	2-15	2
174	<i>n</i> -octanal	5-40	tr-10	2
177	C ₃ -benzene	2-10	1-6	2
193	C ₄ -benzene	1-5	tr-2	2
196	C ₄ -benzene	2-10	tr-4	2
199	C ₄ -benzene	1-5	tr-2	2
200	1-chloro- <i>n</i> -octane	(10)	(10)	standard
206	C ₄ -benzene	2-10	tr-4	2
209	C ₄ -benzene	2-10	tr-4	2
219	C ₄ -benzene	2-5	tr-2	2
224	C ₄ -benzene	2-5	tr-3	2
225	<i>n</i> -nonanal	5-70	tr-20	2
226	C ₄ -benzene	2-10	tr-4	2
240	C ₁₀ H ₁₂	2-10	tr-4	2
242	C ₄ -benzene	2-10	tr-4	2
258	naphthalene	5-40	tr-10	1
275	<i>n</i> -decanal	5-50	tr-20	1
300	1-chloro- <i>n</i> -decane	(10)	(10)	standard
309	2-methylnaphthalene	2-25	tr-5	1
316	1-methylnaphthalene	1-20	tr-5	1
320	<i>n</i> -tridecane	0-5 tr	1	
357	2-ethylnaphthalene	0-15†	—	1
362	2,6-dimethylnaphthalene	0-20†	—	1
369	<i>n</i> -tetradecane	0-10	tr	1
370	C ₂ -naphthalene	0-20†	tr	2
371	C ₂ -naphthalene	tr-20†	—	2
397	acenaphthalene	tr-15†	—	2
400	1-chloro- <i>n</i> -dodecane	(10)	(10)	standard
405	C ₁₅ H ₃₀	—	tr-5	3
410	C ₃ -naphthalene	tr-10†	—	2
413	C ₁₅ H ₃₀	—	1-3	3
417	<i>n</i> -pentadecane	5-100	5-15	4
421	C ₃ -naphthalene	tr-10†	—	2
423	C ₃ -naphthalene	tr-10†	—	2
430	C ₃ -naphthalene	tr-10†	—	2
440	C ₃ -naphthalene	tr-10†	—	2
466	<i>n</i> -hexadecane	1-20	1-3	1
505	C ₁₇ H ₃₄	—	1-12	3
509	C ₁₇ H ₃₄	—	1-3	3
515	<i>n</i> -heptadecane	1-30	5-30	1
517	pristane	tr-5	—	2

* Based on peak heights relative to 1-chloro-*n*-octane, corrected for inefficient recovery where necessary.

† Assuming same recovery as naphthalene.

‡ Sampled in late June and July 1977.

§ 1. GC-MS using EI and CI spectra and by conjection with authentic standards; 2. GC-MS using EI and CI spectra; 3. tentative (GC-MS-CI spectra). All EI spectra were compared to library spectra.

Some of the chronological changes in hydrocarbon concentrations shown in Fig. 3 were major. For example, in early March, several samples taken before a period of severe storms showed considerably higher levels of *n*-alkanes and aromatic hydrocarbons, presumably derived from a single source (oil contamination). After this stormy period, the concentrations were markedly reduced. Chemical or biological removals seem unlikely to produce such an abrupt change, but mixing, air-sea exchange, and particulate adsorption followed by sedimentation from the water column may all have been involved. Later in the year, pentadecane and heptadecane showed separate major concentration changes, suggesting that specific (biological?) processes had become dominant.

Most of the pentadecane and heptadecane observed probably came from biogenic sources. We suggest that they were primarily derived from the local benthic algae, rather than the phytoplankton. The standing crop and productivity of the benthic algae were much greater in this shallow nearshore zone (average depth about three meters for several hundred meters offshore) than that of the phytoplankton (Blinks, 1955). Also, the phytoplankton produce unsaturated hydrocarbons along with pentadecane and heptadecane (Blumer *et al.*, 1971), and we would expect to see these if the phytoplankton were responsible for the hydrocarbons in the water. Youngblood *et al.* (1971) found that local brown benthic algae contained predominantly pentadecane, while green and red benthic algae contained mainly heptadecane. They reported that these compounds occurred at about 0.02% of the total algal dry weight. If we assume a spring-summer benthic primary productivity in this area of 10 g C/m²/day (Kanwisher, 1966) and a g C/dry weight ratio of 0.5, then the growing season production of these compounds is about 4 mg/m²/day. The standing stock near CD of these compounds determined by stripping was about 10 ng/kg seawater, or about 30 μg/m². These very rough estimates imply that if all the primary production of these hydrocarbons passed through a stage accessible as VC, the standing stock could be turned over many times per day. Alternatively, if most of this material cycles through the marine environment in forms inaccessible to determination as VC, a slower turnover of these VC is required.

If these and other alkanes are present in the dissolved state or a weakly complexed form in seawater, they should be subject to air-sea gas exchange processes. By extrapolating the data of McAuliffe (1966) and Button (1976), we estimate the thermodynamic solubility of pentadecane in distilled water is 20–40 ng/kg and heptadecane is 1–2.5 ng/kg. Thus, we suggest that at 10 ng/kg pentadecane is probably at the borderline of its thermodynamic solubility in seawater, while heptadecane is probably not all present in a simple, aqueous solution. The possibility that many other forms of hydrocarbons exist in seawater is well-known, from the cellular material suggested

above through material sorbed on clays (Meyers and Quinn, 1973), or hydrophobically bonded to other organic materials (Boehm and Quinn, 1973). Nevertheless, an approximate maximum air-sea gas exchange flux can be estimated by assuming that these compounds are truly dissolved in seawater at 10 ng/kg, the approximate levels found for extended periods in calm weather. The extremely low water solubilities of these compounds (and other alkanes) in combinations with their known vapor pressures at 20°C lead to partition coefficients (*w/v* in air per *w/v* in water) in the range of 10⁴–10⁵. Since we could not detect these compounds in CD air, we will assume the atmosphere is thermodynamically a perfect sink, and use the stagnant boundary layer model (Broecker and Peng, 1974) to estimate the flux across the air-sea interface. Assuming a 100 μm stagnant boundary layer thickness (corresponding to mean windspeed ~9 kts.), and molecular diffusivity for this non-polar compound similar to that of radon (10⁻⁵ cm²/s):

$$\begin{aligned} \text{Flux}_{\max} &= -D \left(\frac{dC}{dz} \right) \\ &= \frac{(-10^{-5} \text{ cm}^2 \text{ s}^{-1})(10^{-11} \text{ g cm}^{-3})}{10^{-2} \text{ cm}} \\ &= -10^{-14} \text{ g/cm}^2/\text{s} \\ &= -10^{-10} \text{ g/m}^2/\text{s}. \end{aligned} \quad (1)$$

For gas exchange in the extensive shallow area <3 m deep:

$$\begin{aligned} \tau_{\text{exchange}} &= \frac{A}{-dA/dt} \\ &= \frac{(10^{-11} \text{ g/cm}^3)(<3 \times 10^6 \text{ cm}^3/\text{m}^2)}{10^{-10} \text{ g/m}^2/\text{sec}} \\ &< 3 \times 10^5 \text{ s or less than 4 days.} \end{aligned} \quad (2)$$

If alkanes are present in solution in shallow waters, they will exchange rapidly into the atmosphere. In fact, any dissolved VC for which the atmosphere can be presumed to be a perfect sink, will have similar residence times with respect to air-sea exchange independent of concentration.

The absence of numerous other hydrocarbons at CD (in the absence of petroleum contamination) deserves comment. Most notably, the terpenes released to the atmosphere in large quantities from terrestrial vegetation (Went, 1960), do not appear to be transferred to the coastal waters we have studied. (We have achieved excellent recoveries of limonene and pinene spiked into seawater at about 100 ng/kg.) The unfavorable partition coefficients for alkanes could prevent effective gaseous input to the water. The absence of nearby rivers minimizes waterborne transport of land-derived materials. Moreover, production of such compounds as pentadecane and hep-

tadecene (Youngblood *et al.*, 1971), C_{11} alkenes (diclopterenes, Moore, 1977) and pristane (Blumer *et al.*, 1964) at CD is probably much less than that of $n-C_{15}$ and $n-C_{17}$. Assuming the same turnover time with respect to air-sea gas exchange [Equation (2)], the resultant steady-state concentrations can be expected to be undetectably low. Additional sinks, such as adsorption and mixing with offshore waters can only lower the steady-state levels even further.

Aromatic hydrocarbons

Toluene and many of the isomeric C_2 to C_4 alkyl benzenes are present; together they form the group of compounds most abundant and consistently present at CD. They are found in all samples, despite our precautions to minimize or eliminate contamination by these compounds. They are absent in the blanks and in five liter samples of air from CD. Therefore we believe that they are not artifacts, but are actually present in the samples. Toluene (No. 45) is often a major peak; the other alkylated benzene concentrations covary. The isomer distributions are conveniently displayed as $(M + 1)^+$ mass chromatograms of the CI (methane) mass spectra data files. Making the reasonable assumption that these isomers show similar proton affinities, the normalized $(M + 1)^+$ mass chromatograms give the isomer distributions directly. Figure 5 shows the CI-MS spectra of representative C_2 -, C_3 -, and C_4 -alkyl benzenes. Figure 6 shows $(M + 1)^+$ mass chromatograms revealing the relative isomer distribution. Relative ratios can be seen less definitely in the reconstructed chromatograms themselves. Similar patterns were found for all CD samples, suggesting that similar processes determine the concentrations of all these related compounds. Ethylbenzene (No. 101) and propylbenzene (No. 142) show changes in relative concentration, perhaps due to an enhanced ease of biodegradability. Many of these compounds have been reported before in municipal and natural fresh waters (Grob, 1973; K. Grob and G. Grob, 1974; Grob *et al.*, 1975; Bertsh *et al.*, 1975; Saunders *et al.*, 1975; Giger *et al.*, 1976) and in air (Bertsch *et al.*, 1975). K. Grob and G. Grob (1974) have suggested that atmospheric transport of gasoline-derived compounds was the source. The estimated (w/v air per w/v water) partition coefficients for alkylbenzenes are $\sim 0.1-1$, so atmospheric transport and subsequent dissolution is reasonable if w/v air concentrations are greater than or equal to 0.1-1.0 times the observed w/v water concentrations (see Table 2). However, since we detected no VC in a preliminary measurement of air, the atmosphere would appear to be an insignificant or, at best, irregular source. The ubiquitous toluene has obvious potential anthropogenic sources, but may also be of natural geochemical origin. Moderately high toluene levels have been found in Recent sediments (J. Whelan, personal communication).

Naphthalene (No. 258) and the methylnaphthalenes (No. 308, No. 316) both showed concentration max-

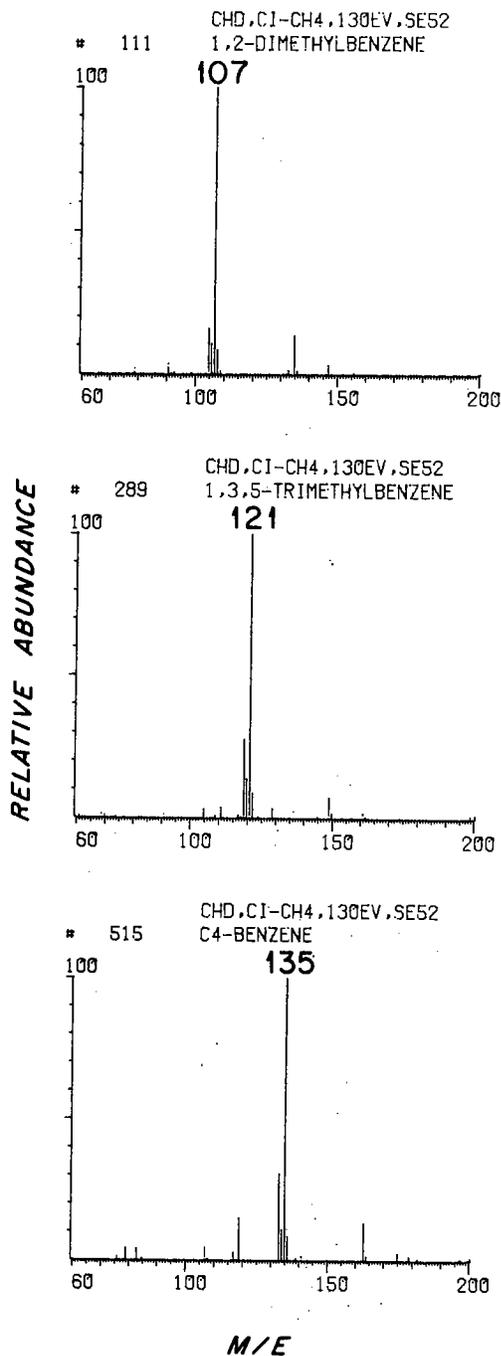


Fig. 5. Selected chemical ionization (methane) mass spectra of alkylated benzenes (A) 1,2-dimethylbenzene, (B) 1,3,5-trimethylbenzene, and (C) C_4 -benzene.

ima during the period of oil contamination (Fig. 2A) and also again late in April, suggesting multiple inputs. The C_2 - and C_3 -alkylated maphthalenes were only found in the samples presumed to contain petroleum-derived hydrocarbons. Figure 7 shows CI (methane)-MS $(M + 1)^+$ mass chromatograms for these compounds. The isomer distribution is similar to that found in a No. 2 fuel oil sample analyzed (see Figure 7).

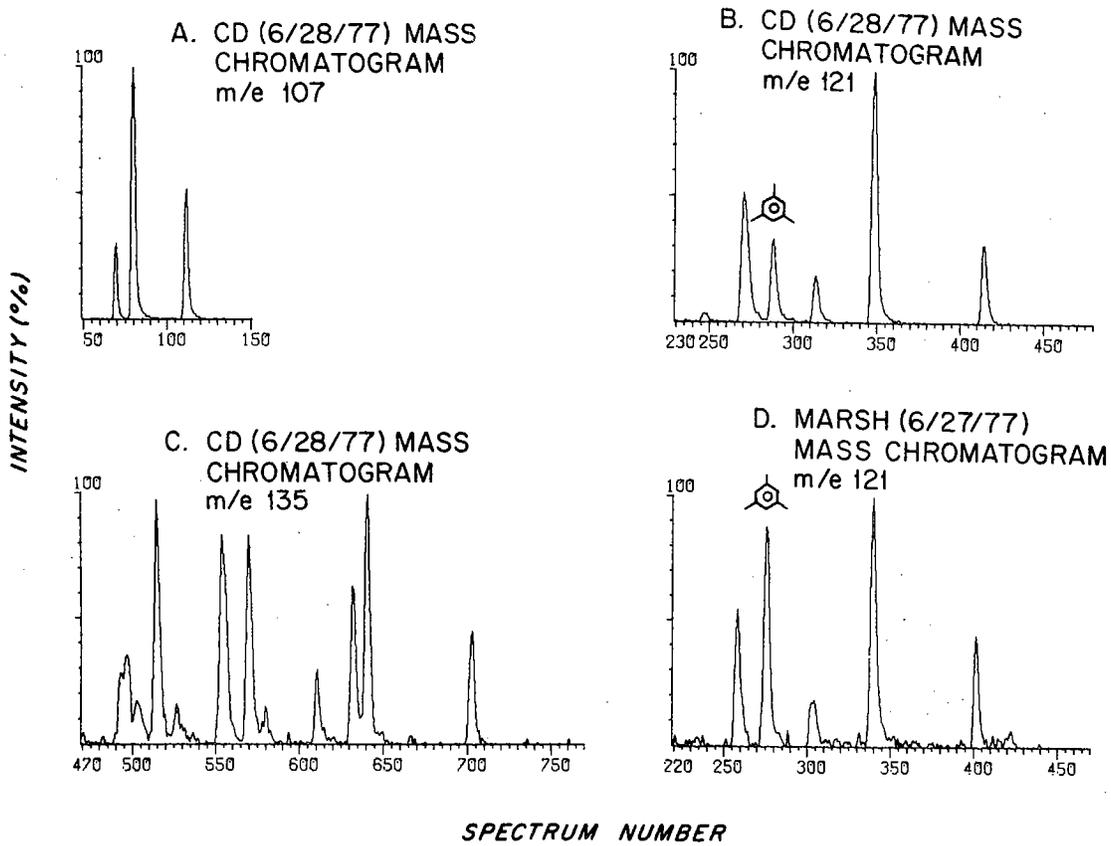


Fig. 6. Mass chromatograms of alkyl benzene isomer distributions.

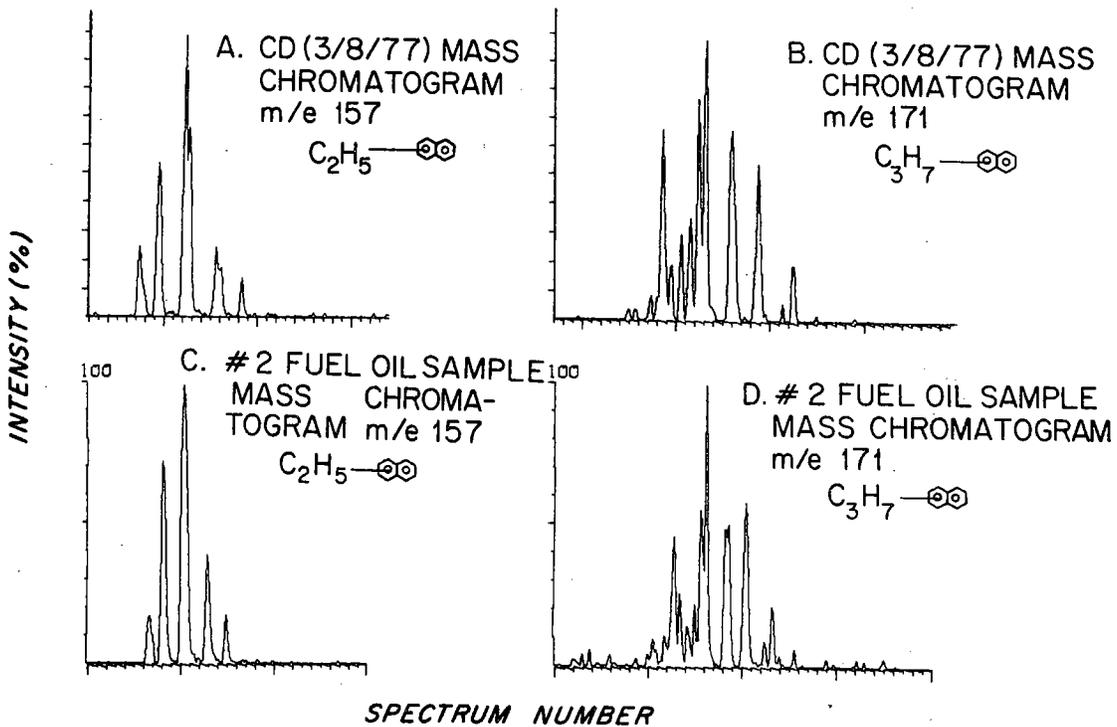


Fig. 7. Mass chromatograms of alkyl naphthalene isomer distributions.

Oxygen compounds

The normal six- to ten-carbon aldehydes (Nos. 61, 121, 174, 225, 275) were the only oxygen-containing compounds identified. No other peaks had MS properties suggestive of oxygen functionality. At times, these aldehydes were major constituents of the VC, especially just after the spring chlorophyll a maximum (Fig. 3). At that time hexanal (No. 61) reached approx 100 ng/kg and heptanal (No. 121) about 40 ng/kg. These compounds have been detected before in fresh water samples (Zürcher and Giger, 1976). They are known constituents of fresh water diatoms (Kikuchi *et al.*, 1974), fresh water yellow-green algae (Collins and Kalnins, 1965), and of marsh grass (Miles *et al.*, 1973). Hexanal has been suggested to arise from the metabolism of linoleic and linolenic acids (Jadhav *et al.*, 1972). Nonanal (No. 225) and decanal (No. 275) show poor quantitative reproducibility and are found in traces in some blanks. It is therefore difficult to assess their concentration in seawater. They have been found as constituents of essential oils of terrestrial plants (Guenther *et al.*, 1975).

Aldehydes are recovered in only moderate yield in our system (Table 1). Model ketone and ester compounds were recovered in better yield, yet no representatives of these compound classes have been found in our coastal water samples. The balance of sources and sinks for these compounds apparently does not favor their reaching detectable levels. While esters may rapidly hydrolyze (preliminary work suggests a half life with respect to hydrolysis in seawater of a few days—P. M. Gschwend, unpublished results), ketones would be expected to be chemically more stable than aldehydes. Alcohol and phenols are very difficult to strip from seawater, and for practical purposes our method is insensitive to them.

Sulfur compounds

The sulfur compounds dimethyldisulfide (DMDS, No. 37) and dimethyltrisulfide (DMTS, No. 149) were found at moderate concentrations in many of the CD water samples. Their concentrations tended to increase in restrips (Fig. 1B), especially after 24 hr (Fig. 1C). Therefore, there seems to be a biological or chemical source within the water. In contrast, these two peaks were invariably present at low tide in marsh creek water (Fig. 4A), often as the largest peaks. They occurred at lower levels in marsh water restrips. We suggest that the same process forms these compounds in both environments. While this formation process is virtually complete in the marsh waters before sampling, it continues to occur in CD water during our analysis.

DMDS has been reported as a major component in the gaseous emission from bacteria and fresh water blue-green and green algae isolated from various soil types (Banwart and Bremner, 1974) and from eutrophic and less productive natural waters (Rasmussen, 1974), and from blue-green algal cultures (Jenkins *et*

al., 1967). Kadota and Ishida (1972) postulated methyl mercaptan as a precursor to DMDS from microorganisms. DMTS has been found in lake waters (Grob and Grob, 1974), waste waters (Keith, 1976), and in a variety of terrestrial plants, especially vegetables (e.g. Carson and Wong, 1961). These compounds may be related to the cyclic polysulfides reported in a red alga (Wratten and Faulkner, 1976). These sulfur compounds may have special potential as process tracers if their source can be more specifically understood. Their flux from marshes to the atmosphere may be significant in the S budget in these environments (Maroulis and Bandy, 1977).

Miscellaneous compounds

Selected mass searches were made in an effort to identify other compound classes, especially those which might be expected on the basis of previous work on marine samples or fresh water stripping. Tetrachloroethylene (No. 60) and bromoform (No. 109) were frequently present, but other volatile halogenated compounds found in marine organisms (Moore, 1977) were not detectable in our samples. Most of the many unidentified peaks in our samples are currently recovered in such low concentrations (<1 ng/kg) that blank and GC-MS sensitivity problems prevent us from quantifying them or identifying them unambiguously.

Marsh creeks

The tidal influence on VC composition at CD is negligible. In contrast, it is major in the marsh creek studied (Fig. 4). At high tide (Fig. 4B), the chromatograms resemble those of Buzzards Bay water, with some trace of the components seen in marsh water at low tide as well (Fig. 4A). At low tide, the C₁₅ and C₁₇ monoenes (No. 405, 413, 505, 509), DMDS (No. 37), and DMTS (No. 149) are very prominent components. The alkylated benzene concentrations varied considerably in marsh samples at low tide (1–10 ng/kg total), and the isomer distribution always differed from CD. Mesitylene (No. 151) was present in higher relative amounts in the marsh at low tide (Fig. 6B and 6D). Further work may reveal more about the processes responsible for this difference.

Temporal variations

In addition to inventorying VC at CD, it was our purpose to elucidate the processes affecting these organic compounds at this coastal site. To this end, we sought temporal correlations among VC concentrations and other environmental parameters. Although marked variations in specific VC concentrations were found (Fig. 3), no direct or inverse correlations were observed with nutrients (PO₄³⁻, SiO₂, NO₃⁻, NO₂⁻, NH₃) or temperature. The decline of the spring phytoplankton bloom, as demonstrated by chlorophyll *a*, may correspond to a period of organic remineralization, and this in turn, may be reflected in the pronounced increase in aldehyde concen-

trations, as demonstrated by hexanal in Fig. 3. Except for such uncertain features, related trends in temporal variations of the VC were not apparent.

This situation may simply reflect inadequacies in the amount or spatial and temporal resolution of these preliminary data. Alternatively, it may be that individual organic compounds typically have rather specific biological sources and sinks. In that case, biologically relevant parameters such as nutrient concentrations, chlorophyll level, and temperature, which are highly non-specific, would not show strong correlations with individual VC levels; instead, compound levels would correlate best with their specific sources and sinks. These may frequently be the metabolic activities of individual genera, species, or even sub-populations of the same species. The likelihood of these and other such complexities has been discussed (Blumer, 1975). Despite these potential problems, the variations observed in VC levels suggest that they are intimately involved in various coastal marine processes.

VC and VOC

Although it was not our purpose to assess the amount of seawater organic matter which is 'volatile', the rather low levels of individual and total VC that occur in the coastal waters of Cape Cod is rather striking. Early Russian work (Vityuk, 1965 quoted in Skopintsev, 1966) had suggested that the VOC represented 12% of the TOC in seawater. MacKinnon (1977, personal communication), utilizing an approach which he felt provided an upper limit to the amount of volatile carbon in seawater, stripped HgCl_2 -poisoned unfiltered samples with N_2 using varying temperatures and times. Subsequently, he determined the Tenax adsorbable volatiles by thermal desorption and combustion analysis. He found about 1% of the coastal TOC was volatile by this procedure at 35°C. Thus MacKinnon recovers about 10–30 μg VOC/kg.

In contrast, we find only about 0.2–1.0 $\mu\text{g}/\text{kg}$ by summing the concentrations of the VC and converting to VOC. There are several possible explanations for this discrepancy:

(1) Volatiles are non-uniformly distributed and data cannot be intercompared.

(2) Volatiles do not survive some steps in our procedure (charcoal trap, active or hot GC surfaces).

(3) Low boiling volatiles are included in MacKinnon's measurement, while they are masked by the solvent peak in ours.

(4) MacKinnon's procedure provides an overestimate.

While all of these factors may be involved to some degree, the first is unlikely to be responsible for the major part of the discrepancy, as we both see a moderate degree of spatiotemporal homogeneity within our respective methods. We doubt that factor two is dominant, as we obtain chromatograms using thermally desorbed Tenax similar to our routine char-

coal trap chromatograms. Also we have found that some standards difficult to determine by low-level GC (polysulfides and aldehydes) survive our techniques at low levels. However, by prolonged stripping MacKinnon may measure relatively polar compounds which we do not determine. Also, low-boiling compounds may exist in seawater at high levels; our CS_2 peak obscures compounds boiling below 100°C. We have observed large amounts of carbon dioxide, pentane, hexane, methylene chloride, acetone, and benzene in samples analyzed by the 'Tenax' method. While much of these materials is likely to be laboratory contamination, micrograms of these compounds may come from the sample. In summary, it is difficult to compare our results with the results of other workers who use different methodological approaches.

SUMMARY AND CONCLUSIONS

The 'stripping' method is a viable and useful approach for studying the volatile organic components in coastal seawater samples, marine marshes, etc. It has been feasible to attain the blanks, recoveries, reproducibility and sensitivity required for quantitation and identification of a structurally varied set of organic compounds. Potentially this set includes compounds within the boiling range $n\text{-C}_7\text{--}n\text{-C}_{18}$ that are not too water soluble or reactive. The method is relatively trouble-free, rapid, and shows good reproducibility under realistic environmental sampling conditions. Incomplete recovery of volatiles from highly turbid samples may complicate interpretation, but also yields information about VC adsorption and formation processes.

About 50 compounds have been identified in samples from the coastal waters of Cape Cod, Massachusetts with individual abundances of ~1–100 ng/kg; individual levels above 20 ng/kg are rare. These compounds include alkanes, alkenes, aromatic and alkyl-aromatic hydrocarbons, n -aldehydes, methyl sulfur compounds, and some halogenated compounds. No ketones, esters, or terpenoid hydrocarbons were recovered. With the possible exception of compounds attributed to petroleum contamination, n -alkanes in the $\text{C}_7\text{--}\text{C}_{12}$ range, branched alkanes, and alkenes were also absent or present only in trace quantities.

Some sources of individual compounds have been suggested. Within the biological realm, there are examples of compounds that are probably derived from different classes of benthic algae ($n\text{-C}_{15}$, $n\text{-C}_{17}$), marsh algal mats (alkene Nos. 405, 413, 505, 509) and bacterial processes (e.g. DMDS and DMTS). Several classes of compounds that might be expected to have an atmospheric source were not found, such as branched saturated hydrocarbons from gasoline and terpenoid compounds from terrestrial vegetation.

The time variability of the data suggest that sources and sinks may change volatiles levels within the

course of a few days. Air/water partition coefficients and exchange estimates suggest that gas evasion from shallow water may be an important sink, especially for alkanes. Since water insolubility, rather than high volatility, is the major factor determining the large air/water partition coefficients for many non-polar compounds, adsorption on particles and sediment is a physico-chemically parallel potential sink. Inefficient recovery of VC in turbid samples also suggests an association between particles and these compounds. No obvious biological effects were revealed by a search for correlations of concentrations of VC with nutrients. The nearly constant isomer patterns and similar time behavior of numerous C₂-C₄ alkyl benzenes demonstrates that the available sinks do not discriminate within this class of compounds, despite variations in physical properties.

The total amount of VOC recovered by this method is about 0.2-1.0 µg/kg, considerably below the VOC content of seawater determined by other methods. It is likely that part of the cause of this discrepancy is that we analyze a fraction of the organic matter in seawater with different volatility limits than that studied by other workers.

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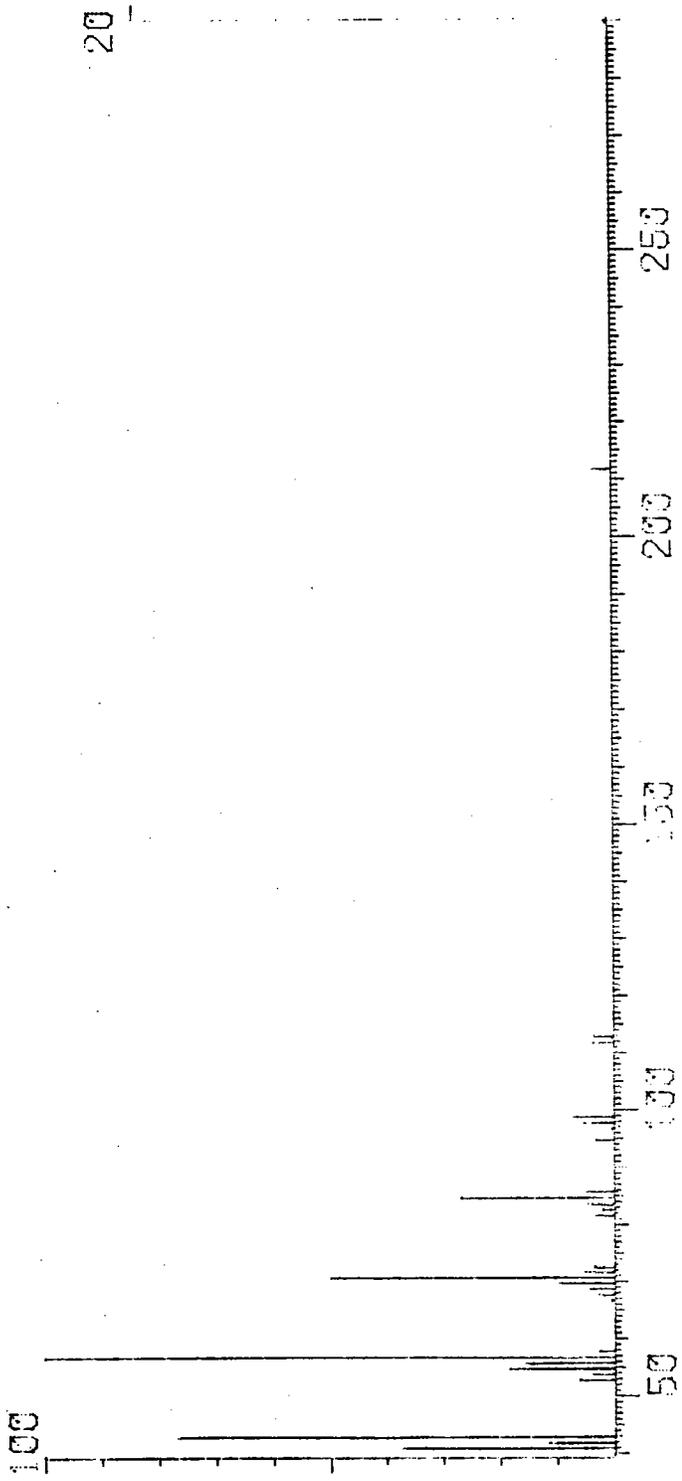
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Appendix IV. Physical chemical data for C₂- and C₃-benzenes taken from Handbook of Chemistry and Physics (1969) and from Sutton and Calder (1975).

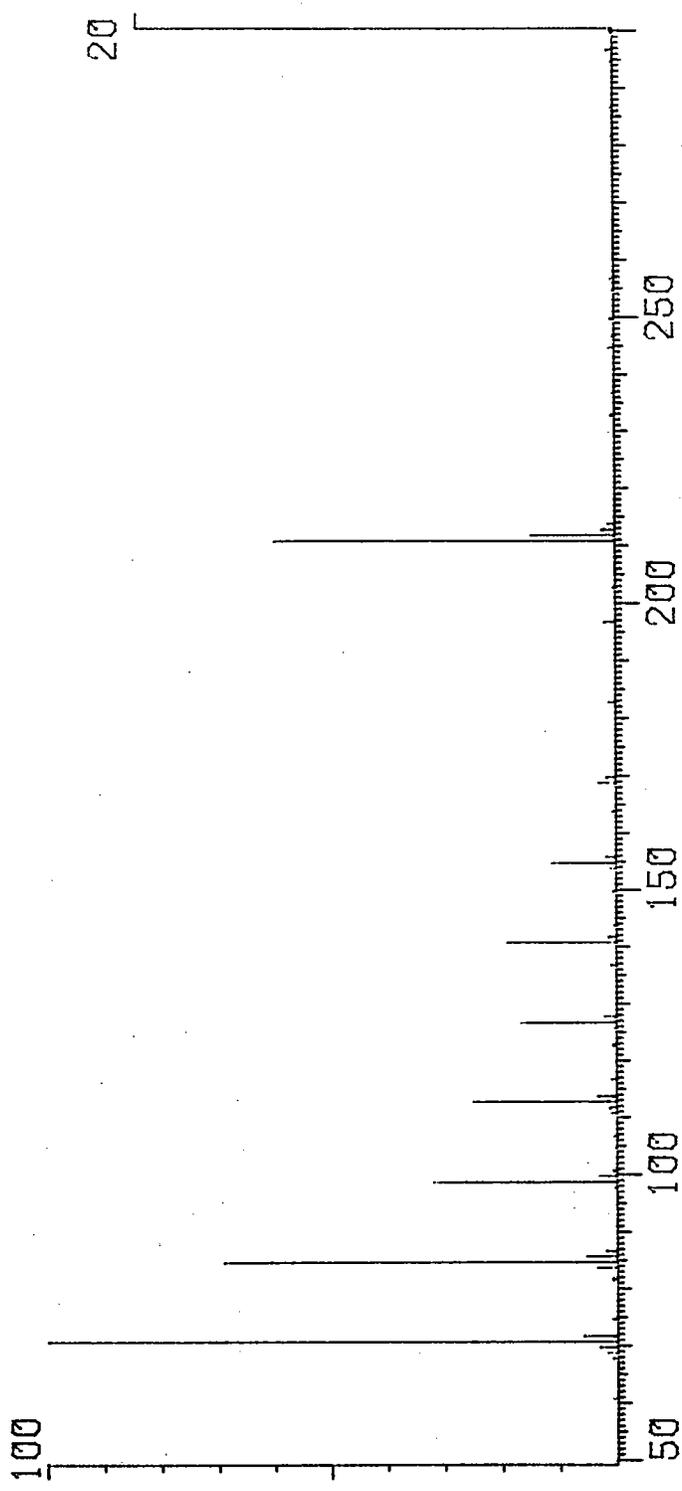
compound	mw	bp(°C)	\bar{V} (ml/M)	seawater solubility (mg/l)	(freshwater solubility) (mg/l)	vapor pressure (mm at 20°C)	K(air/seawater)	K(air/freshwater)
ethyl benzene	106	136.2	122.5	111.0	(161.2)	7.53	0.398	(0.274)
1,4-dimethyl benzene	106	138.35	123.3	110.9	(156.0)	6.50	0.344	(0.245)
1,3-dimethyl benzene	106	139.1	122.9	106.0	(146.0)	6.09	0.337	(0.245)
1,2-dimethyl benzene	106	144.4	120.6	129.6	(170.5)	4.96	0.225	(0.171)
propyl benzene	120	159.2	139.4	36.3*		2.61	0.477	
1,4-ethyl-methyl benzene	120	162	139.5	36.1*		2.39	0.440	
1,3-ethyl-methyl benzene	120	161.3	139.0	37.0*		2.44	0.438	
1,3,5-trimethyl benzene	120	164.7	138.9	31.3	(48.2)	2.10	0.444	(0.288)
1,2-ethyl-methyl benzene	120	165.2	136.5	42.2*		2.10	0.329	
1,2,4-trimethyl benzene	120	169.35	137.2	39.6	(59.0)	1.68	0.283	(0.190)
1,2,3-trimethyl benzene	120	176.1	134.4	48.6	(75.2)	1.31	0.179	(0.116)

* calculated from molar volume relationship and data of Sutton and Calder (1975).

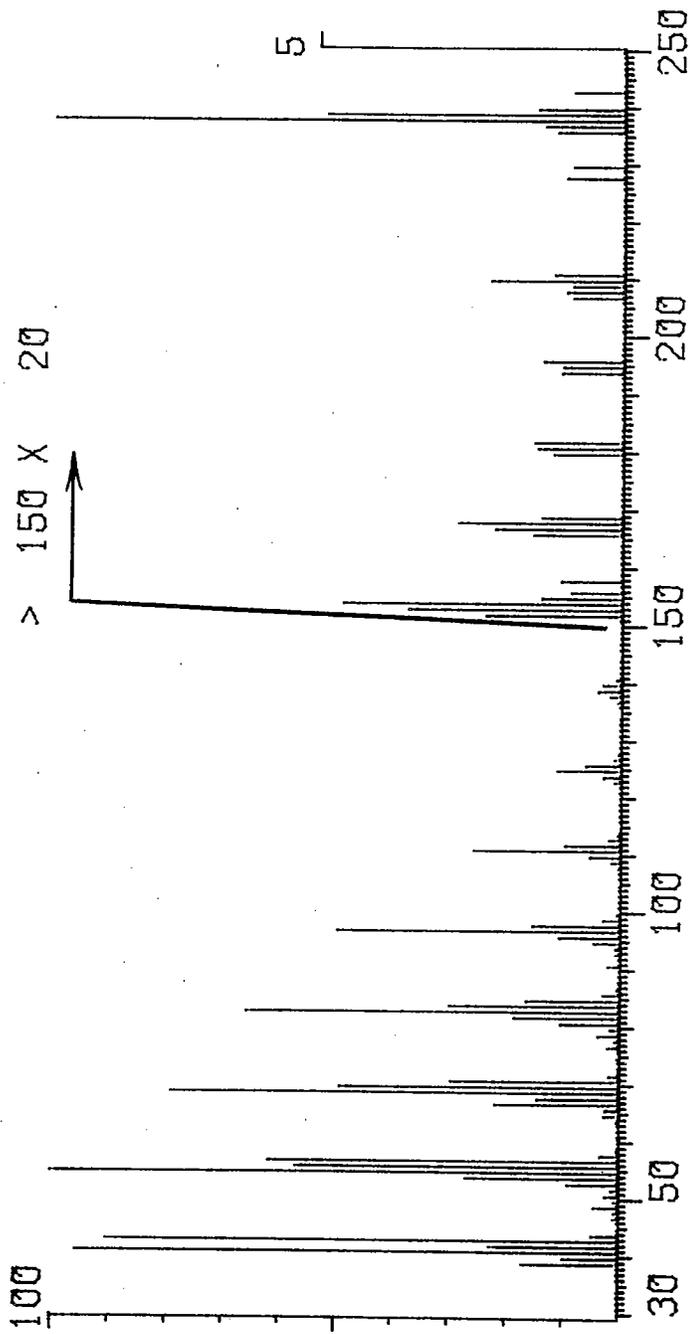
Appendix V. Mass spectra of some hydrocarbons and halomethanes released by benthic algae into seawater.



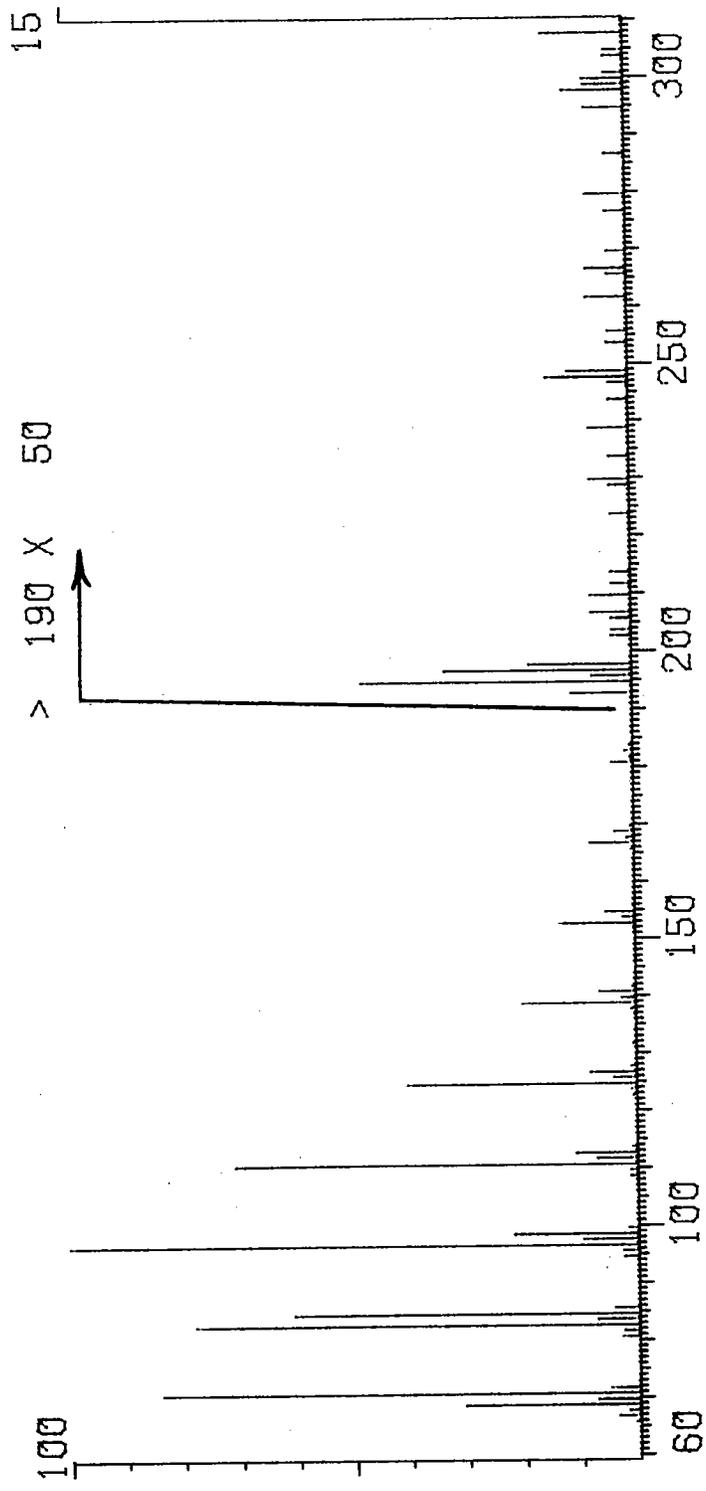
Pentadecane C₁₅H₃₂ EI



Pentadecane $C_{15}H_{32}$ $CI-CH_4$

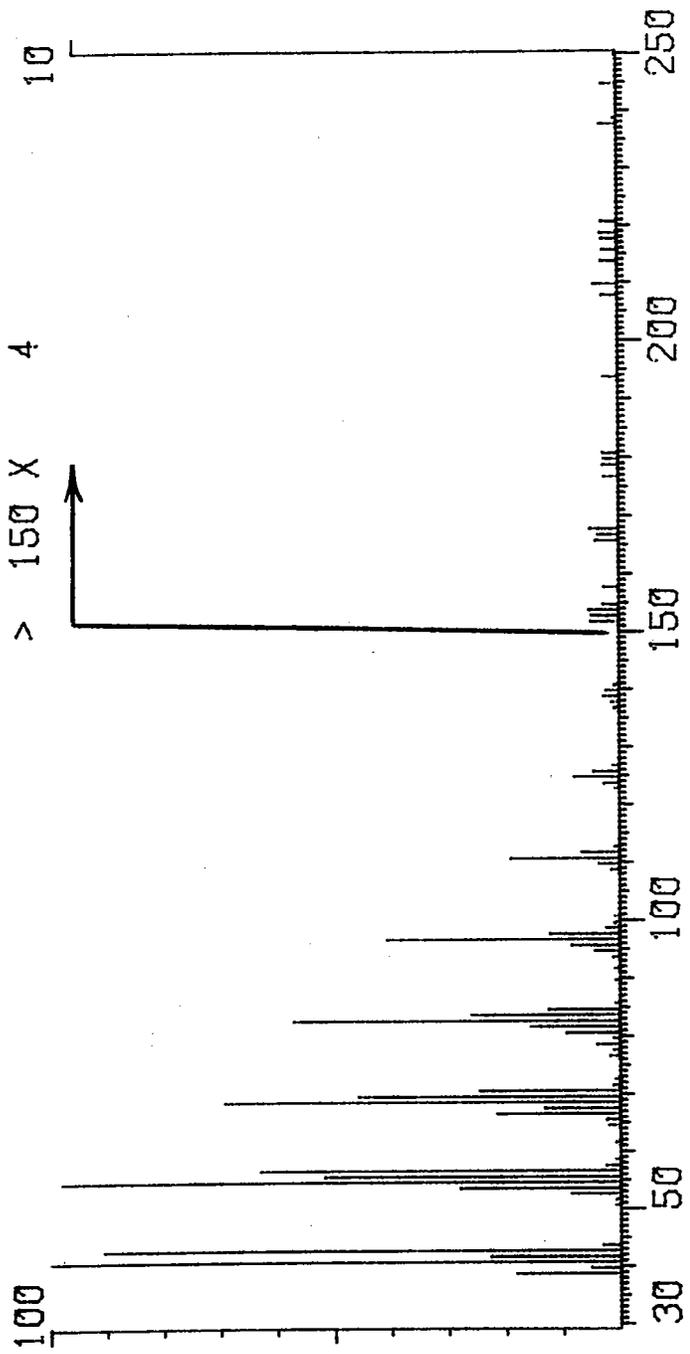


Heptadecene $C_{17}H_{34}$ EI
(*Enteromorpha* spp.)

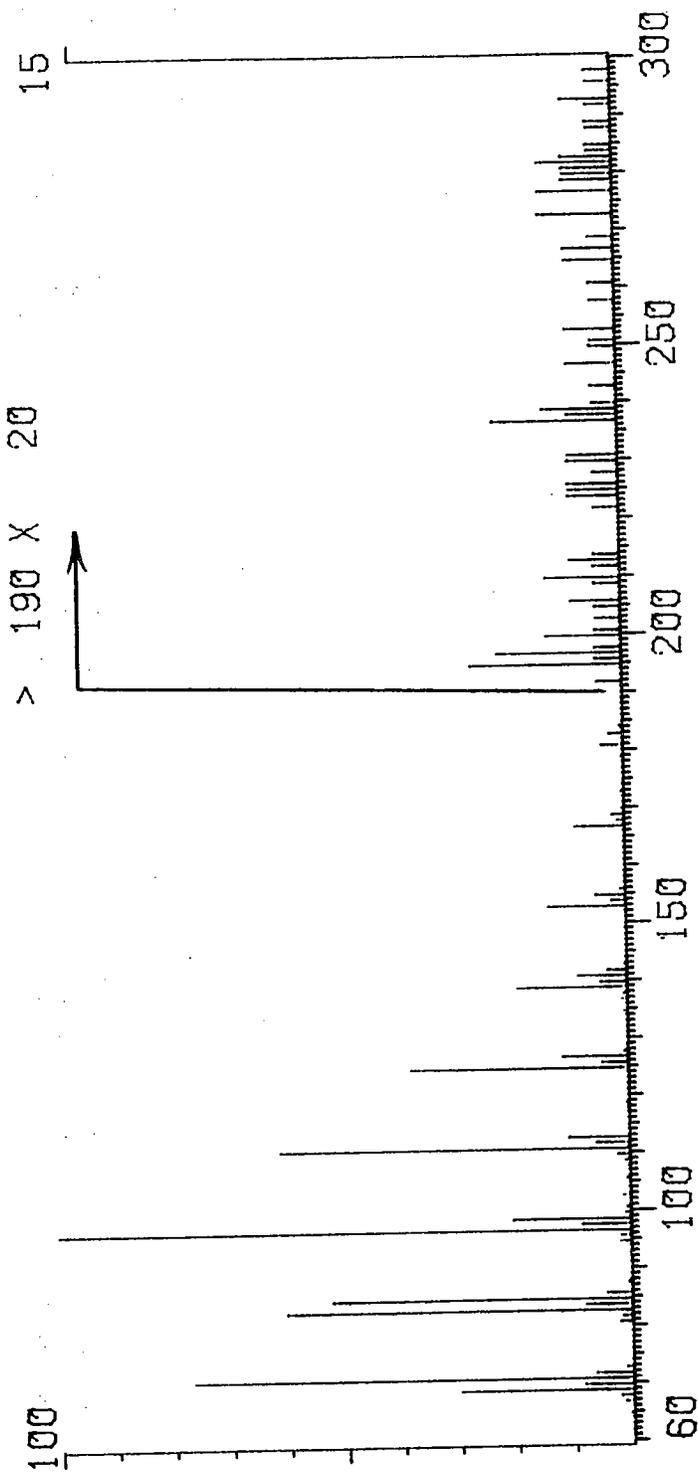


Heptadecene $C_{17}H_{34}$ $CI-CH_4$

(Enteromorpha spp.)

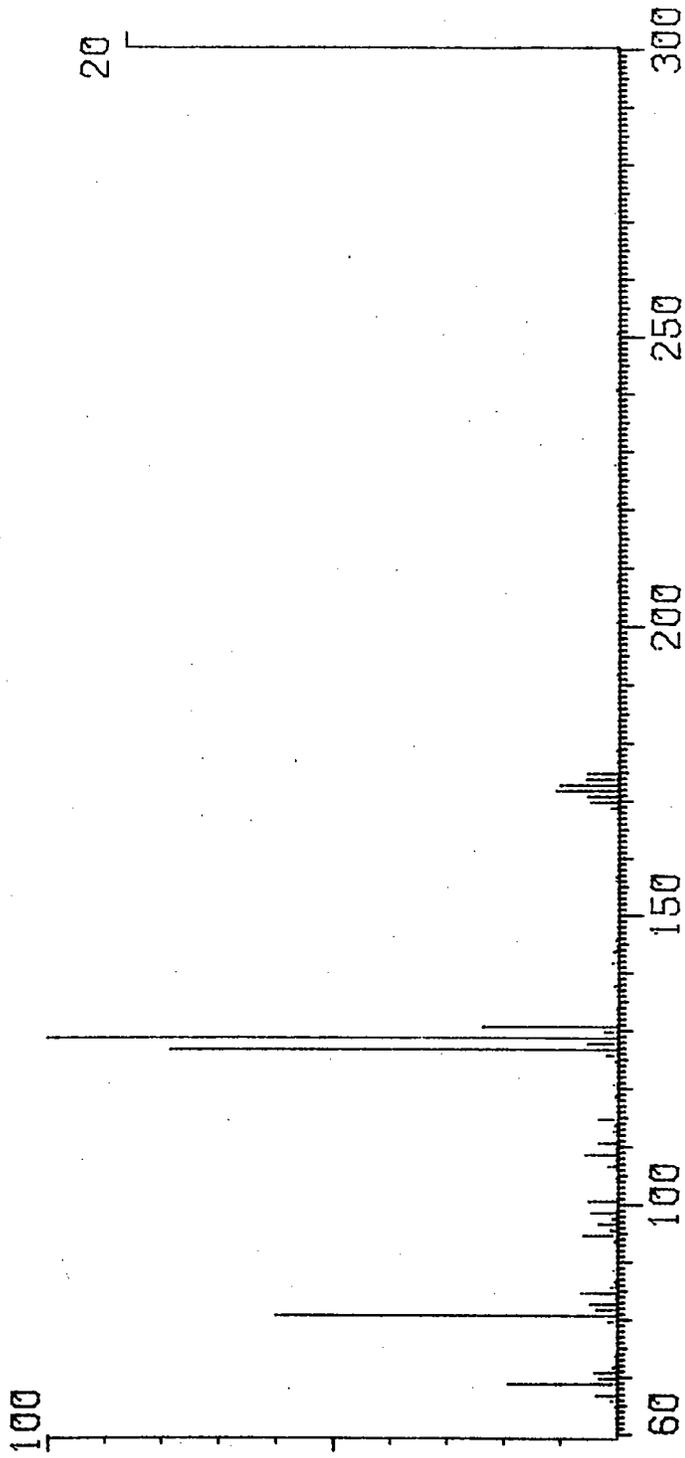


Heptadecene $C_{17}H_{34}$ EI
 (Codium fragile)

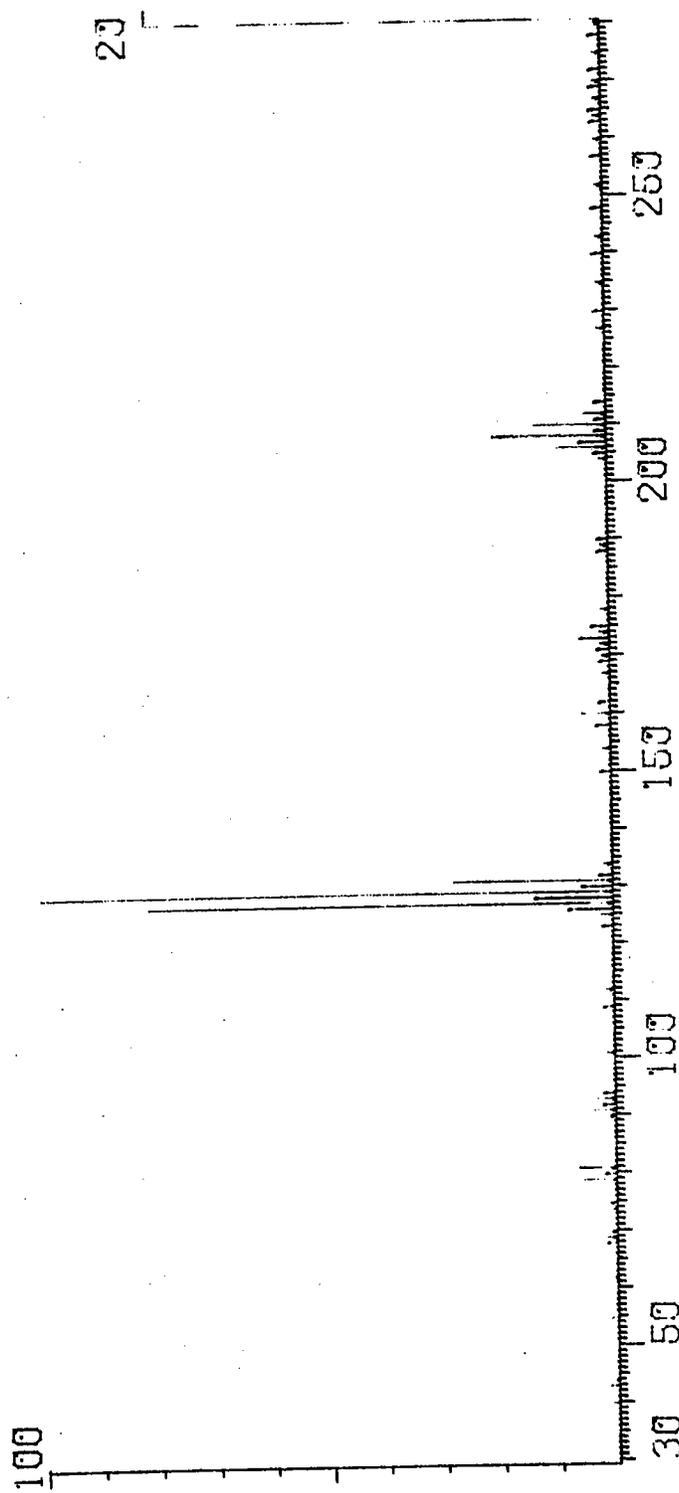


Heptadecene $C_{17}H_{34}$ $CI-CH_4$

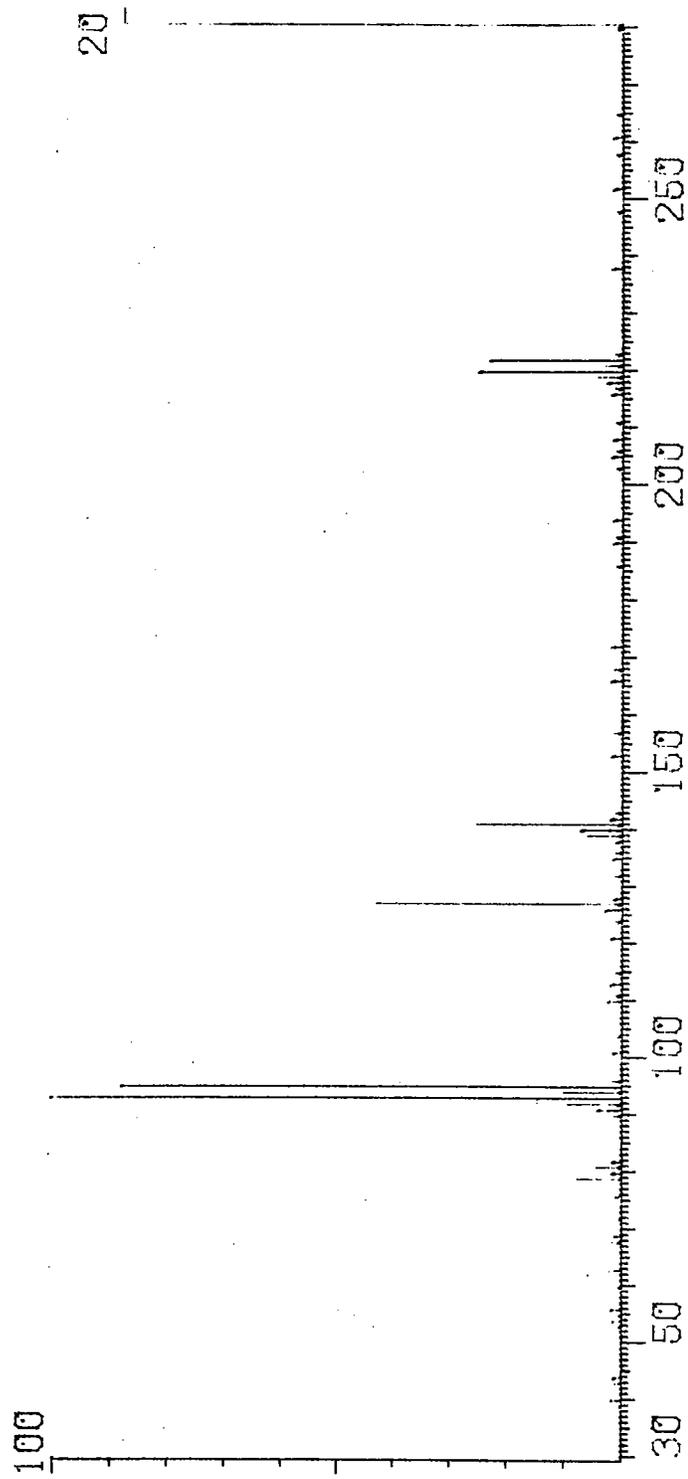
(Codium fragile)



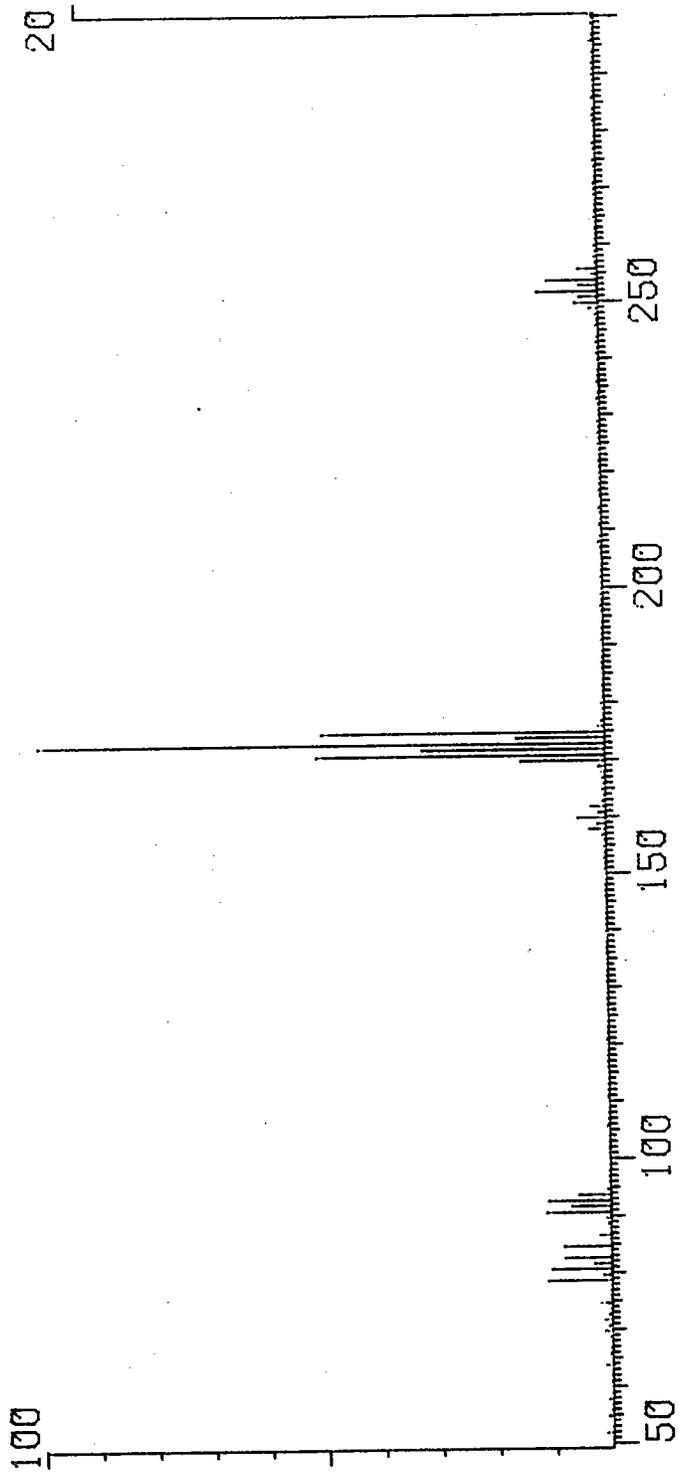
Chlorodibromomethane CHBr_2Cl Cl-CH_4



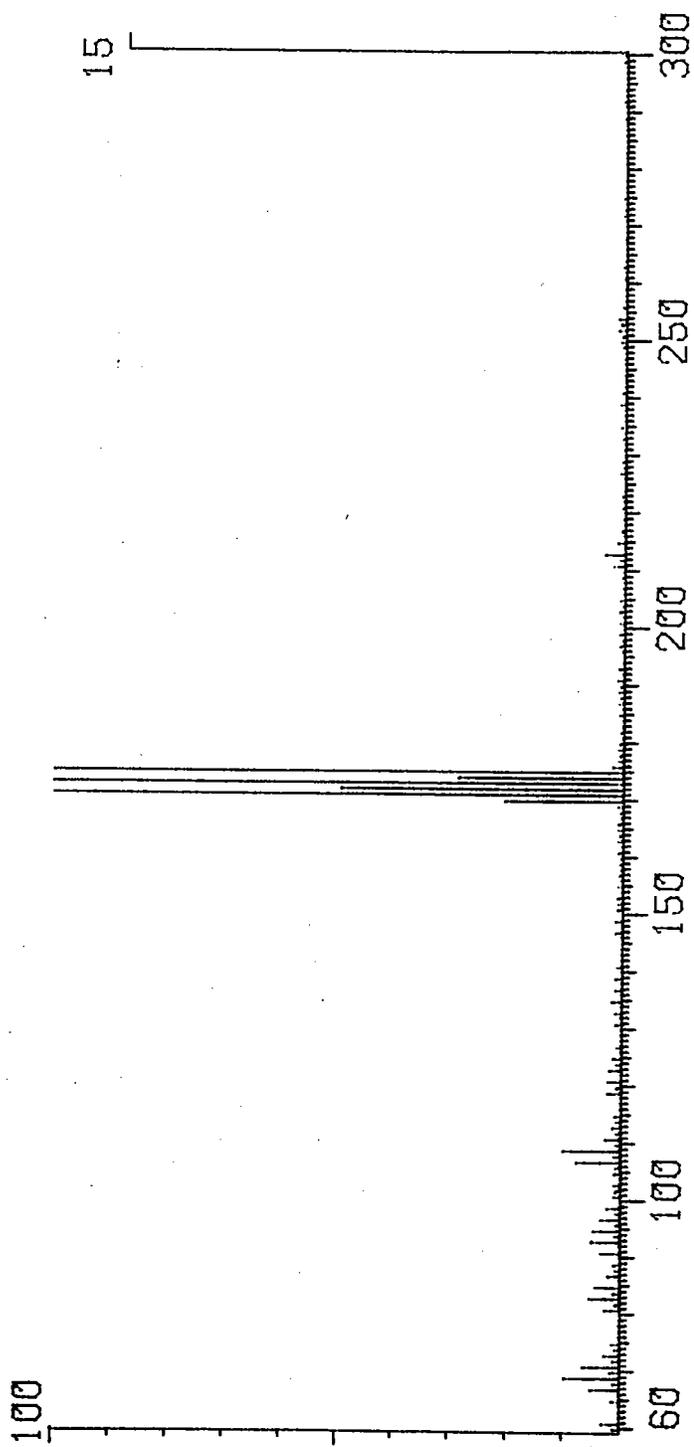
Chlorodibromomethane CHBr_2Cl EI



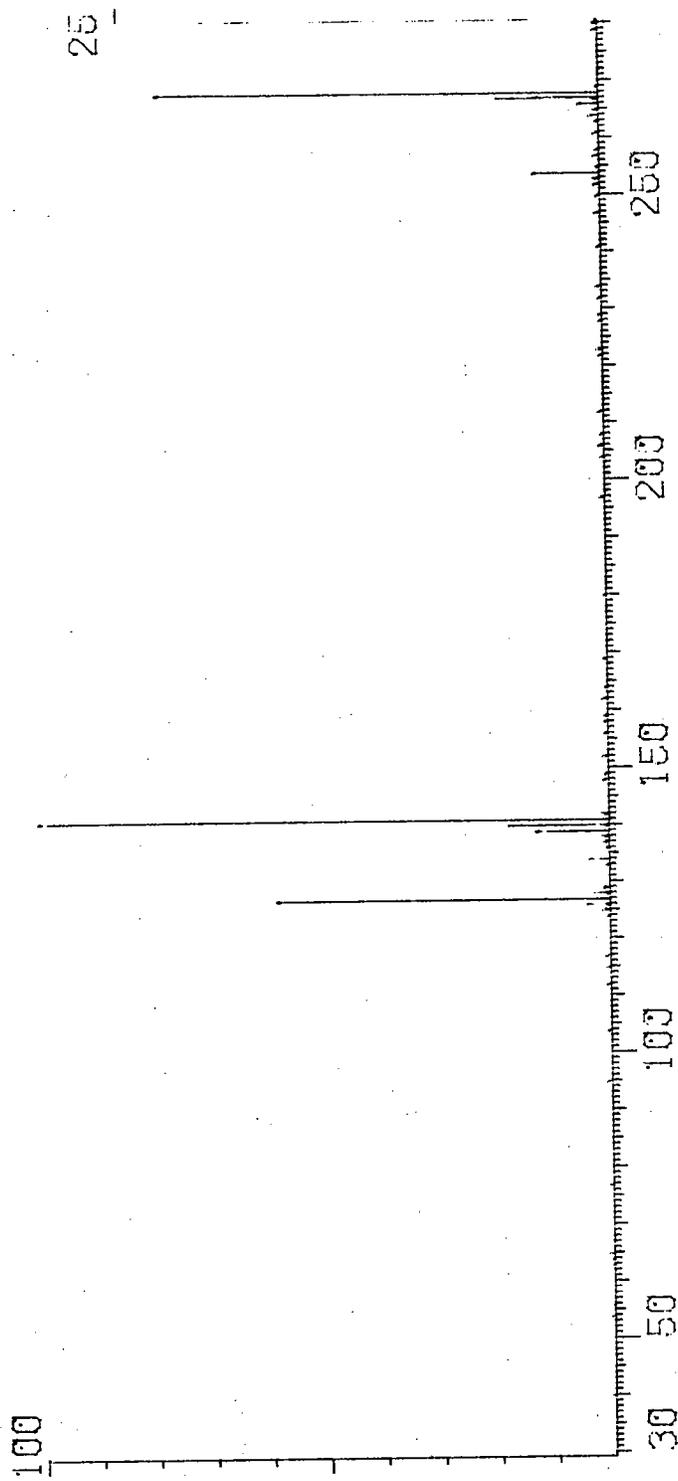
Bromiodomethane CH_2BrCl EI



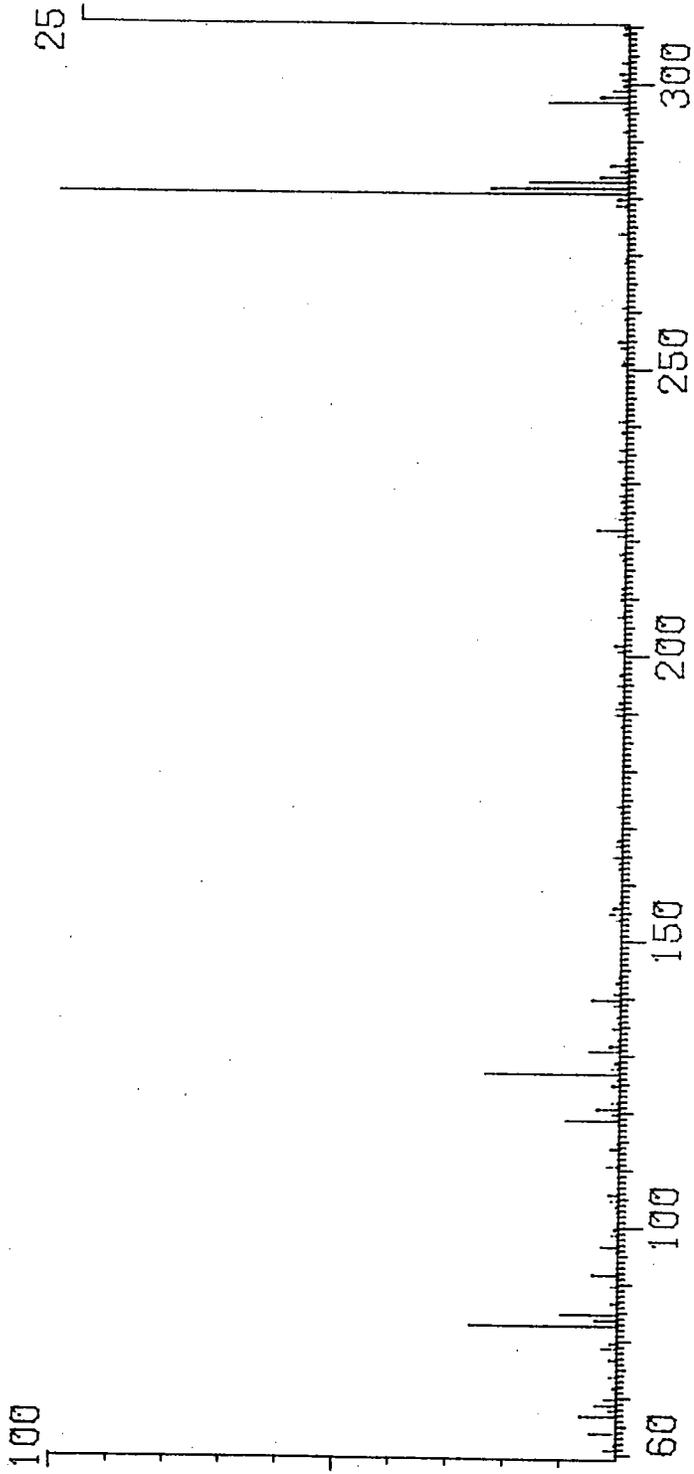
Tribromomethane CHBr₃ EI



Tribromomethane CHBr_3 CHCl_3



Diiodomethane CH_2I_2 EI



Diiodomethane CH_2I_2 CI-CH_4

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