

Volatile Organic Compounds at a Coastal Site. 1. Seasonal Variations[#]

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■ Alkylaromatics, alkanes, aldehydes, dimethyl polysulfides, and miscellaneous compounds were determined over a 15-month period at a coastal site. Alkylbenzenes appear dominated by anthropogenic inputs and air-sea exchange, with selective biodegradation showing minor effects in the summer. Offshore mixing and adsorption to sediments seems minor. Alkynaphthalenes showed a contrasting pattern, best explained by a dominant wintertime source such as space heating oil use. Alkanes were frequently petroleum derived, but pentadecane, heptadecane, and pristane showed evidence of strong biogenic sources as well. The aldehydes exhibited complex behavior, with evidence for autoxidative as well as plankton sources. The dimethyl polysulfides had great variability; they may contribute significant sea-to-air sulfur fluxes if our measured levels are typical of the larger coastal region. An incompletely identified octatriene occurs briefly; it may be an algal product related to the pheromone "fucoserraten".

Introduction

Recently there have been several broad studies of volatile organic compounds (VOCs) in the marine environment (1-6). The study of VOCs has added to our understanding of the marine organic carbon cycle and marine organic chemistry. One approach to studying the VOCs is to monitor their year-round variations at a station. This report describes the results of analyses of seawater samples collected biweekly over a period of 15 months at a single coastal site; in a following paper (7) we address shorter-term variations. The temporal variations are interpreted in terms of probable sources and sinks by utilizing correlations with ancillary data and by considering covariations of structurally related (homologous or isomeric) volatile compounds. Additionally, supplemental sampling and laboratory experiments were conducted to test specific hypotheses.

Methods

The sampling location and methods have been described (4). Briefly, seawater samples were collected biweekly from a wooden pier (Chemotaxis Dock (CD)) which extended into Vineyard Sound, MA, to a point about 2 m deep (Figure 1). The sediment in the immediate region is sandy, with extensive seasonal algal and sea-grass growth. The shore is cobbled and backed by a mixed oak and pine forest band. Water was taken by dipping a 1-L flask attached to an aluminum pole about 20 cm below the surface and transferring 4 L to a 5-L round-bottom flask. Volatile organic compounds were determined by using the stripping procedure of Grob and Zurcher (8), glass capillary gas chromatography with flame ionization detection (GC), and

combined glass capillary gas chromatography-mass spectrometry (GC-MS). Compound identifications were based on GC retention data from a single capillary column (SE-54), and on electron impact (EI) and methane chemical ionization (CI) mass spectra. Compound concentrations were calculated on the basis of GC peak areas relative to an internal standard added to the charcoal microtrap after stripping. Corrections for differential stripping efficiencies (and inefficient recoveries from charcoal in the case of the naphthalenes) were made by using the results of standard compounds spiking experiments (4, 5). Blank levels were ≤ 1 ng/L and were due to erratic laboratory contamination or sample container hysteresis. Replicate samples were determined with a precision of about $\pm 10\%$.

Seawater samples for salinity, nutrients, chlorophyll *a*, and phytoplankton were collected concurrently with those for volatile analyses. Chlorophyll *a* was measured by using the fluorescence technique of Strickland and Parsons (9). Phytoplankton were identified and enumerated in fresh or formaldehyde-preserved samples by light microscopy.

Results and Discussion

Hydrographic Data. Seawater temperature varied sinusoidally from about 23 °C in August to about -1 °C in February. Salinity was 30-32‰ year-round. Daily salinity variations of a few tenths of a part per thousand reflect saltier water flowing from the west and freshwater outflow from neighboring coastal ponds (e.g., Oyster Pond 1-3‰, Figure 1) during the ebbing eastern tide. This salinity variation suggests that the pond waters are diluted about 100 times by coastal seawater in the region of the sampling site.

The inorganic nutrient concentrations varied seasonally (Figure 2), reflecting the changing activities of the biological community. The precipitous decrease in all nutrients in February was caused by the late-winter diatom bloom, as evidenced by chlorophyll *a* concentrations rising above 10 $\mu\text{g/L}$ (Figure 2). Cell counts made during the 1978 late-winter diatom bloom revealed a population density of nearly 7×10^6 cells/L, more than 85% *Thalassiosira nordenskioeldii*. For the remainder of the spring and summer, phytoplankton counts remained low (ca. 10^4 - 10^5 cells/L); thus, the abundant benthic algae near CD probably maintained inorganic nitrogen at low levels. We interpret simultaneous minima in phosphate and silicate in September and October, coincident with high ammonia, as the result of a phytoplankton and zooplankton bloom. Abundant zooplankton could produce the large ammonia levels (10); their grazing may explain the absence of a fall chlorophyll *a* maximum. A fall diatom bloom is common in this region (11, 12). The elevated nutrient concentrations between November and February suggest that algal production was limited by other factors during this period.

Variations of Volatile Organic Compounds. Several groups of volatile organic compounds were found, including all those mentioned in our preliminary report (4) and some new ones. The major groups include alkylated benzenes, alkylated naphthalenes, alkanes, normal aldehydes, and dimethyl polysulfides. Previously unobserved compounds, including an incompletely identified alkene, long-chain

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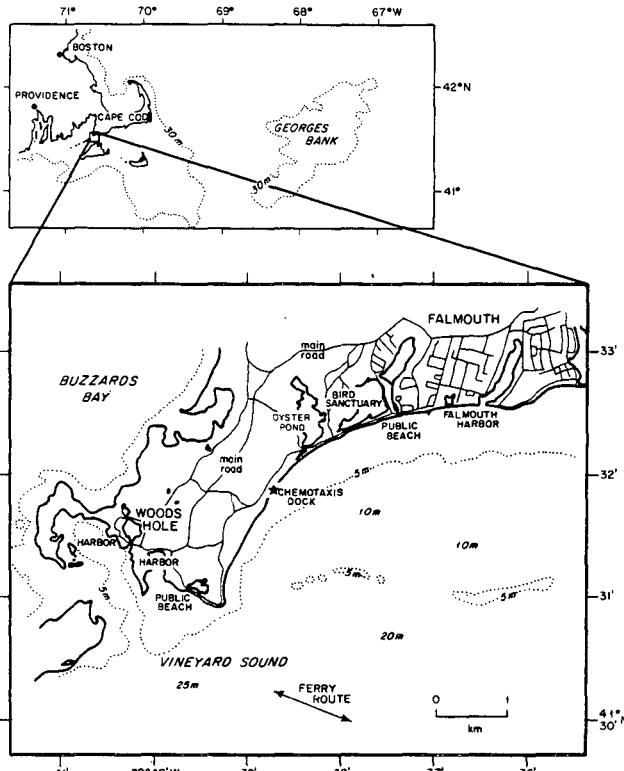


Figure 1. Map of region near Chemotaxis Dock, Vineyard Sound, MA.

($>C_{10}$) aldehydes, and dimethyl tetrasulfide, were only present during part of the year. The mean concentrations, the relative standard deviations, and the concentration ranges for each VOC are reported in Table I. The temporal variations of each group are reported and discussed individually below.

Alkylbenzenes. Toluene through a least C_4 -alkylbenzenes were invariably recovered. The concentrations of these compounds showed no obvious seasonality, and their biweekly variability was great (shown for 1,2-dimethylbenzene and 1,2,4-trimethylbenzene in Figure 3). However, these compounds covaried strongly, and from this behavior we infer that they shared a common source(s) and environmental fate(s).

Since the alkylbenzenes are important constituents of vehicular fuels and exhausts, we hypothesized that gasoline and diesel-fuel use by cars and boats in the region was an important alkylbenzene source. Marine traffic and automotive traffic increase tremendously on Cape Cod on weekends during the summer. Consequently, if the sinks are fairly constant (first-order loss kinetics) and this fuel use was an important source, the alkylbenzene concentrations should peak during and immediately after summer weekends. The year-round 1,2-dimethylbenzene concentrations replotted as a function of season and day of the week show that Monday and Tuesday summertime samples were typically much more contaminated than their late-week counterparts (Figure 4). Thus, vehicular fuel uses are strongly implicated as important sources of alkylbenzene at this Vineyard Sound site.

Additionally, the summer weekend-generated transient pulse of alkylbenzenes decays by Wednesday or Thursday to levels very similar to those observed in the winter for these compounds—possibly a normal “background” at this site. We suggest that these weekend inputs are removed predominantly by air-sea gas exchange, a process that can account nicely for the observed time scale. We previously presented a conservative estimate based on the classical

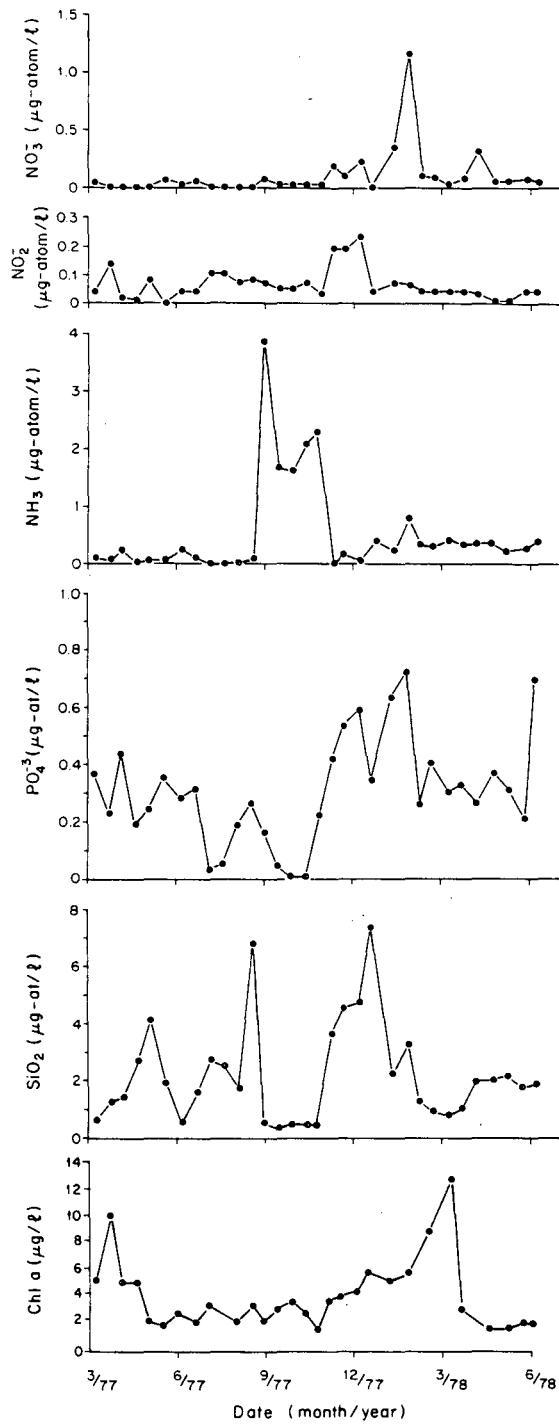


Figure 2. Nutrient (μM) and chlorophyll a ($\mu\text{g/L}$) concentrations in this seasonal study of coastal seawater.

air-sea exchange models (13, 14) that suggested a residence time with respect to atmospheric exchange for VOC in seawater at this site of a few days (4). Under conditions following a pulse input, where the concentration in seawater is much greater than the atmospheric concentration divided by the Henry's law constant (2, 5), the residence time of VOCs with respect to air-sea exchange is equal to the stagnant boundary layer thickness times the volume of seawater per unit area divided by the molecular diffusion coefficient. Inserting reasonable estimates for these parameters at CD yields

$$(30 \times 10^{-4} \text{ cm}) \times$$

$$(5 \times 10^2 \text{ cm}^3/\text{cm}^2)/(0.8 \times 10^{-5} \text{ cm}^2/\text{s}) \simeq 2 \text{ days}$$

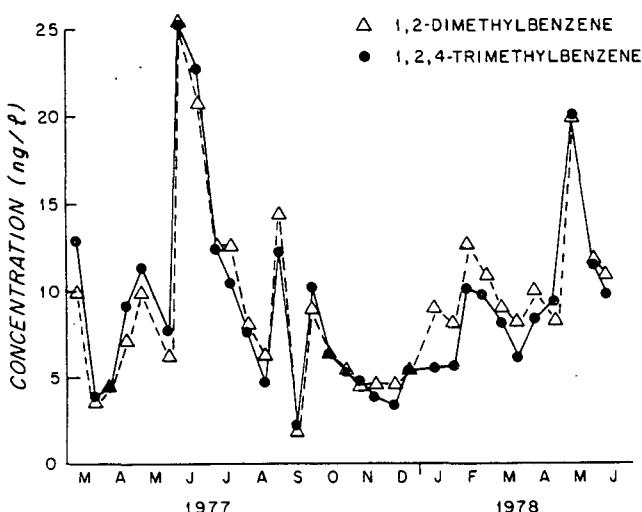


Figure 3. 1,2-Dimethylbenzene and 1,2,4-trimethylbenzene concentrations (ng/L) in this seasonal study of coastal seawater.

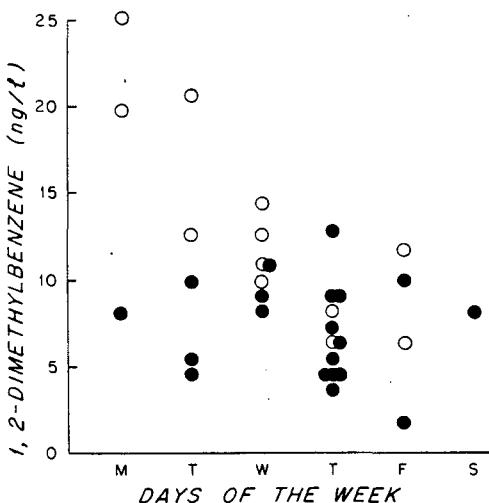


Figure 4. 1,2-Dimethylbenzene concentrations (ng/L) of these seasonal-study samples replotted according to the day of the week and season (summer: open circles; "off-season": closed circles) when they were collected.

where the boundary layer thickness is estimated from Peng et al. (15), the molecular diffusion coefficient is obtained from an empirical relationship (16), and 5 m is taken as the average water depth in the region near CD (Figure 1). The calculated exchange rate and the observed behavior at CD (Figure 4) are in remarkably good agreement, considering the crude approximations, the assumptions involved, and the complexity of the site.

Furthermore, other sinks are probably slow and unimportant compared to air-sea exchange. Dilution by mixing further offshore requires offshore waters to be lower in alkylbenzenes. On four separate occasions, spatial surveys of the surface waters of Vineyard/Nantucket Sounds showed fairly homogeneous alkylbenzene concentrations (the maximum variability was $\pm 27\%$ relative standard deviation).

Although the biodegradation rate of the alkylbenzenes is difficult to assess, it is probably relatively slow also. Biodegradation of hydrocarbons varies as a function of molecular structure (17), implying that biodegradation would result in isomeric discriminations. For most of the year, the alkylbenzene isomer pattern is very similar, despite the fact that biologically mediated rates undoubtedly

Table I. Mean Concentrations (\bar{x}), Relative Standard Deviations, and Concentration Ranges of Volatile Organic Compounds Over 15 Months

compd	\bar{x} , ng/L	$100\sigma/\bar{x}$, %	concn range, ng/L
dimethyl disulfide (DM2S)	18	80	2.7-60
toluene	27	46	10-54
tetrachloroethylene	1.3	88	0.3-5.7
hexanal	18	66	3.8-58
ethylbenzene	11	54	1.8-22
incompletely identified olefin (mol wt 108)	20 ^{a,c}		0-20
1,3- and 1,4-dimethylbenzene	20	64	4.5-66
tribromomethane	2 ^a		0-2
1,2-dimethylbenzene	9.4	54	1.8-25
heptanal	13	91	2.5-61
n-propylbenzene	1.1	61	0.2-2.9
1,3- and 1,4-ethylmethylbenzene	5.7	65	1.4-17
dimethyl trisulfide (DM3S)	6.1	97	2.0-27
1,3,5-trimethylbenzene	3.4	77	0.8-11
1,2-ethylmethylbenzene	2.5	53	0.6-5.7
1,2,4-trimethylbenzene	9.1	59	2.2-25
octanal	12	70	3.6-42
1,2,3-trimethylbenzene	3.1	58	1.1-8.9
dimethyl tetrasulfide (DM4S)	20 ^{b,c}		0-20
nonanal	18	54	5.4-53
naphthalene	12	79	0.5-35
n-dodecane	5 ^a		0-5
decanal	18	51	6.5-44
2-methylnaphthalene	6.3	73	0.5-22
1-methylnaphthalene	4.4	46	0.5-14
n-tridecane	0.9	127	0.1-5.3
undecanal	3.4 ^{b,c}		0-3.4
2-ethylnaphthalene	1.9	122	0.0-4.1
1,6-dimethylnaphthalene	1.9	122	0.0-4.2
n-tetradecane	1.8	138	0.5-12
dodecanal	23 ^{b,c}		0-23
acenaphthalene	2.2	124	0.0-3.8
n-pentadecane	13	131	2.6-79
tridecanal	150 ^{b,c}		0-150
n-hexadecane	2.4	170	0.3-21
tetradecanal	5.9 ^{b,c}		0-5.9
n-heptadecane	6.6	87	0.6-22
pristane	1.1	111	0.0-5.4
pentadecanal	4.1 ^{b,c}		0-4.1

^a Maximum concentration observed, usually undetectable. ^b Maximum concentration observed (uncorrected for stripping efficiency), usually undetectable. ^c Not previously reported in coastal seawater.

varied greatly as environmental conditions changed. Moreover, the year-round isomer distribution closely resembles those determined in the lab for prestripped coastal seawater equilibrated with auto and boat exhausts (5). Finally, on the basis of experiments in which ¹⁴C-labeled toluene was spiked into estuarine water samples at 6-20 $\mu\text{g/L}$ and recovered as ¹⁴CO₂ (intermediate metabolites appeared to be rapidly degraded), Lee (18) reported 3-4-month turnover times with respect to biodegradation for this alkylbenzene.

Biodegradation was generally slower than air-sea exchange; however, an exception occurred in August, when three successive coastal seawater samples showed marked depletions for n-propylbenzene (ca. 80% relative loss) and ethylbenzene (ca. 50% relative loss). Grob and Grob (19) reported similar depletions in Lake Zurich in the summer; they attributed these to biodegradation. In both cases, water temperatures were 20-25 °C, the optimal range for oil biodegradation by natural microbial populations (20). Since it is very hard to imagine a nonbiological mechanism to account for the isomer ratio changes, we suggest that under some conditions the most vulnerable alkylbenzene

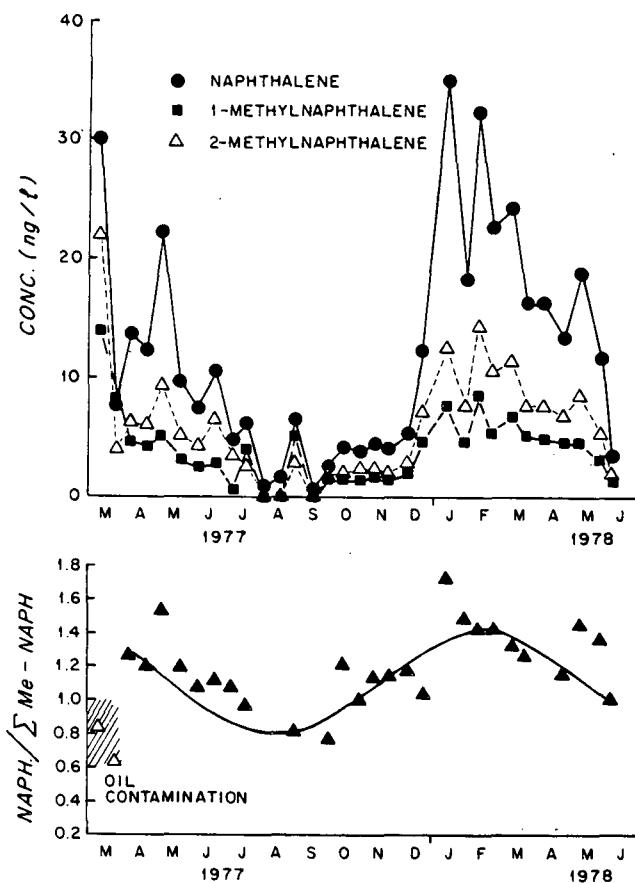


Figure 5. (a) Naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene concentrations (ng/L). (b) Naphthalene-to-methylnaphthalenes ratio in this seasonal study of coastal seawater.

can be degraded in just a few days.

Finally, adsorptive losses of alkylbenzenes to the sediments were probably small, based on the empirical relation of sedimentary adsorption tendencies with octanol-water partition coefficients (21, 22). If one assumes 3% organic carbon content for the Vineyard Sound coastal sediments, the sediment-to-water partition coefficients for C_2 - and C_3 -alkylbenzenes ranges from 10 to 40. Only during severe storms would more than ~ 1 g of sediment (a few centimeters of sediment column) be equilibrated with the ~ 500 cm³ of overlying water on a time scale of a few days. As a result, less than 10% of the most easily adsorbed C_3 -alkylbenzene would be lost to the sediment (fraction adsorbed to sediment = $(1 + \frac{500}{40})^{-1}$). Only a few percent of any C_2 -alkylbenzene would be adsorbed. Thus, we conclude that adsorptive losses were also generally small.

To summarize, anthropogenic sources clearly supplied relatively large pulse inputs of alkylbenzenes on summer weekends. These were probably largely lost by air-sea exchange into relatively clean air over the next few days; some biodegradation of ethyl- and propylbenzene occurred. Mixing offshore and uptake by sediment were probably much less important sinks.

Naphthalene and Methylnaphthalenes. These compounds and higher homologues were observed year-round; their concentrations showed a strong seasonal pattern, with the highest levels occurring in the winter and the lowest in the summer (Figure 5). There was no correlation of naphthalene and alkylated benzene concentrations (linear correlation coefficient (naphthalene vs. 1,2-dimethylbenzene = 0.19, $N = 26$)). The naphthalene/methylnaphthalenes ratio varied seasonally, peaking during the winter and bottoming in the summer (Figure 5). The

exception in March 1979 reflects the effects of an oil spill in the area (4).

We offer two simple hypotheses to explain these seasonal variations. First, the strengths of two (or more) sources with different naphthalene/methylnaphthalene ratios may vary year-round. Alternatively, nearly constant sources, but varying sinks, may cause the variation. This second hypothesis requires the sink(s) to be strongest in summer and to remove naphthalene more efficiently than the methylnaphthalenes. This second hypothesis appears unreasonable. Photooxidation and biodegradation of naphthalenes are probably most effective in the summer, when light intensity and temperature are most favorable. However, in contrast to the observed temporal variation of the homologue ratio, these processes would cause naphthalene/methylnaphthalene to increase in the case of photooxidation (23) or remain unchanged in the case of biodegradation (24). Benthic adsorption would remove methylnaphthalenes more effectively than naphthalene (21), causing a rising summertime ratio. Air-sea exchange acting as a sink could diminish the ratio only slightly, but the higher average wind speeds of the winter in New England (average 6.2 m/s in December–February as compared to 4.5 m/s in July–September) (25) should cause air-sea exchange to be more efficient in the winter.

Thus, the more attractive hypothesis is that changing source strengths caused the seasonal variations. An obvious source of naphthalenes with the required seasonality is space heating oil use. Maximum naphthalene concentrations coincided closely with the coldest time of year (Figure 5). Burning fuels for heat has also been proposed as the source of the relatively high wintertime atmospheric concentrations found for other polycyclic aromatic hydrocarbons (26). This source is also consistent with the observation that naphthalene concentrations correlate with rainfall in a second winter time series study (7). This scenario implies that, during the remainder of the year, weaker combustion sources of naphthalenes, such as marine traffic, became the dominant sources. Since some of this delivery would involve a direct injection into the water, little homologue fractionation occurs and the resultant ratio is lower. Seawater directly exposed to diesel exhaust in the laboratory acquired a ratio very similar to that found in summertime coastal seawater (5).

Alkanes. Straight-chain alkanes from $n\text{-C}_{13}$ to $n\text{-C}_{17}$ and pristane (2,6,10,14-tetramethylpentadecane) were found in the coastal seawater of Vineyard Sound but did not demonstrate clear seasonal patterns. Pentadecane and heptadecane showed some month-long concentration fluctuations during the year as reported previously (4), sometimes reaching concentrations as high as tens of nanograms per liter (Figure 6). Other alkanes were much less abundant, generally present at a few nanograms per liter (Figure 6). Sauer et al. (1, 2) found $n\text{-C}_6$ – $n\text{-C}_{14}$ alkanes at about 1 ng/L in Gulf of Mexico surface water.

We distinguish alkane sources as anthropogenic or biogenic on the basis of an odd–even carbon preference index (CPI) calculated as $(n\text{-C}_{15} + n\text{-C}_{17})/(n\text{-C}_{14} + n\text{-C}_{16})$ (Figure 6). (Typically, organisms produce odd-chain-length alkanes far in excess of the even homologues. Diagenetic processes produce homologous series with members in very similar relative abundances). The high alkane concentrations of March 1977 were due to an oil spill in the vicinity (4), confirmed by the low CPI of 1.2. A second acute anthropogenic input seems to have occurred in May 1978 since the alkane concentrations all increased, but the CPI was near 1. Some naphthalene homologues also increased then. However, no oil spill is known to have oc-

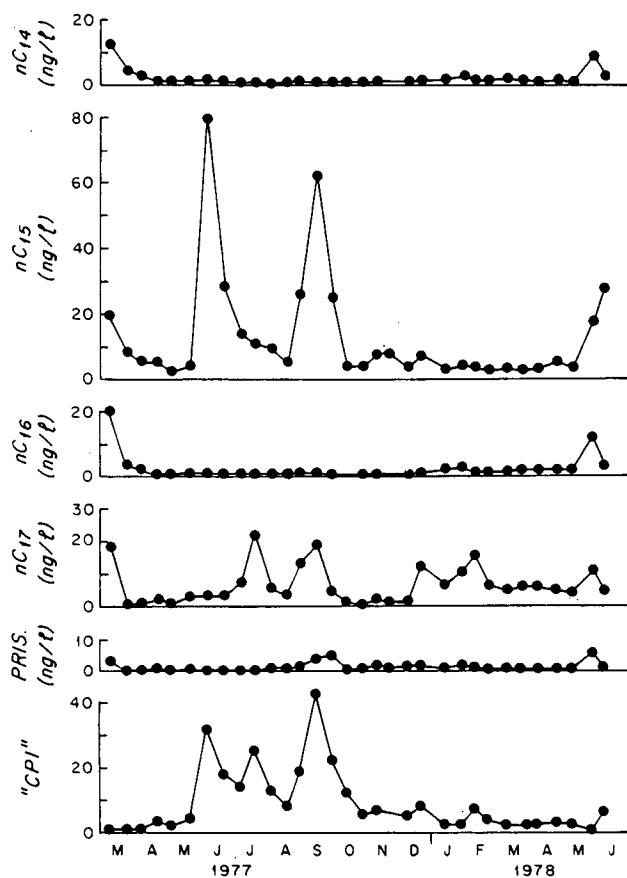


Figure 6. n -Alkane concentrations (ng/L) and the carbon preference index (CPI) in this seasonal study of coastal seawater.

curred in the region at that time. The persistent alkane levels also appear to be partially anthropogenic, since the CPI remains near or below 5 throughout much of the year. Sauer's results for the chronically polluted Gulf of Mexico show no odd-even hydrocarbon preference (1, 2).

The pentadecane and heptadecane maxima correspond to CPI values >5 , clearly not of petroleum origin. Schwarzenbach et al. (4) attributed the large inputs of pentadecane and heptadecane to benthic algae, since these hydrocarbons are abundant in marine plants (27-29) and since benthic algae flourish near CD during the summer when the largest maxima occurred. In a series of batch incubation experiments, Gschwend and Geiselman (5) showed that several benthic algal species release pentadecane and heptadecane into seawater at rates of nanograms per gram of dry algae per day.

Alternatively, phytoplankton may have supplied these alkanes, especially in the winter. Many species of marine phytoplankton contain both pentadecane and heptadecane (28). Several workers have concluded that pentadecane and heptadecane observed in open ocean seawater must have been produced by phytoplankton (2, 6, 30). The winter episodes of heptadecane input occurred during the chlorophyll *a* buildup and maximum (Figures 2 and 6). Additionally, both pentadecane and heptadecane appeared at high levels in the fall when a diatom bloom was expected (see discussion on hydrographic data). Clearly either planktonic or benthic algae may be significant n -alkane sources at CD.

Pristane was moderately enriched in September (Figure 6); it was not of petroleum origin, as shown by the low values of other hydrocarbons. Pristane is an important constituent of lipids of Cape Cod zooplankton (31); the water chemistry at this time suggested a heavily grazed

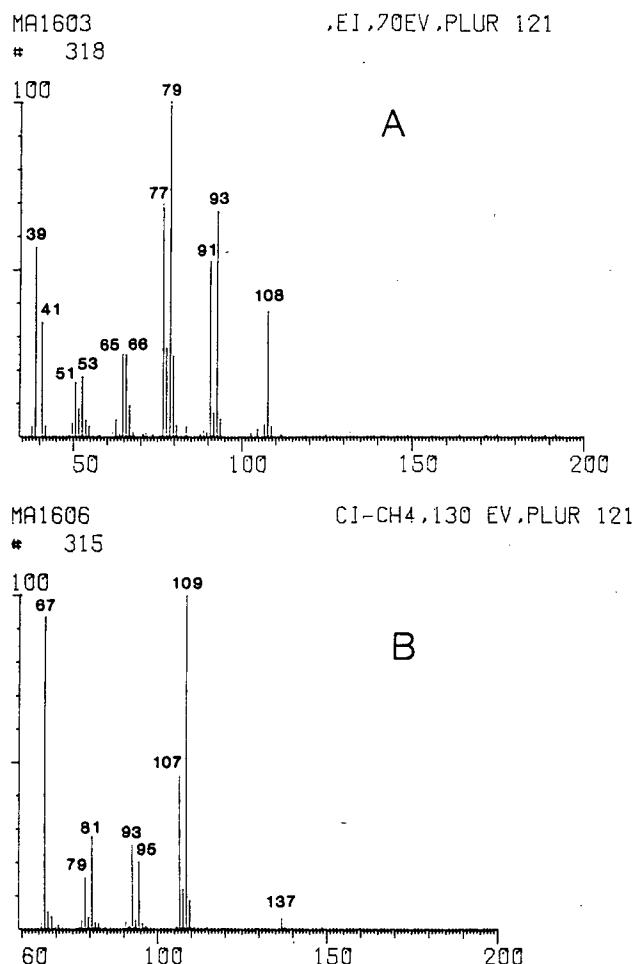


Figure 7. (a) Electron impact and (b) methane chemical ionization mass spectra of incompletely identified olefin, mol wt 108, recovered occasionally from coastal seawater in this study.

diatom bloom (see Hydrographic Data), and the 100-mL chlorophyll subsample contained visible zooplankton suggesting their unusually high abundance. Release of only 0.2% of the pristane content reported for a single *Calanus hyperboreus* (31) would supply the maximum pristane content that we observed. Goutz and Saliot (30) have observed high pristane in zooplankton-rich samples from the Mediterranean Sea.

Incompletely Identified Alkene. An alkene of molecular weight 108 was found occasionally at high levels at CD during this study and in the following year (7). This material is especially interesting in that it has also been found in the Marine Ecosystems Research Laboratory tanks of the University of Rhode Island (32), in the coastal seawater off Peru (6), and in Cook Inlet, AK (33). This compound coelutes with the ubiquitous ethylbenzene on SE-54, but is has been subsequently resolved by using a glass capillary column coated with Pluronics 121. The molecular-weight assignment is based on the presence of *m/e* 109 (*M* + 1), 137 (*M* + 29), and 149 (*M* + 41) in the methane CI spectrum (34) and *m/e* 108 in the EI spectrum (Figure 7). Since the CI and EI spectra are very similar to those of authentic 1,3,5-octatriene spectra (35, 36), we propose that this compound is one of the geometric isomers of this octatriene; less likely, it is a double bond position isomer, since published EI spectra for the 1,3,6, 1,3,8, and 1,4,6 isomers (36) show important differences.

The chemical nature and temporal occurrence of this compound suggest that it is related to the sexual gamone of *Fucus serratus*. This benthic brown alga releases *trans*,

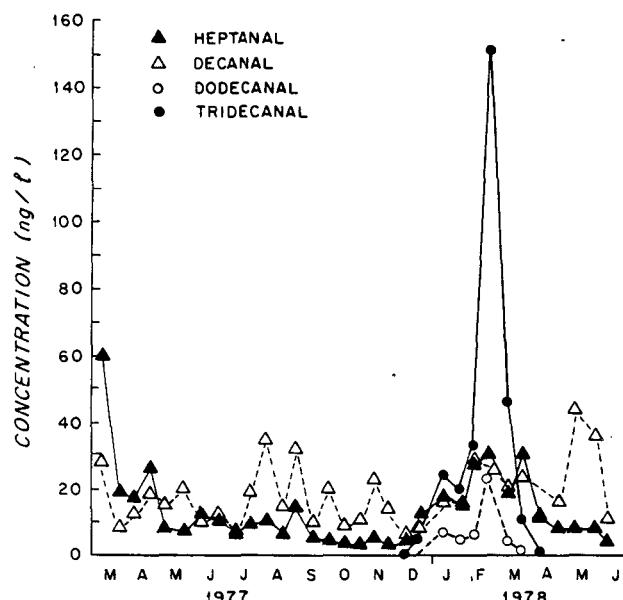


Figure 8. Heptanal, decanal, and dodecanal, and tridecanal concentrations (ng/L) in this seasonal study of coastal seawater.

cis-1,3,5-octatriene (fucoserraten) from its eggs into seawater to attract sperm (37, 38). However, the unknown and fucoserraten did not coelute on SE-54 column.

Since the alga in Vineyard Sound is actually *Fucus vesiculosus* rather than *F. serratus*, we hypothesized that this closely related species may utilize a geometric isomer of fucoserraten. When 500 g of mature (by microscopic observation) female receptacles were excised from productive plants, washed in filtered seawater, and incubated 3 days at 5 °C in order to promote liberation of ova and chemotactic substances, no octatriene compound was detected. *F. vesiculosus* is thus unlikely to be the source of the octatriene in Vineyard Sound seawater. Benthic algae are unlikely sources for the other locations (see above) at which this compound has been found; the compound seems to correlate fairly well with the occurrence of diatom blooms. However, log and stationary-phase cultures of *T. nordenstokioeldii*, the dominant late-winter bloom species in Vineyard Sound, also did not yield any of this material; other diatoms may be involved (7).

Like fucoserraten, the octatriene may be an important chemical signal. Its apparent wide distribution is extremely intriguing in this respect; hopefully, its source(s) and structure can be established in future studies. It is interesting to note that the concentrations at which this olefin occurred in seawater were similar to those of other hydrocarbons such as alkylbenzenes. Since various petroleum hydrocarbons interfere with chemotaxis in marine organisms (38-42), elucidation of the source and function of this olefin may have important ecological implications.

Aldehydes. We found the homologous series of normal aldehydes from hexanal to decanal year-round. In the winter as the chlorophyll *a* levels peaked, the concentration of hexanal, heptanal, and octanal increased from a few ng/L, found during the rest of the year, to about 20 ng of each/L (Figure 8). Nonanal and decanal also maximized at that time but were recovered at similarly high levels sporadically throughout the year (Figure 8). Schwarzenbach et al. (4) previously pointed out the reproducibility and blank problems with these latter two aldehydes. Also, precisely coincident with the maximum chlorophyll *a* levels and phytoplankton cell numbers were peak concentrations of longer-chain aldehydes from dodecanal to pentadecanal (Figure 8). Tridecanal was by far most abundant (13 >

12 > 14 > 15) and peaked at ~150 ng/L (uncorrected for stripping efficiency). During May-December when only the C₆-C₁₀ aldehydes were present at very low concentrations, nonanal and decanal occurred in the highest relative abundance, while during January-April the C₆-C₁₀ homologues were found in nearly equal abundance.

Aldehydes may originate from various sources. First, they may be produced in situ by marine microbes. Marine microorganisms have been shown to produce aldehydes as intermediates during the monoterinal oxidation of *n*-alkanes (43, 44). Freshwater diatoms (45) and chrysophytes (46) also produce aldehydes. However, these in situ biogenic sources were probably unimportant in this case since the appropriate *n*-alkane precursors for monoterinal oxidation were not observed and since pure cultures of *Thalassiosira nordenstokioeldii*, the dominant phytoplankton of the 1978 late-winter bloom, did not produce aldehydes. Possibly heterotrophic utilization of the phytoplankton-derived lipids produces aldehydes; occasionally we have observed large enrichments of short-chain aldehydes in seawater samples containing numerous zooplankton. Autoxidation of unsaturated fatty acids, as occurs during food spoilage or rancidification, may also form aldehydes. It is known (47) that *cis*-9-octadecenoic (oleic) acid, a very abundant algal fatty acid (48-50), is autoxidized to octanal, nonanal, and decanal. Similarly, *cis*-9-hexadecenoic acid, a second particularly abundant algal fatty acid, would autoxidize to yield hexanal, heptanal, and octanal.

Some aldehydes produced in the atmosphere or in the sediments may be transported into the coastal seawater. Sauer (2) proposed the atmospheric oxidation of petrogenic hydrocarbons to be a source of aldehydes to Gulf of Mexico surface seawater. We have noted the n-C₆-n-C₁₀ aldehydes to be the most prominent volatiles in two rainwater samples collected near CD. Recently, we made a preliminary attempt to examine sedimentary material collected in the region of our sampling site; we found these short-chain aldehydes to be particularly abundant. Thus, diagenetic processes may produce these aldehydes, and subsequently they may be released to the overlying waters via diffusion or resuspension of the sediments. Such processes may explain the low year-round levels.

Dimethyl Polysulfides. CH₃SSCH₃ (DM2S), CH₃SS-SCH₃ (DM3S), and CH₃SSSSCH₃ (DM4S) were also observed. They were frequently recovered in greater amounts in a second 2 h of stripping (restrips) than in the original 2 h. As discussed in Schwarzenbach et al. (4), a capacity for producing these polysulfides must be contained within the seawater samples. DM2S was recovered chiefly in the spring and summer samples, while DM3S and DM4S were found in the restrips of winter samples and in both the strips and restrips of spring samples of 1978.

DM2S and DM3S have been reported previously from lake-water samples (19, 51). DM2S is produced by cultures of freshwater bacteria, blue-green, or green algae (52, 53). DM2S may be formed by the oxidative coupling of methyl mercaptan (54), a common product from microorganisms (55, 56). DM2S, DM3S, and DM4S can all be produced by reacting methyl mercaptan with elemental sulfur at room temperature (57, 58). The polysulfides observed at our study site may originate in reducing environments such as sediments of coastal ponds and marshes lining Vineyard Sound. In support of this contention, the dimethyl polysulfides were recovered in very large amounts in our preliminary examination of sedimentary material. Finally, dimethyl polysulfides may be derived from other sulfur-containing metabolites. Cyclic polysulfides (59) and acyclic

forms (60-62) have been reported, and their degradation may be the source of these sulfur volatiles.

We demonstrate the possible importance of these polysulfides to the global sulfur cycle with an air-sea exchange calculation. The coastal seawater contained roughly 10 μg of S/m^3 in the form of these polysulfides (estimates based on the first 2 h of stripping only). If the atmosphere were a perfect sink, air-sea exchange would introduce between 20 and 80 μg of $\text{S}/(\text{m}^2 \text{ day})$ (using a range of piston velocities expected on the basis of the results of ref 15), or 7-28 mg of $\text{S}/(\text{m}^2 \text{ yr})$. This flux is greater than the 2 mg of $\text{S}/(\text{m}^2 \text{ yr})$ calculated for H_2S or the 6-10 mg of $\text{S}/(\text{m}^2 \text{ yr})$ for dimethyl sulfide for the coastal region of Chesapeake Bay (63) and similar to the 20 mg of $\text{S}/(\text{m}^2 \text{ yr})$ as dimethyl sulfide estimated for the surface Atlantic Ocean (14). However, a much larger global source of sulfur to the atmosphere is needed to balance the sulfur cycle (64).

Halogenated Volatile Organic Compounds. Tetrachloroethylene concentrations were about 1 ng/L, similar to the 0.5 ng/L reported for the Northeast Atlantic, but much lower than the concentration in Liverpool Bay, 120 ng/L (65). Tetrachloroethylene is used primarily in a direct dispersal manner and has recently been discovered in Falmouth, MA, drinking waters at ng/L to $\mu\text{g}/\text{L}$ levels (32).

Tribromomethane was also found occasionally in the summer. Benthic algae are known to produce it (5, 66). However, since chlorinated sewage is discharged into the coastal region at Woods Hole harbor, tribromomethane may also have derived from this source (67).

Total Organic Carbon Collected by Stripping. The total combined volatile extract in our work was between 200 and 500 ng of C/L. This total is roughly comparable to the 70-1500 ng of C/L found by Sauer (2) in the Gulf of Mexico using similar methods. In contrast, MacKinnon (68) collected 15-60 μg of C/L by using much more exhaustive stripping methods. No matter which operationally defined volatile extract is considered, these volatiles account for only a very small fraction of the total mass of dissolved organic matter. This does not imply insignificant importance of this fraction, since these compounds appear to be rapidly cycling in the environment.

Conclusions

Aside from the large number of specific events or probable source-process-sink relationships noted in this paper, several points of more general interest arise.

First, a very great variety of compounds seems to be present and to show roughly the same variability levels (Table I), suggesting that the variability is controlled by some common process. This theme is explored in the following paper (7).

Second, the very rapid rate of gas exchange likely at this site can explain almost completely the observed alkylbenzene level decreases; it is most unfortunate that we do not have comparison atmospheric concentration measurements to corroborate our hypothesized scenario. The rapid evaporation rate suggests that shorter time scale studies might prove more informative.

Third, for the favorable case of the alkylbenzenes, it has been possible to estimate the relative importance of four potentially competing sinks: evaporation, biodegradation, offshore mixing, and adsorption in sediments.

Fourth, preliminary work on the very difficult problem of quantifying potential sedimentary sources of volatile organic compounds suggests that the sedimentary source may be significant in some cases, e.g., aldehydes and dimethyl polysulfides.

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