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Volatile organic compounds in seawater from the Peru upwelling region[1,2]

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Abstract

The concentrations and distributions of individual volatile organic compounds in seawater were determined at six stations in the upwelling region off the coast of Peru by vapor phase stripping, glass capillary gas chromatography, and gas chromatography-mass spectrometry techniques. Saturated and unsaturated hydrocarbons, alkylated benzenes, and aldehydes were found. Individual compound concentrations varied from <2 ng·kg^{-1} to about 60 ng·kg^{-1}. All of the volatile compounds were present at higher concentrations in surface than in deeper waters, but each class of compounds had a unique horizontal distribution. Spatial distributions and correlations with hydrographic data suggest possible sources and transformations.

Several groups of specific volatile organic compounds have been identified and quantified in coastal seawater samples. Schwarzenbach et al. (1978) recovered alkanes, alkylbenzenes, naphthalene and alkylnaphthalenes, aldehydes, and dimethylpolysulfides from seawater collected from Vineyard Sound, Massachusetts. Sauer et al. (1978) determined individual C_6–C_{14} alkanes, benzene, and alkylbenzenes in coastal waters of the Gulf of Mexico. These workers used mild purging conditions to obtain their volatile concentrates and focused on the occurrence of individual specific organic compounds, the sum of which amounted to only 0.05–1.5 μg C·kg^{-1} (Sauer 1978; Gschwend 1979). Somewhat harsher purging methods recovered about 50 μg C·kg^{-1} from coastal seawater acquired off Nova Scotia, but the composition of this volatile extract is unknown (MacKinnon 1979). Although these volatile isolates amount to a very small proportion of the total organic carbon in seawater, study of the spatial and temporal distributions of the specific volatile organic compounds has provided information concerning some sources and transport processes of dissolved organic matter in seawater (Sauer et al. 1978; Sauer 1978; Schwarzenbach et al. 1978; Gschwend 1979). Further work on these volatile compounds may extend our insights and indicate environmental transformations characteristic of their organic functional groups.

We report here a study of volatile organic compounds in seawater from the Peru upwelling region. The intense biological productivity associated with upwelling provides an opportunity to focus on the distribution, sources, and sinks of biogenic volatile organic compounds. Terrestrial and anthropogenic inputs of organic materials from the sparsely populated, arid Peruvian coast should be minimal. We have analyzed a series of seawater samples from profiles along an offshore transect taken in March 1978 (a period of active upwelling) using vapor phase stripping, glass capillary gas chromatography, and gas chromatography-mass spectrometry techniques for the "volatile organic compounds." These are operationally defined as those compounds which may be purged from seawater by bubbling with a gas stream and retained by a solid adsorbent (Schwarzenbach et al. 1978; Gschwend 1979). We report the compounds identified, their distribution in the water column, and correlations with hydrographic, nutrient, and pigment data.

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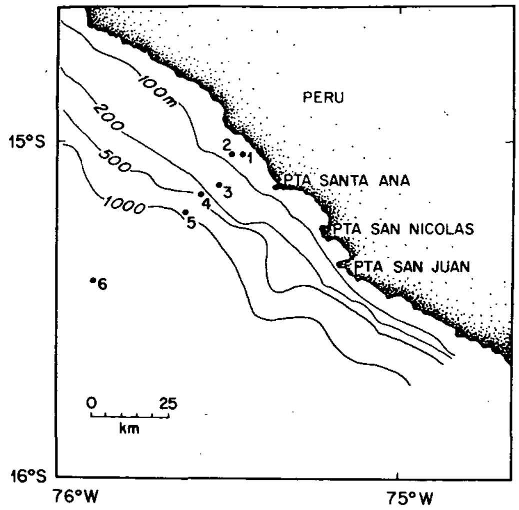

Fig. 1. Station locations, RV *Knorr* Cruise 73-2 (March 1978).

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Sampling and analysis

Seawater samples were collected with a single 30-liter Niskin bottle with Teflon-coated spring at six stations in March 1978 on Cruise 73, Leg 2 of RV *Knorr* (Fig. 1). Immediately after retrieval, samples were drawn from the bottle at the ships bow, heading into the wind, to minimize contamination from the ship. Water flowed by gravity from the bottle through a polypropylene tube to an inline 142-mm glass-fiber filter (previously cleaned by baking at 450°C overnight) in a stainless steel holder; these components were rinsed with a portion of the the sample. Glass reagent bottles (2 liters) with ground-glass stoppers were then filled completely, poisoned with 0.5 ml of saturated $HgCl_2$ solution (67 μM Hg in the samples), stoppered tightly, and stored at 4°C in the dark for 3–6 weeks before analysis at Woods Hole.

Samples for salinity, oxygen, nutrients, and chlorophyll *a* were drawn from the same Niskin bottle and analyzed on shipboard. Salinity was determined with a Guildline Autosal salinometer (model 8400), oxygen by a modified Winkler procedure (Carpenter 1965). Nutrients were measured with an AutoAnalyzer, and chlorophyll *a* was determined by the fluorometric technique (Yentsch and Menzel 1963; Holm-Hansen et al. 1965).

The seawater samples were analyzed by the "Grob" method (Grob 1973; Grob and Zürcher 1976; Schwarzenbach et al. 1978; Gschwend 1979). Just before analysis, 200 ml of water were poured off at a nearby isolated beach to provide clean-air headspace; Schwarzenbach et al. (1978) showed that this procedure eliminated erratic airborne contamination of samples by lab air. The samples were stripped for 2 h at 35°C by repeatedly cycling the headspace air through the sample and a charcoal microtrap to collect the volatile compounds. After the water was stripped, a standard, 20 ng of 1-chloro-*n*-octane in 2 μl of CS_2, was added to the trap, which was then extracted with 15 μl of CS_2. Aliquots of this extract were analyzed by glass capillary gas chromatography on a model 2101 Carlo Erba gas chromatograph equipped with a flame ionization detector, or by combined gas chromatography-mass spectrometry (GC-MS) with a Finnigan 3200 quadrupole mass spectrometer. A single 20-m × 0.32-mm-i.d. SE-54 column (Jaeggi, Switzerland) was used throughout. Electron impact (EI) spectra were acquired at 70 eV ionization potential, methane chemical ionization (CH_4-CI) spectra at 130 eV and a source pressure of 950 μ.

As a check for possible contamination effects of filtering and poisoning, some samples were not treated; others were poisoned only. Untreated samples were drawn first, followed by unfiltered samples, and finally by filtered ones. Comparison of treated with untreated samples showed that filtering and poisoning procedures did not contaminate the samples.

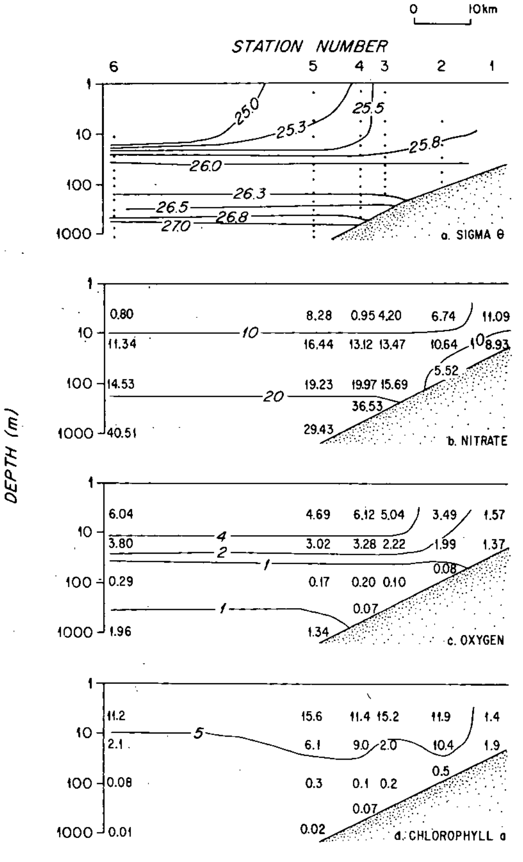

Fig. 2. Sections showing sigma θ (‰), nitrate ($\mu M \cdot kg^{-1}$), oxygen ($ml \cdot kg^{-1}$), and chlorophyll *a* ($\mu g \cdot kg^{-1}$) in seawater from Peru upwelling region. Depth scale is logarithmic.

Coastal seawater samples were filtered, poisoned, and spiked with model volatile compounds (*n*-tridecane; 2,6-dimethyl-3-heptene; 1-ethyl-2-methylbenzene; 2-ethylhexanal) at 25 $ng \cdot kg^{-1}$ and stored for 4 weeks to evaluate sample storage effects. Stored samples showed reproducible (±8%) changes in volatile concentrations from unstored replicates. All three hydrocarbons were recovered at 30–40% lower concentrations from the stored samples than from the unstored ones. The aldehyde, however, was recovered at 50% greater efficiency after storage. The volatile compound variations we discuss here are much greater than these storage effects. Although the absolute quantities recoverable may change during sample storage, the relative distributions within each compound should not be influenced.

The analyses provided a detection limit of about 2 $ng \cdot kg^{-1}$. Schwarzenbach et al. (1978) found reproducibility to be about ±10%; blanks were <2 $ng \cdot kg^{-1}$. Nonpolar and slightly polar compounds were recovered with >80% efficiency; relatively polar compounds were recovered at lower efficiencies, e.g. aldehydes ≈30%. Reported concentrations are corrected for stripping efficiency and storage effects by using results from model compounds. Results reported here are for filtered, poisoned samples.

Results

The hydrographic data showed active upwelling between stations 1 and 4 during sampling (Fig. 2a). Nutrients were enriched at station 1 and dropped to relative minima in the surface seawater at stations 4 and 6 (as shown for nitrate in Fig. 2b). An oxygen-deficient subsurface layer was encountered at all stations at about 100 m (Fig. 2c), reflecting the strong remineralization activity which occurs at that depth. Chlorophyll *a* concentrations were particularly high (>10 $\mu g \cdot kg^{-1}$) in the surface waters offshore of station 2 (Fig. 2d), indicating intense biological productivity at these sites during sampling. A diatom bloom was present in the region of stations 2 and 3 and a dinoflagellate bloom at stations 4 and 5 (J. Hobbie pers. comm.).

The seawater samples contained representatives of several classes of volatile organic compounds, including saturated and unsaturated hydrocarbons, alkylated benzenes, and aldehydes (Fig. 3 shows representative chromatograms). In general, concentrations for all volatiles were higher in surface samples than in deeper ones; however each class had a unique horizontal distribution. Normal pentadecane was the only prominent *n*-alkane; its C_{13}–C_{16} homologues were only found at trace levels. Surface samples contained the highest concentrations of pentadecane, with a maximum at station 6 of more

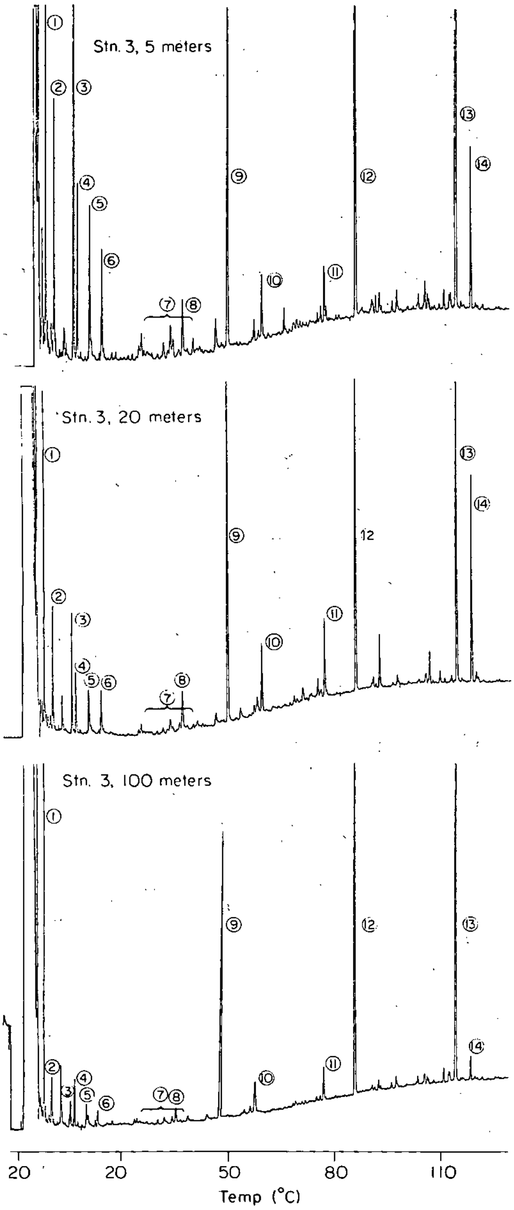

Fig. 3. Chromatograms showing volatile organic compounds isolated from three depths at station 3. Compounds identified are: 1—toluene; 2—hexanal; 3—ethyl benzene + unknown (mol wt 108); 4—1,3- + 1,4-dimethylbenzene; 5—1,2-dimethylbenzene; 6—heptanal; 7—C_3-benzenes; 8—octanal; 9—1-chloro-*n*-octane, internal standard; 10—nonanal; 11—decanal; 12—1-chloro-*n*-decane, internal standard; 13—1-chloro-*n*-dodecane, internal standard; 14—pentadecane.

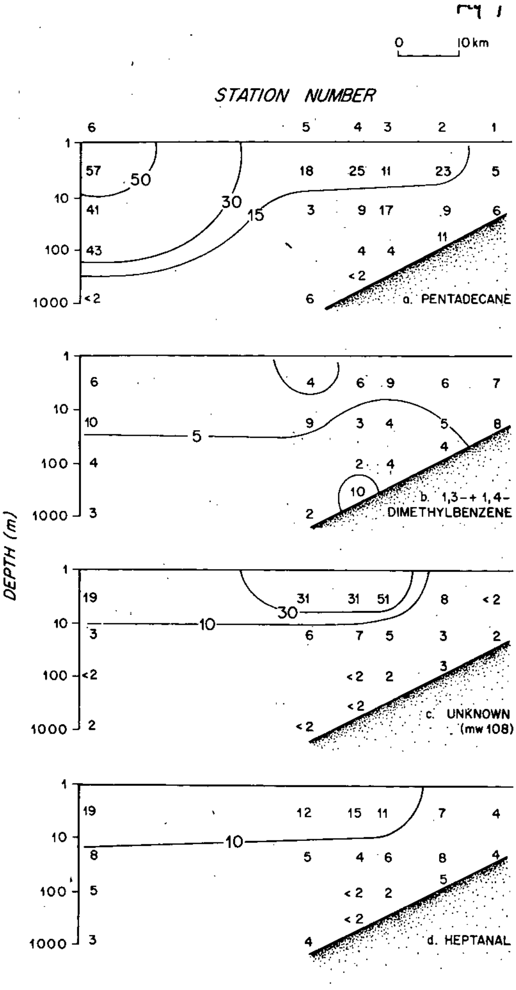

Fig. 4. Sections showing pentadecane, 1,3- + 1,4-dimethylbenzenes, unknown (mol wt 108), and heptanal concentrations (all in ng·kg^{-1}) in seawater from Peru upwelling region. Depth scale is logarithmic.

than 50 ng·kg^{-1} (Fig. 4). C_1–C_3 alkylated benzenes were found, but only the C_2-alkylated benzenes were sufficiently abundant and free from blank problems to provide interpretable data (deep-water toluene concentrations were similar to shallow sample levels). These C_2-aromatic hydrocarbons were present at <10 ng·kg^{-1}. Surface seawater contained 2–3 times more of these compounds than 1,000-m samples (as shown for 1,3-dimethylbenzene + 1,4-dimethylbenzene in Fig. 4).

A relatively abundant unidentified compound, which cochromatographed with ethylbenzene, was found in several surface samples. A molecular weight of 108 was assigned to this compound based on the presence of m/e 109 (M + 1), 137 (M + 29), and 149 (M + 41) ions in the CH_4-CI spectrum and m/e 108 in the EI spectrum. Losses of 13 and 27 mass units (giving m/e 95 and 81) in the CH_4-CI spectrum indicate a terminal vinyl group ($-CH=CH_2$) (Field 1968). The loss of 15 mass units (giving m/e 93) in both the EI and CI spectra suggested a methyl substituent. These data are consistent with an octatriene or possibly a methyl-branched heptatriene structure. Authentic *trans,cis*-1,3,5-octatriene showed the same major fragment peaks as the unknown in the sample. However, *trans,cis*-1,3,5-octatriene did not cochromatograph with ethylbenzene; thus the unknown was not this particular isomer.

The peak heights of this (mol wt 108) unknown were estimated by subtracting the ethylbenzene contribution from the mixed GC peak, assuming that ethylbenzene peak heights were proportional to the peak heights of other C_2-benzenes in the same sample. This assumption is reasonable since ethylbenzene levels covary with other C_2-benzene isomer concentrations in most fossil fuels and in many other seawater samples (Gschwend 1979). These estimates by difference agreed very well with peak heights inferred from GC-MS mass chromatography data.

The derived spatial distribution of the unknown compound (mol wt 108) is shown in Fig. 4c. Maximum values were always found near the surface. Station 3 showed the highest level, with concentration decreasing slowly offshore.

Mass chromatograms for m/e 109 in the GC-MS analyses of CI-CH_4 showed only one "octatriene" at station 3, but additional isomers appeared in the surface seawater at station 6. Mass spectra indicated that the compounds are probably *cis-trans* or positional olefinic isomers.

The homologous series of straight-chain aldehydes from hexanal to decanal was also found. Individual aldehyde concentrations covaried; hexanal and heptanal were the most abundant. As in the case of the other volatiles, concentrations were highest in offshore surface samples (shown for heptanal in Fig. 4d).

Discussion

The organic carbon recovered in the "analytical window" defined by our methods amounted to <0.01% of the total organic carbon in the seawater. Total levels detected in surface samples, where primary productivity was intense, were about 100 ng $C \cdot kg^{-1}$. Deep water samples contained 20 ng $C \cdot kg^{-1}$ or less. These total levels are approximately equal to or less than the lowest volatile fraction concentrations found in the Gulf of Mexico by Sauer (1978) or in Vineyard Sound, Massachusetts, by Gschwend (1979), both of whom used methodology similar to that used here. The maximum concentration observed for an individual volatile organic compound was only 60 $ng \cdot kg^{-1}$.

One hypothesis to explain the generally low levels of volatile organic compounds in these waters is that there may be a lack of sources. The coastal region of Peru near the area where the samples were collected is a sparsely populated desert. Therefore, terrestrial biogenic and anthropogenic sources are unlikely to be large, despite offshore winds. However, primary production in this upwelling region was very high at the time of sampling, and total volatile concentrations were higher near blooms. Thus, biogenic production is implied, and therefore sinks for these volatile organic constituents must act to limit their concentrations to parts per trillion (w/w) levels.

Concentrations of volatile compounds (especially biogenic compounds) may be limited by rapid remineralization. Menzel (1975) suggested that dissolved organic carbon is rapidly decomposed after pulse inputs, since primary productivity correlated only poorly with dissolved organic carbon values. Also, the low concentrations of specific organic metabolites imply that these compounds are quickly removed after release into seawater. Turnover times of only a few days have been calculated for amino acids (Williams and Gray 1970; Lee and Bada 1975, 1977) and glucose and acetate (Wright and Hobbie 1966) dissolved in natural waters and have been attributed to heterotrophic utilization. Concentrations of biogenic volatile organic compounds may also be limited by microbial degradation.

A second potentially important sink for volatile organic compounds is gas exchange into the atmosphere. The mixed layer of the open ocean exchanges gases of low water solubility with a residence time of about 1 month (Broecker and Peng 1974). The shallow mixed layer off Peru (10–20 m: Fig. 2a) should degas several times faster. Therefore, volatile organic compounds produced by the highly active planktonic community of the upwelling region off Peru may be removed from the seawater into the atmosphere on a time scale of days. As a result, we cannot determine the relative importance of heterotrophic utilization and evaporation as sinks for the volatile organic compounds.

Pentadecane—The concentration of pentadecane in these surface waters (Fig. 4) approached its calculated solubility (based on an extrapolation of data from McAuliffe 1966; Button 1976). It has also repeatedly been found in coastal seawater (Schwarzenbach et al. 1978), in Gulf of Mexico surface seawater (Sauer 1978), and in Sargasso Sea and equatorial Atlantic surface water (Gschwend 1979). Known sources for this hydrocarbon include fossil fuels and terrestrial and marine plants. The absence (<2 ng$\cdot$kg^{-1}) of homologues—tetradecane and hexadecane—rules out a fossil fuel source. Land-derived dust sampled over the ocean does not contain detectable amounts of pentadecane (Simoneit et al. 1977). The air–water partition coefficient (ca. 10^4) for this saturated hydrocarbon favors the vapor phase so strongly that ca. 100 mg$\cdot$m^{-3} in air would be required to maintain the tens of nanograms per kilogram concentrations observed in seawater. Such atmospheric levels are very unlikely; e.g. Cautreels and van Cauwenberghe (1978) found only 60 ng pentadecane$\cdot$m^{-3} in the vapor phase of urban air.

In situ biological production is a probable source of pentadecane. Many phytoplankters contain pentadecane (Blumer et al. 1971). Clark and Blumer (1967) reported between 300 and 600 ng pentadecane$\cdot$g^{-1} dry algae for three species. To estimate the magnitude of this source for the Peru upwelling region, we assume that average phytoplankton have 500 ng pentadecane$\cdot$g^{-1} dry weight and that twice the surface particulate organic carbon (POC) values approximate the dry phytoplankton biomass. For the Peru upwelling region, where values between 500 and 2,300 μg POC$\cdot$kg^{-1} were found, these plankton could contain about 1 ng pentadecane$\cdot$kg^{-1} seawater. If we assume a 2–4 week degassing equilibration time as a minimum sink, these hypothetical phytoplankters would have to produce and release all of this estimated pentadecane stock into solution in seawater at a rate of once per day. Although this rate corresponds to algal doubling rates observed in the Peru upwelling region (Strickland et al. 1969; Beers et al. 1971; Walsh 1975), it seems unlikely that all of the pentadecane should be released as dissolved organic matter. Thus, while phytoplankton may contribute some pentadecane to seawater, other biogenic sources may also be important.

Another reasonable source of pentadecane might be the biochemical decarboxylation by zooplankton of phytoplankton-produced hexadecanoic acid, analogous to the pathway proposed for the formation of pristane (2,6,10,14-tetramethylpentadecane) (Blumer et al. 1964; Avigan and Blumer 1968). Since phytoplankton contain about 10 mg hexadecanoic acid$\cdot$g^{-1} dry weight (Ackman et al. 1968; Chuecas and Riley 1969; Fisher and Schwarzenbach 1978), the standing stock of this proposed starting material could be up to 20 μg$\cdot$kg^{-1} seawater. Conversion of 0.1–1% of this hexadecanoic acid would yield tens of nanograms of pentadecane per kilogram of seawater. Tetradecane and hexadecane would not be found in similar abundance because phytoplankton contain very little of the C_{15} and C_{17} fatty acid precursors. Consequently, in addition to direct phytoplankton inputs, a zooplankton-mediated transformation of hexadecanoic acid to pentadecane may contribute an important fraction of the dissolved pentadecane in seawater.

Alkylated benzenes—The C_1–C_3 alkylated benzenes—common constituents of petroleum and combustion exhausts—were recovered from the coastal waters off Peru. The spatial distribution shown by 1,3- + 1,4-dimethylbenzene suggests a surface water or atmospheric source (but not general shipboard or analytical contamination above about 2 $ng \cdot kg^{-1}$, the deep water levels). Since oxygen concentrations in recently upwelled waters at station 1 were quite low, the transfer of gases from the atmosphere was far from complete. If the atmosphere were the source, dimethylbenzene air concentrations in this region would have to be several times >2 $ng \cdot liter^{-1}$ air [$K(wt \cdot vol^{-1}$ $air)/(wt \cdot vol^{-1}$ $water) = 0.34$], the value calculated for equilibrium with observed C_2-benzene levels; this is greater than the 3–5 $ng \cdot liter^{-1}$ air measured in rural areas of Florida (Lonneman et al. 1978) and much greater than the 0.02 $ng \cdot liter^{-1}$ air detected along the west coast of Ireland (Eichmann et al. 1979). It seems unlikely that air at this remote Peruvian site would be much more contaminated.

Direct surface water pollution of alkylbenzenes from marine traffic therefore seems most likely. Sauer et al. (1978) have noted that the research vessel is a significant source of alkylated benzenes to surface waters; nonetheless, taking precautions to avoid ship-derived sample contamination, they also found between 2 and 10 ng 1,3- + 1,4-dimethylbenzene$\cdot kg^{-1}$ seawater in nonpolluted Gulf of Mexico surface seawater. We cannot at present determine whether the recovery of low levels of these aromatic hydrocarbons in this relatively remote region is due to ubiquitous fossil fuel-related contamination or simply the result of inputs from the research vessel.

Unknown (mol wt 108)—The surface maximum in the unidentified olefin concentration at station 3 suggests a phytoplankton source, possibly associated with the diatom bloom. The discovery of what seem to be isomers of the unidentified olefin in the surface sample at station 6 implies that the decline in concentration between stations 3 and 6 is not due solely to dilution but also to isomerization reactions.

This same unidentified compound was found at high concentrations in Vineyard Sound seawater during late winter 1978 (Gschwend 1979), but its source is not known. *Fucus* spp., benthic brown algae, release an octatriene (*trans,cis*-1,3,5-octatriene) into seawater as a sex attractant (Müller and Jaenicke 1973), but the mol wt 108 compound is not this triene. Knowledge of the detailed structure and the biological source of this occasionally abundant and geographically widespread compound would obviously permit very interesting studies of the transport, transformation, and biological function of what may be a chemical messenger (as is the *Fucus* compound).

Aldehydes—The C_6–C_{10} straight chain aldehydes were found primarily in surface waters offshore of station 3 (Fig. 3d), indicating a biogenic source. Aldehydes have been found in other seawater samples (Sauer 1978; Schwarzenbach et al. 1978), in freshwater diatoms (Kikuchi et al. 1974), and in a freshwater chrysophyte (Collins and Kalnins 1965). The hypothesis that they are produced directly by phytoplankton is also supported by the covariation of cell counts and aldehyde concentration in a time series of seawater samples from Vineyard Sound (Gschwend 1979). The linear correlation coefficient for heptanal with chlorophyll *a* in the Peru upwelling region samples was 0.76 ($P < 0.001$).

On the other hand, these aldehydes may be produced by heterotrophic oxidation of algal organic matter. To test this hypothesis, we plotted the aldehyde concentrations against dissolved oxygen (e.g.

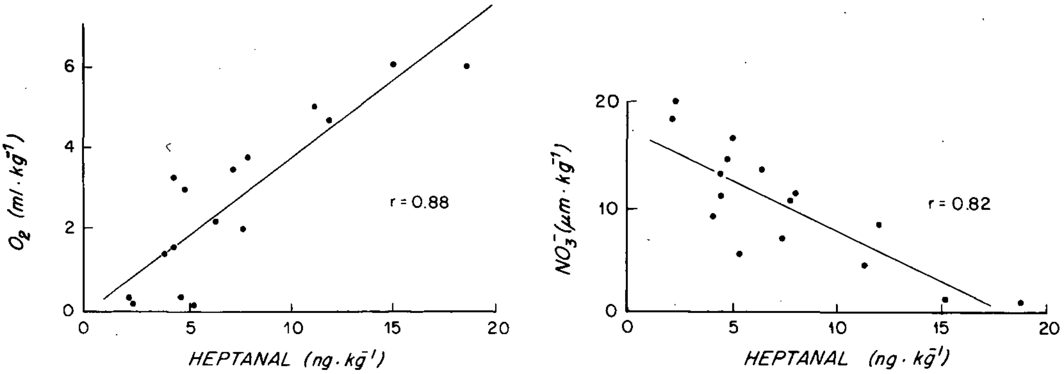

Fig. 5. Heptanal vs. dissolved oxygen and vs. nitrate. r is linear regression coefficient.

heptanal: Fig. 5). Rather than the inverse correlation expected for a heterotrophic oxidation mechanism, we found strong direct correlations [e.g. linear correlation coefficient of 0.88 ($P < 0.001$) for heptanal vs. oxygen]. This aldehyde-oxygen correlation indicates a source related to the atmosphere, to primary production, or to chemical oxidation. Since there is also a strong inverse correlation for heptanal vs. nitrate (−0.82, $P < 0.001$) in the 5-, 20-, and 100-m samples (Fig. 5), the source appears to be related to primary production rather than to atmospheric gas exchange.

Chemical oxidation of algal metabolites released during intense primary production may be responsible for the aldehyde distribution observed. Unsaturated fatty acids are potential metabolite reactants for chemical oxidation to aldehydes. Two of the most common fatty acids in phytoplankton are *cis*-9-hexadecenoic acid and *cis* 9-octadecenoic (oleic) acid (Ackman et al. 1968; Chuecas and Riley 1969; Fisher and Schwarzenbach 1978). Autoxidation of *cis*-9-octadecenoic acid has been shown to yield C_7–C_{10} alkanals (Badings *cited in* Schauenstein et al. 1977). Corresponding degradation of *cis*-9-hexadecenoic acid would produce C_5–C_8 alkanals. These two fatty acids are found at $\mu g \cdot kg^{-1}$ concentrations in seawater (Jeffrey 1966) and are particularly abundant in surface slicks (Kattner and Brockman 1978) which may be the site of (photo?) oxidation reactions (Wheeler 1972; Zafiriou 1977) that produce these aldehydes.

The occurrence of aldehydes in seawater is noteworthy since they may be involved in the formation of refractory polymeric substances. They are highly reactive and may combine with other organic compounds through condensation reactions and thus contribute to the introduction of the extensive aliphatic character of marine humic materials (Stuermer and Payne 1976; Gagosian and Stuermer 1977; Stuermer and Harvey 1978).

Conclusion

The detection of volatile organic compounds in seawater from the Peru upwelling region suggests their use as tracers of some sources and sinks of organic matter in the sea. In situ biological processes dominate as the source of dissolved volatile organic constituents in seawater from this region, and other processes, possibly heterotrophic remineralization or gas exchange with the atmosphere, are responsible for limiting the concentrations of these substances. Anthropogenic contamination must also be considered for some compounds observed at this remote site, but it is difficult to be certain that this pollution did not come from the research vessel.

Our study also suggests the occurrence of three specific environmental transformation processes of organic compounds in seawater: carboxylic acids may be converted to hydrocarbons by zooplankton; polyolefinic moieties may interconvert to yield other geometric isomers; unsaturated lipids may be autoxidized to produce *n*-aldehydes.

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