Reports

Hydrocarbons in Open Ocean Waters

Abstract. *Nonvolatile hydrocarbons in Atlantic Ocean and nearby waters were found to contain aromatics at lower concentrations than would be expected if the source of the hydrocarbons were crude oil or petroleum refinery products. Hydrocarbons appear to persist in the water to varying degrees with the most persistent being the cycloparaffins, then the isoparaffins, and finally the aromatics.*

In 1972–1973 we carried out a base line study to measure the concentration and composition of nonvolatile hydrocarbons as found dispersed in open ocean water. Water samples were collected off moving tankers as they traveled tanker routes in the Atlantic Ocean as well as some waters of the Mediterranean Sea and the Indian Ocean. Other areas of the North and South Atlantic were sampled during the Geochemical Ocean Section Study (GEOSECS) voyage. The hydrocarbons in ocean water were found to be complex mixtures comprising saturated and aromatic compounds having from 14 to 32 carbon atoms per molecule (*1*). Aromatics are present in smaller relative concentrations than one would predict if the source of the hydrocarbons were crude oil or refinery products. This finding is of interest from both a scientific and a public viewpoint, because aromatic hydrocarbons are potentially more toxic to the environment than saturated hydrocarbons.

Prior to carrying out the measuring program, we conducted an extensive study to develop suitable sampling and analytical procedures to identify and measure the small concentrations of hydrocarbons found in open ocean water. These methods, described elsewhere (*2*), give accurate results for concentrations as low as 1 part per billion (ppb) of hydrocarbons. The method of analysis is applicable to the measurement of nonvolatile hydrocarbon compounds having 14 or more carbon atoms per molecule. With this technique it is also possible to measure the total organic content as extracted by CCl_4; this quantity, "extractable organics," includes hydrocarbons, esters, and acids.

The actual compositions found for hydrocarbons in the ocean are based primarily upon mass spectrometric analyses, from which it was possible to identify and measure the relative concentrations of *n*-paraffins, isoparaffins, cycloparaffins, aromatics by ring number, and sulfur-containing aromatics such as benzo- and dibenzothiophenes. The isoparaffins are long chains having from one to several short-chain substituents. Cycloparaffins include ring systems varying primarily from one to six rings, and alkyl substituents are present on the rings. Aromatics are composed principally of one- to three-ring molecules with short- to long-chain alkyl substituents. Aromatics include benzenes, naphthalenes, and phenanthrenes and also mixed molecules which contain both aromatic and cycloparaffinic rings. One example of the latter class is an indan which consists of a cycloparaffinic ring fused with a benzene and having alkyl substituents at locations around the total ring system. Sample aliquots were analyzed by gas chromatography to obtain the *n*-paraffin contents.

Samples were taken principally from the top meter of seawater (surface samples) and at a depth of approximately 10 m. For Atlantic Ocean water, the median concentration of nonvolatile hydrocarbons was 4 ppb with values from 1.3 to 13 ppb falling within 1 standard deviation from the median (*3*). Vertical profile samples at eight stations generally showed concentrations of 1 ppb or less for depths of 100 m or more.

Hydrocarbons in the sea can originate from a biogenic source or from petroleum. If the source is petroleum, hydrocarbons may be introduced via seepage or by man's activity. Evidence available at present (*4*, pp. 1–12) suggests that petroleum hydrocarbons in ocean water are primarily introduced by man. Recent reviews indicate

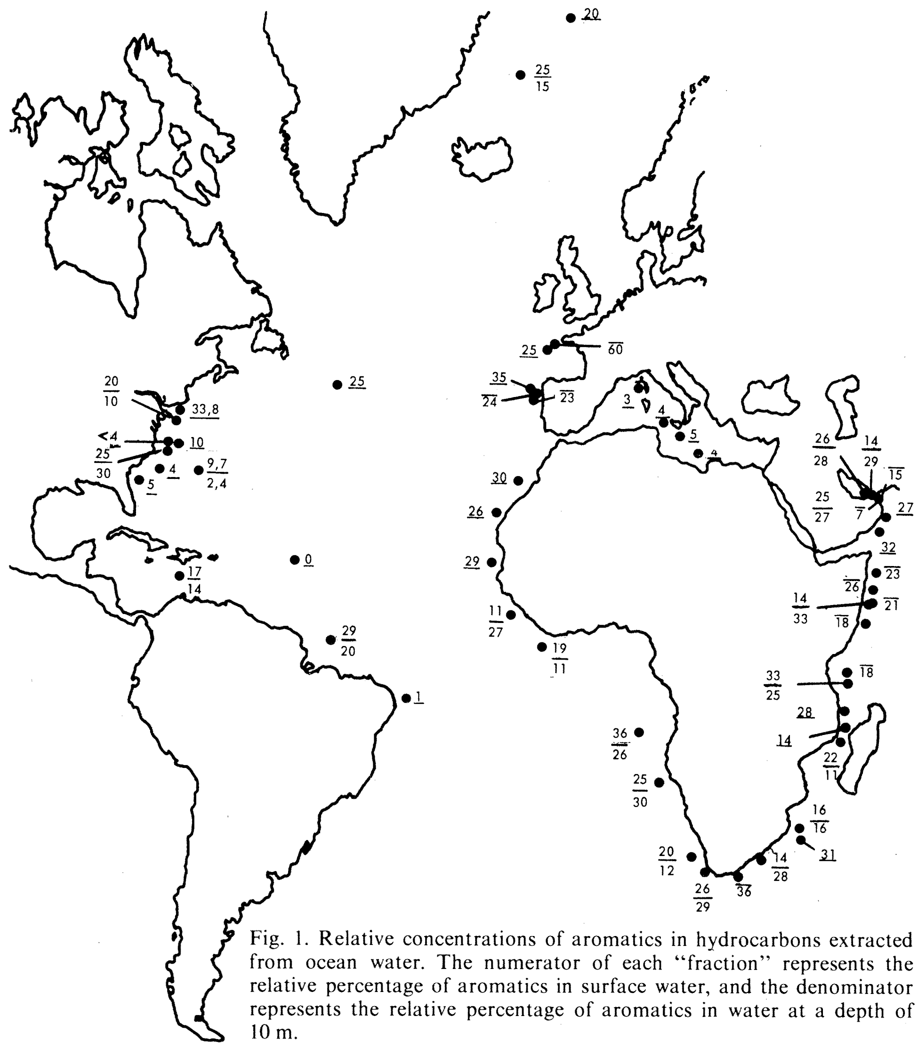

Fig. 1. Relative concentrations of aromatics in hydrocarbons extracted from ocean water. The numerator of each "fraction" represents the relative percentage of aromatics in surface water, and the denominator represents the relative percentage of aromatics in water at a depth of 10 m.

Table 1. Composition of nonvolatile hydrocarbons in crude oil and typical open-ocean samples from the Persian Gulf tanker route in 1972.

Hydrocarbon types	Relative percent (by weight) of crude oil		Relative percent (by weight) of sample			
			Surface		−10 m	
Paraffins						
n-Paraffins	7				1	
Isoparaffins	22		26		29	
Cycloparaffins	32		57		54	
Aromatics						
One ring	12	39	7	16	9	16
Two rings	11		5		5	
Three rings	4		2		0	
Four rings	2					
Sulfur-containing*	10		2		2	

*Benzo- and dibenzothiophenes.

that the biogenic hydrocarbons in petroleum may be limited to a finite number of *n*-paraffins or olefins with possibly a smear of polycyclic hydrocarbons (5).

During our sampling along the Persian Gulf tanker route in 1972, the daily shipments of crude oil [in millions of barrels (1 barrel = 159 liters)] were comprised of the following: Arabian light (4.5 to 6), Iranian light (2.5), Iranian heavy (2.5), and Kuwait (2.5). On the basis of the measured composition of each crude oil and the relative proportion, an average crude oil composition was calculated as shown in column 2 of Table 1. There is little variation in the aromatic content of the four crude oils so that in this respect the average is uniquely representative of the cargo carried along this tanker route. Columns 3 and 4 of Table 1 show compositional data for typical samples as collected along this tanker route. These samples and most others for which compositions were measured are actually blends of two or more individual samplings. This blending was necessary in order to get sufficient material for analysis by gas chromatography and mass spectrometry.

The data in Table 1 indicate that, as compared with the crude oil, the samples are significantly lower than the average crude oil in the *n*-paraffin content (1 versus 7 percent) and aromatic content (16 versus 39 percent). On the basis of our experience, low *n*-paraffin content is characteristic of open ocean hydrocarbons as will be discussed more fully below. A relatively low concentration of aromatics (< 39 percent) was also observed in all samples collected along the Persian Gulf tanker route. This behavior is shown in Fig. 1 where the relative percentages (by weight) of aromatics are shown for surface and subsurface water samples from around Africa and into the waters of the Atlantic off western Europe. Of 49 samples analyzed, only one contained hydrocarbons having more than 39 percent aromatic content. The mean relative aromatic concentration is 24 percent. No correlation is apparent between aromatic content and either geographical location or depth of sample.

Also shown in Fig. 1 are some values for the Mediterranean Sea. Four samples taken in open areas of the Mediterranean contained relative aromatics concentrations of 3 to 5 percent. At the time of sampling in 1972 the Suez Canal had been closed for several years, and in the intervening years the principal tanker cargo in this area of the Mediterranean had been Libyan crude oil, comprised of ~ 18 percent aromatics. The 3 to 5 percent aromatics as observed for nonvolatile hydrocarbons in the Mediterranean are significantly lower than the aromatic content of the crude oil.

Figure 1 also shows the aromatic concentrations as observed for hydrocarbons in ocean water along two well-traveled tanker routes, namely, the Gulf of Mexico to New York City and the Caribbean to New York City. At the time of this sampling in 1972, Gulf Coast crude oils and residual fuels were the principal cargo items. Aromatic contents for these fuels are typically 19 and 60 percent, respectively. These concentrations are higher than generally found for hydrocarbons in the water along these tanker routes.

Data are shown for only a small number of samples outside of regular shipping lanes. Of these, the North Greenland Sea contained aromatics concentrations of 15 to 25 percent. Other locations from as far south as South America show a range of 0 to 29 percent.

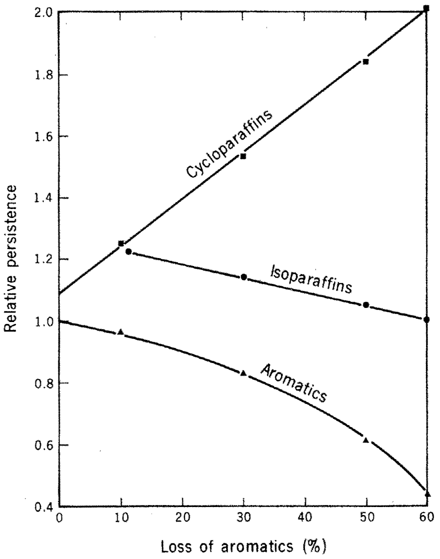

Fig. 2. Relative persistence of hydrocarbons in the water off the African coast.

Table 2. Aromatic content of profile samples containing ≥ 1.5 ppb of nonvolatile hydrocarbons.

Depth (m)	Relative percent of aromatics (by weight)				
	GEOSECS station number				Bermuda (32°18′N, 65°32′N)
	17 (74°56′N, 01°07′W)	27 (42°00′N, 42°00′W)	30 (31°48′N, 50°46′W)	34 (18°01′N, 53°59′W)	
0	20	25		0	9*, 7*
10					2*, 4*
20					7*, 3*
100	3		2	4	10
120	0	2			
3500		12			

*Duplicate samples from separate casts of Niskin bottles.

At eight stations in the Atlantic, vertical profile studies were made in which the water column was sampled to depths of 4000 m. Most of these samples contained low concentrations of hydrocarbons, and only a small proportion contained hydrocarbon concentrations high enough to warrant a hydrocarbon type analysis. Samples judged to be suitable for analysis were those whose total hydrocarbon content was 1.5 ppb or higher. Data for such samples are summarized in Table 2.

The data presented here show qualitatively that hydrocarbons in ocean water have lower aromatic concentrations than would be expected if the hydrocarbon source were petroleum. Of the various tanker routes that were sampled, the Persian Gulf route was particularly unique in having tanker traffic in which only crude oils of very similar composition were carried. The similarity of composition presented an opportunity to examine the data for more quantitative relationships.

To do this, relative persistence values were plotted against the percentage loss of aromatics as observed in each sample. The relative persistence of a given type of hydrocarbon is represented by the ratio of its relative concentration in hydrocarbons as found in water to that present in Persian Gulf crude oil. The loss of aromatics is the percentage difference between concentrations in the crude oil and in the sample. For the surface sample of Table 1, the relative persistence of cycloparaffins is (57 percent/32 percent) = 1.78 and the loss of aromatics is $[(39 - 16)/39 \times 100] = 59$ percent.

Data from the 49 samples were used to prepare the graph shown in Fig. 2. The relative persistence of types of hydrocarbon in decreasing order are: cycloparaffins, isoparaffins, and aromatics. The *n*-paraffins were not plotted; they appear to be the least persistent of the hydrocarbons as indicated by their consistently low concentrations in ocean water.

There are numerous possible mechanisms that may account for the low relative aromatic hydrocarbon content of ocean water. Evidence available at present suggests that biogenic sources do not yield aromatic hydrocarbon mixtures (*5*). On this basis then, hydrocarbons from biogenic sources serve as a diluent to aromatics. In principle, for example, a 50/50 mixture of biogenic and petroleum hydrocarbons would cause the aromatics of the petroleum mix to be diluted by a factor of 2. Two different methods for estimating hydrocarbon sources (*3, 6*) were applied to our data, and the results from both methods suggest that hydrocarbons along tanker routes are primarily from petroleum. Based on available knowledge, then, it does not appear that low aromatic concentrations are caused by a dilution effect from the presence of biogenic hydrocarbons.

Our study provides no explanation of why the aromatics may be preferentially removed from ocean water. Numerous processes give rise to changes in hydrocarbons. An evaluation of these processes has been presented in a workshop on petroleum in the marine environment convened by the National Academy of Sciences (*4*, pp. 45–48 and 58–60). One conclusion was that evaporation accounts for extensive loss of C_{15} and lighter hydrocarbons from the environment. Dissolution of hydrocarbons into the water column is another mechanism for the disappearance of hydrocarbons, and this pathway seemed to be particularly applicable to C_{10} and lighter hydrocarbons.

Neither evaporation nor dissolution, however, explains the selective disappearances of C_{14} and heavier aromatics. Other processes that may contribute to this behavior include degradation of hydrocarbons caused by chemical or biological reactions, or both. Still another possibility is removal of the hydrocarbons by absorption onto particulate matter followed by settling of the particulate to the ocean bottom. There would appear to be sound reasons to investigate all of these possibilities.

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15 September 1975; revised 3 November 1975

Mineral Inclusions in Diamond: Temperature and Pressure of Equilibration

Abstract. *Two distinct suites of minerals included in natural diamond occur and probably represent different physical and chemical conditions during diamond growth. Minerals of the ultramafic suite appear to have equilibrated in the range 1000° to 1300°C between 45 and 65 kilobars, whereas the temperature range for minerals of the eclogitic suite is 850° to 1250°C. At present, models relating the partitioning of magnesium and iron between coexisting phases are not sufficiently rigorous to determine a value for the pressure of equilibration of these eclogitic suite inclusions.*

The occurrence of large, clear, and well-formed diamonds has led to the general belief that natural diamond has formed as a stable phase within the upper mantle of the earth (*1, 2*). Accordingly, detailed mineralogical and chemical study of the minerals included within diamond during its growth can provide significant data regarding the chemistry and physics of the upper mantle, as well as providing an insight into the genesis of diamond.

At the present time there is considerable interest in the use of chemical relationships among coexisting minerals as a means of elucidating the temperatures and pressures of formation (*3–6*). Perhaps the most interesting result of such studies to date has been the development of petrological models for the upper mantle based upon the study of xenoliths from kimberlite and basalt (*5, 7–9*). These models have been criticized (*10–12*) but do represent a major step forward in petrological studies and interpretation of mantle xenoliths.

In general the initial crystallization and subsolidus changes in silicate minerals are well documented from both experimental and naturally occurring systems. In contrast, little is known concerning the initial and subsequent stages of diamond growth; however, it is possible to suggest probable pressure and temperature conditions in which diamond crystallized by applying the knowledge of silicate systems to the pertinent minerals included in natural diamond.

Several silicate minerals occur as primary inclusions, and abundant among them are olivine, garnet, enstatite, and diopside (*2, 13, 14*). Depending upon their major element chemistry the minerals may be assigned to one of two distinct mineral suites. For example, olivine (Fo_{92-96}), enstatite (En_{94}), chrome-pyrope garnet (*15, 16*), and diopside belong to the ultramafic suite, whereas pyrope-almandine garnet and clinopyroxene with appreciable contents of Na and Al are assigned to the eclogitic suite. Although minerals of each individual suite may coexist in a single diamond, the presence of minerals from both suites together within the same diamond has not been observed. It is thus probable that these two suites represent either different chemical or physical conditions, or both, in which diamond has formed.

There is, at present, insufficient data for a statistical analysis of the relative abun-

Table 1. Temperature and pressure of equilibration for mineral inclusions of ultramafic suite in diamond.

Diamond No.	Assemblage	Temperature (°C)	Pressure (kb)	Reference
1 Pre-7-75	Diopside-enstatite-chrome pyrope	1270	65	(*26*)
2 Jag-4-75	Diopside-enstatite	1010	53	(*26*)
3 No. 1	Diopside-enstatite-pyrope almandine	1050	45	(*14*)
4 No. 3	Diopside-enstatite	970	60	(*14*)