

Observation of a Subsurface Oil-Rich Layer in the Open Ocean

Abstract. A layer of water at a depth of 200 meters containing 3 to 12 milligrams per liter of oil was found during February and March 1978 over a distance of 800 nautical miles in the southwest North Atlantic and the eastern Caribbean. The geochemistry and carbon-14 activity of the oil shows it to be a weathered crude, probably from a submarine seep. Although the dimensions of the oily layer were not determined, conservative estimates indicate that more than 1 megaton could have been present.

During February and March 1978, on a cruise investigating the chemistry of the subtropical underwater (1), we found an extended layer of unusually oil-rich water about 200 m below the surface of the southwestern North Atlantic Ocean and the eastern Caribbean Sea (Fig. 1). At stations 11 to 24, a transect of 800 nautical miles, hexane extracts of seawater obtained from depths of 150 to 250 m yielded 3 to 12 mg of weathered oil per liter (average of 6 mg per liter). Extracts of samples from both above and below the oily layer at stations 11 to 24 and from all depths at stations 26 to 38

had hydrocarbon concentrations (micrograms per liter) and distributions typical of the open ocean (2). Because the sampling at each station was centered about the subtropical underwater, the discovery of the oily layer was serendipitous.

Water was collected in a 90-liter polyvinyl chloride drop-top sampler and transferred into 20-liter glass bottles through steel tubing. Forty liters of each sample was batch-extracted with hexane within 1 hour of collection. The extracts were concentrated by means of a vacuum within 1 hour of collection, esterified with boron trifluoride-methanol reagent,

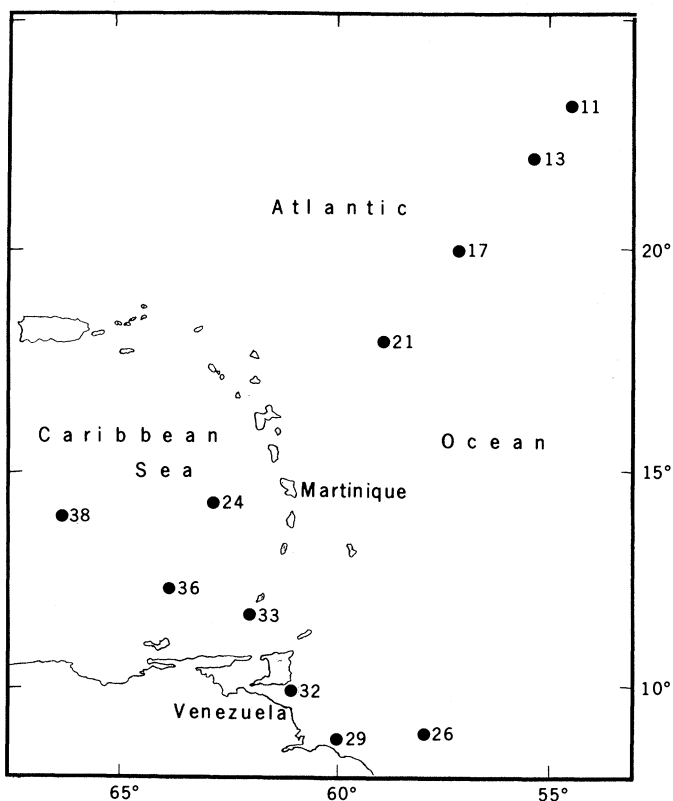


Fig. 1. Sampling stations of NOAA Researcher cruise R-78-1. The oily layer was found at stations 11 (12.6 mg, 200 m), 13 (5.8 mg, 200 m), 17 (9.6 mg, 270 m), 21 (3.2 mg, 145 m), and 24 (2.8 mg, 150 m and 5.7 mg, 200 m).

Table 1. Percentage of fatty acid distributions.

Station	Depth (m)	14:0*	15 br	15:0	16:1	16:0	17 br	17:0	18:1	18:0	20:1	20:0	22:0	24:0
11	56	10	1.7	3.0	6.5	33.6	2.9	1.5	13.6	15.4	0.5	0.8	0.8	0.8
11	200	0.2	0.0	0.0	0.0	32.1	0.4	0.0	33.2	13.6	1.0	5.0	0.8	2.9
17	130	6.2	2.0	3.0	9.6	26.8	1.9	2.3	4.3	10.3	0.6	0.6	0.1	0.2
17	270	0.0	0.0	0.0	0.0	28.1	0.3	0.0	31.1	12.7	0.9	6.1	0.3	5.1

*In this nomenclature, 14:0 is a 14-carbon straight-chain acid with no pi bonds, 16:1 has one pi bond, and br indicates branching as determined by the GC retention index and mass spectral analysis.

and fractionated (3). The paraffinic and aromatic hydrocarbons, fatty acid methyl esters, and silylated sterol fractions were analyzed at sea by gas chromatography (GC) on 30 m by 0.25 mm wall-coated, open tubular glass capillary columns coated with either SE-30 silicone oil or Dexsil 300. During the cruise, all likely sources of extraneous contamination, such as the ship's fuel, lubricants and hydraulic fluid, the water sampler, and other associated hardware, were extracted, fractionated, and analyzed by GC. None of these extracts resembled those from the oily layer. Procedural blanks, run at regular intervals during the cruise, did not resemble the subsurface oil.

The fractionated oil consisted of 60 to 70 percent hydrocarbons, 5 to 10 percent fatty acids, and 4 to 8 percent sterols and fatty alcohols. The GC of the paraffin fraction showed a narrow-range (C_{16} to C_{26}) symmetrical, unresolved complex multiplet (4) centered at $n-C_{20}$ with only traces of n -alkanes evident. Such symmetrical distributions are usually not observed in pelagic tars (5). The pristane to phytane ratio varies from 0.9 at station 24 to 1.2 at station 11. The C_{18} to phytane ratio of 0.3, the C_{22} to background ratio of 0.2, and the absence of alkanes above C_{25} indicate a biochemically weathered oil that has not undergone evaporative weathering (6). Comparison of these ratios with those from sunken tar weathering studies (7) indicates that the subsurface oil was weathered for 1 to 2 years when we found it. The infrared and mass spectra indicate only normal, saturated, cyclic and branched hydrocarbons in fraction 1 (3). Gravimetric and GC calculated weights agree within 10 percent. The aromatic fraction was analyzed by computer-assisted GC and mass spectrometry. In addition to abundant ions due to alkylated naphthalenes, anthracenes, and phenanthrenes, mass fragmentograms of mass to charge ratios of 184, 198, and 212 revealed the presence of dibenzothiophenes. Dibenzothiophenes are not biosynthesized and are known only in fossil fuels.

The nonhydrocarbon fractions in the extracted oil were distinct from those ex-

tracted from samples outside the oily layer and must have a different source. Table 1 shows the fatty acid distribution at two typical stations above and in the oily layers. The shallower samples had distributions similar to those observed by others in open-ocean waters (8). In contrast, the distribution of acids associated with the oil is biased toward the longer chain lengths, and $C_{18:1}$ accounts for one-third of the total acids.

The sterol distribution of open-ocean water has been studied by Gagosian (9). In the present study, analyses of water outside the oily layer agree with his work and indicate that cholesterol is the dominant sterol at a concentration of about 1 μg per liter. In contrast, the dominant sterol in the oil was β -sitosterol or clio-nasterol (9) at a concentration of more than 300 μg per liter; cholesterol was only a minor component at 5 μg per liter.

Because of its quantity, quality, and observed distribution, we believe this oil layer results from a natural seep. This is supported by the absence of natural ^{14}C activity in the sample from station 11, which thus has an apparent age of >22,000 years before present. The total amount of oil entering the sea from natural seeps is unknown. On the basis of limited data from known seeps and conservative extrapolations, Wilson *et al.* (10) estimated that between 0.2×10^6 and 6.0×10^6 tons of oil per year enter the oceans from seeps. Blumer (11) argued that such estimates were too high. The currently used estimate of 0.6×10^6 ton/year reported in a workshop of the National Academy of Sciences (12) is obviously a compromise figure.

The breadth and thickness of the oily layer reported here is not known, but integrating over a conservative estimate of its dimensions, that is, 800 nautical miles long, 1 nautical mile wide, and 100 m thick, results in a total of more than 1 megaton.

Accurate assessment of the quantity, frequency, and duration of subsurface oil seeps is beyond present resources or technology. Similar discharges of crude oil may occur elsewhere and would pass undetected except by chance. The quantity of the oil described here may have

been greater than the total estimated oil entering the sea annually (12). An attempt was made, on another cruise in January 1979 to determine the width of the oily layer. Sampling was done between 10° and 21° north latitude on a course of 130° . This cruise crossed the 1978 track near Martinique. Gravimetric and GC analyses of detailed profiles from seven stations revealed no trace of the oil found 11 months before.

We believe the most likely source of the oily layer is a seep located on the Venezuelan shelf at a depth of about 200 m. This is an area where offshore seeps have been reported. Such oil could be carried north at depth, probably in a dispersed state, by the Guyana and Antilles currents until entrained by midwater easterly flows into the southern Sargasso Sea as discussed by Reid (13). In fact, observations of subsurface oil east of the Antilles represent independent evidence supporting physical indications of a mid-depth easterly return of water into the subtropical North Atlantic (13).

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References and Notes

1. L. V. Worthington, *On the North Atlantic Circulation* (Johns Hopkins Press, Baltimore, 1976), chap. 14.
2. R. A. Brown and H. L. Huffman, Jr., *Science* **191**, 847 (1976).
3. The fractionation is adapted from J. W. Farrington and B. W. Tripp, *Geochim. Cosmochim. Acta* **41**, 1627 (1977). A portion of the oil not exceeding 5 mg was chromatographed on 3 cm of alumina (5 percent deactivated with H_2O) over 3 cm of silica (5 percent deactivated with H_2O) in a disposable Pasteur pipette. Eight fractions (F) were eluted with 1.5 ml of each of the following: hexane, 10 percent benzene-hexane, 20 percent benzene-hexane, 50 percent benzene-hexane, benzene, 5 percent methanol-benzene, 10 percent methanol-benzene, and 20 percent methanol-benzene. Saturated hydrocarbons were in F-1, aromatics were in F-2 and F-3. Fatty acid methyl esters were in F-4 and F-5. Sterols were in F-7 and F-8.
4. J. W. Farrington and B. W. Tripp, in *Marine Chemistry in the Coastal Environment*, T. M. Church, Ed. (ACS Symposium Series No. 18, American Chemical Society, Washington, D.C., 1975), pp. 267-284.
5. J. N. Butler, B. F. Morris, J. Sass, "Pelagic tar from Bermuda and the Sargasso Sea," *Bermuda Biol. Stn. Res. Spec. Publ. No. 10* (1973), appendix 3.

6. M. Blumer, M. Ehrhardt, J. H. Jones, *Deep-Sea Res.* **20**, 239 (1973).
7. A. Zsolnay, *ibid.* **25**, 1245 (1978).
8. P. M. Williams, *J. Fish. Res. Board Can.* **22**, 1107 (1965).
9. R. B. Gagosian, *Geochim. Cosmochim. Acta* **39**, 1443 (1975).
10. R. D. Wilson, P. H. Monaghan, A. Osanik, L. C. Price, M. A. Rogers, *Science* **184**, 857 (1974).
11. M. Blumer, *ibid.* **176**, 1257 (1972).
12. *Petroleum in the Marine Environment* (National Academy of Sciences, Washington, D.C., 1975).
13. J. L. Reid, *J. Geophys. Res.* **83**, 5063 (1978).

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