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13. We thank Lynn Sykes, Bryan Isacks, Reuben Kachadoorian, and Jerry P. Eaton for critically reviewing the manuscript. Data for the Lunar Module impact conditions were furnished by John Gurley, Manned Spacecraft Center, Houston, Texas. Jonathan B. Haussler, Marshall Spaceflight Center, Huntsville, Alabama, furnished the data for the S-IVB. Supported by NASA contract NAS9-5957. Lamont-Doherty Geological Observatory contribution No. 1501.

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## Petroleum Lumps on the Surface of the Sea

**Abstract.** *Lumps of crude oil residue floating on the sea surface have been observed widely. Samples were taken with surface-skimming nets in the Mediterranean Sea and eastern North Atlantic Ocean; their displacement volumes were as large as 0.5 milliliter per square meter. An isopod, Idotea metallica, appears to be associated with the lumps, and a barnacle, Lepas pectinata, grows upon them. Lumps were found in stomachs of Scomberesox saurus, a surface-feeding fish important in ocean food webs. Films on the lumps, presumably consisting mostly of bacteria, consumed oxygen at the rate of 4 cubic millimeters per hour per square centimeter of lump surface. Chemical analysis suggested that certain lumps had been at large for only a few weeks; data from barnacle size and growth rate suggested that other lumps were at least 2 months old.*

Although oil pollution of the sea, particularly pollution resulting from spills and blowouts, has recently received considerable attention (1), little has been said (2) about the tarlike lumps that occur widely on the sea surface. We first noticed these lumps about 5 years ago when we began sampling the neuston, the fauna of the upper few centimeters of the sea, with surface-skimming nets (3). Since then we have found these variously sized, black or brownish-black lumps in many places in the North Atlantic. The lumps are so abundant that they regularly foul the neuston nets, which have to be cleaned repeatedly with solvents. Peter David of the National Institute of Oceanography, Wormley, England, has observed lumps since 1954 in the Mediterranean Sea and in the Atlantic and Indian oceans (4).

During cruise 49 of the R.V. *Atlantis II* between Rhodes (10 May 1969) and Ponta Delgada, Azores (28 June), tarry lumps were present in at least 75 percent of the 734 neuston tows made; the substance was recorded as absent in only 16 percent, and for a few tows no remark about the presence or absence of the tar was made. The displacement volumes of 41 samples of

tar are shown in Fig. 1 (5). Estimates from the neuston tows indicated that the amount of tar on certain areas of sea surface was as high as 0.5 ml/m<sup>2</sup>.

The lumps were irregular in shape, with the greatest dimension varying from 1 or 2 mm to about 10 cm. Black lumps were commoner than brownish-black ones. Hardness varied, although all lumps were easily deformed by a

touch of the finger. The hardness of the softer ones could not be measured with the penetrometer used (6); the harder ones gave values of 0.1 to 0.3 kg/cm<sup>2</sup> (unconfined compressive strength). Some of the lumps were very sticky, had a rough, uneven surface, and were relatively soft and black. Other lumps were firmer with a smoother, more even surface and were usually lighter (brownish-black); this type frequently had barnacles attached and appeared to be older than the first. A sample of this tar (from 34°00'N, 26°00'E on 13 May) was soluble in chloroform and behaved in chromatography (7) as a typical crude oil.

The low-boiling fraction of crude oil, which contains the most immediately toxic substances (8), was retained in the lumps. It is evident that the formation of the petroleum into lumps tends to conserve these poisons. The presence of volatile components (7) suggests that this sample of tar had been at large for no more than a few weeks. One sample of tar collected on 18 May about 160 km off the coast of Libya contained bits of grass and leaves; it had probably been washed ashore and then out to sea again.

Several organisms were found on or were associated with the lumps. *Idotea metallica*, a pelagic isopod which ranged from 10 to 25 mm in length and varied from light gray to black in color, was collected in large numbers in the neuston nets and was frequently found clinging to lumps when a collection was dumped into the sorting tray. These isopods were also dipped from the sea surface together with the lumps.

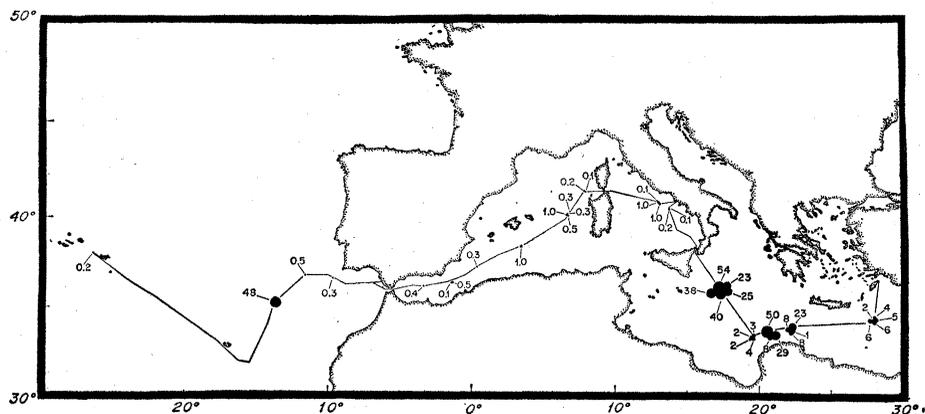


Fig. 1. Chart showing the distribution of petroleum lumps along a track in the Mediterranean Sea and the eastern North Atlantic. The area of the dots is proportional to the volume of the lumps collected; the numbers are the volumes in milliliters per square meter multiplied by 100. Collections were made nightly all along the track. Although some collections, particularly some west of Gibraltar, had too little tar to measure, almost all collections had at least a trace.

When placed in shipboard tanks together with tar lumps, the isopods collected on the lumps and remained there almost continuously (9).

*Lepas pectinata*, a goose barnacle, was frequently found attached to the lumps, particularly the firmer, "older-looking" ones. At one station, 150 barnacles ranging from 2 to 8 mm in length (10) were attached to four lumps that displaced 40 ml. Lumps with barnacles attached were kept in an aquarium with running seawater pumped through an all-plastic system. All barnacles were removed except those between 1 and 2 mm long. Barnacle lengths were measured once a week for 3 weeks. The growth rate was approximately 1 mm per week. The largest barnacles found on the oil lumps were 8 mm long; therefore, it can be inferred that these barnacles are about 2 months old and that the lumps to which they are attached are at least that old.

Neither barnacles nor isopods appeared to suffer short-term ill effects when confined for several days with lumps of tar in minimal volumes of water at 15° to 20°C. However, the maximum length of barnacles found on tar lumps was 8 mm, but barnacles growing on floating pumice in the same region reached a length of 11 mm. The smaller size on the tar may indicate either that the tar is slightly toxic to barnacles or that the softer tar is a mechanically inferior substrate.

The saury, *Scomberesox saurus*, an epipelagic fish that is abundant in temperate seas, occurs commonly in neuston tows. In a sample of ten specimens collected in 38°28'N, 3°41'E on 2 June 1969 and ranging from 164 to 255 mm in standard length, we found large amounts of tar (11) in the stomachs of three. The saury is said to feed on small crustaceans and perhaps upon small fish (12). "Vegetable debris" was found in one saury stomach examined (12), which suggests that the species is not a very discriminate feeder. The saury, in turn, is fed upon by "porpoises and by all the larger predaceous fishes" (12). Thus, this ingestion of the tar by sauries provides a direct introduction of a material known to be toxic into the oceanic food web.

The oil lumps seemed to be covered with a grayish film, presumably composed mostly of bacteria. This assumption was supported by measuring the oxygen uptake (13) at 10°C of a lump with a displacement volume of 10 ml

and with no barnacles attached before and after the water containing the lump was poisoned with Formalin. Oxygen consumption decreased by 125 mm<sup>3</sup> per hour with the addition of the Formalin; the residual uptake was indistinguishable from zero. The value obtained for the respiration of the film was about 4 mm<sup>3</sup> per hour per square centimeter.

Taken altogether our observations indicate that lumps of petroleum exist in surprisingly large amounts on the sea surface and have a complicated history during their residence there. These lumps form a chronic type of oil pollution, which may significantly affect the marine ecosystem.

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5. Generally, we measured the displacement volume of the tar lumps from the first two neuston tows of each of two nighttime watches (when there was a measurable amount). The neuston nets, which are about 1 m wide, were towed at about 3 knots. Duration of tow varied from 25 to 130 minutes and the surface area skimmed from about 2,200 to about 11,500 m<sup>2</sup>. The data in Fig. 1 come from a net the bag of which was made of 00 plankton netting whose aperture size is 0.75 mm.
6. Pocket penetrometer, Soiltest model CL-700.
7. The saturated hydrocarbon fraction was prepared by chromatography of the whole tar on alumina and silica gel; *n*-pentane was used as the eluent. The waxy, semiliquid saturate fraction was then analyzed by gas chromatography on a 1/8-inch (outside diameter) column packed with 2.1 percent Apiezon L on Chromosorb G, DCMS. Hydrocarbons from *n*-decane (C<sub>10</sub>) to *n*-dotriacontane (C<sub>32</sub>) were identified. Pristane was abundant; the ratio of *n*-heptadecane to pristane was about 3 : 1. Normal paraffins exceeded the branched and cyclic saturates by a factor of 3 to 4. No odd carbon predominance was observed.
8. M. Blumer, in *Oil on the Sea*, D. P. Hoult, Ed. (Plenum, New York, 1969), p. 5.
9. Similar observations have been made by P. J. Herring [*J. Mar. Biol. Ass. U.K.* 49, 766 (1969)], who notes in discussing the species' color-change mechanism that "the brown and black colours thus produced are an almost perfect match of the colours of the lumps of oil with which this species is so often associated may be no more than coincidental, but it almost certainly affords the animal some protection against predation. . ."
10. Barnacle length was taken as the distance from the tip of the tergum to the junction of the body with the stalk.
11. A sample studied by thin-layer chromatography behaved as a typical crude oil residue.
12. H. B. Bigelow and W. C. Schroeder, *U.S. Fish Wildl. Serv. Fish. Bull.* 53, 170 (1953).
13. Oxygen uptake was measured in glass vials stoppered with an oxygen electrode. Rate was calculated from the slope of the resulting oxygen versus time curve. Ratio of water to tar in the vials was between 6 and 3 to 1.
14. Supported by National Science Foundation grants GZ-259 (to M.H.H.), GB-7355 (to J.M.T.), and GB-7108 (to R.H.B.). Shiptime was provided under NSF grant GA-1298 and contract Nonr-4029(00). We thank our shipmates on *Atlantis II* cruise 49 for their help, especially Captain E. H. Hiller and Dr. J. E. Craddock, overseer of the neuston fishing; we thank Dr. Max Blumer, who made and interpreted the chemical analyses; and we thank Dr. Blumer, Dr. Richard L. Haedrich, David Masch, and Dr. Paul T. McElroy for criticizing the manuscript. Contribution 2426 of the Woods Hole Oceanographic Institution.

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## Secular Changes in the Lunar Elements

Abstract. Corrections to the adopted values for centennial rates of change of four elements of the lunar orbit, the location of the FK4 equinox, and the obliquity of the ecliptic are presented. They are derived from analyses of lunar occultations distributed over several centuries. Generally, these corrections help to resolve existing discrepancies between theory and observations.

Investigations of lunar motion from occultation observations covering the time periods 1627-1860 (1) and 1950-1968 (2) have recently been completed. These investigations have incorporated the Watts limb corrections (3) and improvements in astronomical constants, lunar theory, and star positions, as well as many other refinements over earlier investigations.

When the results of the two investigations are combined, fairly accurate values may be obtained for the rates of change of the lunar elements over

a period of 1½ centuries (the small number of observations before 1780 contribute very little to the rates because of large observational errors). Values derived for rates of change of six elements are given below (in seconds of arc per century), together with their standard deviations:

$$\begin{aligned}\Delta d\Omega/dT &= +4.31 \pm 0.37 \\ \Delta d\omega/dT &= +1.11 \pm 0.40 \\ \Delta dI/dT &= -0.04 \pm 0.09 \\ \Delta de/dT &= +0.10 \pm 0.04 \\ \Delta dE/dT &= +1.36 \pm 0.06 \\ \Delta de/dT &= -0.13 \pm 0.10\end{aligned}$$