



UNITED NATIONS ENVIRONMENT PROGRAMME

# A. Golik: Tar pollution in the Mediterranean Sea

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#### PREFACE

Sixteen years ago the United Nations Conference on the Human Environment (Stockholm 5-16 June 1972) adopted the Action Plan for the Human Environment, including the General Principles for Assessment and Control of Marine Pollution. In the light of the results of the Stockholm Conference, the United Nations General Assembly decided to establish the United Nations Environment Programme (UNEP) to "serve as a focal point for environmental action and co-ordination within the United Nations system" [General Assembly resolution 2997(XXVII) of 15 December 1972]. The organizations of the United Nations system were invited "to adopt the measures that may be required to undertake concerted and co-ordinated programmes with regard to international environmental problems", and the "intergovernmental and non-governmental organizations that have an interest in the field of the environment" were also invited "to lend their full support and collaboration to the United Nations with a view to achieving the largest possible degree of co-operation and co-ordination". Subsequently, the Governing Council of UNEP chose "oceans" as one of the priority areas in which it would focus efforts to fulfill its catalytic and co-ordinating role.

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans.

The Regional Seas Programme at present includes ten regions  $\frac{1}{2}$  and has over 130 coastal States participating in it. It is conceived as an action-oriented programme having concern not only for the consequences but also for the causes of environmental degradation and encompassing a comprehensive approach to combating environmental problems through the management of marine and coastal areas. Each regional action plan is formulated according to the needs of the region as perceived by the Governments concerned. It is designed to link assessment of the quality of the marine environment and the causes of its deterioration with activities for the management and development of the marine and coastal environment. The action plans promote the parallel development of regional legal agreements and of action-oriented programme activities  $\frac{2}{2}$ .

The Mediterranean Action Plan was the first one developed in the framework of the Regional Seas Programme. It was adopted in early 1975 in Barcelona $\frac{3}{}$  and since then has shown a remarkable progress.

3/ UNEP: Mediterranean Action Plan. UNEP, 1985.

<sup>1/</sup> Mediterranean, Kuwait Action Plan Region, West and Central Africa, Wider Caribbean, East Asian Seas, South-East Pacific, South Pacific, Red Sea and Gulf of Aden, Eastern Africa and South Asian Seas.

<sup>2/</sup> UNEP: Achievements and planned development of UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No. 1, UNEP, 1982.

A centrally co-ordinated monitoring of the sources, levels and effects of pollutants, as well as research related to this monitoring (MED POL) $\frac{4}{2}$ ,  $\frac{5}{2}$  was organised by UNEP as one of the cornerstones of the Action Plan. The contamination of the Mediterranean by petroleum hydrocarbons was one of the early targets of MED POL.

This publication, prepared by Dr. A. Golik, was commissioned by UNEP and IOC to review the contamination of the Mediterranean basin by tar on the basis of results obtained through MED POL and other programmes.

<sup>4/</sup> FAO/UNESCO/IOC/WHO/WHO/IAEA/UNEP: Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL) - Phase I: Programme Description. UNEP Regional Seas Reports and Studies No. 23, UNEP, 1983.

<sup>5/</sup> UNEP: Long-term programme for pollution monitoring and research in the Mediterranean (MED POL) - Phase II. UNEP Regional Seas Reports and Studies No. 28, Rev.1, UNEP, 1986.

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SUMMARY

Tar balls in the marine environment are a derivate of oil or oily compounds which were released into seawater, lost their volatile fraction by evaporation and turned into soft black lumps called tar balls. Due to the relatively high intensity of oil activity in the Mediterraneam Sea, tar pollution became a problem in this area. The severity of this problem is accentuated by the fact that stranded tar on the beach is a serious nuisance to sea bathers, and the Mediterranean Sea is becoming more and more attractive to coastal oriented tourism.

Measurements of pelagic tar have been carried out in the Mediterranean since 1969, but mostly in the western Mediterranean. The findings show that between 1969 and 1983, mean tar concentrations in the Mediterranean ranged from 0.6 to  $130 \text{ mg/m}^2$  and that, at least between 1969 and 1975, the Ionian Sea was the most tar polluted area in the Mediterranean Sea. Mean quantities of stranded tar on Mediterranean beaches were found to range between 0.2 and 4388 g/m (grams per linear metre of beach front). On the basis of geographical considerations, it seems that the areas in the Mediterranean where deballasting of oily waters and release of oily compounds into the sea were permitted until 1978 were foci for tar contamination. However, measurements of pelagic and beach-stranded tar which were conducted after 1980 indicate that there might have been a reduction in tar quantity during the last few years.

Examination of data and information relevant to oil transport rate in the Mediterranean Sea and outside of it shows that several factors combined in 1978/79 to cause a reduction in oil and as a result in tar pollution. In 1978, the 1969 amendment to the International Convention OILPOL 54 entered into force. This amendment permits release of oil only in restricted areas and even there only at certain rates and quantities. At about the same time, the oil crises of 1979 caused an increase in oil prices and a reduction in oil transport, and therefore encouraged tanker owners to reduce to a minimum the loss of oil through spillage or otherwise. The continuing grim economic condition of oil transportation facilities, high oil prices, the adoption of the Mediterranean Sea as a special area (into which no oil release with concentrations higher than 15 ppm is permitted) in the MARPOL 73/78 convention, and the enforcement of this convention caused a tighter control on oil pollution as well as development of innovative techniques and procedures aimed at preventing the waste of oil into the sea. It is suggested that these developments indeed reduced oil pollution, as indicated by a few examples of tar reduction in the Mediterranean Sea and beaches.

As it is not yet certain that reduction in tar pollution is indeed a fact, and the recent reduction of oil prices and the new discoveries and exploitation of offshore oil in the Mediterranean constitute a threat for a new wave of tar pollution, it is recommended to invest a multi-national, co-ordinated effort to determine a new baseline for tar level today in the Mediterranean. Old findings of tar pollution could be compared to this baseline to determine the present trend of this problem. In addition, it is recommended that studies related to "fingerprinting" of tar as well as tar processes should be continued to ensure means of combating this type of pollution if it persists.

#### 1. INTRODUCTION

Tar in the marine environment is formed as a result of the release of hydrocarbon compounds into the sea. The sources of these hydrocarbon compounds may be natural seeps from the sea bottom, accidental or intentional release from oil tankers or ships, or release from land-based oil installations or industry. Once it is released into the marine environment, the oil loses its light fraction by evaporation and its viscosity increases, until it becomes soft, sticky brownish black material often termed tar balls or simply tar. The specific gravity of the tar is usually lower than that of seawater and therefore it normally floats on the water. The dispersal of tar is thus affected by winds and currents.

Very little is known about the effect of tar on marine organisms. In a study aimed at finding whether tar constitutes a threat to marine life, Zsolnay <u>et al.</u> (1978) examined concentrations of tar and of aromatic hydrocarbon, which is the most toxic component in crude oil, at the same stations. They found that there is no relationship between the two, presumably due to different dispersion mechanisms. However, there is no question that once tar lands on the beach, it forms a serious nuisance to bathers. It sticks to the body, ruins clothing, and it is very hard to get rid of it. Tar is therefore a serious threat to the tourist industry. This is especially so in the Mediterranean Sea, because this is a warm sea in which coastal oriented tourism is constantly growing.

Systematic studies of tar distribution in the Mediterranean started in 1969 with sampling of pelagic tar by the R/V "Atlantic II" (Horn <u>et al.</u>, 1970). Since then, pelagic tar sampling was conducted by several expeditions of various oceanographic vessels, mostly in western Mediterranean. Many studies on tar stranded on Mediterranean beaches were carried out between 1975 and 1978, most of them within the MED POL Programme (UNEP, 1980). These were conducted mostly in the eastern Mediterranean. At the same time, studies were made on the distribution of dissolved and dispersed petroleum hydrocarbons, their chemical behaviour and their effect on the biosphere. These were recently reviewed in UNEP (1986).

The Mediterranean Sea was considered to be the most oil polluted sea in the world (U.S. National Academy of Sciences, 1975). This was because of the heavy oil traffic on it relative to its size, and because it is an enclosed body of water with very restricted passages to other oceans. During the last three decades, efforts were made, at national and international levels, to reduce the input of oil into the Mediterranean. There are signs that these, together with the increase in oil prices in 1979, have indeed caused reduction of oil and tar pollution in the Mediterranean.

The purpose of this document is to review the available information on tar pollution in the Mediterranean Sea and its shores, to assess the magnitude of this pollution in terms of space and time, to examine the methods for monitoring this pollution, and to evaluate the feasibility of assessing oil pollution of the Mediterranean through monitoring tar contamination.

#### 2. THE MEDITERRANEAN SEA

Surrounded by Europe, Asia and Africa (see Figure 1), the Mediterranean is an enclosed sea, extending over an area of  $3.7 \times 10^6 \text{ km}^2$  with an average depth of 1,500 m and maximum depth of 5,092 m. Its passages to other oceans are restricted: through the Straits of Gibraltar (320 m deep and 20 km wide) to the Atlantic Ocean and through the man-made Suez Canal to the Red Sea and Indian Ocean. In addition, it is connected through the Bosphorus to the Black Sea. The time required to exchange the water of the Mediterranean is estimated at eighty years, implying that the average residence time of substances in the water in the Mediterranean is about eighty years.



Figure 1. The Mediterranean Sea.

The Straits of Sicily, with a 400 m deep sill, divide the Mediterranean into western and eastern basins. These basins are further divided into quasi-natural internal basins: the Alboran, Balearic, Ligurian and Tyrrhenian Seas in the western basin and the Adriatic, Ionian and Aegean Seas in the eastern basin. Many islands are found in the Mediterranean; the larger of them are Sicily, Sardinia, Cyprus, Corsica and Crete. In addition, many small islands are found in the Aegean Sea. The major rivers that empty into the Mediterranean are the Ebro, Rhone and Po Rivers, and until the activation of the Aswan Dam, the Nile River as well. These rivers created large alluvial plains and deltas on the Mediterranean shores.

The water circulation in the Mediterranean (see Figure 2) is determined by its geographical shape, evaporation-precipitation ratio, and wind system. Surface Atlantic water enters the Mediterranean through the Straits of Gibraltar and flows eastward along the coast of North Africa. Some of the water is deflected northward to form circulation in the Ligurian and Tyrrhenian Seas, where its density increases because of evaporation and cooling, and it sinks to form a deep water layer. The remaining water continues eastward through the Straits of Sicily, where again part of the water participates in a counterclockwise circulation in the Ionian and Adriatic Seas and the rest continues to the eastern part of the Mediterranean. There, the salinity and temperature of the water increase due to the excess of evaporation over precipitation and runoff. The water becomes denser and sinks. The outflowing water from the Mediterranean goes through the deeper part of the Straits of Gibraltar and sinks in the Atlantic Ocean to a depth of about 1,000 m. It spreads in the Atlantic Ocean but is still distinct, by its high salinity and temperature, at large distances from Gibraltar, towards the west and north.

#### 3. FACTORS CONTROLLING TAR CONCENTRATION IN THE MEDITERRANEAN

Any discussion on tar ball concentration in the sea or the beaches must be related to the quantity and distribution of petroleum hydrocarbon discharge into the Mediterranean Sea. This subject has been described and discussed in a recent publication (UNEP, 1986). The following is a short summary based on this as well as other publications.

Figure 3, taken from Le Lourde (1977), shows the locations of the various activities in the Mediterranean which are related to oil. Although this map needs updating, its basic elements are still valid today. Middle Eastern oil, which reaches the eastern shores of the Mediterranean via pipelines and the Suez Canal, is shipped from there westward. North African oil is shipped from the southern part of the Mediterranean to its northern shores. Concentrations of refineries are found in the northwestern part of the sea, with a smaller concentration in its southwestern part. Offshore oil discoveries were recently made in Algeria, Tunisia, Libya, Egypt, Greece, Italy and Spain, and in some of these oil exploitation has already started.

Table 1 provides two estimates of petroleum hydrocarbon input into the world oceans according to various sources of input. The first estimate was published in 1975 by the U.S. National Academy of Sciences on the basis of 1973 data. The second estimate is an update based on data from 1982 (U.S. National Academy of Sciences, 1985). Comparison of the two shows a reduction of close to 50 per cent between the first and second estimates. There is no information on the input of oil into the Mediterranean Sea, but various authors used the world estimates to relate it to the Mediterranean. Le Lourde (1977) estimated that between 0.5 to 1.0 million tons of oil were released into the Mediterranean. Steinman et al. (1979) and also Montford (1984), assuming annual oil transport through the Mediterranean to be 600 million tons, and introducing various corrections for the short distances between oil loading and unloading ports, reached an estimated 1.1 million tons/year of oil release due to transportation and 0.6 million tons/year. It is not clear in the above mentioned studies what is the source of information for the volume of oil transport in the Mediterranean. Table 2 is based on information published by Maritime Transport (1976-1984) which provides also a breakdown of the sources of the oil transported in the Mediterranean: North African, Suez Canal/Sumed and pipelines to the eastern Mediterranean. According to this information, the volume of oil transported in the Mediterranean is smaller than



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Figure 2. Surface currents and main winds in the Mediterranean in summer. (From Le Lourd, 1977).





Source	Ac	U.S. National ademy of Science 1975	2	U.S. National Academy of Sciences 1985
Natural seeps		0.600		0.20
Sediment erosion		, 		0.05
Offshore production		0.080		0.05
Transportation: Load-on-top tankers	0.310)		0.70	
Non-load-on-top tankers	0.770 )		0.10	
Dry-docking	0.250		0.03	
Terminal operations	0.003		0.02	
Bilges-bunkering	0.500	-	0.30	
Tanker accidents	0.200		0.40	
Non-tanker accidents	0.100		0.02	
Transportation sub-total		2.133		1.47
Coastal refineries		0.200		0.10
Atmosphere		0.600		0.30
Coastal municipal wastes		0.300		0.70
Coastal non-refining industrial wastes		0.300		0.20
Urban runnoff		0.300		0.12
River runoff		1.600		0.04
Ocean dumping		-		0.02
Total	<u> </u>	6.113	<u></u>	3.25

### Table 1. Input of petroleum hydrocarbons into the oceans (in million tons/year)

¥ear	North Africa	East Med. pipelines	Suez Canal/Sumed	Total
1975	119.3	54.5	11.0	184.8
1976	147.2	10.3	33.8	191.3
1977	157.1	15.5	38.8	211.4
1978	161.0	22.2	27.2	210.4
197 <del>9</del>	163.8	29.6	71.7	265.1
1980	140.2	34.9	53.4	228.5
1 <b>981</b>	107.9	34.4	117.2	259.5
1982	106.3	35.1	143.0	284.4
1983	108.2	36.5	146.0	290.7

Table 2. Oil movement in the Mediterranean Sea (in million tons)

Source: Maritime Transport (1976-1984)

those quoted by the authors who computed oil input into the Mediterranean, and it is therefore probable that at least for the period 1975-1983, the rate of oil input was smaller than the estimates cited above.

It is of interest to note the difference in trend between the rate of oil transport in the Mediterranean (Table 2) and the global rate of oil transport (Table 3). In 1979 the global oil transport reached a maximum but not so for the Mediterranean, in which oil transport increased almost continuously until 1983. Percentage-wise the proportion of oil shipment in the Mediterranean in comparison to the world shipment has doubled between 1975 and 1983 (see Table 3). Therefore, if tar ball concentration had a direct relationship to volume of oil transport, a decrease in tar concentration should be expected in world oceans during the last seven years but not in the Mediterranean.

However, two main factors caused a reduction in oil release into the Mediterranean Sea in spite of increase in oil activity. These are international regulations to control oil discharge and technological developments leading to the same effect.

The two most important international conventions for the control of oil release into the sea are OILPOL and MEDPOL 73/78. The first, International Convention for Prevention of Pollution of the Sea by Oil 1954, prohibits discharge of oil or oily mixtures into the sea in water closer than fifty miles from land. According to the 1969 amendment, which entered into force in January 1978, beyond that distance, discharge was permitted only at certain rates and quantities. This convention was ratified by all the Mediterranean coastal countries except Turkey. According to OILPOL, there were two restricted areas in the Mediterranean, one east of Crete and the other west of it (see Figure 3), which were at distances larger than fifty miles from land in which deballasting of oily water and discharge of other forms of oil was permitted, at least until 1978, and restricted in quantity thereafter. The second convention is the International Convention for the Prevention of Pollution from Ships, 1972, as modified by the Protocol of 1978 (MARPOL 73/78). According to MARPOL 73/78, the Mediterranean is considered a special area in which any discharge into the sea of oil or oily mixture at concentrations above 15 ppm from any oil tanker or any ship of more than 400 grt is prohibited. MARPOL 73/78 entered into force in October 1983 but to date has been ratified only by eight Mediterranean countries: France, Greece, Israel, Italy, Lebanon, Spain, Tunisia and Yugoslavia.

Year	World	Mediterranean	Mediterranean per cent of world	
1975	1,934.4	184.8	9.5	
1976	1,930.4	191.3	9.9	
1977	2,016.8	211.4	10.5	
1978	1,975.9	210.4	10.7	
1979	2,051.3	265.1	12.9	
1980	1,853.2	228.5	12.3	
1981	1,662.8	259.5	15.6	
1982	1,483.5	284.4	19.1	
1983	1,413.3	290.7	20.6	

## Table 3. Comparison between world and Mediterranean oil movement (in million tons)

Sources: World shipment from British Petroleum, 1985 (converted to tons/year); Mediterranean shipment from Maritime Transport, 1976-1984

The entry into force of these conventions and the increase in oil prices resulted in two lines of action, both leading to a decrease of oil input into the water. On the one hand, the rate of installation of coastal reception facilities increased, policing and enforcing regulations against oil spillages became stricter, and awareness of the impact of oil pollution on the marine environment increased. On the other hand, the industry developed new techniques and procedures of oil handling, such as equipping all new tankers with segregated ballast, developing a clean ballast system in new tankers, and developing a crude oil washing system which allows collection of the washed oil. All these help in saving the oil and at the same time stop its disposal into the sea.

The impact of the above mentioned regulations and technological developments on tar quantity and distribution must be noticed. One would expect higher quantitites of tar, pelagic and beached, before 1978 and in the vicinity of the areas where discharge of oily residues was permitted. From then on, tar quantities had to decrease if the above mentioned measures are indeed effective.

#### 4. METHODOLOGY

#### Determination of pelagic tar quantity

Pelagic tar is sampled by neuston net, which is commonly used for sampling organisms from the

quantitative results. Morris (1971) improved it to provide quantitative results. This sampling system (see Figure 4) consists of a sled which is built of two skis and keels connected to each other by cross members. A brass drum which holds a flowmetre and a plankton net is connected to the sled between the keels below water level. A dacron sleeve, with holes in its upper part, leads the surface water into the drum. When the sled is towed behind the boat, the sleeve skims the sea surface, the air escapes through the holes and the water activates the flowmetre. In this way the volume of water entering the net is known and the area covered by the net may be computed. It is reported that this system operates well at speeds of 2 to 4 knots in sea states to force 5 (Butler et al., 1973).

An important point to consider, while sampling pelagic tar, is the effect of the wind on the tar distribution. Persistent winds above 4-5 m/s usually generate wind-rows causing floating items to be arranged along the wind-rows. To prevent biased sampling, it is recommended to sample either in a circle or perpendicular to the wind-rows. The surface area skimmed by the net should be computed (by the length of the tow times the width of the net or by the measured water flow if available). The results should be expressed in terms of weight of tar per  $m^2$ .

#### Determination of tar quantity on the beach

Review of the literature on monitoring of tar ball quantities on the beach reveals, as Golik (1982) pointed out, a confusion over the parameter which is monitored. One should distinguish between the rate at which tar lands on the beach and the standing stock of tar on the beach. The former, rate of tar landing from the sea, is very important for understanding the dynamics of tar on the beach, which in turn is important for the estimation of tar balance on a given beach. However, when an experiment is designed to measure this parameter, one must realize that waves cause lateral movement of tar balls along the beach. Therefore, repeated sampling of a narrow beach strip yields the rate of tar accumulation from both the sea and the beach on either side of the sampling strip. Golik (1982) demonstrated that even under conditions of calm sea, tar balls moved laterally by the small waves along the beach at a rate of several metres per day, and speculated that under stormy conditions this transport rate may reach even hundreds of metres per day. Therefore, monitoring of the rate of tar accumulation from the sea on a beach requires a thorough cleaning from tar of a long section of the beach (a few hundreds of metres) and then collecting daily the tar balls which accumulate on a narrow strip at the centre of that section. If the experiment continues for a long period of time, the beach on both sides of the sampled strip should be repeatedly cleaned to prevent lateral movement of tar into the sampled strip. This is, of course, a laborious and costly venture.

Standing stock of tar is simpler to monitor but, of course, yields less information than rate of tar accumulation. Here, only the quantity of tar at a given moment is measured, and therefore if repeated sampling is made from the same beach at relatively short time intervals (weeks), care should be taken not to sample the same strip in order to give a true picture of tar quantity.

Many of the studies aimed at monitoring tar quantities on beaches in the Mediterranean Sea failed to distinguish between the two parameters mentioned above, and although measurements of tar were made on a narrow strip of beach (1-2 m) at a rate of once a week or once a month, the results are reported in units of tar quantity per unit length of beach (or unit area of beach) per unit time, implying rate of accumulation. Furthermore, in some of the studies, it is clearly stated that the same strip of beach was repeatedly measured, which makes the measured value a guestionable one even for the purpose of standing stock evaluation.

Techniques of sampling is another problem related to tar measurement on the beach. Two basic methods were employed in various studies: measurement of tar per unit area of beach, and measurement of tar per unit length of beach. In the former, tar from a unit area (in most cases  $m^2$ ) was collected and reported. In the latter, the tar from a strip (usually 1 m wide) perpendicular to the beach was collected. Here also there is confusion as to the length of this strip. Some select the strip from mean low water to mean high water, and some from the waterline to the back of the beach as defined by the foot of the cliff or dune or the highest storm mark.



Figure 4. Diagram of modified neuston net for quantitative sampling. (From Morris, 1971).

UNEP (1985) provides a detailed description of a method for quantitative sampling of tar on the beach. It emphasizes the importance of random selection of the sampled beach to avoid erroneous results due to conscious or subconscious bias. According to that method, tar should be collected from one metre strip of beach which is normally oriented to the coast from the waterline to the foot of the cliff, dune or highest storm line at the back of the beach. Tar may be collected by hand, or gently brushed by a long handled brush to form small mounds of sand and tar. These mounds are transferred into a bucket, with the bottom replaced by a 2 mm mesh screen. The bucket is carefully immersed in seawater, washing out all the sand. The remainder, which contains tar and other material, is later spread on a tray in the laboratory. The tar is allowed to dry in open air and the foreign material is removed by hand. The remaining dry tar is then weighed. Frequency of sampling depends on resources available, but one should be careful to sample a new strip each time, especially if sampling frequency is high.

This method may be used in sandy beaches but not in rocky or pebbly beaches. There is no way to remove effectively the tar from the rocks or separate it from the pebbles in a way that reliable quantified information is obtained.

Measurement of tar on the beach is very laborious, and only a few samples may be taken per day by a team of 2-3 persons. It is therefore proposed to attempt quantitative estimation of tar on the beach by the use of air photos and analysis using image processing equipment (Golik and Rosenberg, 1987).

#### 5. TAR POLLUTION IN THE MEDITERRANEAN SEA

#### Quantities of pelagic tar in the Mediterranean

The first systematic measurement of pelagic tar in the Mediterranean was carried out by Horn <u>et al.</u> (1970), who collected floating tar lumps using neuston nets during a cruise they conducted aboard the R/V "Atlantis II" from Rhodes to the Azores in 1969. They reported their findings in terms of displacement volume of tar per unit area of sea surface. Of the 734 neuston tows, only 16 per cent were reported as clean from tar. The largest concentration of tar was found in the Ionian Sea off Libya and between Libya and Sicily, where tar values were up to  $0.5 \text{ ml/m}^2$ . Morris <u>et al.</u> (1975) used the original data of Horn <u>et al.</u>, converted them to mg/m<sup>2</sup> and provided the statistics for various parts of the Mediterranean (see Table 4). According to them, the average tar quantity found in the expedition of Horn <u>et al.</u> in the Mediterranean was 37 mg/m<sup>2</sup>.

Oren (1970) conducted two cruises in the eastern Mediterranean in 1970 (between Israel and the Straits of Sicily) in which he collected floating tar using a neuston net. He provided his results in relative, rather than absolute, terms. Nevertheless, his findings suggested that the most polluted areas in the eastern Mediterranean were off the Gulf of Sirte, Libya and between Cyprus and Syria. Secondary foci of tar pollution were found between Sicily and Tunisia and in the southeastern Aegean.

Another measurement of pelagic tar, in the western Mediterranean, was conducted on board the R/V "Westward" in 1974/75 by Morris <u>et al.</u> (1975). They collected forty-eight neuston samples in the Alboran, Balearic, Tyrrhenian and Ionian Seas, fairly close to the sampling track used by Horn <u>et al.</u> (1970). All of the tows contained tar ranging between 0.1 and 109.9  $mg/m^2$  with an average of 9.7  $mg/m^2$ . The detailed results of that study are provided in Table 4.

Ros and Faraco (1979) conducted three cruises in the western Mediterranean in 1975, 1976 and 1977 aboard the R/V "Cornide de Saavedra". They collected tar from one hundred and forty three neuston nets and found that tar quantity ranged between 0-77.7  $mg/m^2$  with an average of 2.9  $mg/m^2$ ; 13.3 per cent of their tows contained less than 0.1  $mg/m^2$ , 49.6 per cent between 0.1 and 1, 25.2 per cent between 1 and 5, and 11.9 per cent of the samples contained more than 5  $mg/m^2$ .

Area	Period	Range	Arithmetic mean	Geometric mean	Reference
Alboran Sea					· · · · · · · · · · · · · · · · · · ·
	1969		6.5		Horn et al., 1970*
	1974-75	0.35-45.11	11.0	4.4	Morris et al., 1975
	1976	0.04-6.6	0.6	0.22	Ros and Faraco, 1979
	1981-82	0.01-25.6	0.8	0.17	De Armas, 1985
Balearic Sea					
	1969		2.4	2.2	Horn et al., 1970*
	1972-73		3.1	2.5	Polikarpov and Benzhitsky, 1974*
	1974-75	0.1-27.9	0.5	0.4	Morris et al., 1975
north	197577	0-77.7	5.4	1.06	Ros and Faraco, 1979
south	1975-77	0.05-26.8	3.9	1.18	Ros and Faraco, 1979
	1981-82		3.6	0.63	De Armas, 1985
Tyrrhenian Sea					
	1969		1.5		Horn et al., 1970*
	1972-73		4.7		Polikarpov and Benzhitsky, 1974*
	1974-75	0.2-14.7	3.2	1.4	Morris et al., 1975
	1975-77	0-10	0.9	0.3	Ros and Faraco, 1979
Ionian Sea					
	1969		130.0	60.0	Horn et al., 1970*
	1974-75	0.9-109.9	16.0	5.0	Morris et al., 1975
East Mediterranean					
Egypt	1970-71	0-58.3	5		El Hehyawi, 1979
	1977-79	0.2-1.33**			Wahby and El Deeb, 1981
	1978-79	0-8.91	2.82		Aboul-Dahab and Halim, 1981a
NE Mediterranean	1983-84	0-33.4			Saydam et al., 1985

Table 4. Statistics of pelagic tar in the Mediterranean Sea  $(mg/m^2)$ 

\* Values are those quoted in Morris et al., 1975

\*\* mg/m<sup>3</sup>

De Armas (1985) reports the results of pelagic tar collected on board the R/V "Cornide de Saavedra" in October 1981 and May 1982 in the Alboran and Balearic Seas. The arithmetic means of tar concentrations for both seas, 0.8  $mg/m^2$  in the Alboran and 3.6  $mg/m^2$  in the Balearic, were very close to the results of Ros and Faraco (1979) collected in 1975/77. The two highest values, 19.8 and 25.6  $mg/m^2$ , reported by De Armas, were from intensive oil tanker traffic lanes off the Spanish and Algerian coasts.

El-Hehyawi (1979) collected pelagic tar in 1970-1971 using a neuston net from the Mediterranean off the western coast of Egypt between El Sallum and Damietta as far as 150 km offshore. Later, in 1974-1978, he collected samples from five shallow water stations in the vicinity of Alexandria. He found distinct differences in tar quantitites which were related to distance from shore and to season. At a distance of 100 km offshore, tar ranged from zero to 1.2  $mg/m^2$ , at 60 km offshore from zero in the summer to 18.6  $mg/m^2$  in the winter, and at 10 km offshore from 2.9 in the summer to 58.3  $mg/m^2$  in the winter. He also noted a general decrease in concentrations as one goes from El Sallum westward to Abu Qir Bay near Alexandria. El-Hehyawi attributed the tar distribution described above to wind and current conditions that, during winter, are from the northwest to the east. These bring the tar from the northern coast of Africa to the Egyptian coast. Based on these findings and extraction of hydrocarbon from sand on the beach, El-Hehyawi estimated that 5,200 tons of pelagic tar existed in 1971 in the coastal waters of the area of his study, and that about 150 tons of tar were at that time on the beach between El Sallum and Alexandria, a distance of some 600 km.

Floating tar in the coastal waters of Alexandria, Egypt, was measured by Wahby and El Deeb (1981) between May 1977 and April 1979. They did not report how far offshore samples were collected, but they commented that they used a plankton rather than a neuston net because of the lack of a boat, which indicates that sampling was carried out in very shallow water. They found that floating tar quantities ranged between  $0.2 - 1.22 \text{ mg/m}^3$ . Tar quantities were higher east of the Sumed oil pipeline than to the west of it. Since the wind and current regime is directed from west to east, the authors implied, though did not state it clearly, that spills from this pipeline cause pollution of floating tar.

In another study in the coastal waters off Alexandria, Egypt, pelagic tar was measured by Aboul-Dahab and Halim (1981a), who collected floating tar balls between September 1978 and June 1979 on a monthly basis from seven fixed stations off Alexandria. They found that the average tar quantity was 2.82 mg/m<sup>2</sup>, with values ranging from zero to 8.91 mg/m<sup>2</sup>. It was found that during the winter months, quantitites of tar were higher than in the summer months, and the authors attributed this phenomenon to the water temperature. According to them, the higher water temperature during summer enhances evaporation and degradation of tar. They also found that high tar values were recorded in the vicinity of the oil terminal west of Alexandria, and attributed this to leakages from the pipeline.

Off Turkey, Saydam <u>et al.</u> (1985) collected pelagic tar aboard the R/V "Bilim" in 1983. He collected ten samples in coastal waters and in five of them no tar was found. In the remaining five, one sample contained 33.4  $mg/m^2$  and the rest between 0.01 and 1.5  $mg/m^2$ . In the offshore, five samples were collected with a mean content of 0.6  $g/m^2$ .

#### Spatial and temporal distribution of pelagic tar

Table 4 provides a summary of all the statistics available on pelagic tar in the Mediterranean. Comparison between results of various studies does not require any assumptions except, of course, that measurements (of length of tow, of area skimmed by the neuston net, of weight of tar) were done accurately. Comparison of tar quantitites between various parts of the Mediterranean presents several difficulties:

- (a) The sampling coverage of the Mediterranean is poor and geographically imbalanced. During the nineteen years that passed since the expedition of the R/V "Atlantis II" (Horn <u>et al.</u>, 1970), only six studies on pelagic tar took place and five of them in the western Mediterranean. In the eastern Mediterranean the only studies on this subject were that of Oren (1970), which produced only relative values of tar, and that of Saydam <u>et al.</u> (1985), which is restricted to the northeastern corner of the Mediterranean and consists of a few stations only. The rest of the studies in the eastern Mediterranean are only in coastal waters.
- (b) The spatial distribution of tar does not follow the pattern of normal distribution, but rather that of a log-normal distribution. Handling data with this type of distribution is rather difficult, especially if the original data are not available and the author did not provide the suitable statistics.

In spite of these difficulties, the data suggest that the Ionian Sea was the most polluted by tar balls. The highest values for tar concentration in the studies of Horn <u>et al.</u> (1970) and Morris <u>et al.</u> (1975) were from the Ionian Sea. Oren (1970) also reported this area as highly polluted by tar balls. Other areas of large concentrations of tar were the Alboran Sea and, probably, off the eastern coastline of the Mediterranean. The reasons for this tar pollution pattern were the heavy traffic of oil from North Africa to Europe and the deballasting area in the Ionian Sea which, at least during the time that the above mentioned studies were conducted, was still a legitimate area for disposal of oily residues. It is possible that the heavy pollution in the Ionian Sea influenced also the coastal waters of Egypt where, as El-Hehyawi (1979) reported, the pelagic tar concentration was high near the border with Libya, gradually decreasing eastward to Damietta.

An attempt to detect changes in tar concentration as a function of time suffers from the same difficulties mentioned above. Many students in this field (Butler <u>et al.</u>, 1973; Morris <u>et al.</u>, 1975; Ros and Faraco, 1979) have noticed that concentrations of tar balls have normal or close to normal distribution on a logarithmic scale. Therefore the central tendency of tar samples is better expressed by the goemetric mean rather than by the common arithmetic mean. Morris <u>et al.</u> (1975) uses this statistic and its 90 per cent confidence limits to determine changes in tar with time. In the Ionian Sea there was a significant reduction in tar quantities between 1969 and 1975, from 130 to 16 mg/m<sup>2</sup> (arithmetic mean) or from 60 to 5 mg/m<sup>2</sup> (geometric mean). Morris <u>et al.</u> (1975) attributed this reduction to the closing of the Suez Canal that caused a shift in the routes of the oil traffic from the Mediterranean Sea to the Indian and Atlantic Oceans.

Another significant decrease in tar concentration was found by Morris <u>et al.</u> (1975) in the Balearic Sea. There, the geometric mean has decreased from 2.2 in 1969 and 2.5 in 1972/73 to 0.4  $mg/m^2$  in 1974/75. However, in a later study in 1975/77 by Ros and Faraco (1979), this mean has increased again to 1.06 and 1.18  $mg/m^2$ , dropping again in 1981/82 to 0.63  $mg/m^2$  (De Armas, 1985).

If data for all of the western Mediterranean are compared, we obtain the following results (in arithmetic mean):

1969	37.0 mg/m <sup>2</sup>	Horn <u>et al.</u> (1970)
1974/75	9.7 mg/m <sup>2</sup>	Morris <u>et al.</u> (1975)
1975/77	2.9 mg/m <sup>2</sup>	Ros and Faraco (1979)
1981/82	1.6 mg/m <sup>2</sup>	De Armas (1985)

which indicate a reduction in tar pollution in that part of the Mediterranean for the period 1969/82. This trend of reduction is distorted and probably not as sharp, because the data of Ros and Faraco (1979) and De Armas (1985) do not include the Ionian Sea which, as mentioned above, was the most polluted, whereas in the earlier studies, those of Horn <u>et al.</u> (1970) and Morris <u>et al.</u> (1975) were included.

#### 6. TAR POLLUTION ON MEDITERRANEAN BEACHES

Table 5 provides tar quantities on various Mediterranean beaches. The table clearly reflects the great variability in approach to sampling and sampling techniques. Some authors report their findings in terms of tar weight per area of beach, implying measurement of standing stock. Others provide their results in terms of weight of tar per unit area per unit time, therefore implying, and sometimes even stating, measurement of rate of tar landing on the beach. These authors failed to recognize that lateral movement of tar along the beach does not permit a true measurement of this parameter. Furthermore, there are even differences in the units of area, or time, used by various authors. Some express their results in terms of tar quantity per unit length of frontal

Country	Beach	Sampling period	Sampling frequency	Mean tar	Range	Units	Reference
Libya	- <u></u>	3/80-3/81	Once	1228	-	g/m	El Ghirani 1981
Egypt	Alexandria	4/77-4/78	15 days	133.8	3.5-380	g/m <sup>2</sup> /15 days	Wahby 1979
		4/77-10/79	15 days	135.5	21-347	$g/m^2/15$ days	Wahby and El Deeb, 1981
		4/78-9/79	7 days	97.6	2.85-405.7	$q/m^2/7$ days	Aboul-Dahab and Halim, 1981
	El Arish	4/75-6/76	Monthly	884	30-2055	g/m	Golik, 1982
Israel	Ashkelon	4/75-6/76	15 days	3014	391-11,133	g/m	Golik, 1982
	Ga'ash	4/75_6/76 <sup>`</sup>	15 days	4186	254-12, 150	g/m	Golik, 1982
	Bet Yanay	4/75-6/76	15 days	4114	375-14,759	g/m	Golik, 1982
	Atlit	4/75-6/76	15 days	4388	678-13,052	g/m	Golik, 1982
	Rosh Hanigra	4/75-6/76	15 days	3902	481-13,502	g/m	Golik, 1982
	Haifa	7/81-8/84	Daily	26.2	0-662	g/m	Golik, 1985
Lebanon	Ramlet	4/77_6/78	Monthly	4	0-14.8	g/ <del>m<sup>2</sup></del>	UNEP, 1980
	Sidar	4/77-8/78	Monthly	3.4	0-33.6	g/m <sup>2</sup>	UNEP, 1980
Turkey	Erdemli	6/77-7/78	3 samplings	26.7	17.9-34.3	g/m <sup>2</sup>	UNEP, 1980
Cyprus	Paphos	10/76-11/78	Every 9 days	268.4	13.9-967.1	g/m <sup>2</sup>	UNEP, 1980
•••	•	1/83-12/83	Monthly	67.3	29.2-99.7	g/m <sup>2</sup>	Demetropoulos, 1985
	Limassol	10/76-11/78	Every 9 days	23.0	1.1-102.0	g/m <sup>2</sup>	UNEP, 1980
	Makronisos	1/83-12/83	8 samples	33.0	13.9-61.0	g/m <sup>2</sup>	Demetropoulos, 1985
Malta	Anchor Bay	4/77-9/78	Monthly	4.15	0.9-10.0	g/ <del>m<sup>2</sup></del> /day	UNEP, 1980
	Marsaxldele	4/77-9/78	Monthly	0.42	0-1.7	g/m²/day	UNEP, 1980
	Qawra	4/77-9/78	Monthly	0.19	0-1.0	g/m²/day	UNEP, 1980
Yugoslavia	-	12/77-4/78	10 samples	0.91	0-8.6	g/m <sup>2</sup>	UNEP, 1980

Table 5.	Tar concentrations on Medite	rranean beaches	
		-	

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beach (usually 1 m), whereas others per unit area  $(1 m^2)$ ; some provide rates of tar accumulation in terms of one day and others in terms of fifteen days. In some cases, tar was measured every nine days but reported in terms of monthly accumulations. It is obvious that these data do not permit analysis of the results in terms of space and time for the whole Mediterranean. A search for the factors which control tar distribution on the beach may be conducted for some of the studies quoted in Table 5 but hardly for all of them.

In Libya, El-Ghirani (1981) reported large quantities of tar along the coast of Cyrenaica and in the vicinity of Tripoli (see Figure 5). El-Ghirani explained this distribution: (a) the deballasting area off the Gulf of Sirte, in his opinion, was the major contributor of tar balls to the area. These are carried by winds and currents to the northwestern coast of Cyrenaica; (b) the oil terminals in the Gulf of Sirte were a secondary contributor of tar to that region; (c) domestic activity created oil residues which flow out to the sea from the beach, as may be seen by the high values of tar near Tripoli. It must be noted that at least in 1980 (one year before the study of El-Ghirani), in four out of five oil ports in Libya, no reception facilities for oil residues existed (UMEP, 1986, table 3). This must have contributed to the tar pollution along the Libyan coast. El-Ghirani estimates that 2,000 tons of tar contaminate the Libyan coastline.

In Egypt, off Alexandria, Wahby (1979), Aboul-Dahab and Halim (1981a) and Wahby and El Deeb (1981) found that tar concentrations were higher during winter than during summer. Wahby (1979) and Wahby and El Deeb (1981) proposed that this seasonal distribution was caused by the winter storm winds which drive the floating tar balls from the open sea to the beaches. Aboul-Dahab and Halim (1981a) also observed a direct relationship between wind intensity and tar accumulation on the beach. In addition, they suggested that during summer, quantities of pelagic tar are smaller due to the higher water and air temperature which enhances tar degradation. In another paper, Aboul-Dahab and Halim (1981b) tried to relate pelagic tar, the rate of tar accumulation on the beach and the concentration of dissovled and dispersed hydrocarbon. They found that there was no correlation between floating tar and dissolved hydrocarbon (see Figure 6A), and reasoned that those two are from different origins. The tar resulted from tanker ballast, whereas dissolved and dispersed hydrocarbon resulted from coastal waste discharge. On the other hand, they found a good correlation (see Figure 68) between pelagic tar and the rate of tar accumulation on the beached the conclusion that both of them are from the same sources, and that the distribution of both depends on the same factors, such as winds and temperature.

Golik (1982) found that in 1975/76 the beaches in the northern and central part of Israel were significantly more polluted than those in its southern part and Sinai (see Figure 7). He attributed this distribution to several factors: (a) for seven years prior to the study, the Suez Canal was closed and there was no oil traffic in the vicinity of Sinai; (b) most of the oil traffic at that time took place between the oil terminals in the eastern Mediterranean (Israel, Lebanon and Syria), thus affecting the northern beaches of Israel; (c) Oren (1970) and Burman and Oren (1973) found high concentrations of pelagic tar between Cyprus, Israel and Lebanon. There are indications (S. Brenner, personal communication, 1986) that an eddy exists in that location. If this is proven, tar would accumulate in the no-motion centre of that eddy, to feed the Israeli northern coast with tar.

In Cyprus, a comparison between the western side of Cyprus (Paphos) and its eastern side (Limassol) for the period of 1976/78 shows that the western side of the island was more polluted by tar than its eastern side by about ten times (UNEP, 1980). In a similar way, the beach on the western side of Malta (Anchor Bay) contained ten times as much tar as those on its eastern shores (UNEP, 1980). The reason for this difference between both sides of the two islands is probably the wind, which is generally a western one. Most of the tar lands on the exposed, western side of the island, whereas the lee, eastern side of the island remains relatively clean.



Quantitative distribution of tar in g/m on the Libyan coast in 1980/81. (From El-Ghirani, 1981). Figure 5.









Figure 6. Dissolved and dispersed petroleum hydrocarbon concentrations as a function of pelagic tar (A) and Tar deposition rate as a function of pelagic tar (B) off Alexandria, Egypt. (From Aboul-Dahab and Halim, 1981b).

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Figure 7. Quantitative distribution of tar in g/m on the coast of Israel and Sinai in 1975-76. (From Golik, 1982).

A drastic reduction in tar contents on the beaches of Israel between 1975/76 and 1984 was found by Golik (1985) in Haifa. Although the sampling frequency in Golik's study in 1984 was daily in comparison to the bi-weekly sampling in the study of 1975/76, the results reported in Table 5 for the 1984 study are only from newly sampled beach strips, and therefore a comparison between the two studies is valid. Table 5 shows that the reduction in tar quantity between 1975/76 and 1984 was of two orders of magnitude. A comparison of low flying air photos from beaches in Israel at various periods between 1975 and 1985 (Golik and Rosenberg, 1987) clearly shows the gradual and drastic reduction in tar concentrations, as may be seen in Figure 8.

A similar reduction in tar quantity between 1976/78 and 1983 was reported (UNEP, 1980; Demetropoulos, 1985) from Paphos, Cyprus. During that period, mean tar concentration was reduced from 268.4  $g/m^2$  to 67.3  $g/m^2$ .

Golik (1982) made an attempt to compare tar quantities on various beaches in the Mediterranean. For that purpose he had to re-compute reported values from various studies so that all of them were expressed in the same units. This procedure has undoubtedly introduced some error into the comparison, but still, for an order of magnitude, this comparison is valid. Also, most of the compared studies were carried out at about the same period, 1975-1978, and therefore provide the state of beach tar pollution at some parts of the Mediterranean at that time. The result of this comparison is given in Table 6. According to the comparison, Paphos, Cyprus and Alexandria, Egypt were the most polluted beaches at that time (1975–78). These two beaches were both closest to and downwind of the deballasting area which existed at that time between Crete, Cyprus and Egypt (see Figure 3). This geographical relationship indicates the role of the deballasting area on the pollution of seawater and nearby beaches by tar. The geographical relationship between the highly polluted coast of Cyrenaica in Libya (El-Ghirani, 1981) and the nearby deballasting area in the Ionian Sea (see Figure 5) supports this conclusion. Although the study of El-Ghirani (1981) was conducted in 1980/81, 2-3 years after deballasting and releasing of oily water into the whole Mediterranean was forbidden, the effect of the deballasting area certainly still persisted in that area.

Country	Beach	Period of study	Sampling rate	Mean tar quantity (g m <sup>-2</sup> )
Malta	Anchor Bay	Apr. 77 - Sep. 78	Every 15 days	62.3 <sup>a</sup>
Malta <sup>b</sup>	Marsaxlokk Bay	Apr. 77 - Sep. 78	Every 15 days	6.3 <sup>a</sup>
Cyprus <sup>b</sup>	Limassol	Nov. 77 - Nov. 78	Every 9 days	31.5
Cyprus <sup>b</sup>	Paphos	Nov. 77 – Nov. 78	Every 9 days	360.3
Egypt <sup>b</sup>	Alexandria	Apr. 78 - May 79	Every 15 days	132.0
Lebanon <sup>b</sup>	Ramlet	Apr. 17 - June. 78	Monthly	4.0
Lebanon <sup>b</sup>	Sidar	Apr. 77 - Jun. 78	Monthly	3.8
Turkeyb	Erdemli	1977 - 1978	Only 3 samplings	24.3
IsraelC	Mean of six beaches	Apr. 75 - Jun. 76	Every 15 days	14.6

Table 6. Tar quantities on various Mediterranean beaches (from Golik, 1982)

<sup>a</sup> Values are reported as  $g m^{-2} day^{-1}$  and recalculated here back to  $g m^{-2}$  (15 days<sup>-1</sup>) to permit comparison

<sup>b</sup> UNEP, 1980

<sup>C</sup> Golik, 1982



Figure 8. A series of air photographs of the same 25 m beach section at different dates showing the change in tar concentration on the Israeli coast between 1975 and 1985. From Golik and Rosenberg (1987).

#### 7. TAR PROCESSES

The chemical changes that petroleum hydrocarbon undergoes until it becomes a "tar ball", the movement of tar balls on the sea surface and in the water column, the landing of tar on the beach and its final fate, are defined here as "tar processes". A good understanding of these processes may help in coping with the tar problem. For example, the chemical composition of tar may indicate its source and thereby the agent causing oil pollution. The chemical composition may also indicate the age of a tar ball and thereby provide insight into the tar balance on a beach, which in turn is important for feasibility evaluation of cleaning tar from beaches. Information on degradation of tar may help in designing methods to hasten this process. Unfortunately, only very few studies were conducted on tar processes in the Mediterranean; these will be reviewed here.

#### Sources of tar in the Mediterranean

Shekel and Ravid (1977) investigated the origin of tar balls that land on the beaches of Israel. They carried out gas chromatographic (GC) analyses as well as analyses of the ratio of vanadium to nickel and sulphur content of 788 tar samples collected fortnightly from eight stations along the Israeli coastline between September 1973 and January 1975. On the basis of the GC analyses, the authors classified their samples into four categories as follows:

GC 1 weat	hered crude oil	149	samples	19	per	cent	of	samples
GC 2 crud	e oil sludge	451	samples	57	per	cent	of	samples
GC 3 weat	hered fuel oil	139	samples	18	per	cent	of	samples
GC 4 high	ly weathered oily residues	32	samples	4	per	cent	of	samples
Unidentif	ied samples	17	samples	2	per	cent	of	samples
Total:	788 samples	100	per cent					

To evaluate the results of the V/Ni ratio and S content, Shekel and Ravid prepared a log-log chart of the content of these elements in oils from Algeria, Libya, Egypt, Simai, and the Persian Gulf (see Figure 9A). It can be seen that the Middle Eastern oil differs greatly from the North African oils, with the oil of Egypt and Sinai found between them. The results of the analyses of the tar balls were plotted on this chart, and it was found that 96 per cent of the tar balls originating from crude oil or crude sludge originated from Middle Eastern oil (Figure 9B). Since fuel oil is an artificial refinery product, with which ships load their tanks at a great variety of places, there was no sense in attempting to find its geographical source.

Using the first n-hydrocarbon appearing in the chromatogram, Shekel and Ravid tried to determine the degree of the tar weathering. They found that in 46 per cent of the tar balls originating from crude oil or crude oil sludge, the first n-hydrocarbon was C12-C14, indicating an age of about two weeks, and in 41 per cent degradation reached C15-17, indicating an age of about two months. It was also found that tar with low n-hydrocarbon was more abundant in summer than in winter, but no explanation was offered for this phenomenon.

Albaiges <u>et al.</u> (1979) analyzed forty-two samples of floating tar collected in the western Mediterranean between Spain and Italy in order to determine their source. The analyses consisted of gas chromatography as well as analytical chemistry to determine sulphur, vanadium and nickel content in the tar. It was found that almost all the samples were already subjected to degradation - in 75 per cent of the samples C13-C14 n-paraffins were present and in the rest n-C15 was always present. There was no evidence of biological degradation nor of a difference between



North African oil: □ Algerian, O Libyan, △ Egyptian. Middle Eastern oil: ● tranian, × Kuwait, + Saudi Arabian, ▲ Sinai



Figure 9. Sulphur content vs V/Ni showing geographical sources of crude oil (A) and in the four groups of tar ball samples in Israel (B). (After Shekel and Ravid, 1977).

the inner part and outer part of the tar ball. It was concluded that the tar sampled originated from crude oil, weathered marine fuel oil and weathered crude oil sludges; 82 per cent of the samples were the result of discharged oil tanker washings. The S, Ni, and V content of the samples indicated that the tar originated from Middle Eastern oil.

The significance of these studies is that at the time they were conducted, the origin of the tar which polluted the eastern Mediterranean must have been oil which reached the area from oil terminals in the eastern Mediterranean and not from great distances in the Mediterranean. Still it is surprising that the origin of tar in the western Mediterranean was also from Middle Eastern oil and did not show traces of North African oil, which was shipped in large quantities to European ports in the Mediterranean. Albaiges <u>et al.</u> (1979) suggest that the North African oil is low in asphaltane and paraffin content and evaporates without leaving solid content. This explanation is not satisfactory in view of the large quantities of tar found by El-Ghirani (1981) on the Libyan coast. This problem must be further investigated.

In a later paper, Albaiges (1980) points out that common analytical procedures for determining S, Ni and V content in samples, as well as the hydrocarbon gas chromatography, including the phytane/pristane ratio, are not enough for "fingerprinting" of oil residues in the Mediterranean. This is because of two reason: (a) a large number of types of oil are transported in the Mediterranean, and some of them show great similarity in terms of the above mentioned parameters; (b) in many cases the above mentioned parameters change with the degradation that oil undergoes after it has been released into the marine evironment. This would especially affect tar analysis. Albaiges recommends making use of multi-fingerprinting using selective detectors (FP and NP detectors) on the GC, which provide profiles of sulphur and nitrogen compounds. With the aid of these profiles, a better differentiation of the oil compound is obtained. However, these are good only for detection of a chronic source of oil pollution but not for degraded, old oil residues. For these, the author recommends the use of mass-fragmentation of petroleum biological markers such as acyclic isoprenoids, steranes, rearranged steranes and hopanes. These compound are hardly changed during degradation of the oil and preserve their original fingerprinting even in old tar balls.

#### Dispersion of tar

Very little is known on the transport of tar in the sea. Floating tar is affected mostly by winds and to a lesser extent by currents. However, tar is found also suspended in the water column as well as on the seabed. Balkas <u>et al.</u> (1982) tried to find whether sunken tar differs chemically or physically from floating tar. They analysed floating and sunken tar ball samples using Infra-red (IR), H-Nuclear Magnetic Resonance (H-nmr), gas chromatography (GC) and GC/Mass Spectrometry (MS) techniques. They found that it is very difficult to separate the floating from the sunken tar on the basis of their chemical or even physical properties. In many cases the density of the sunken tar was higher than that of the floating tar but not always. Usually the density of the tar is very close to that of the water. Therefore, the water temperature is probably the factor that controls whether the tar will sink or not. An example was brought of oil released from a tanker which caught on fire in the Bosphorus. A few weeks later, when the weather grew colder, the tar floated in a matter of hours.

Saydam <u>et al.</u> (1985) found high concentrations of pelagic tar in the Gulf of Iskadrun. Associated with the tar, anthropogenic litter was found as well, which consisted, among others, of plastic bags. These carried commercial writings on them indicating that this material, and presumably the tar too, was swept with the Mediterranean counter-clockwise current from as far south as Egypt along the eastern shores of the Mediterranean (Israel, Lebanon, Syria and Turkey) to that Gulf. There, the tar was trapped by two eddy systems which are usually located there. The authors attributed another area of tar concentration, east of Cyprus and south of Turkey, also to eddy currents found there. It has already been mentioned that another permanent eddy system is probably located south of Cyprus, which may be the reason for the high tar concentration reported there by Oren (1970).

#### Fate of tar

Eventually, the tar is swept to the beach and lands there. Once it lands, sand grains are attached to it, increasing the specific gravity of the tar ball and preventing it from floating. The tar may sink to the sea bottom, but the net transport of particles in the breaker zone is such that these are always carried shoreward. At times, they may be carried by rip currents back to the sea and start their voyage shoreward again. Therefore, the tar is destined to land on the beach.

On the beach, the tar balls are spread along the waterline, and each successive wave drives the tar to the back of the beach. With the fluctuation of sea level due to tide or storms, elongated strips of tar, parallel to the waterline, are formed (see Figure 8). The further a strip of tar is on the back of the beach, the older this strip is, indicating a higher sea elevation. Golik (1982) observed that during storms, the waves push the tar as far to the back of the beach as to the foot of the cliff. Longshore currents cause the tar to move along the beach until it reaches a section of the coast which is not cliffy and where the beach is wide. In a storm, the waves may carry the tar to a distance of 200-300 m landward on a flat beach, but then the water percolates into the sand and the tar remains behind on the beach. The result of this process is that in flat beaches, such as near river outlets, large deposits of tar may be found.

Golik (1982) conducted observations on a fresh tar lump on the beach for several months, and reports that during that period the lump developed a hard skin, then started to shrink, forming fissures in the skin, and later broke into small particles 1-3 mm in size. These are blown easily by the wind. It is not known as yet how long it takes for the average tar ball to disintegrate in this way.

#### 8. HAS THERE BEEN ANY REDUCTION OF TAR POLLUTION IN THE MEDITERRANEAN?

The period 1978/79 may be considered as a milestone in the history of marine oil pollution. The oil crisis that occurred at that time caused a sharp increase in oil prices (see Figure 10), which caused a chain reaction of reduction in oil consumption (see Table 3), reduction in marine transportation and a decline in tanker fares. At the same time, the 1969 amendment to OILPOL 54 entered into force, restricting oil disposal into the sea.

As mentioned earlier, these brought about a series of activities, technological and legal, which caused a reduction of oil release into the sea and increased the awareness of marine pollution by oil. Indeed, recent information indicates, as shown in Table 7, that the number of oil spill incidents is decreasing. In some cases, e.g. Israel (Y. Cohen, personal communication), systematic cleaning of long (scores of km) beach sections has been undertaken since 1984 and is conducted at least once a year.

To examine the impact of these developments on the state of tar pollution in the Mediterranean, one must compare data of tar concentration prior to 1978/79 to those after that year. Examination of Tables 4 and 5 shows immediately that almost all of the data were collected prior to 1978/79, and in only two or three locations is a comparison possible. The only studies that were conducted after 1978/9 are those of De Armas (1985) on pelagic tar in the western Mediterranean in 1981/82, Demetropoulos (1985) on beach tar in Cyprus in 1983, Saydam et al. (1985) on pelagic tar off Turkey in 1983/84, Golik (1985) on beach tar in Israel in 1984, and Golik and Rosenberg (1987) on comparison of beach tar content during the period 1975-1985. With the exception of the work of Saydam et al. (which cannot be compared to any previous one), all these works show reduction in tar quantity in comparison to data collected prior to 1978/79 and, as demonstrated earlier, in some cases the reduction is quite dramatic.





۲	ear	No. of spills	Oil spills attented on-site
1	974	26	5
١	975	23	7
١	976	25	7
١	977	20	3
١	978	24	8
١	979	37	13
. 1	980	13	9
١	981	5	14
Į	982	3	10
1	983	11	17
•	1984	7	13
1	1985	8	13
1	lotal	202	119

Table 7. Incidence of oil spills over 5,000 barrels from tankers worldwide (1974-1985)

From: International Tanker Owners Pollution Federation Ltd. (1986).

It is of interest to find whether similar examples of tar reduction are found outside of the Mediterranean. One example is the stranded tar on the beaches of Bermuda. Three tar studies were conducted on these beaches: in 1971/72 by Butler <u>et al.</u> (1973), in 1978/79 by Knap <u>et al.</u> (1980), and in 1982/83 by Robertson Smith and Knap (1985). The results of these studies show that between 1971/72 and 1978/79 there was an increase in tar content, but a statistical test was not conducted because different beaches were sampled each time. A comparison between 1978/79 results and those of 1982/83 (for the same beaches) showed a decrease of 59 per cent and 78 per cent in the arithmetic mean, and 79 per cent and 87 per cent for the geometric mean.

Though encouraging, the described cases are very few and could be considered only as signs of tar reduction. Only if similar comparisons in other parts of the Mediterranean show the same trends, may one conclude that the tar problem is indeed decreasing.

#### 9. ASSESSMENT OF OIL POLLUTION THROUGH MONITORING TAR CONTAMINATION

The rationale that marine oil pollution and tar concentrations are quantitatively related is basically valid because tar is a derivate of oil. However, this is true only in general terms when comparing two geographic areas, or two periods, which greatly differ from one another in oil pollution. The reduction in tar concentration during the last seven to ten years, presented above, may be considered as an example for the relationship between oil and tar pollution. As mentioned above, this still needs proof.

At the present state of our knowledge, direct, quantitative correlation between the two types of pollution is impossible. This is because:

(a) The exact process by which tar is formed from oil is not yet fully understood. How much tar is formed from a given quantity of oil? Of what kind of oil? How much time is required for

this process? These and similar questions must be answered before such a correlation may be attempted.

(b) The dispersion mechanism of oil in the sea is different from that of tar. The dominant agent for oil dispersal is currents, whereas wind is the dominant agent for tar dispersal. Therefore, tar may move much faster than the oil slick which generates it, making a correlation between them impossible.

Indeed, the few attempts that were made to find a relationship between oil and tar showed that there is none. It was mentioned above that Zsolnay <u>et al.</u> (1978) searched for a relationship between tar concentration and aromatic hydrocarbons in the same water samples, and concluded that there was none. Aboul-Dahab and Halim (1981b) also showed that there was no relationship between dissolved/dispersed hydrocarbons and pelagic tar, as may be seen in Figure 68. Similarly, Faraco and Ros (1979), working on pelagic tar as well as on dissolved/dispersed hydrocarbons in the western Mediterranean, reported that they did not find any relationship between the two.

Intensive field and laboratory work is required to verify a quantitative relationship between tar and oil pollution. This should include many expeditions to various geographical areas under various climatic and sea conditions, in which simultaneous tar and water sampling is carried out and later chemically analyzed in the laboratory. The few examples brought above, though not conclusive, indicate that such an effort may be in vain.

#### 10. CONCLUSIONS

As mentioned earlier, during the period of 1976/78 many studies of tar pollution were conducted in the Mediterranean as part of the MED POL programme (UNEP, 1980). These provided a baseline to which one could refer later. The reduction in tar concentration in Cyprus and in Israel in the early 1980s would not have been noticed if it were not for the studies carried out there in the mid 1970s. These findings raise the question whether similar reductions in tar quantities have not occurred in other areas in the Mediterranean.

We are now at a time when a similar concentrated effort must be made to provide data which will help to decide whether the signs of tar reduction are real or not. Furthermore, the trend of reduction in oil consumption which the world has experienced since 1979 may be reversed in the future with the recent reduction in oil prices. Another threat is the discovery and exploitation of offshore oil in the Mediterranean Sea which, as mentioned above, is now in fast progress. Will those cause a new wave of oil and tar pollution? Monitoring of oil and tar pollution must therefore continue.

Many oceanographic vessels conduct studies in the Mediterranean. It is recommended that a central agency (presumably UNEP) should undertake the mission to encourage the research institutions sending these ships to conduct pelagic tar samplings on their way between the stations they occupy for their missions. This may cost an extra day or two of shiptime but the reward is great, because it will provide data from all over the Mediterranean in a short time. Efforts should be made to carry out these studies simultaneously all over the Mediterranean.

It is very important to determine the origin of beach-stranded tar. Such information will indicate whether the focus of pollution is in the coastal water or in the open sea. In the former case, treatment should be local and on the responsibility of the country controlling the pollution source; in the latter, international action would be required. Therefore, each coastal State should carry out studies on the chemical constituents (GC, S, V/Ni, etc) of the tar landing on its coast. In addition, a central reference "library" of as many oil samples as possible should be established to permit such studies.

Although monitoring is of higher priority at a time when changes in the oil industry are taking place, other studies aimed at understanding the transformation of oil into tar, tar

dynamics, age of tar, tar degradation and its final fate, must go on and be supported, because these will provide the tools to combat the tar problem if it continues to exist.

At the present moment, tar is not an efficient tool to assess the degree of oil pollution, and it seems that it will not be one in the future. Both oil and tar are a menace to the marine environment, having their own deleterious effects on various aspects of the environment and on the economy. Both should be monitored, studied and handled, each in its appropriate way.

#### 11. RECOMMENDATIONS

- 1. Co-ordinate a Mediterranean multi-national effort to collect pelagic and beach stranded tar all over the Mediterranean in order to evaluate the present state of tar pollution in this sea.
- 2. Encourage each State to carry out chemical analyses (GC, S, V/NI, etc.) to determine the source of tar landing on its coast.
- Establish a central "library" of oil samples with their chemical characteristics to allow efficient "fingerprinting" of tar.
- Support and encourage studies which investigate various aspects of tar processes.

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