MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION

ASSESSMENT OF THE STATE OF POLLUTION OF THE MEDITERRANEAN SEA BY PETROLEUM HYDROCARBONS

EVALUATION DE L'ETAT DE LA POLLUTION DE LA MER MEDITERRANEE PAR LES HYDROCARBURES DE PETROLE

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This series contains selected reports resulting from the various activities performed within the framework of the components of the Mediterranean Action Plan: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas and Regional Oil Combating Centre.

Ce volume constitue le dix-neuvième numéro de la série des Rapports techniques du Plan d'action pour la Méditerranée.

Cette série comprend certains rapports élaborés au cours de diverses activités menées dans le cadre des composantes du Plan d'action pour la Méditerranée: Programme de surveillance continue et de recherche en matière de pollution (MED POL), Plan Bleu, Programme d'actions prioritaires, Aires spécialement protégées et Centre régional de lutte contre la pollution par les hydrocarbures.

INTRODUCTION

The Mediterranean States meeting in Barcelona in 1975 adopted an Action Plan for the Protection of the Mediterranean Sea against pollution. The legal framework for this co-operative regional programme is the Convention for the Protection of the Mediterranean Sea against pollution and its related protocols (also known as Barcelona Convention) which has been ratified by 17 Mediterranean states and the European Economic Community. So far, four protocols have been adopted and entered into force, one of them being the Protocol for the Protection of the Mediterranean Sea against pollution from Land-based Sources (LBS protocol).

The MED POL programme is the scientific/technical component of the Mediterranean Action Plan and is concerned with the assessment and evaluation of the environmental problems. The environmental assessment undertaken provides a basis for assisting national policy makers with the management of their natural resources in a more effective and sustainable manner.

The specific objectives of the MED POL programme are designed in such a way as to provide the Contracting Parties to the Barcelona Convention, inter alia, with:

- information required for the implementation of the Convention and the protocols;
- indicators and evaluation of the effectiveness of the pollution prevention measures taken under the Convention and the protocols;
- scientific information which may lead to eventual revisions and amendments of the relevant provisions of the Convention and the protocols and for the formulation of additional protocols;
- information which could be used in formulating environmentally sound national, bilateral and multilateral management decisions essential for the continuous socio-economic development of the Mediterranean region on a sustainable basis.

The Contracting Parties to the LBS protocol, which entered into force in 1983, agreed to take all appropriate measures to prevent, abate, combat and control pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources within their territories.

For the achievement of the above goal, the Meeting of Experts for the Technical Implementation of the LBS Protocol (December, 1985) proposed, inter alia, that prior to recommending specific measures to the Parties, "assessment documents" should be prepared for selected substances listed in the LBS Protocol, over a certain period of time. According to the proposal, which was adopted by the Fifth Ordinary Meeting of the Contracting Parties to the Barcelona Convention (September 1987), such assessments should include inter alia chapters on:

- sources, points of entry and amounts of pollution for industrial, municipal and other discharges to the Mediterranean Sea;

- levels of pollution;

- effects of pollution;

- present legal, administrative and technical measures at national and international level.

The present document on the assessment of the state of pollution of the Mediterranean Sea by petroleum hydrocarbons summarizes information on the sources of inputs and observations of petroleum hydrocarbon levels in the Mediterranean, and on the biological effects of the contamination. The document was prepared jointly by the Co-ordinating Unit for the Mediterranean Action Plan and IOC and was presented to the Fifth Meeting of the Working Group for Scientific and Technical Co-operation for MED POL (Athens, 6-10 April 1987) as part "A" of Document UNEP/WG.160/11. The Meeting approved the document and recommended that it be published. This was subsequently endorsed by the Fifth Ordinary Meeting of the Contracting Parties to the Barcelona Convention (Athens, 7-11 September 1987).

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ASSESSMENT OF THE STATE OF POLLUTION

OF THE MEDITERRANEAN SEA BY PETROLEUM HYDROCARBONS

On the basis of the available data on the distribution of petroleum hydrocarbons in the different environmental compartments, a mass balance is estimated. The very preliminary estimate suggests a total amount of petroleum hydrocarbons of approximately 716 x 10^3 tonnes $year^{-1}$. This amount should be compared with the estimated yearly input of 635 x 10^3 tonnes $year^{-1}$ indicating a possible accumulation of hydrocarbons in the Mediterranean ecosystem. However, the uncertainty of the mass balance is such that no firm conclusions can be drawn; however, there is a clear need for more data so as to improve the mass balance.

Practically no observations exist on the effects of petroleum hydrocarbons on marine organisms in the Mediterranean and thus no conclusions can be drawn on the effects of oil pollution in this area.

The major gaps of information concern inputs and levels of petroleum hydrocarbons along certain parts of the Southern shore. Information is also sparse on levels in the deep-sea sediments and in the open waters especially in the Eastern Mediterranean; finally there is a great need for information on the effects of long term input of low level contaminants on marine organisms in the entire area.

1. GENERAL INFORMATION

The Mediterranean, a semi-enclosed sea, with a surface area of 2.96 million km^2, is surrounded by mountains except on the south-eastern desert coast. The coastal plains are small and narrow compared to the general features along the Atlantic Ocean. Large alluvial plains are situated in the deltas of great rivers such as the Ebro, Rhône and Po. In addition, the Nile delta is an essential part of the Eastern Mediterranean environment, although its hydrographical significance has changed with the construction of the Asswan dam. Fig. 1 shows the Mediterranean and its regional seas.

The average depth of the Mediterranean is 1500 m with maxima of 5000 m. The sea has a volume of 3.7 million km^3 and a renewal period of 80 years for its water. There are three important sills in the Mediterranean: the Straits of Gibraltar (365 m depth), the Sicilian Channel (350 m) and the Dardanelles (100 m). The first one, with a width of 15 km separates the Mediterranean from the Atlantic Ocean and makes it an almost enclosed sea; the second divides it into a western and an eastern basin, the third separates it from the Sea of Marmara and the Black Sea.

The evaporation rate is extremely high, so that surface circulation results in a net influx of surface waters from the North Atlantic and Black Sea. The rate varies over the entire area. In the Aegean Sea, the Adriatic Sea and the Ligurian Sea (Fig. 1), the evaporation balance is zero, whereas a high evaporation rate is found in the Eastern Mediterranean, the Gulf of Sirte and in the Central Western Mediterranean. The average salinity of the Mediterranean is $38^{o}/oo$ against $35^{o}/oo$ in the Atlantic Ocean. The Mediterranean is surrounded by 18 countries, some of which are among the most industrialized countries in the world. Over 200 million people live along its coasts and in areas which contribute to river run-off into this sea.

Oil pollution is not a new phenomenon in the Mediterranean. Natural seeps have existed over geological times, particularly in the northeastern parts. However, the oil pollution of anthropogenic origin is substantial and considerable amounts are frequently observed, mainly as lumps of tar on beaches or off-shore, often together with surface film contamination. In fact, the Mediterranean is considered to be relatively more polluted by oil than any other sea from which data are available (US Natl. Acad. Sci., 1975; UNEP, 1980).

The Mediterranean has so far been spared major oil spills. However, a large number of minor accidental or deliberate spills occurs each year in connection with oil transport activities within the region. Pollution has been observed along the tanker routes particularly in the eastern parts of the sea (IOC, 1981). In addition, considerable quantities of oil are released from coastal urban and industrial areas (UNEP, 1977).

A number of monitoring activities to assess the oil pollution in the region has been carried out by Mediterranean research centers. These studies have mostly been part of the Mediterranean Action Plan. Although there is still a lack of knowledge in a number of fields, parts of the problem have been studied during the last decade, for example the quantitative and qualitative assessment of dissolved/dispersed hydrocarbons in water and of tar on beaches and in surface waters. More recently, interest in other components, especially benthic and marine atmospheric environments and marine biota, has been developed, giving rise to the first rough estimates of fluxes and mass balance of petroleum hydrocarbons in the Mediterranean.

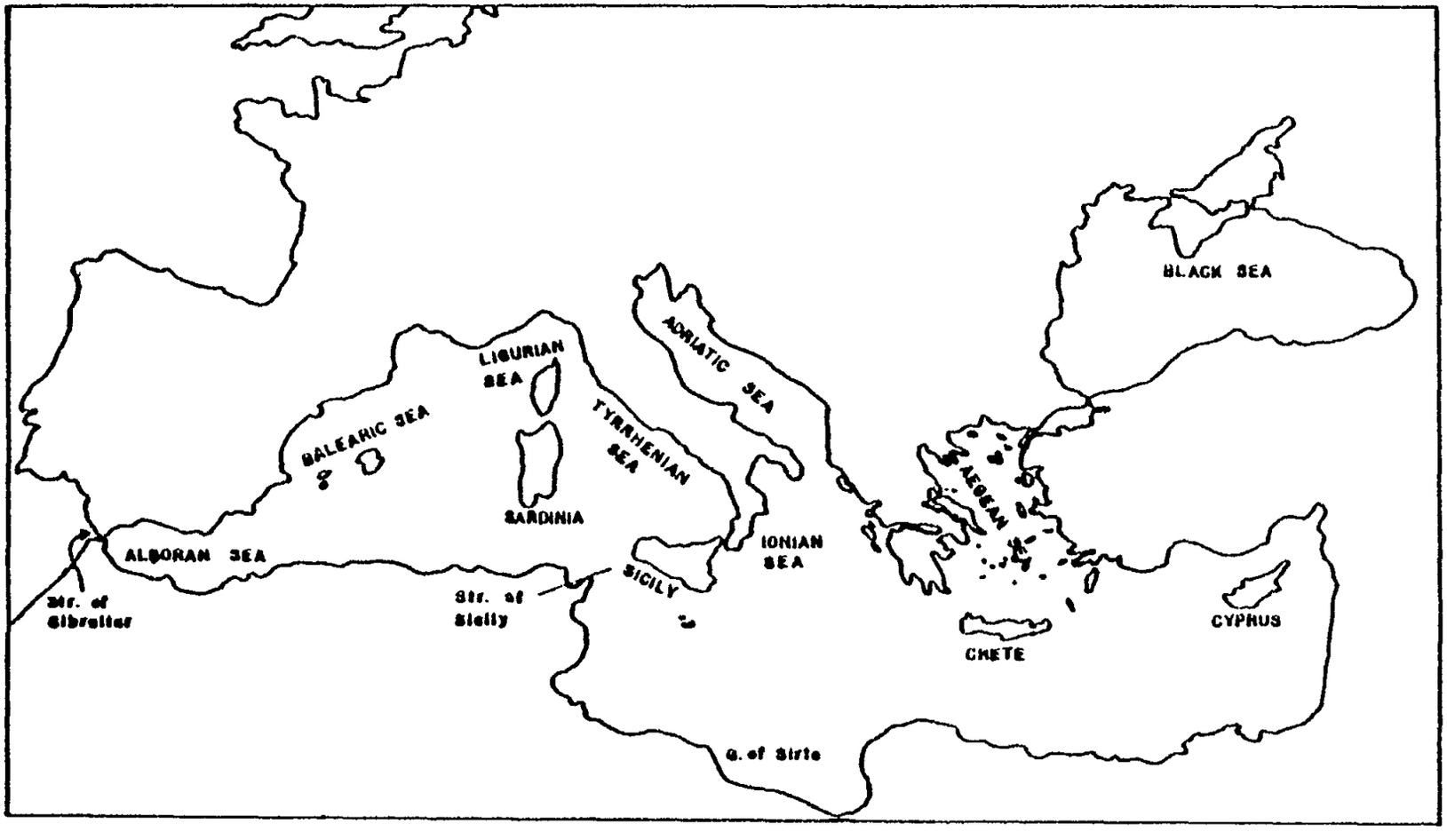

Figure 1: The Mediterranean Sea and its regional seas

2. SOURCES AND INPUT OF PETROLEUM HYDROCARBONS IN THE MEDITERRANEAN

Input of petroleum hydrocarbons into the marine environment ranges from diffuse chronic inputs (terrestrial run-off and natural seeps) to large point source releases (e.g. tanker spills). Deliberate release of oil into the world's oceans from marine operations or land-based activities is a relatively more important pollution source than accidents involving single massive inputs of oil (Table I). Although there are very few data on the relative importance of the different sources in the Mediterranean, the deliberate chronic oil pollution is considered far more important compared to accidental pollution (Jeffery, 1974; Le Lourd, 1977).

In 1979, Le Lourd estimated that the amount of oil released into the Mediterranean was between 0.5 and 1 million tonnes per year, with half being discharges from the coast and half in the open sea. These represent about a fifth of the total marine oil inputs (around 4 million tonnes) which are released in a region representing no more than 1% of the total world oceans' surface. Other authors (Longé, 1980) evaluated this quantity as 1.7 million tonnes, which is probably overestimated.

Le Lourd's estimate was based on local tanker practices and remains a reasonable figure. The amount of oil transported over the world's oceans has considerably increased (Table II) but despite this there has been a significant reduction of the quantity of oil discharged into the sea during transportation, due to the entering into force of the MARPOL Convention. Based on these estimates and on the 350 million tonnes of oil crossing the Mediterranean each year (Smith, 1975) it can be assumed that the quantity of oil entering the Mediterranean through these practices is around 330×10^3 tonnes. Even a figure of 500×10^3 tonnes has not been considered unreasonable by IMO (UNEP, 1984). It must be considered that in late 1978, 10 loading terminals out of the 19 existing in the Mediterranean did not possess any deballasting installations, although they handled over 190 million tonnes of oil traffic (Table III). On the basis of published data it does not appear possible to give a quantitative estimate of the input caused by the lack of reception facilities for ballast water from tankers or for sludge and bilge water from all ships, although it is expected that the resulting inputs may be considerable; this source of petroleum hydrocarbons should therefore be estimated in the future.

The estimates of inputs from other sources can be arrived at if we include the land-based industrial discharges summarized by UNEP (1977). These are more than 60 oil refineries located along the coasts of the Mediterranean (Table IV). The input of petroleum hydrocarbons from these sources into the Mediterranean has been conservatively estimated at 20,000 tonnes per year (Rouit, 1975). The main part of this oil comes from the old refineries, which were not designed with water treatment as a priority (Table V). Their water consumption is high and effluent streams are often not segregated. In many cases the waste water is only subjected to primary treatment. These refineries have a higher waste water flow and a much higher pollutant load per tonne of crude processed, if compared to the modern refineries. The latter use either air or recirculating water for cooling purposes and they generate minimal quantities of waste water.

No figures or estimates are available regarding the amounts of petroleum hydrocarbons carried directly through land run-off into the Mediterranean or indirectly via rivers. As the pollution load and pollution pattern vary widely in rivers it seems impossible to transfer to the Mediterranean the results of detailed analysis from rivers outside the region without substantial amendments. However, as several of the countries surrounding the Mediterranean are among the most industrialized in the world, it seems very likely that considerable amounts of oil enter the sea through run-offs from land. The overall input of oil from different industrial sources is estimated at 110,000 tonnes.

Urban inputs can be computed by using the estimates of Eganhouse and Kaplan (1981) of 1,014 per year per person for urban populations and 398 per year per person for rural areas. If we take into account the Mediterranean population distribution given by Henry (1977) we get a total input of 160,000 tonnes of oil per year.

Finally, only very few studies are available on the quantities of hydrocarbons entering the Mediterranean through atmospheric fall-out. However, it can be expected that considerable quantities arrive via the atmosphere since many of the Mediterranean countries are heavily industrialized and consequently burn large amounts of oil.

Combustion products are estimated from atmospheric fluxes given by Ho et al. (1983) at 35,000 tonnes per year, including dry and wet deposition. Although these fluxes were derived from two shipboard transects in the western basin, which is probably the area most affected by this type of pollution, the estimate represents a contribution of only about 10% of the total worldwide input (Table I).

The resulting value of 0.6 million tonnes (Table VI) falls within the Le Lourd estimates.

Table I

Inputs of petroleum hydrocarbons in the marine environment
(million metric tonnes per year)
(from IMCO, 1981; Baker, 1983; US Nat. Acad. Sci., 1985).

	Best estimate	Probable range	US Nat. Acad. Sci., 1985
Transportation	1.49	1.00-2.60	1.47
Tanker operation	0.71	0.44-1.45	0.7
Drydocking	0.03	0.02-0.55	0.03
Marine terminals	0.02	0.01-0.03	0.02
Bilge and fuel oil	0.32	0.16-0.60	0.3
Tanker accidents	0.02	0.02.0.04	0.02
Production platforms	0.05	0.04-0.07	0.05
Atmospheric	0.30	0.05-0.50	0.3
Municipal, industrial wastes, run-off	1.40	0.70-2.80	1.18
Natural seeps/erosion	0.03	0.03-2.60	0.25
Total	3.27	1.82-8.57	3.25

Table II

Quantities of oil movement at sea and the size of the world's merchant and tanker fleets in 1970 and 1980
(from IMCO, 1981).

	1970	1980	Ratio 1980/70
Oil movement at sea (million tonnes)			
Crude oil	1,100	1,319.3	1.20
Product oil	255	268.9	1.05
Total	1,355	1,588.2	1.17
World's merchant fleet			
No. of ships	55,041	73,832	1.34
Tonnes gross tonnage	247,202,634	419,910,651	1.70
World's tanker fleet			
No. of ships	6,292	7,112	1.13
Total deadweight tonnes	169,354,743	339,801,719	2.0
Average deadweight tonnes	36,900	47,800	1.78

Table III

Loading terminals in the Mediterranean
(Adjusted after Longé, 1980).

Port	Max. ship tonnage	Facilities	Oil shipment (in million tonnes)	
TURKEY				27.5
Dortyol	35,000	YES	2.5	
Botas	150,000	YES	35.0	
SYRIA				38.0
Banias	120,000	NO	34.0	
Tartous	100,000	NO	4.0	
LEBANON				41.0
Tripoli	140,000	NO	23.0	
Sidon	150,000	NO	18.0	
EGYPT				41.5
Sidi Kreir	250,000	YES	40.0	
Marsa Al Hamra	100,000	YES	1.5	
LIBYA				108.5
Marsa Al Hariga	120,000	YES	17.5	
Zueitina	250,000	NO	31.5	
Marsa El-Brega	300,000	NO	12.5	
Ras Lanuf	265,000	NO	12.5	
Es-Sider	250,000	NO	34.5	
TUNISIA				16.0
La Skhirra	120,000	YES	14.0	
Ashtart	100,000	NO	2.0	
ALGERIA				36.0
Skikda	50,000	YES	7.5	
Bejaia	100,000	YES	13.0	
Arzew	100,000	NO	15.5	
			Total	318.5

Table IV

Weighted average volume of liquid effluent discharged (m^3) per tonne of crude oil processed in European refineries (CONCAWE, 1977).

	Refineries constructed		
	before 1960	1960-1969	since 1969
1969 performance	10.45	2.17	
1974 performance	6.37	0.92	0.38

Table V

Weighted average oil content of European refinery effluents expressed as kg oil in effluent per 1000 tonnes of crude oil processed (CONCAWE, 1977).

Refinery location	before 1960	1960-1969	since 1969
Coastal	80	10.6	1.82
Inland	56	4.1	0.92

Table VI

Inputs of petroleum hydrocarbons in the Mediterranean (10^3 tonnes per year).

Source	Estimate
Spilled oil from tankers, ballasting and loading operations, bilge and tank washings	330
Land based discharges, run-off	
Municipal	160
Industrial	110
Atmospheric deposition	35
Total	635

3. PROCESSES AFFECTING THE BEHAVIOUR OF PETROLEUM HYDROCARBONS

Any anthropogenic input of hydrocarbons into the marine environment, once introduced to the recipient water body, is subject to a subsequent series of physical, chemical and biological processes which define the biogeochemical cycle of oil in the sea. The understanding of the transport and fate of these inputs is of major importance for interpreting their environmental consequences and particularly for evaluating the capacity of the receiving waters to accept wastes without detrimental effects.

Physical factors and processes have the most significant initial effect upon oil discharged into the marine environment. Factors like spreading, dispersion, evaporation, dissolution and aerosol formation, emulsification, sorption onto particulate matter and settling of the oil alter the potential impact on the living marine resources. Meanwhile dynamic processes such as current, wave and tidal movements also have a pronounced effect on marine oil pollution, as they together with the wind control the advective and dispersive behaviour of oil in the sea. Talbot (1972) and Weidemann and Sendner (1972), among several others, investigated the effect of these factors and processes in greater detail. However, some consideration is given here to the transport processes of oil pollutants in the Mediterranean, concerning the way in which they affect the distribution and fate of oil pollutants in the Mediterranean, i.e. attention is paid to factors mainly connected with winds and surface currents which are the main advective agents affecting these pollutants.

In general, the circulation of the Mediterranean is influenced by several factors : the internal density distribution, the surface wind speed, the Coriolis force and the topographic features of the sea bottom. The tidal current has a negligible role in the general circulation of the Mediterranean. Except in certain limited areas such as the Gibraltar region, the Strait of Messina, the Gulf of Gabes, the North Adriatic and at Bosphorus and the Dardanelles, the tidal amplitudes are small by world ocean standards. This, together with the existence of narrow continental shelves, results in very little tidal amplification along the Mediterranean coasts. Thus, as far as the net circulation is concerned, the tidal movements themselves generate very little net motion and are not considered as contributing to the net circulation. Particularly poorly flushed regions include the N. Adriatic and the Saronikos Gulf.

The Mediterranean circulation pattern has some stationary general features, but with noticeable seasonal variability. The winter pattern of the circulation has been obtained by using geostrophic calculations by Ovchinnikov (1966) and a numerical model by Gerges (1976, 1977). The principal features of the winter circulation as obtained by both authors, as well as by previous investigators who used the distribution of the hydrographic properties of the different water masses (e.g. Nielsen, 1912; Lacombe and Tchernia, 1960 and 1972; Wüst, 1961), indicate a general eastward flow along the north African coast, then a flow along the shore of Asia Minor into the Aegean and back to the Western Mediterranean as a general westward flow. The summer pattern is shown in Fig. 2.

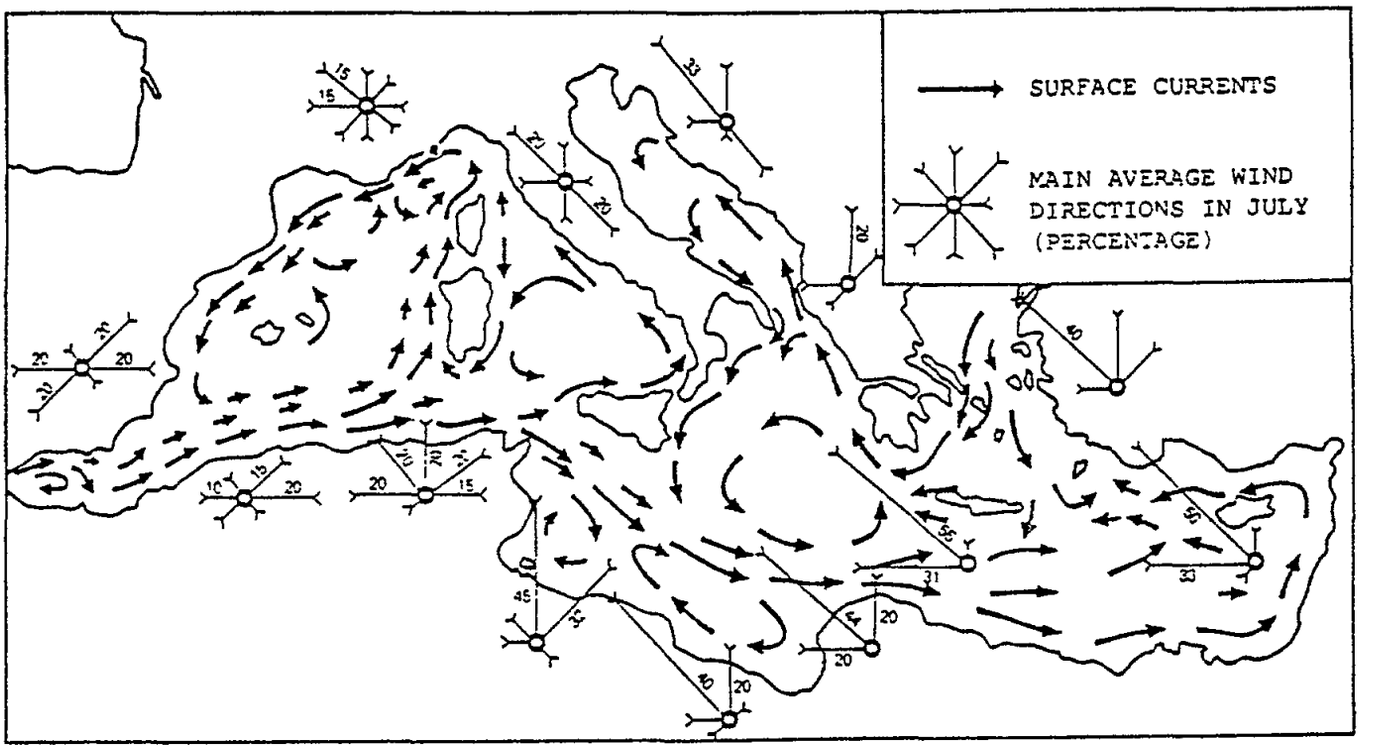

Fig. 2 Surface and main winds in the Mediterranean in summer (from Lacombe and Tchernia, 1972).

According to Gerges (1977), the velocities of the surface drift currents range from 15 to 30 cm sec^{-1} and have a general cyclonic direction. Due to the narrowness of the Gibraltar Strait, the velocities of the drift currents in this region are weaker (5-10 cm sec^{-1}). Greater velocities are noticed in the Ionian Sea, where values exceeding 35 cm sec^{-1} are indicated.

In addition, the existence of some interbasin scale features has also been confirmed, e.g. the cyclonic features between Cyprus and Crete and between Crete and Cyrenaica. Another cyclonic feature is dynamically reminiscent of the Alboran anticyclone (Hopkins, 1983a). These features of gyratory motions are of particular importance, since in some other ocean areas, such as the Sargasso Sea, gyres of the surface circulation tend to accumulate floating tar (IOC, 1981). Thus, one might expect that higher concentrations of oil will be observed in the areas where gyres are usually the dominating features.

This general surface circulation of the Mediterranean has in fact much greater detail, particularly in the coastal areas. Moreover, it is also well known that the summer surface flow is more complex owing to more diverse and smaller-scale wind regimes. The increased complexity in summer is often manifested in smaller gyre-like flow cells; for example, the Tyrrhenian may have several summer cyclonic surface features but one basin-wide winter cyclone (Hopkins, 1983b). However, the principal features of the Mediterranean surface circulation as described by Ovchinnikov (1966) and Gerges (1976, 1977) are generally valid.

Dispersal systems such as those discussed do not remove the pollutants from the environment but only redistribute them into the various reservoirs or compartments. An important point to be stressed here is that during transport, petroleum can be chemically fractionated by partitioning into the atmosphere, surface microlayer, water column (dissolved and particulate phases), sediment and biota, depending on the volatility, solubility and adsorptive properties of the components.

Selective chemical compositional changes of oil can also occur during weathering, both as a result of microbiological degradation and processes such as atmospheric oxidation. In the late sixties it was believed that degradation processes were the main answer to the question of the ultimate fate of oil spilled at sea. However, it was demonstrated later that they are usually slower than the disappearance of the oil from the sea surface, although both mechanisms are interrelated.

Although it is difficult to assess the relative importance of the above processes in the ultimate fate of petroleum hydrocarbons in the Mediterranean, some estimates are given in Table VII.

Evaporation removes the most volatile fractions of the spilled oils which contain a large portion of the acutely toxic volatile aromatic hydrocarbons. These fractions compose 20 to 50% of most crude oils and 10% or less of residual fuel-oils. Several mathematical models have been developed to give a quantitative description of this process (Butler, 1975). An average loss to the atmosphere of 30% of spilled oil inputs and 10% of land-based residues can be estimated, taking into account the particular hydrogeographical conditions of the Mediterranean. Recent studies have shown the air/sea exchange route to be the only route of importance for volatile hydrocarbons in seawater, compared to other possible sinks such as particle adsorption and sedimentation (Gschwend et al., 1982).

Tar formation from oil residues followed by stranding on shores has been estimated to occur for approximately 30% of spilled oil in the Mediterranean US Natl. Acad. Sci., (1975). This is higher than in the open ocean because of the increased probability of suspended tar contacting shores in an enclosed sea.

Table VII

Outputs of hydrocarbons in the Mediterranean
(10^3 tonnes per year).

Process	Estimate
Evaporation	125
Tar formation and stranding	100
Sedimentation	230
Biodegradation and biological uptake	180
Total	635

Nevertheless, although petroleum tars are currently found on beaches, long-term buildup concentrations have not been reported; this indicates that degradation of stranded tar occurs and that coastal stranding is not the only removal mechanism of the pelagic residues. Blumer et al. (1973) found that in temperate climates the oil remaining on a beach retained, after one year, practically all of the original hydrocarbons above n-C_{22} (b.p. 320°C). Whether the ultimate fate of petroleum residues is due to biodegradation (in water and sediment) or sedimentation (burial) remains to be determined.

Sedimentation rates have been estimated from a long-term sediment trap experiment conducted off Monaco in the Western basin (Burns and Villeneuve, 1983). The rate reflects the situation of coastal waters but probably is an underestimate for estuaries where sedimentation is enhanced and substantial accumulation of petroleum in sediments has been noted (Albaiges et al., 1985). The processes occurring during sedimentation and particularly the mediation of biological faeces have also been investigated but will be discussed in another section.

On the basis of the lack of positive evidence of large scale petroleum accumulation in the Mediterranean, except in areas where petroleum inputs are large, we can state that biodegradation accounts for the disappearance of the remaining residues. As estimated in Table VII, this is one of the major output pathways.

The Mediterranean is a warm sea with bottom water temperatures above 10°C even in winter (Lacombe and Tchernia, 1972). Given favorable conditions, micro-organisms will degrade 50% or more of crude oil (Bayona et al., 1986). Microbial degradation greatly depends on the degree of dispersion of oil in water, hence, biodegradation becomes the preferential process by which dissolved hydrocarbons are removed from the sea (Button, 1976).

Outputs to adjacent bodies of water are considered to be insignificant for the flux calculations, since the levels of petroleum residues are low in subsurface waters (Ho et al., 1983), i.e. those that are generally exchanged into adjacent water masses.

4. CONCENTRATIONS OF PETROLEUM HYDROCARBONS IN THE MEDITERRANEAN

The number of reported data on hydrocarbon concentrations in water and on beaches has been steadily increasing during the last 10 years, mainly as a result of the activities generated by the projects MED POL I (Baseline studies and monitoring of oil and petroleum hydrocarbons in marine waters, UNEP and MAPMOPP IOC/WMO IGOSS Marine Pollution Monitoring Pilot Project). In this respect, the availability of reference methods (UNESCO, 1982 and 1984) and the training facilities provided to the participating laboratories were of much importance. MED POL - PHASE II is yielding data obtained from laboratories which have participated in intercalibration exercises and which are using reference methods for sampling and analysis.

Comparatively little is known about the occurrence of hydrocarbons in benthic sediments, probably because of the later issue of a reference method (UNESCO, 1982) and the greater complexity involved in the determination. The information is even lower with respect to levels in marine biological samples, where a reference method has not yet been adopted.

The first large survey was devoted to the evaluation of pelagic tars and dissolved/dispersed hydrocarbons in open water. After the cruise by the R/V Atlantis II in 1969 (Horn et al., 1970), the region was surveyed in 1975 by the R/V Westward (Morris et al., 1975; Zsolnay, 1979), in 1975 and 1977 by the R/V Cornide de Saavedra (Faraco and Ros, 1979; Ros and Faraco, 1979) and in 1978 by the R/V Meteor (Ehrhardt, unpublished data). Unfortunately, the large survey undertaken by the R/V Calypso in 1977-1978 (Cousteau, 1979) was only focussed on metals and organochlorinated compounds.

Since then, monitoring programmes in several mainly coastal areas are under way, involving dissolved/dispersed hydrocarbons, surveys of tar on beaches and petroleum hydrocarbons in sediments and marine biota. The Western Mediterranean basin has been more extensively studied than the Eastern. The coasts of the Western Mediterranean are the most potentially affected by pollution due to the major concentration at its boundaries of urban populations, industrial activities and river discharges (UNEP, 1977).

The available data are presented in Tables VIII to XII.

Analytical techniques and quality assurance studies

The large number of analytical measurements performed in a regional monitoring programme and the participation of several laboratories necessitate the existence of a common basis for comparing data, so that they can be integrated into a coherent data set. At present, there are several difficulties, some arising from the analytical methodologies themselves and others derived from the limited knowledge on the comparability of hydrocarbon data from the various laboratories of the area.

From a methodological point of view, it should be considered that petroleum hydrocarbon contains a large suite of molecular types of hydrocarbons (namely saturated and unsaturated aliphatic, aromatic and heteroaromatic) which require elaborate protocols for their isolation and analysis. Hydrocarbons are also supplied by other sources, such as coal-tars and combustion products, each one contributing with characteristic compounds or mixtures of compounds. Finally, the marine environment also contains a variety of biogenic hydrocarbons related to the primary productivity which are

particularly abundant in the surface waters of the coastal zones. Therefore, it is practically impossible to select any one technique suitable for the analysis of all hydrocarbon types in all matrices. Excellent reviews have been published, enabling laboratories to select the most appropriate methods (Farrington et al., 1980; Clark and Brown, 1977). In this respect there is some controversy about which methodology to use in order to assess petroleum contamination. Some advocate simple, rapid and less discriminatory analytical methods for survey type monitoring (e.g. UV-fluorescence), while others advocate sophisticated and more specific methods for measuring a suite of indicator compounds (e.g. COM-GC-MS), although usually economic considerations and the availability of trained personnel are the major constraints in such studies.

Another difficulty arises from the variety in quantification methods. Although a description of recommended techniques for measuring oil in water and beaches is given (UNESCO, 1984), results of beach tar for example are expressed sometimes in units of weight $area^{-1}$ and sometimes in weight $meter^{-1}$ of beach line. Concentrations of petroleum hydrocarbons measured by UV-fluorescence are often reported in terms of chrysene equivalents or in crude oil units. Sediment and biological tissues can be analyzed fresh or dried and consequently the results can be reported on a wet or dry weight basis. When GC analysis is carried out, there is a large suite of parameters through which to assess petroleum pollution (n-alkanes, pristane, UCM, PAHs etc.).

On the other hand, the frequency distribution of any data set for a given area is very variable. The possibility should be considered not to publish the data until a sufficiently large number of samples allows an adequate statistical analysis for the assessment of spatial and temporal variations.

The problem of data quality control must be seriously considered. One method to increase quality control is through the participation of laboratories in intercomparison exercises. Ideally, an intercomparison exercise should be conducted with a specified method applied to reference material that has been certified to contain a known amount of constituents of concern. These materials are not available for petroleum hydrocarbons, because of the complexity in defining and quantifying the analyte.

Alternatively, interlaboratory comparison exercises may be performed using field samples (sediment or tissue homogenates) that have been collected in sufficient quantities to permit wide distribution and homogenized as well as possible. In addition, the fact that analysts carry out a common exercise, comparing their individual methods and discussing analytical differences in order to investigate their sources, will guarantee the validation of data on a regional basis. This is absolutely necessary when the component to be analyzed is sea water, because of the difficulties in distributing samples.

Very recently, several laboratories in the region had the opportunity to participate in different exercises concerning hydrocarbons in water (DDPH), sediment and biota.

In November 1984, an intercalibration exercise for oil and petroleum hydrocarbons was held in Barcelona (IOC/CSIC/UNEP/MED CAL I) following a recommendation of the Working Group for Scientific and Technical Co-operation for MED POL (Athens, 21-25 November 1983). The participants in the exercise came from 9 countries.

Each laboratory group made an analysis for DDPH in water samples collected in a fairly polluted area, following the procedure given in M/G No. 13 (UNESCO, 1984). Measurements gave a concentration of 1.65 ug l^{-1} of chrysene equivalents (excluding two outliers) with a 33% relative standard deviation (RSD), which was considered satisfactory for this level of concentrations. In a similar exercise held in Bermuda (December, 1984), a 60% RSD was obtained for measurements at much lower levels (0.057 ug l^{-1}). The method is indeed very sensitive, so that the problem of blanks must always be carefully checked. In 1986 a similar intercalibration exercise was repeated in Barcelona with 11 participants, also with a satisfactory result.

Although there is a question about the meaning of measurements in the open ocean samples, as fluorescence is not only related to the occurrence of petroleum hydrocarbons but also to other biogenic compounds, the method is adequate for "hot spot" determinations. In addition, the scanning of the whole spectra in the normal or synchronous modes provides useful information about the hydrocarbon sources (Solonas et al., 1982).

During the IOC-CSIC-UNEP exercise (1984) a freeze-dried and sieved (250 um) sediment sample was also analyzed following the procedure given in M/G No. 11 (UNESCO, 1982). Total n-alkanes and the unresolved complex mixture (UCM) were calculated by GC, aromatic hydrocarbons by UV-fluorescence. The precision of the results improved from total n-alkanes (RSD=70%) to UCM (RSD=45%) and to total aromatics (RSD=26%), which is consistent with the degree of difficulty in sample handling and analysis. Obviously GC analysis, especially with capillary columns, permits known individual compounds to be quantified, thus eliminating many of the ambiguities arising from UV-fluorescence, although at the expense of precision. Notice however that even though the method involves a chromatographic separation, the precision of the results obtained for aromatic hydrocarbons using UV-fluorescence is of the same order of magnitude as that of hydrocarbons in water.

Finally, twelve laboratories (6 from France, 3 from Spain and one each from Monaco, Malta and Cyprus) participated in 1984 in the ICES/IOC Intercomparison Exercise for hydrocarbons in biological tissue, performed on a freeze-dried mussel homogenate sent to each laboratory by the Bermuda Biological Station.

The number of laboratories was rather low if we take into account the fact that 129 laboratories which could carry out analytical chemistry were contacted. It is interesting to note that none of the laboratories used GC-MS. Although in this case no particular method was suggested, the results reported had a confidence limit of about 80%, which was not very different from that reported by other participating regional groups.

However, these variation coefficients should serve as a warning against overinterpretation of measurements when designing and interpreting results of any future pollution monitoring programme.

The lack of uniformity in reported data, the differences in sampling frequencies in different areas and the quality control of data generated by the different monitoring programmes are some of the questions that require further attention. Finally, a major training effort will be required in the Mediterranean region to ensure a widespread participation of laboratories in a petroleum monitoring programme.

Dissolved/dispersed petroleum hydrocarbons (DDPH)

Results of MAPMOPP in the Mediterranean Sea

The results of MAPMOPP have been reported in the IOC Report "Global Oil Pollution" (IOC, 1981). The data base consisted of 465 values, mainly concentrated in the eastern and central basins. Concentrations were generally between 0 and 5 ug l^{-1}, although a small number of values exceeded 10 ug l^{-1}. The overall arithmetic mean was 2.0 ug l^{-1}, however this is not an appropriate indicator of central tendency when populations are highly skewed, as in this case. The frequency distribution after a logtranformation of the data suggested the presence of two different groups, one comprising samples with concentrations less than 0.4 ug l^{-1} and a second with higher concentrations. Geometric means of 0.04 and 2.0 ug l^{-1} provided acceptable estimates of central tendency for these populations (Table VIII).

A possible interpretation is that the lower values represent the background level of DDPH in the region, whereas the higher group indicates recent inputs of petroleum which had not yet become diffused. Another possibility is that of an artifact arising from the procedures used to obtain the data. However, the more heavily polluted samples came from the eastern region along the tanker routes (Table VIII). Contamination levels in the western Mediterranean were lower, although there were insufficient samples for a meaningful statistical analysis. Despite the uneven sampling coverage of the whole area it is apparent that the levels found in the Mediterranean were significantly higher than those reported for other oceanic regions (Table VIII). With the entering into force of the International Convention for the Prevention of Pollution from Ships (1973), as modified by the Protocol of 1978 (MARPOL 1973/78), this picture is likely to improve gradually.

In the following section an extended list of DDPH data is shown, particularly for areas that were not covered well by MAPMOPP. However, the following preliminary assessment can be made on the basis of the concentrations reported so far.

Taking into account that the Mediterranean has:

(i) a surface of 2.96×10^6 square kilometers,
(ii) a yearly input of 0.6 million tonnes of petroleum hydrocarbons (Table VI),
(iii) that most of the input occurs in the nearshore areas (Table VI),
(iv) the mean residence time in the top 100 metres is one year Burns et al., 1985),

we can reach an estimate of the order of 0.2 ug l^{-1} of total petroleum compounds for the top 100 metres of the open Mediterranean.

Errors in these assumptions which could change the estimate by one or more orders of magnitude are highly unlikely, so that any values exceeding this level in offshore areas should be considered cautiously since they are likely to represent either contamination in sample handling or a contribution by fluorescing biogenic compounds.

Western Mediterranean

The concentrations of dissolved/dispersed petroleum hydrocarbons in this part of the Mediterranean have been obtained from a number of cruises. Samples collected nearshore frequently show concentrations above 10 ug l^{-1}, particularly if they were taken close to industrialized areas or river mouths (Table IX).

Table VIII

Concentrations of dissolved/dispersed petroleum residues in the Mediterranean (n = number of values; c = arithmetic mean; s = standard deviation; G.M. = geometric mean). All values in ug l^{-1} (IOC, 1981).

Region	Normal statistics			Logtransformed data	
	n	c	s	n	G.M.
Mediterranean	466	2.0	5.0	462	0.33
0.4 ug l^{-1}	219	0.07	0.08	215	0.04
0.4 ug l^{-1}	247	3.7	6.4	247	2.0
Aegean Sea	134	1.3	0.79	134	1.1
Eastern Region	133	5.5	8.3	131	1.5
0.4 ug l^{-1}	29	0.04	0.06	27	0.03
0.4 ug l^{-1}	104	7.0	8.8	104	4.0
Central Region	176	0.17	0.42	175	0.06
0.4 ug l^{-1}	156	0.07	0.07	155	0.05
0.4 ug l^{-1}	20	1.0	0.86	20	0.77
Western Region	22	0.02	0.01	22	0.02
Baffin Bay	104	0.11	0.12	93	0.09
Indian Ocean	45	60.1	92.7	36	8.09
Japan	1666	0.31	1.21	1640	0.13
North Am. East Coast	80	0.10	0.10	71	0.09
North Sea	90	0.02	0.12	9	0.15
South China Sea	272	0.20	0.28	256	0.10
Strait of Malacca	14	0.11	0.12	10	0.13

From the Spanish coast between Castellon and Cartagena results have been reported from sampling along nine transects (De Leon, pers. comm.). This study showed concentrations between 0.06 and 8.26 ug l^{-1} as mean values at each station. In Mar Piccolo, Taranto, Italy, concentrations ranging from 0.1-36 ug l^{-1} have been reported (Strusi, pers. comm.). Mean values are 3.26, 7.42 and 7.98 ug l^{-1} from three sampling occasions. More precise determinations (GC) were carried out during the PHYCEMED cruises (Ho et al., 1983; Sicre et al., 1985). Concentrations of petrogenic hydrocarbons ranged between 1.1 - 4.5 ug l^{-1} for the aliphatic fraction and 0.1 - 0.8 ug l^{-1} for the aromatic one. During these cruises, relevant information was obtained on the accumulation of hydrocarbons in the air-seawater interface. Enrichment factors up to 50 were observed in the surface microlayer (Sicre et al., 1985), although the effect was more evident for the biogenic hydrocarbons. Table X summarizes the information obtained in this study and it can be compared with that reported in Table IX for the same area. Few or no values are available from countries along the North African coast.

Adriatic

Results of the analysis of water samples are reported in Table IX. Most of these studies have dealt with the Rijeka Bay area, although recently data from Sibenik and Split have also been obtained. Concentrations from these areas range from 0.1 ug l^{-1} or below in unpolluted zones, to 50 ug l^{-1} in polluted parts.

Central Mediterranean

The only concentrations reported from sampling offshore are those reported by Monaghan et al. (1974). From nearshore areas (Libyan coast) Gerges and Durgham (1983) report concentrations between 0.6 and 28 ug l^{-1}. The highest values (10 - 28 ug l^{-1}) are reported from areas far from major industrial activities. Similar concentrations ranging from 0 (unpolluted) to 27.6 ug l^{-1} (polluted) were reported in a study carried out by the Marine Fisheries Research Center, Tripoli (MFRC, 1981). From the coastal waters around Malta, concentrations between 0.02 and 0.29 ug l^{-1} have been reported (UNEP, 1980).

Table IX

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Western Mediterranean (offshore)				
Northern part	1973	10-2200 (surface) (av. 450)	Fluorescence	Monaghan et al., 1974
		3-37 (10 m) (av. 15)	"	"
	1975-77	2-6 (surface) (av. 3.3)	"	Faraco and Ros, 1979
	1981	1.5-21.1 (surface)	GC-n-alkanes -UCM	Ho et al., 1983
		3.5-4.6 (surface)		"
		0.5-0.8 (chr. eq.)	Fluorescence	"
	1983	1.9 (surface)	GC-n-alkanes -UCM	Sicre et al., 1985
		1.3 (surface		"
Central part	1981	0.33 (chr. eq.)	Fluorescence	Ho et al., 1983
	1983	0.68 (surface)	GC-n-alkanes -UCM	Sicre et al., 1985
		1.37 (surface)		"

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Western Mediterranean (offshore)				
Southern part	1973	2-17 (surface) (av. 8.5) 2.7 (10 m)	Fluorescence	Monaghan et al., 1974
	1974-75	av. 6.9 (surface)	"	Zsolnay, 1979
	1975-77	1-123.5 (surface (av. 17.5)	"	Faraco and Ros, 1979
	1981	0.23 (surface) 0.81 (surface) 0.078-0.2 (chr. eq.)	GC-n-alkanes -UCM Fluorescence	Ho et al., 1983 " "
	1983	0.31 (surface) 1.15 (surface)	GC-n-alkanes -UCM	Sicre et al., 1985 "
Alboran Sea	1975-77	4.3-14.6 (surface) (av. 7.9)	Fluorescence	Faraco and Ros, 1979
	1981	0.2 (chr. eq.)	"	Ho et al., 1983

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Western Mediterranean (nearshore)				
Spanish coast				
Castellon	1983	1.36-2.40	Fluorescence	De Leon, pers. comm.
Sagunto	"	0.06-3.40	"	"
Valencia	"	0.63-4.35	"	"
Cullera	"	0.06-3.10	"	De Leon, pers. comm.
Benidorm	"	0.60-0.26	"	"
Alicante	"	0.85-8.26	"	"
Guardamar	"	1.15-3.15	"	"
Portman	"	0.26-6.50	"	"
Cartagena	"	0.26.3.22	"	"
French coast	1975-78	50-5000 (av. 580)	IR	UNEP, 1980
Banyuls-sur-Mer				
Var Estuary	1981	0.4-1.0	GC-UCM	Burns and Villeneuve, 1983
Golfe de Fos	1983-84	30-200		MEDPOL Phase II
Golfe d'Ajaccio	1983-84	0-100		MEDPOL Phase II

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Italian coast				
Tyrrhenian Sea	1973	8-614 (surface) (av. 180) 3-19 (10 m) (av. 7)	Fluorescence	Monaghan et al., 1974
	1974-75	av. 4.8 (surface)	"	Zsolnay, 1979
	1975-77	1.9-20.5 (av. 7.4)	"	Faraco and Ros, 1979
Taranto, Mar Piccolo	1983	0.2-11.6 (av. 3.26)	GC	Strusi, pers. comm.
"	"	0.5-23.0 (av. 7.42)	"	"
"	"	0.1-36.0 (av. 7.98)	"	"

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Central Mediterranean				
South Ionian Sea	1973	3-423 (surface) (av. 58)	Fluorescence	Monaghan et al., 1974
		2-120 (10 m) (av. 16)	"	"
	1974-75	av. 14.9 (surface)	"	Zsolnay, 1979
Malta, coastal waters	1977-78	0.02-0.29	"	UNEP, 1980
	1984	0.03-1.70 (av. 0.51)	"	(MEDPOL Phase II-data)
Libyan coast	1974-75	av. 24.9 (surface)	"	Zsolnay, 1979
W. Sedra, Tripoli harbour Zawia	1980	20-28	"	Gerges & Durgham, 1983
Janzur, W&E. Brega, Zawia W. Khoms	"	12.5-19	"	"
Zlitan, Zwetina, Benghazi, E. Sirte, Tajura		4.6-5.3	"	"
Sabratha, Derma, Sidi Blal		0.6-2.9	"	"

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Libyan coast; 171 samples from coastal areas	1980	0.0-27.6 (av. 3.6)	Fluorescence	MFRC, Tripoli 1981
Adriatic				
Yugoslavia, Rijeka Bay	1976-77	1-50 100-1100 below 0.1	Fluorescence IR GC	UNEP, 1980 Ahel & Picer, 1979
" "	1976-78	1-7 ("polluted") 0.2-0.5 ("unpolluted")	Fluorescence "	Ahel, 1985
Yugoslavia, Sibenik area	1984	0.2-16.4 (av. 1.4)	"	(MED POL Phase II - data)
Yugoslavia, Split	1984	av. 24.9 (surface)	"	" "
Eastern Mediterranean				
Aegean Sea	1974-75	av. 20.5	Fluorescence	Zsolnay, 1979

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Greece				
Coastal waters		below 3	Fluorescence	Mimicos, 1981
Saronikos Gulf	1980-81	1.6-5.6	"	Gabrielides et al., 1984
Aegean Sea	"	2.9-13.7	"	"
Thessaloniki harbour	1976-79	1500	IR	UNEP, 1980
Cavala harbour	"	2600	"	"
Strymonikos Bay	"	1100	"	"
Patraikos Gulf	1977-83	0.12-28.2	Fluorescence	Mimicos et al., 1985
Acheloos River estuary	"	1.3-4.5	"	"
Turkey				
Mersin-Akkuyu	1977-78	8.2-39.4	"	UNEP, 1980
Southern coast	1980-82	0.5-3.5 (av. 1.5)	"	Sunay et al., 1983
Offshore between Turkey and Cyprus	1980-82	2.0-6.0	"	Sunay et al., 1983
Iskenderun Bay	"	0.7-7.0	"	"
Sea of Marmara	1983	0.88 (max. 8.07)	"	Sakarya et al., 1985
Izmit Bay	"	0.75-5.0	"	"

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Aegean Sea	1983	0.14-1.39	Fluorescence	Sakarya et al., 1985
Mediterr. coastal waters	"	0.02-1.1	"	"
Iskenderun Bay	"	0.11-1.0	"	"
Candarli Bay	1983-84	1.20-80.0	"	Topcu & Muezzinoglu, 1984
Aliaga	"	0.53-7.30	"	"
Saros Bay	1983	0.77	"	"
Izmir Bay	"	9.40	"	"
Southern Aegean Coast	"	0.86	"	"
Eastern Mediterranean				
Offshore, South of Cyprus, Southeast of Crete	1975-76	10-40	Fluorescence	UNEP, 1980
Israel				
Ashkelon	1975-76	9.4-19.4	"	"
Haifa Bay	"	15.0-15.6	"	"
Plamachin	"	10.7-12.5	"	"
Bardawil Lagoon	"	20.6	"	"
Tel Shikmona	"	1.1-45.3	"	"

Table IX (cont'd)

Dissolved/dispersed petroleum hydrocarbons (ug l^{-1}).

Area	Year	Concentrations	Technique	Reference
Egypt				
Alexandria	1978-79	0.7-35.2 (av. 3.7)	Fluorescence	Aboul-Dahab & Halim, 1981a
Alexandria	1979-80	6.6-41.4 (nearshore)	"	Wahby & El Deeb, 1981
		0.7-3.9 (offshore)	"	"
Mouth of Suez Canal	1980-81	0.5-14	"	El Samra et al., 1983
Cyprus, Limassol Bay	1983	2.6-8.1	"	MED POL - Phase II
	1984	1.15-1.48	"	"
Larnaca Bay	1983	4.2-13.6	"	"
	1984	1.74-2.53	"	"

Table X

Hydrocarbons in the surface microlayer.

Area	Year	Concentrations (in ug l^{-1})		Technique	Reference
off-Monaco	1981	6.0 - 11.4	(n-alk)	GC	Burns and Villeneuve, 1983
		23 - 61	(UCM)*	GC	
		4.3 - 4.9	(arom.)	GC	
North Western basin	1981	1.0 - 13.48	(n-alk)	GC	Ho et al., 1983
		8.11- 22.1	(UCM)	GC	
		0.26- 0.35	(arom.)	UV-fl.	
	1983	0.55	(n-alk)	GC	Sicre et al., 1985
Central Western basin	1981	0.69	(n-alk)	GC	Ho et al., 1983
		6.8	(UCM)	GC	
		0.70	(arom.)	UV-fl.	
	1983	0.96	(n-alk)	GC	Sicre et al., 1985
South Western basin	1981	0.57	(n-alk)	GC	Ho et al., 1983
		0.25 - 5.15	(arom.)	UV-fl.	
	1983	1.67 - 1.86	(n-alk)	GC	Sicre et al., 1985
Alboran Sea	1983	1.4	(n-alk)	GC	Sicre et al., 1985

* UCM : unresolved complex mixture.

Values ranging from 0.1 to 2.6 ug l^{-1} are reported from Greek coastal waters (Table IX), while concentrations in the range 1 to 2.6 ug l^{-1} were reported from harbour areas and were measured with infrared spectroscopy. However, some studies in areas quite far from major land-based industrial activities, such as off-shore in the Aegean Sea, show concentrations exceeding 10 ug l^{-1}. Sakarya et al., 1985 reported values between 0.14 and 1.39 ug l^{-1} from the Aegean Sea.

From Turkish waters, data ranging from 0.02 to 40 ug l^{-1} are reported (Sunay et al., 1983 ; Sakarya et al., 1985). Concentrations of around 1.5 ug l^{-1} are reported from coastal waters southwest of Mersin (Sunay et al., 1983). However, the same authors report concentrations of 2.0 to 6.0 ug l^{-1} from off-shore areas between Turkey and Cyprus. Concentrations up to 7.0 ug l^{-1} were reported from the industrialized Iskenderun Bay (Sunay et al., 1983). Sakarya et al., 1985 reported concentrations ranging between 0.11 and 1.0 ug l^{-1} from the northeastern Mediterranean coast off Turkey.

Concentrations between 10 and 20 ug l^{-1} have been reported from areas close to harbours, oil refineries, river mouths, etc. in Israel. High concentrations of dissolved hydrocarbons were found south of Cyprus (25 - 40 ug l^{-1} and southeast of Crete (10 to above 40 ug l^{-1}), although more recently concentrations ranging between 2.6 and 8.1 ug l^{-1} were reported from Limassol Bay, Cyprus and levels from 4.2 to 13.6 ug l^{-1} from Larnaca Bay, Cyprus, (unpublished report to IOC, 1984). This is another situation where an offshore contamination by ship traffic may have occurred.

Several reports are available on the oil contamination of coastal waters off Egypt (Aboul-Dahab and Halim, 1981,1981a; Wahby and El Deeb, 1981; El Samra et al., 1983). Concentrations up to 30-40 ug l^{-1} have been reported in areas influenced by various industrial activities (Aboul-Dahab and Halim, 1981, 1981a; Wahby and El Deeb, 1981). The same authors report concentrations below 10 ug l^{-1} and usually below 5 ug l^{-1} in offshore waters. One study of the petroleum hydrocarbon content of the waters reaching the Mediterranean from the Suez Canal has been reported by El Samra et al., 1983. This study showed that the water contained 0.5 - 14 ug l^{-1}.

However, some noteworthy observations can be made . Zsolnay et al. (1978) report that the concentrations of aromatic hydrocarbons in Baltic Sea water are almost twice as high as those in the Mediterranean and almost 10 times higher than in the northwest Atlantic, including the Sargasso Sea.

By contrast, the Mediterranean is reported to be more heavily polluted with surface-floating tar balls than the Baltic and the northwest Atlantic . It would seem that there is little or no correlation between the quantity of tar derived from oil spills (and, by reference, the quantity of oil spilled) and the degree of contamination by DDPH. Indeed Zsolnay et al. (1978) and Faraco and Ros (1979) found no such correlation in a group of samples taken throughout the Mediterranean. This can be explained if we assume that dissolved hydrocarbons are derived from coastal industrial and municipal waste discharges, whereas pelagic tars are derived from tanker ballasts. However, another possibility is that dissolved hydrocarbons are leached out during initial deposition of tarry materials in the marine environment and their subsequent accumulation and transport then depends on different factors, including currents and concentration of other substances with which the materials interact. Currents partly driven by winds are the main transport actions for the surface layer materials.

Oil slicks, floating tar and tar on beaches

As a part of the MAPMOPP (IOC/WMO Marine Pollution Monitoring Pilot Project) visual observations of oil slicks were carried out from ships (IOC, 1981). Position, date, time and slick size were noted for observed slicks. Since it is as important to know which areas are not polluted as it is to know which ones are, a report was made during each 24-hour period, even if no pollution was observed. In the Mediterranean, surface slicks were present in more than 10% of the observations almost throughout the region. These data compared with MAPMOPP results from other regions provide evidence of relatively extensive surface pollution in the Mediterranean.

Available data on pelagic tar from the Mediterranean (Table XI) show that between 1969 and 1983 mean concentrations in the Mediterranean ranged from 0.5 to 130 mg m^{-2} and that the Ionian Sea was the most tar polluted area in the Mediterranean Sea. The data also suggest that normal values for offshore areas are up to 5 mg m^{-2}, while in nearshore waters, concentrations can be much higher and range between 10 and 100mg m^{-2}.

The data also suggest that the eastern basin was the relatively most heavily contaminated by this pollutant source, although some indication of an improving situation was observed during the last ten years. Confirmatory evidence of the nature and sources of these floating tars (tanker deballasting waters) has been obtained (Torrados and Albaiges, 1978).

The data on tar on Mediterranean beaches show considerable variation and mean quantities were found to range between 0.2 and 4388 g m^{-1} (Golik, 1986).

On the basis of geographical considerations, it seems that the areas in the Mediterranean where deballasting of oil waters and release of oily compounds into the sea were permitted until 1978 were areas of tar contamination. However, measurements of pelagic tar conducted after 1980 indicate that there may have occurred a reduction in tar quantity especially in the Eastern Mideterranean during the past few years.

Measurements on tar on beaches in Cyprus and in Israel conducted during a 10-year period (Golik, 1985; Demetropoulos, 1985) suggest a similar reduction of the quantities of tar in the Eastern Mediterranean. These findings show a drastic decrease in the amount of tar on beaches.

Table XI

Pelagic tar in the Mediterranean Sea (mg m^{-2}) (Golik, 1986).

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 & 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	Benzhitsky A.G. and G.G. Polikarpov, 1974
	1974-75	0.1 -27.9	0.5	0.4	Morris et al., 1975
North	1975-77	0 -77.7	5.4	1.06	Ros & Faraco, 1979
South	1975-77	0.05 -26.8	3.9	1.18	Ros & Faraco, 1979
	1981-82		3.6	0.63	De Armas, 1985
Tyrrhenian Sea					
	1969		1.5		Horn et al., 1970
	1972-73		4.7		Benzhitsky A.G. and G.G. Polikarpov, 1974
	1974-75	0.2 -14.7	3.2	1.4	Morris et al., 1975
	1975-77	0 -10	0.9	0.3	Ros & 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					
	1970-71	0 -58.3	5		El Heyawi, 1979
	1977-79	0.2 -1.33**			Wahby & El Deeb, 1981
	1978-79	0 -8.91	2.82		Aboul-Dahab & Halim, 1981a.
NE Mediterranean					
	1983-84	0 -33.4			Saydam et al., 1985

** mg m^{-3}

Petroleum hydrocarbons in sediments

The application of the concept that sediments represent a sink for some pollutants and hydrocarbons among them has only recently been attempted in the Mediterranean. Studies have been conducted primarily in the Western basin (Mille et al., 1982 and 1983) (Table XII).

Along the French coast between Fos-sur-Mer and Monaco, Mille et al. (1983) reported concentrations of aliphatic and aromatic hyrdocarbons ranging between 20 and 950 ug g^{-1}. The highest concentrations were found outside a refinery.

Comparable results have been reported by Albaiges et al. (1983) in sediments collected along the Spanish coast outside harbours, oil terminals and river mouths (1-62 ug g^{-1} of aliphatics and 2 - 66 ug g^{-1} of aromatics). In order to get some insight into the sources of these hydrocarbons, the extracts were analyzed for individual components by GC-MS. Levels of pyrolytic-like PAHs range from 0.3 to 2.3 ug g^{-1} dry weight. These concentrations are also similar to those reported by Mille et al. (1982) and Burns and Villeneuve (1983) (0.6 - 0.7 ug g^{-1}) for the French coast. Two samples collected in the central part of the Western basin provided information about the background levels of petrogenic hydrocarbons for the area (1.2 ug g^{-1} of aliphatics, and 0.6 ug g^{-1} of aromatics).

In Mar Piccolo, Taranto, Italy, average concentrations of 14.7 ug g^{-1} aliphatic and aromatic hydrocarbons were found at 8 stations at depths from 1 to 10 metres (Strusi, 1984). Similar results have recently been reported for the Yugoslavian coast.

From the eastern Mediterranean, results are available from Cyprus and Turkey. From Cyprus concentrations of 0.114 to 1.35 ug g^{-1} are reported in sediment samples collected at 90m depth. From Iskenderun Bay, Turkey, average sediment concentrations of 0.24 ug g^{-1} were reported by Sunay et al. (1983). The samples were collected at 10 to 90 metres depth and the range of concentrations was 0.04 - 0.68 ug g^{-1}. Recent measurements in Turkish waters have shown very low levels of petroleum hydrocarbons (Table XII).

In general, the hydrocarbon concentrations encountered in the area indicated a moderate contamination compared with other sites for which petroleum contamination has been assessed (2 - 1200 ug g^{-1} for the New York Bight and 45 - 730 ug g^{-1} for the California Bight). Nevertheless, the use of sediments for monitoring programmes of coastal zones looks promising for the recognition of land-based pollutant sources and particulary of "hot spots".

Petroleum hydrocarbons in organisms

Few studies have been carried out on the uptake of petroleum hydrocarbons in organisms from the Mediterranean. From the Spanish coast analyses of samples of fish and molluscs, collected from the mouth of the river Ter and south to the Ebro delta, have been reported by Albaiges et al. (1983); Ballester et al. (1982); Albaiges et al. (1985a); and Risebrough et al. (1983).

Risebrough et al. (1983) used the technique employed in the Mussel Watch project in a study of petroleum hydrocarbons in molluscs from the Ebro delta. Mussels (Mytilus galloprovincialis), oysters (Ostrea edulis), and clams (Venus gallinae) were selected as the indicator organisms. Petroleum hydrocarbons were measured on the basis of the unresolved complex mixture (UCM) in the chromatograms of the saturated and aromatic fractions. The levels found were generally in the order of 100 - 300 ug g^{-1}. These concentrations were equivalent to those in mussels in the most polluted harbours and bays in California.

In another study by Albaiges et al. (1983), relatively high concentrations of petroleum hydrocarbons were found in bivalves from the same area (190 - 215 ug g^{-1}) (dw)) (Table XIII). Pelagic fish showed lower concentrations in tissue samples (less than 10 ug g^{-1}). A study by Ballester et al. (1982) of mussels from a drilling platform in the Ebro river delta showed concentrations of up to 20-30 ug g^{-1} of n-alkanes.

Table XII

Petroleum hydrocarbons in benthic sediments.

Area	Concentrations (in ug g^{-1})					Reference
French coast						Mille, et al., 1982
(Fos sur Mer to Monaco) (1979)						
Côte Bleue	13	-952	aliphatics + aromatics			
Les Embiez	69	-93	"		"	
Monaco	51	-77	"		"	
Spanish coast (1980-1982)	0.6	-2.3	(D/w)	C_{14}-C_{20}	(GC)	Garcia-Regueiro, et al., 1983
off Valencia 3-10m (0-5cm)						
off Alicante	0.1	-5.8	(D/W)	D_{14}-C_{24}	(GC)	
off Delta del Ebro	0.3	-1.1	(D/W)	C_{15}-C_{24}	(GC)	
off other Catalan rivers - river mouths and cities	0.07	-0.56	(D/W)		(GC)	Sanchez-Pardo and Rovira, 1985
Ter river mouth (10-60m) (3 samples)	0.5	- 1.9	(D/W)	n-alkanes	(GC)	Albaiges et al., 1983 and 1985
	1.8	- 9.8		UCM		
	5.1	-10.1		aromatics		
off Barcelona (10-80 m) (9 samples)	1.3	-17.0	"		"	
	24.5	-52.8				"
	3.1	-66.8				
off Tarragona (17-95 m) (6 samples)	0.9	- 5.0	"		"	"
	4.8	-77.1				
	7.8	-21.2				
Ebro Delta (10-100 m) (5 samples)	0.4	- 3.2	"		"	"
	1.3	-12.9				
	0.6	-15.2				

Table XII (cont'd)

Petroleum hydrocarbons in benthic sediments.

Area	Concentrations (in ug g^{-1})		Reference
off Valencia (10-100 m) (5 samples)	0.8 - 1.0 (D/W) 3.8 -12.3 4.8 -26.0	(GC)	Albaiges et al., 1983 and 1985
off Benidorm (10-100 m) (2 samples)	0.8 - 0.9 (D/W) 1.9 - 4.0 2.8 - 5.5	(GC)	"
Western Mediterranean (1000 m)	1.2 - 1.6 " 0.6 - 2.3	UCM aromatics	"
Italy, Taranto, Mar Piccolo, 1983 8 stations (1-10m depth)	1.3-45 (av. 14.73) (D/W)		(Strusi, 1984, pers. comm.)
Yugoslavia, Split, 1984	1.0-18.9	Fluorescence	MED POL - PHASE II
Cyprus,			
Larnaca Bay, 1983 (90 m)	0.114-0.135 (4 samples)	"	"
1984	0.442-1.301 (4 samples)	"	"
Limassol Bay 1984 (18-90m)	0.308-0.417 (2 samples)	"	"
Turkey, Iskenderun Bay 1980-82, 10-9m depth	0.04-0.68 (av. 0.24 ug g^{-1}	PAHs (GC)	Sunay et al., 1983
Turkey			
Candarli Bay, 1983-84	0.0043-0.375 (fw)	Fluorescence	Topcu & Muezzinoglu, 1984
Aliaga, 1983-84	0.0175-0.025 (fw)	"	"
Saros Bay, 1983	1.0 (fw)	"	"
Izmir Bay, 1983	0.047 (fw)	"	"
Southern Aegean Coast, 1983	0.1575 (fw)	"	"

Petroleum concentrations of tissues of three species of fish (Mullus barbatus, Merluccius merluccius, Trachurus trachurus) have been reported by Albaiges et al. (1985). This study showed that baseline levels in muscle tissues for the area between Barcelona and the French border were 1.5 - 12 ug g^{-1} and 1.7 to 8.4 ug g^{-1} (dw) of saturated and aromatic hydrocarbons respectively. Higher concentrations were found in fish off Barcelona and the Ebro river. The results are summarized in Table XIII. In this study, it was also shown that hydrocarbons are largely accumulated in liver and in adult species.

From the data available it cannot be concluded that the higher concentration of petroleum hydrocarbons existing in the Mediterranean with respect to other oceanic areas has biological effects on pelagic fish. However monitoring of selected species is desirable.

Few studies of the petroleum hydrocarbon contamination of marine organisms from other parts of the Mediterranean are available. From the coast of Turkey, notably from Iskenderun Bay, a study of the concentration of PAHs in fish has been carried out (Sunay et al., 1983). The average concentrations in muscles and livers were 0.13 and 0.79 ug g^{-1}, respectively.

From Mar Piccolo, Taranto, Italy, a study has been reported on the levels of hydrocarbons in mussels (Strusi, 1984). The results, which are given as wet weight concentrations, range from 0.5 - 10.1 ug g^{-1} with an average of 2.7 ug g^{-1}. If these concentrations were to be transformed into dry weight figures, they could become roughly ten times higher.

Table XIII

Hydrocarbons in biota samples from the Spanish Mediterranean Coast (in ug g^{-1} dry wt) (Albaiges et al., 1983 and 1985).

Species	Area (year) fraction (UCM)	Saturate fraction (crude oil eq.)	Aromatic
Mytilus (10 samples)	Palamós	106- 190	-
	Barcelona	500-3200	-
	Ebro Delta	8- 216	-
Mullus sp.	Palamós	12.6	4.4
(muscle) (14 samples)	Barcelona	22.2	9.3
	Ebro Delta	5.8	11.1
Merluccius sp.	Palamós	1.5	1.7
(muscle) (14 samples)	Barcelona	0.2	3.9
	Ebro Delta	0.2	2.4
Trachurus sp.	Palamós	11.2	4.2
(muscle) (14 samples)	Barcelona	1.4	10.9
	Ebro Delta	5.4	3.7
Engraulis sp. (muscle) (19 samples)	Barcelona	7.7	7.8

5. DISTRIBUTION OF PETROLEUM HYDROCARBONS IN MEDITERRANEAN ECOSYSTEM COMPARTMENTS AND TENTATIVE MASS BALANCE ASSESSMENT

A considerable amount of data is available on the distribution of petroleum hydrocarbons in some environmental components of the Mediterranean. A critical point in any long-term monitoring programme is the management and interpretation of the data generated. Monitoring is not simply an exercise in data accumulation (Albaiges and Frei, 1982), but should be designed to answer specific questions. It should be coupled with concurrent research and, as new information becomes available, be adjusted accordingly.

An assessment of the information available requires an adequate knowledge of the biogeochemical processes controlling the transport and fate of petroleum residues introduced into the sea. This is why more recently attention has been focused on the investigation of these processes. Thus, in 1981 and 1983, the PHYCEMED cruises were concerned with the evaluation of the atmospheric budget of hydrocarbons in the Western Mediterranean and with the investigation of mechanisms of exchange of these materials across the air/sea interface (Ho et al., 1982 and 1983; Sicre et al., 1985).

The relative importance of these exchanges, as far as atmospheric deposition is concerned, is assessed in Table XIV. The atmospheric compartment, however, has been recognized not only as a source of hydrocarbons mainly derived from combustion, but also as a sink for those which are volatized from the petroleum discharged to the sea. This two-way flux across the air-sea boundary is difficult to measure but requires further investigation.

In addition, semi-permanent traps have been set up by the International Laboratory of Marine Radioactivity in Monaco (at 100 m depth in a 250 m water column, approximately 2 km off the Monaco coast) to obtain information on the downward flux of anthropogenic substances in the Ligurian Sea and particularly on the dominant processes controlling the transport to and retention of hydrocarbons in the sediment reservoir. These include biological uptake and concomitant faeces production, biological/chemical degradation and physical/chemical partitioning between marine compartments (Burns et al., 1985).

Table XIV

Estimated annual input of atmospheric hydrocarbons into the Western Mediterranean (Ho et al., 1983).

Transect (Fig. 6)	HCs	Deposition (mg $m^{-2}yr^{-1}$). wet	dry
a-b	aromatic	0.04 - 0.44	0.025 - 0.25
	total	1.67 -16.70	0.94 - 9.4
b-c	aromatic	0.05 - 0.5	0.03 - 0.3
	total	0.84 - 8.4	0.47 - 4.7

Table XV

Hydrocarbon fluxes at Monaco trap station
(Burns et al., 1983 and 1985).

Fluxes	Hydrocarbons (ug/ $m^{-2}yr^{-1}$)	
	Petroleum	Unresolved mixture
On zooplankton faeces	8.2-9.0	-
At 100 m (a)	0.8-1.0	0.6-0.9
At sediments (b)	0.9	0.8

a) estimated from sediment trap material
b) estimated from sedimentation rate and average sediment concentrations.

The quantitative importance of zooplankton faeces in transporting organic contaminants and particularly petroleum hydrocarbons into sediments was estimated by Burns et al. (1985), by computing pollutant flux based on analyses of residues in faeces and on estimates of faecal pellet production rates and average zooplancton biomass off Monaco. Average fluxes of the site (Table XV) were higher by a factor of six than those estimated for the Sargasso Sea (Sleeter and Butler, 1982).

On the other hand, Table XIV shows that although petroleum is relatively non-soluble and rapidly transported to depth on faeces at the site, only about 10% of the falling through the water column survives long enough to be incorporated into the sediments. This discrepancy implies rapid biodegradation of the majority of petroleum hydrocarbons delivered to these sediments. In this way, sediments incorporate the most refractory components which can be used as tracers for flux and mass balance assessment.

The chemical characterization of the different marine compartments (dissolved, particulate and sedimentary), through the application of the molecular marker concept, has been carried out to gain some insight into the input sources and their fate in the sea (Albaiges et al., 1984; Grimalt et al., 1985). Hydrocarbon inputs from domestic wastes, used oils, coal tars and fossil combustion were identified, providing evidence of urban run-off as the most important hydrocarbon input to coastal areas. PAHs are particularly abundant in sediments, thus being useful markers for establishing couplings between surface inputs, particle transport and sediment incorporation.

Residence times of hydrocarbons in surface waters were computed (by Burns et al., 1985) according to recent partitioning models and compared with those calculated from fluxes of settling particles and from sediment data (Table XVI). The agreement in flux rates calculated from faeces and sediment trap material suggests that the residence time of about 1 year is a reasonable estimate. The discrepancy with the calculation based on sediment concentrations again demonstrates the rapid rate of biological degradation at the sediment interface.

Table XVI

Estimated residence times of hydrocarbon residues in the top 100 m. of the Mediterranean water column (Burns et al., 1985).

Data base	Petroleum (years)
Surface particles and seawater conc.	0.6
Sediment trap material	1.0
Seawater and sediment conc.	10.5

Table XVII

Distribution of hydrocarbons in the ecosystem compartments. (in 10^3 tonnes $year^{-1}$).

Beach tar	100
Surface microlayer	0.018
Floating tar	8.8
Surface water (0-5 m)	30
Subsurface water	72
Sediment flocculent layer	230
Sediments	120
Biomass	0.220
Atmosphere	155
Total	716

These calculations imply that significant changes in the input of organic contaminants to the Mediterranean should be detectable as changes in surface water concentrations within a one-year period.

Tentative mass balance assessment

From these investigations on fluxes by Burns et al. (1985), as well as from the data derived from monitoring activities (Tables VIII to XIII) a crude estimate can be made of the amount of petroleum hydrocarbons associated with the different ecosystem compartments and the fluxes involved.

Using the above estimates and following the rationale established by the GIPME Programme (IOC, 1984) for mass balance calculations which inventories equal inputs on an annual basis, and thus assuming that inputs are continuously replacing residues in each compartment as they are lost by the output processes, we obtain the results computed in Table XVII. These estimates represent an updated calculation of one made previously by a GEMSI ad hoc Group to identify existing gaps in mass balance/flux type information for contaminants in the oceans. The estimates were made on the basis of a Mediterranean surface of 2.96×10^{12} m^2 and a volume of 3.7×10^{15} m^3. It is understood that the mass balance is very crude.

Beach tar can be estimated as 30% of the spilled oil input as discussed under outputs. The estimate could be verified if large scale monitoring data were published for comparison.

Surface microlayer concentrations have been listed in Table X. Values corrected for the thickness of microlayer sampled with each technique (0.44 mm for Ho et al., 1983 and Sicre et al., 1985 and 0.11 mm for Burns and Villeneuve, 1983) gave an average of 6 ug m^{-2} of petrogenic hydrocarbons in the microlayer. Pelagic tar can be estimated by averaging measurements reported in Table XI to yield an average of 3.0 ug m^{-2}.

Many authors have reported values of petroleum hydrocarbons in surface seawater (Table VIII) and levels range between 0.05 and 423 ug l^{-1} with averages in the range of 1 to 20 ug l^{-1}. The tabulated estimate is based on an average concentration of 2 ug l^{-1} down to a depth of 5 m as found in MAPMOPP (Table IX). Much uncertainty however exists for measurements of levels of petroleum in seawater and the estimate can only be regarded as giving the order of magnitude. Even greater uncertainty exists for concentrations in subsurface waters. The few values reported indicate levels at least an order of magnitude lower than surface waters. The estimate for this compartment has been made assuming an average concentration of 0.02 ug l^{-1}.

The amounts within the sediment flocculent layer cannot be estimated on the basis of data. However, if it is assumed that the amount sedimented through the water column measured in the Monaco trap experiment (8 ug cm^{-2}) gives an order of magnitude value we can obtain a crude estimate for the Mediterranean (Table XV). Coastal sediment content can be estimated from the calculated flux at the sediments underneath the sediment traps as 0.9 ug cm^{-2} yr^{-1}. Integrating this down to a 2 cm depth and over 20% of the total area we get the value given in Table XVII. The open sea sediment load can be computed by assuming that the open sea sediments receive deposits at the rate of 10% of the coastal flux per year. The few reports of sediment concentrations generally support this order of magnitude difference between concentrations in coastal and off-shore sediments (Albaiges et al., 1983).

The biomass load in the western basin can be computed by assuming an average hydrocarbon concentration of 225 ug g^{-1} dry weight and a standing stock of zooplankton biomass of 1 g m^{-2} when integrated over the top 100m of the water column (Burns et al., 1985).

As it has already been mentioned, the atmosphere could be assumed to be a sink for volatile hydrocarbons discharged to the sea surface but also a source of combustion products. The atmosphere petroleum hydrocarbon budget has been computed from Tables VI and VII.

The mass balance approach permits an assessment of the rates of dissipation of pollution inputs and of the ecosystem components more severely affected. Ambient levels of petroleum in surface waters cause relatively high levels of hydrocarbons in organisms and their faeces. Values exceeding 6,000 ug g^{-1} dry weight have been measured in freshly defaecated faeces from surface zooplankton (Burns et Villeneuve, 1983). This and other indirect evidence suggests that high levels of petroleum hydrocarbons are contained at the sea-sediment interface even in areas where levels in underlying sediments may be misleadingly low. There is urgent need to examine the deep sea sediments and their associated flocculent layers. Other critical reservoirs are the sea surface microlayer and the near surface seawater, as these determine the pollution load in the biota.

The uncertainty in measurements of petroleum trace levels in seawater limits the usefulness of such data for determining long term trends in major ecosystem compartments.

The major weak parts in the mass balance for the Mediterranean are the estimates for the amounts in the deep sediments, the magnitude of atmospheric fluxes and the levels in oceanic particles and biota. More attention should be paid to the determination of these parts in the mass balance. An assessment of the inherent uncertainties in the chemical measurements and the identification of critical ecosystem compartments will help devise more effective monitoring strategies.

6. EFFECTS OF PETROLEUM HYDROCARBONS

Oil tainting of seafood products has been reported sporadically from various areas in the Mediterranean Sea. Thus, some reports of oil taste in fish and mussels have come from Spain, France, Italy and Yugoslavia (Le Lourd, 1977). Environmental deterioration owing to oil pollution has also been reported in the Marmara Sea and Bay of Izmir in Turkey, as well as the Gulf of Naples and Cagliari, the lagoons of Venice and the Bay of Muggia in Italy (Le Lourd, 1977). In all these cases the reproduction of fish and molluscs has been affected and fisheries have suffered. Apart from this, no studies of the effects of oil pollution on the Mediterranean ecosystems are available.

In other regions some investigations have been carried out showing the full spectrum of effects of oil-spills on the various parts of the ecosystems. Such studies are the ones carried out after the accidental discharges from the "Torrey Canyon", Cornwall, England, 1967 (Southward and Southward, 1976; Smith, 1968);the "Florida", west Falmouth, Massachusetts, USA, 1969 (Sanders, 1978); the "Amoco Cadiz", Brittany, France, 1978 (Laubier, 1980); the "Argo Merchant", Georges Bank, NW Atlantic Ocean, 1976 (Univ. Rhode Island, 1978); and the "Thesis", Baltic Sea, 1977 (Linden et al., 1979). All these spills have occurred in temperate climatic zones. The higher temperature of the Mediterranean environment may produce a slightly different impact. Thus, the acute effect might be somewhat more pronounced, while in the long-term, a recovery may occur more rapidly. However, it appears very likely that the general conclusions that can be drawn from these studies are also applicable to spills occurring in the Mediterranean. Therefore, a brief summary of the general conclusions from the above mentioned spills will be given below.

The recovery of ecosystems affected by oil pollution varies considerably. In some cases, large spills have caused a minor impact, while in other cases only very small quantities have caused severe and indeed long-term effects on large parts of the marine ecosystem. Both abiotic and biotic factors govern the extent of the biological consequences of each oil spill and it is the interaction and relative contribution of each of these factors that are important.

An abiotic parameter of importance for the extent of biological damage and the time required for complete recovery is the capacity of the polluted area of water to be diluted to concentrations too low to cause any lethal or important sublethal effects. It is clear that the quantity of oil and the morphology and hydrography of the affected area are important here. Therefore it seems quite obvious that single oil spills in off-shore areas with considerable water depth cause less biological damage than oil spilled close to the coast or in shallow and confined water bodies. The impact on sea bird populations may however be serious in any of these cases. The impact of the "Argo Merchant" accident seems to be an example of a spill which caused comparatively little damage to the ecosystems in the area, while the "Florida" spill in West Falmouth, Massachusetts is an example of a spill close to the shore where the oil concentrations in the confined water body rapidly reached toxic concentrations. However, the type of oil involved is also important in these two cases (see below).

In addition, the spills close to open coasts (i.e. no tidal flats or marshes) in areas with large tidal water amplitudes and good water exchange appear to cause considerably less damage than spills in atidal bays and archipelagoes where winds and currents cannot dilute the oil. Although locally extensive, the damage caused by the large quantities of oil from the "Torrey Canyon" did not seem to cause long-term negative effects. This however does not apply to the areas where dispersants were used extensively in the clean-up of the oil. Considering the large amount of spilled oil, the limited damage caused so far by the "Amoco Cadiz" may also indicate a fairly rapid recovery, at least in exposed locations. The "Thesis" oil spill on the contrary, although involving only a very small quantity of oil, caused comparatively long-lasting damage in the enclosed low-turbulent archipelago.

Most of the spill studies have shown that considerable long-term damage to the marine communities has been caused by spills in which the oil is accumulated in fine-particle sediments in the inter-tidal or sub-tidal regions, where the degradation and evaporation of the oil is slow or almost non-existent. The long-term action of the higher molecular weight aromatic hydrocarbons on living organisms will become important under such circumstances. Examples of spills where the oil has accumulated in sediments, thus prolonging the impact, are the "Florida" (West Falmouth), the "Arrow" and the "Thesis" oil spills.

Another abiotic factor of high significance for the extent of the damage is the composition of the spilled oil. The light refined products such as the No. 2 fuel oil or similar oils containing high proportions of light, readily soluble, aromatic hydrocarbons are considerably more toxic than normal crude oils or heavy refined oils. Furthermore, the light refined oils are usually more easily emulsified into the water body by wave action. The "Florida" (West Falmouth) oil spill involved such a light diesel oil with considerable long-term effects on the near-shore communities. The "Thesis" oil spill, also occurring close to the coast and involving approximately the same quantity of heavy distillate (No. 5 fuel oil) caused less impact on the coastal ecosystem.

The extent of damage in different communities

Few studies exist on the effects of single oil spills on planktonic communities. Some effects were observed on phytoplankton following the "Torrey Canyon", and "Thesis" oil spills. These effects were, however, minor. Some impact on zooplankton was observed after the "Torrey Canyon" spill, although the effect was probably related to the toxicity of dispersants rather than oil. The "Amoco Cadiz" oil spill apparently resulted in effects on zooplankton up to a few months after the spill in off-shore areas. Following the "Argo Merchant" spill some effects were observed on zooplankton in the oil contaminated area. These effects did not, however, appear to be very drastic. After the "Thesis" oil spill zooplankton was severely affected only immediately after the spill and in the close vicinity of the wreck. Effects have also been observed in the Santa Barbara channel (Straughan, 1971)

Based on these observations it would appear that the impact of the oil spills on the planktonic community is not of a long-term nature. The water exchange and turbulence in off-shore areas rapidly dilute the oil and replace the affected communities. It seems likely that the period necessary for recovery of the plankton community from single spills is usually a question of weeks rather than months.

Studies in the littoral zone are more frequent. Extensive and lasting damage was caused to the littoral communities after the "Tampico Maru", "Florida", "Arrow" and "Thesis" oil spills. These accidents occurred in bays and estuaries where the spilled oil was not diluted sufficiently. In several cases the oil also accumulated and was retained in sediments. The spills from the "Tampico Maru" and "Florida" also involved highly toxic products. The "Amoco Cadiz" spill caused severe acute effects along the coast of Brittany. Except in the estuaries, however, the spill does not appear to have caused a long-term impact in the littoral zone. It appears from these studies that whether the impact on littoral communities is drastic and lasting depends on a number of factors. The recovery of affected littoral communities is usually a question of several years. In the worst cases, the time necessary for a complete recovery of the ecosystem may take one or more decades.

Only a few studies are available on the impact of acute oil spills on benthic sub-tidal and sub-littoral communities. The studies following the "Florida" and "Thesis" oil spills indicate however, that the impact in this zone may be severe and may perhaps last longer than in any other part of the ecosystem. The "Thesis" oil spill caused effects in soft bottom sub-littoral communities that lasted longer than those in the littoral zone. The oil was incorporated into sediments and organisms and as the water exchange was limited and the temperature and oxygen content low, the oil was preserved for a longer period than in the littoral zone.

The immediate effects of catastrophic oil spills may be obvious although their long-term consequences are often difficult to quantify, since the abundance of plants and animals in any locality fluctuates naturally from year to year and catches vary with fishing effort and for other reasons as well.

Assessing the impact of chronic pollution, which is the most common in the Mediterranean, is even harder, as it may not cause an appreciable increase in mortality and since other forms of pollution are usually also present. With these limitations in mind however one can make some generalizations about the biological effects of long-term, low level pollution of marine habitats by oil.

Among individuals, young stages are more sensitive than adults, while some species are more sensitive than others at any stage, as it has been described in comprehensive reviews (Nelson-Smith, 1975; GESAMP, 1977). Some illustrative examples are given below.

It is well documented that even 1 ug l^{-1} of oil dispersed in seawater or 1 ug l^{-1} of water-soluble oil components can harm sensitive organisms. For example, it has been recognized that it may have a negative effect on the health of the larvae hatched from fish eggs. Also, trace amounts of oil components in sea-water interfere with the sex behaviour of marine animals and they may have an effect on the chemical orientation of marine organisms. Salmon fry for example avoid oil concentrations as low as 1.6 ug l^{-1}, which may frequently occur around a river mouth and which therefore disrupt their migration patterns. Exposure to low-boiling hydrocarbons at 12 ug l^{-1} halves the rate at which mussels can assimilate food; the effect is enhanced by low salinities and high temperatures to the extent that bivalves inhabiting estuaries or bays, where these conditions often occur, may not be able to breed in spring. Synergistic effects particularly between aromatic hydrocarbons and trace metals may also occur in natural environments.

Some organisms are of course more tolerant than others of chronic pollution. Sublethal effects will soon exclude particular groups and those surviving may be able to take advantage of the extra space or food which becomes available, so that there may not be a drop in the overall abundance of biomass, but in the species diversity. If the organisms which are excluded occupy a key ecological role, a major change may occur in the nature of the community. This has been demonstrated in shores crossed by refinery effluents (Crapp, 1971).

These ecosystem disturbances may have unforeseen effects on fishes and birds, simply because of the limitations of food.

Bearing in mind the importance of chronic inputs in certain Mediterranean coastal areas, where many effluents are incorporated into the sea without any treatment or regulatory constraint,it is expected that chronic effects occur, although at present there is little or practically no information on the subject.

7. EVALUATION OF THE AVAILABLE DATA BASE AND STATE OF KNOWLEDGE

The review of the available data base on hydrocarbon levels in the Mediterranean Sea shows that most of the data are from coastal and nearshore areas with a lack of data from the open sea. Most of the data are not comparable in the sense that they have not been obtained by intercalibrated methods. Very little information is available on the biological effects of petroleum hydrocarbon pollution from the Mediterranean Sea. A reliable scientific evaluation of the state of pollution and the possible associated biological effects cannot be made with confidence on the basis of existing data.

In order to improve the pollution assessment there is a need for data covering various parts of the Mediterranean Sea obtained through agreed Reference Methods that have been intercalibrated. This could be achieved through one or more baseline studies so as to cover as large a part of the Mediterranean Sea as possible.

There is also a need for investigations of coastal ecosystems and wildlife on oil-sensitive shorelines to determine their relative vulnerability to spilled oil; this information may provide a basis for oil spill response priorities and aid in the selection of protection and clean-up methods for oil-sensitive areas.

Furthermore, there is a need for studies of the possible biological effects of chronic petroleum hydrocarbon pollution.

There is finally a need for further studies on the fate of petroleum hydrocarbons in the marine environment in the Mediterranean Sea.

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