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PRELIMINARY REPORT ON THE STATE OF POLLUTION OF THE MEDITERRANEAN SEA

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1. INTRODUCTION

This is an extract from a preliminary report on the state of pollution of the Mediterranean Sea.

Many contributions received from the specialized parts of the United Nations system and from individual scientists made it possible for the Secretariat to prepare this partially completed preliminary report.

The valuable assistance of three consultants (M. Bernhard, A. Cruzado and Lj. Jeftić) is acknowledged in particular.

The first draft of this report (UNEP/WG. 11/4 (Prov.) was submitted for consideration and comments to the Mid-Term Review Meeting on the Progress of the Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL) and Related Projects of the Mediterranean Action Plan (Monaco, 18-22 July 1977), and widely distributed to the Mediterranean scientific community.

Taking into account the suggestions and additional information received the present document has been prepared. Due to the short time available it was impossible to finish the report and it therefore contains only those sections which could be considered as partially or almost finished. The missing sections are indicated by italics in the table of contents.

Although fully aware that the coverage of the various sections is not yet homogeneous enough and that many essential sections are missing or incomplete, it was felt nevertheless that even in its present form the report could serve as the basis for a wider discussion on its purpose, scope and expected final form.

The final, although somewhat ambitious, aim of the report is to present in an authoritative volume the present state of pollution of the Mediterranean as the result of the environment assessment activities initiated through the co-ordinated Mediterranean Pollution Monitoring Programme (MED POL) and other related projects of the Mediterranean Action Plan. Naturally, such a presentation cannot rest only on the latest results obtained through MED POL but should also take into account the accessible results obtained through other research and monitoring efforts.

In its final form the report is intended to be a fully documented (referenced) publication with a significantly expanded text compared with the present draft.

The Secretariat regrets that it has not been able to prepare the translation of this document.

2. THE MEDITERRANEAN BASIN

The Mediterranean is a remnant of a vast waterway, at least half a billion years old, that formerly extended from what is now Portugal, the Alps, south-east Europe, Anatolia, Iran, the Himalaya to south-east Asia and the Pacific. This ancient sea, called Tethys, separated the northern continent of Eurasia from the southern one of Gondwanaland. As a result of constant interactions between these two great continents, and in particular of the Alpine orogenic evolution which began in late Cretaceous time, the present shape of the Mediterranean Basin gradually evolved.

The Mediterranean Sea proper, excluding the Sea of Marmara and the Black Sea, extends 3,800 km from east to west and 800 km from north to south, covering an area of about 2.5 million km^2 (Tixeront, 1970) and has a volume of about 3.7 million km^3 (Miller and Stanley, 1965) with an average depth of 1,500 m, although depths of over 4,000 m are not uncommon all along the Herodotus Fault, with a recorded maximum depth of 5,121 m in the centre of the Ionian Sea (Lacombe and Tchernia, 1974).

The Mediterranean, as a whole, is separated from the Atlantic Ocean by the straits and sill of Gibraltar and communicates with the Black Sea via two sills (Bosphorus and Dardanelles) between which extends the Sea of Marmara. The Suez Canal joining the Mediterranean with the Red Sea has little significance for the Mediterranean. On the other hand, the Siculo-Tunisian sills and the sill of Messina divide the Mediterranean Sea into eastern and western Basins which, in many respects, show distinct hydrographical conditions.

The western basin has poorly defined compartments: the Tyrrhenian Sea, defined by the sill of Elba and Bonifacio,is relatively open between Sardinia and Sicily; the sill of the Balearic islands and the poorly marked sill of the Alboran Sea do not play an important role in the general characteristics of the basin.

The eastern basin, on the other hand, has clearly defined compartments: the Adriatic Sea bound by the straits and sill of Otranto and the Aegean Sea open to the eastern basin by the arched sills that, from the Peloponesus to Anatolia, support the islands of Kythira, Antikythira, Crete, Kasos, Karpathos and Rhodes. The Aegean Sea contains several sills and depressions in a region of complicated topography among the large number of islands. Due to its complex and interrelated climatic, hydrological and hydrographical conditions the Mediterranean Basin today represents a uniquely integrated ecoregion with common and very distinctive social, cultural and political features.

The following chapters give a short review of those characteristics of the Mediterranean Basin which have a major bearing on the origin, fate and effects of the various pollutants entering it.

2.1 CLIMATE AND HYDROLOGY OF THE MEDITERRANEAN REGION

The climate of the Mediterranean region is highly diverse with desert occupying a large part of the eastern and southern shores and with well irrigated basins in the north-western shores where the main rivers maintain a regular flow of water throughout the year. Summers are dry and winters are humid. Average precipitation on the northern shores and on the islands is 400 to 1000 mm/annum while on the southern and eastern shores it is less than 100 mm/annum. At a rough estimate, in 1975 there were 2000 m^3/annum of potential water resources for each inhabitant on the northern shores while he was using only 400 m^3/annum of high quality supply. On the southern shores the potential water resources seldom exceed 100 m^3/annum per inhabitant. Therefore, water shortage is endemic in the greater part of the Mediterranean region and, by reason of the climate it may attain dramatic proportions in certain exceptionally dry years which occur once or twice in a decade. Even in normal years water deficiences in summer (July - September) are made worse by the influx of tourists into the coastal zones. Considerable expense is thus necessary to fulfil this need for water and basin transfers or sea-water desalination plants are being built in many countries around the Mediterranean.

For the basin as a whole, meteorological data available can be considered as from average to good but hydrological information is extremely poor and does not permit of valid historical reconstructions except for the major basins. Very little is known also about evaporation of the sea-water and precipitation on the sea. There is, too, a complete lack of knowledge about the importance of coastal and submarine groundwater contributions, which may certainly not be negligible, as well as the effects of deep hydrothermal inflows in the tectonically active zones that cross the Mediterranean seabed from east to west.

Table 2.1.I shows a distribution by regions of the water inflow through rivers, urban sewage systems and direct run-off from agricultural land. Two regions II and V are exceptionally well watered and have positive water balances but the remainder of the Mediterranean is one of the arid zones of the ocean, i.e., the rate of evaporation exceeds that of run-off and precipitation. The major rivers entering the Mediterranean are the Ebro, the Rhône and a number of smaller ones in region II, and the Po, Adige and a number of minor Italian rivers in region V (Adriatic Sea). Therefore, some of the basins are in a better situation than others, but the Mediterranean as a whole has a negative water balance which must be compensated by a flow of less saline waters from the Atlantic ocean through region I (Alboran Sea) and from the Black Sea through region VIII (Aegean Sea).

Atmospheric circulation is mainly driven by the Azores anticyclone which in summer advances towards western Europe, and by the low pressures arising from the intense solar heating over the large continental masses of western Asia and eastern Africa. Thus, anticyclonic winds are generated that tend to blow in the entire region from the north-west. In winter, atmospheric depressions cross all western Europe carried by the jet stream in medium atmospheric altitudes and sweeping the basin from west to east and often

Table 2.1.1 Flow of fresh water from river run-off and other sources (in million m^3/annum)

Area		Total	Domestic		Industrial		Agricultural		Rivers		Population ($\times 10^3$)
				%		%		%		%	
I	Alboran	6,150	116	1.9	141	2.3	2,140	34.8	3,750	61.0	2,690
II	North-west	100.000	786	0.8	2,520	2.5	12,200	12.2	84,500	84.5	8,870
III	South-west	8,640	105	1.2	244	2.8	4,930	57.0	3,360	39.0	4,439
IV	Tyrrhenian	32,200	341	1.1	565	1.8	19,100	59.1	12,200	38.0	8,131
V	Adriatic	162,000	283	0.2	1,060	0.7	53,200	32.9	107,000	66.2	3,625
VI	North Ionian	26,600	77	0.3	242	0.9	20,600	77.5	5,680	21.3	1,883
VII	South Ionian	4,330	120	2.8	170	3.9	4,040	93.3			2,904
VIII	Aegean	46,200	163	0.4	696	1.5	18,500	40.0	26.900	58.1	4,584
IX	North Levantine	20,400	19	0.1	25	0.1	3,120	15.3	17,300	84.5	1,320
X	South Levantine	17,700	191	1.1	134	0.8	1,580	8.8	15,800	89.3	5,388
	Total	424,220	2,201	0.5	5,797	1.4	139,410	32.9	276,490	65.2	43,834

halting in certain regions producing small hurricane-like tempests that frequently flood the areas with torrential rainfalls. In winter too, some regions are placed under the influence of inflows of dry continental air blowing with high intensity especially when funnelled by the major mountain ranges or into the river valleys (Tramontana, Mistral, Bora). This happens especially when the southern front of the anticyclone located over central and eastern Europe covers the northern shores of the sea.

Whenever precipitation occurs, especially on the northern shores, it is of a particularly high intensity and suddeness. Substantial water masses laden with terrigenous solid materials are then discharged into the coastal stretch by the normally dry beds of the rivers, now filled by the storm, often flooding adjacent zones. The sediments are deposited on the shelf and might then be carried down the slope of existing canyons in turbidity currents which are capable of playing a major role in the transport and disposal of sediments even at great depth.

2.2 HYDROGRAPHY AND CIRCULATION

2.2.1 Water Balance

The Mediterranean Sea is a concentration basin. Its waters always have a higher salt concentration than those of the adjacent regions in the Atlantic Ocean and the Black Sea. Therefore, the Mediterranean Sea must have a negative water balance. That is to say that the water losses through evaporation exceed, by and large, the gains due both to precipitation and to river inflow. In order to maintain, on the human time scale, the total water mass and thus the level of the Mediterranean, the balance is achieved by means of a net inflow of water from both the Atlantic Ocean and the Black Sea.

Since the salt content of the Mediterranean Sea is constant and the incoming water is not pure water, a two-directional flow has to be established both at the straits of Gibraltar and at the Bosphorus (Sverdrup et al., 1943) with an incoming flow of less saline water larger than the outgoing flow of more saline water. This, together with the precipitation and the river inflow, compensates for the high evaporation rate of the region due both to the high temperatures during summer and the strong, cold and dry continental winds in winter time.

Table 2.2.I gives different estimates for the various components of the water budget based sometimes on very dubious data that require extreme care in their use, especially when it comes to the computation of the over-all residence time of the water in the whole Mediterranean or of the several water masses in each of the basins, parameters normally used when studying the fate of the pollutants that enter the sea.

Lacombe and Tchernia (1972), using very careful studies of the currents and of the hydrographical conditions in the straits of Gibraltar, and the data given by Merz (1928) for the straits of Dardanelles, give an estimate of the flow of water entering and leaving the Mediterranean, to and from the adjacent seas, in the order of 1.2 million m^3/sec. Since the volume of

Table 2.2.I Water budget for the Mediterranean Sea (units in m^3/sec)

Process	Tixeront 1970	McGill 1969	Lacombe & Tchernia 1974	Morel (*) 1971
Evaporation	95,000 (1)	92,000 (2)	-	70,000
Precipitation	28,000 (3)	33,000 (2)	-	13,000
River Run-Off (**)	16,000 (4)	14,000 (2)	-	9,000
Net Inflow Through:				
Dardanelles	6,000 (5)	6,000 (5)	6,000 (5)	6,000 (5)
Gibraltar	45,000 (6)	40,000 (7)	54,400 (8)	-
Strait of Sicily	-	-	-	42,000 (6)
Total Inflow Through:				
Dardanelles	-	-	12,500	-
Gibraltar	-	-	1,187,500	-
Strait of Sicily	-	-	-	1,000,000

(*) Only for the eastern basin

(**) MED X estimate for total run-off is 13,250 for the whole Mediterranean and 8,663 for the eastern basin

(1) Estimated from studies made in the Lac de Tunis (Berkaloff, 1952)

(2) Based on Carter, 1956

(3) Estimated from pluviometric charts and sailors' accounts

(4) Direct measurements on some rivers and from pluviometric charts and area of all other river basins

(5) Based on Merz and Moeller, 1928

(6) Estimated by balance

(7) Based on Schink, 1967

(8) Estimated by salinity difference between incoming and outgoing waters and an estimate of mean flow through Gibraltar

the Mediterranean, according to Miller and Stanley (1965) is of 3.7 million km^3, the over-all residence time of the water would be in the order of 100 years. These figures, however, can only be considered as a rough indication of the fate of the water entering the different basins of the Mediterranean due to the uncertainty in all the estimates and to the large differences in residence time for the different water masses that range from a few years to several centuries.

Considering the data used by Morel (1971) for the ingoing and outgoing flux through the sills of Sicily and the volume of 2.3 million km^3 for the eastern basin given by McGill (1971) the over-all residence time of the water in the eastern basin would be about 75 years.

According to Morel, the eastern basin plays a role with regard to the western basin similar to the role of the whole Mediterranean with respect to the Atlantic Ocean, that is of a concentration basin. He underlines the analogy of the situations in the straits of Gibraltar and Sicily reinforced by the similarity in the flows of water exchanged across both narrows. (See Table 2.2.I).

2.2.2 Water Masses of the Mediterranean Sea

The mechanism by which the incoming surface Atlantic water with salinity slightly above 36 ppt is transformed into the outgoing deep Mediterranean water with salinity around 38 ppt is perhaps the most important oceanographical problem encountered in the Mediterranean Sea (Lacombe, 1974). It implies not only large horizontal displacements covering the whole basin but also a general downwards vertical movement of the water with a net increase in density. During the passage through the different basins the water is submitted to varying climatic circumstances which altogether establish, in a fairly steady state condition, the identity of several characteristic water masses: the Atlantic surface water, the intermediate Levantine water and the deep waters in each of the eastern and the western basins (See Fig. 2.2.1).

Atlantic surface water. This water enters the Alboran Sea in a surface layer 150 to 200 m thick driven by the lower mean level of the Mediterranean Sea relative to that of the Atlantic Ocean. This difference in the level is produced by the predominance of evaporation over precipitation plus river run-off and by a lower mean atmospheric pressure in the eastern Mediterranean over that in the Atlantic Ocean and creates a permanent sucking effect towards the east (Oren, 1977). Due to its lower density the Atlantic water always remains at the surface except in the Levantine basin, east of longitude 22°E, where it is overlaid by more saline water with a higher temperature and therefore lower density (Oren, 1971) (see Fig. 2.2.2).

The Atlantic water, due to the rotation of the Earth (Coriolis effect), tends to pile up against the southern shores of the Mediterranean. However, it reaches the northern regions as well, in locations that range from the NW Mediterranean (Furnestin, 1960; Cruzado et al., 1977) to the Tyrrhenian Sea and even to the Adriatic (Zore-Armanda, 1969), the Aegean and the Cretan Seas (Oren, 1977).

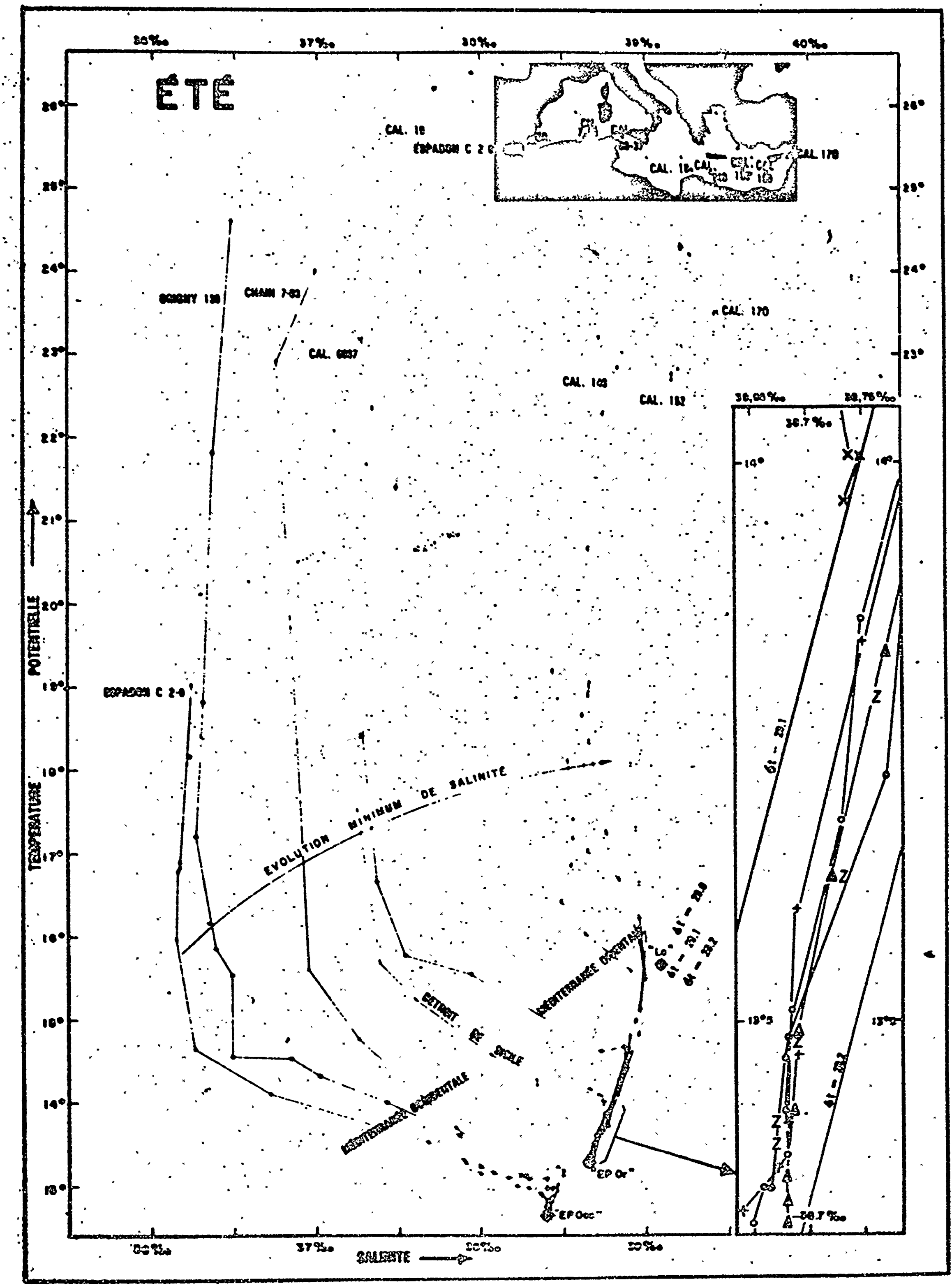


Fig. 2.2.1 (a) - Temperature-salinity (TS) in summer (from Lacombe et Tchernia : Caractères hydrologiques et Circulation des Eaux, 1972 a)

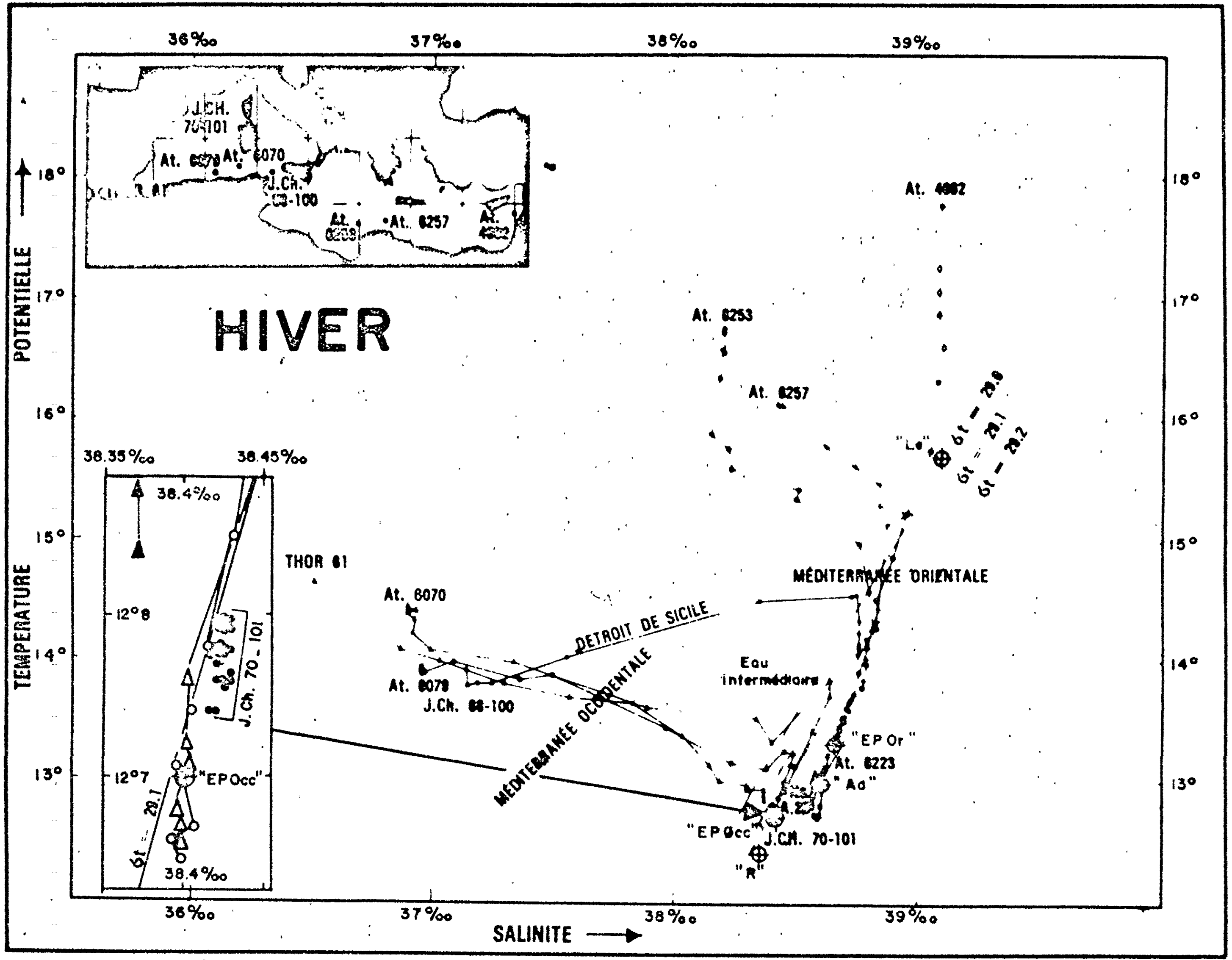


Fig. 2.2.1 (b) - Temperature-salinity (TS) in winter (from Lacombe et Tchernia: Idem)

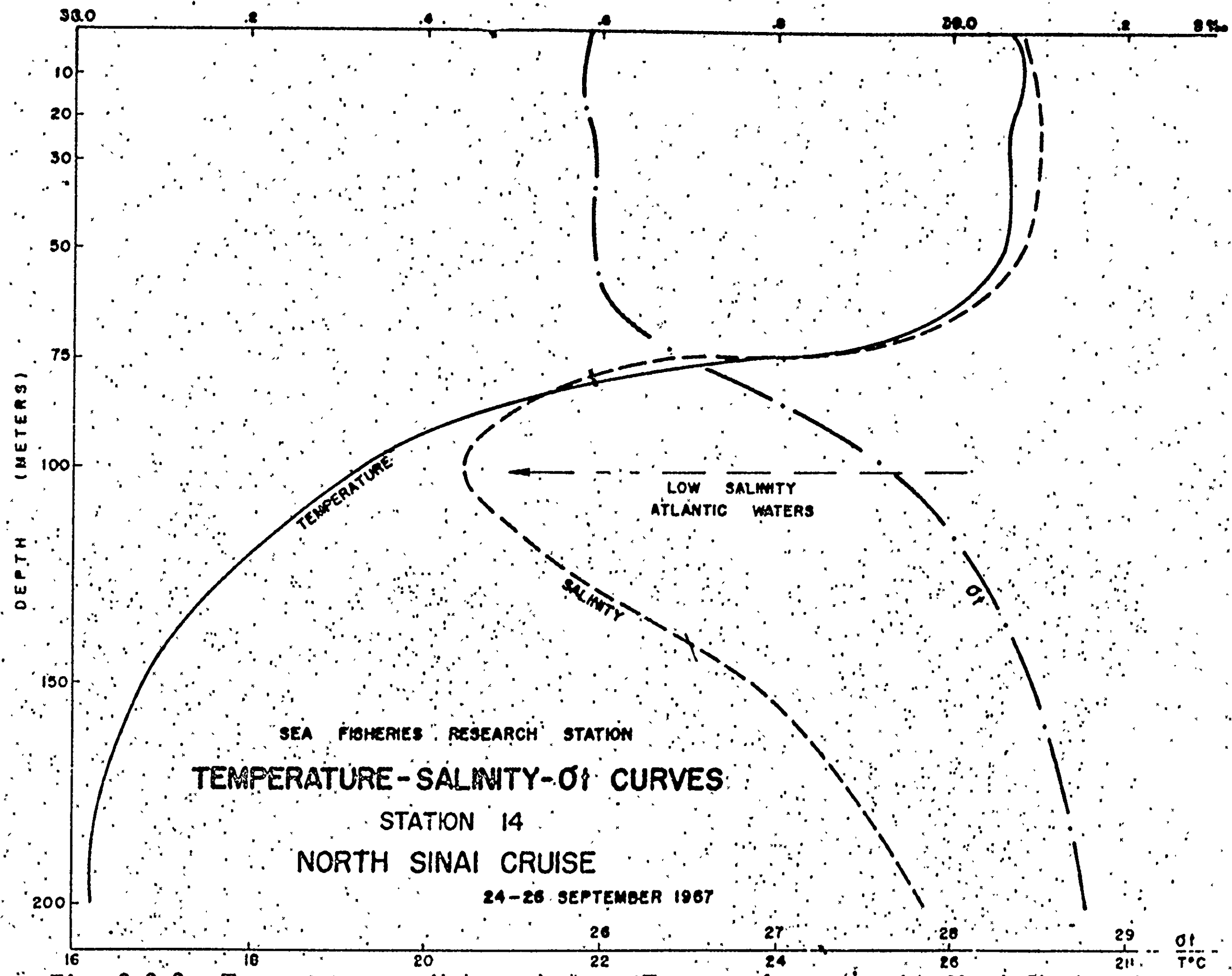


Fig. 2.2.2 - Temperature, salinity and sigma-T curves for station 14, North Sinai cruise. (24-26 Sept. 1967). (Oren, 1971)

The evolution of this water mass as it moves from west to east is highly dependent on the climatic circumstances encountered:

In summer, the intensive solar heating originates a strong thermocline which forces the less dense Atlantic water to remain in a layer of 20 to 40 m thick practically covering the whole western basin, except in places of strong divergence such as the NW Mediterranean and other less well known areas, and a large part of the eastern basin until at least 22°E of longitude. (See Fig. 2.2.3). Because of the heating, strong evaporation takes place as the water moves eastwards and the salinity of the incoming water (36.15 ppt) increases steadily to about 37.50 ppt in the straits of Sicily (Morel, 1971) and to about 38.00 ppt at longitude 22°E (Lacombe, 1974). At this stage the Atlantic water becomes heavier than the surface water from the Levant Sea, warmer although more saline, and sinks to a depth of 30 to 75 m (Oren, 1977) where it remains sandwiched between waters of higher salinity and is only revealed by the existence of a salinity minimum that exceeds 38.90 ppt.

In winter (Fig. 2.2.4) the heat flow is reversed and the surface water is markedly cooled by the dry continental winds blowing in the northern half of the Mediterranean basin especially (Tramontana, Mistral, Bora). Evaporation is however as intense as or even more than during summer, and the consequent increase of density by the combined effects of cooling and evaporation forces the water to enter into a convective movement of a high intensity that stirs the water column vertically to an eventual depth of several hundred metres. Therefore, the water of Atlantic origin soon loses its identity by being mixed with the underlying and more saline waters (See Fig. 2.2.5).

Intermediate Levantine water: A layer between 250 and 400 m deep, with temperature around 15.7°C and salinity up to 39.10 ppt, covers the entire eastern basin, underlying the subsurface layer of Atlantic water and revealed by a salinity maximum above the colder and less saline deep water. This intermediate water, often called intermediate Levantine water, especially in the eastern basin, is formed, according to Lacombe and Tchernia (1974) by the cooling of the highly saline surface water (up to 39.5 ppt), found in summer south of Turkey and around Cyprus, and its merging with the remains of the subsurface Atlantic water, especially in the north-east of the eastern basin.

In the western basin, the intermediate water is formed as a result of the flow of intermediate Levantine water over the sills of the Siculo-Tunisian straits. The high density eastern deep water, denser than the deep water in the western basin does not cross the sills (Morel, 1971) and only the top layer formed by the intermediate Levantine water does so, (Lacombe and Tchernia, 1972) contributing therefore to the formation of the intermediate water in the western basin.

Although the salinity of this intermediate water is high east of the sills of Sicily (above 38.8 ppt) it drops to about 38.75 ppt as it proceeds through the eastern sill, fills the Sicilian trough and then through the western sill flows into the western basin. This drop in salinity is due to the active vertical mixing with the overlying less saline subsurface Atlantic water.

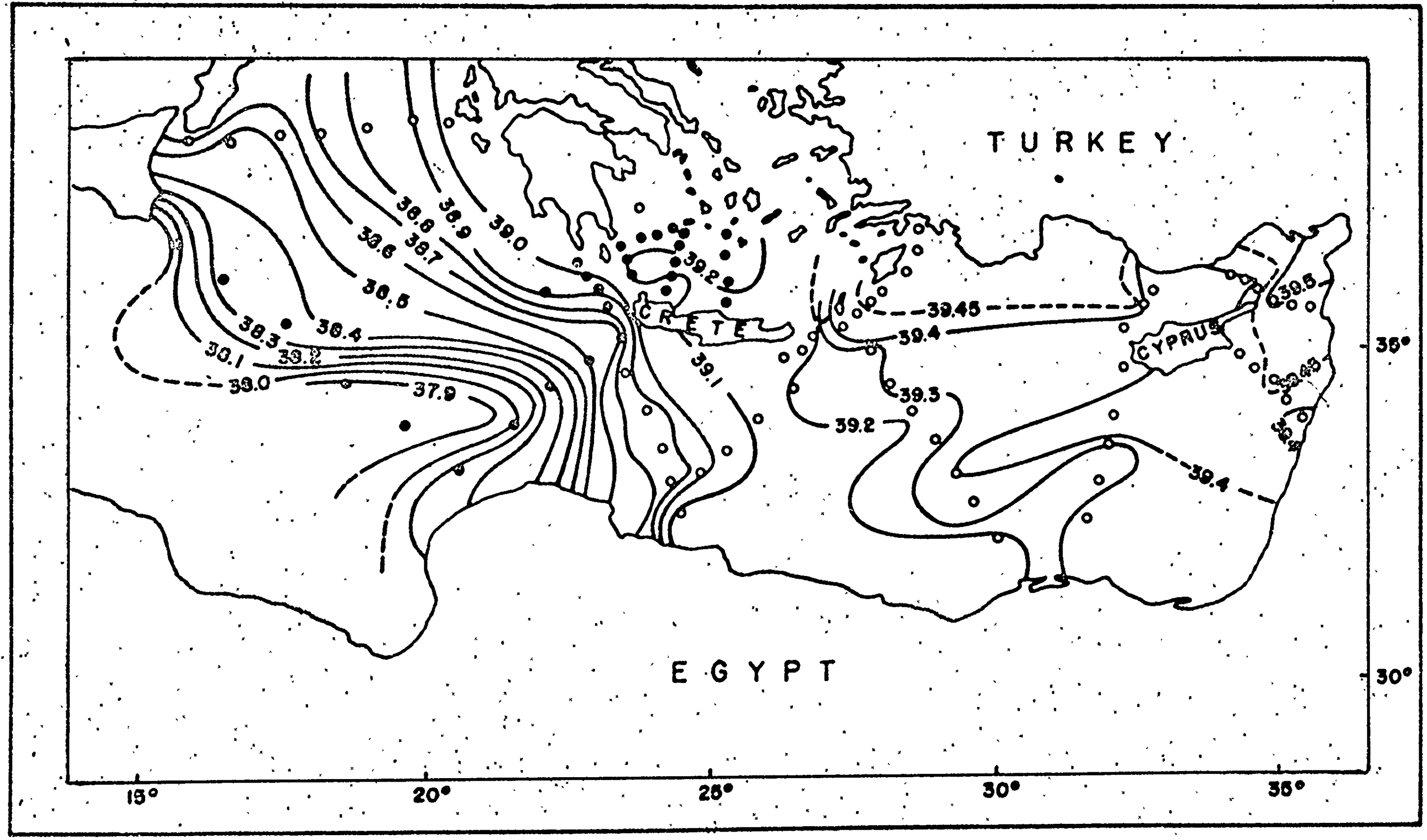


Fig. 2.2.3 - Surface isohalines for the eastern Mediterranean during summer.
(Lacombe et Tchernia, 1960)

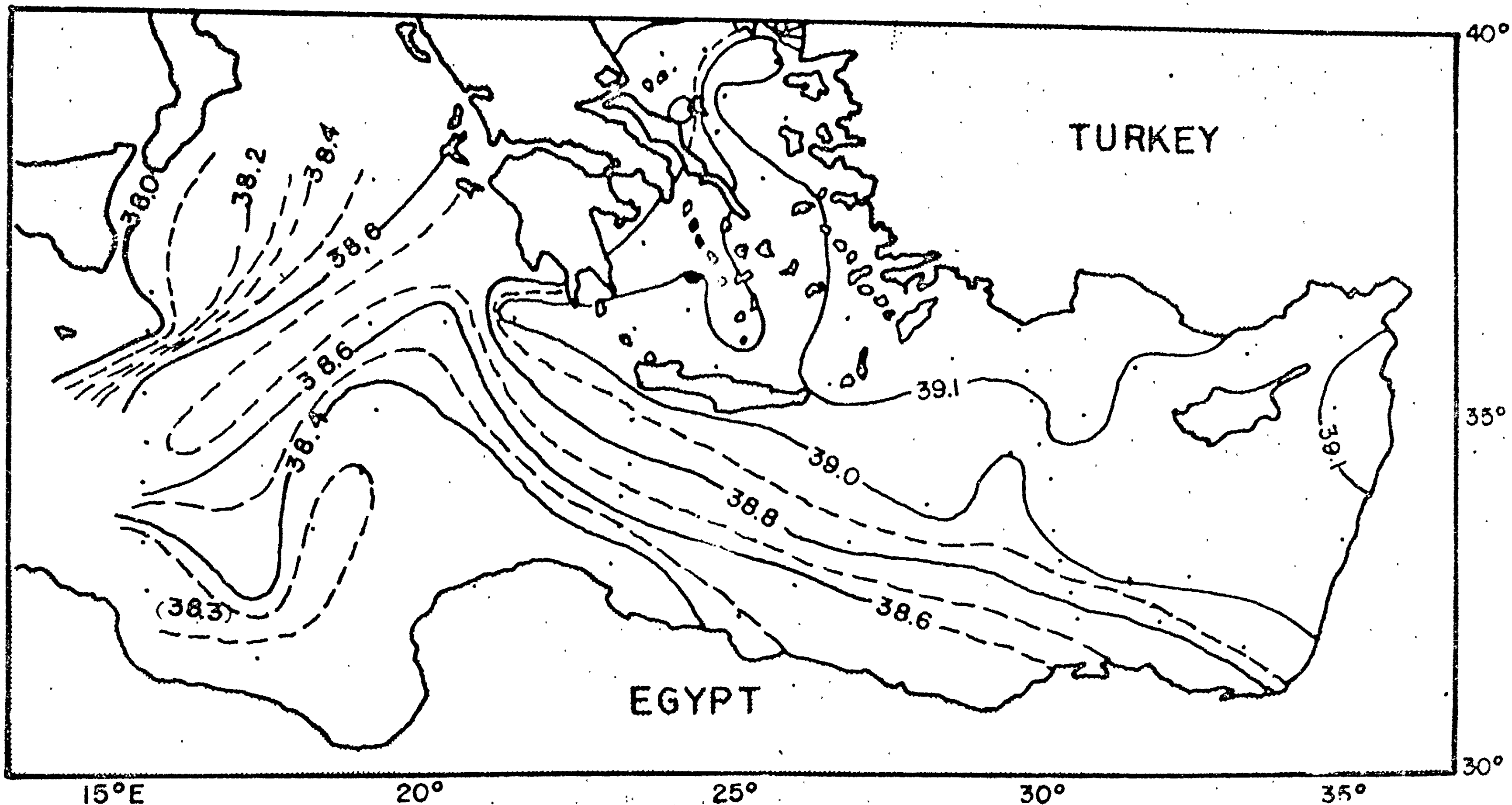
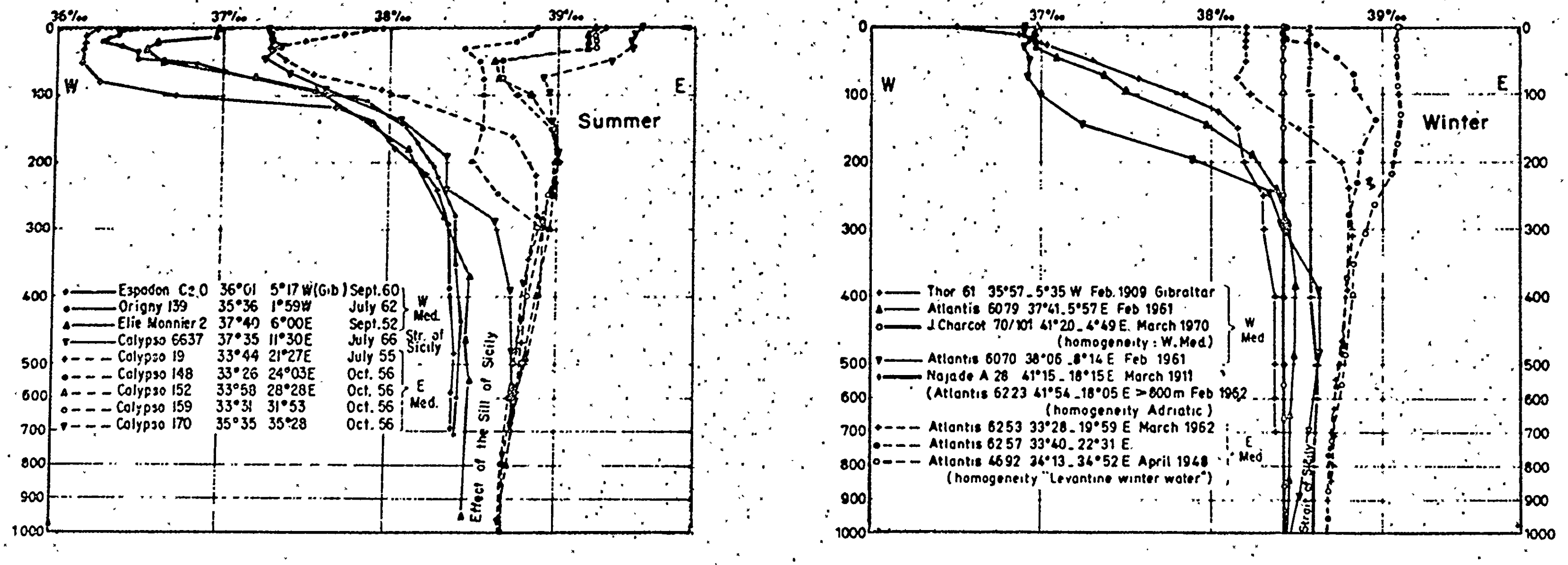


Fig. 2.2.4 - Surface isohalines for the eastern Mediterranean during winter. (Lacombe et Tchernia, 1960) <u>Cahiers Océanogr.</u> 12 (8) 527-548.



EVOLUTION OF THE VERTICAL PROFILE OF SALINITY FROM WEST TO EAST, IN SUMMER AND IN WINTER

Fig. 2.2.5 - Mixing of water of Atlantic origin with the underlying and more saline waters. (based on Lacombe, 1974). Bulletin of CIM No. 7 : 5-27.

This intermediate water entering the western basin has a lower density than the western deep water and therefore does not sink to the bottom but is, rather, interleaved with the deep water and spreads practically throughout the whole basin. (See figure 2.2.6). As it proceeds to the north-west and to the west, both temperature and salinity approach closely those of the surrounding deep water, and it can only be identified by a very slight rise in temperature and salinity between 400 and 600 m which completely vanishes in the Alboran Sea.

Deep water: The vertical convection referred to above is what produces the deep water masses lying at depths of over 600 m both in the eastern and in the western basins. In spite of the transient nature of the processes that produce these deep water masses, they are of remarkably constant characteristics: T = 15°C and S = 39.0 ppt in the eastern basin, T = 13°C and S = 38.4 ppt in the western basin. Although following different processes, the formation of these water masses takes place essentially in three regions of the north Mediterranean where the necessary meteorological and hydrographical conditions are met (Lacombe, 1974).

In the western basin, the extreme winter conditions in its northern half promote the mixing of the cooled surface water with the intermediate water to give rise to the deep water which then fills the entire basin, including the Alboran Sea, and flows into the Atlantic Ocean through the straits of Gibraltar. This process has been studied in great detail by Lacombe (1974) and by the Medoc Group (1970). In this area the surface water at the end of the summer is relatively low due to the influence of the river Rhône and in winter the temperature can reach 12°C uniformly over depths of more than 600 m.

In the eastern basin, the process takes place both in the Adriatic and in the south-eastern Aegean Seas, starting over shallow areas with relatively low salinity water due to the influence of the river Po and of the Black Sea. The dense water flows from both areas into the Ionian Sea, the Adriatic water crossing the straits and sill of Otranto, and, after mixing, covers the entire basin between about 400 m and the bottom. The process in the Adriatic Sea has been studied by Buljian (1953) and reviewed by Zore-Armanda (1969) who has pointed out the unsteadiness of the characteristics of such water from year to year, depending on the prevailing atmospheric conditions.

Other water masses: Although not as important as the foregoing due to their more localized existence, three more water masses should be mentioned if only because they make an important contribution to the formation of the characteristics of the water masses described above.

Levantine surface water has a high salinity (up to 39.5 ppt) and can be considered as the end product of the Atlantic water once it has travelled across the entire Mediterranean Sea from the straits of Gibraltar to the Levantine shores undergoing high summer evaporation. This water is important however as the main source of the Levantine intermediate water and its high salinity is probably the result of a somewhat closed circulation in the eastern part of the Levantine basin.

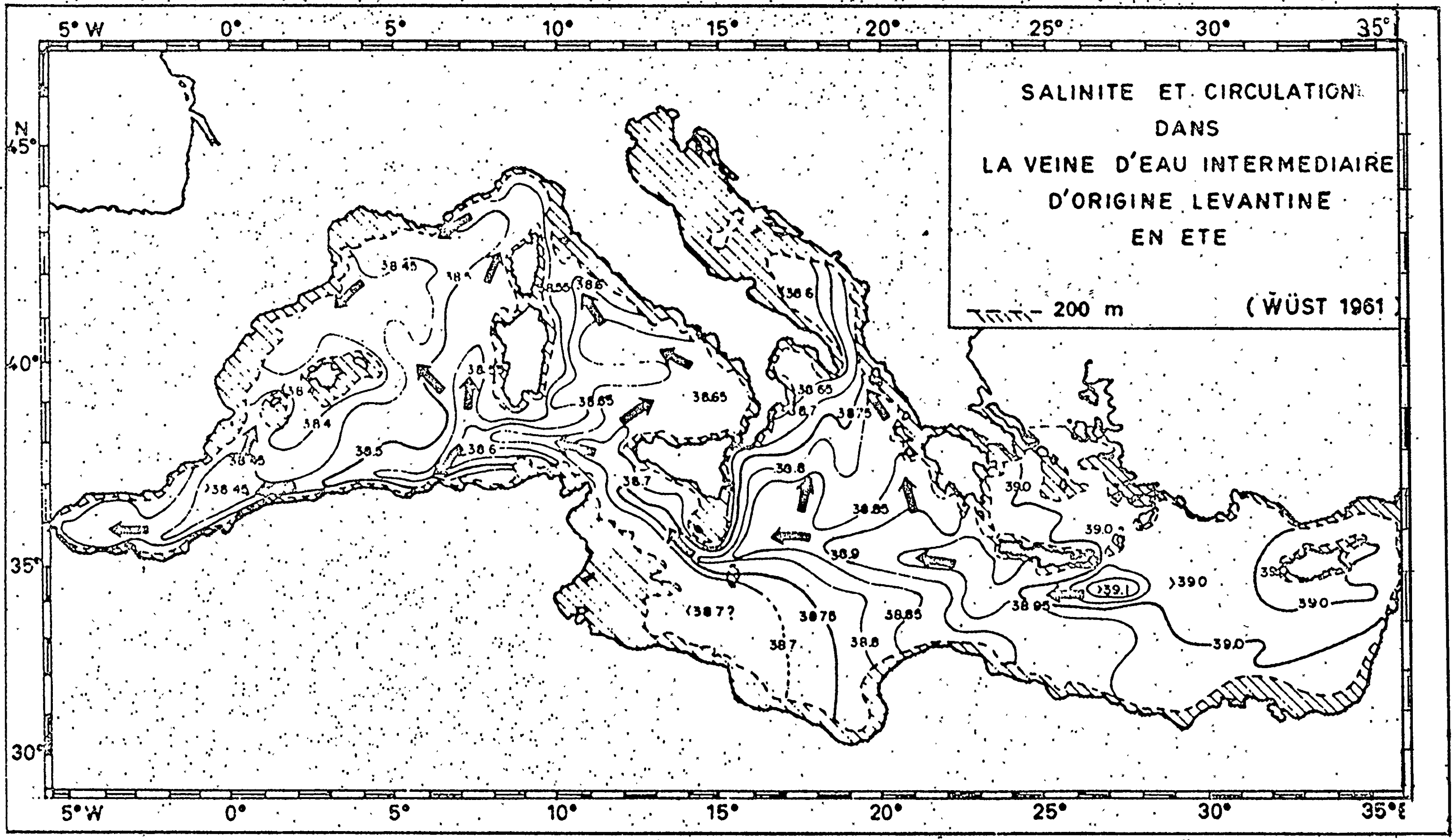


Fig. 2.2.6 - Salinity and circulation in the layer of intermediate water of Levantine origin in summer. (after Wüst, 1961) (from Lacombe and Tchernia, 1972).

Northern Adriatic surface water is strongly influenced by the discharges of the Po and other rivers contributing altogether to about one third of the total discharges of fresh water into the Mediterranean (Stirn et al., 1974). This water, with salinity well below 37 ppt, is fundamental for the formation of the eastern basin deep water. (See Fig. 2.2.7).

North-west Mediterranean surface water, like the latter made up of discharges mainly by the river Rhône, influences a large area especially in summer, mainly in the Golfe du Lion and adjacent coastal stretches (Cruzado et al. 1977) playing also an important role in the formation of the deep water of the western basin.

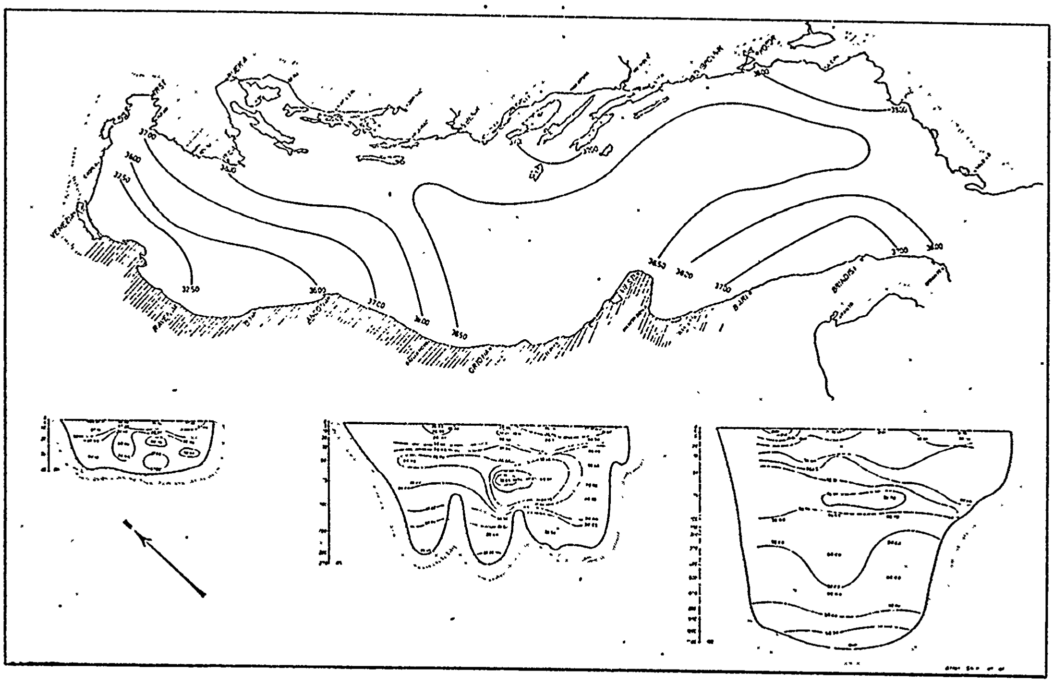
2.2.3 General Circulation of the Mediterranean

Due to the weakness of the tidal forces in the Mediterranean Sea, tidal circulation is in general negligible except in the neighbourhood of the straits of Gibraltar and of the amphidromic points like the straits of Sicily and south of Crete as well as in the north Adriatic. Therefore, the main components of the velocity field are due both to the wind stress and atmospheric pressure distribution and to the thermohaline forces created by the hydrographic structure already described in the previous section.

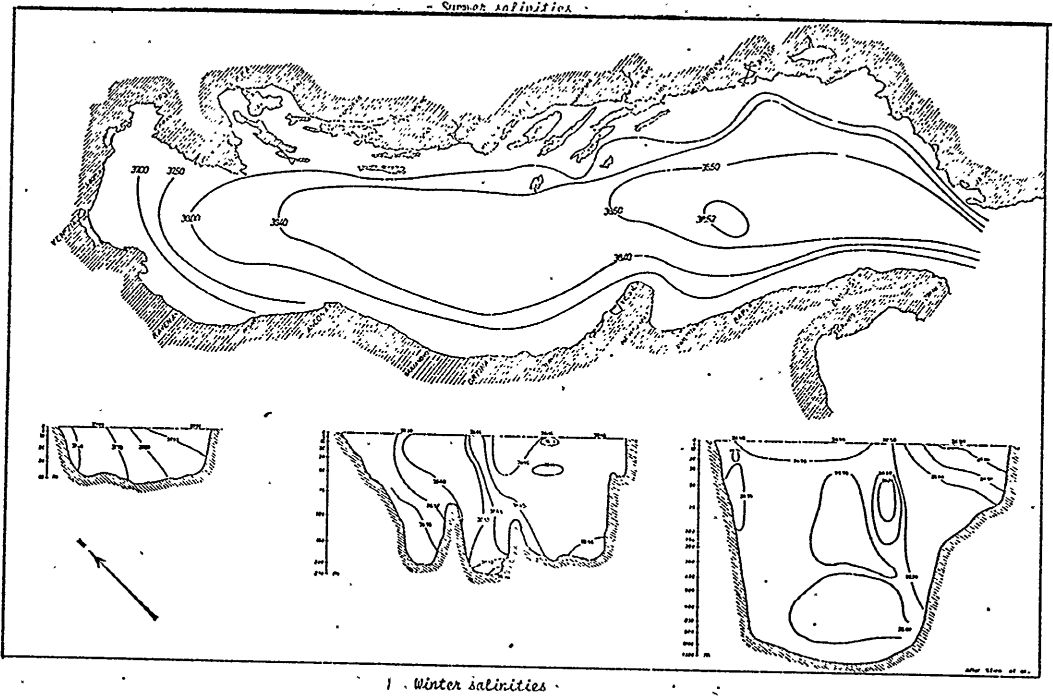
The spatial distribution of the density suggests a general circulation of the surface Atlantic water entering the Mediterranean Sea towards the east and of the Levantine intermediate water and western deep water towards the west. Due to the rotation of the Earth (Coriolis effect) this general flow pattern should be deflected to give a cyclonic (anti-clockwise) general circulation in each of the basins. However, the large number of straits and sills, especially in the eastern basin, much complicates the actual circulation pattern not only of the surface layer but also of the intermediate and deep water layers.

Summer general surface circulation. Based on the data gathered by the "Thor" expedition in 1908-1910, Nielsen established the pattern of surface general circulation for the entire Mediterranean Sea (Fig. 2.3.1). Although a large amount of research has been carried out on the matter in the last 70 years, this pattern is still used by authors summarizing the knowledge on surface currents (Lacombe, 1974a; Lacombe and Tchernia, 1972 and 1974). However, according to Allain (1960), the network of observations made during that expedition was too sparse for the circulation pattern to have more than just a very limited value.

A number of authors have studied the currents system of both the western and the eastern basins and contributed to the improvement of the simple Nielsen model. Allain (1960) taking into consideration the work done in the western basin as well as his own dynamic computations, has produced a highly improved version of the summer general surface circulation for the western basin (Fig. 2.3.2). The main features are a number of counter-clockwise gyres found all over the basin especially active along the northern shores from the Alboran Sea to the Tyrrhenian Sea. These gyres seem to carry the largest part of the Atlantic water all the way through the Balearic Islands and into the Golfe du Lion area. The



- Summer salinities -



I. Winter salinities

Fig. 2.2.7 Summer and winter salinities of the Adriatic (1972-1973) Stirn et al., 1974

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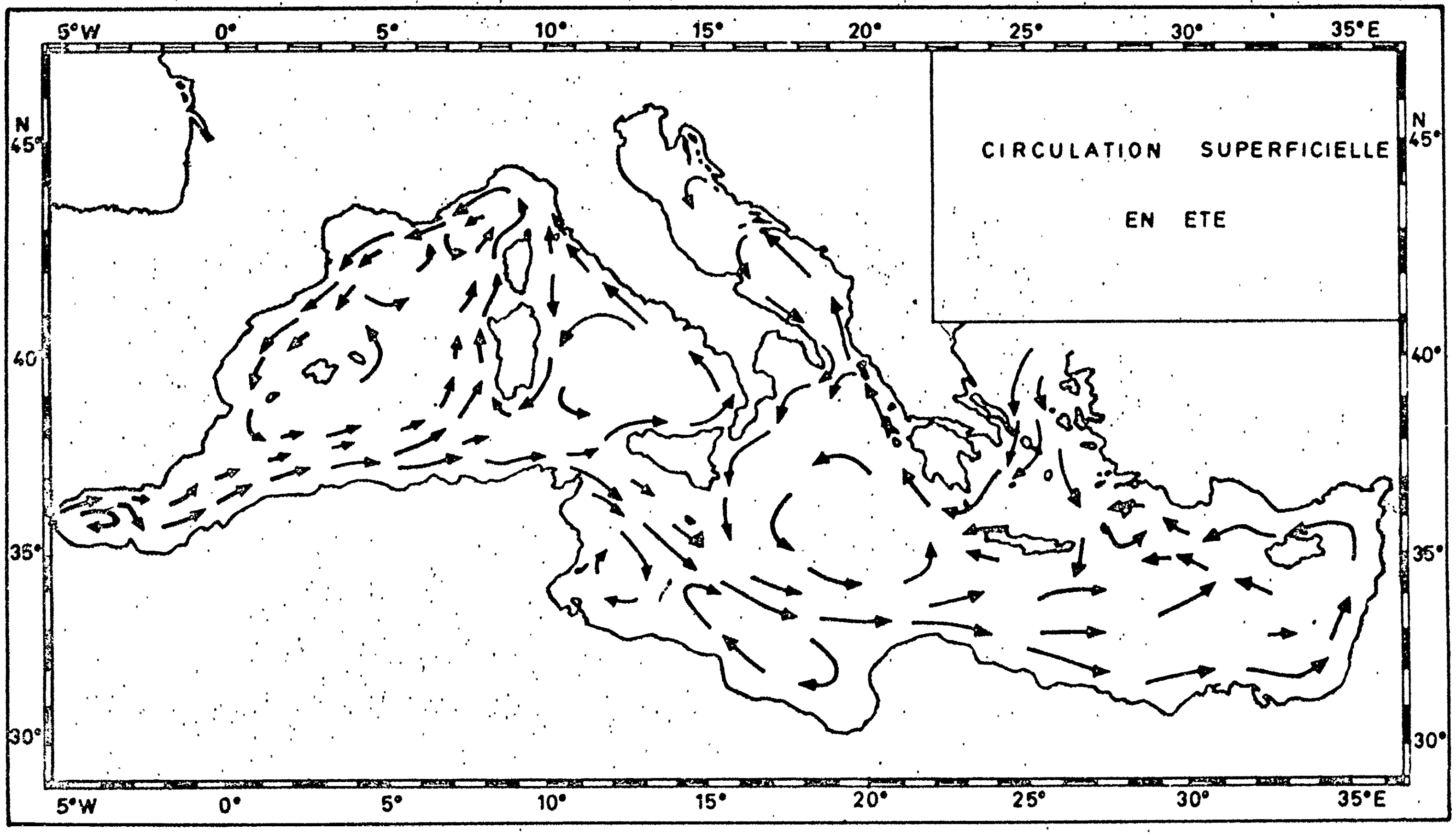

Fig. 2.3.1 - Pattern of surface circulation in summer (Schmidt-Nielsen) (from Lacombe, 1974)

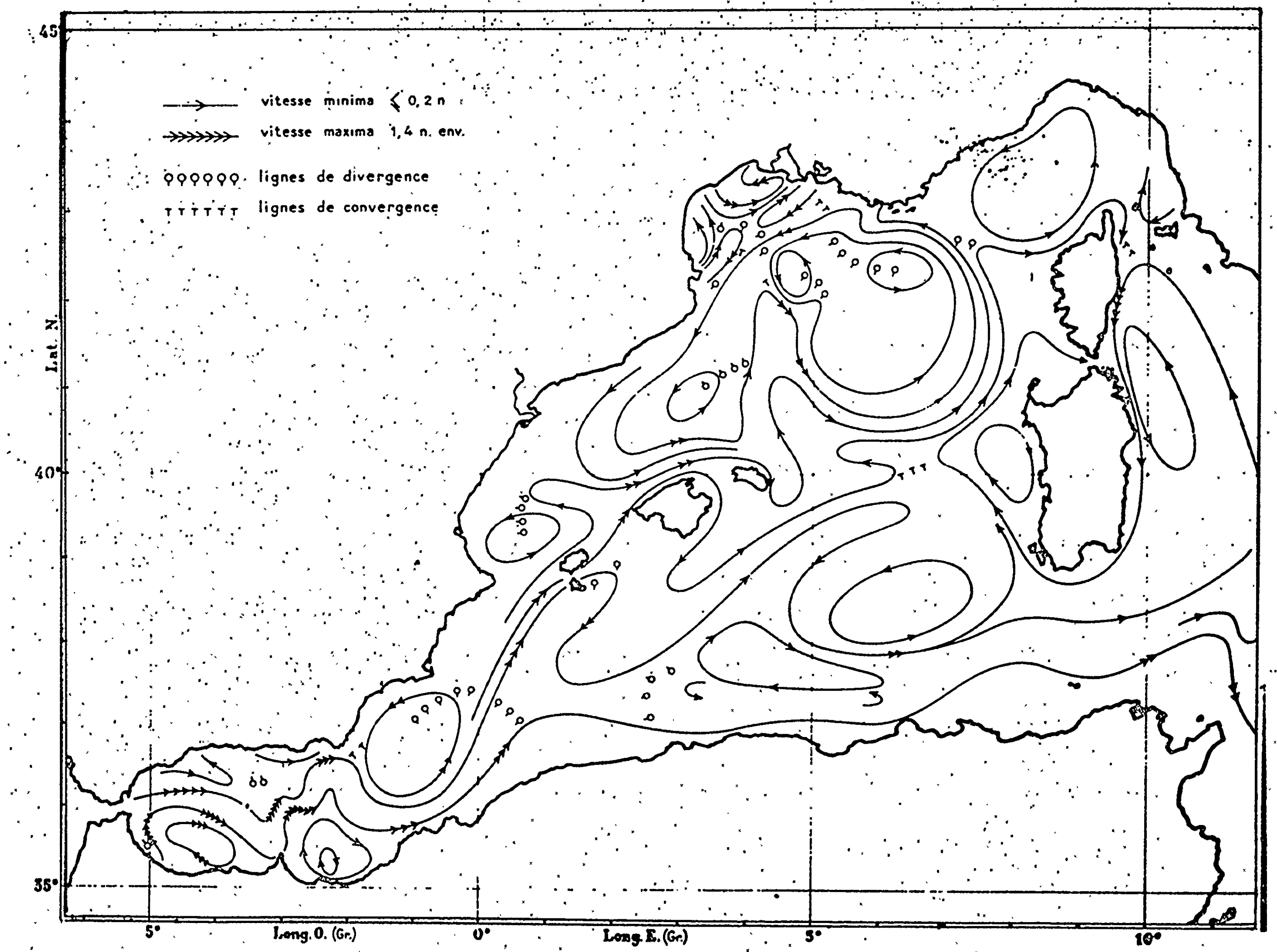

Fig. 2.3.2 - Pattern of surface currents in summer in the west of the western basin. (Allain, 1960).

remaining Atlantic water would be involved in the North African flow, generating several weak clockwise gyres and, crossing the straits of Sicily, flow towards the eastern basin with part of it entering the Tyrrhenian Sea and circling it also in a counter-clockwise direction.

This pattern of circulation has been substantiated at least for the Catalan Sea and around the Balearic Islands during the MED POL phase by geostrophic computations made during a spring cruise in the area (Cruzado et al., 1977).

According to this pattern, any pollutants entering through the sills of Gibraltar would soon reach the shores of the Balearic Islands and join the north to south coastal circulation along the southern shores of France where the Rhône waters would contribute to the main Atlantic vein and, along the Catalan coast, reach the Ebro outlet and then off-shore towards the Balearic Islands closing the large NW Mediterranean gyre. This water would therefore continue to recirculate this rather closed gyre until the winter winds completely disrupted the summer circulation and transformed the surface water into deep western water.

Unfortunately, a similar synthesis of the recent knowledge of the eastern basin has not been carried out so far. Geostrophic computations for the Levantine Sea were made by Burman and Oren (1970) (Fig. 2.3.3) showing some features not included in Nielsen's model circulation such as the long circuit of the surface Atlantic water entering through the straits of Sicily and being taken into a number of clockwise and anti-clockwise gyres before flowing into the Aegean Sea through the narrows between Rhodes and the Turkish mainland where it is converted during the winter into eastern deep water. Gerges (1976) has also given an estimate of the currents driven both by wind and by density for the eastern basin east of 20°E (Fig. 2.3.4) showing the strong large-scale cyclonic eddy also pointed out by Nielsen. This large gyre is undoubtedly responsible for the strong thermohaline front between the incoming Atlantic water and the older surface water trapped in a rather closed circulation in the Levantine Sea accounting for its high salinity.

Finally, the Adriatic Sea, the only basin with a positive water balance due to the discharges of the Po and other rivers, has a basically cyclonic circulation pattern with a number of small eddies which recirculate the fresh water entering in the NW as it flows southwards and out into the Ionian Sea (Fig. 2.3.5). This general cyclonic pattern has been substantiated during the MED POL phase by the general displacement of surface drifters in the high Adriatic.

Winter surface circulation: Basically the summer circulation seems to hold also for winter time although the general movement seems to be stronger. Along the French shores the volume transported in winter is about twice as large as in summer (Lacombe, 1974a). The transport in the 100 m above the slope off the Catalan coast shows a maximum in spring and autumn and a minimum in winter (Cruzado et al., 1977) tentatively attributed by the authors to a larger inflow of fresh water to the coastal stretch during the equinoctial rainfalls.

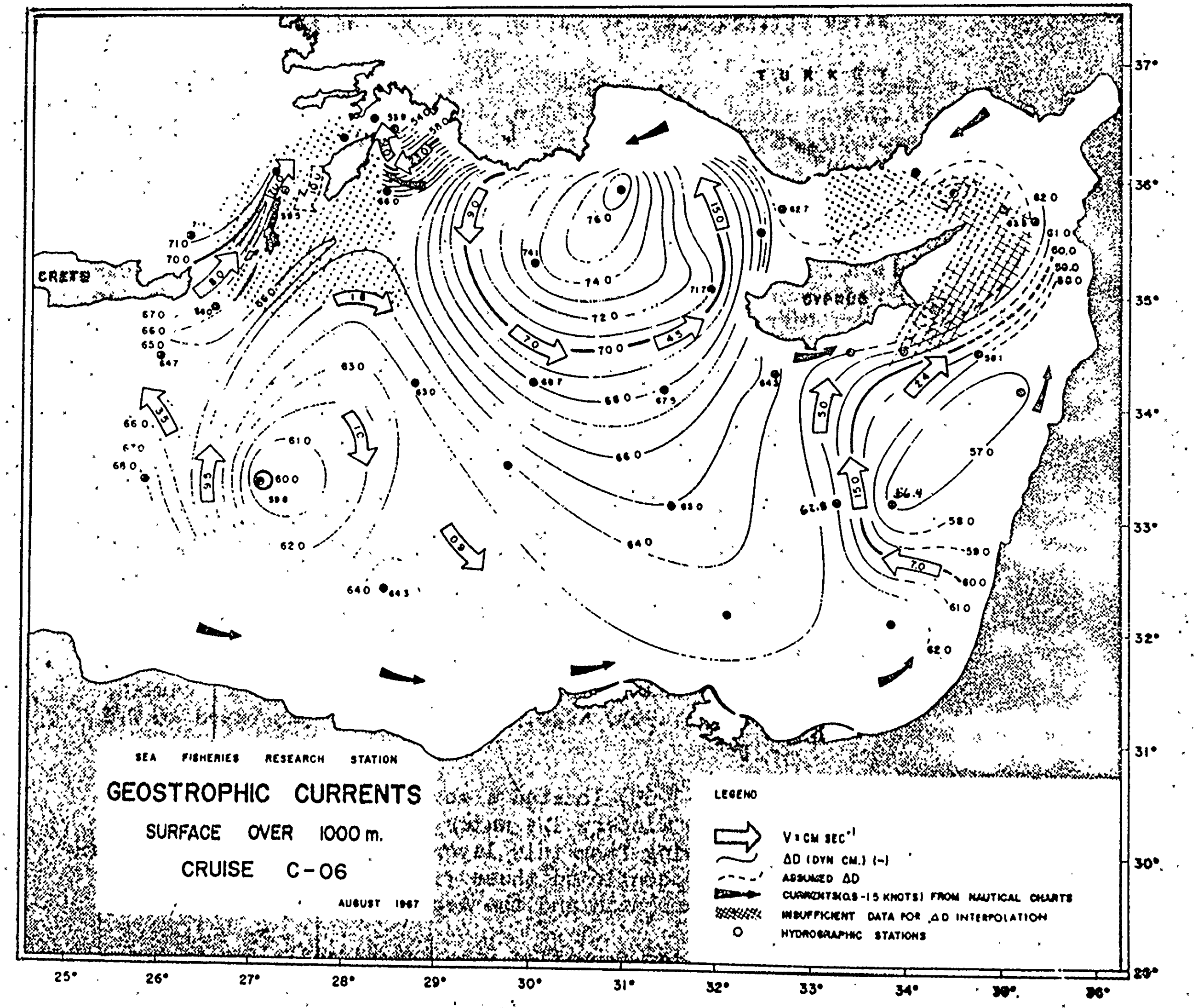

Fig. 2.3.3 - Geostrophic currents. (Burman and Oren, 1970)

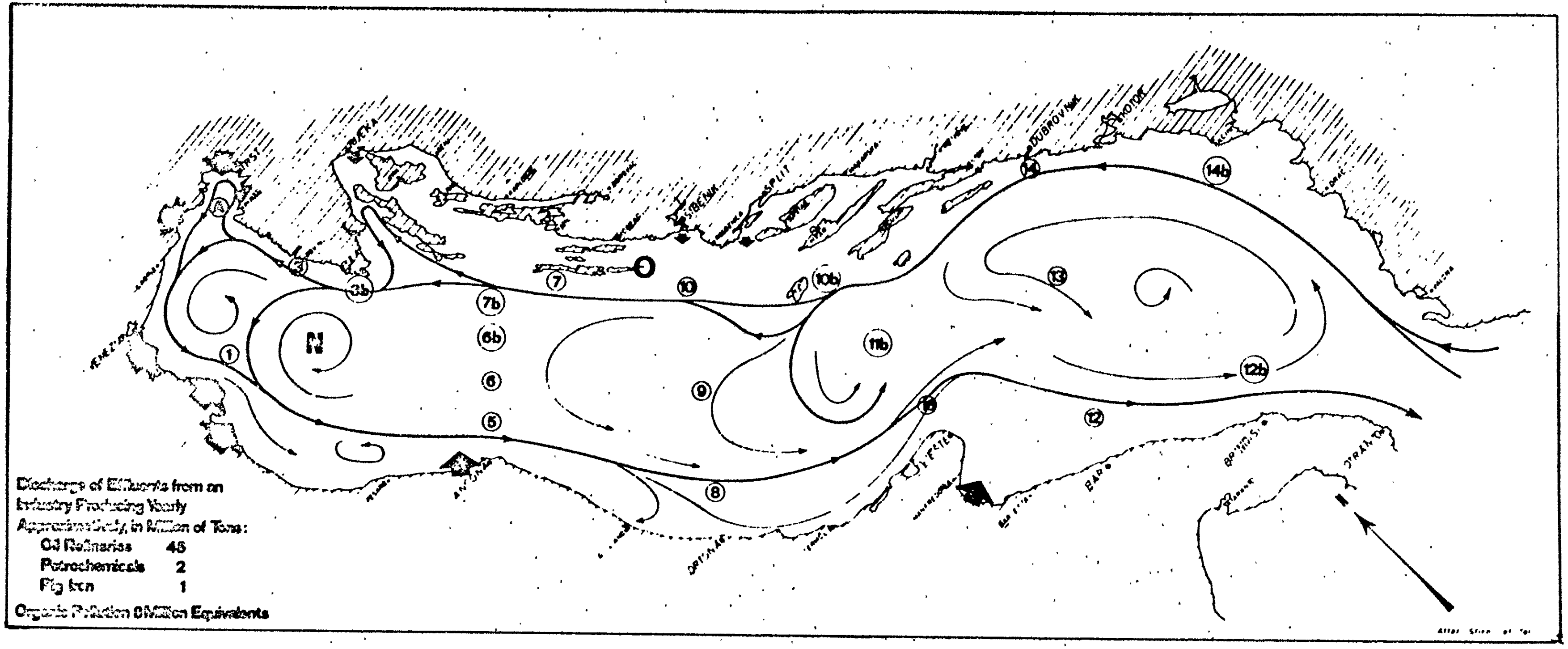

Fig. 2.3.5 - Map of the Adriatic showing its circulation, major-pollution sources and stations of the cruise A. Mohorovicic (March 1973). (Stirn 1974)

On the other hand, the correlation between surface current and local wind which in summer is very definite, appears less clear in winter when the water is vertically homogeneous in density (Gonella, 1973) due to the existence of vertical currents with the same order of magnitude as the horizontal ones. It can be concluded that, in general, information on hydrography and circulation in winter is sadly lacking, much more so than in summer.

Intermediate circulation: If the circulation of the surface layer is known rather imprecisely, even less is known about the circulation of the intermediate layer both in the eastern and in the western basins. As has been pointed out above, the general displacement is from east to west and, except in the straits of Sicily where velocities up to 50 cm/sec have been cited, very few velocity measurements have been carried out. Lacombe and Tchernia (1972) give an estimate of 5 to 10 cm/sec as the maximum velocities for the more important veins of intermediate water.

A cyclonic circulation is presumed (Fig. 2.2.6) although in some cases departures from this rule would not be surprising. The velocity could be much more important in the Alboran Sea since this layer is contributing to a high extent to the flow of the Mediterranean water into the Atlantic Ocean. However, in this area, the intermediate water mass no longer keeps its identity.

Deep water circulation: Because of the strong homogeneity of the density of the deep waters of the Mediterranean, weak velocities are suspected and perhaps the vertical component is not the least important. In these layers, as in the case of the intermediate water, a general east to west displacement occurs, although it is much weaker in the eastern basin than in the western one since the deep water is not flowing across the sills of the straits of Sicily. Here again information is very scanty.

Coastal circulation: Basic knowledge of the circulation in most coastal regions of the Mediterranean is severely limited and fragmented. The velocities in the coastal zones are mostly due to the transient disturbances caused by successive gusts of wind and the corresponding waves and eddies are the dominant processes. Yet these processes are likely to vary on different shelves and with seasons.

One of the main sources of information has been the release of drifters and driftcards in several regions carried out in the past 20 years. There is a great drawback, however, in this procedure: the speeds computed upon recovery are minimal velocities due to the trapping of the drifters in closed eddies between the shoreline and the general circulation streamlines. Therefore, they do not represent the actual coastal circulation and can even be contradictory.

In spite of the lack of <u>in situ</u> observations, several exercises are being conducted within the general framework of MED POL. Consequently certain results are emerging for different coastal areas in the Mediterranean. A very well controlled driftcard experiment was launched in the Ligurian Sea to serve as a model for a more ambitious exercise covering the entire Mediterranean. A network of in situ recording current meters is being set up in these areas and data produced ought to be checked against computations of the velocity components generated by local wind stress, general atmospheric circulation and density structure from open water hydrographic studies.

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3. ASSESSMENT OF POLLUTION

In the following sub-sections the present state of the pollution of the Mediterranean is reviewed in relatively general terms. The data used in this review are primarily those reported by the participants in the Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL) although a deliberate use has been made of other data made available through publications, reports or personal communications. The results reported through MED POL are very recent indeed, most of them having been received in May and June 1977. It was therefore impossible to prepare a complete and in-depth analysis of these data and they are reported in a somewhat selective and incomplete way.

For the sake of convenience and to follow the presentation of pollutants from land-based sources which is under preparation, the Mediterranean was sub-divided, disregarding national boundaries, into ten areas of the Mediterranean proper and three adjacent areas. The geographic boundaries of the areas and the interim terminology used for their description are indicated in figure 3.0.1.

The state of pollution of each of these areas has been described separately whenever possible.

3.1 HEAVY METAL CONCENTRATIONS IN SEA-WATER, SEDIMENTS AND ORGANISMS

Many toxic or potentially toxic heavy metals are released into the oceans, especially into the coastal zones. Iron, copper, zinc cobalt, manganese, chromium, molibden, vanadium, nickel and zinc are known to be essential for living organisms. But even these essential metals become toxic, if present in excessive quantities. An idea of the toxicity and (very important) their availability can be obtained from table 3.1.1.

Apart from waste discharge the oceans receive heavy metals (together with other materials) through the atmosphere, land run-offs and rivers. Natural processes such as degassing, weatherng and erosion mobilize these metals. Heavy metals mobilized by man enter into the natural biogeochemical cycles at rates comparable to or even exceeding the natural rates. The prediction of the rate and the pathway of a heavy metal mobilized by man is further complicated by the observation that the pathways and rates of mobilization depend on the physico-chemical state of the element. Often, however, anthropogenic mobilization produces physicochemical forms which are different from the natural ones observed. As a consequence an artificially mobilized heavy metal can appear in a component of the marine system in which it was not anticipated and cause unexpected damage to marine biota and create hazards for human health.

In order to facilitate a distinction between natural and anthropogenic increased levels, open sea data and coastal data are discussed in separate sections. Coastal areas are much more likely to suffer than the open sea from anthropogenic inputs of metals.

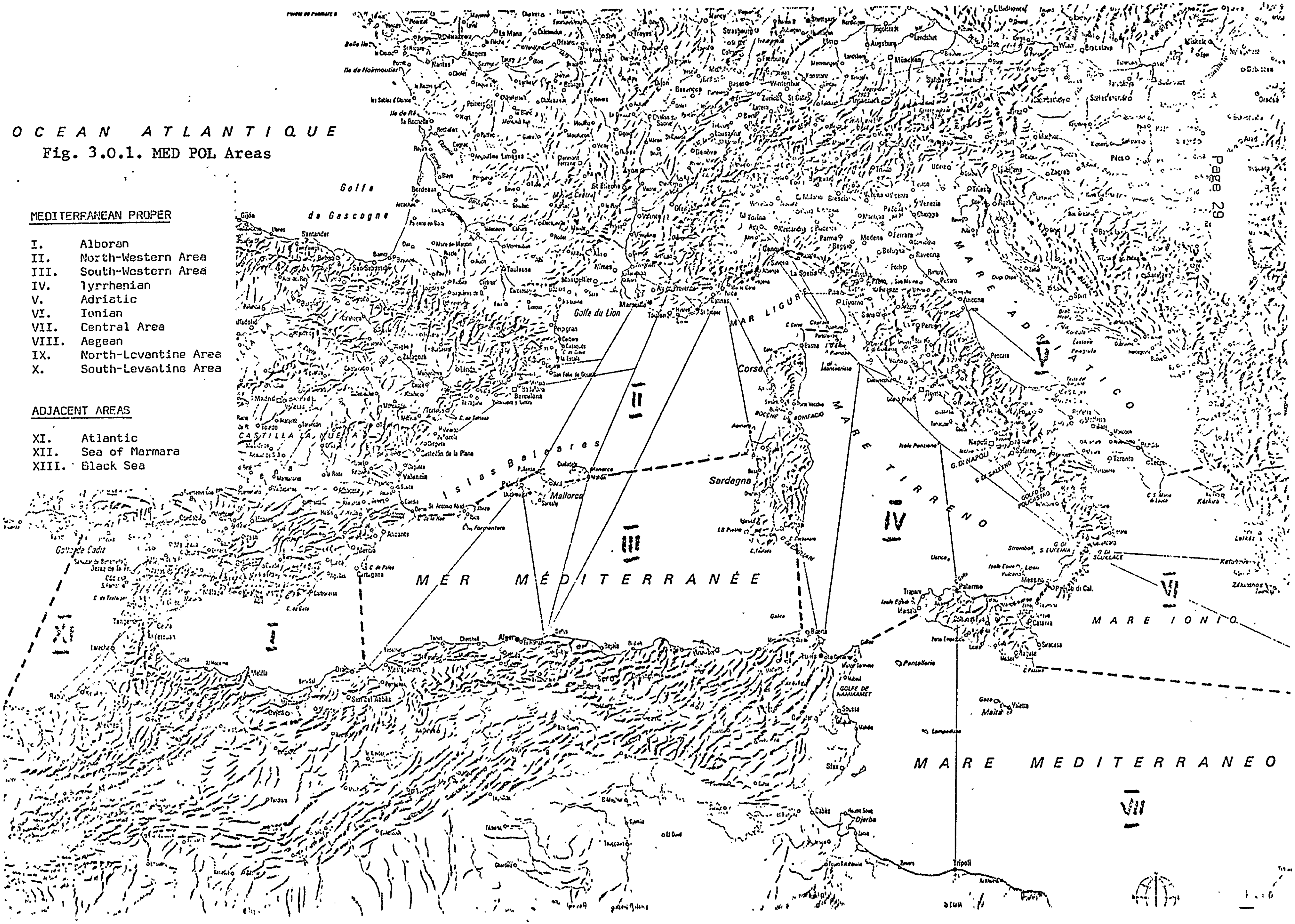


Fig. 3.0.1. MED POL Areas

MEDITERRANEAN PROPER

I.	Alboran
II.	North-Western Area
III.	South-Western Area
IV.	Tyrrhenian
V.	Adriatic
VI.	Ionian
VII.	Central Area
VIII.	Aegean
IX.	North-Levantine Area
X.	South-Levantine Area

ADJACENT AREAS

XI.	Atlantic
XII.	Sea of Marmara
XIII.	Black Sea

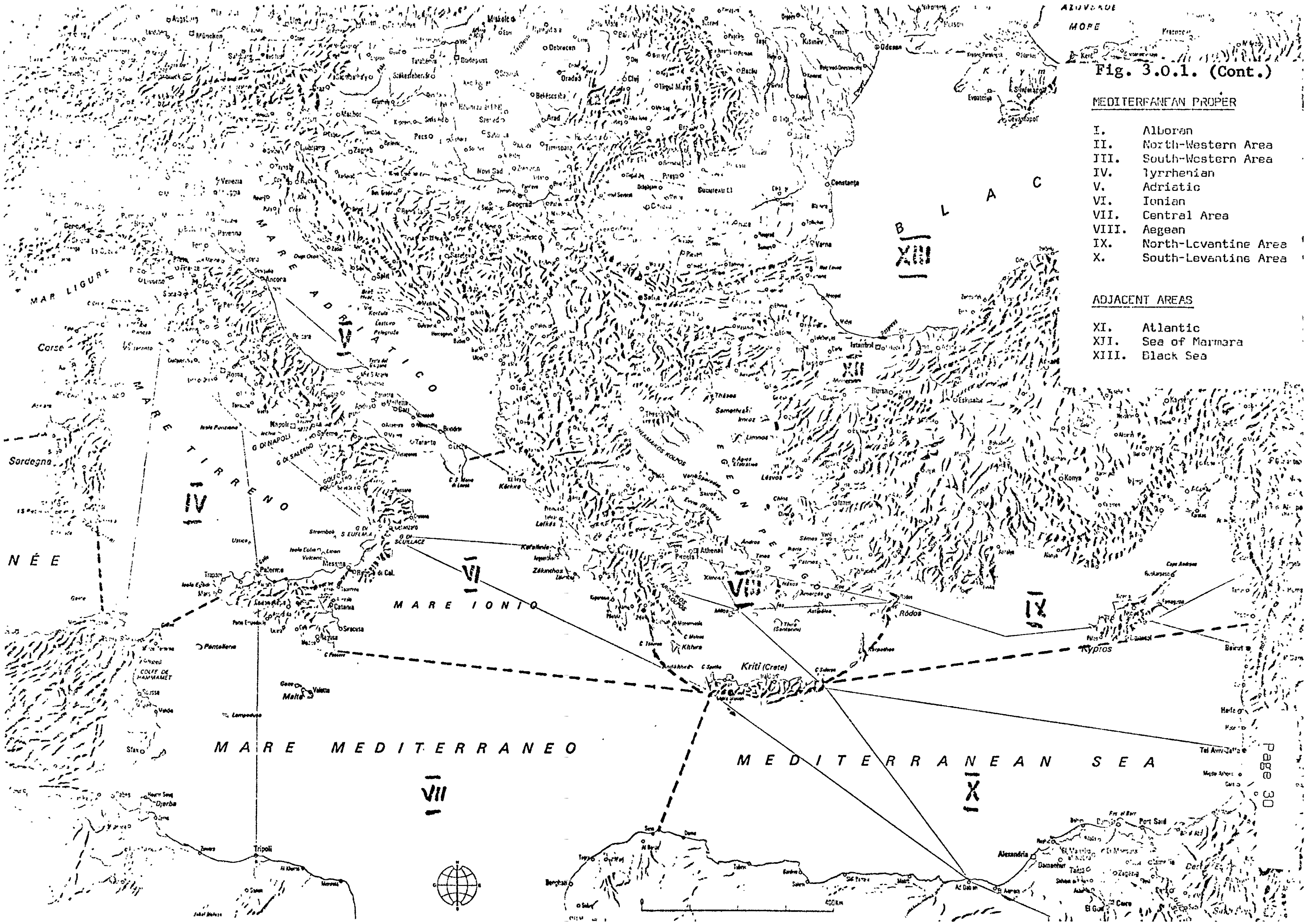


Fig. 3.0.1. (Cont.)

MEDITERRANEAN PROPER

I. Alboran
II. North-Western Area
III. South-Western Area
IV. Tyrrhenian
V. Adriatic
VI. Ionian
VII. Central Area
VIII. Aegean
IX. North-Levantine Area
X. South-Levantine Area

ADJACENT AREAS

XI. Atlantic
XII. Sea of Marmara
XIII. Black Sea

Table 3.1.1

Classification of elements according to their toxicity [a]

(Wood and Goldberg 1977)

Non-critical	Very toxic and relatively accessible	Toxic but very insoluble or very rare
Na	Be	Ti
K	Co	Hf
Mg	Ni	Zr
Ca	Cu	W
H	Zn	Nb
O	Sn[c]	Ta
N	As[c]	Re
C	Se[c]	Ga
P	Te[c]	La[d]
Fe	Pd[c]	Os
S	Ag	Rh
Cl	Cd	Ir
Br	Pt[c]	Ru
Fe	Au[c]	Ba
Li	Hg[c]	
Rb	Tl[c]	
Sr	Pb[c]	
Al	Sb	
Si	Bi	
F[b]		

[a] Elements omitted from this table should not be neglected in the environmental sense. For example, iodine and manganese are important elements, but they fit more than one category for the above classification.

[b] Some may argue with this designation, but we do add fluoride to drinking water.

[c] Metals having metal alkyls which are stable in aqueous systems have been reported to be biomethylated.

[d] All the lanthanides are very insoluble and some are very rare.

3.1.1 Characteristics of heavy metals

The distinction between different physico-chemical forms is very important because different physico-chemical forms will participate in different ways in the biogeochemical cycles. They also have different effects on marine organisms. For example ionic forms are preferentially accumulated by some marine organisms and particulate forms by others (for a recent review see Bernhard and Zattera 1975). Organo-mercury compounds are more toxic than inorganic mercury compounds. On the other hand most heavy metals are more toxic in ionic than in complexed form. Also heavy metal/ sediment interactions depend very much on the physico-chemical form of the metal and of the granulometric and mineralogical composition of the sediment. Only in recent years has the chemical speciation of sea-water obtained the attention it deserves (e.g. Kester et al. 1975).

Three groups of chemical states of a metal in sea-water can be distinguished: dissolved, colloidal and particulate. A scheme for their differentiation is shown in figure 3.1.1. The dissolved metal can occur as a free metal ion, as an inorganic ion pair, or as an inorganic or organic complex. These ions and compounds are in general smaller than 1 nm. Metal ions complex bound to high molecular weight (MW) organic substances (>10 nm) can be separated by dialization. Membrane filtrable compounds include highly dispersed colloids. The metal compounds which remain on the membrane filter are precipitates, inorganic and organic particules, metal adsorbed to particles and small marine organisms such as bacteria and microscopic algae. The different physico-chemical forms of mercury are given as an example in the lower part of figure 3.1.1.

3.1.2 Sources and inputs of heavy metals into the ocean

A general schema of the inputs and outputs of a marine ecosystem consisting of the three principal components is shown in figure 3.1.2. In order to obtain a general idea of the present anthropogenic inputs into the oceans, world mining production and potential global heavy metal inputs are compared in table 3.1.2. Through MED X input of some heavy metals into the Mediterranean has been very approximately estimated (figures 3.1.3 to 3.1.6). Since so far no data on the 'natural' inputs are available for a comparison, the previously cited global values may serve for a first approximation (table 3.1.2). At a later date, when an adequate data base exists, the particular characteristics of the Mediterranean, for example the mercury anomalies (see below), have to be taken into consideration for a better estimation of the inputs in this area.

3.1.3 Heavy metals in the marine environment

3.1.3.1 Heavy metals in sea-water

The accurate and sometimes also the precise determination of heavy metals is rendered more difficult by many still unsolved problems in sampling, sample preparation, sample conservation and analytical procedure. As a consequence only relatively few measurements have

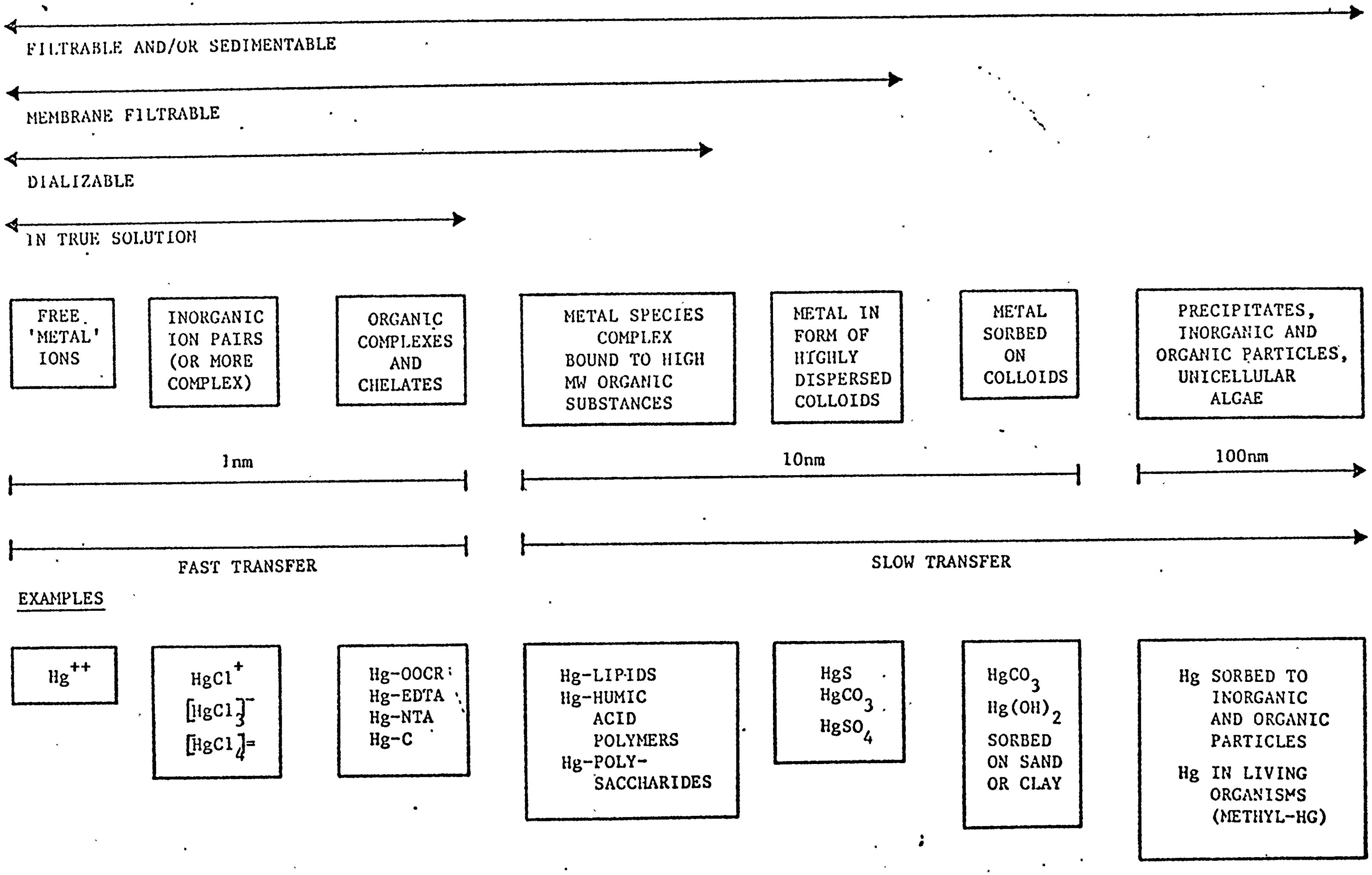


Fig. 3.1.1 Scheme of "heavy metal" species in a sea-water sub-system (UNESCO 1977)

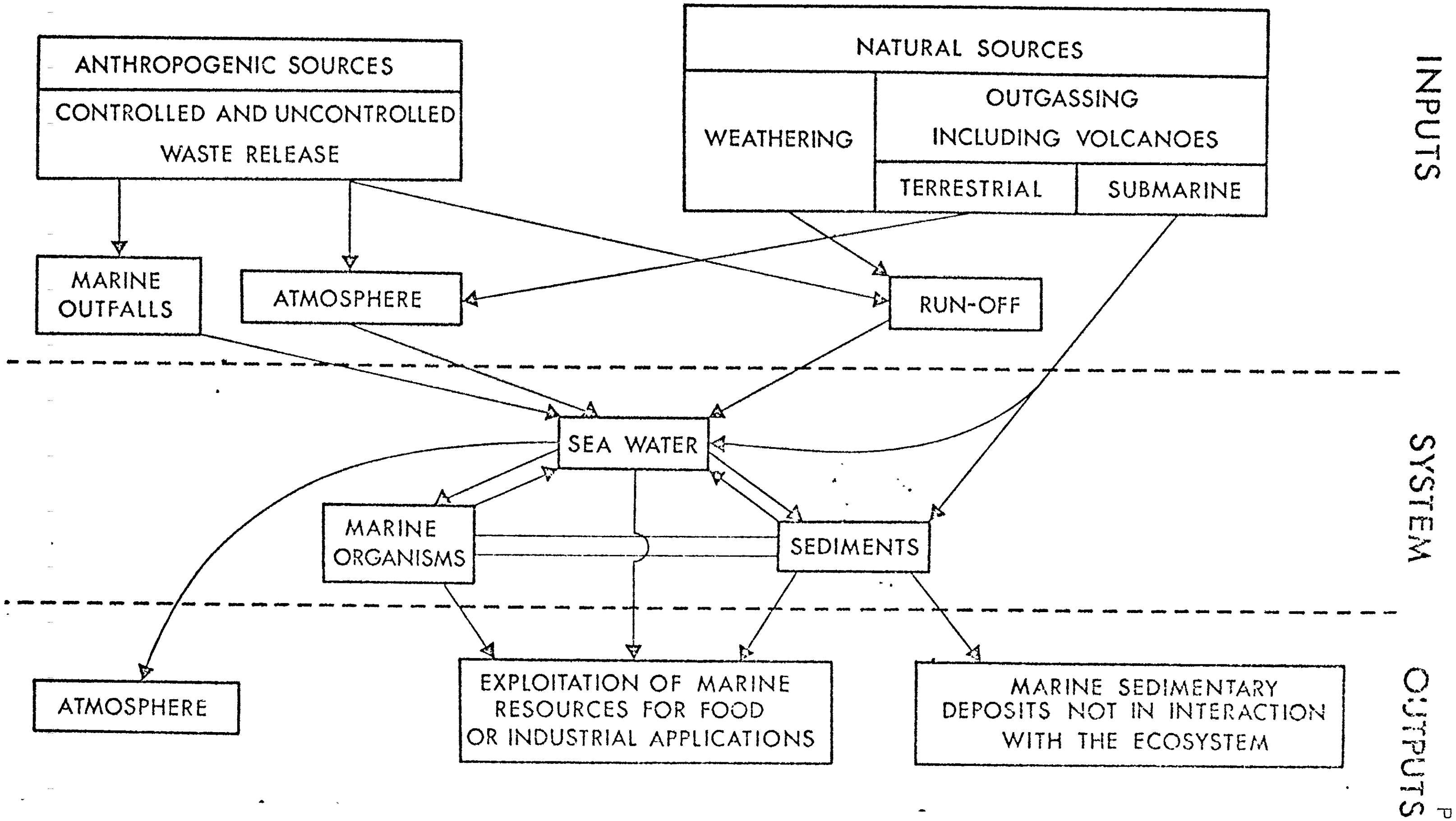


Fig. 3.1.2 Schema of the inputs and outputs of a 3 component marine system (UNESCO 1977)

Table 3.1.2.
World heavy metal production and potential ocean inputs
(Marine Environmental Quality 1971)

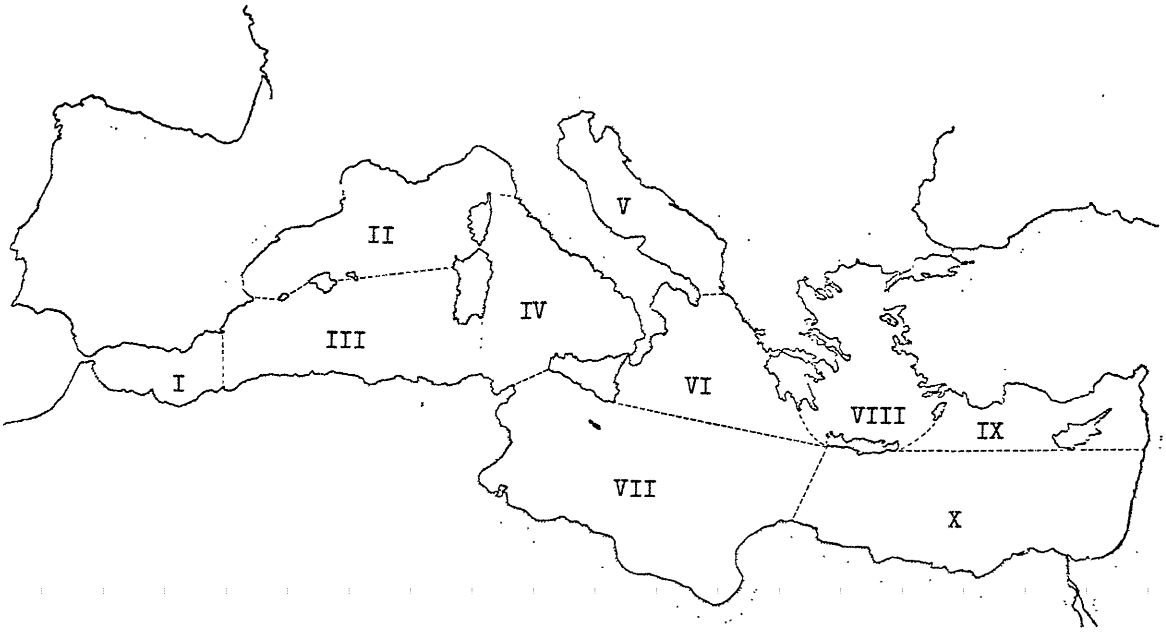
Substance	Mining Production[a] (million tons/yr)	Transport by rivers to oceans[b] (million tons/yr)	Atmospheric Washout[c] (million tons/yr)
Pb	3	0.1	0.3
Cu	6	0.25	0.2
V	0.02	0.03	0.02
Ni	0.5	0.01	0.03
Cr	2	0.04	0.02
Sn	0.2	0.002	0.03
Cd	0.01	0.0005	0.01
As	0.06	0.07	-
Hg	0.009	0.003	0.08
Zn	5	0.7	-
Se	0.002	0.007	-
Ag	0.01	0.01	-
Mo	-	0.03	-
Sb	0.07	0.01	-

[a] US Department of Interior, (1970 a and b).

[b] Bertine and Goldberg, (1971)

[c] Estimated from aerosol data of Egorov *et al.*, (1970) and Hoffman, (1971)

[d] Goldberg, unpublished data



I

Total	2.5 t/a
Dom.	2%
Ind.	24%
Agri.	-
Riv.	74%

II

Total	33 t/a
Dom.	1%
Ind.	8%
Agri.	-
Riv.	91%

III

Total	2.7 t/a
Dom.	1%
Ind.	7%
Agri.	-
Riv.	92%

IV

Total	10.7 t/a
Dom.	1%
Ind.	10%
Agr.	-
Riv.	89%

V

Total	41 t/a
Dom.	0%
Ind.	1%
Agri.	-
Riv.	99%

VI

Total	9.8 t/a
Dom.	~ 0%
Ind.	2%
Agri.	-
Riv.	98%

VII

Total	1.7 t/a
Dom.	2%
Ind.	9%
Agri.	-
Riv.	88%

VIII

Total	14.3 t/a
Dom.	~ 0%
Ind.	2%
Agri.	-
Riv.	98%

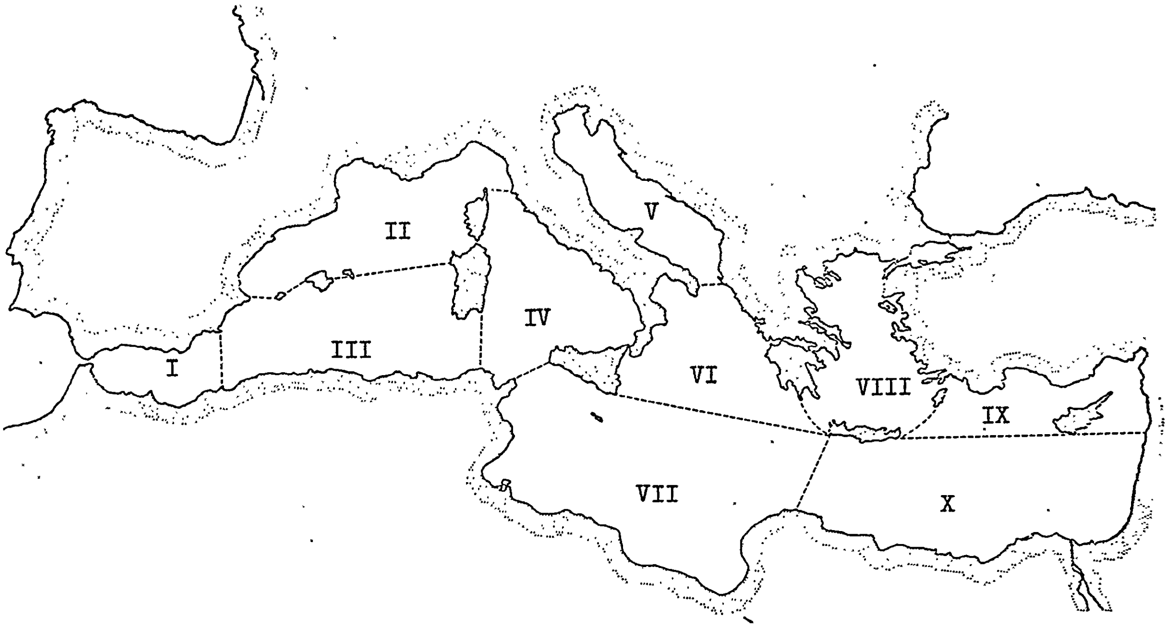
IX

Total	7.1 t/a
Dom.	~ 0%
Ind.	1%
Agri.	-
Riv.	99%

X

Total	6.9 t/a
Dom.	1%
Ind.	17%
Agri.	-
Riv.	82%

Fig. 3.1.3. Inventory of Hg-pollution sources along the Mediterranean coastlines (data from MED X project)



I	Total	104 t/a
	Dom.	10%
	Ind.	58%
	Agri.	-
	Riv.	32%

II	Total	1,000 t/a
	Dom.	9%
	Ind.	37%
	Agri.	-
	Riv.	54%

III	Total	122 t/a
	Dom.	10%
	Ind.	52%
	Agri.	-
	Riv.	39%

IV	Total	379 t/a
	Dom.	10%
	Ind.	42%
	Agri.	-
	Riv.	48%

V	Total	197 t/a
	Dom.	14%
	Ind.	44%
	Agri.	-
	Riv.	42%

VI	Total	207 t/a
	Dom.	4%
	Ind.	9%
	Agri.	-
	Riv.	87%

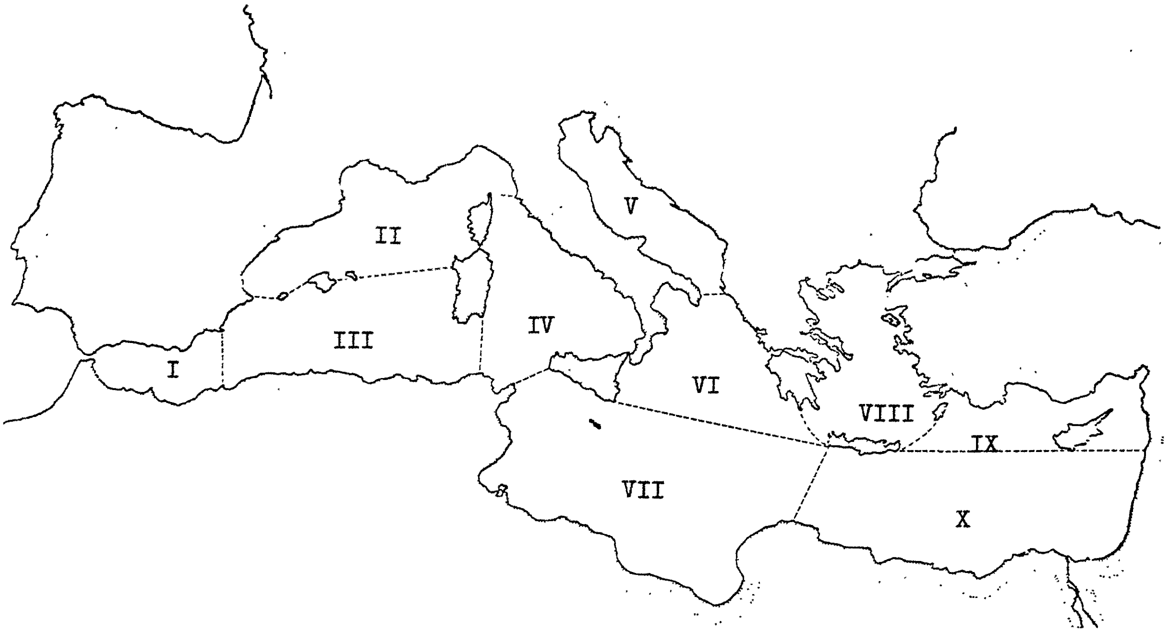
VII	Total	54 t/a
	Dom.	17%
	Ind.	33%
	Agri.	-
	Riv.	50%

VIII	Total	293 t/a
	Dom.	6%
	Ind.	9%
	Agri.	-
	Riv.	85%

IX	Total	145 t/a
	Dom.	2%
	Ind.	2%
	Agri.	-
	Riv.	96%

X	Total	261 t/a
	Dom.	7%
	Ind.	58%
	Agri.	-
	Riv.	35%

Fig. 3.1.4 Inventory of Cr-pollution sources along the Mediterranean coastlines (data from MED X project)



I	Total 262 t/a
Dom.	32%
Ind.	57%
Agri.	-
Riv.	10%

II	Total 5,170 t/a
Dom.	13%
Ind.	41%
Agri.	-
Riv.	46%

III	Total 690 t/a
Dom.	15%
Ind.	30%
Agri.	-
Riv.	55%

IV	Total 3,000 t/a
Dom.	12%
Ind.	40%
Agri.	-
Riv.	47%

V	Total 8,600 t/a
Dom.	2%
Ind.	6%
Agri.	-
Riv.	92%

VI	Total 1,640 t/a
Dom.	4%
Ind.	11%
Agri.	-
Riv.	85%

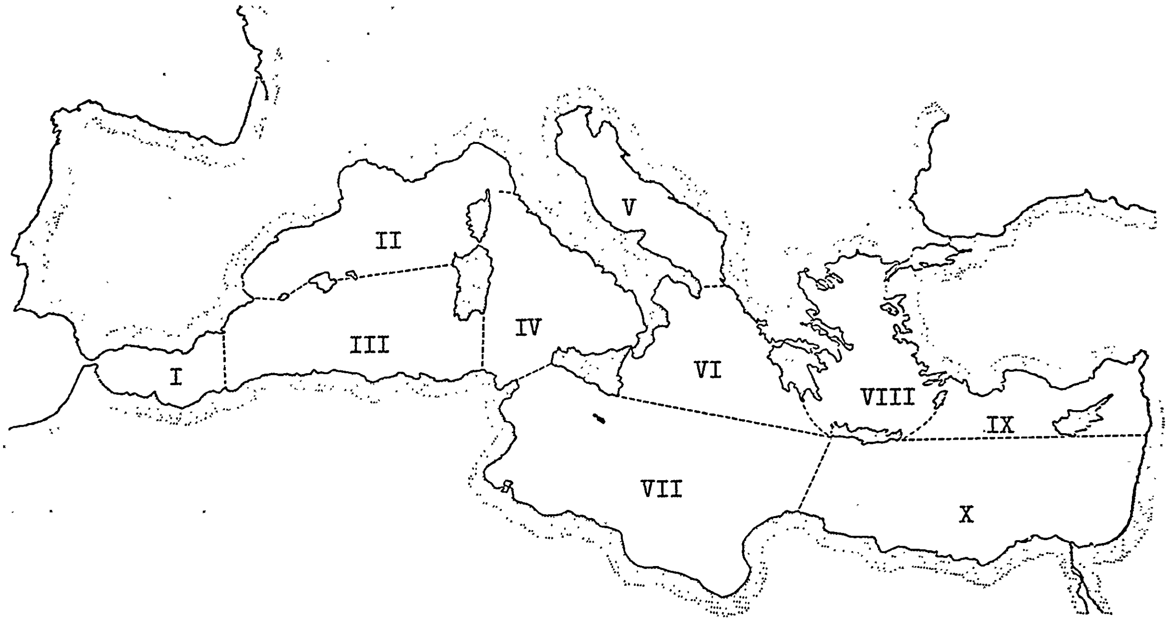
VII	Total 467 t/a
Dom.	16%
Ind.	34%
Agri.	-
Riv.	50%

VIII	Total 2,490 t/a
Dom.	6%
Ind.	10%
Agri.	-
Riv.	84%

IX	Total 1,150 t/a
Dom.	2%
Ind.	2%
Agri.	-
Riv.	96%

X	Total 1,200 t/a
Dom.	14%
Ind.	20%
Agri.	-
Riv.	66%

Fig. 3.1.5 Inventory of Zn- pollution sources along the Mediterranean coastlines (data from MED X project)



	Total	Dom.	Ind.	Agri.	Riv.
I	93 t/a	9%	46%	-	45%
II	1,360 t/a	5%	36%	-	59%
III	121 t/a	8%	43%	-	49%
IV	629 t/a	5%	59%	-	36%
V	1,440 t/a	1%	8%	-	91%
VI	232 t/a	3%	2%	-	95%
VII	98 t/a	8%	56%	-	36%
VIII	444 t/a	3%	25%	-	72%
IX	180 t/a	1%	4%	-	95%
X	232 t/a	7%	41%	-	52%

Fig. 3.1.6 Inventory of Pb-pollution sources along the Mediterranean coastlines (data from MED X project)

been made so far in the Mediterranean. The use of different analytical methods, which often determine different physico-chemical forms and thus only fractions of the 'total' amount present, has further complicated a comparison between values given by different authors. Methods such as instrumental neutron activation (INAA) or chelating resin extraction will yield 'total concentrations', while extracting sea-water with organic solvents at pH 4 - 6 will only determine fractions of the total amount present. In most cases it is not even easy to decide which physico-chemical form or fraction of the total amount has been determinated by a certain method.

Since influence from land will obviously influence the concentration of heavy metals in near-shore areas, a distinction is made between determinations of 'open-sea-samples' and samples taken in the vicinity of the coast. The former will supply an indication of the general level of heavy metal concentration in the Mediterranean while the latter will reveal mainly local influences. At the same time an attempt is made to indicate the most likely forms determined by each method. It is realized that, due to the scarce knowledge of the actual forms determined, the indication of the forms is very approximate and its main purpose is to draw attention to the chemical speciation problem and stimulate further research on the speciation.

Heavy metals in 'open-sea-samples'.

The first to compare the Hg-concentration in open-sea-water-samples from the Mediterranean with samples from other areas were probably Robertson and collaborators (1972). A summary of published data according to MED POL areas together with a 'typical' concentration i.e. a concentration considered average for unpolluted water, is given in table 3.1.3. Hg-concentrations in samples from tropical NW Atlantic, Irish Sea, North Sea and English Channel were not significantly different from those of the Mediterranean. The 'typical value' is 0.1 ug Hg-T/l with a range of 0.06 to 0.17. Determining hydrolysable soluble (< 0.45 u) mercury in various MED POL regions, Fukai and Huynh-Ngoc (1976 b) found lower values in several areas of the Mediterranean. According to Robertson and collaborators (1972) the particulate fraction of 'typical' open sea sea-water constitutes maximally only 2.5 per cent of the total Hg (Hg-T). Therefore, it is not very likely that the particulate fraction of mercury in sea-water is considerable. The differences between values obtained by the two groups are probably caused by the use of different methods.

Fukai and Huynh-Gnoc (1976 b) also determined Cd, Cu and Zn in MED POL areas II, III, IV, VI and VIII. Their values can be compared with those of Bubic and collaborators (1977) for Cu and Zn (MED POL area V), with those of Fonselius and Koroleff (1963), and for Zn with Fonselius (1970) and Bernhard and collaborators (1977) data. The 'typical' concentration for ionic cadmium plus labile complexes (Traube, 1955) of cadmium seems to be 0.1 ug/l. This value is similar to average concentrations from other non-Mediterranean regions (Bernhard and Zattera 1975, Fukai and Huynh-Ngoc 1976 b). In

Table 3.1.3. Concentration of mercury, cadmium, copper and zinc in the open Mediterranean (in ug/l)

Sampling depth (m)	n	Hg	Species	Cd	Species	Cu	Species	Zn	Species	Sampling area and date	References
15 - 300	(3)	0.11 M (0.062-0.11)	T	-	-	-	-	-	-	Str.Gibraltar (VII/68-VIII/68)	Robertson et al., 1972
0	(13)			<0.1 M (<0.05-0.5)	I + L MF	<0.2M (0.1-4.9)	I + L MF	2.1M (0.8-7.7)	I + L MF	NW Mediterranean (VI/73-VI/74)	Fukai & Hyunh-Ngoc, 1976a
0 - 5	(5)	0.024 M (0.016-0.03)	TH MF	0.09 M (<0.05-0.51)	I + L MF	<0.06 M (10)(<0.06-0.62)	I + L MF	(10) 1.0 M (0.1-2.6)	I + L MF	SW Mediterranean (V/75-IX/75)	
0 - 5	(4)	0.021 M (0.017-0.03)	TH MF	0.12 M (0.05-0.43)	I + L MF	0.07 M (0.06-0.93)	I + L MF	1.3 M (0.5-4.8)	I + L MF	W. Ligurian Sea (VII/75-IX/75)	
0	(11)	-	-	-		3.7 M (1.0-12.7)	I + D + P	30.0 M (9.6-86.0)	I + D	Ligurian Sea (V/62)	Fonselius & Koroleff 1963
20	(11)	-	-	-		0.72 M (0.15-1.16)	I + D + P	5.4 M (3.9-10.6)	I + D + P	Ligurian Sea (IX/62)	
10 - 2250	(15)	-	-	-		0.23 (<0.03-3.32)	I + D + P	0.23 M (3.3-16.4)	I + D + P	40 km S-Imperia (IV/63)	
0 - 175	(121)	-	-	-	-	-		7.6 $\bar{x}$ (0.84-12.5)	HT	20 km SW La Spezia (II/67-II/69)	Bernhard et al., 1977
5	(4)	0.025 M (0.02-0.03)	TH MF	0.1 M (0.08-0.33)	I + L MF	<0.06 M	I + L MF	0.7 M (0.2-2.3)	I + L MF	Tyrrhenian Sea (IX/75)	Fukai & Huynh-Ngoc 1976a
0 - 500	(69)	-	-	-	-	-	-	10.5 $\bar{x}$ (5.8-28.4)	HT	Taranto Gulf (IV/69-XI/70)	Bernhard et al., 1977
0	(3)	-	-	0.06 M (0.06-0.12)	I + L MF	0.33 M (0.08-0.74)	I + L MF	1.1 M (0.7-2.4)	I + L MF	Ionian Sea (V/75)	Fukai + Huynh-Ngoc 1976a

Table 3.1.3.(contd.) Concentration of mercury, cadmium, copper and zinc in the open Mediterranean (in ug/l)

Sampling depth (m)	n	Hg	Species	Cd	Species	Cu	Species	Zn	Species	Sampling area and date	References
0.5	(40)	-	-	0.14 $\bar{x}$ (<0.05-0.60)	I + L MF	1.12 $\bar{x}$ (0.1-1.6)	I + L MF	5.35 $\bar{x}$ (0.8-23.6)	I + L MF	G.Kvarner, North Adriatic (VIII/73-II/76)	Bubic et al., 1977
0 - 495	(10)	-	-	-	-	0.57 M (<0.03-2.86)	I + D + P	18.0 M (0.1(?)-29.4)	I + D + P	Off Crete (VII/63)	Fonselius, 1970
0	(3)	-	-	0.07 M (<0.05-0.12)	I + L MF	0.36 M (0.08-0.74)	I + L MF	4.7 M (1.5-5.8)	I + L	Aegean + Cretan S. (V/75)	Fukai & Huynh-Ngoc 1976a
15 - 300	(2)	0.12 (0.09-0.14)	T	-	-	-	-	-	-	Off Cyprus (IV/68)	Robertson et al. 1972
.....	....	....	....	....	....	.....	....	....	....	....	....
typical conc. range		0.02-0.2 (T)		0.06-0.07	T	0.5-2		0.5-10		World oceans	Robertson and Carpenter, 1976

$\bar{x}$ = mean; M = median; (...) before $\bar{x}$ or M number of samples analysed; concentration range in (...) below the $\bar{x}$ or M; I = ionic species; P = particulate species; L = labile complexes with regard to anodic stripping voltametry; D = labile complexes with regard to dithizone; H = hydrolysed by acid treatment; MF = filtrate through 0.45 u millipore filter; T = total comparing the data one has to keep in mind that, for example, the range of a normally distributed population of 2 data estimates 1.25 sigma, a range from 4 data estimates 2 sigma and a range of 9 data 3 sigma (Snedecor 1962). Since the ranges from the different areas overlap (with sample number n between 3 and 13) no significant difference was observed. Bubic et al. (1977) observed the highest value, but here we have to keep in mind that their sample stations are located on the fringe of the Gulf of Kvarner (Rijeka). The copper concentrations vary considerably between authors and areas. Contamination during sampling may be one reason. Also the Zn-concentrations observed show differences which are not easy to explain. Fukai and Huynh-Ngoc (1976) and Bubic et al. (1977) have determined the ionic plus labile complex fraction, with anodic stripping voltametry (ASV), Fonselius and Koroleff (1963) and Fonselius (1970), using a method based on dithizone, probably determined particulate zinc and the zinc which is bound to complexes which have a smaller stability constant than dithizone, while Bernhard and collaborators (1977) have determined hydrolysable zinc with ASV at pH 2. This method includes all zinc which can be liberated from complexes at pH 2. According to the last-named authors, in Ligurian sea-water the ionic fraction is about 10 - 15 per cent, the particulate 20 - 35 and the complexed zinc 45 - 50 per cent of the total hydrolyzable zinc. Chelex extraction yielded about 10 per cent higher zinc concentration than those determined with ASV at pH 2.

Although these data are by no means conclusive and additional data are badly needed, it seems that the concentration of Hg, Cd, Cu and Zn in open-sea-water-samples is similar to those of other oceans and seas.

Heavy metals in coastal waters.

Anthropogenic sources, river inputs and land run-offs markedly influence the concentrations of heavy metals in coastal sea-water. In region I, Establier (1969) observed seasonal fluctuations of copper and high Cu concentrations in the coastal waters near Cadiz (table 3.1.4). In the near hinterland of Cadiz are the Huelva copper mines, so anthropogenic Cu pollution is superimposed on a geochemical Cu anomaly which is very probably reflected in the Cu-concentration of the marine sediments of the Bay of Cadiz. Fukai and Huyhn-Ngoc (1976 b) investigated the concentration of Cu, Zn and Cd in the coastal and off-shore waters in area II from Sète to Genoa. They observed no significant differences between concentrations in coastal and off-shore waters except for areas of significant anthropogenic inputs, e.g. in March high Cu-concentration (6 ug/l) near Marseilles and between Cap de l'Aigle and Cap Camarat (20 ug/l). Their values were obtained by ASV at pH 8 and hence they determined the ionic and labile complexes with regard to the electrochemical method i.e. the electroreducible forms of Cu, Zn and Cd. Capelli and collaborators (1977) collected water samples in ports and harbours from San Remo to Viareggio (MED POL area II) in the same sites from which they also sampled Mytilus (see below). Their values should be considered 'total' concentrations, since they extracted the trace elements with a

Table 3.1.4. Cd, Cu, Zn, Pb, Ni and Ag in the coastal waters of the Mediterranean Sea (in ug/l).

MED POL Areas	Sampling sites	Cd	Cu	Zn	Pb	Ni	Ag	References
XI	Gulf of Cadiz	-	(40) 5.2; I + P (2.6 - 8.6)	-	-	-	-	Establier, 1969
II	Sète to Genoa	(14)?; I (DL - 8.0)	(14)?; I (DL - 22.4)	(14)?; I (DL - 11.2)	-	-	-	Fukai & Huynh-Ngoc, 1976b (MED POL II)
II	San Remo to Livorno (mainly in ports)	(7) 0.1; T (0.1 - 0.28)	(14) 2.4; T (0.8 - 4.0)			(12) 1.7; T (0.6 - 5.7)		Capelli *et al.*, 1976
II	Gulf of La Spezia			(40) 10.5; T (6.5 - 15)				Bernhard *et al.*, 1977
II + IV	Ventimiglia to Anzio	(222)0.15; H (0.005 - 0.45)	(221)3.5; H (0.13 - 3.6)	-	(227) 0.15; H (0.018 - 2.42)	-	-	Nürnberg *et al.*, 1977
V	Trieste to Ravenna	-	-	(21) 13.6; T (1.4 - 36.4)	-	-	(22) 0.83; T (2.6 - 19.0)	Grancini *et al.*, 1975
V	Plonim to Nin (Adriatic) (surface)	(85) 0.12;I (<0.05 - 6.9)	(85) 1.2; I (0.2 - 3.6)	(85) 13.8; I (1.5 - 365)	(85) 1.2; I (0.02 - 2.8)	- -	- -	Bubic *et al.*, 1977
	10 - <85 m	(255) 0.9; I (<0.05 - 2.25)	(225) 1.1; I (0.2 - 3.5)	(225) 6.2; I (1.5 - 63.6)	(225) 0.55; I (0.1 - 3.3)	- -	- -	Bubic et al., 1977
VIII	Saronikos Gulf (Athens)	-	(1?) 3.0; ?	(1?) 20; ?	-	-	-	Papadopoulou, 1972
	Rhodes Island	-	(1?) 8.0; ?	(1?) 25; ?	-	-	-	Papadopoulou, 1972
X	Rosh Haniqra to Haifa	(60) 0.94; TF (0.6 - 2.9)	(60) 3.7; TF (0.8 - 31.2)	(60) 38.3; TF (1.0 - 256.9)	(59) 6.4; TF (2.1 - 11.4)	(60) 3.3; TF (2.0 - 5.4)	- -	Roth & Hornung,1975
		(53) 0.15; TP (DL) - 0.8)	(53) 0.53 TP (DL - 2.1)	(51) 5.7; TP (1.0 - 24.2)	(52) 2.4; TP (0.6 - 13.3)	(53) 0.48;TP (DL - 2.4)	- -	Roth & Hornung,1975
	Hazardous conc. minimal risk c.	10 0.2	50 10	100 20	50 10	100 2	5 1	WQC - 1972 (1973)

? = unknown, I = ionic (incl. labile complexes), P = particulate, T = total, F = filtered (0.45), H= hydrolysed with acid
DL = detection limit

chelating resin (Chelax-100). In MED POL areas II and IV total hydrolyzable Cd, Pb and Cu were determined by ASV at pH 2 near the coast from Ventimiglia to Anzio (Rome) in 225 sampling stations in May/June 1976 (Nuernberg et al. 1977). Bernhard et al. (1977) determined total hydrolyzable, ionic and particularized zinc in the harbour of La Spezia and its immediate surroundings (MED POL area II). They found that total hydrolyzable zinc increased towards the harbour, while the percentage of the ionic and particulate zinc remained practically constant until the outskirts of the harbour were reached. In the outer and inner harbour the ratios between particulate and ionic vary considerably, probably due to anthropogenic inputs from the shipbuilding industry and town of La Spezia.

The influence of an anthropogenic Hg source on the Hg concentration in sea-water and biota was studied south of Livorno (MED POL area II) by monitoring the Hg-discharges of a chlor-alkali plant (Solvay, Rosignano) along the coast of Tuscany (table 3.1.5; figure 3.1.7) (Renzoni et al. 1973). Near the outfall (1 km south) he observed relatively high values around 0.2 ug/1, but at 10 km south and north of the outfall the Hg concentration was already below his detection limit of 0.02 ug/l.

Heavy metal concentrations in the Adriatic (MED POL area V) received attention by several workers. Grancini et al. (1975) analysed with neutron activation analysis (NAA) millipore filtered sea-water of the Northern Italian Adriatic coast from Trieste to Ravenna. Cs, Rb, Se and U mean concentrations of the area were comparable to those of open sea, while the means of Ag, Co, Sc, Sb and Zn were significantly higher. The authors did not exclude the possibility of sample contaminations as an explanation for these high Hg and Cr values. Bubic et al. (1977) determined ionic Zn, Cd, Pb and Cu in the Kvarner area with ASV at pH 8 (Rijeka), four times from November 1973 to August 1974. They observed a seasonal, horizontal and vertical variation of ionic zinc, but not of ionic Cd, Pb and Cu. The average Zn-concentration was much higher (365 ug/l) near anthropogenic inputs (town of Rijeka) than at the more 'open sea' stations. At different depths in the same stations they often found greatly varying concentrations, an indication of either very heterogeneous distribution of the heavy metals or possible sample contamination by the sampling gear or the ship. Strohal and Dzajo (1975) determined Hg-T concentrations near Banjole and Limski Kanal on the Istrian coast with NAA. They found values near the 'typical' open-sea concentrations. In the MED POL area VIII Papadopoulou (1972) compared the concentrations of several elements in samples from the 'clean-waters' of the island of Rhodes with those from the polluted Saronikos Gulf (Athens). In most elements examined no direct pollution was evident. But the collateral data on the sediment concentration in heavy metals (see below) indicate pollution by heavy metals in the Saronikos Gulf. Also the As-concentrations in fish from the Saronikos Gulf were higher than from other areas (see below).

Table 3.1.5 Hg, Cr, Co, As, Ag and Mn (ug/l) in coastal waters of the Mediterranean

Hg		
Tuscan coast		
10 km N. Solvay plant	< 0.02	Renzoni *et al.* 1973
near Solvay plant	0.180	
10 km S. Solvay plant	< 0.02	
Trieste to Ravenna	(1 - 7.3) (?)	Grancini *et al.* 1975
Limski Kanal & Banjole (Istria)	0.04	Strohal and Dzajo 1975
Rosh Haniqra to Haifa	0.06 (0.01-0.18)	Roth and Hornung 1975
"Minimal risk conc."	0.1	WQC - 1972 (1973)
Cr		
Monte Carlo	0.1 - 0.57	Fukai and Vas 1967
Trieste to Ravenna	0.6 - 50	Grancini *et al.* 1975
Rosh Haniqra to Haifa	0.4 (0.4 - 5.8)	Roth and Hornung 1975
"Minimal risk conc."	10.0	WQC - 1972 (1973)
Co		
San Remo to Ventimiglia	0.1 - 1.5	Capelli *et al.* 1976
Trieste to Ravenna	0.2 - 0.76	Grancini *et al.* 1975
"Minimal risk conc."	2	WQC - 1972 (1973)
As		
Rhodes Island	2	Papadopoulou 1972
Saronikos Gulf	3.5	
"Minimal risk conc."	10.0	WQC - 1972 (1973)
Mn		
Rhodes Island	1.6	Papadopoulou 1972
Saronikos Gulf	2.0	
"Minimal risk conc."	20.0	WQC - 1972 (1973)

(?) High concentration probably due to sample contamination

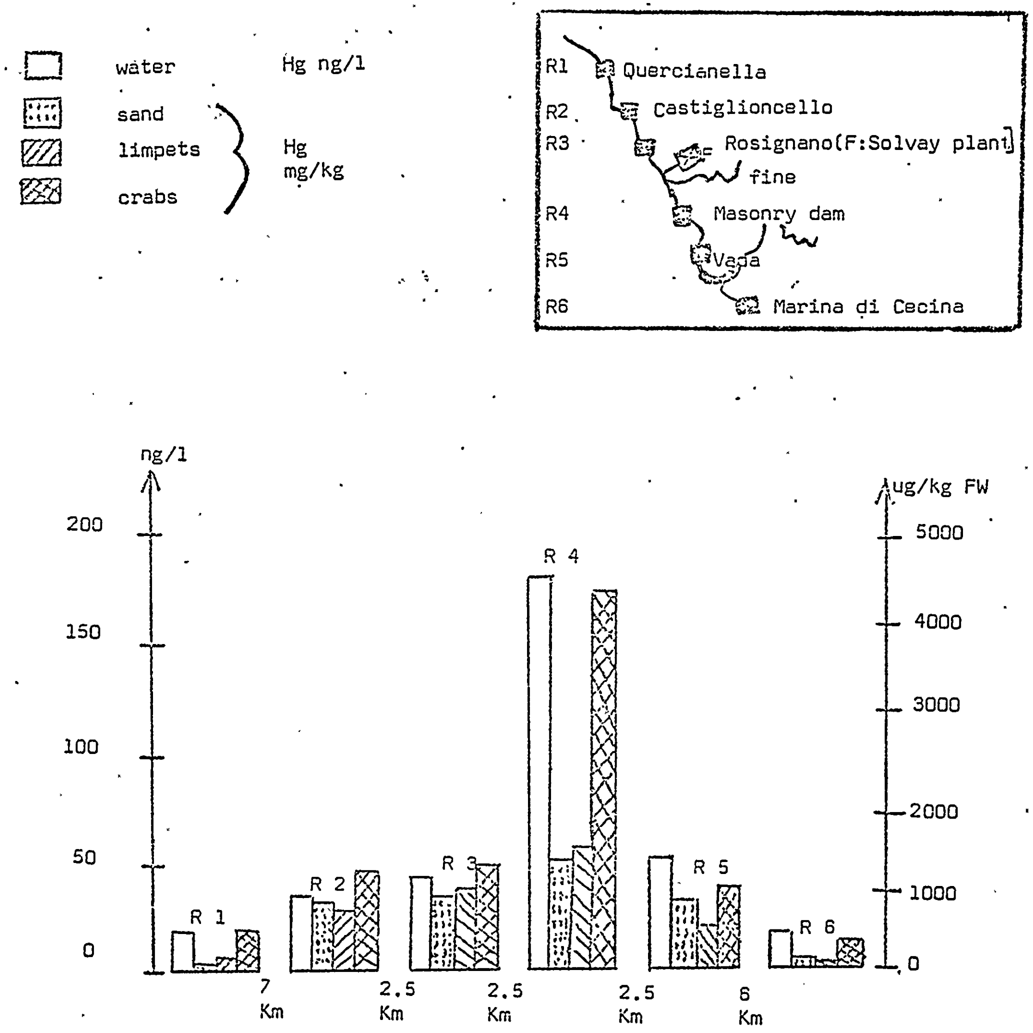


Fig. 3.1.7 Mercury concentration in waters, sediments, limpets and crabs in six stations near the Solvay plant

(Renzoni *et al.*, 1973)

Using a chelating resin Roth and Hornung (1975) investigated the distribution of soluble (<0.45 u) total Hg, Cd, Cu, Pb and Ni and particulated (<0.45 u) Cd, Cu, Pb, Ni and Cr mainly in surface waters along the Israel coast line from Rosh Haniqra to Haifa (MED POL area X). In general they found concentrations near the mean values except for high concentrations near densely populated and industrialized areas. High values could also be attributed to the run-off of the river Qishon, heavily polluted by industrial discharges, and the river Na'amon polluted by agricultural and domestic wastes.

A summary of available data for Hg, Cd, Cu, Zn, Pb, Ni, Ag from the different MED POL areas together with concentrations considered hazardous and a minimal risk are listed in tables 3.1.3 and 3.1.4.

3.1.3.2 Heavy metals in sediments

Natural sediments are mixtures of sands, clays and organics. For many elements and substances sediments are the ultimate 'sink' or deposit. For this reason information on the heavy metal concentrations in sediments can indicate a build-up of pollution in a given area.

The relative abundance of these components varies considerably with different types of sediments. Since each component has its particular physico-chemical characteristics, the interaction of heavy metals with natural sediments (sorption, ion-exchange, complexation and chelation with inorganic and organic substances) depends on the mineralogical composition of the sediments. Higher heavy metal concentrations are generally found in mud, silt, muddy sand and mixtures of them, rather than in pure sand. The interpretation of the values observed is in most cases very difficult, if not impossible, if the mineralogical and sedimentological characteristics of the sediment samples are not reported.

In addition, the analytical methods for sediment analysis vary widely and results of intercalibration exercises conducted in the Mediterranean area have not yet been published. It is, therefore, very difficult to compare data obtained by different authors.

Despite the great public concern about mercury, only few and sporadic data on Hg in sediments are published.

It is astonishing that the quite extensive work on the mercury distribution on land around mercury mines, especially in MED POL area IV, (Dall'Aglio 1968; Costa et al. 1974a,b, 1975; Benvegni and Brondi 1974; Cigna-Rossi et al. 1976) and the possibility of an environmental impact has not also stimulated investigations into the Hg concentration in marine sediments near areas of known terrestrial geochemical Hg anomalies. These areas should be quite frequent in many parts of the Mediterranean (see below). The 'natural' concentration of Hg in sediments range from 0.05 to about 1700 ug/kg DW (table 3.1.6). The high values are found in apparently unpolluted

Table 3.1.6 . Hg in marine sediments from the Mediterranean

MED POL Area		n	ug/kg DW			References
			mean		range	
I	Alboran Sea	(1)	0.26	±	0.14	Robertson *et al.* 1972
	(2720 m)					
II	off Monte Carlo	(2)	0.3	±	0.22	
IV	Tyrrhenian Sea					
	(bottom samples)	(10)				
	(93 - 1715 m)	(9)	0.1	M	(0.05 - 0.24)	Selli *et al.* 1973
	(68 m - 5 Km					
	WSW Mignone)	(1)	1.57			
	(core samples)	(4)	0.1	M	(0.045 - 0.16)	
	(390 - 3520 m)					
	(0 - 700 cm)					
	108 m Fiora 9.5 Km SW					
	0 - 1 cm		0.58			
	60 - 61		0.13			
	Tuscany coast					
	Solvay plant	(2)			(1.1 - 1.3)	Renzoni *et al.* 1973
	4 km S and N	(18)			(0.1 - 0.8)	
	10 km S and N	(6)			(0.04 - 0.1)	
	(conc. proportional to sand grain size)					
V	Adriatic Sea					
	(bottom samples)	(20)	0.11	M	(0.07 - 097)	
	(5 - 1195 m)					
	(core samples)	(2)	0.08	M	(0.05 - 0.1)	
	(64 + 888 m)					
	(0 - 720 cm)					
	Off Trieste	(1)	3.0	+	0.3	Robertson *et al.* 1972
	Po to Ancona	(?)	0.3		(0.06 - 0.97)	Frascari *et al.* 1972

Table 3.1.6 (Contd) Hg in marine sediments from the Mediterranean

Area		n	ug/kg DW mean	range	References
VII	S. off Crete (2360 m)	(1)	< 0.3		Robertson *et al.* 1972
VIII	Saronikos Gulf background		0.5		Grimanis *et al.* 1976
	Elefsis Bay		(0.5 - 1)		
	Athens outfall		(0.5 - 3)		
	Piraeus harbour		10		
X	Haniqra to Haifa	(60)	0.13	(0.01 - 0.57)	Roth and Hornung 1975

sediments in the coastal zone west of the Monte Amiata where the Italian mercury mines are located. A systematic survey will probably reveal the extent to which this off-shore area presents Hg anomalies. Mud feeding fish (Mullus barbatus) collected in this region have a much higher Hg concentration than those sampled in areas of normal Hg sediment concentrations (table 3.1.11), indicating the great importance of the sediment content of heavy metals for the heavy metal concentration of the biota. In this respect it is very interesting that in two areas the anthropogenic influence of mercury on sediments (and biota: see below) has been investigated. Renzoni et al. (1973) near the chlor-alkali plant (Solvay,Rosignano, Tuscany) and Grimanis and collaborators (1976) in the Gulf of Saronikos (Athens) could clearly show the influence of the Hg waste release from the Solvay plant and the discharge of mercury and other pollutants from the Athens sewage and industrial waste outfall (tables 3.1.6 and 3.1.7; figure 3.1.7). In both sites at a distance of 10 to 15 km the pollutant concentrations decrease to background values. It is remarkable that even taking into consideration the different methods used on sediments of various mineralogical composition the highest 'natural' concentrations are not much lower (except in Piraeus harbour) than the concentration in 'polluted' sediments (Solvay plant and Athens outfall table 3.1.6). Viviani et al. (1973) studied the Hg-concentration in sediments off the Po delta. As anticipated, he found a significant correlation between Hg concentration and relative amount of clay. Very recently Paul and Meischner (1976) studied the concentration of Fe, Mn, Cr, Cu, Ni, Pb and Zn in sediments from the Adriatic. Their values for Cu, Ni, Pb and Zn were not significantly different from those of Stefanini (1971). Paul and Meischner (1976) concluded that Cu, Ni, Cr, Zn and Pb did not exceed 'typical' concentrations and hence do not indicate pollution. Cr concentrations were higher in the S-E Adriatic. This was explained by natural river inputs.

Frascari et al. (1976) analysed with factor analysis the granulometric data of the sediments from Chioggia to Ancona and their Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn and $CaCO_3$ concentrations. 90 per cent of the first factor covered the coastal zone from the Po delta south to Ancona. This zone was characterized by a higher than 'typical' concentration of Pb, Cu, Zn, Hg, Cr, Co and Ni in this order of importance. The second factor which covered up to 90 per cent of the area between the Po delta and Chioggia had slightly higher concentrations of Mn, Co and Ni. The third factor was characterized by a high $CaCO_3$ content. The authors conclude that due to the different mineralogical characteristics of the sediments investigated it is not possible to associate level of pollution with the concentration of heavy metals in these sediments.

Grancini et al. (1975) determined 8 elements (Ce, Co, Cr, Cs, Sc, Rb, Tb and Yb) with NAA in sediments from the Northern Adriatic. The concentrations observed are related to the geochemical nature of the sediment matrix showing an increase of the element concentrations in silt and clay containing sediments of fluvial origin.

Table 3.1.7. Heavy metals (mg/kg DW) in marine sediments from the Mediterranean

Area	Type of sediment	n	Cd	Zn	Pb	Ni	Ag	Mn	Cr	References
II Nice - Monte Carlo (50 + 100 m) (0 - 6 cm)	?	(18)	1.7 (0.1 - 2.3)	70.6 (45 - 114)	57.5 (35 - 95)	23.7 (28 - 33)	2.5 (1.9 - 3.6)	227 (95 - 320)	18.8 (12 - 30)	Renfro & Oregioni, 1974
V Adriatic (3 - 7 m) (0 - 4 cm)	sand	(4)	-	35 M (31 - 50)	14.5 M (8 - 24)	<20 M	-	290 M (250 - 305)	14 M (10 - 18)	Pauls & Meischner,1976
	silty sand	(5 - 6)	-	62.5 M (40 - 76)	12 M (9 - 21)	<20 M	-	525 M (450 - 1275)	75 M (17 - 83)	
	muddy sand	(1)	-	85.5 M	11.5 M (11 - 12)	<20 M	-	890 M (780 - 1000)	75.5 M (72 - 79)	
	mud	(10-18)	-	117 M (105 - 131)	12 M (7 - 17)	<20 M (<20 - 35)	-	1250 M (680 - 1770)	112 M (35 - 222)	
Po to Cattolica	(<60)		0.71 (0.44-1.52)	89 (66 -113)	32 (10 - 92)	50 (35 - 64)	-	585 (410 - 695)	45 (24 - 86.5)	Frascari <u>et</u> <u>al</u>., 1976
VIII Saronikos Gulf (0 - 5cm)										
background	?	(?)	-	50	-	-	0.04	-	80	Grimanis <u>et</u> <u>al</u>., 1976, and Papakostidis <u>et</u> <u>al</u>., 1975 + WHO report
Elefsis Bay	?	(16)	-	(<100 ->500)	-	-	?	-	(80 ->150)	
Athens outfall	?	(>40)	-	(50 - 1800)	-	-	(<0.25 - 2)	-	(80 - 1100)	
Piraeus harbour	?	(?)	-	2500	-	-	2.7	-	250	
X .Rosh Haniqra to Haifa		(40)	0.72 (0.3 - 2.2)	7.0 (2.1 - 18.2)	8.4 (4.3-19.7)	4.8 (2.3 -9.3)	- -	- -	4.2 (1.7 - 12.4)	Roth and Hornung, 1975
... average near-shore clays-shales				95	20	68		850	90	Turekian & Wedepohl, 1961 Wedepohl, 1970
... average carbonate rocks				23	9	15		700	11	Wedepohl, 1970

n = number of samples; M = median; the concentrations are given in mean or median and the range beneath in brackets.

Roth and Hornung (1975) studied the heavy metal concentrations in sediments from the northern Israel shore line. Comparing their data with those of Amiel and Navrot (1974) for the southern shore line shows that the concentrations of Cu, Zn and Cr are higher along the northern shore line while the Ni and Hg concentrations are about the same in both areas. As expected, element concentrations are higher in estuarine sediments. The highest values were found near Akhziv, Nahariyya and Akko:

	ug/kg DW		ug/kg DW
Cd	2200	Zn	18,200
Pb	19,700	Ni	9,300
Cu	2800	Cr	12,400

Relatively high values of Hg (210 - 570 ug/kg DW) were found near Fruarom.

A summary of the published concentrations of heavy metal in marine sediments from the Mediterranean is given in tables 3.1.6 and 3.1.7 together with average heavy metal concentrations in near-shore clay-shales and in carbonate rocks.

3.1.3.3 Heavy metals in marine organisms

The concern about heavy metals in food items has also stimulated the analysis of mercury especially in contamination of fisheries products: edible crustaceans, molluscs, and especially fish. In order to obtain an idea of the general level of concentration of heavy metals, the concentrations in pelagic organisms are discussed separately from those in coastal and benthic organisms, since the latter are more subject to local influence. As will be shown below, different species collected at the same site have shown great differences in their heavy metal concentrations and often a correlation between body burden of a pollutant and length and weight is observed. Therefore, if the heavy metal concentration in marine organisms is to serve as an indicator for pollution, only concentrations from the same species of approximately the same length can be compared. On the other hand, concentration ranges in commercially available fishes and other marine organisms can give an indication of the possible contribution of fishery products to the intake of certain pollutants. It must, however, be remembered that a comprehensive assessment of the routes from marine products to man requires an investigation into the frequency distribution of the different fisheries products offered to the public (i.e. a market analysis).

Heavy metals in pelagic organisms

Only a few authors (Fowler et al. 1976, Vucetic et al. 1974) have analysed mixed plankton samples. Since plankton samples vary widely in species composition and contain phyto- and zooplankton and predators feed selectively on different plankton species it is very difficult to draw conclusions about heavy metal concentration in the marine environment from these data. More interesting are analyses of single zooplankton species (e.g. Fowler et al. 1976; Zafiropoulos and Grimanis 1977; Vucetic et al. 1974; Belloni et al. 1977)). Here too, however, only very few data exist.

Heavy metal concentrations in pelagic fishes are more numerous. Of special interest are surveys in which both Mediterranean and Atlantic specimens of the same species have been analysed by the same author with the same method. This will facilitate the comparison between areas, since possible systematic errors can be neglected. In table 3.1.8 Hg-concentrations are listed from authors who have analysed anchovy, European hake, sardine, mackerel and bluefin tuna both from the Mediterranean and the Atlantic. Since the Hg-concentration is expected to increase with age, the length of the fishes, where available, is also reported. It is realized that length is only a very approximate estimator for age, but, so far, age has not been reported for the species analysed. In comparing the data one has to bear in mind what has been said about sigma estimation from ranges. Allowing for the fact that the data are not normally distributed and hence the range will estimate smaller sigmas the differences are still significant for anchovy, sardines, mackerel and tuna (n = 130: 5.2 sigma), while it is very likely that significant differences will be revealed for hake if a comparison with more specimens were carried out. The concentrations determined by the authors who investigated only Mediterranean fishes support, with few exceptions, the hypothesis that Mediterranean fishes of the same species have higher Hg-concentrations than fishes from the Atlantic. On the other hand, they show the great importance of single-specimen-analysis for a statistical treatment of the results, and that intercalibration is absolutely necessary for a comparison of data. No data on other elements have come to the reviewer's attention which would allow a similar comparison.

Sardines and anchovies have been analysed for Hg, Co, Ni, Cd and Pb throughout a seven-month fishing season in the northern Adriatic. A few data on Cr chromium are supplied by Fukai and Broquet (1965). Too few data are as yet available to allow a comparison between levels in pelagic fishes from different areas of the Mediterranean.

The Hg-levels in tuna, swordfish and marine mammals deserve special consideration. Cumont et al. (1972, 1977) systematically analysed a large number of tuna from the Mediterranean and the Atlantic (table 3.1.8). The only swordfish data so far published were those from Establier (1972 b), unfortunately without length and weight measurements. The Hg-concentrations range from 1000 to 2000 ug Hg-T/kg FW. The mercury concentrations in tuna are the highest reported for teleost fish from the Mediterranean, but are by no means uncommon in other large teleost fish from other oceans. Merlin caught off N-E Australia, where specimens reach 2 to 3.5 m, had Hg-body burden of between 500 and 15500 ug Hg-T/kg FW (Mackay et al. 1975, Shultz et al. 1976). Only in marine mammals have similar and higher concentrations been observed. In the blue dolphin (Stenella

Table 3.1.8. Comparison of mercury concentrations (ug Hg-T/kg FW) in pelagic fishes from the Mediterranean and Atlantic

Species	n	Atlantic mean	Atlantic range	Mediterranean mean	Mediterranean range	Length (cm) x	Length (cm) range	Sampling area and date	References
Engraulis encrasicholus	5 H (5 - 6n)	50	15 - 80			13	11.5 - 14	SW French Atlantic coast	Thibaud, 1971
	1 H (5 - 6n)			165		?		off Marseilles	
	17	95	50 - 140			13.2	10.5 - 13.6	Str. Gibraltar (VII/76)	Stoeppler et al., 1977
	17			380	210-590	16.3	16.0 - 16.5	off N. Sardinia (VI/76)	
	?	60				?		Atlantic Ocean (?)	Cumont et al.,
	2			230	210-250	15.5	15 - 16	off Corsica (?)	
	37			250	40-1040	?		Mediterranean Sea (?)	
	10	70	50 - 90			12.6	11.5 - 14	off Ceuta (VII/77)	Bernhard and Renzoni, 1977
	10	160	70 - 330	160	70-330	14.6	13.5 - 16	off SW Sardinia (VI/77)	
Merluccius merluccius	1 H (5 - 6n)	50				?		Charente coast (VII/71)	Thibaud, 1971
	1 H (5 - 6n)			125		?		off Sète (III/71)	
Sardina pilchardus	2 H (5 - 6n)	65	60 - 70			15	12 - 18	Gulf of Gascony (III/71)	Thibaud, 1971
	1 H (5 - 6n)			235		?		off Sète (III/71)	
	1 H (5 - 6n)			205		?		off Marseilles (IV/71)	
	28	28	5 - 52			13.7	12 - 14.7	Str. Gibraltar (VII/76)	Stoeppler et al., 1977
	26			220	120-310	15.4	14 - 16.5	off La Spezia (VII/76)	
	19			300	160-475	16	14.5 -16.5	off N. Sardinia (VI/76)	
	?	26	20 - 40			?		Atlantic Ocean (?)	Cumont et al.,1972
	24			150	110-250		16 - 17	off Corsica (IV/75)	Cumont et al.,1977
	10	54	47 - 70			15.8	15.5-16.5	off Tangiers (VII/77)	Bernhard and Renzoni, 1977
	10	65	35 - 110			13.4	9.0-16.0	off Monte Carlo (VII/77)	
	10	150	100 - 210			14.0	13.0-14.5	off SW Sardinia (VI/77)	
Scomber japonicus	9	76	43 - 96			19.5	17.3-24.7	Str. Gibraltar (VII/76)	Stoeppler et al., 1977 (MED POL II)
S. scombrus	15			340	125-510	19.9	14.7-21.5	off La Spezia (IX/76)	
S. scombrus	?	70	15 - 160			?		Atlantic Ocean (?)	Cumont et al., 1972
	11			230	100-580	?		Mediterranean Sea (?)	Cumont et al., 1977 (MED POL II)
Thunnus thynnus	285	485	200 - 760			?		Atlantic Ocean (?)	Cumont et al.,1972
	132			1145	200-2460	?		Mediterranean Sea (?)	

H = composite sample

coeruleoalba) from the Mediterranean the Hg-T concentration in the muscle tissue reached 23 800 ug/kg FW, in the liver 344 000 ug Hg-T/kg FW and in the spleen even 530 000 ug Hg-T/kg FW (Thibaud and Duguy 1973).

Marine mammals with high Hg-T concentrations have relatively low methyl- mercury concentrations (1 to 10%). In teleost fish with low Hg-T concentration, the methyl mercury makes up between 75 and 95% (Cumont et al. 1972, 1977). In the merlin and in marine mammals and birds a positive correlation between Hg and Se concentration has been observed (Koeman et al. 1975, Mackay et al. 1975). The correlation between Hg and Se is of very great practical importance since it has been suggested that a synergism exists between Hg and Se reducing the toxicity of both metals (see below).

Coastal and benthic organisms

Very few data are available on macroscopic algae and marine plants (Strohal et al. 1975, Fukai and Broquet 1965, Roth and Hornung 1975). The values for Hg are low (10 to 100 ug Hg-T/kg FW) and the concentrations of other metals are similar to those of the higher organisms investigated. The data available on crustaceans are also scarce.

Mytilus galloprovincialis is probably the marine organism which has received the widest attention in the Mediterranean area (table 3.1.9) followed by the oyster, especially in the area of Cadiz. These sessile organisms show wide variations in heavy metal concentration indicating local conditions. Establier (1969 a, b, 1972 a, b, 1973) studied heavy metals in oysters in the Gulf of Cadiz and along the north-west African coast. He observed very high Cu content in oysters from the Huelva river (Gulf of Cadiz) with more than 1 500 000 ug Cu/kg FW (= 0.15%). The Cu and Zn concentrations in the Gulf of Cadiz are high in comparison with oysters from non-Mediterranean areas (Bernhard and Zattera, 1975). On the other hand, Hg-concentrations of various molluscs from the Gulf of Cadiz were in the range of non-Mediterranean areas.

Thibaud (1973) and Alzieu et al. (1976) compared Hg concentrations in Mytilus collected on the French Atlantic and Mediterranean coasts. The over-all average concentrations in the Mediterranean tend to be higher than those from the Atlantic although the ranges overlap. The wide ranges are caused by contamination from local sources, especially noticeable in the Seine estuary, the roads of Morlaiz and Brest and the mouths of the rivers Charente and Adour. In some sampling sites Crassostrea gigas, Patella vulgata, Pecten maximum and Murex trunculus, are also collected and analysed. The Hg-levels in the two bivalves were similar, but the Hg-concentrations in the gastropods were markedly lower.

Table 3.1.9 Heavy metal body burden in *Mytilus galloprovincialis* from different MED POL areas

Area	Element	n	ug/kg FW		Length (cm)		Sampling area and date	References
			mean	range	mean	range		
I	-	-	-	-	-	-	-	-
II	Hg	3 H (>6n)	130 M	70 - 160	?	2 - 6	Spanish NE coast	Ballester *et al.* (MED POL II)
	Hg	230 H (>6n)	-	20 - 310	-	2 - 7	French NW coast VI, XII/76	Thibaud 1973 Alzien *et al.* 1976 and MED POL II
	Cd	82 H (>25)	-	140 - 5900	-	3 - 5	France/Italy coast	Fowler and Oregioni 1976; Capelli *et al.* and MED POL II FW = DW/5; Macchi 1967
	Cu			1380 - 190,000				
	Ni			900 - 141,000				
	Pb			2700 - 117,000				
	Zn			27,800 - 644,000				
	Cr	> 69 (>25)		500 - 28,800				
	Ag	69 (>25)		100 - 18,900				
	Hg	7 - 52	35 M	6 - 93	-	2.3 - 5.3	La Spezia X/75 - VI/76	Stoeppler *et al.* 1977 (MED POL II)
III	-	-	-	-	-	-	-	-
IV	Hg	7	160	120 - 215	5.2	4.8 - 5.7	N Sardinia	Stoeppler *et al.* 1977 (MED POL II)
V	Hg	3		65 - 1500			Adriatic Sea	Caracciolo *et al.* 1972 Strohal and Dzajo 1975 Lulic and Strohal 1974

Table 3.1.9 (contd.) Heavy metal body burden in *Mytilus galloprovincialis* from different MED POL areas

Area	Element	n	ug/kg FW mean	ug/kg FW range	Length (cm) mean	Length (cm) range	Sampling area and date	References
VI	-	-	-	-	-	-	-	-
VII	-	-	-	-	-	-	-	-
VIII	Hg	2 H (>10n)		40 - 50	?		Saronikos Gulf	Papadopoulou and Kanias 1976 and MED POL II FW = DW/5
	Cd	1 H (>10n)	100					
	Co		3900					
	Zn	2 H (>10n)		17,500 - 20,000				
	Se	1 H (>10n)	300					
	Mn		2700					
	Ag		5000					
	Cr		1550					
	Ni		7800					
	Cu		800					

Fowler and Oregioni (1976) determined the Cd, Cu, Ni, Pb, Zn, Cr, Ag, Co, Fe, Mn content in mussels from Sète to Genoa. They found that near ports and river discharges the heavy metal content of the mussels increased. Seasonal variation in the concentrations was evident and may, in part, be due to the great changes in biomass during the life of the mussel. In some cases the seasonal variation observed in the mussels could be related to high metal concentration in the ambient water collected simultaneously (Fukai and Huynh-Ngoc, 1976 b). Fowler and Oregioni (1976) point out that the filtered sea-water analysed by Fukai and Huynh-Ngoc (1976 b) does not contain the particulate metal fraction available to the filter-feeding mussels. They also draw attention to the fact that water samples represent short time situations in heavy metal concentrations, while mussels will integrate water concentrations over a certain time interval. Comparing their values with those obtained by other authors reveals that the Mediterranean values do not differ significantly from those of other regions.

For a period of two years (1963-1964) Macchi (1967) examined monthly the Cd, Cu and Pb concentrations in M. galloprovincialis collected from a mussel bed situated near Palmaria Island (La Spezia). Capelli and collaborators (1977) investigated the concentrations of Cd, Cu, Ni, Pb, Cr, Co, Mn in Mytilus collected in ports and harbours from San Remo to Viareggio. In La Spezia one of their collection sites (Palmaria Island) is practically in the same location as the sampling station of Macchi (1967) where the latter examined monthly Cd, Zn, Cu and Pb. Contrary to Fowler and Oregioni (1976), Macchi (1967) did not observe a significant seasonal variation, probably because their sampling site was less exposed to the influence of run-offs and anthropogenic contamination sources. Table 3.1.9 gives an over-all view of the concentration ranges observed.

Papadopoulou and Kanias (1976) analysed seven molluscs from the Saronikos Gulf for several heavy metals. Their Hg concentrations in M. galloprovincialis are in the 'typical' range for the Mediterranean. Cr and Ni values are similar to those of other non-Mediterranean areas; no Mediterranean data are available for Cr and Ni.

Of considerable interest is the multi-element analyses carried out on seven molluscs from the coastal waters of the Saronikos Gulf (table 3.1.10). The concentration of a given element varied remarkably between different species collected at the same site. These data supply a Mediterranean example of similar observations made earlier by Segar et al. (1971) in the English Channel who analysed 17 elements in seven Lamellibranchia and four Gasteropoda. For example, the Cu-concentrations ranged from 360 ug/kg FW for Anodonta sp. to 40 500 ug/kg FW in Crepidula fornicata. The Ni-concentration showed an even wider range for these two species (40 to 127,500 ug/kg FW). This shows that the concentration of heavy metals from different species cannot be easily compared.

Table 3.1.10 Multi-element analysis of the soft part of molluscs from the coastal waters of the western part of Saranikos Gulf between Megara and Slamis Island. Samples were collected between 0 and 12 m depth during October 1969. All concentrations are in ug/kg dry weight. (Papadopoulou and Kanias 1976)

	Hg	As	Sb	Cr	Ni	Co	Mg (x 10^6)
Mytilus galloprovincialis	210	25,500	140	7800	39,000	19,400	5.5
Venus verrucosa	22	15,000	40	4700	-	1700	7.2
Glycymeris glycymeris	15	7300	100	4900	14,000	520	6.0
Enis enis	2350	15,000	60	12,500	-	510	6.0
Meretrix chionae	70	59,000	37	4100	26,000	14,000	6.7
Ostrea edulis	320	83,000	50	12,500	15,000	730	4.5
Tapes decussatus	290	56,000	100	18,000	45,000	22,500	4.3

	Cu	Zn	Mn	Sr	V
Mytilus galloprovincialis	(4500)	(87,000)	(13,500)	(26,000)	(230)
Venus verrucosa	(5200)	(17,500)	(2100)	(24,300)	(100)
Glycymeris glycymeris	(28,000)	(75,000)	(3500)	(135,000)	(750)
Enis enis	(9400)	(24,000)	(13,000)	(15,000)	(700)
Meretrix chionae	(4100)	(33,000)	(26,000)	(38,000)	(450)
Ostrea edulis	(100,000)	(685,000)	(2000)	(24,000)	(20)
Tapes decussatus	(10,500)	(83,000)	(650)	(32,000)	(320)

Coefficient of variance ~ 10%

Values in brackets are calculated from ash weight/dry weight ratio (Papadopoulou pers. comm.)

The few data available on other molluscs show relatively high Hg concentrations for cephalopods (Octopus and Sepie). Both are of a greater age and higher position in the food chain compared to mussels, which may be the explanation.

Great attention has been focused on mercury after the Minamata incident. A large number of different fish species have been investigated in various parts of the Mediterranean. Establier (1972 b and 1973) has compared the Hg concentrations of fishes from the N-W African coast with those from the Gulf of Cadiz. Ballester et al. (1977) investigated species from the northern Spanish coast-line, Thibaud (1971), Cumont et al. (1972, 1977) and Aubert et al. (1975) those from the French Mediterranean coast; Renzoni et al. (1973), Renzoni (1975), Ciusa et al. (1973) and Stoeppler et al. (1976) examined species from the Italian west coast. Of special interest for a correct interpretation of Hg-body burdens are the very recent findings of Bernhard and Renzoni (1977) who observed that M. barbatus, from the area along the Tuscan coast bordering the Monte Amiate (a geochemical Hg anomaly, had very high Hg body burden (up to 3700 ug Hg-T/kg FW) far away from possible Hg anthropogenic sources. From table 3.1.11, it can be seen that M. barbatus caught between the Isle of Elba and the Isle of Giglio have considerably higher Hg concentrations than the M. barbatus from other regions. The previously reported concentrations for Piombino and Orbitella by Ciusa et al. (1973) confirm these observations.

The very few Hg analyses carried out on sediments from this area (table 3.1.6) seem to justify this assumption. Only the low Hg body burden found in the samples taken at very shallow depth (20 m) off-shore of Talamone does not seem to fit this explanation. Most probably the Hg concentration in the sandy sediments of the Talamone trawling ground is low in comparison with the sediments of the Hg anomaly. However, this has still to be verified. The often observed Hg concentration versus length correlation was only observed in M. barbatus specimens which had relatively low body burden. In all samples with the high Hg body burden the data scattered widely.

At the moment no reason can be given to explain this phenomenon. Similar high 'natural' body burden might well be found in the other areas. A few well-known areas with Hg anomalies are indicated in figure 3.1.8. Ciusa et al. (1973) also determined the concentration of Cu, Zn, Cd and Pb. For the Italian east coast data are available from Perna et al. (1972), Caracciolo et al. (1972) and Ciusa and Giaccio (1972) who also determined Cu, Pb and Zn. Strohal and Dzajo (1975) determined Hg in fishes from the northern coast of Yugoslavia, while Papadopoulou et al. (1973) analysed the concentration of Ni, Ca, Mg, As, Pb, Co, Sr, Zn, Fe and Mn in Pagellus erythrinus showing considerable body burden of As in muscle tissue. Comparing P.erythrinus from unpolluted waters (Rhodes Island) with specimens from the polluted Saronic Gulf found that the As- concentration in fish from polluted waters was 2 - 2.5 times higher than in fish from the unpolluted waters. No difference could be established for the Hg-concentrations. Finally Roth and Hornung (1975) analysed fish from

Table 3.1.11 Heavy metal body burden in *Mullus barbatus* from different MED POL areas

Area	Element	ug Hg-T/kg FW n	 mean	 range	Fork length (cm) mean	 range	Sampling site and date	References
I	-	-	-	-	-	-	-	-
II	Hg	9 H(6n)	170 M	110 - 360	?	9 - 20	Barcelona X/75 - III/77	Ballester *et al.*, 1977 (MED II)
	Hg	4H (1-4n)		100 - 150				(MED II)
		25	215	40 - 760	12.9	10.5 - 15.3	off Palmeria Isle III/76 - VI/76	Stoeppler *et al.*, 1977 (MED II)
		31	75	20 - 190	10.7	8.0 - 14.0	off Carrara X/75 - IV/76	" " " "
		10	100	45 - 220	13.9	13.0 - 14.5	off 5-Terre (La Spezia) V/76	" " " "
		51	221.2	60 - 900	12.2	10.5 - 18	off River Arno	Bernhard and Renzoni, 1977 (MED II)
		1 F	1500		18			
III		-	-	-	-	-	-	-
IV	Hg	41	1434	500 - 3700	13.2	11 - 16.5	N. Isle Elba XII/76 - III/77	Bernhard and Renzoni, 1977 (MED II)
	Male	15	495	180 - 940	16.4	14 - 18.0	I. Monte Cristo	
	Fem.	7	965	360 - 1740	19.4	16 - 23	" " "	
	Male & Fem.	22	644	180 - 1740	17.4	14 - 23	Same sample as above	
		19	200	55 - 335	14.1	13.5 - 16.0	Talamone VII/77	Bernhard and Renzoni, 1977 (MED II)

Table 3.1.11 (contd.) Heavy metal body burden in Mullus barbatus from different MED POL areas

Area	Element	ug Hg-T/kg FW n	 mean	 range	Fork length (cm) mean	 range	Sampling site and date	References
		2	100	55 - 143	17	14 - 20	off Pescara 1971	Caracciolo et al., 1972
VI	-	-	-	-	-	-	-	-
VII	Hg	10	240	90 - 560	13.5	10.5 - 17.0	Isle Pilau, Tunis (V/76)	Stoeppler et al., 1977 (MED II)
VIII	Hg	4 H (6n)		48 - 145				(MED II)
	Cd			32 - 65				
	Zn			3.2 - 4.25				
	Se			0.184 - 0.32				
IX	Cd	1 H (6n)	20		?			(MED II)
	Cu	1 H (6n)	680					
	Zn	1 H (6n)	6400					
	Pb	1 H (6n)	120					
	Mn	1 H (6n)	220					
	Cr	1 H (6n)	140					
	Ni	1 H (6n)	6190					

Table 3.1.11 (contd.) Heavy metal body burden in *Mullus barbatus* from different MED POL areas

Area	Element	ug Hg-T/kg FW			Fork length (cm)		Sampling site	References
		n	mean	range	mean	range	and date	
	Hg	61	775	100 - 2500	13.5	9.5 - 18	S. Isle Giglio XI/76 - III/77	Bernhard and Renzoni, 1977 (MED II)
		5	205	165 - 245	14.6	13.2 - 14.5	Maddalena (Sardinia) II/76 - III/77	Stoeppler *et al.*, 1977 (MED II)
		5	3030		20		Piombino (market) VI/72, VI/73	Ciusa *et al.*,1973
		5	1300		19		Orbetello VI/72, VI/73	
		30	310 M	120 - 680	17 M	14 - 22	Civitavecchia, Fiumicino, Pozzuoli, Salerno, Vibo Valentia, Reggio Calabria, markets VI/72, VI/73	
	Cd	1 H (5n)	<1					(MED II)
	Zn			2800 - 3280				
	Cu			316 - 481				
	Pb		<50					
	Mn			170 - 239				
V	Hg	35	250 M	140 - 1060	?		Trieste to Pescara 7 major fish markets VII/71, X/71	Ciusa and Giaccio, 1972

Table 3.1.11 (contd.) Heavy metal body burden in Mullus barbatus from different MED POL areas.

Area	Element	ug Hg-T/kg FW n	mean	range	Fork length (cm) mean	range	Sampling site and date	References
X	Hg			220 - 290		11 - 16	Netanya/El Arish Israel II-VI/74	Roth and Hornung,1975
	Cd	2 H (2-18n)		130 - 150				
	Pb			670 - 710				
	Cu			880 - 1340				
	Zn	1 H (18n)	3120					
	Ni	2 H		290 - 330				
	Cr	2 H		590 - 1090				
	Hg	1 H (10n)	50		14		Bardawil, Israel IX/74	Roth and Hornung
	Cd		50					
	Pb		10					
	Cu		1310					
	Zn		5430					
	Ni		440					
	Cr		720					
XI	-	-	-	-	-	-	-	-
XII	-	-	-	-	-	-	-	-

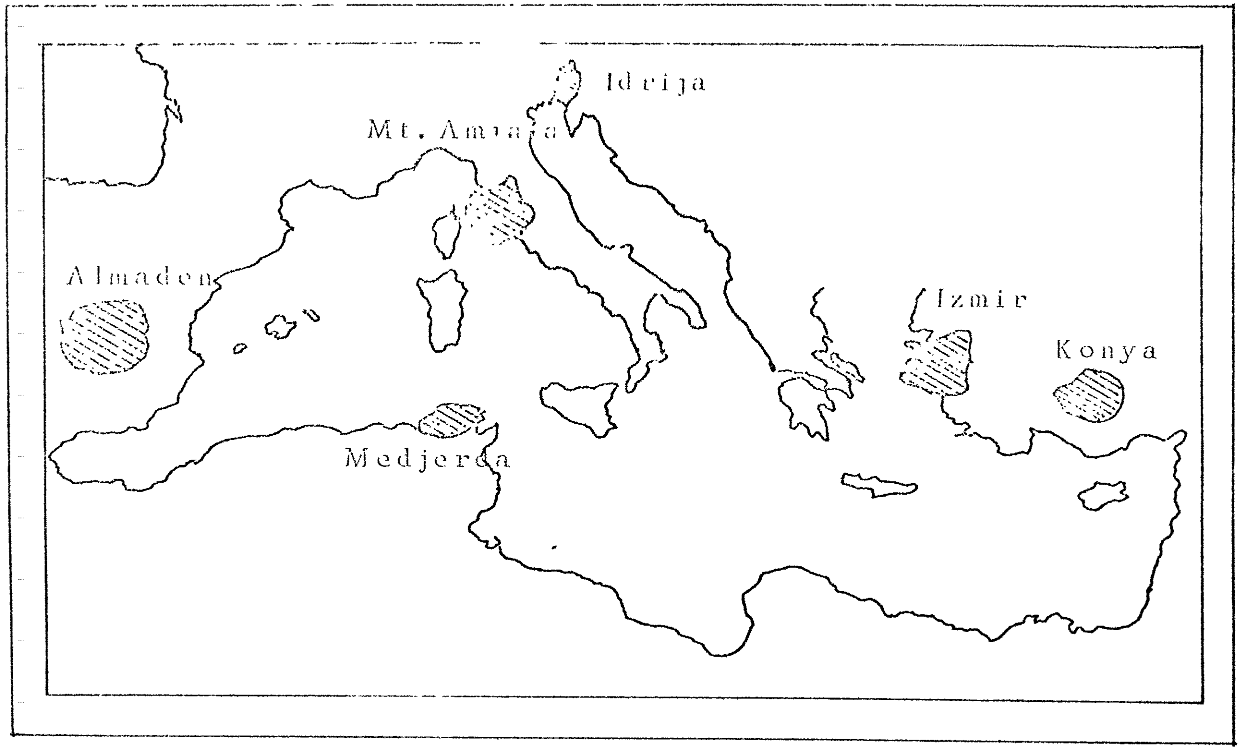


Fig. 3.1.8 Areas with possible mercury anomalies deduced from known mercury mining activities

the Israel coast, determining Cd, Pb, Cu, Zn, Ni and Cr in addition to Hg. Unfortunately, despite the diverse species analysed, only very few species were analysed by several authors, making a comparison of the data from all the regions mentioned impossible. A wide variation of concentrations has to be observed. At present it is not possible to say whether these observed differences in the body burden are actually due to anthropogenic sources, as is undoubtedly the case for the fish from the Saronic Gulf, or if the differences are caused by Hg anomalies or special enrichment factors inherent in the species which show higher Hg concentrations. Last, but not least, since no intercalibration exercise data are as yet available, methodological difficulties may also be the cause of high and low Hg body burdens. Only for health protection purposes have some typical concentrations of the more important heavy metals been summarized (table 3.1.12). These data are still only approximate and their use for an estimation of the contribution of fishery products to the total heavy metal intake by humans is still difficult to determine since the relative amounts of the various species in the 'normal' diet is not known. In a later section an attempt will be made to give such an estimation.

3.1.4 Pathways of heavy metals

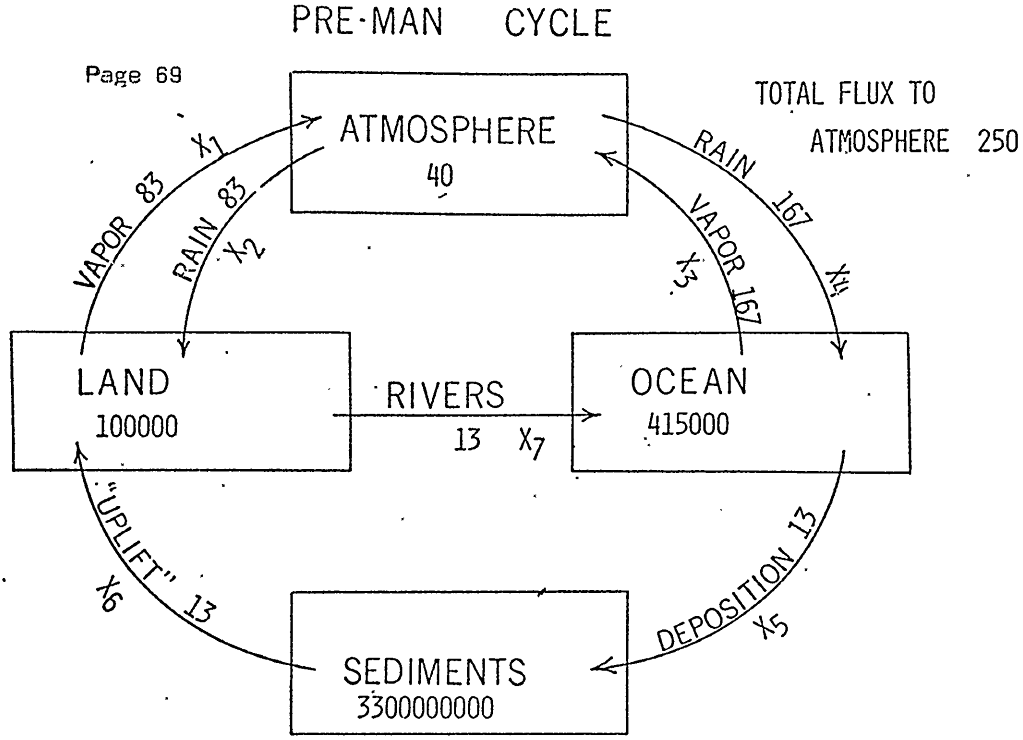
The best way to understand the fate and long-term implications which may be expected from changed environmental conditions due to pollution is to consider first the cycles (input, fluxes, residence-time, transformation, distribution, reservoirs and sinks) of those substances which determine the basic characteristics of an area. The Mediterranean, being a semi-enclosed sea with only limited exchange of its water masses, provides an ideal opportunity for such a study, although at present it would be premature due to the lack of a sufficiently large Mediterranean data base. In order to give an idea of possible pathways and fates of heavy metals, the global geochemical cycles of two metals are illustrated. As soon as a better Mediterranean data base is available these models have to be adapted to typical Mediterranean situations.

A comparative model of global cycling of mercury before and after man's radical intervention in geochemical processes is shown in figure 3.1.9. Although the figures speak for themselves it is worth emphasizing the "gain" indicated for the oceans. The increased fluxes are mainly due to the mobilization of load increase from mining, and to atmospheric inputs due to combustion of fossil fuel (oil in particular), chlor-alkali and cement production, and other activities involving mercury processing. By extrapolation one could estimate that in the year 2000 the present mercury concentrations in the surface layer of the oceans (3-15 x 10^{-5} ppm) will be increased by 30%.

The most important forms of mercury reaching the marine environment are inorganic (metallic) mercury and to a lesser degree various organomercurial compounds. Inorganic mercury is only moderately toxic but in the marine environment it undergoes a number of transformations

Table 3.1.12 'Typical' heavy metal concentrations in selected pelagic and benthic marine organisms of economic importance

	Hg	Cd	Pb	Cr	Cu	Zn	Ni	As
Mytilus galloprovincialis	50	350	(1500)	1000	1500	30,000	500	5000
Sardina pilchardus	200	20	100	40	1000	10,000	300	-
Merluccius merluccius	100	50	-	-	1000	3000	-	-
Mullus barbatus	300	20	-	-	500	3000	300	-



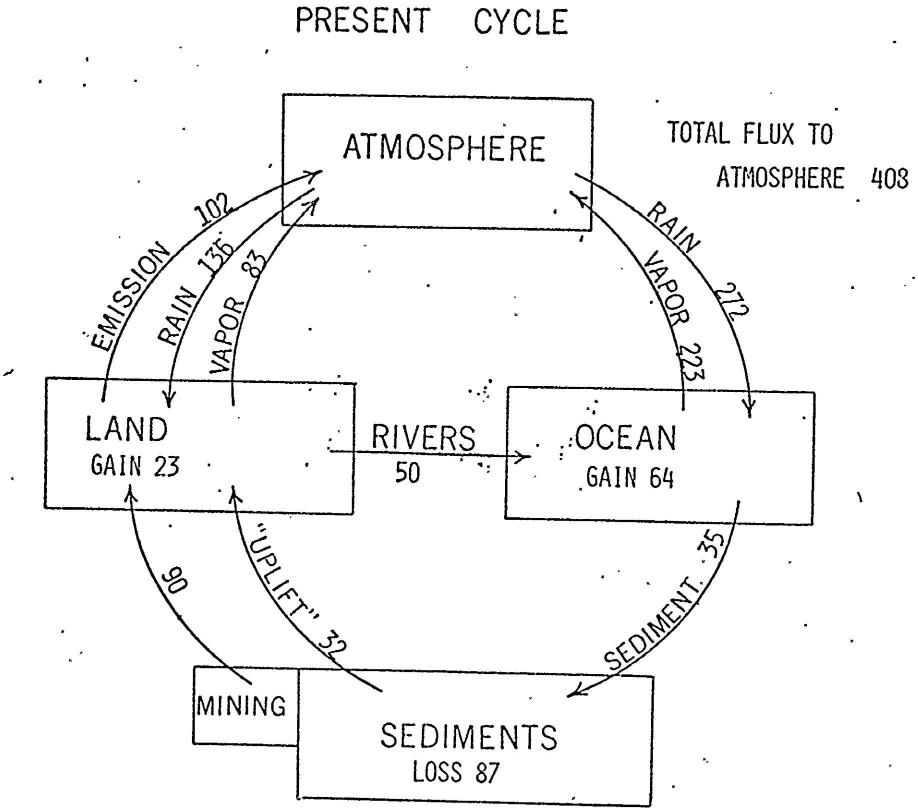


Fig. 3.1.9 Model of pre-man and present-day cycle of mercury. Reservoir masses in units of 10^8 g; fluxes in 10^8 g/year. (Garrels et al., 1975)

(see below). One of these transformations leads to a biological methylization of inorganic mercury. Methly-mercury is only slightly more toxic than inorganic mercury, but transformation into other more toxic mercury organic compounds may also occur and thus present considerably more hazardous substances than the inorganic mercury released from an anthropogenic source. The geobiochemical cycle of mercury is characterized by the high volatility of inorganic mercury. In fact the pathway through vapour from land and from the ocean in the pre-man cycle is considerable. River inputs on the other hand are very small. Also in the present-day cycle the pathways through the atmosphere predominate over the other pathways.

Manganese, a less volatile metal, shows the behaviour of a non-volatile metal (figure 3.1.10). Consequently the inputs through rivers are more important than the pathways through the atmosphere. Biogeochemical cycles of other pollutants can be developed for the Mediterranean as soon as enough 'hard facts' become available.

3.1.5 Effects on marine organisms, ecosystems and human health

It is relatively easy to demonstrate under laboratory conditions the effects of pollutants on marine organisms. However, it is not so easy to extrapolate from usually short-term laboratory experiments in which relatively high concentrations of pollutants have been used, and only a limited number of very crude physiological (mortality, immobilization) changes have been determined. In nature the interaction of pollutants with marine life is much more complex and does not submit so easily to exact measurements reflecting dose-effect or even cuase-effect relationship because the number of varied influences which may modify the response of an organism, not to mention that of an ecosystem, is practically limitless. Furthermore, in nature it occurs only rarely that an organism, or a community, is exposed to a sinlge pollutant; usually the effects of several pollutants are superimposed on the same time-scale often leading to a definite synergistic end-effect.

Due to the intricate built-in feed-back mechanisms governing the response of marine communities to any external stress, the changes caused by pollution are rarely abrupt and tend to be slow and subtle, making it difficult to differentiate them from naturally occurring structural and functional fluctuations.

The duration of MED POL (the first work started in late 1975) is obviously too short to produce new and substantive evidence on the effects of pollutants on Mediterranean ecosystems and human health. Therefore, most of the results reported below in general terms in the subsequent sections are based on observations and measurements in past decades.

There has been the choice in the MED POL project to agree, at its very beginning, on a limited number of species to be commonly used in experimental work. These species should have been preferably the same as those monitored in MED III for their body burdens. This, of

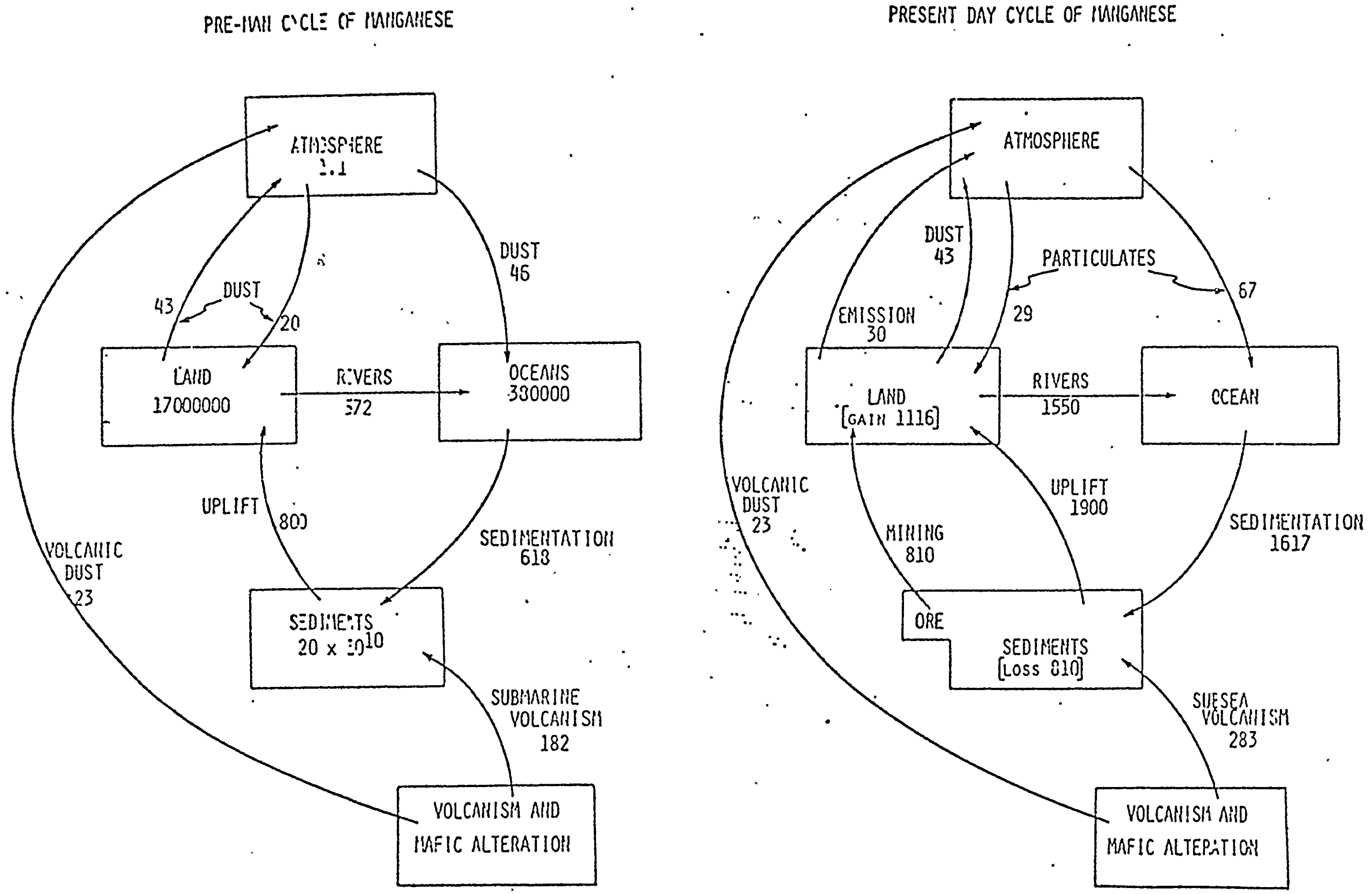


Fig. 3.1.10 Model of pre-man and present-day cycles of manganese. Reservoir masses in 10^8 g; fluxes in 10^8 g/year. (Garrels et al., 1975)

course, would have required a certain time for the participating laboratories to become familiar with new test organisms. Or the laboratories could go on using the same species they were already acquainted with. In most cases the latter choice was made. This had the advantage that, in spite of the relatively short time, some very valuable data concerning threshold concentrations could be furnished.

Potential reproductive effects, which could prevent replacement of current populations, are also under investigation. Altered developmental patterns and morphological effects are additional areas of concern and may also interfere with recruitment into depleted stocks. These effects could prove to be direct or they may be genetic. Potential genetic effects, their induction and reversal, are being studied by analysis of enzyme markers utilizing field collections, as well as the maintenance of animals in the laboratory for several generations. This interdependence of laboratory and field research is reflected by most projects.

Fishery may also be impaired by toxic effects on feeding behaviour and growth rate. It may be possible to detect effects on growth rate at the molecular level in studies on a regenerating sponge by examining protein synthesis using as indicator the incorporation of labelled precursors into DNA, RNA, and proteins. Several other biochemical studies are assessing the effects of contaminants on particularly sensitive enzymes and related metabolic pathways.

Sublethal effects of contaminants which indirectly produce increased mortality are also being investigated. Several institutes are performing histopathological examination of speciments exposed to pollution; others are comparing hematological parameters; and one is investigating possible interference with physiological mechanisms responsible for osmoregulation in marine organisms. All of those studies contribute to the understanding of the mode of action of toxic pollutants and provide information on subtle changes such as metabolic and physiological malfunctions.

The simple comparison of concentrations of contaminants found in the field and the occurrence of characteristic species in appreciable abundance at the same site and time can furnish very valuable information implementing laboratory data. To give one example: Cyclotella, Scelettonema and Arcatia occurred in appreciable abundance in the Gulf of Fos where they were apparently not affected by a concentration of 5 ug Cd and 10 ug/Pb/l (Blanc and Leveau 1975).

The study of the structure of benthic communities often reflects exposure to pollution. Qualitative and quantitative benthic analyses are under way as part of MED POL involving benthic communities in unpolluted coastal areas and those exposed to various human influences. Mapping the distribution of these communities will indicate change over time, providing a tool to evaluate the effects of increased human settlement and industrialization. Taxonomic diversity, biomass, production potential of populations and studies of community dynamics are being completed and provide further indications of the effects of pollutants on communities and ecosystems.

The ecological approach in determining pollution effects is extremely time-consuming and provides information that requires very careful interpretation. Therefore it might appear that this subsection is less an anlysis of currently observed effects of pollutants on Mediterranean ecosystems and human health than a review of ongoing MED POL activities, notably projects MED IV, MED V and MED VII, which will ultimately lead to a better understanding of the "biological" response to increased pollution.

Organisms are adapted to the chemical composition of ocean water. They evolved in this environment, most can acclimate to minor changes, but survival and acclimation to greater changes of natural concentrations of some marine constituents (i.e. mercury) may be beyond the capability of a population, community or ecosystem to adapt.

3.1.5.1 Effects on human health

Marine foods do not constitute a large part of the diet of the general public. Except for Spain (approx. 17 per cent) and Tunisia (approx. 12 per cent) less than 10 per cent of the animal protein intake is of marine origin (table 3.1.13). Much fish is imported into the Mediterranean countries. From the few estimates available the percentage of Mediterranean fish consumed by the general public ranges from 10 to 50 per cent.

The higher than average Hg concentrations found in Mediterranean fishes obviously raises the question of possible health risks. After the Minamata incident, maximum permissible concentrations of mercury in fish and other marine organisms were established. Limits for other heavy metals do not seem to exist, so mercury may serve as an example for an evaluation of these limits. The mercury limits vary in different countries from 500 to 1000 ug Hg-T/kg FW. In some countries higher limits are set for tuna. All limits must be referred to fresh weight, since in the early days of discussing these limits great confusion and commotion had already arisen because the differences between fresh weight concentrations and dry weight concentrations were confused. A justification of these limits can be deduced from the provisional weekly intakes established by FAO expert panels (e.g. FAO 1973) (table 3.1.14). 300 ug has been suggested as the maximum provisional intake for Hg-T and 200 ug for methyl-mercury.

Since food habits are quite variable, two categories of persons can be distinguished in a first approximation:

a) The general public which consumes the national average of fish food from Mediterranean and non-Mediterranean origin as offered on a typical market;

b) The general public which consumes the national average of fish but exclusively from Mediterranean origin;

Table 3.1.13 Consumption of fishery products in Mediterranean countries (Data for 1972 - 1974 from FAO (1977) and Crispoldi, pers. comm.)

Country	Population in millions	Per caput consumption kg edible, FW*** per year	per week	g protein per day tot. animal	% fish	Sea food of Mediter. origin
Algeria	15.78	0.92	0.018	10.4	5.7	?
Cyprus	0.65	2.3	0.044	40.6	4.2	?
Egypt FW*	35.82	0.9	0.016	10.3	4.85	?
SW*		0.65	0.0125		2.9	?
France FW*	52.115	0.15	0.003	61.2	<0.2	
SW*		7.33	0.141		6.5	10%
SWI*		2.75	0.053		1.3	
Greece FW*	8.81	0.62	0.012	44.7	0.9	
SW*		6.15	0.118		8.7	50%
Italy FW*	54.9	0.21	0.004	42.8	0.2	
SW*		4.38	0.083		7.2	?
Lebanon	2.7	1.1	0.023	18.0	5.0	?
Libya	2.15	2.13	0.04	20.1	9.45	?
Malta	0.32	4.3	0.083	40.6	8.6	?
Morocco	16.5	2.18	0.042	20.1	8.0	?
Spain FW*	34.6	2.31	0.045	44.9	0.2	
SW*		13.91	0.268		16.7	10%
SWI*		4.91	0.095		4.5	
Syria	6.8	0.51	0.01	13.7	2.9	?
Tunisia	5.49	3.25	0.062	13.7	12.4	?
Turkey FW*	37.95	0.17	0.004	17.9	0.6	
SW*		2.18	0.042		7.8	3%
Yugosl. FW*	20.96	0.472	0.009	28.7	1.7	
SW*		1.06	0.021		2.4	?

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kg FW equiv. = kg of fresh weight equivalent: processed fish products have been converted into the original fresh weight

Tot. animal = total animal protein available

FW* = fresh water fish; SW* = marine fish; SWI* = marine invertebrates

Countries without subdivision into SW* etc. marine fish only

*** edible portion of fish has been estimated as being 0.5 of live weight equivalent

Table 3.1.14 Provisional weekly intake of heavy metals by human beings (FAO 1973, Bernhard and Zattera 1975)

Total heavy metal	ug element/'70 kg man'
total mercury	300
methyl mercury	200
total copper	24,500
total cadmium	400
total lead	2800
total arsine	2450

Table 3.1.15 Mercury in agricultural products used for human consumption and an estimation of mercury intake through these products

	ug Hg/kg*	consumption in kg FW daily	weekly	weekly intake in ug Hg
Meats	5	0.3	2	10
Bread etc.	15	0.4	3	45
Vegetables	4	0.2	1.5	6
Fruits	6	0.1	0.7	3
Milk products	5	0.2	1.5	8
			total	72

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* Data from Schelenz and Diehl (1973)

Schelenz R., and J.F. Diehl (1973) Anwendung der Neutronenaktivierungsanalyse zur Quecksilberbestimmung in Lebensmitteln, Z. Anal. Chem. 265, 93-97

c) So-called critical groups which, because of special food habits and/or because of facilitated access to fish (fishermen, fish vendors, workers in fish food processing industries and their families) consume considerably larger quantities.

Before proceeding with the estimate, the mercury contribution of the other food items has to be estimated. From table 3.1.14 it can be seen that about 70 ug Hg-T or about 25 per cent of the normal Hg intake (300 ug; table 3.1.15) comes from terrestrial foods.

Although on the average only 80 per cent of the mercury in fishes is methyl-mercury (see above) we will assume that all mercury is methyl-mercury (Hg-M). So our allowance for marine foods is 150 ug Hg-M.

For the average fish consumption we can use the FAO estimates (table 3.1.13). For the critical groups we have to rely on the very few estimations available which range from 300 g to 800 g fish per day (Jokelainen, 1967; Preston, 1967; Bernhard et al. 1972). This corresponds to about 5.5 kg fish per week. Taking Spain as an example, for the three population groups the following estimates can be made:

a) General public eating fish of Mediterranean and non-Mediterranean origin: 27 g (= 10% of 0.268 kg) shall contain less than 150 ug Hg-M. Therefore, the maximum Hg-M concentration in fish is not to exceed 7500 ug Hg-M/kg FW. This corresponds to about 10,000 ug Hg-T/kg FW or 10 ppm FW, a value 10 times higher than the legal limit.

b) General public eating only fish of Mediterranean origin: 270 g shall not contain more than 150 ug Hg-M. From this follows that the Hg-M concentration must not exceed 750 ug/kg FW or 1000 ug Hg-T/kg FW. This corresponds to the 1 ppm or higher legal limit.

c) Critical groups eating 5.5 kg/week of Mediterranean fish. In this case 40 ug Hg-M/kg FW and 50 ug Hg-T/kg FW respectively are not to be exceeded. This value corresponds to one tenth of the lower legal limit.

Comparing these data with the actual Hg-T concentrations found in Mediterranean fish (tables 3.1.9 - 12) shows that the general public is protected, but that the critical groups are exposed to an apparent health risk. Since it is extremely unlikely, if not impossible, that the higher than normal Hg concentration in Mediterranean fishes and other marine organisms is caused by anthropogenic or man-made pollution, and that, on the other hand, the critical groups have eaten these large amounts of fish for generations without ill effects, another explanation must be sought.

The observations showing that selenium considerably reduces the toxic effects of inorganic and organic mercury and vice versa may supply the solution. Ever since Parizek et al. (1967) had observed that small amounts of selenite could clearly contract the toxicity of $HgCl_2$, many other workers have investigated the antagonistic effects of selenium on inorganic and organic Hg compounds. It could be shown that, in particular, selenite prevents inhibition of growth, neurotoxicity and lethality caused by the simultaneous administration of methyl-Hg with selenite to rats (e.g. Iwata et al., 1973; Stilling et al., 1974) and to Japanese quails (Gather and Sunde, 1974; Stoewsand et al., 1974).

In view of the high Hg body burden found in several larger marine organisms (especially tuna and swordfish), investigations which demonstrate the antagonistic effects of mercury and selenium when supplied in a tuna diet are of special interest (e.g. Ganther et al., 1972; Ohi et al., 1976).

The few data that exist on a positive correlation of mercury and selenium concentrations, both in marine organisms and human beings having been exposed to higher than average mercury concentrations in their environment, point to natural protection mechanisms (table 3.1.16). Kosta and collaborators' data (1975) have shown clearly that mercury mine workers who had high Hg concentrations in their organs also have high Se concentrations. The molar ratio is 1. Controls from the general 'not-exposed' public have Hg/Se molar ratios of 0.02 and 0.002. Marine fishes with low Hg body burden have similar low molar ratios around 0.02, while marine organisms with high Hg body burden have molar ratios of about 1, similar to human beings. The most extensive data available at present are those of the large teleost fish Makaira indica from the Pacific (Mackay et al. 1975) and of various marine mammals (Koeman et al 1973; 1975). Very preliminary data obtained through MED II suggest that in the Mediterranean tuna with relatively high body burden, the Hg/Se molar ratio is also 1. If further data confirm these observations on the 'coaccumulation' (Kosta et al. 1975) of selenium and mercury in organisms exposed to higher than average mercury concentrations, the new tolerance limits for many must take selenium concentrations in food into serious consideration.

3.1.5.2 Effects on marine organisms, ecosystems and living organisms

Research carried out within the MED POL project showed that 1 ug Hg/l inorganic can cause already sublethal effects on Crustacea; 0.7 ug D Cd/l are definitely noxious to adult Mytilus (George and Coombs, 1977). MED POL studies also revealed that 2.5 ug Cu/l constitute a hazard to sensitive marine forms (tables 3.1.16 and 17). Compared to these substances, Pb seems to be less hazardous when considering the concentrations found in the water and those proving toxic according to laboratory experiments.

Table 3.1.16 Mercury and selenium concentration in humans and marine organisms

		ug/kg FW		molar ratio	
Man	n	Hg	Se	Hg/Se	References
Mine worker (Idrija)	(1)	5000	1500	1.3	Kosta *et al.* 1975
	(1)	7800	3200	0.95	
	(1)	26,500	12,300	0.87	
	(1)	29,700	12,600	0.95	
	(1)	101,000	41,100	0.98	
Idrija population	(1)	14,400	5700	0.98	
	(1)	26	160	0.06	
Control	(1)	39	790	0.02	
	(1)	2.3	460	0.002	
Marine organisms					
Makaira indica					
muscle	(42)	7300	2200	1.3	Mackay *et al.* 1975
liver	(40)	10,400	5400	0.75	
High- Hg tuna	?	2870	2900	0.4	Ganther *et al.* 1972
Low- Hg tuna	?	320	1900	0.07	
Marine mammals	(25)	1000	2700	1.1	Koeman *et al.* 1973
Solea sp.	?	?	?	0.02	
Clupea heringa	?	?	?	0.02	
Scomber sp.	?	?	?	0.01	

Table 3.1.17. Effects of heavy metals on marine organisms

(1)

Comparison between the "typical concentration" of some heavy metals in sea-water with their concentration of saturation, the "safe concentration" for marine organisms and the concentration for which effects on marine organisms were observed. All concentrations in ug/l, data as quoted by Bernhard (1977) and MED POL.

Metal (compound) (solubility in sea-water)	Sea-water concentration (1)	Minimal risk (2)	Effective concentration	Effect	Species/stage	References
Hg inorganic	0.1	0.1	1	inability to acclimate	Artemia salina	MED IV
			2	adhesion stress	Arbacia lixula	MED IV
			8 and 11	LC 50	Penaeus keraturus, Protozoea and Mysis larva respectively	MED IV
			100	severe liver damage	Mugil auratus	MED IV
			200	reduction of O_2 consumption	Monodonta	MED IV
Hg organic Phenyl mercury acetate			0.06	20% growth inhibition	Phaeodactylum tricornutum	Nuzzi, 1972
Methyl mercury			4.8 and 69	LC 50	Penaeus keraturus Protozoea and Mysis larva respectively	MED IV
Cd (4000 - 1,000,000)	0.02	0.2	1	inability to acclimate	Artemia salina	MED IV
			5000	abnormal shell movements	Crassostrea angulata adults	MED IV
			0.7	excessive mucus production	Mytilus edulis	George and Coombs, 1977

Table 3.1.17. (contd.) Effects of heavy metals on marine organisms (2)

Metal (compound) (solubility in sea-water)	Sea-water concentration (1)	Minimal risk (2)	Effective concentration	Effect	Species/stage	References
Cd (contd.)			1020 - 1250	LC 50	*Penaeus kerathurus* *Nauplius*, *Protozoea* and *Mysis* larva	MED IV
			50,000	Severe damage to liver and kidneys within four days	*Halobatrachus didactylus*	MED IV
Pb (300-400/1)	0.02	10	200	Abnormal larval development	*Psammechinus miliaris*	Bernhard and Zattera, 1975
			500	Decrease of 5-aminolevulinate-dehydrogenase-activity	*Mugil capito*	MED IV
			1036	Below threshold of acute toxicity	*Nereis diversicolor*	Aubert *et al.*, 1976
Cu (400-800/1)	1	10	6	Increased frequency of shell movements and closure	*Crassostrea angulata*	Establier and Pascual, 1974
			500	26 days LC 50	*Crassostrea angulata*	Establier and Pascual, 1974
			80 and 105	24 hours LC 50	*Penaeus kerathurus* *Protozoea* and *Mysis* larva respectively	MED IV
			2.5 - 9	decreased mobility	*Acartia clausi* and *Oncea mediterranea*	MED IV

Table 3.1.17. (contd.) Effects of heavy metals on marine organisms.

Metal (compound) (solubility in sea-water)	Sea-water concentration (1)	Minimal risk (2)	Effective concentration	Effect	Species/stage	References
Cu (contd.)			50	reduced growth	*Artemia salina* larva	MED IV
			25,000	48 hours LC	*Palaemon elegans*	MED IV
			50	reduced growth	*Ophryotrocha labronica* larva	Saliba and Ashanullah, 1973
			25	reduced growth (permanent exposure 2nd generation larva)	*Ophryotrocha labronica* larva	Saliba and Ashanullah, 1973
	1		39.7	8 days acute toxic threshold	*Nereis diversicolor* adults	Aubert *et al.*, 1976.
Zn (1200–2500/1	10	~ 20	30	inhibition of larval development	*Psamechinus miliaris*	Bernhard and Zattera, 1975
			2000	increased frequency of shell movements	*Crassostrea angulata*	Establier and Pascual, 1974
			817.5	threshold of acute toxicity	*Carcinus maenas* adults	Aubert *et al.*, 1976
Cr (VI)	0.04	10	100	no spawning and embryo development	*Neanthes arenaceodentata*	Oshida, 1976
			1300	8 days acute toxic threshold	*Carcinus maenas*	Aubert *et al.*, 1976

Table 3.1. 17 (contd.) Effects of heavy metals on marine organisms

Metal (compound) (solubility in sea-water)	Sea-water concentration (1)	Minimal risk (2)	Effective concentration	Effect	Species/stage	References
Ni	5	2	1180	48 hours LC 50	*Crassostrea virginica*	Bernhard and Zattera, 1975
As	2	10	2200	96 hours incipient lethality	*Argopecten irradians*	Nelson *et al.*, 1976
Ag		0.1	0.7	photokinesis decreased	*Carcinus maenas Zoea* larva	Amiard, 1976
B	0.00002	1	12.2	283 hours LC 50 in sea-water	*Onchorhynchus kisutch* under yearlings	Thompson *et al.*, 1976
Co		0.1	0.6	photokinesis decreased	*Carcinus maenas*	Amiard, 1976

(1) Goldberg (1965) and Brewer (1976)

(2) WQC - 1972 (1973)

Table 3.1.18 Toxic effects of heavy metals and body burden in bioassay and body burden observed in the field (1)

	Bioassay					Field observations	
	Exposure concentrations and corresponding body (organ) burdens (concentration in ug/l - burdens in ug/kg)					(Particularly high) body and organ burdens found in the Mediterranean	
Metal compound	Exposure time Concentration	Species	Effects	Corresponding burden	References	Burden and if different from the preceding: species	References
$HgCl_2$	50 days 100	Mugil auratus (22 cm length)	severe liver damage	liver 100,000 intestine 21,000 muscle 2200 FW	MED IV	Mugil cephalus liver 11,220 muscle 660 FW	Renzoni et al. 1973
$HgCl_2$	49 days 100	Halobatrachus didactylus (20 - 33 cm length)		liver 53,000 muscle 9600 FW	MED IV		
$HgCl_2$	7 days 100	Nereis diversicolor	1/5 of the threshold of acute toxicity	13,200 FW	Aubert et al. 1976		
$CdCl_2$	96 hours 50,000	Halobatrachus didactylus (20 - 33 cm length)	severe liver and kidney damage, caryorhexis of blood cells	liver 5000 intestine 39,000 kidney 13,000 muscle 200 FW	MED IV	intestine 231 liver 57.5 kidney 228 muscle 40 FW controls	MED IV
$CdCl_2$	96 hours 75,000	Crassostrea angulata adults	LC 50	>40,000 FW	MED IV	<400 FW controls	MED IV
115 $Cd\ Cl_2$	120 hours 0.7	Mytilus edulis	excessive mucus production	120,000 DW	George and Coombs 1977	4700 FW in Mytilus galloprovincialis	Fowler and Oregioni 1976
$Pb(NO_3)_2$	7 days 103	Nereis diversicolor	<1/100 threshold of acute toxicity	3500 DW	Aubert et al. 1976		

Table 3.1.18 (Contd) Toxic effects of heavy metals and body burden in bioassay and body burden observed in the field (2)

	Bioassay					Field observations	
	Exposure concentrations and corresponding body (organ) burdens (concentration in ug/l - burdens in ug/kg)					(Particularly high) body and organ burdens found in the Mediterranean	
Metal compound	Exposure time Concentration	Species	Effects	Corresponding burden	References	Burden and if different from the preceding species	References
$Pb(NO_3)_2$	15 days	*Carcinus maenas*	< 1/100 threshold of acute toxicity	[illegible]70-8590 FW without pancreas	Aubert *et al* 1976	*Nephrops norvegicus* 131 FW	MED IV
$CuSO_4$	77 days 200	*Sparus aurata*	severe lesions of intestine	liver 20,700 intestine 2400 spleen 8900 FW	MED IV	liver 4070 intestine 1200 spleen 4430 FW controls	MED IV
						Engraulis encrasicolus liver 8500 FW fillet 1100	Gilmartin and Revelante 1975
$CuCO_4$	7 days 40	*Nereis diversicolor* adults	< threshold of acute toxicity	6430 FW	Aubert *et al.* 1976		
$CuSO_4$	4 days	*Nereis diversicolor* adults non-resistant	LC 50	200,000 - 300,000 DW	Bryan 1974	500,000 - 1,000,000 (resistant)	Bryan 1974
$CuSO_4$	26 days 500	*Crassostrea angulata*	lethal	391,000 DW	Establier and Pascal 1974	*Mytilus edulis* 3700 FW 149,000 DW	Sheppard and Bellamy 1974, Fowler and Oregioni 1976, respectively
CuSO4	15 days 31.7	*Carcinus maenas*	< 1/100 threshold of acute toxicity	9900-16,400 whole body without pancreas FW	Aubert *et al.* 1976		

Table 3.1.18 (contd) Toxic effects of heavy metals and body burden in bioassay and body burden observed in the field (3)

	Bioassay					Field observations	
	Exposure concentrations and corresponding body (organ) burdens (concentration in ug/l - burdens in ug/kg)					(Particularly high) body and organ burdens found in the Mediterranean	
Metal compound	Exposure time Concentration	Species	Effects	Corresponding burden	References	Burden and if different from the preceding: species	References
$ZnSO_4$	7 days 33	*Nereis diversicolor*	< 1/100 threshold of acute toxicity	39,000 FW	Aubert *et al.* 1976		
						Mytilus galloprovincialis 248,000 FW 543,000 DW	Sheppard and Bellamy 1974, Fowler and Oregioni 1976, respectively
$ZnSO_4$	15 days 33	*Carcinus maenas*	(4/100 threshold of acute toxicity)	49,700 - 62,500 FW whole body without pancreas	Aubert *et al.* 1976	*Nephrops norvegicus* 13,580 FW	MED IV
$K_2Cr_2O_7$	7 days 26	*Nereis diversicolor*	< 1/100 threshold of acute toxicity	805 FW	Aubert *et al.* 1976		
							MED IV
$K_2Cr_2O_7$	15 days	*Carcinus maenas*	~ 1/50 threshold of acute toxicity	560 - 810 FW whole body without pancreas	Aubert *et al.* 1976		
$NaAsO_2$	96 hours 2220	*Argopecten irradians* (North American)	incipient lethality LC 50	~ 30,000 ~ 40,000 FW	Nelson *et al.* 1976	*Ostrea edulis* 83,000	Papadopoulou and Kanias 1976

Arsenic did not receive much attention within MED POL. The burdens assessed in organisms were very low (FIR PM/77/7). Those found in earlier surveys only seldom exceeded 100,000 ug/kg. The highest concentration found was 182,000 (Papadopoulou and Kanias, 1976). However, concentrations up to 100,000 ug/kg can still be acquired naturally, and most of the As incorporated is present in alkylated and only slightly toxic form (Edmonds and Francescone, 1977). In addition to this, there is no evidence of accumulation in the food chain (Kennedy, 1976).

Determination of tolerance limits for the ecosystem requires evidence of interference with the survival of the most sensitive species and life stages. This information is largely unknown for the Mediterranean. Knowledge of threshold levels for reversible effects on individual, population, community and ecosystem levels is required to determine what a tolerable level of pollution might be.

Uptake via food, which accounts for most of the body burdens, particularly in the case of mercury (Pentreath, 1976) seems to be much less harmless than uptake from water. Test organisms, have, for the most part, been exposed to contaminants in the water. But as it has been found elsewhere, 1,800,000 ug Hg/kg DW of algae were harmless to Acartia tonsa. Besides this, no accumulation was assessed in this zooplankton species (Parrish and Carr, 1976). This shows how little is known about the environmental impact, even of a contaminant as important as mercury (generally believed to be biomagnified).

Communities are complex webs of species interrelationships - the removal of one species may be critical to the structure and function of the whole community. Similarly the excessive growth of one species (as in eutrophication), or its accumulation of chemicals toxic to others, can also have detrimental effects. Detergents are suspected of decreasing species diversity of some benthic communities in North-Western area (II) and have been associated in the Tyrrhenian (IV) with sea spray "kills" of coastal pine trees. A loss of diversity and accompanying increases in population of a few pollution-tolerant species have also been reported in the Adriatic (V). Differential sensitivity of both phyto and zoo-plankters to chlorinated hydrocarbons is known, the potential effect of shifts in community species composition is not known.

Changes in the genetic composition of population, physiology and behavioural patterns may be a more sensitive detection technique for low-level contamination than changes in community structure although marked community changes have resulted from major pollution incidents. The identification of especially susceptible, indicator organisms can facilitate the demonstration of pollution effects.

Knowledge of biochemical and physiological changes associated with contaminant exposure and related survival and reproductive alternations in populations is generally inadequate to prove cause-effect relationships conclusively.

3.1.6 Highlights of the most important problems and measures to remedy

The main problem in heavy metal pollution concerns mercury and possibly arsenic in fishery products for human consumption and the effects of these metals on marine organisms and ecosystems in near-coastal zones, especially semi-enclosed water bodies like harbours, bays, etc.

Mercury concentrations exceeding several times the legal limits have been observed in several large fish species such as the commerically very valuable tunas and swordfish, but also in smaller fishes (Mullus barbatus, Merluccius merluccius, Pagellus erythrinus). There seems to be no doubt that the high mercury concentrations in the large pelagic tunas and swordfish are natural and have existed in these fishes for geological ages. The high mercury concentrations in coastal and benthic fishes from areas where such concentrations exist in their environment, particularly in the sediments, also show that high levels of mercury in marine organisms are not necessarily linked to anthropogenic pollutions.

The recent findings (see 3.1.5.1 above) that (i) selenium acts antagonistically towards mercury and vice versa, and (ii) that both in man and some marine organisms high mercury concentrations are associated with high selenium concentrations, suggest that under 'natural' conditions selenium is "coaccumulated" with mercury to counteract the toxic effects of high mercury levels.

This Hg/Se coaccumulation does not seem to occur in the case of anthropogenic release of organic mercury. In the Minamata incident organic mercury was directly released into the sea-water and accumulated in this form by marine organisms used for human consumption, while the natural accumulation process seems to start with the uptake of inorganic mercury by organisms from water and sediments and only then does the transformation to organic Hg take place. This illustrates the importance of distinguishing between different physico-chemical forms of mercury both from the point of view of health protection directly (organic mercury is more toxic than inorganic) and indirectly, since organic mercury follows different pathways from inorganic when released into the marine environment.

Comparing arsenic concentrations in marine biota with the tolerable intake limits suggests, despite the few data as yet available from the Mediterranean and other areas, that arsenic is also a critical element in fishery products. Recent investigations on the different physico-chemical forms of arsenic and the mechanisms which control organometallic compounds in the natural environment have shown that arsenic occurs to a large extent in methylated forms (Braman and Foreback, 1973; Brinckman and Iverson, 1975; Edmonds and Francesconi, 1977; Wood, 1977). Since dimethylarsenic acid is, for example, about 25 times less toxic than As(III), tolerance intakes based on total arsenic would be misleading if large fractions of arsenic in fishery products were present as metal organic compounds.

The determination of the total amounts of heavy metals in fishery products is inadequate for the evaluation of health hazards. The determination of the total amount of heavy metals, only, is insufficient to justify neglecting important health hazards on the one hand, or, on the other, placing unnecessary restrictions on important industries such as fisheries and the associated food industry.

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3.3 PETROLEUM HYDROCARBONS

3.3.1 Introduction

Concern has evolved during recent years regarding the fate and effects of petroleum hydrocarbons in the marine environment. This concern is prompted by the increasing additions of these substances to the marine environment, an environment that is an intimate part of the world ecosystem, and recognized as having finite carrying or assimilative capacities. The fact that the time-scales involved in natural ocean processes are quite large, ranging from months to decades for coastal waters and from a hundred to a hundred million years for open ocean waters, intensifies the problem. This means that non-degradable fractions of toxic inputs to the oceans can remain for extremely long periods of time before finding their respective sinks. In such a system, it becomes imperative to detect small adverse changes from some baseline state if corrective action is to be taken. The ultimate objective of such research on lethal and sublethal effects of oils on marine organisms is the ability to predict levels of oils in sea-water that are safe under conditions of continuous exposure and are conducive to the survival, growth, reproduction, and general well-being of the species.

In an attempt to understand the state of oil pollution in the Mediterranean the following problems are discussed briefly in this chapter:

a) Properties and composition of oil.

b) Sources of oil pollution in the Mediterranean.

c) Level of petroleum hydrocarbons in the Mediterranean.

d) Fate and pathways of oil in the marine environment.

e) Effects of oil pollution.

f) Highlights of the most important problems and measures to remedy the situation.

3.3.2 PROPERTIES AND COMPOSITION OF OIL

The word oil is used synonymously with the terms mineral oil, crude oil, crude, or petroleum, although there are many other types of oils that are not of fossil origin and are distinct from petroleum. Oil varies in chemical composition, colour, viscosity, specific gravity, and other physical properties depending on the source. The colour of petroleum varies from light yellow-brown to black and the viscosity varies from water-like to almost solid. The specific gravity of most petroleum oils lies between 0.735 and 0.950. We need to understand the composition of oil to understand its fate at sea.

Crude oils are complex mixtures of thousands of pure hydrocarbons (50 - 98%), trace amounts of metals (primarily nickel, vanadium, and iron) complexed with organic chelates and porphyrins and with other organic compounds containing sulphur, nitrogen and oxygen. The principal classes of hydrocarbons in crude petroleum are alkanes, cycloalkanes and aromatics. The alkanes, commonly referred to as paraffins, are saturated straight or branched chain hydrocarbons having the general formula C_nH_{2n+2}. Cycloalkanes are saturated ring structures of the general formula C_nH_{2n} which may have alkyl groups substituted for certain hydrogen atoms. The aromatic hydrocarbons are unsaturated compounds primarily composed of one or more benzene ring structures that may also have alkyl substitutions.

Olefins, a fourth general class of hydrocarbons, are unsaturated compounds with two or fewer hydrogen atoms per carbon atom. Although they are found only in trace amounts in crude petroleum, they may account for as much as 30 per cent of the weight of refined petroleum products such as gasoline.

Natural plant and animal hydrocarbons are ubiquitous in both terrestrial and aquatic environments. Normal alkanes in the C25 to C35 range predominate in plant waxes where molecules of odd numbers of carbon are in excess of those of even numbers by a factor of ten or more. Although there is a tendency for biogenic hydrocarbons to be characterized by an abundance of odd-carbon types, this is not a sufficient criterion for identifying a source as non-petroleum.

The quantitative separation of hydrocarbons found in the ocean into those due to petroleum sources and those due to biogenic sources is nearly impossible with the present state of analytical competence. Part of the problem is due to the ubiquitous occurrence of plant and animal hydrocarbons and part is due to a lack of information regarding the eventual weathered products of both petroleum and biogenic hydrocarbons.

A National Academy of Sciences report, 1975, listed four characteristics considered indicative of petroleum sources:

(i) Petroleums are complex mixtures of hydrocarbons with a wide range of molecular weights and structures.

(ii) Petroleums contain several homologous series (such as n-paraffins) with adjacent members present in nearly the same amounts.

(iii) Petroleums contain a greater variety of cycloalkanes and aromatics. Also the occurrence of alkyl-substituted ring compounds, characteristic of petroleums, has not been reported in marine organisms.

(iv) Petroleums contain naphtheno-aromatic hydrocarbons that have also not been reported for marine organisms.

A crude oil may contain up to 2 per cent of total oxygen. The principal species include phenols (cresols and higher boiling point alkylphenols) and both straight chain and linked carboxylic acids, such as hexanoic acid and 3-methyl pentanoic acid. Nitrogen varies between 0.05 and 0.8 per cent in crude oils chiefly in pyridine and quinolines. Sulphur exists both as the element and in compounds from trace amounts to 5 per cent by weight in crudes. Hydrogen sulphide, mercaptans and aliphatic and cyclic sulphides are included in these compounds.

The metallo-organics encompass the nickel and vanadium porphyrin complexes permitting these metals to attain concentrations of 5-40 ppm. Added to these are very small concentrations of other metals e.g. iron, sodium and zinc, whose associations with other elements are still undetermined.

The refined products produced by the distillation of crude oils are as follows:

Straight-run petrol, which boils at temperatures up to 200°C and contains compounds with 4 to 12 carbon atoms.

Middle distillate, with compounds of 12 to 20 carbon atoms and a boiling range of 185°-345°C. Products such as kerosene, heating oils, diesel oils and jet, rocket and gas turbine fuels fall into this category.

Wide-cut gas oil with 29 to 36 carbon atoms and boiling points between 345° and 540°C. This group contains waxes, lubricating oils and starting materials for the production of gasoline by catalytic cracking processes.

Residual oils, usually asphaltic in nature.

The alkenes may be found in concentrations of up to 30 per cent in petrol and about 1 per cent in jet fuel. The exact composition of any particular refined product is determined by the character of the crude oil from which it came and by the nature of the distillation process.

The attention given to the pollution of the ocean by oil should be concentrated on crude oil since it is in this form that it is usually transported by sea. Except in coastal waterways, harbours and bays it is a far greater source of pollution than refined products and residual oils. Crude oil accounts for approximately 80% of oil spilled directly at sea (NAS, 1975). Inputs of waste oils and incompletely combusted fuels via the atmosphere, river run-off, and industrial or municipal sewage are not included in this estimate. Although there are undoubted inputs of petroleum from these sources, their composition and behaviour in the sea are diverse and not clearly understood.

3.3.3 SOURCES OF OIL POLLUTION IN THE MEDITERRANEAN

The actual input of oil to the Mediterranean as well as to world oceans is unknown. Best estimates are based on very limited availability of reliable data concerning the rates of input from each significant source.

In order to make the best estimate of a global input of oil to the ocean a panel was assembled by the US National Academy of Sciences (Anon., 1975) and its estimates are given in table 3.3.1.

The largest single source is marine transportation which contributes 35% of the total. Land-based sources of pollution (coastal refineries, industrial waste, municipal waste, urban run-off and river run-off) combined, are a bigger source than marine transportation. Subdistribution among different categories within marine transportation is given in table 3.3.2.

According to Jeffery, 1974, the major sources of oil pollution in the Mediterranean are the following: ballasting/deballasting operations of the tankers; discharge of oily bilge-water; tank washing; refinery effluents; discarded lubricants and other oils. Minor sources are: accidents to tankers and other vessels (a small annual contribution but each incident can pose a major local problem); off-shore exploration and exploitation; accidents to pipe-lines and terminals; natural seepages; atmospheric rain-out.

Accidental pollution by oil takes second place to chronic pollution in the Mediterranean. The general sssumption is that marine operational losses and land-based discharges are equally responsible for this chronic pollution. The location of the different sources is indicated in figure 3.3.1 which shows that the situation differs from one basin to another: the Eastern Mediterranean is essentially an area of oil production and there are fewer industrial zones able to pollute the coastal waters directly and these are located in specific zones. The western basin, on the other hand, has many oil treatment industries and there is heavy transit of these products. At present Algeria is the only large oil-producing country in the Western Mediterranean.

Table 3.3.1.

Estimate of input of petroleum to the marine environment

Source	Input (10^6 t/y)	%
Marine transportation	2.133	35
Off-shore production	0.08	1
Land-based		
- Coastal refineries	0.2	3
- Industrial waste	0.3	5
- Municipal waste	0.3	5
- Urban run-off	0.3	5
- River run-off	1.6	26
Natural seepage	0.6	10
Atmospheric	0.6	10
Total	6.113	

Table 3.3.2.

Input of oil to the ocean from marine transportation

Source	Input (10^6 t/y)	%
LOT tankers	0.31	14.6
Non-LOT tankers	0.77	36.1
Dry-docking	0.25	11.7
Terminal operations	0.003	0.1
Bilges, bunkering	0.5	23.5
Tanker accidents	0.2	9.4
Other accidents	0.1	4.6
Total	2.13	

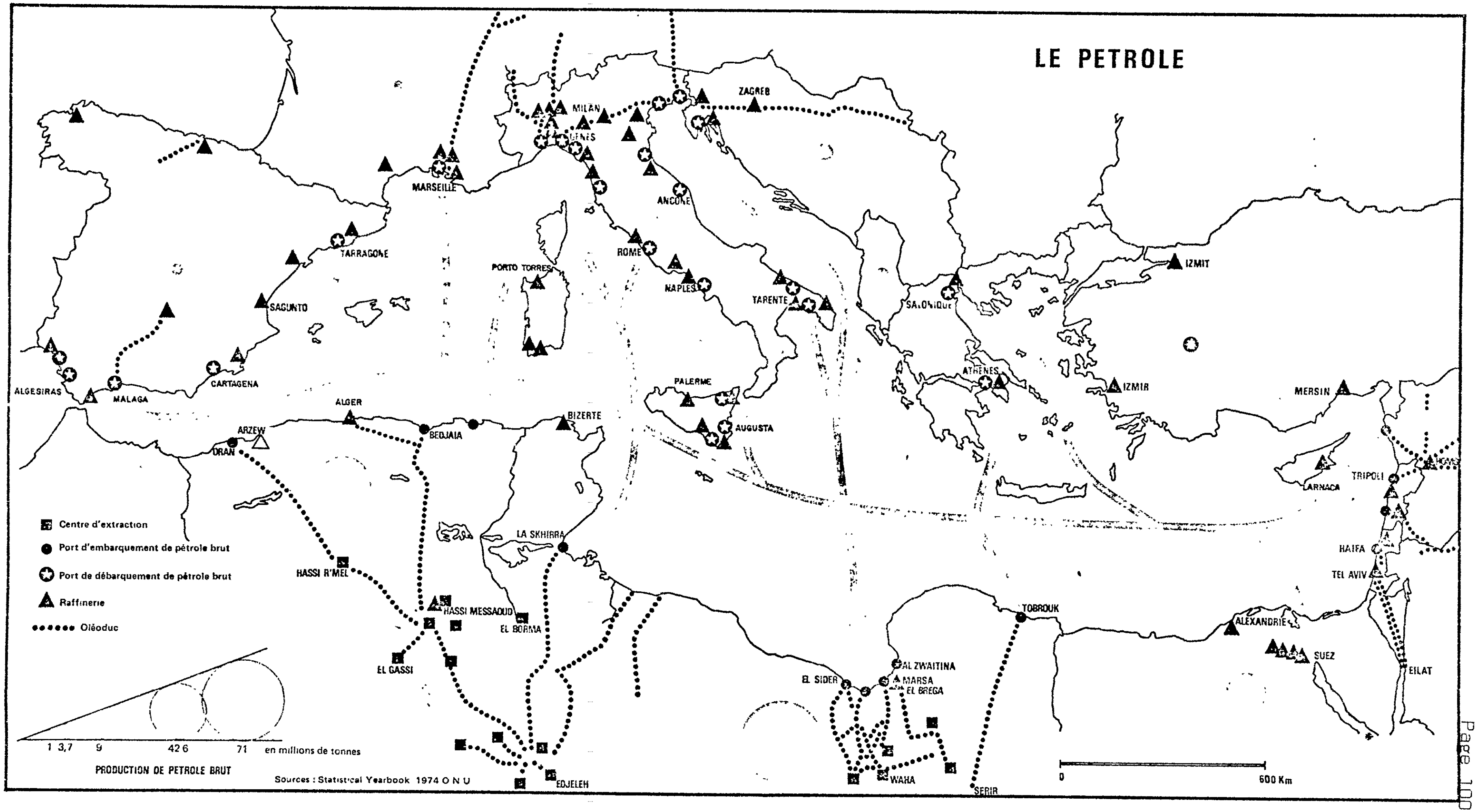


Fig. 3.3.1 Sources of oil pollution in the Mediterranean (data from United Nations Statistical Yearbook, 1974)

The quantity of petroleum hydrocarbons released into the Mediterranean Sea depends on several factors:

(i) The quantity of oil produced within the region;

(ii) The quantity of crude oil brought into the region by pipe-lines from crude oil sources outside;

(iii) The quantity of oil transported within or through the Mediterranean;

(iv) Land-based sources of pollution;

(v) Maritime accidental.

Oil production

It is very difficult to obtain the latest data on oil production within the areas concerned which are partially responsible for the oil pollution of the Mediterranean. This information is essential for the estimation of the extent of pollution as well as for the all-important question of finding means to reduce the pollution from this source. Table 3.3.3 gives recently published data. The quantity of oil produced within the area is only partly used and/or processed within the area itself; a major part of it is intended for export.

Oil brought into the area by pipe-line

The development and exploitation of the large oil fields in the Middle East, the Libyan Arab Jamahiriya and Algeria, together with Europe's rapid industrial development, have made the Mediterranean Sea one of the major world regions for the transit of oil. The transport of crude oil by sea from terminals situated in the Eastern Mediterranean and North Africa has been made possible by an efficient system of pipe-lines for crude oil, connecting internal and rather distant oil fields to the Mediterranean coast.

When considering only the larger lines, such as that from Iraq to Tripoli in the Lebanon and to Banias in Syria, the TAPline from Saudi Arabia to Sidon in the Lebanon, from Eilat to Ashkelon in Israel for the Iranian oil, and from the town of Suez to the Mediterranean coast of Egypt for the Sinai and South Egyptian oil, we reach a capacity of 230-300 million tons per year of crude oils from areas outside the Mediterranean region. By cautious estimate, the over-all quantity reached in 1976 was already 460 x 10^6 tons per year. On the other hand, in the consumer countries, the main pipeline terminals in Marseilles, Genoa and Trieste, having a capacity at present of over 300 million tons per year, supply oil to France, Federal Republic of Germany, Switzerland, Italy, Austria, etc.

Table 3.3.3 and figure 3.3.1 also include some information on oil-processing facilities in the region.

Table 3.3.3.
Oil production and refining capacity of Mediterranean countries
(adapted from: The Oil and Gas Journal, 29 December, 1975)

	No. of producing wells 7.1.1975	Estimated oil production, 1975 (1000 b/d)	% change from 1974	No. of refineries 1.1.1976
EUROPE				
Cyprus	-	-	-	1
France	274	20.0	-13.0	24
Greece	-	-	-	4
Italy-Sicily	117	20.0	-5.3	32
Spain	25	38.0	2.1	10
Yugoslavia	1,100	70.0	-	-
MIDDLE EAST				
Israel	15	185.0	-2.3	2
Lebanon	-	-	-	2
Syria	346	175.0	32.6	1
Turkey	354	60.0	-7.7	4
NORTH AFRICA				
Algeria	384	935.0	-5.2	3
Egypt	319	225.0	51.0	4
Libya	851	1400.0	-6.7	6
Morocco	17	0.7	-28.6	2
Tunisia	60	95.0	8.0	1

There are also plans to increase the capacity of pipe-lines and of oil terminals (Le Lourd, 1977). The new SUMED pipeline of 80 million t/y capacity was opened in December 1976 with its new oil terminal in Egypt but an increase to 100 million t/y is already being contemplated. In Turkey too, a new pipe-line from Iraq of 25 million t/y capacity will this year extend to the new oil terminal of BOTAS. During the next ten years or so we can also expect the development of off-shore oil production on some parts of the continental shelf such as those bordering Spain, Tunisia, Libyan Arab Jamahiriya, in the Adriatic and in the Aegean Sea. Thus, what was considered, until now, as a minor source of oil pollution in the Mediterranean may well be significantly increased by these new factors.

Oil transported within or through the Mediterranean

Smith, 1975, has estimated the annual amount of oil which has crossed or been landed in the Mediterranean in that year, at some 350 million tons, compared to the 1500 million tons throughout the world (Sasamura, 1977). 150 million tons of this were transported from North Africa to Europe.

Shipping in the Mediterranean is characterized by the short distances covered, and tankers are no exception. In order to maintain adequate manoeuvrability and propeller immersion, tankers need to carry sea-water ballast in their empty tanks on their return journey to their loading terminal. In the very large crude carriers (VLCCs) the amount of sea-water ballast is about a third of the dead-weight. Unloading of this sea-water ballast must of course take place before the loading of crude but the water has been heavily polluted by the previous cargo. The direct discharge of this water ballast into the sea can reach up to 0.5 per cent of the dead-weight of the ship (Le Lourd, 1977). The situation has been improved since the early 1960s by introducing a procedure, known as the Load on Top (LOT), whereby washings and oily sea-water from ballast are kept on board for settling and separation of oil from water; the separated oil is then merged with the next cargo. Eighty per cent of the world tanker fleet use this procedure which has gone a long way to reducing operational oil pollution despite the greater quantities of oil carried by sea. To be efficient this procedure needs at least 72 hours which corresponds to a tanker's voyage of more than 1200 miles. If these requirements are considered in conjunction with the main routes taken by tankers in the Mediterranean as illustrated in Figure 3.3.1, and if we bear in mind that the dimensions of the Mediterranean are 4000 km east-west and 800 km north-south, it appears that a great number of tankers cannot use the LOT system. According to the 1954 Convention on the prevention of oil pollution at sea ratified by all the riparian States, appropriate reception facilities have to be provided for the unloading of the oily residues contained in the sea-water ballast. However, these reception facilities exist in only about half of the 17 loading terminals in the Mediterranean and their capacity is often insufficient thus causing delay and making the tankers lose precious time. Most of them, therefore, make use of the possibility offered by the 1962 amendment to the Convention of 1954 which allows the discharge of oil residues at a distance of over 100 miles from land. Two areas in the Mediterranean can thus be used; one between Italy and the Libyan Arab Jamahiriya, and the other south-west of Cyprus.

In 1970 it was estimated that the quantity of tanker ballast and wash water adds approximately 300,000 t/y to the Mediterranean.

Bilges and bunkering, stemming from day-to-day operations in the engine-room, and drippings from faulty valves, present another operational source of oil pollution. According to Goldberg, the quantity released is of the order of 10 tons oils per ship and year. Estimates of quantities of oil introduced as bilges into the sea from a 60,000 ton tanker plying between Ashkelon - Europe - Ashkelon were between 3 and 5 tons of oil per voyage (Shekel, 1972a,b).

Transportation of oil by tanker might be the most important operational source of oil in the sea, and particularly within the Mediterranean. This is due primarily to the large ratio between the quantity of oil transported within this sea and the surface of the Mediterranean: 40% of the world oil transport passes through the Mediterranean, while its area is only 0.7% of the total area of the world oceans.

Land-based sources of oil pollution

In order to estimate the amounts of pollutants entering the Mediterranean Sea from land-based sources a detailed study of that problem was carried out by the MED-X project. In their report they give amounts of land-based sources of oil pollution in the Mediterranean and the results are in figure 3.3.2 for all 10 areas. The total amount for the whole Mediterranean region is 115,000 t/y. It can be seen from figure 3.3.2 that the most polluted are areas VII and IX.

Maritime accidental

The largest single spillages of oil at sea result from accidental damage to a tanker's hull. Collisions and groundings are by no means rare, perhaps because over 50% of sea traffic is now in oil. The yearly number of tanker collisions in the Mediterranean is not known. After the Torrey Canyon affair, in the three years ending April 1967, 238 tankers were involved in collisions and 91 went aground. Nine per cent of the collisions and 19% of the groundings resulted in cargo loss (39 incidents in all). An analysis of 285 tanker damages in the United States (Fletcher, 1967) showed that 36% were caused by collision and 25% by grounding or striking submerged objects. In this analysis, crew negligence (38 cases) and heavy weather damage (37 cases) were the next most common causes (13% each).

The structure and operation of modern tankers do not make them markedly less prone to accidental stranding or collision, nor do they reduce the pollution risk from such accidents. In the case of the Torrey Canyon, the combined effects of the lack of manoeuvrability, faulty crew-training and communication, and inadequate navigational aids were responsible for the catastrophe. Two of the most severe handicaps of a tanker are its directional stability and its stopping distance. Torrey Canyon, when approaching the Seven Stone Reef, was making about 16 knots and would have required two miles to come to a dead stop; a super tanker requires as much as seven miles.

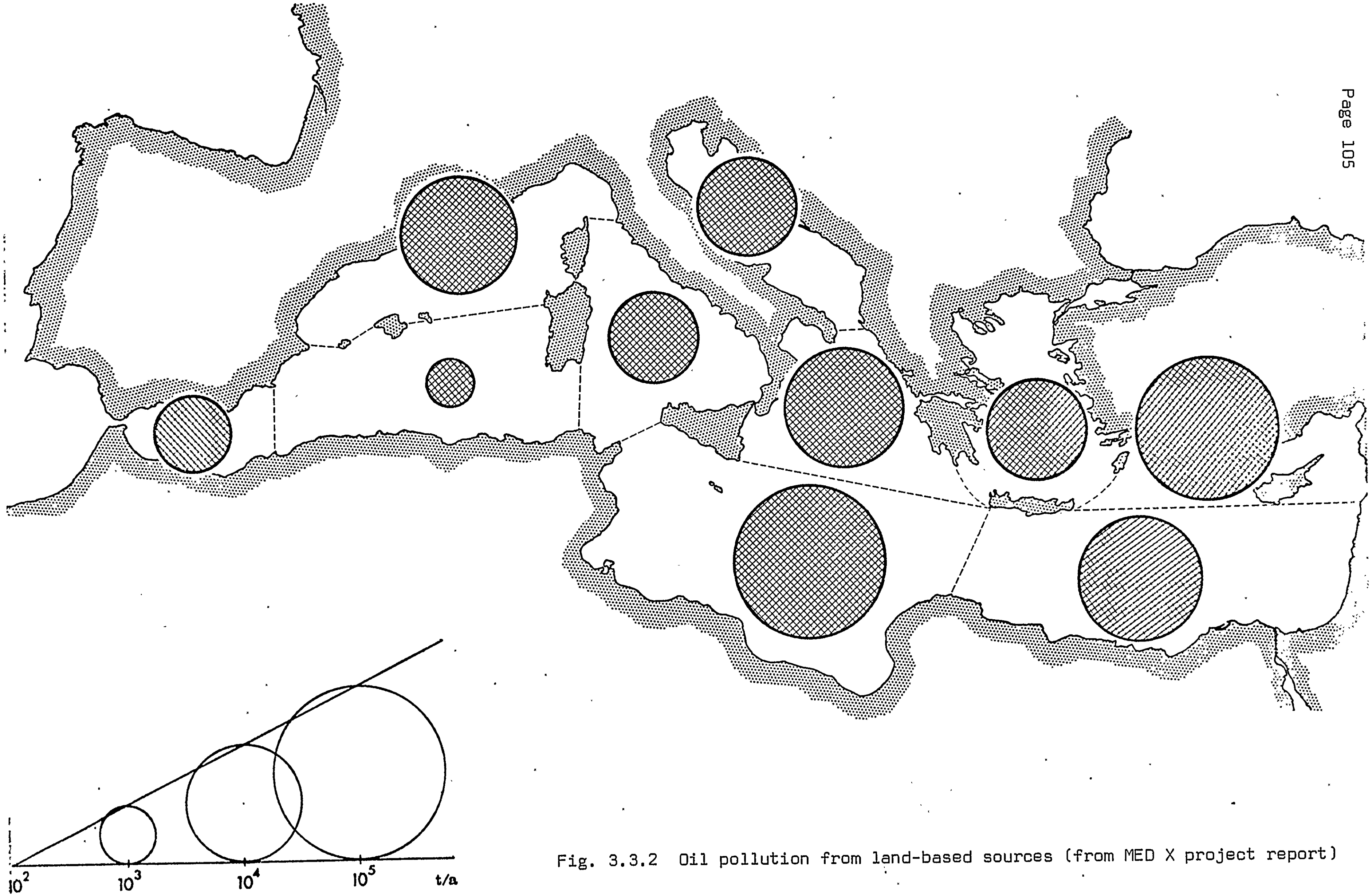


Fig. 3.3.2 Oil pollution from land-based sources (from MED X project report)

The majority of oil spills occur at, or very close to, the oil terminal, usually while the tanker is actually transferring cargo or bunker fuel. Of the 331 incidents reported, 311 occurred in port.

It is difficult to determine how much oil has been spilled, but many of the reports have made some estimate. About one third are specified as "slight" and the quantity spilled is usually a few barrels. However, one or two of the spills have been a good deal bigger, the largest being 3,750 barrels (excluding 2,000 tons jettisoned at sea). Although half of the spills reported do not exceed five barrels each, the few large incidents bring the average of the reported spills to 127 barrels (Keith and Porricelli, 1973).

The most recent serious tanker accident in the Mediterranean was off the coast of Spain. Small-scale spillages are reported constantly from different coastal and off-shore areas. The spills are estimated to contain up to 250-300 tons of oil. A recent spill in Haifa was caused by damage to the pipe-line carrying oil from the terminal to the refinery. One hundred and fifty tons of oil were released into the coastal area. More than 800,000 litres of oil was spilled after sabotage of the TAPline near its Mediterranean terminal in November 1969 (Nelson-Smith, p. 68). Spillage rates in terminal operations at well-controlled ports are of the order of 0.00011 to 0.00022% of the amount pumped for large tankers.

Estimate of the total input of oil to the Mediterranean

To give an accurate estimate of the inputs of the different sources of oil in the Mediterranean is well-nigh impossible because of the almost total lack of appropriate statistics in the different countries and the absence of coherent monitoring figures on oil in the whole area. It seems better, therefore, to refer to the estimates of world-wide input.

In 1975, 2700 million tons of oil were produced in the whole world. 350 million tons of oil crossed the Mediterranean or were loaded/ unloaded at its ports in the same year, which represents 13% of the total production (Le Lourd, 1977). The same percentage of the total input can be assumed to enter the Mediterranean Sea. This makes 795,000 t/y (from 6,113 million t/y) which shows that this region is effectively one of the most polluted by oil in the world.

3.3.4 LEVEL OF PETROLEUM HYDROCARBONS IN THE MEDITERRANEAN

In spite of the fact that pollution by oil and petroleum hydrocarbons has been receiving considerable attention, very few data exist on measured levels in the Mediterranean.

Pollution by oil appears in different forms, as oil slicks on the surface of the water, surface films, hydrocarbons dissolved in water, tar balls at or near the surface of the water, tar on beaches and hydrocarbons in sediments and in living organisms.

In order to get as clear a picture as possible about the level of oil pollution, all available data from the Mediterranean region will be presented and compared with some data from outside the Mediterranean.

Following the general outline accepted for this report the whole Mediterranean has been divided into 12 areas and data will be reported for each area separately.

Dissolved hydrocarbons and surface films

AREA I

No relevant data have been reported.

AREA II

Barbier et al., 1974, measured the content of dissolved hydrocarbons from one sample taken at 50 m depth near Villefranche-sur-Mer, France and the concentration was 75 ppb.

Monaghan et al., 1974, report on the measurements taken using Exxon tankers for sampling during their regular trips. In the course of three trips in 1973 from Brega, Libya, to La Spezia, Italy, while the ship was under way, samples were taken simultaneously from near the surface water and from the 10 m depth. Samples were taken at approximately 12 hour intervals, stations being about 200 miles apart. In total 54 surface and 51 samples at 10 m depth were taken. Six of the 51 sampling stations were in area II and all six were in the most eastern part of it. Concentrations were from 10 to 2200 ppb (average 448) and from 3 to 37 ppb (av. 15) for surface and 10 m depth, respectively.

For the MED POL project, 1977 data were reported from area II obtained from surface samples taken at two stations near the coast twice a week from October 1975 to June 1976. In all, 30 samples were taken and concentrations ranged from 50 to 4000 ppb with an average of 580 ppb.

The average for the area is 560 ppb for surface waters and 15 ppb for 10 m depth.

AREA III

During the same cruise as mentioned under area II (Monaghan et al., 1974), surface and 10 m depth samples were taken at four stations in the eastern-most part of the area. Concentrations for surface samples were in the range from 2 to 17 ppb with an average of 8.5 and for 10 m depth values were from 2 to 7 ppb with an average of 4.3 ppb.

Since these were the only results reported for this area they represent the area averages.

AREA IV

As for area III the only data reported are from Monaghan et al., 1974. Samples were taken at 13 stations and concentrations were from 8 to 614 ppb (av. 180) for surface and 3 to 19 ppb (av. 7) for 10 m depth.

AREA V

It was in this area that the most data were reported. In all about 700 samples were measured. Majori et al. (1973a,1973b,1973c) measured the content of hydrocarbons in the surface film layer (1 cm) of the Lagoon of Venice and the Bay of Trieste. In their investigations 266 surface samples were taken and concentrations were from 0 to 80,000,000 ug/m^2 with an average of 2000 ug/m^2 for 126 samples.

Other measurements in the area (Jardas and Munjko, 1974; Picer, 1975, 1976a,1976b; MED POL) dealt with surface waters (not with surface films) and with deeper waters. Concentrations varied from 0 to 223,000 ppb with an estimated average of 4000 ppb. All samples were taken in the Yugoslav part of the Adriatic Sea.

AREA VI

No data have been reported.

AREA VII

During above-mentioned cruises (Monaghan et al., 1974) 31 surface and 29 samples from 10 m depth were taken. Concentrations were from 3 to 423 ppb (av. 58) for surface and 2-120 ppb (av. 16) for 10 m depth samples.

In 1973, at 10 stations in the eastern Mediterranean, samples were taken in order to study lipid composition of surface films and oil pollution in that area (Morris, 1974). One of the stations was in area VII and surface film concentration for one sample gave a value of 190,000 ug/m^2.

AREA VIII

During the MED POL project, 1977, investigations were carried out at three locations. In total 108 samples were taken, of which 40 were from the surface, 32 at 10 m depth, and 36 at 50 m depth. No significant depth variation was found and results ranged from 100 to 3500 ppb (av. 2000).

AREA IX

Only one surface sample from the above-mentioned cruise (Morris, 1974) was taken and its concentration was 65 ug/m^2.

AREA X

Seven surface samples were taken during the above-mentioned cruise. (Morris, 1974) and the concentration was from 30 to 480 ug/m^2 (av. 230).

Simultaneously, four surface film samples were taken (Morris, 1974) and reported concentrations were in the range from 40,000 to 230,000 ug/m^2 (av. 150,000). Estimated thickness of surface film was 0.0005 to 0.003 cm. Oil slick observed six days after the Torrey Canyon grounding would have had an average thickness of 0.003 cm (Smith, 1967). Films were composed of both natural product organics (< 5% extract) and pollutant hydrocarbons (> 85% total extract). The major fatty acids were 16:0 and 18:1 in both free and esterified forms, together with minor amounts of the longer chain mono-unsaturated acids, 20:1 and 22:1. The surface film hydrocarbon composition was similar to that of the surface samples.

AREA XI

In the period 1974 - 1976, 213 surface samples were taken in Cadiz harbour and its vicinity. Results ranged from 0.8 to 3858 ppb with an average of 85 ppb.

All available data from the Mediterranean region are presented in table 3.3.4.

In figure 3.3.3 approximate averages for all available Mediterranean data are given. Unfortunately, results for some areas are based on only a few or even only one measurement. On the other hand, in the case when there were more measurements, very often samples were taken only in one part of the area. Besides, it is extremely difficult to compare data published by different scientists since they most often use different sampling techniques and analytical procedures. Also, results are expressed sometimes in units of weight/area and sometimes in weight/volume. Extreme care should therefore be taken when interpreting data and drawing conclusions as to the state of the pollution.

In order to be able to compare the state of oil pollution in the Mediterranean with other regions of the world, table 3.3.5 was prepared. The comments on table 3.3.4 are equally valid for table 3.3.5: i.e. about the variability in the number of samples, sampling techniques and analytical procedures. Concentrations vary greatly from one locality to another but generally most of the results are in the range of several ppb.

Comparing table 3.3.4 and table 3.3.5 it is abvious that the concentration of oil in surface waters of the Mediterranean is quite a bit higher than in most of the other regions in the world where investigations have been made.

Pelagic tar and tar on beaches

All data collected on the content of pelagic tar and tar on beaches in the Mediterranean region are presented in table 3.3.6.

Table 3.3.4

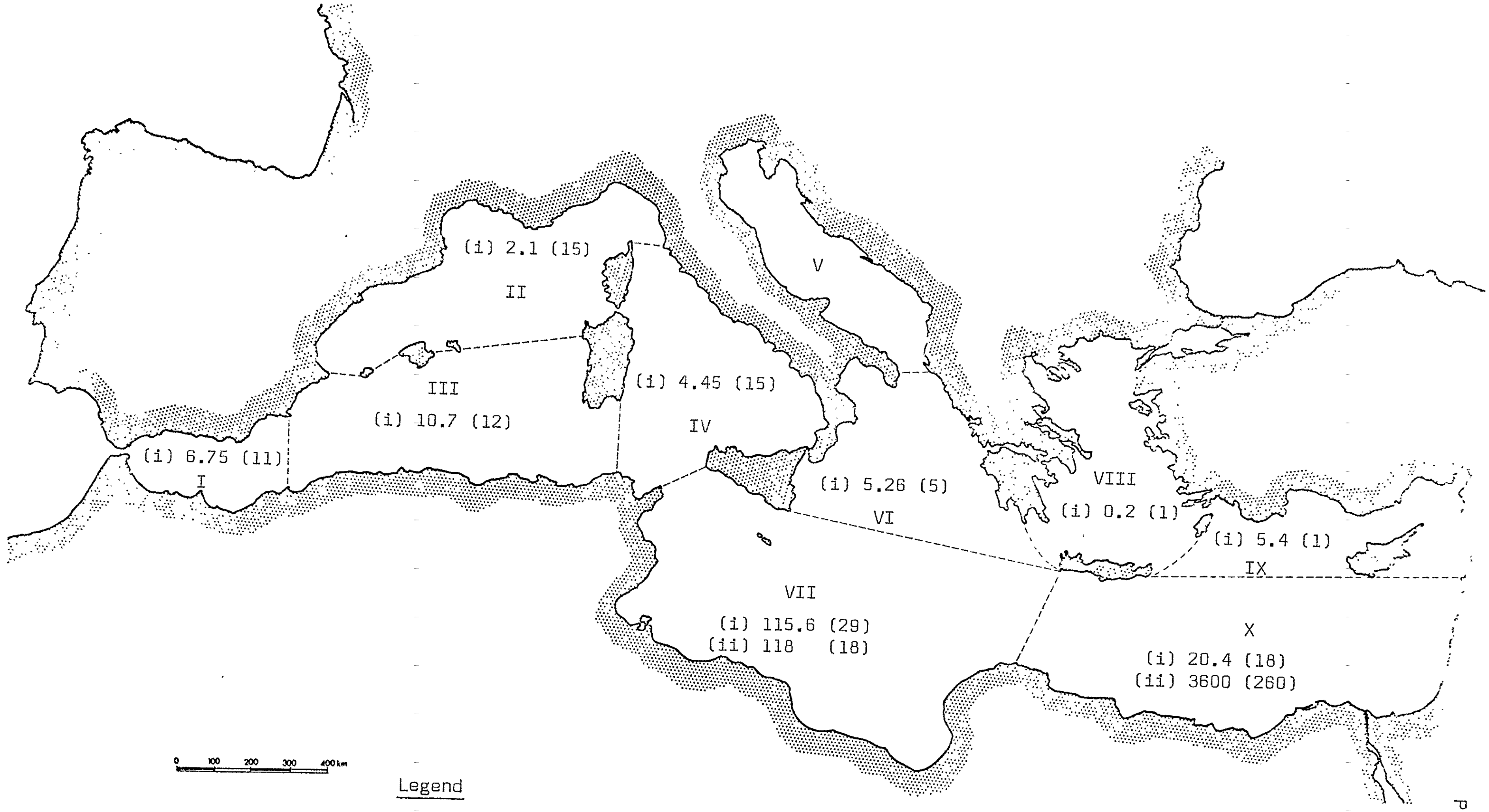
Hydrocarbons in Mediterranean sea-water

Area	Period of investigation	No. of samples	Depth	Concentration, ppb	References
I	-	-	-	-	No data available
II	1972	1	50 m	75	Barbier et al. 1973
	1972	6	Surface	10 - 2200 (av. 448)	Monaghan et al. 1974
	1972	6	10 m	3 - 37 (av. 15)	Monaghan et al. 1974
	1975 - 1976	30	Surface	50 - 4000 (av. 580)	MED POL 1977
III	1972	4	Surface	2 - 17 (av. 8.5)	Monaghan et al. 1974
	1972	4	10 m	2 - 7	Monaghan et al. 1974
IV	1972	13	Surface	8 - 614 (av. 180)	Monaghan et al. 1974
	1972	12	10 m	3 - 19 (av. 7)	Monaghan et al. 1974
V	1970 - 1973	163	Surface	200 - 26,000 (av. 3250)	Jardas and Munjko, 1974
	1970	126	Surface film	0 - 80,000,000 (av.2000) ug/m^2	Majori et al. 1973 a
	1971 - 1972	53	Surface film	1700 - 760,000 ug/m^2	Majori et al. 1973 b
	1971 - 1972	87	Surface film	800 - 26,000 ug/m^2	Majori et al. 1973 c
	1973	15	var. depth	8000 - 223,000	Picer, 1977
	1974 - 1976	177	var. depth	100 - 63,800 (av. 4900)	Picer, 1977
	1976 - 1977	72	var. depth	0 - 1100	MED POL 1977
VI	-	-	-	-	No data available
VII	1972	31	Surface	3 - 423 (av. 58)	Monaghan et al. 1974

Table 3.3.4 (contd.)

Hydrocarbons in Mediterranean sea-water

Area	Period of investigation	No. of samples	Depth	Concentration, ppb	References
VII (contd.)	1972	29	10 m	2 - 120 (av. 16)	Monaghan et al. 1974
	1973	1	Surface film	190,000 ug/m^2	Morris, 1974
VIII	1976 - 1977	24	Surface	1000 - 2000 (av. 1500)	MED POL 1977
		20	10 m	100 - 2600 (av. 1550)	
		20	50 m	1600 - 2500 (av. 1550)	
		8	Surface	2700 - 3500 (av. 3100)	MED POL 1977
		4	10 m	3100	
		8	50 m	1700 - 2000 (av. 1850)	MED POL 1977
		8	Surface	900	
		8	10 m	1100 - 1700 (av. 1400)	MED POL 1977
		8	50 m	800 - 900 (av. 850)	
IX	1973	1	Surface	65 ug/m^2	Morris, 1974
X	1973	7	Surface	30 - 480 ug/m^2 (av. 230)	Morris, 1974
	1973	4	Surface film	40,000 - 230,000 ug/m^2 (av. 150,000)	Morris, 1974
XI	1974 - 1976	213	Surface	0.8 - 3858 (av. 58.0)	Calderon, 1977



Legend

(i) Pelagic tar, mg/m^2
(ii) Tar on beaches, g per metre of coastline
Number in brackets indicates number of samples

Fig. 3.3.4 Pelagic tar and tar on beaches

Table 3.3.5.*

Hydrocarbons in sea-water

Region	Depth m	Concentration ppb	References
ATLANTIC OCEAN Sargasso Sea	0.1 - 0.3 mm	14 - 559 (av. 154)	Wade and Quinn, 1975
	0.2 - 0.3	13 - 239 (av. 73)	Wade and Quinn, 1975
		40.3 ug/m^2	Gordon *et al.*, 1974
Nova Scotia - Bermuda	0 - 3 mm	av. 20.4	Gordon *et al.*, 1974
	1 - 5 mm	av. 9.3	Gordon and Keizer, 1974
	1	av. 0.8	Gordon *et al.*, 1974
	1	av. 0.6	Gordon and Keizer, 1974
	5	av. 0.4	Gordon *et al.*, 1974
	5	av. 0.4	Gordon and Keizer, 1974
	10 - 1000	negligible	Gordon and Keizer, 1974
Nova Scotia - Gulf of Mexico	1, 10, 25	av. 4.9	Zsolnay, 1974
New York - Gulf of Mexico	0 - 0.3	av. 8.9	Brown *et al.*, 1973
	10	1 - 50 (av. 3.8)	Brown *et al.*, 1974
Near Bermuda	<10	1 - 22	Brown *et al.*, 1974
	100	1.0	Butler *et al.*, 1973
Gulf of Mexico -	<10	12 - 52	Iliffe and Calder, 1974
Caribbean Sea	>10	0 - 75	Levy, 1976
Gulf of Mexico	?	2.0	McAuliffe, 1976

Table 3.3.5 * (contd.)

Hydrocarbons in sea-water

Region	Depth m	Concentration ppb	References
ATLANTIC OCEAN			
off-shore Louisiana	micro-layer	360 ug/m^2	Ledet and Laseter, 1974
off-shore Florida	micro-layer	180 ug/m^2	Ledet and Laseter, 1974
Narragansett Bay	micro-layer	8.5	Duce *et al.*, 1972
Gulf of St. Lawrence	<10	1.5 - 4.2	Levy, 1971
	<10	0 - 5	Levy and Walton, 1973
	>10	1.3 - 3.0	Levy, 1971
	>10	0 - 10	Levy and Walton, 1973
Scotian Shelf	<10	0.2 - 1.9	Levy, 1971
	>10	0.2 - 3.2	Levy, 1971
NW Atlantic	<10	0.1 - 1.4	Levy, 1976
	<10	0 - 1.8	Levy, 1975
	>10	0 - 1.3	Levy, 1975
North Sea	micro-layer	13 - 75 ug/m^2	Hardy *et al.*, 1975
	<10	2 - 7	Hardy *et al.*, 1975
	>10	1 - 11	Hardy *et al.*, 1975
United Kingdom			
in-shore	micro-layer	14 - 145 ug/m^2	Whittle *et al.*, 1975
	<10	0.4 - 5	Whittle *et al.*, 1975
off-shore	micro-layer	4 - 84 ug/m^2	Whittle *et al.*, 1975
	<10	0.2 - 12	Whittle *et al.*, 1975
Norwegian Sea	>10	100 - 1000	Smagin and Rachkov, 1975
NE Atlantic	<10	1 - 49	Monaghan *et al.*, 1974
	>10	10 - 95	Barbier *et al.*, 1973

Table 3.3.5* (contd.)

Hydrocarbons in sea-water

Region	Depth m	Concentration ppb	References
NE Atlantic (contd.)	>10	0 - 13,450	Monaghan et al., 1974
Baltic Sea	<10	50 - 90	Carlberg and Skarstedt, 1972
	>10	50 - 120	Carlberg and Skarstedt, 1972
	>10	0.5 - 2.3	Zsolnay, 1971
INDIAN OCEAN			
	<10	3 - 601	Monaghan et al., 1974
	>10	6 - 105	Monaghan et al., 1974
PACIFIC OCEAN			
Seas around Japan	<10	0 - 56	Anon., 1974
	<10	0 - 123	Anon., 1974
	<10	0 - 39	Anon., 1976
Major bays of Japan	<10	2 - 10	Anon., 1974
	<10	0 - 27	Anon., 1974
	<10	0 - 12	Anon., 1976
NE Pacific	0 - 0.3	0.012 - 0.071	Cretney and Wong, 1974
Santa Barbara Channel	1	16	Koons and Brandon, 1975
	10	0.4	Koons and Brandon, 1975
	55	1.0	Koons and Brandon, 1975
	1 - 400	0.3	Koons and Brandon, 1975

* Some results in this table were taken from McAuliffe, 1976 and Levy, 1976

Table 3.3.6.

Pelagic tar and tar on beaches in the Mediterranean

Area	Period of investigation	No. of samples	Sampling location	Concentration ug/m^2	References
I	1969		W surface	1 - 5 (av. 3.3)	Horn et al., 1970
	1973	1	W surface	0.6	Polikarpov and Benzhitsky, 1974
	1974 - 1975	7	W surface	0.4 - 45 (av. 9.2)	Morris et al., 1975
II	1969	3	w.s.	1 - 3 (av. 2)	Horn et al., 1970
	1973	5	w.s.	0.9 - 7 (av. 4.6)	Polikarpov and Benzhitsky, 1974
	1974 - 1975	7	w.s.	0.1 - 10 (av.0.5)	Morris et al., 1975
III	1969	5	w.s.	3 - 10 (av. 6)	Horn et al., 1970
	1974 - 1975	7	w.s.	1.4 - 27.9 (av. 13)	Morris et al., 1975
IV	1969	5	w.s.	1 - 10 (av. 5)	Horn et al., 1970
	1973	4	w.s.	2 - 11 (av. 6)	Polikarpov and Benzhitsky, 1974
	1974 - 1975	6	w.s.	0.2 - 14.7 (av. 3)	Morris et al., 1975
V	-	-	-	-	No data available
VI	1973	2	w.s.	2 - 12 mg/m^2	Polikarpov and Benzhitsky, 1974
	1974 - 1975	3	w.s.	0.5 - 7.7 (av. 4)	Morris et al., 1975
VII	1969	16	w.s.	10 - 540 (av. 200)	Horn et al., 1970
	1974 - 1975	13	w.s.	0.9 - 109.9 (av. 14.4)	Morris et al., 1975
	1977	18	tar on beaches	0 - 800 g/m (av. 118 g/m)	MED POL

Table 3.3.6 (contd.)
Pelagic tar and tar on beaches in the Mediterranean

Area	Period of investigation	No. of samples	Sampling location	Concentration ug/m2	References
VIII	1973	1	w.s.	0.2	Policarpov and Benzhitsky, 1974
IX	1973	1	w.s.	5.4	Morris, 1974
X	1969	5	w.s.	20 - 60 (av.45)	Horn *et al.*, 1970
	1973	7	w.s.	0.7 - 10.0 (av. 4.4)	Morris, 1974
	1974 - 1975	5	w.s.	1.1 - 86.6 (av. 20)	Morris *et al.*, 1975
	1975 - 1976	260	tar on beaches	30 - 14,759 g/m (av. 3625)	MED POL, 1977
	1977	18	tar on beaches	1 - 5.6 g/m	MED POL, 1977

Data on pelagic tar are from four papers (Horn et al., 1970; Morris, 1974; Polikarpov and Benzhitsky, 1974; Morris et al., 1975). Data from three papers (Horn et al., 1970; Morris, 1974; Morris et al., 1975) i.e. almost all data available on tar balls in the Mediterranean, are presented in figure 3.3.4.

In the excellent paper by Morris et al., 1975, data were reported for the cruise taking place during December 1974 - January 1975 and compared with data published by Horn et al., 1970 and Polikarpov and Benzhitsky, 1974. Comparing data for 1969 and 1974 it was concluded that in areas I and III there had been some, but not a very significant, increase in tar concentration from 1969 to 1974. On the other hand in area VII there was a very significant decrease in tar concentration from 1969 to 1974. These changes were explained as being the result of closing the Suez Canal. It will be important to repeat such measurements to see the effect of the re-opening of the Canal.

Average data on pelagic tar for every Mediterranean region are presented in figure 3.3.4. Although most of the data are based on a low number of samples it can be concluded that the southern part of the Mediterranean is more heavily polluted than the northern.

A survey was made to find the sources of tar balls polluting the Mediterranean coast of Israel, where samples were collected fortnightly from eight stations along the shore from September 1973 to January 1975. According to chromatographic analysis, 76% of the tar balls were formed from weathered crude oil (GC-1) + crude oil sludge (GC-2), 18% from weathered fuel oil (GC-3), 4% were greatly weathered, and 2% of the samples were unidentified. According to the vanadium/nickel ratio and sulphur contents, 96% of the tar balls formed from GC-1 + GC-2 were from Middle Eastern sources. The degree of weathering of the samples shows that 46% of the tar balls formed from GC-1 + GC-2 were exposed at sea for about a fortnight; 41% for more than 2 months, and 13% probably for one to two years (MED POL, 1977).

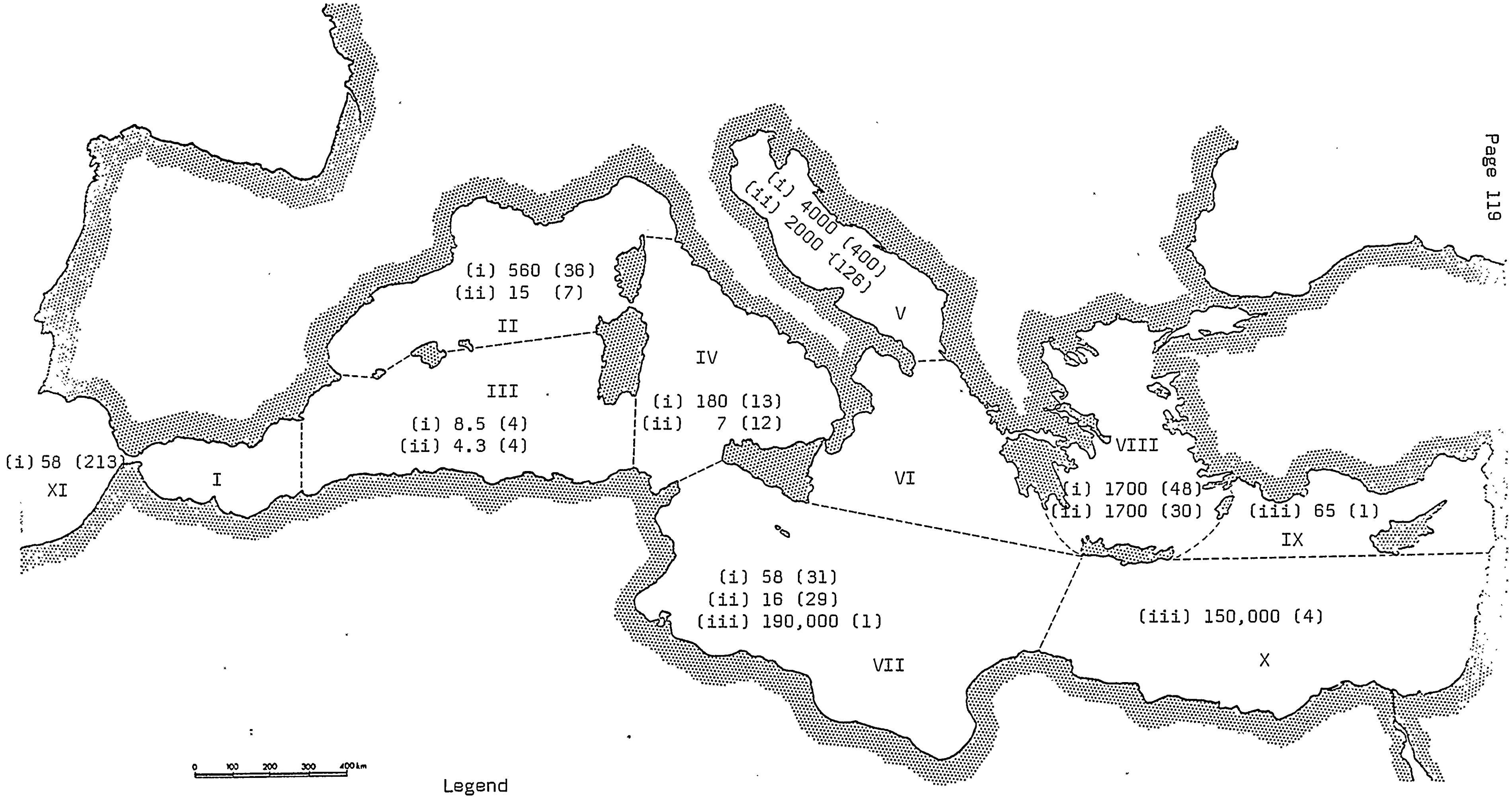
In order to compare the state of pollution of the Mediterranean by pelagic tar, table 3.3.7 gives results of measurements taken in other world regions.

Comparing tables 3.3.6 and 3.3.7, it is obvious that the concentration of tar in the Mediterranean is much higher than in other regions.

Another comparison of pelagic tar concentration in different regions of the world is presented in table 3.3.8 (NAS, 1975). The original mean value for the Mediterranean was changed from 20 to 38 based on data presented in this report.

NAS, 1975, presents a case for a strong co-variance between observed high levels of pelagic tar and known tanker routes of high traffic (table 3.3.9).

The tar flux for a given area is assumed to represent 35% of the oil spilled, assuming no inputs from oil seep.



Legend

(i)-------- surface samples, average value, ppb
(ii)------- -10m samples, average value, ppb
(iii)------ surface film samples, average value, ug/m^2

Number in brackets indicates number of samples

Fig. 3.3.3 Level of petroleum hydrocarbons in the Mediterranean Sea

Table 3.3.7 *

Some representative concentrations of tar measurements

Region	No. of samples		Range (mg/m^2)	Average concentration (mg/m^2)	References
	Total	% with tar			
ATLANTIC					
Arctic Regions	>400	~0	Virtually non-existent		Levy, 1975; Levy and Walton, 1976
Labrador Current			Almost non-existent		Levy, 1975 Levy and Walton, 1976
	?	?	0-0.003	0.00	
North Atlantic	>400	~100	0-91.8	1.16	Levy, 1975; Levy and Walton, 1976
North Atlantic Current	?	?	0-1.8	0.12	McGowan *et al.*,1974
North of 32°N	34	71	0.02-5.4	1.6	Attaway *et al.*,1974
South of 32°N	25	96	0.05-17.4	3.5	Attaway *et al.*,1974
Gulf Stream					
winter	32	78	0-?	0.23	Sherman *et al.*,1974
summer	48	90	0-?	1.22	Sherman *et al.*,1974
			0-10.7	1.15	McGowan *et al.*,1974
	14	100	0.7 - 9.7	2.24	Morris, 1974
	16		0.1 - 9.7	2.2	Morris and Butler, 1973
	18			3.4	Attaway *et al.*,1974
Sargasso Sea	34		0.1 - 40	9.4	Morris and Butler, 1973
			0-21.6	2.6	McGowan *et al.*,1974
			0.9 - 91	22.2	Sleeter *et al.*,1974
	70			6.47	Butler *et al.*, 1973
Bahamas/Antilles					
winter	39	87	0-?	3.9	Sherman *et al.*,1974
summer	47	96	0-?	4.8	
Coastal U.S.A.					
winter	29	31	0-?	0.18	Sherman *et al.*,1974
Off-shore U.S.A.					
winter	52	83	0-?	0.77	Sherman *et al.*,1974
summer	51	59	0-?	0.05	
Scotian Shelf	5	100	0.2-2.4	0.94	Morris, 1971
	8	?	0-2.4	0.2	Morris and Butler, 1973
Canary Current/ Gibraltar region	35%	<0.01 mg/m^2	0-2270		Ehrhardt and Derenbach, 1975
			0- 480		Horn *et al.*, 1970
			0.2-23	6.2	Sleeter *et al.*,1974
Caribbean	20	?	0-4.5	0.7	Jeffrey *et al.*,1974
	64	?		0.16	Sherman *et al.*,1974
Gulf of Mexico	84	?	0-10	1.2	Jeffrey *et al.*,1974

../..

Table 3.3.7 (contd.)

Some representative concentrations of tar measurements

Region	No. of samples Total	% with tar	Range (mg/m^2)	Average concentration (mg/m^2)	References
Gulf of St. Lawrence	52	62	0-0.1	-	Levy and Walton, 1973
PACIFIC					
North-west	15		0.3-14	3.8	Wong _et_ _al_., 1974
North-east	18		0-2.9	0.4	

* Table taken from Levy, 1976

Table 3.3.8

Tar densities in the world oceans

Location	Area (10^{12} m^2)	Tar (mg/m^2)		Total tar (10^3 tons)
		Maximum	mean	
North-West Atlantic Marginal Sea	2	2.4	1	2
East Coast Continental Shelf	1	10	0.2	0.2
Caribbean	2	1.2	0.6	1.2
Gulf of Mexico	2	3.5	0.8	1.6
Gulf Stream	8	10	2.2	18
Sargasso Sea	7	40	10	70
Canary and North Equatorial Current	3	1000?	?	? (large)
Mediterranean	2.5	540	38	95
Indian Ocean	75	?	?	? (large)
South-West Pacific	45		<0.01	<0.5
South-East Pacific	45		?	?
Kuroshio System	10	14	3.8	38
North-East Pacific	40	3	0.4	16

Table 3.3.9.

Relation between occurrence of spilled oil and occurrence of tar concentration

Location	Area (10^{12} m^2)	Spilled petroleum ($mg/m^2/yr$)	Tar supply rate ($mg/m^2/yr$)	Tar found mean (mg/m^2)
North Atlantic	33	17.45	6.13	5
Mediterranean	2.5	108	38	38
Kuroshio System	10	33	11.6	3.8
North-East Pacific	40	0.74	0.26	0.4
South-West Pacific	45	<0.05	<0.02	<0.005

3.3.5 Fate and pathways of oil in the marine environment

The fate of oil in the marine environment is multiform and depends on the physical, chemical, and biological characteristics of the ambient environment and on the physical and chemical properties of the oil. Several processes, of importance for the dispersion and degradation of oil in the marine environment, will be briefly described in this chapter.

a) Physical changes

In view of the relatively large amount of oil spilled in the world ocean and its potential effects on living organisms and aesthetic values, it is important to assess its fate, to determine how long it can be expected to last, and what forms it may eventually take.

The moment oil is spilt on the ocean it begins to disperse. The rate of this dispersal depends on various environmental factors such as the speed of the wind, size of the waves, temperature, salinity, depth of the water, and currents as well as on the nature of the oil, its specific gravity, degree of refinement, and the quantity involved (Zobell, 1964). In theory, the oil will spread until it becomes a monomolecular layer, but this tendency is counteracted by viscosity and other factors. Consequently, a small slick on an infinite water surface is about 1.5 to 10 x 10^{-4}mm thick (Nelson-Smith, 1970). The thickness of a uniform oil slick decreases exponentially with time. The viscosity, density, chemical composition, and discharge point of the oil and the wind speed and currents will influence the rate of spread. Emulsification reduces the tendency of the oil to spread (Berridge *et al*., 1968a).

As the oil spreads out, its polar components begin to dissolve and leach out of the oil slick (Pilpel, 1968). Waters in equilibrium solution with oil can have 10-30 ppm dissolved hydrocarbons (McAuliffe, 1973b). About one half of these are the more soluble aromatic hydrocarbon compounds, the other half are chiefly low molecular weight and the more polar compounds (NAS, 1975). At the same time the volatile components are evaporating. The sum of these processes is termed "weathering" and its product is "weathered oil". The nature of the oil (i.e. its content of low-boiling-point components) and, in addition, the air and water temperatures, wind conditions, etc. obviously determine the portion that evaporates.

The percentage of components lost to the atmosphere by evaporation correlates well with the carbon number. Figures vary, but there is general agreement that all hydrocarbon fractions containing approximately 13 carbon atoms or less are subject to great losses after the first few days, with heavier fractions, up to about 20 carbon atoms, evaporating after a few weeks. Evaporation therefore selectively depletes the lower-boiling-point components of the oil, increasing the specific gravity as the oil loses its volatile fraction. These more volatile fractions make up 20% to 50% of most crude oils, 75% or more of refined petroleum fuel and 10% or less of residual oils such as Bunker C. The process can aid the formation of thick residuals, oil sludges, and, eventually, the possible creation of tar balls. In any case the specific gravity of the remaining oil will increase, and the residual oil may become denser than sea-water, thus increasing the possibility of sinking.

Dissolution and evaporative losses are hindered by the emulsification of the oil. Emulsions of both oil-in-water and water-in-oil occur. Water-in-oil emulsions have a water content of between 10 and 80%. The term "chocolate mousse" has been used to describe water-in-oil emulsions with a water content of from 50 to 80%. "Mousse" has a solid or a semi-solid, grease-like appearance, maintaining a rigid configuration that can be altered only by applied force, and cannot be changed to an oil-in-water emulsion by agitation with sea-water (Berridge et al., 1968b). Water-in-oil emulsions are very difficult to ignite (Pilpel, 1968). In the presence of natural or artificial emulsifiers, ocean turbulence can also bring about the formation of oil-in-water emulsion consisting of small drops of oil dispersed in sea-water. These oil droplets in water are more susceptible to weathering, adsorption to suspended organic and inorganic matter, consumption by zooplankton with incorporation of the oil into faecal pellets, and to hydraulic transport (Forrester, 1971; Parker et al., 1971). By adhering to suspended sediments of greater density, oil droplets dispersed in water may also sink to bottom waters and sediments (Conomos, 1974).

Spray from waves and bursting bubbles also help to remove petroleum hydrocarbons from the sea surface as well as evaporation and dissolution. The transfer into the atmosphere depends on wind speed, the state of the sea, and the extent to which wave-breaking and whitecap formation are suppressed by oil films, which in turn is largely dependent on the thickness and horizontal extent of the film. The process seems to be accelerated by solar radiation, which can cause the formation of polar, surface-active molecules in the film.

A considerable quantity of spilt oil sinks naturally. In shallow waters where bottom material is churned up, the oil clings to particulates and settles on the bottom. Masses of sunken oil are rolled along the bottom by wave and current action, accumulate larger particles of sand, shells, and stones, and are eventually washed up on the beaches as tar balls (Nelson-Smith, 1970). These tarry deposits can be buried in the intertidal zone or carried back by tidal currents and deposited on the sea bed (Pilpel, 1968).

b) Chemical degradation

Oil is also subject to oxidation or photo-oxidation. Sunlight starts off free-radical reactions that convert hydrocarbons into hydroperoxides. These hydroperoxides are then further transformed into alcohols, acids, and other oxygenated compounds. The free radical reactions also bring about the polimerisation of the partially oxidized hydrocarbons. The resulting "tar" is denser, more polar, and more viscous than the parent hydrocarbons (Pilpel, 1968). Although almost all hydrocarbon compounds are subject to this oxidation, there is preferential UV absorption and subsequent decomposition of the cycloalkane and aromatic hydrocarbons (Hansen, 1975), especially those compounds with side branches. Low molecular weight compounds (n-alkanes in particular) are relatively transparent, and may not photo-oxidize rapidly.

The rate of oxidation depends on temperature, intensity of sunlight and the physical state of the oil. Emulsions of oil-in-water and thin films of oil are more likely to be oxidized than large coherent masses (Zobell, 1964). Minerals in sea-water can serve as catalysts for oxidation (Zobell, 1964). Some of the metallic compounds in crude oil such as vanadium porphyrins also catalyse oxidation (Berridge et al., 1968a). On the other hand, sulphur compounds in oil act as antioxidants and inhibit oxidation. Therefore, high-sulphur oils such as Kuwait oil are more recalcitrant to oxidation than low sulphur oils. In crude oils, paraffins and aromatics with suitable side chains will be most vulnerable to attack. Iso-alkanes will be oxidized more readily than straight chain alkanes. Hydrocarbons such as cumene and tetralin, whose alkyl radicals are resonance-stabilized, are susceptible to rapid oxidation.

c) Microbial degradation

After evaporation and solution, most of the oil remaining at sea is believed to be destroyed by microbial oxidation. Over 200 species of bacteria, yeasts and moulds that metabolize oil compounds have been isolated from the sea (Zobell, 1973).

The ability of microbes to oxidize oil compounds has been demonstrated by laboratory cultures. These studies have determined that microbial species are selective for certain classes and molecular weights of hydrocarbon compounds. Practically all classes of petroleum compounds can be oxidized by marine microbes (Perry, 1973). Normal-alkanes in the C_{10}-C_{19} range are attacked by most species while only a few species have been isolated that will make any use of cycloalkanes.

It is commonly found that n-alkanes are the most rapidly degraded hydrocarbons in petroleum, but it is not known whether this is because they are more easily metabolized and are oxidized faster, or because there are simply more microbial species in the sea that are able to attack them rather than other classes (Zobell, 1973).

There is now substantial evidence that the low-molecular weight alkanes and aromatics are the first to degrade. After them the higher molecular weight alkanes degrade more rapidly than other types of hydrocarbons of similar weight. However, since the low-molecular compound weights are also the first to be lost by evaporation and solution, microbial oxidation may not play so large a part in this process (Morris, 1976).

Within each hydrocarbon class, higher molecular weight compounds are oxidized most slowly. Above n-C_{20} microbial degradation is very slow, and decreases with increasing chain length. Low molecular weight aromatics (such as toluene) may be rapidly utilized (Gibbs, 1975) but not the higher molecular weight aromatics such as fluorene and benzopyrene (Lee and Takamashi, 1975). Some microbial species specifically attack certain aromatics and naphthenic compounds (Soli, 1973), probably by way of the longer paraffinic side chains. Asphaltenes are resistant to microbial decay and may persist for years (Friede, 1972; Traxler et al., 1965; Johnston, 1975).

Oxidation of petroleum leads to diverse and complex intermediate organic compounds and little is known of their role in the sea. Some of these compounds may be more toxic than their hydrocarbon precursor and may hinder further microbial action. The role of intermediates in the pathway to complete mineralization of hydrocarbons is worthy of special attention in the future.

Measured rates of oil degradation in the laboratory are generally not applicable to the field, since the natural rates of microbial degradation are affected by many environmental factors. Nutrients and temperature can critically limit natural rates. Although laboratory rates of 100 to 1000 mg m^{-3} day^{-1} can be attained (Zobell, 1964), under natural conditions degradation may be no faster than 1-10 mg (Gibbs, 1975; Johnston, 1975).

Complete mineralization of oil needs about 3.3 kg O_2 per each kg oil (Gunkel, 1973): this is the equivalent of an O_2 content of about 400,000 m^3 ocean per ton of spilt oil. An upper limit of oil concentrations under non-limiting O_2 concentration would be 25 g oil/m^3 (or 25 ppm) of sea-water for complete microbial oxidation. Assuming an average of 5 mg m^{-3} day^{-1} as the natural rate of microbial degradation (Gibbs, 1975; Johnston, 1975), 500 days would be required for complete mineralization of the oil under static conditions. Such high concentrations of oil are found only in very polluted harbours.

At degradation rates of 5 mg m^{-3} day^{-1} hydrocarbon concentrations in ocean water maintained at 0.5 to 5 ppm may exceed the oxidizing capacity of microbes. Concentrations of this density may now be found in many inland waters.

Bacteria that make use of hydrocarbon occur in low concentrations in ocean water but are abundant in coastal waters and especially in the chronically polluted waters of harbours of ship channels. Open ocean water off Hawaii failed to yield cultures of bacteria utilizing hydrocarbon in 75% of the water samples (Anderes, 1973). Considerable delay in the initiation of microbial oxidation of oil can be caused by this scarcity of microbes in the ocean.

d) Oil residues

After low and medium molecular weight compounds have dispersed or degraded, a significant fraction of oil remains in the sea in a physically changed but chemically unaltered form. A semi-solid residue is left, dispersal is halted, and oxidative processes are restricted primarily to the surface boundary of the oil mass (Koons, 1973).

Tar balls are the most common form of residual oil. Because of the high molecular weight and resultant inertness of these oil residues, the time needed for their decay may be a matter of years.

Since degradation is limited to their surface boundary, these oil residues usually have a weathered crust. Some volatile or degradable compounds can be effectively sealed inside.

Oil residues are little affected by evaporative weathering as the lighter molecules that may be enclosed in the balls are effectively contained. The time for n-C_{14} to diffuse through 1 cm^2 of a tar ball has been calculated at over 250 days (Ehrhardt and Derenbach, 1975). Higher weight n-alkanes take much longer.

The relatively small surface area of a tar ball that is exposed to the water, oxygen, and to microbes also protects it from oxidation or biodegradation (Zobell, 1973). Oil residues either slowly degrade in a year or more, or they are stranded on beaches or they sink through increase in density.

e) Fate of oil in sediments

The degradation of petroleum hydrocarbons in aquatic sediments is caused by the interaction of microfauna, meiofauna and macrofauna. Populations of hydrocarbon-degrading microbes are high in areas of oil input, resulting in a rapid degradation of the alkanes and a much less marked effect on isoalkanes, cycloalkanes and aromatic hydrocarbons. In the feeding process, the interstitial community (meiofauna), and benthic macrofauna expose deeper sediments to the water-sediment interface where there is more microbial activity. The polychaete worms take up hydrocarbons from the sediment and the active enzyme system in the lower portion of their intestine metabolizes these compounds. Hydrocarbons on re-suspended sediments are recycled by passing through filter-feeding bivalves. Bacteria and animals metabolize aromatic hydrocarbons by different mechanisms: bacteria produce cis-diols while animals degrade them to trans-diols. Since bacteria use hydrocarbons as a carbon source there is a cleavage of the ring of diols which eventually degrade to carbon dioxide. Animals excrete the diols or their conjugated products (Lee, 1976).

f) Uptake of oil by biota

Petroleum hydrocarbons are presented to pelagic organisms as dissolved or dispersed materials, adsorbed on to particulate material, or as small floating tar balls. Lee and Benson, 1973, suggested that hydrocarbons enter the marine food web in several ways:

(i) adsorption on to particles, both living and dead, followed by ingestion of these particles;

(ii) active uptake of dissolved or dispersed oil;

(iii) passage into gut of fish which gulp or drink water.

A considerable portion of oil is adsorbed on to or dissolved in particulate matter because the partition coefficient should favour the solution of hydrocarbons in the lipids of detritus. Detritus would then carry the adsorbed or dissolved hydrocarbons to the sea floor to be consumed by benthic organisms.

Dissolved hydrocarbons are taken up by the gill tissue of the Mytilus edulis and are then transferred to other tissues (Lee et al., 1972a). Subsequent work on the uptake of dissolved hydrocarbons by marine fish demonstrated the entrance of hydrocarbons through the gills (Lee et al., 1972b). It was also reported that phytoplankton appeared to absorb hydrocarbons but that there was no transfer inside the cell.

It is currently believed that large floating aggregates are not taken up by marine organisms and do not, therefore, have a direct and immediate impact on the marine ecosystem.

In some cases, the biota may be severely affected by the presence of oil in their habitat, but they are not a major reservoir for spilled oil. However, they may act as a temporary storage site or transfer point. It is apparent that marine animals are probably not of great significance in influencing the distribution patterns of spilt oil.

After petroleum hydrocarbons are taken up by an organism, they may be excreted unchanged, they may be metabolized, or they may be stored with possible elimination at a later date.

Lee et al., 1972c, found in particular that saturates and aromatics were taken up rapidly by mussels but were also discharged without metabolic breakdown after the return of the mussels to clean sea-water.

Conover, 1971 suggests that under the conditions observed in Chedabucto Bay, the plankton could graze as much as 20 per cent of the oil particles (less than 1 mm in diameter) in the water column and make sediment of them in their denser than sea-water faeces. Parker, 1970 also demonstrated that copepods can ingest considerable quantities of oil and pass the oil, unchanged, into the faecal material.

It is a matter of some interest that oil can enter marine organisms and be discharged unchanged. Oil from a slick can be grazed by plankton and the ingested oil precipitated in the faeces. Faecal matter is usually denser than sea-water, thereby providing a means by which oil can continue to exist through the water column and ultimately within the sediments, where it will be exposed by marine organisms. It is also a well-known fact that faecal pellets can be ingested by marine organisms, thus providing a possible mechanism for passage and/or concentration in marine produce.

Oil that has been taken up by marine organisms can also be stored at high or low concentrations and possibly eliminated at a future date. Morris, 1974, has demonstrated that the surface zooplankton from the Mediterranean takes up large quantities of petroleum hydrocarbons from the heavily polluted surface film. Hydrocarbons, having the same complex molecular weight distribution as those in the surface film, made up some 17-33 per cent of the total lipid material in the zooplankton organisms. This was considered to be indicative of their storage and concentration of pollutant hydrocarbons.

Studies by Lee and Benson, 1973, have indicated the accumulation of hydrocarbons in the liver of marine fish and in the hepatopancreas of several invertebrates. Since the liver and hepatopancreas are generally high in lipid, this observation was predictable. The gall bladder in fish was also found to be a temporary storage site, but apparently it serves mainly as an avenue for discharge. Hydrocarbons could also possibly accumulate in the complex lipoproteins of cell and organelle membranes of all tissues.

Marine fish tested by Lee _et al_., 1972, were found to take up aromatic hydrocarbons via the gills. Metabolism then occurred in the liver, followed by transfer of the hydrocarbons and metabolites to the bile, and finally excretion. This offered evidence of an efficient detoxification mechanism in the fish which made provision for the removal of polycyclic aromatics from the body tissue.

g) Pathways of the fate of oil in the marine environment

Oil in the marine environment will disperse and degrade through different processes briefly described above.

The relative yield of such processes to dispersion and degradation of oil is given in table 3.3.10 (Butler _et al_., 1976).

A schematic summary of the fate of oil in the marine environment stressing the links between atmosphere, sea-water and bottom sediments in the biogeocycle of petroleum hydrocarbons is given in figure 3.3.5.

Table 3.3.10

Processes of dispersion and degradation of oil

Pathway	Time Scale (days)	%
Evaporation	1 - 10	25
Solution	1 - 10	5
Photochemical	10 - 100	5
Microbial	50 - 500	30
Disintegration and sinking	100 - 1000	15
Oil residue	100	20
		100

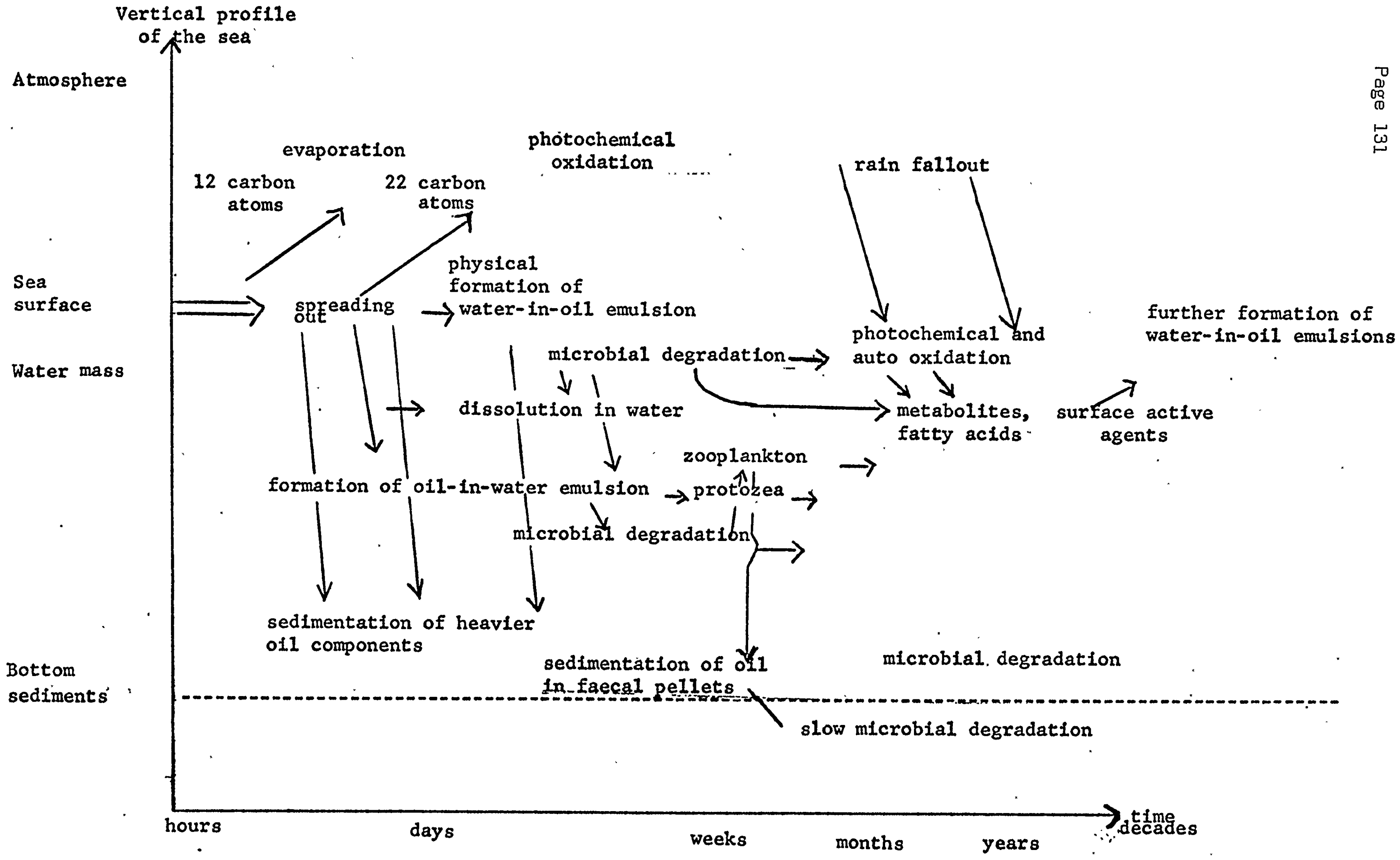


Fig. 3.3.5 Diagramatic summary of fate of oil (from GESAMP No.6 1977)

3.3.6 Effects of Oil Pollution

The public has been concerned - or at least it has complained - about coastal pollution for fifty years or more. Unlike most other pollutants the presence of oil is obvious even to the uninstructed and attracts immediate and constant attention. Its nuisance value is evident and if fouling of tourist beaches were the only consequence of oil pollution, it would not be difficult to decide upon policies with regard to control and treatment. However, there are other consequences of oil pollution, all of which are, in one way or another, biological. This introduces new problems and often gives rise to a conflict between amenity and biological interests.

Because of the extensive interactions between organisms in an environment like the sea, the biological problems raised are nearly always very complex. No answer can be simple and most will be hesitant. Moreover, because the ecological sciences have been relatively neglected in the past, there are considerable areas of ignorance so that in any discussion of the impact of oil pollution on biological systems there is inevitably as much supposition as fact. The layman is understandably tempted to dismiss biological considerations because of their complexity and apparent inconclusiveness. But it is wrong to take this attitude; we should be greatly concerned that we are ignorant of the consequences of our activities. More than at any other stage in our history, we are becoming increasingly aware of our dependence on the natural environment of which we are a part, but at a time when we are compelled to exploit it as fully as possible we also have the capacity to inflict damage upon it to such an extent that it may have serious repercussions on our own welfare and livelihood. In this situation we must guard and treasure the whole natural environment and to this end we must not only endeavour to understand the consequences of our actions, but also to heed the first warning signs of damage and investigate its potential danger. (R. B. Clark, 1971).

Physical, chemical and biological factors alter the composition of oil immediately after the discharge and possibly for months, even years, afterwards. In addition, the oils themselves have a variety of physical, chemical and biological effects on the marine environment. In this chapter such physical, chemical and biological effects will be discussed briefly.

Physical and Chemical Effects

a) Gas transfer and deoxygenation

From time to time, fears have been expressed in scientific journals and in contributions to national and international meetings, that oil pollution in the form of a layer floating on the surface of the sea will result in substantial if not total depletion of oxygen in the sea. The argument runs that if such depletion were to arise, the conditions necessary for the growth of marine organisms would be destroyed, and severe limitations would then be imposed upon sea life in general, particularly on the production of plankton and other marine organisms at the foot of the food chain that are essential for the survival of a marine biosystem, including sea food resources utilized by man.

The topic of oxygen exchange across a sea/water atmosphere boundary, and the extent to which oil films limit or interfere with this exchange, do not appear to have received a great deal of attention from the scientific community. The data available on transfer rates were regarded as poor and conflicting and, since much of the information predates the present concern about oil pollution, it must be interpreted with present-day oil slicks in mind.

Data relating to the transfer of carbon dioxide across the air/sea interface are almost non-existent, and few papers have been found describing the effects on marine sediments of oil layers on the surface of sea-water.

It is important to realize that there are a number of processes affecting the oxygen concentration in water. These will not affect the transfer rate of oxygen to the water unless the concentration falls below the saturation level. To measure the transfer rate adequately it would be necessary tq remove, or at least reduce considerably, the existing oxygen concentration, as the rate is determined by the oxygen deficiency. Work by Garret, 1972, on the effects of capillary wave dampening may be considered as more significant to re-aeration limitation than to an oxygen transfer barrier established by oil "membranes".

In the laboratory, thick layers of oil have been found to interfere with gaseous exchange, but no indication has yet been discovered to support any suggestion that, under open sea conditions, the presence of oil layers such as those that arise from pollution of the sea by oil, will give rise to a depletion of oxygen in sea-water. No areas have yet been identified where local conditions give rise to local problems of oxygen depletion under an oil slick, although it has been recognized that such areas may exist. It is likely that in these areas other effects of oil such as acute toxicity or smothering would be important.

b) Heating Effects

Fears have been expressed that when layers of crude oil of high optical density are exposed to solar radiation, the absorption of this radiation by the oil could give rise to elevated temperatures, and that these could bring about, or contribute to, the mortality of marine organisms.

This fear relates to those marine organisms such as coral that live in an intertidal zone, and those areas of shallow, quiescent water such as intertidal pools. In these areas, the absorption of solar radiation by layers of oil could result in elevated temperatures to which the organisms are exposed. In such areas it is difficult to separate the mortality effects due to direct smothering, acute toxicity and temperature changes.

It is probable that black body effects - which do not always have a determinant influence on a given marine species - would be reported only from the intertidal zone. The organisms most adversely affected are likely to be those at or near their geographical limit. At these limits, the species are probably more sensitive to other factors as well, and some realignment of the exact species distribution and population numbers might occur from time to time.

No experimental data have so far been found to support a significant heating effect due to absorption of solar radiation by oil films. Heating effects of stranded oil on corals and in intertidal zones have been noted.

c) Pollutant Sorption

It has been reported that high concentrations of pesticides, especially DDT, and heavy metals, chief among them mercury, can arise by sorption from the atmosphere into surface films and layers of oil. If substantiated, this could give rise to bioaccumulation problems in certain marine organisms.

In a similar way, oil films and surface layers could serve as extractants for both pesticides and heavy metals from the body of the sea. This could result in exposing certain marine organisms to increased concentrations of pollutants.

The basic fear underlying this topic of concern appears to relate to the general toxicity to marine organisms of such materials as pesticides and heavy metals. Any concentration of either in an oil layer may give rise to an appreciable decrease in microbial activity and hence to an appreciable decrease in the rate at which oil and oil products are removed from the marine environment by this activity. Further fears relate to the possibility that pesticides may bioaccumulate by this mechanism.

The evidence to date shows that oil of petroleum origin can serve to concentrate pesticides from sea-water into an oil slick, but further work must be done to prove this to be a general phenomenon. Bioslicks that may be of land origin have been observed with high pesticide values, but there is little to indicate that any concentration mechanism is in action in the marine environment or that oil of petroleum origin is solely or significantly implicated.

Biological Effects

A great number of factors, acting both individually and in combination, govern the effects that an oil spill may have on marine life. The biological damage that ensues depends on the following:

(i) the type of oil involved, particularly with respect to its content of aromatic compounds;

(ii) the dosage of oil to which the organism is exposed and the duration of exposure;

(iii) whether the oil is in a fresh, weathered or emulsified form;

(iv) whether it is in solution, suspension, dispersion or adsorbed on particulate material;

(v) whether plankton, neuston, nekton or benthos are involved and within these categories the individual species affected;

(vi) the season of the year with respect to the annual cycle of the organism and whether it is in a dormant state or actively feeding and reproducing;

(vii) whether adult or juvenile forms are involved;

(viii) the effects of the oil on competing biota;

(ix) previous history of exposure of the organisms to oil or other pollutants;

(x) whether a coastal, estuarine or open ocean area is involved and especially if it is a nesting or wintering ground for sea birds, a migration route for birds or fish, etc;

(xi) natural environmental stresses imposed by meteorological conditions or fluctuations in water temperature, salinity and other oceanographic parameters, particularly currents and wave action;

(xii) the cleaning procedures, if any, that have been used and particularly whether chemical agents have been employed;

(xiii) and all other stresses of both natural and pollutant origin to which the organisms are subjected.

In general, the biological damage is much more severe if the spill occurs in a coastal or estuarine environment, especially if the intertidal zone is affected, than if it occurs in the open ocean because there are generally many more types and numbers of organisms in these areas as well as the sensitive juvenile stages of many oceanic species (Evans and Rice, 1973).

a) Marine Organisms

Marine toxicology is a new science. Consequently, many of the earlier attempts to assess the toxic potential of petroleum and petroleum products to marine life have led to confusing and often incorrect conclusions. For example, lack of standardized techniques with respect to type of oil, test organism, or duration of exposure has greatly confused the interpretation of reported effects. Moreover, bioassays have been performed in the laboratory under static conditions, little care being taken to simulate natural conditions which influence the behaviour of the test organisms. Analytical techniques to measure the exact amount of oil in solution were rarely used. Instead, investigators reported the amount of oil initially added to aquaria on a volume to volume basis. Hence, concentrations causing biological effects were often over-estimated.

Death has often been used as a measure of biological response and has been reported in a form such as the LD-50, i.e. the concentration of oil responsible for the death of 50 per cent of the test population over a given period. The literature is full of references to such values (Moore et al., 1973). Too often these LD-50 values were calculated for resistant species that were easy to manage in the laboratory, while fragile species were often excluded from studies. Obviously, "safe" levels of oil contamination for all marine organisms lie well below the LD-50 values calculated for tolerant species.

The authors of recent reviews (Moore et al., 1973; Moore, 1973; Nelson-Smith, 1973; Boesh et al., 1974; NAS, 1975; Cowell, 1976; Hyland and Schneider, 1976) on the subject of oil pollution have synthesized much of this fragmentary information, and as a result a great deal more has been learned concerning types of biological responses at the organism level and the fractions of oil responsible for such effects. Accordingly, Moore, 1973, has identified five major categories of effects from oil on individual organisms:

(i) direct lethal toxicity;

(ii) sublethal disruption of physiological or behavioural activities;

(iii) the effects of direct coating by oil;

(iv) incorporation of hydrocarbons in organisms which may cause tainting of edible species and/or accumulation of potentially carcinogenic polycyclic aromatic hydrocarbons in food chains; and

(v) changes in biological habitats.

Lethal toxicity refers to interference with subcellular, cellular, and physiological processes (e.g. disruption of membrane activitie leading directly to the death of the organism (Moore, 1973). As a result of the literature evaluation by Moore et al., 1973 and their analysis of the type of compounds causing toxicity in variously reported bioassays, the conclusion was reached that soluble aromatic hydrocarbon derivatives (mono- and dicyclic aromatics, and naptheno-aromatics) are the primary cause of organism mortality. Low molecular weight paraffins can bring about narcosis, while certain heterocyclic compounds are lethally toxic; but concentrations capable of having such effects are extremely high and are unlikely to be caused by oil spills (Moore, 1973; Goldacre, 1968).

Table 3.3.11 (Hyland and Schneider, 1976) summarizes the minimum concentrations of soluble aromatic hydrocarbon derivatives (S. A. D.) needed to being about lethal toxicity for a wide variety of marine organisms. Minimum lethal concentrations for particular categories of organisms are based on estimates of S. A. D. in solution made by Moore et al., 1973 from relevant bioassays that were reported in the literature. The factor of ten uncertainty observed for each category of organisms in table 3.3.1 is a result of the confusion created when interpreting results from such a large number of bioassays carried out before the development of standardized techniques. Table 3.3.11 also shows estimated maximum per cent S. A. D. for several types of petroleum products. Thus, refined products such as No. 2 Fuel oil which contain a high content of S. A. D., are considerably more toxic than equal amounts of crude oil or residual products.

Apparently, lethal effects of S. A. D. make their appearance in the 1 to 100 part per million range for the adult forms of most marine organisms. Crustaceans and certain benthic organisms, especially burrowers, are the most sensitive (1 to 10 ppm), while fish and bivalves are moderately sensitive (5 to 50 ppm), and gastropods and marine flora the least sensitive (10 to 100 ppm). Lethal toxicity from S. A. D. may occur at lower concentrations, 0.1 to 1 ppm, for the more sensitive larval and possibly juvenile life stage.

Sublethal effects follow cellular and physiological interferences, usually causing some form of abnormal behaviour, particularly the disruption of normal feeding and reproductive patterns (Moore, 1973; Neff et al., 1976). Such behaviour often depends on sensitive levels of communication by way of chemical cues, which may be disrupted by very low levels of petroleum hydrocarbons in solution. Sublethal responses may lead indirectly to lethal effects. Table 3.3.12 (Hyland and Schneider, 1976), summarizes sublethal effects of petroleum on marine organisms. From this synthesis it is clear that many organisms respond to sublethal effects of S. A. D. in the part per billion range, particularly between 10 and 100 ppb. However, several

Table 3.3.11

Summary of lethal toxicity[a]

Class of organisms	Estimated conc. (ppm) of S.A.D. b/ causing toxicity	Estimated amount (ppm) of various petroleum substances containing equivalent amounts of S.A.D.				
		# Fuel oil (est. max. % S.A.D. = 1-30)	Crude oil (est. max. % S.A.D. = 0.1-10)	Kerosene (est. max. % S.A.D. . 1-20)	Dispersant (BP 1002) (est. max. % S.A.D. . 1-20)	Residual (est. max. % S.A.D. . 0-1)
Flora	10-100	50-500	10^4-10^5	10^2-10^3	10^2-10^3	10^3-oo (no effect)
Finfish	5- 50	25-250	10^4-10^5	50-500	50-500	500-oo
Larvae (all species)	0.1-1.0	0.5- 5	10^2-10^3	1- 10	1- 10	10-oo
Pelagic crustaceans	1- 10	5- 50	10^3-10^4	10-100	10-100	10^2-oo
Gastropods	10-100	50-500	10^4-10^5	10^2-10^3	10^2-10^3	10^3-oo
Bivalves	5- 50	25-250	10^4-10^5	50-500	50-500	500-oo
Benthic crustaceans	1- 10	5- 50	10^3-10^4	10-100	10-100	10^2-oo
Other benthic organisms (polychaetes, etc.)	1- 10	5- 50	10^3-10^4	10-100	10-100	10^2-oo
Birds			←	Coating	→	

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[a] Adapted from Hyland and Schneider, 1976

[b] Soluble aromatic hydrocarbon derivatives (mono - and dicyclic, naptheno-aromatics)

Table 3.3.12

Summary of some sublethal effects of petroleum products on marine organisms[a]

(1)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Marine flora	Marsh plants (*Festuca rubra, Distichlis maritime*)	Baker, in Cowell, 1971	Crudes and refinery effluents.	Single or successive coatings with crude.	Inhibition of germination and growth. Repeated coatings cause disappearance of some plants (increasing order of tolerance: shallow rooted plants, shrubby perennials, filamentous green algae, perennials, perennials with large food reserves).
	Phytoplankton (*Chlorella vulgaris; Chlamydomonas angulosa*)	Kauss *et al.*, 1973	Crude Naphthalene	1 ppm 3 ppm	Suppression of growth. Reduction of bicarbonate uptake (i.e., photosynthesis).
	Phytoplankton (*diatoms* and *dinoflagellates*)	Mironov 1970	"Oil"	10^{-1} 10^{-4} ppm	Inhibition or delay in cellular division
	Phytoplankton (*Asterionella japonica*)	Aubert *et al.*, 1969	Kerosene	3 ppm; 38 ppm	Depression of growth rate.
	Phytoplankton (*Phaeodactylum tricornutum*)	Lacaze, 1967	Kuwait crude	"1 ppm"	Depression of growth rate

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[a] Adopted from Hyland and Schneider, 1976

Table 3.3.12 (continued)

(2)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Marine flora (continued)	Phytoplankton (Monochrysis lutheri)	Strand et al., 1971	Kuwait crude; dispersant emulsions	20-100 ppm	Inhibition of growth; reduction of bicarbonate uptake at 50 ppm.
	Phytoplankton (Phaeodactylum tricornutum, Skeletonema costatum, Chlorella sp., Chlamydomonas sp.	Nuzzi, 1973	Extracts of outboard motor oils, No. 6 fuel oil, No.2 fuel oil.	1 ppm	Inhibition of growth with No. 2-stimulation with No. 6 and outboard motor oil.
	Phytoplankton (mixed natural samples)	Gordon and Prouse, 1973	Venezuelan crude, No. 2 and 6 fuel oils.	10-200 mg/1 (ppm)	Stimulation of photosynthesis at 10-30 ug/1 , decrease in photosynthesis at 100-200 ug/1 No. 2 fuel oil.
	Kelp (Macrocystis angustifolia)	Wilber, 1969	Toluene	10 ppm	75% reduction in photosynthesis within 96 hrs.
	Lichen (Lichen pygmaea)	Brown, 1972	Kuwait crude, BP 1002	0.1-100 ppm	1 ppm emulsifier decrease total C^{14} fixation.
	Spartina marsh grass	Lytle, 1975	Crude	Poured into pond.	Decrease in productivity.
	Algae (Ulva lactuca, Grateloupia dichotoma, Polysiphonia opaca)	Davavin et al., 1975	Crude	.1-10 ml/1 (100-10,000 ppm)	Complete inhibition of biosynthesis of DNA and RNA at higher conc. for Ulva.

Table 3.3.12 (continued)

(3)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Larvae and eggs	Pink salmon fry (Onochorhynchus gorbuscha)	Rice, 1973	Prudhoe Bay crude	1.6 ppm	Avoidance effects; could have effect on migration and behaviour.
		1975	Prudhoe Bay crude	0.73 ppm	Decrease in growth
	Black sea turbot (Rhombus maeoticus)	Mironov, 1967	"Oil"	0.01 ppm	Irregularity and delay in hatching-resulting larvae deformed and inactive.
	Plaice larvae (Pleuronectes platessa)	Wilson, 1970	BP 1002	0-10 ppm	Disruption of photoactic and feeding behaviour.
	Cod fish larvae (Gadus morhua)	Kühnhold, 1970	Iranian crude	Aqueous extracts from 10^3 ppm, 10^4 ppm	Adverse effects on behaviour leading to death.
	Lobster larvae (Homarus americanus)	Wells, 1972	Venezuelan crude	6 ppm	Moult delayed to 4th stage.
	Sea-urchin larvae (Strongylocentrotus purpuratus)	Allen, 1971	Extracts of Bunker C	0.1-1 ppm	Interference with fertilized egg development.
	Barnacle larvae (Balanus)	Mironov, 1970	"Oil"	10-100 ul/1 (ppm)	Abnormal development.
	Crab larvae (Pachygrapsus marmoratus)	Mironov, 1970	"Oil"	10-100 ul/1 (ppm)	Initial increase in respiration.

Table 3.3.12 (continued)

(4)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Larvae and eggs (continued)	Polychaete larvae (*Sabellaria spinulosa*)	Smith, 1968	BP 1002	0.5-1 ppm	Abnormal irritability in larvae revealed by stiffening out of median setae.
	Oyster larvae (*Ostrea edulis*)	Simpson, 1968	BP 1002	1 ppm	Inhibition of growth
	Herring larvae (*Clupea harengus*)	Kühnhold, 1969 1971	Crude	5 ppm	High % deformed larvae (stunted tail and constricted yolk mass) among hatching eggs: normal hatched larvae became narcotized within 2 days of hatching and died by 3rd.
	Herring and anchovy larvae (*Clupea pallasi; Engraulis mordax*)	Struhsaker, *et al.*, 1974	Benzene	15-45 ppm	35-45 ppm causes delay in development of eggs and produces abnormal larvae; 10-35 ppm causes delay in development of larvae; decreases in feeding and growth, and increase in respiration.
Fish	Chinook salmon (*Onchorhynchus tshawytscha*, striped bass (*Morone saxatilis*)	Bracksen and Bailey, 1973	Benzene	5-10 ppm	Initial increase in respiration
	Menidia menidia	Gardner, 1975	Crude (whole fractions) (water-soluble) (water-insoluble)	140 ppm (v/v) 12 ppm estimated 588 ppm (v/v)	Histological damage to chemoreceptors.
	Cyprinodon variegatus, Lagodon themboides, Micropogon undulatus	Steel and Copeland 1967	Petrochemical wastes	0.2-2.0 ppm in addition to 0.4-4.0 phenol	Respiratory inhibition.

Table 3.3.12 (continued)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Fish (continued)	Lagodon rhomboides	Wohlschlag and Cameron, 1967	Petrochemical wastes	50% of wastewater	Respiratory inhibition.
	Ictalurus natalis	Todd, 1972			Alteration of social behaviour
	Menidia menidia	Gardner et al., 1975	Waste motor oil	>20 ppm	Incidence of lesions in vascular systems (pseudobranch, heart, arterial system)
	Siganus rivulatus	Eisler, 1975	Dispersant Crude	.010 ml/l (10 ppm) .3-10 ml/l (300-10,000 ppm)	Reduction in blod hematocrit. Increase in somatoliver index.
Crustaceans	Lobster, (Homarus americanus)	Blumer et al., 1973	Crude, Kerosene	10 ppm	Effects on chemoreception feeding times, stress behaviour, aggression, grooming.
	Barnacle, (Pollicipes polymerus)	Straughan, 1971	Crude - Santa Barbara	Field study after blowout	Apparent decrease in adult brooding; no recruitment in oiled areas.
	Lobster (H. americanus)	Atema and Stein 1972, 1974	La Rosa Crude	Extracts; whole oil at 1:100,000 (10 ppm)	Delay in feeding with whole crude fractions
	Crab, (Pachygrapsus crassipes)	Kittredge, 1971	Crude	Dilutions of diethyl ether extracts (1:100)	Inhibition of feeding
	Crab, (Uca pugnax)	Krebs, 1973	No. 2 fuel oil	Field observations after W. Falmouth spill	Adverse effects on sexual behaviour Mortality in heavily-oiled areas.

Table 3.3.12 (continued)

(6)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Crustaceans (continued)	Copepod (Calanus helgolandicus)	Spooner and Corkett, 1974	Suspended oil droplets in lab vessels	10 ppm	Decrease in feeding and metabolic activity among survivors, based on amount faecal pellets deposited by controls vs. experimentals
	Benthic amphipods (Gammarus oceanicus, Onisimus affinis) isopod (Mesidotea entomon)	Percy, 1976	3 Crudes	Oil-soaked object; oil-tainted food	Avoidance of oil measures and oil-tainted food for amphipods; neutral response for isopod.
	Crab, (Pachygrapsus crassipes)	Kittredge et al., 1975	Naphthalene	1 ppb	Inhibition of feeding (reduction in intensity of response)
			Crude	(extracts)	Inhibition of feeding and response to sex pheromone (male mating stance).
Molluscs	Mussel (Mytilus edulis) Modiolus demissus	Gilfillan 1973, 1975	Crude	1 ppm	Reduction in carbon budget (increase in respiration; decrease in feeding and assimilation).
	Snail (Nassarius obsoletus)	Blumer et al., 1973	Kerosene	Saturated extract diluted 10^{10}	40% reduction in chemotactic perception of food.
	Snail (Nassarius obsoletus)	Jacobson and Boylan, 1973	Kerosene	0.001-0.004 ppm	Reduction in chemotactic perception of food.
	Clam (Mya arenaria	Barry and Yevich, 1975	No. 2 fuel oil	Collected from field	Gonadal tumours.

Table 3.3.12 (continued)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Molluscs (continued)	Oyster (*Crassostrea virginica*)	Mackin and Hopkins, 1961	Bleedwater	Spray	Reduced growth and glycogen content.
	Snail (Littorina *littorea*)	Perkins, 1970	BP 1002	30 ppm	Significant inhibition to growth
	Oyster (*Crassostrea virginica*)	Menzel, 1948 ; in Nelson-Smith, 1973	"Oil"	0.01 ppm	Marked tainting.
	Mussel (*Mytilus edulis*)	Blumer *et al*., 1971	No. 2 fuel oil	Collected from field after spill.	Inhibition in development of gonads.
	Gastropod drill (*Drupa granulata*), Mussel (*Mytilus variabilis*)	Eisler, 1973	Iranian crude, dispersant	10 ml/1 (10,000 ppm)	Decrease in predation rate of drill on mussel when exposed to crude; decrease in fecundity of drills when exposed to dispersant.
	Oyster (*Crassostrea virginica*), Scallop (*Aquipectins irradians*)	Gardner *et al*., 1975	Waste motor oil	>20 ppm	Incidence of lesions in branchial efferent vein, mantle, and gastro-intestinal tract of oyster; and in mantle, gill, and kidney of scallop.
	Mussel (*Mytilus variabilis*)	Eisler, 1975	Dispersant Iranian crude	.020 ml/1 (20 ppm) 3 ml/1 (3000 ppm)	Decrease in ability to attach to surfaces
	Mussel (*Mytilus edulis*)	Gonzalez *et al*., 1976	No. 2 fuel oil, water accommodated-fractions	10 ppb - 1 ppm	Decrease in filter feeding activity; and byssal thread attachment at the higher concentrations.

Table 3.3.12 (continued)

(8)

Type of organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Molluscs (continued)	Oyster (*Crassostrea virginica*)	Kittredge *et al.*, 1975	Naphthalene	1 ppm	Irritation of gill cilia
	Snail (*Littorina littorea*)	Hargrave and Newcombe, 1973	Bunker C. dispersant	.750-80 ppm	Increase in crawling and respiration rates (decreased in response to undefined conc. of dispersant or dispersant plus oil).
Other benthic invertebrates	Polychaeta (*Capitella capitata*)	Bellan *et al.*, 1972	Detergent	0.01-10 ppm	Decrease in survival, fecundity.
	Octocoral (*Heteroxenia fuscescens*)	Eisler, 1975	Crude	10 ml/1 (10,000 ppm)	Reduction in tentacular pulsation.
	Hermatypic corals (*Porites furcata*)	Birkeland and Reimer, 1976	Bunker C, diesel	exposed to oil layer	Exposures caused decrease in growth and variation of heads.
	Corals (*Pavonia*, *Psammocora*, *Porites*)	Reimer, 1975	Bunker C, diesel	exposed to oil layer	Caused prolonged "mouth opening" responses, followed by reduction in feeding.

citations from table 3.3.12 disclose sublethal responses in the low part per billion range, i.e. 1 - 10 ppb. A wide variety of effects across animal and plant kingdoms and their components are included. Among these effects are: delaying cellular division in phytoplankton (Mironov, 1970); producing abnormal fish spawn (Mironov, 1968); reducing chemotactic feeding responses in snails (Jacobson and Boylan, 1973); and in crabs (Kittredge et al., 1975); inhibiting mating responses of male crabs to sex pheromones (Kittredge et al., 1975); decreasing filter feeding activity of mussels (Gonzales et al., 1976); and decreasing survival and fecundity in worms (Bellan, 1972). Little is yet known of the ecological implications, as well as the exact mechanisms causing sublethal responses.

The effects of a direct coating of oil include the disruption of physiological or behavioural processes, as a result of smothering, entanglement of appendages or filtering devices, and dislodgement of sessile organisms from their substrates (Moore et al., 1973; Moore, 1973; Nelson-Smith, 1973; Boesh et al., 1974). Residual oil fractions are implicated as the primary cause of these effects which are most significant along exposed shorelines populated by attached or relatively immobile species (barnacles, mussels, limpets, snails, algae, etc.).

The incorporation of petroleum hydrocarbons in marine organisms may result in the tainting of edible species and/or the accumulation of potentially carcinogenic, polycyclic aromatic fractions in marine food chains (Moore, 1973). The exposure of some animals, particularly filter-feeding bivalves and fish, to as little as 1 ppb dissolved petroleum hydrocarbons can result in tainting (Moore, 1973). Humans can taste petroleum hydrocarbons in animal tissue at concentrations between 5 and 50 ppm (Moore, 1973; McKee and Wolf, 1963). The belief that oil can cause cancer in marine organisms is based on the following reasoning:

(i) polycyclic aromatic hydrocarbons have been identified as carcinogenic agents;

(ii) they are widely distributed over the ocean;

(iii) they are found in the residual fractions of crude oil;

(iv) they have been found to concentrate in animal tissues (Moore, 1973).

Cases of cancer have been attested among clams sampled from oil spill sites (Barry and Yevich, 1974; Yevich and Barszcz, 1976). However, there has been no conclusive evidence to date which positively implicates oil as the direct cause of the observed neoplasms.

Much of the oil split in the marine environment eventually finds its way to bottom sediments. As a result, bottom habitats are potentially subject to changes in their chemical and/or physical integrity. Benthic organisms depend a great deal on this integrity. To have a complete insight into the effects of these alterations, one must seek beyond the organism level of response for shifts in species composition and distribution, functional community changes, etc.

b) Marine Populations and Communities

As demonstrated in tables 3.3.11 and 3.3.12 individual organisms are killed by soluble oil fractions in the 0.1 to 100 part per million range, and may show sublethal responses at very low concentrations (1 to 10 ppb). However, the ecological significance of these responses is revealed only when considered in conjunction with the population level of the biological organization. An individual organism may be proved extremely sensitive to oil in the laboratory, but under natural conditions, due to effective reproductive and dispersal strategies, or high rates of birth, maturation and immigration, an entire population may recuperate rapidly from a catastrophe. Similarly, the expected rapid recovery of a community of organisms found to be resistant in the laboratory may be seriously delayed under natural conditions as a result of inhibiting interactions, i.e. competition for food and space, dependence on a specific food source, or the ability to compete with other recovering species.

Other than hypotheses, we have very little first-hand information at this stage on the reaction of various populations, communities, or ecosystems to oil contamination. The little we know has been learned from post-spill studies, surveys of chronically polluted areas, or from the few experimental field studies involving artificial oiling of natural or simulated "ecosystems". Interpretation of results from the first two methods has been severely restricted owing to the lack of precise pre-spill control information to use for comparison. The experimental field approach is recommended since it corrects the limitation mentioned above and emphasizes the importance of natural environmental and biological variables in influencing the behaviour of both the oil and the communities affected. For a review of studies following major spills, see NAS, 1975.

For management purposes, it is extremely important for decision-makers to understand how stable various types of marine systems are in response to oil. Such information can be used to help predict the ecological impact of an oil-related operation while it is still in the planning stages. Unfortunately, too little is known at present to make definite conclusions for every type of system. Table 3.3.13 summarizes the responses of marine populations and communities to oil (J. L. Hyland and E. D. Schneider, 1976).

Table 3.3.13

Summary of effects of oil on populations and communities[a]

Community or population type		Expected degree of initial impact		Expected recovery
Plankton	Light to moderate	Impact dependent on chance event of contacting floating slcik. Decrease in population densities may have effect on local productivity. Greastest danger to small local breeding populations. composed of larval fish.	Fast to moderate	Effective reproductive and dispersal mechanisms for most phyto- and zooplankton in open waters (population dense, widely dispersed; individual ubiquitous, prolific, grow quickly to maturity). Local breeding populations of larval fish and shellfish may take much longer to recover.
Neuston	Unknown:	Chance of contact high since communities exist on or near surface. Contamination reported, but effects unknown.	Unknown:	Ecology poorly understood.
Benthic communities		Mortalities lead to decrease in population densities and age distribution; changes in species abundance and distribution; imbalance between interacting populations.		
Rocky intertidal	Light: (with exceptions, e.g., <u>Tampico Maru</u> spill)	Hardiness of organisms. Most damage from coating leading to suffocation or loss of purchase on substrates.	Fast:	Oil rapidly removed by waves. Populations rapidly restored since individuals grown and reproduce rapidly.
Sandy or muddy intertidal	Moderate:	Impact increased by persistence of oil in unconsolidated substrates. Chance for greater mortalities since infaunal organisms may be more sensitive than rocky intertidal organisms that have developed defence mechanisms for living in rigorous and variable environments.	Moderate:	Persistence of oil sediments prolongs. toxic effects.

[a] Adapted from Hyland and Schneider, 1976

Table 3.3.13. (Continued)

Community or population type	Expected degree of initial impact		Expected recovery	
Subtidal offshore	Heavy:	Impact increased by persistence of oil in unconsoildated substrates. Chance for greater mortality since many subtidal organisms may be more sensitive than rocky intertidal organisms that have developed defence mechanisms for living in rigorous and variable environments.	Slow:	Persistence of oil. Possibly, slow rate of biological succession for complex, highly structured communities found in some subtidal areas where abiotic factors have been historically constant.
Fish	Light to moderate:	Possibility of avoiding spills; some resistance offered by mucous coating. Greatest danger to local breeding populations in confined waterways (increased chance of contact; sensitive larval forms present; adults display complex breeding behaviour) of benthic fish heavily polluted substrates.	Fast to moderate	Effective reproductive and dispersal mechanisms for most pelagic populations (fast immigration of larvae and adults). Local breeding populations may take much longer to recover.
Birds	Heavy:	Mortality from ingestion of oil droplets and coating (loss of body heat and buoyancy). Mortality leads to decrease in population densities.	Slow:	Individuals long-lived; low fecundity; gregarious behaviour increases chances of losing entire population
Mammals	Light:	In comparison with other groups, marine mammals not extremely abundant along most coasts. Impact dependent on chance event of small population contracting floating slick. Due to mobility, most mammals can probably avoid heavily-polluted areas. Conclusive evidence of mortality, due to oil pollution, is rare. Possible effects include ingestion of toxic oil droplets during grooming; loss of thermal insulation and/or waterproofing, due to coating; and irritation of eyes and exposed mucous membranes. Eye irritation reported after Arrow spill and spill Alaska.	Slow, if population seriously affected:	Individual long-lived; low fecundity-hence, time for recovery increased. Also, some mammals near extinction. However, no supportive evidence for loss of entire populations as result of oil pollution.

Birds

It would appear from the literature that only sea-bird populations have suffered from oil pollution to the extent that certain species or subspecies are threatened with extinction. For example, there is little doubt that the more southern colonies of puffins (*Fratercula artica*) (Bourne, 1971), razorbills (*Alca torda*) and guillemots (*Urea aalge*) are declining rapidly on both sides of the Atlantic (Tuck, 1960; Clark, 1973). Those that nest on the islands to the north of Scotland have already suffered greatly and are considered to be in a particularly serious predicament (Bourne and Johnston, 1973; Bourne, 1971). It is almost certain that the primary cause of these declines is oil pollution (Nelson-Smith, 1972).

Bird kills were reported following the *Torrey Canyon* spill, south-west England (Smith, 1968); the *Esso Essen* spill, South Africa (Stander and Ventner, 1968); the Santa Barbara spill, California (Straughan, 1971); the San Francisco Bay spill, California (Chan, 1973).

Causes of death include:

(i) disruption of feather surfaces leading to either drowning as a result of the loss of buoyancy, or pneumonia due to the loss of thermal insulation;

(ii) ingestion of toxic oil droplets from excessive preening;

(iii) "accelerated starvation" following increased metabolic activity (to compensate for loss of body heat) coupled with a decrease in feeding.

Since birds are relatively long-lived and are not very prolific, replenishment of losses is often extremely difficult (USCEQ, 1974). Recovery could be a very slow process.

The attempt to clean and rehabilitate sea birds has proved unsuccessful on the whole and is unlikely to contribute in any substantial way to the conservation of the declining population of those species seriously affected by oil pollution, except possibly in small, isolated breeding colonies (Clark, 1973).

Mammals

Despite much publicity and over-reactions from human beings, it does not seem that oil has had serious effects on entire populations of marine mammals. Compared with other animals, marine mammals are not particularly large in number. Hence they rarely come into contact with oil. Also, throughout most of the year many mammals are quite mobile and thus are apparently capable of avoiding heavily polluted areas. A breeding population of seals on an oiled beach is an obvious exception, as are small furred species living in coastal wetlands chronically polluted with oil.

Fish

Oil may have varied effects on free-swimming fish, the most obvious being the lethal effects of concentrations high enough to disrupt the functioning of the gills or bring about the ingestion of large quantities of toxic substances. In general, it would appear that concentrations that are significantly high to be lethal to fish are only encountered in the vicinity of major oil spills or when a spill has occurred in a very restricted area. Less obvious, but perhaps more significant, are the effects on fish at sublethal concentrations which may bring about changes in the feeding, migration or reproduction of the species, or the losses of equilibrium of individuals, and often tainting or carcinogenesis.

Generally speaking, the large amounts of oil associated with major spills tend to remain floating on the surface of the water. As a consequence, adult pelagic fish are only exposed to those components of the oil that dissolve in sea-water or become dispersed through the water columns as droplets either as a result of the use of dispersants or trough wave action.

Despite the possibility of large amounts of oil entering the water column in major spills, there does not appear to be any report in the literature of high mortality in pelagic fish as a result of spills of crude or heavy fuel oil. Unlike birds and mammals, the external surfaces of most fish are coated with a slimy mucous to which oil does not adhere easily although dispersants tend to destroy this protection. Although there is some evidence that adult fish may make an effort to avoid heavily contaminated areas (North et al., 1964; Straughan, 1971 a), a large mortality at sea would probably not be noticed. However, mortality in coastal areas, estuaries, etc., where most major spills occur, would be perceptible so it is possible that adult fish in fact avoid heavily contaminated areas.

In comparison with the apparently minor effects of crude and heavy fuel oils on pelagic fish, spills of light refined oils seem to have considerably more determinant effects. For example, a spill of 22 million litres (5 million gallons) of high octane aviation gasoline, aviation jet fuel, aviation turbine fuel, diesel oil and Bunker C from the tanker R. C. Stoner on Wake Island killed an estimated 2,500 kg of inshore reef fishes (Gooding, 1971), while an "intermediate" oil containing large amounts of aromatic hydrocarbons was identified as the cause of an extensive kill of herring (Clupea harengus) in Nova Scotia in 1969 (Zitko and Tibbo, 1971).

Since the eggs and larvae of many varieties of pelagic fish, many of them of commercial importance, float on the surface or inhabit the upper layers of the sea, they are particularly exposed to the effects of oil pollution and often suffer high mortality. For example, Smith, 1970, reported that 50 to 90% of the pilchard (Sardina pilcardus) eggs were dead and that juvenile fish were scarce or absent in plankton samples collected in the vicinity of the Torrey Canyon spill. This was ascribed to the toxic effects of the emulsifiers used to disperse the spill rather than the oil itself.

Mironov, 1972, found that fish eggs were highly sensitive to oil and oil products and usually died during the second day of exposure to concentrations of 10^{-4} to 10^{-3} ml/l. At concentrations of 10^{-4} to 10^{-5} only 55 to 89% of the eggs hatched and the hatching itself was irregular and prolonged. Larvae were abnormal and died soon after hatching. Mironov, 1968, used fertilized eggs of plaice and found they were highly sensitive to oil products in the water. He found 0.1 - 0.01 ppm caused injury to 40 - 100% of the hatched prelarvae and that 0.001 ml oil/l was toxic to the eggs of anchovy, scorpion fish and sea parrot (Mironov, 1969a). Linden, 1976a, investigated the effects of a Venezuelan oil, with or without the addition of oil spill dispersants, on the embryonic development of Baltic herring (Clupea harengus). The results showed that the toxicity of the oil increased several hundredfold if the oil was dispersed by a certain newly developed (non-toxic) dispersant, and by an additional power of tenth if an older dispersant was used. Linden, 1975, found that newly hatched larvae of Baltic herring were 50 to 100 times more sensitive to an oil dispersion that was brought about by mixing a crude oil and a dispersant, than a "natural" oil dispersion without a dispersant.

Induction of carbohydrate-metabolizing enzymes in fish has been found by several researchers and has been used for monitoring purposes (GESAMP Rep. Stud. 6; Payne, 1977). It was within the studies undertaken in the MED POL project that the effects of an oil spill, reflected by the changes in activity of a hydroxylase in Blennius pavo, a tide pool fish, could be followed up. Enzyme changes do not seem to be a generally suitable indicator of oil contamination. Positive responses could only be found in a few fish species and not in invertebrates (Payne, 1977).

Light refined oils are clearly much more toxic to adult fish than crude and heavy fuel oils. While investigations of the effects of major incidents have concentrated largely on the damage to adult fish or the immediate reduction in fish catches, insufficient attention has been given to damage to the more delicate juvenile forms, effects on fish eggs or the food organisms on which commercial fish feed. All these factors contribute to the long-term effect on fisheries. Damage from oil pollution, therefore, may not become evident immediately, nor necessarily at the location of the spill, but may lead to a gradual reduction in productivity over a large area and a long period.

Furthermore, a gradual and widespread reduction in a fishery would more probably be caused by chronic pollution than by a single acute incident. In the circumstances and bearing in mind other natural and pollutant stresses, the cause of the actual decline in the fishery may not be obvious.

Benthic Organisms

By far the greatest amount of information concerning the effects of petroleum pollution on marine organisms refers to benthic organisms; that is, those organisms which spend a major portion of their lives at the sea bottom. These include a large number of species of molluscs, crustaceans, echinoderms, polychaetes, coelenterates, and hydroids. Many of them, notably lobsters, oysters, scallops, and clams, not only constitute an important fisheries resource but are also amenable to mariculture, an industry which will undoubtedly expand greatly in the future. These creatures are very susceptible to oil pollution because many inhabit the intertidal zone where they become coated with oil and smothered if heavy oil drifts on to the shore. A large number of them are filter-feeders which indiscriminantly extract fine particles of a certain size range from the water and thus ingest oil present in the form of droplets or adsorbed on the other particulate material. Since the intertidal zone is the most accessible region of the marine world and since the consequences of pollution are most readily observed there, the effects of oil on intertidal invertebrates have been extensively studied.

Molluscs: In a large spill in the coastal area, molluscs frequently suffer heavy mortality. For example, a diesel oil spill off the coast of California killed "enormous" numbers of clams (*Tivella stultorum*) and abalones (*Haliotis*) as well as practically all other animals inhabiting the cove at the time of the spill (North *et al*., 1964). While recolonization of most species occurred during the next few years, abalones were still absent after 16 years and many species, while present, were not as abundant as before the spill (North, 1973). During the spill at West Falmouth, large numbers of shellfish perished, while contamination of the survivors resulted in closure of the industry.

The sensitivity of molluscs to oil pollution differs according to species. Tests were carried out in the laboratory to determine the comparative toxicities of crude oils, refined oil products, and oil emulsions to several species of intertidal molluscs common on rocky shores in the United Kingdom. In general, oil products with low boiling points seem to be more toxic than the heavier fuel oils whilst crude oils come between. But heavier oils are more of a physical hazard. No simple relationship appears to exist between, on the one hand the toxicity of mixtures of oil and dispersants, and on the other the toxicity of oil or dispersants alone. In the case of one widely used low toxicity dispersant, the oil and dispersant mixture was more toxic than either the crude oil or the dispersant (Gelder-Ottway, 1976).

That petroleum-derived hydrocarbons were readily taken up by the common blue mussel (Mytilus edulis) was convincingly demonstrated by Clark and Finley, 1973.

Crude oils, oil derivatives and oil-dispersant emulsions cause harm to the larvae of some marine bivalve molluscs as shown by experiments carried out by Renzoni, 1973, on the gametes, developing eggs and larvae of oysters (Crassostrea angulata and Crassostrea gigas) and mussels (Mytilus galloprovincialis).

There is increasing evidence that the effect of outboard motor exhaust is biologically harmful. Using oysters (Ostrea lurida) and mussels (Mytilus edulis), Clark et al., 1974, found that after a 24-hour exposure to diluted effluent (10%) almost all mussels showed stress (gaping) while the oysters reacted by closing their shells and apparently ceasing to pump water. The mussels showed such stress that they were removed and placed in clean water but even so they showed evidence of gill tissue degeneration and after 10 days there was 66% mortality. The oysters resisted rather more successfully, showing 14% mortality after being in the effluent for 10 days. These studies were conducted using an effluent which was probably much more concentrated that what would be found after a spill.

Crustaceans: The mobile crustaceans, lobsters, crabs, etc., generally inhabit the sublittoral zone and are therefore not as likely to come into direct contact with oil as are the intertidal molluscs and attached crustaceans. Furthermore, their mobility makes it possible for them to avoid heavy contamination or, conversely, to be drawn towards it (Blumer, 1970). Mortality is frequently high, for example, as a result of the Tampico Maru incident when lobsters (Panulirus interruptus) and crabs (Pachygrapsus crassipes) suffered heavy losses (North et al., 1964). As is often the case with other juvenile forms of marine life, lobster larvae are very sensitive to oil pollution. Wells, 1972, indicates that emulsions of crude oil are lethal to larvae at concentrations of 100 ppm and appear to have sublethal effects at concentrations down to 1 ppm. The lethal threshold concentration (96 hr LC_{50}) ranged between 2 and 30 ppm. Lobster larvae were particularly sensitive immediately after moulting (Wells, 1972; Engel and Neat, 1974). Atema and Stein, 1972, report that sublethal quantities (0.9 ml/l of sea-water) of crude oil depress the appetite and chemical excitability of adult lobsters (Homarus americanus) and lengthen the period of delay between noticing food and going after it.

According to Mazmanidi et al., 1973, oil at a concentration of 35 mg/l diminishes glycogen content in muscles and hepatopancreases of oyster females in one day. Thus, glycogen has decreased from 190 mg% to 69 mg% in hepatopancreases and from 97 mg% to 28 mg% in muscles, as compared with the control. During chronic exposure experiments, considerable decrease of glycogen content in these organisms was observed (at 7.5 mg/l and 3.7 mg/l of oil concentration).

The sessile crustaceans, particularly those inhabiting the intertidal zone, frequently suffer extensive mortality in the event of an oil spill. For example, an estimated 4.2 million intertidal animals, the majority of them acorn barnacles, were killed by a spill of 840,000 gallons of Bunker C oil in San Francisco in 1971 (Chan, 1973).

Echinoderms and other benthic organisms: Echinoderms are considered to be extremely sensitive to any reduction in water quality (Nelson-Smith, 1970). For example, sea-urchins (Strongylocentrotus franciscanus) and S. purpuratus) were virtually eliminated from the vicinity of the Tampico Maru wreck (North et al., 1964) and did not reappear until two years later nor become plentiful until four years had elapsed. In the absence of these grazing animals, the giant kelp Macrocystis pyrifera proliferated (North, 1973). Water-soluble extracts of a number of crude and fuel oils, diesel and jet fuels seemed to have little effect on fertilization of sea-urchin (Strongylocentrotus purpuratus) eggs, but most of these extracts were toxic to the developing eggs (Allen, 1971).

Many varied benthic invertebrates were killed by diesel oil spilt into Puget Sound in 1971, with mortality for 48 species of intertidal invertebrates ranging from 30 to 100%, the most affected being brittle stars, polychaetes, nemertants, chitons, hermit crabs, and limpets (Chia, 1971; Woodin et al., 1972). Animals from the higher intertidal regions were more severely damaged than those from the lower regions. In January 1972, a continuous leak of fuel oil from the General M. C. Meigs off Washington not only killed sea-urchins (Strongylocentrotus purpuratus) but petroleum hydrocarbons were taken up by the intertidal community as a whole. Goose barnacles (Mitella polymerus) and crabs (Hemigrapsus nudus), healthy in other respects, exhibited the same hydrocarbon patterns as the fuel oil (Clark et al., 1973).

Rates of recovery for oil-impacted benthic communities have ranged from weeks on rocky shores at Santa Barbara (Straughan, 1971) to five years in soft-bottom, offshore and marsh stations at West Falmouth (Michael et al., 1975).

Plankton

The "passively" drifting plankton seems to be in potential danger mainly from the possibility of its coming into contact with a floating slick, or as a result of complications from physical coating by the slick itself. The consequent loss of large populations could have an effect on local productivity.

Generally, however, no dramatic changes in plankton have been observed as a result of oil contamination. Smith, 1968, noticed minor population changes in the ichthyoplankton and phytoplankton following the Torrey Canyon spill, but in general the plankton was apparently unaffected. Likewise, no apparent changes in phytoplankton or ichthyoplankton were reported following the Santa Barbara blow-out (Straughan, 1970, 1971).

With some exceptions, the recovery of phytoplankton and zooplankton communities, particularly in large bodies of water, is apparently rapid. These species are widely dispersed, reproduce quickly and soon grow to maturity, so that pre-spill population densities and/or stable age-distributions are soon restored (USCEQ, 1974). However, in estuarine mursery grounds or other confined areas, small, localized, breeding populations - particularly the larval forms of some fish (ichthyoplankton), or crustaceans and molluscs (meroplankton) - may be seriously affected, and complete recovery may take several years (USCEQ, 1974).

Surface-dwelling zooplankton from the Mediterranean Sea contained hydrocarbons (17 to 33% of their lipids) which were similar to those in the surface film where petroleum slicks were present (Morris, 1974). These high levels of unnaturally produced hydrocarbons in the lipids of the zooplankton were thought to reflect the concentration and storage of pollutant hydrocarbons by these near-surface animals.

Beneath a thick oil slick, light may be obscured by more than 90% (Nelson-Smith, 1968) drastically reducing the rate of photosynthesis in phytoplankton and also interfering with the daily vertical migration of zooplankton which is regulated by light intensity. Many of the large zooplankters seek their food visually so that overshadowing by oil may exert an indirect effect on nutrition and behaviour in addition to its direct chemical or mechanical effects (Nelson-Smith, 1968).

Microbial

The addition of petroleum hydrocarbons to water samples from an oil-free environment can significantly limit the growth of the indigenous bacterial populations of the water. However, addition of petroleum hydrocarbons to water collected from an oil-polluted environment may promote growth of the bacteria already present in the water (Walker and Colwell, 1975c).

In general, the microbial response to an oil spill is of two types: an inhibition of some of the naturally occurring groups of bacteria that may be critical for maintaining the ecosystem balance and/or the development of petroleum-degrading populations that contribute to the removal of the oil. This is an overstatement of course. In areas already exposed to oil, the numbers of petroleum-degraders are higher than in areas never previously exposed to petroleum hydrocarbons of an allochthonous nature.

Marine bacteria are specific in their attraction to organic nutrient sources. Fogel et al., 1971, have shown that most marine bacteria have chemoreceptors and are drawn to a food source by way of chemotaxis. Clearly, one of the major consequences of interference with microbial chemotaxis by petroleum is that the decomposition of organic materials in the sea is not only dependent on the ability of the micro-organisms to degrade the substrate enzymatically, but also on the ability of the degrading organisms to detect its substrate and to become attached to it (Corpe, 1975). The data of Bell and Mitchell, 1972, indicate that marine bacteria are chemotactic to algal culture filtrates. In all cases the response was found to be highest to filtrates from old algal cultures, implying that release of extracellular materials is most important ecologically during the later stages of a plankton bloom. Hence, chemotaxis is a highly important part of the mineralization process in the pelagic ecosystem. Interference by petroleum may have serious consequences.

The water soluble fraction of petroleum would be expected to be most critical, since chemoreceptors are attuned to water soluble substances. The assumption might therefore be made that light oils would have the greatest impact upon microbial chemotaxis.

Effects of Oil Discharges on Human Beings

a) Carcinogenesis

Polynuclear Aromatic Hydrocarbons (PNAHs) of known mammalian carcinogenicity occur in crude and, particularly, in refined oils. Reported levels of named compounds, such as 3.4 Benz-pyrene (BaP) and 1.2 Benz-anthracene (BaAnth), vary widely from 0.005 ppm to over 3 ppm, but the residues from catalytic cracking and pyrolysis may contain over 10^3 ppm.

Compared with biosynthesis and terrestrial run-off, oil does not provide a significant proportion of the PNAH input to the marine environment on a global scale, but there have been incidents that have attracted major attention. Levels of PNAHs in marine produce can be relatively high, particularly in molluscan shellfish, and these high levels are frequently, but not necessarily, associated with known sources of terrestrial pollution, including oil. Fish and crustacea seem to be endowed with the requisite systems for the metabolism of PNAHs and their excretion as the more water-soluble hydroxylation products. Molluscs appear to lack these systems.

There is a greater storage and persistence of aromatics and PNAHs in lipid-rich than in lipid-poor fish types; in lipid-rich than in lipid-poor oyster populations; in lipid-rich gonad of oysters and mussels than in their muscle.

The uptake of aromatic hydrocarbons (including PNAHs) is faster than paraffins. Concentrations in the range of a hundred to a thousand times background levels may be found, the greater part of the aromatic being quickly discharged on return to clean conditions. However, some 1 to 10 per cent of the maximum uptake may persist for longer periods.

PNAHs are poorly absorbed by the mammalian gastro-intestinal tract when ingested. It is apparently still uncertain whether there is any dose-response relationship for cancer-induction in man, or whether a threshold exists below which carcinogens do not induce cancer. We have found no reports of epidemiological studies which link gastro-intestinal cancers in man with the ingestion of oil-contaminated marine fish or shellfish. There are, however, indications of high frequencies of stomach cancer associated with the consumption of smoked fish (which does contain high levels of carcinogenic PNAHs) in Iceland.

b) Loss of Marine Food

It has been impossible to evaluate fully the extent of losses proved or alleged to be due to oil pollution, owing to the inadequate documentation of incidents, claims, closures, or condemnations of produce. However, a few examples have been compiled which serve to indicate the likely extent of the problem. Examples have been found of produce being condemned on the grounds of altered appearance, and of the closure of fisheries because of health risks, but most of the existing data and documentation refer to the problem of tainting.

It was established that:

(i) crustaceans, fish and molluscs exposed to oily conditions can acquire an objectionable, oily taste;

(ii) the ability to taste oily produce is closely associated with the presence of volatile compounds derived from oils, refined products or dispersants;

(iii) the range and quantity of odorous compounds vary with the type of oil and refining process, with the middle distillate fractions, e.g. diesel oil, containing the greatest number.

The use of dispersants facilitates the uptake of oil and its components and their introduction to the lipid pool of the organism. The likelihood of tainting is increased by utilizing oil dispersants. The solvent fractions of older dispersants contained tainting compounds of the same nature as those found in diesel and crude oils. There are indications that the tissue lipid content and the amounts of free lipids increase the susceptibility to tainting. Fatty fishes and lipid-rich organs, such as gonads, will become more strongly tainted and will perhaps remain so for longer. Therefore, the seasonal condition of the produce will also affect the susceptibility and the degree of the tainting as lipid contents and metabolic rates vary.

External contamination by oil does not necessarily mean that the flesh has been tainted, although visible outer contamination may in itself be a reason for rejection of produce. Even ingestion of oil does not necessarily induce tainting of flesh, but some species of crustacea and molluscs are consumed together with their gut contents, which may lead to the produce being condemned. Cooking of whole animals fouled with oil internally or externally may bring about tainting of the flesh. There have been too few studies on the tissue levels of oil components in tainted produce for any tainting threshold levels to be deduced from them. A threshold of 10 - 30 ppm in tissue contaminated with a North Sea crude oil has been reported with an upper limit of 200 - 300 ppm, beyond which no further increases could be detected by a trained tasting panel. Threshold levels of 5 ppm gas oil in tainted mussel tissue, and 4 - 12 ppm extractable from diesel oil in lobsters have also been reported. Exposure to ambient water concentrations as low as 0.01 - 0.02 ppm oil can lead to contamination of flesh.

3.3.7 Highlights of the most important problems and measures to remedy the situation

The extent to which oil pollution has a deleterious effect on the ecology of the sea has been argued in some circles with more emotion than scientific objectivity. Unless we can quantify the problem and so define the scale of the effects, the cost of the damage, the scale and cost of the preventive or remedial measures needed, and the amount of monitoring we require to tell us whether we are succeeding or failing in our aims, we are liable to waste resources we can ill afford.

By far the largest percentage of oil is introduced into the environment as a result of intentional discharges which are capable of being regulated through government policy. With increasing supply and demand, an increase in the rate of oil pollution is inevitable, unless such regulations exist.

Industry has achieved a great deal in planning and in developing new technology to prevent pollution or to clean up any that occurs. The issue for us has been to define with greater precision just how much oil pollution is likely in certain circumstances, and how much it matters; and to define the needs for such measures as environmental impact assessment before development, a certain level of standards and control during development and operation, and monitoring of those operations afterwards. There are two main goals: the controls must be adequate to prevent unacceptable damage and they must be cost-effective.

Pollution control is an applied science. We need to ensure that the data we gather are relevant to policy - that they can be used to guide decisions about the nature and adequacy of controls and standards. We have to make certain that the right research is done, that the information is evaluated and related to the vast amount of existing knowledge, and that it is communicated to policy-makers and industrial operators so that they can make sensible judgements in this dialogue which is vital if we are to find the right solution.

In setting standards for discharge, models of the dispersion pattern are needed so that we can predict and regulate effects. Bioassays and field surveys clearly complement one another: organisms can be used as an aid to chemical monitoring because they accumulate substances; as indicators because their responses integrate the influence of many contaminants, known and unknown; and as measuring devices, where we have been able to calibrate a specific response to a specific situation. In this latter area synergism could be important, i.e. the possible combined effects of detergents, herbicides and traces of persistent organochlorine pesticides in mixed effluent.

The determination of a permissible level of oil contaminants in the marine environment should be based first and foremost on a careful consideration of their potential impact on vulnerable and sensitive marine life forms.

While there are dangers in over-standardization, all serious monitoring programmes must be designed to give a meaningful sample, quantified accuracy, and inter-comparability. Biological and physico-chemical monitoring must proceed together and there is a need for feedback from monitoring and surveillance to research, to seek to establish the causes of observed correlations and hence improve the selection of variables to monitor.

Just as there is a danger in environmental managers striving for disproportionately costly purity, scientists tend to pursue excessive perfectionism in information-gathering which can lead to inaction pending the evaluation of superabundant data, or the ignoring of simple warning signs.

Deciding upon appropriate measures to counter oil pollution therefore demands the assessment of priorities which will vary from place to place and even from time to time. Ultimately the matter is likely to be resolved on some kind of economic basis, but whereas it is not very difficult to evaluate the damage to a fishery or the cost to a tourist resort resulting from oil pollution and decide priorities on these grounds, it is much more difficult to place a cash value on scientific or aesthetic damage to the coastal environment and even more so to consider long-term and insidious damage in these forms. The last is the most serious. Not only is it almost impossible to assess prolonged damage in realistic economic terms (and for this reason it is likely to be ignored altogether) but long-term consequences of oil, or any other kind of pollution, cannot easily be detected until a stage is reached from which recovery will be extremely slow.

In order to solve the above-mentioned problems scientific research should focus on the following issues:

(i) the physical, chemical and biological transport mechanism by which oil moves from its point of entry through the marine ecosystem;

(ii) the mechanism by which oil is taken up, stored, metabolized, and excreted by organisms;

(iii) dispersion and degradation models of oil (including hydrodynamical models of the area of interest):

(iv) effects of oil should be studied at the ecosystem level; attention should be paid to chronic and sublethal effects;

(v) studies should be made and models should be developed on the fate and rate of the degradation of oil and its effects on marine organisms;

(vi) systematic data on the levels of specific carcinogenic polynuclear hydrocarbons in marine produce from clean and polluted waters are needed;

(vii) there is a need for intercalibration of bioassay methods;

(viii) more analyses and more complete analyses of sample materials of all kinds are required;

(ix) methods of surface sampling should be studied and standardized;

(x) all analytical methods should be standardized.

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3.5 EUTROPHICATION IN THE MEDITERRANEAN SEA

An ecosystem may be regarded as a system in which there is a cyclic interchange of material between the biotic and the abiotic. Marine ecosystems in particular are normally considered as having three main components: producers, consumers and decomposers (Hawkes, 1971). Detritus, although not being an active component, is often included since it plays a major role in the trophic chain, especially when interaction with man is considered. Producers are organisms that, using sunlight as energy and inorganic carbon and nutrients as building materials, photosynthesize organic matter which is partly converted upon decay into detritus utlized by saprobic bacteria as a source of both energy and matter. Consumers, partly grazing on the producers and partly preying within their own component, also contribute to the detritus component either upon death or by way of their faeces production. Along this cycle, oxygen is released to the environment in the photosynthetic process by producers only and it is consumed in respiratory processes by all three components. Man acts both as a consumer when using marine organisms as food and as a decomposer when discharging partially digested wastes. However, he is one of the main sources of detritus.

Ecosystems are usually maintained maintained by a very delicate equilibrium between different processes controlling them. This equilibrium is established around some "most probable state" which will depend on the rates of these processes as well as on the external forces acting on the system. Fluctuations induced by outside forces such as incoming solar and mechanical energies, human activities, etc., are only admitted when they occur within "acceptable boundaries". Such is the case in the Mediterranean as well as in other marine ecosystems submitted to strong seasonal changes. Long-term changes of their "mean (average) state" do occur as a partial consequence of global trends but they come about in a far more obvious way through the influence of man-made disasters. One of the aspects more directly related to these human activities because it directly affects the flow of matter through the ecosystem and because of the difficulties encountered in preventing it, is eutrophication.

Naturally occurring biogenic material in the sea is rapidly assimilated in the ecosystem. However, introduction of organic matter (detritus) by man tends to encourage the development of the heterotrophic decomposers component whilst introduction of nutrient salts with partially treated sewage favours the growth of the producers component. In both cases the turnover rate of matter in the ecosystem is accelerated and the system enters into a cycle of assimilation or "self-purification" which tends to re-establish the equilibrium around the old "normal state" if introduction of foreign material is discontinued or change it to a new "polluted state" if introduction persists. Consequently, in order to take into account the complexity of the system, one would conclude that eutrophication is better defined by over-all nutrient and organic matter balances and flow rates rather than by concentrations.

In order to tackle the problem of eutrophication in the Mediterranean Sea one must understand the basic relationships among the components of the carbon/oxygen/nutrients cycle in which the system is involved as well as the critical points at which man-made products interfere with the natural cycle.

The response of biological systems to increasing concentrations of substances which are growth factors of whatever kind, is an increase in the rate of growth or productivity. (See figure 3.5.I) This increase may proceed up to an optimum and be advantageous to the individual species or population but thereafter any increase in the concentration of the added substance merely produces a decline in individual sensitive species or the population and causes a nuisance (Perkins, 1974).

Although the major effect of eutrophication is to change, if not to destroy, the equilibrium of the marine ecosystem, some of these effects are of direct concern to man and therefore measures have to be and have been taken in some cases to avoid them. However, all of them are of a very limited nature. A consideration of the effect of necessary growth substances such as nutrients and organic matter upon biological systems yields a more lucid view of what is meant by eutrophication and gives a clear indication of the essentially complex nature of the system of which the polluting source forms a part.

Nutrient cycles and phytoplankton growth

The essential factors controlling the development of phytoplankton blooms are summarized in table 3.5.1. In the open ocean, in temperate latitudes, diatom blooms occur in spring and autumn while dinoflagellate blooms occur mostly in summer. Diatoms are most abundant where high phosphate and nitrate concentrations occur, sometimes accompanied by a reduced salinity. In tropical seas, as is the case of the Mediterranean Sea during the summer months, the relationship is modified by the development of a thermocline which greatly reduces the nutrient supply from the deep, nutrient rich waters. Off the Castellon coast (NW Mediterranean), significant diatom production does not take place when surface temperatures exceed 18 C (Margalef, 1969). Under these conditions recycling of nutrients may sustain a significant density of phytoplankton organisms in nutrient depleted waters through the so-called regenerated production (Dugdale and Goering, 1967) as opposed to the new production based on freshly supplied nutrients (figure 3.5.2). Nitrogen fixation by blue-green algae may also play an important role. Nevertheless, within limits, the primary production of the sea is largely controlled by the supply of nutrients from below and this is indeed very low in the Mediterranean stratified waters. Other less diffuse sources of nutrients may be river run-off, urban sewage and industrial effluents, but still a number of other ill-defined sources may contribute to the nutrient balance such as seepage from interstitial waters within the sediments or rainfall.

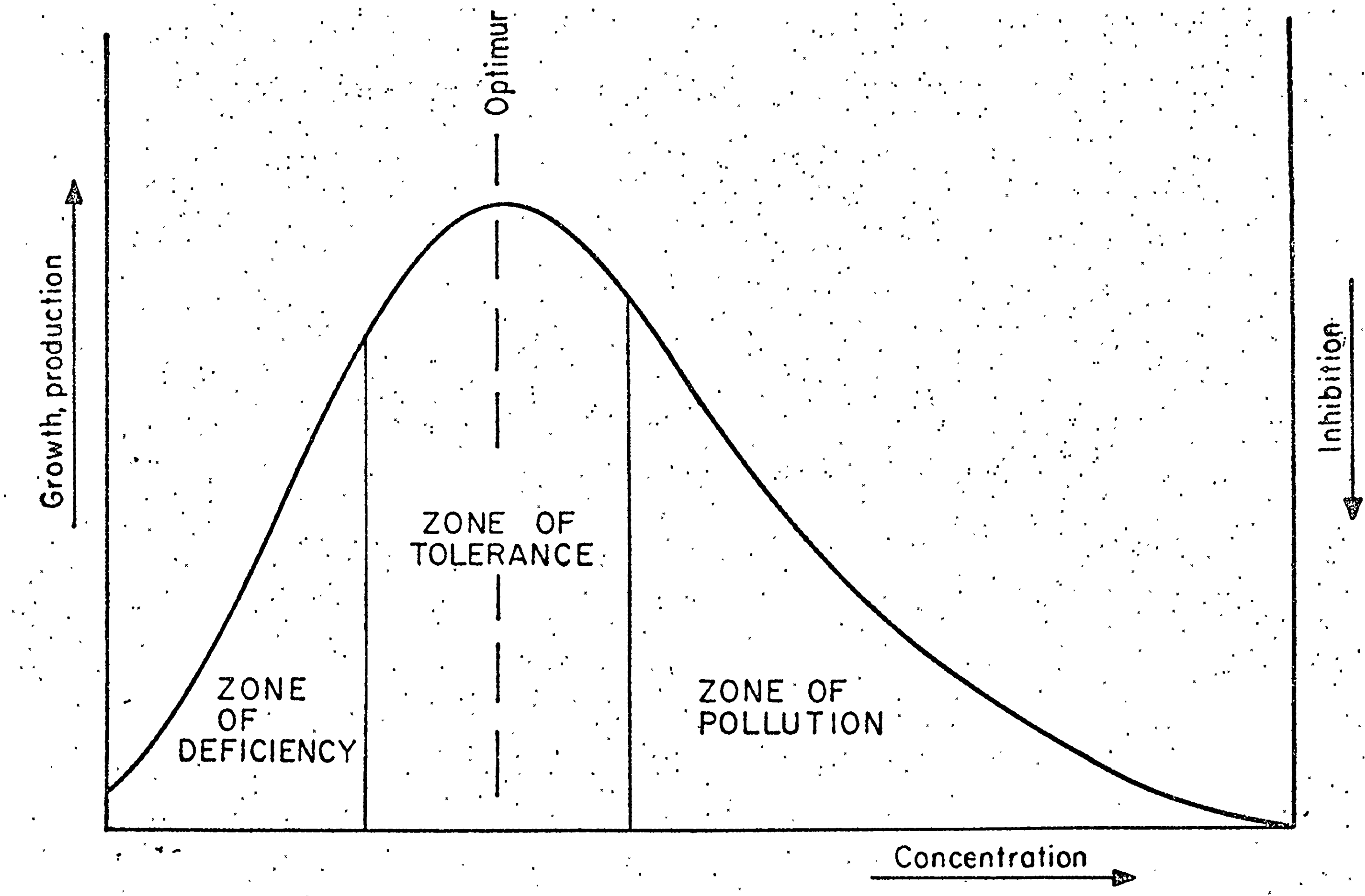

Fig. 3.5.1 - The relationship between the concentration of growth factors, optimal conditions and the development of deficient and polluted environments. (from Perkins, 1974).

Table 3.5.1 Summary of the main factors affecting the growth of phytoplankton

Season	Nutrients	Temperature	Light	Phytoplankton
Winter	abundant	cold	weak	scarce
Spring	abundant	moderate	moderate	major bloom
Summer	scarce	warm	strong	scarce
Autumn	moderate	moderate	moderate	minor bloom

(From Perkins, 1974)

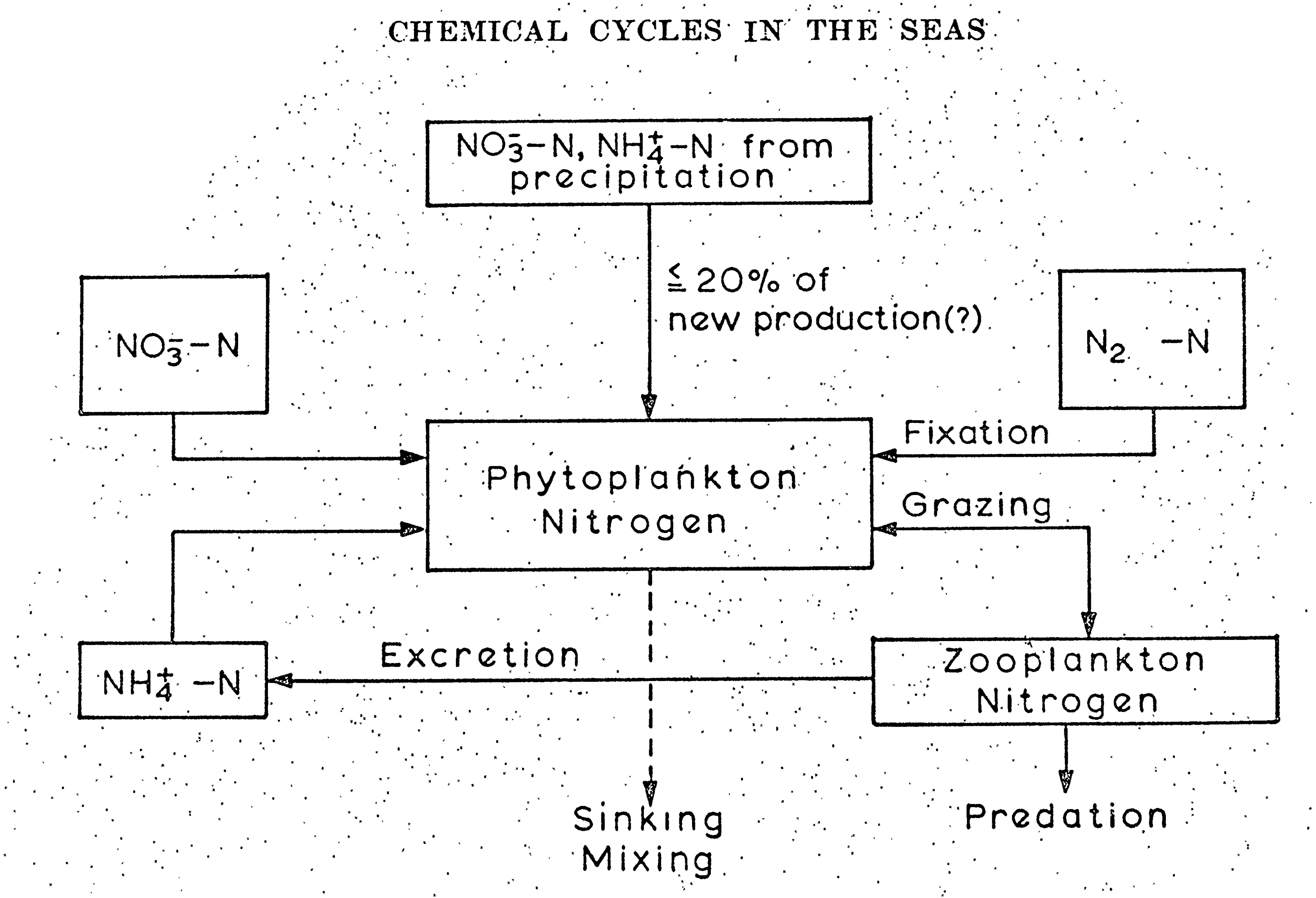

Fig. 3.5.2 - Circulation of nitrogen in the euphotic zone (after Dugdale and Goering, 1967; modified).

Numerous reviews on the nutrients controlling biological production in aquatic systems suggest that nitrogen (N) and phosphorus (P) compounds are normally the limiting factors. According to many authors, algal productivity is largely governed by the concentration of P compounds in the euphotic zone, that is, the region near the surface in which the intensity of incoming light is sufficient to promote photosynthetic activity. Several recent reports however suggest that N is the most important growth-limiting factor under normal conditions as well as in eutrophic situations when P compounds are supplied in much larger proportion than N compounds.

The distribution of nutrients in the seas has long been studied and there is a great deal of literature on the subject. In general (See fig. 3.5.3), concentrations are minimal at the surface and increase with depth until 700 to 1000 m level is reached. In this section however we are more concerned with their biological circulation and especially with that of nitrogen considered as the most important element in controlling the production and distribution of living organic matter in the marine ecosystem both under normal and eutrophicating conditions.

The principal forms of N occurring in marine waters, excluding dissolved gaseous N_2, are nitrate, nitrite, ammonia and organic N. The concentrations of the various forms of N in the water depend not only on the rates of input and output but also on biological processes such as the uptake by phytoplanktonic algae or the mineralization or immobilization by bacterial micro-organisms both in the water and in the sediments underlying it. In sediments, as in soils, the N is primarily in an organic form arising either from particulate material brought in by the terrestrial run-off or formed in the waters above. Figure 3.5.4 shows in a very schematic way the biotic and abiotic paths along which N can circulate in the marine ecosystem. The most important pathways are those determined by plant and bacterial micro-organisms but some animals may contribute in no negligible a way to the mobilization of nitrogen (Dugdale and Goering, 1967). Due to the many complex, competing, biological reactions occurring in a given ecosystem it is extremely difficult to determine the relative importance of each individual microbial process. However, some of them which are likely to be most important in determining the availability of N are ammonification, nitrification, denitrification and nitrogen fixation.

Ammonification: Comparatively little information is available on either the micro-organisms or the environmental characteristics controlling the formation of ammonia from organic matter in marine systems. Early studies show that ammonia can be produced in freshwater lakes in the waters below the thermocline, by the decomposition of sinking detritus, as well as be released from the sediments. Recent work has shown that the process is favoured by anaerobic conditions. On the other hand, ammonia N can also be produced by excretion in fish and smaller animals (Whitledge, 1972).

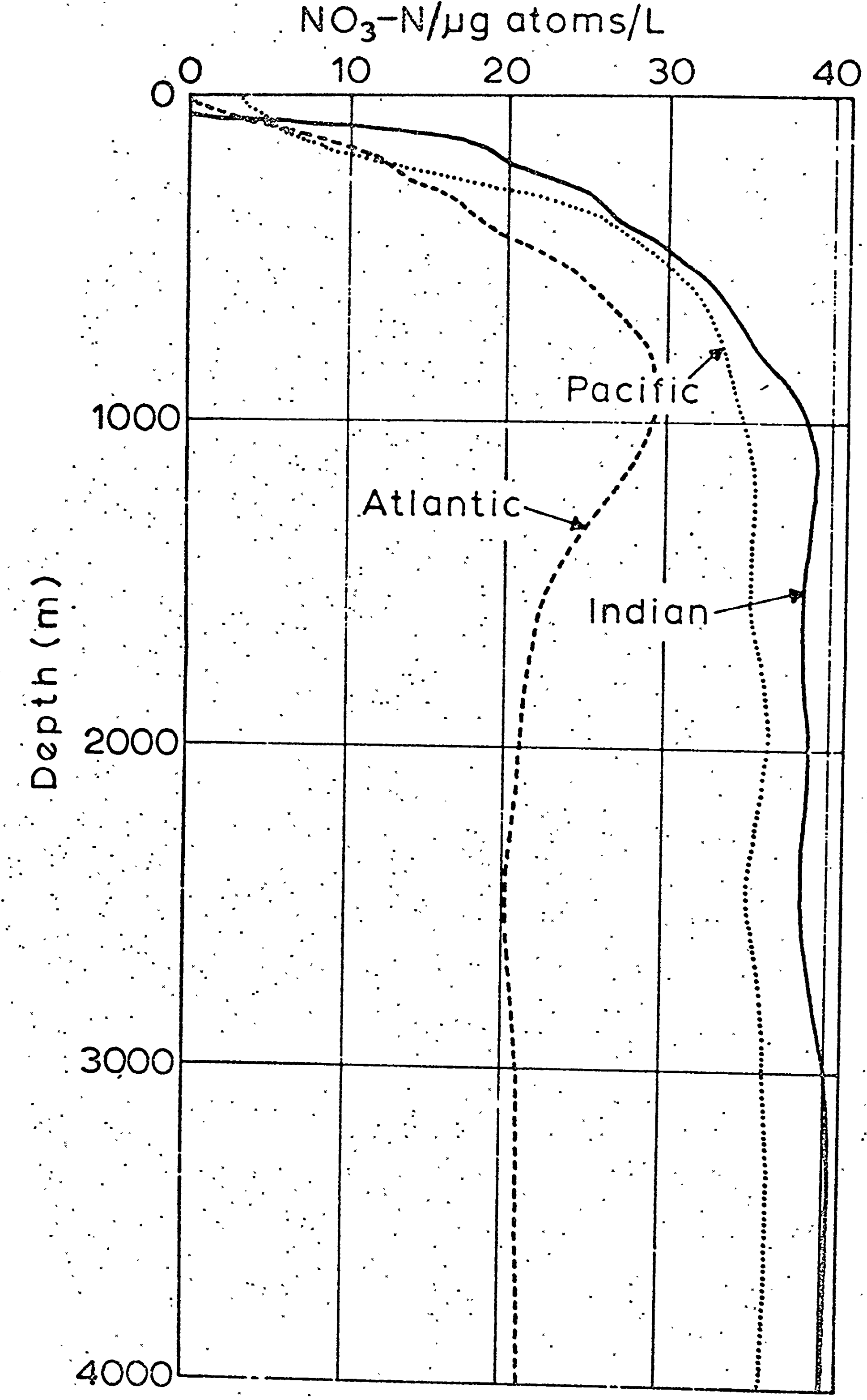

Fig. 3.5.3 - Vertical distribution of NO_3-N in representative areas in the oceans (after Sverdrup and co-authors, 1942).

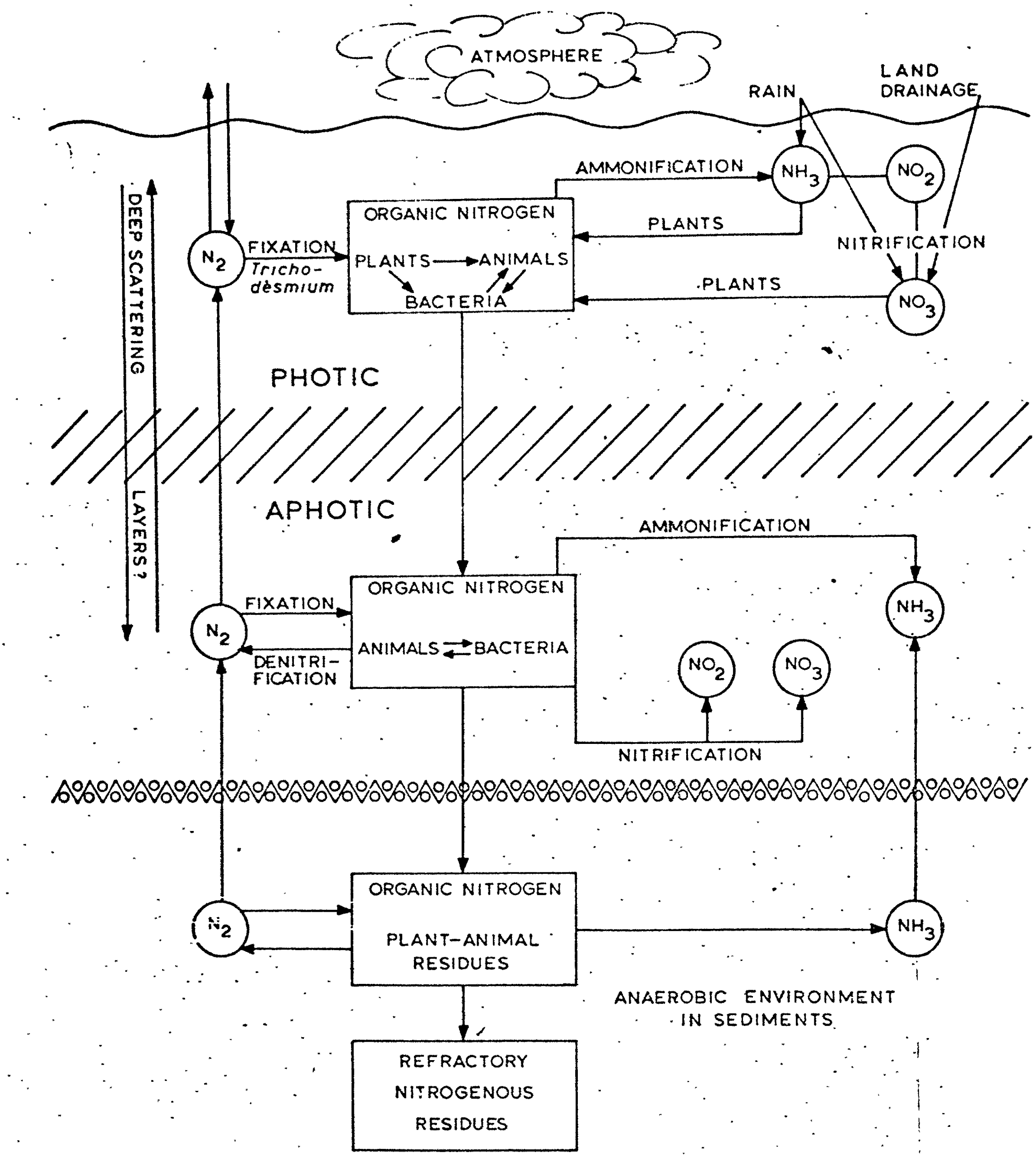

Fig. 3.5.4 - A generalized scheme showing the sources of nitrogen and its organic circulation in the ocean (from A.W. Collier, 1970).

Nitrification: This process, resulting in the conversion of ammonia N to nitrate N, is carried on by obligate aerobic bacteria of the genera Nitrosomonas (ammonia to nitrite) and Nitrobacter (nitrite to nitrate) and has been extensively studied in terrestrial systems and in sewage purification processes. In sea-water, the trophic state may determine whether the process is functional or not and the utilization of molecular oxygen results in an over-all increase in the BOD (Biological Oxygen Demand) in waste-laden waters. In shallow areas with sediments well stirred and aerated by wave action, nitrification may contribute with appreciable amounts of nitrate to the overlying waters. The reverse process (nitrate to nitrite) has been described in Mediterranean waters (Blasco 1972) as being carried out by phytoplanktonic algae submitted to low light intensity and high nitrate concentrations, conditions normally found in summer below the thermocline.

Denitrification: In this process nitrate and nitrite are biologically reduced to gaseous nitrogen oxides (N_2O and NO) and molecular N_2. Nitrogen oxides are not known to be present in the environment and only gaseous N_2 is commonly observed in sewage sludges and wastes. As a consequence of denitrification, a loss of N by the system may be of considerable importance in controlling the over-all amounts of N present in the system especially under eutrophic conditions.

Nitrogen fixation: This is the reverse process to the latter in the sense that molecular N_2 is converted to organic N. A considerable volume of data is available to show that nitrogen fixation occurs, usually in the presence of blue-green algae of the genus Tricodesmium, especially in tropical waters (Goering et al., 1966) and it has also been reported in the Mediterranean Sea. The process appears to be light-dependent and therefore coupled to photosynthesis although certain blue-green algae can fix nitrogen in the dark.

Phosphorus cycle: Unlike nitrogen, which is present in several inorganic forms, phosphorus occurs only in sea-water as the phosphate. Redfield et al., (1963) have established the principle that the different elements involved in the production of organic matter (C:O:N:P:) in the ocean water occur and are taken up by phytoplankters in more or less definite proportions. However, the proportions given for the world ocean do not hold for the Mediterranean Sea and the principle completely fails for waters influenced by river discharges. Figure 3.5.5 schematically reviews the various forms in which phosphorus can be found in the marine ecosystems.

Phosphorus bound to organic matter is released very rapidly. However, even less work has been published on specific bacteria active in the regeneration of phosphate than in the case of the regeneration of nitrate. One would assume that there are many micro-organisms which will bring about the solubilization of phosphate from organic phosphorus compounds present in detrital material.

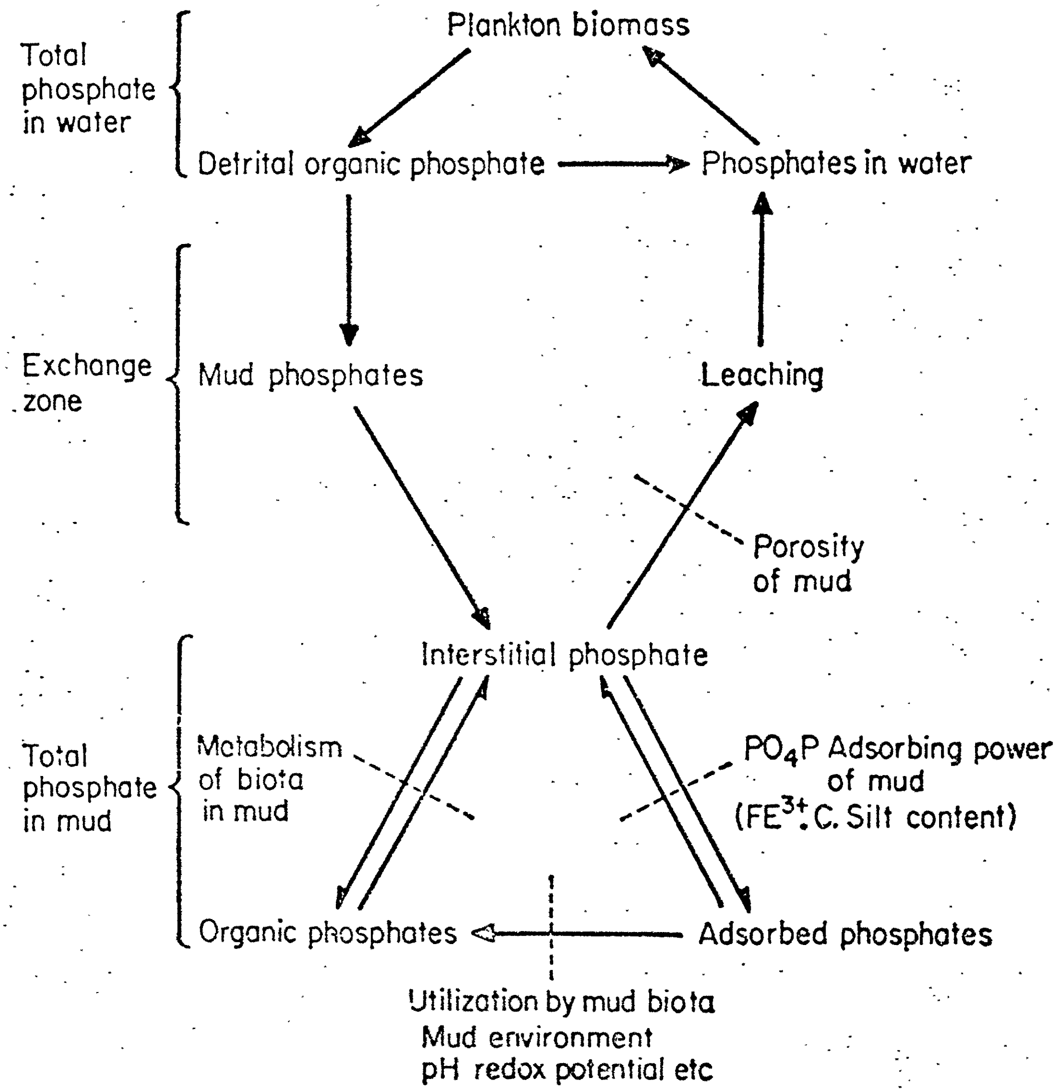

Fig. 3.5.5 - The various forms in which phosphorus can be found in the marine ecosystems (after Rochford).

A large fraction (up to 20%) of the phosphate dissolved in freshwater entering the sea is lost to the sediments through the formation of insoluble phosphates deposited as silt on the bottom. The amount of phosphorus present in a soil is proportional to its silt content (Perkins, 1974). Phosphorus is considered to exist in the sediments in four states:

(a) interstitial phosphate which is present in pore water and can be leached to the water above,

(b) adsorbed phosphate which can be released by chemical processes,

(c) insoluble phosphate bound by such ions as Ca^{2+} and Fe^{3+} and,

(d) phosphorus bound to organic matter.

Insoluble ferric phosphate is strongly bound to the sediments but under reducing circumstances it becomes ferrous phosphate and may leach out to the overlying water. In shallow waters, phosphate attached to bottom sediments may be released to the overlying waters by gales. Evidently, an oxygen deficiency may be expected to facilitate the release of phosphate by the substratum probably by bacterial action in the sediment.

Oxygen cycle in the marine ecosystems

Oxygen not being in itself a growth factor, plays a major role in the process of biological or chemical oxidation of the dead or living organic matter dissolved or dispersed in sea-water, since only in the presence of this element can it be converted by aerobic bacterial action into CO_2 and simple inorganic salts. Oxidation of organic matter can however proceed beyond the availability of oxygen under anaerobic conditions by using SO_4^{2-}, NO_3^- or even NO_2^- as oxygen donors, although this occurs only in extreme eutrophic conditions and, so far, only the bottom of the Black Sea and some other small localized areas in the world ocean are known to be affected by anoxy.

In the presence of the inorganic salts released during the oxidation of the organic matter, acting as fertilizers for plant growth, CO_2 is fixed under the influence of light for them both to be converted into living organic matter by plants and especially by phytoplankton algae through the process of photosynthesis. An amount of oxygen equivalent to the one used in the oxidation is released to the water and eventually to the atmosphere. Inorganic carbon (as CO_2, CO_3^{2-} or HCO_3^-) is normally in excess in sea-water even in the extreme case of algal blooms. Besides it has almost unlimited reserves in the atmosphere. Therefore, we should not concern ourselves with the details of its pathways in the marine ecosystem. On the other hand, oxygen, and to some extent carbon dioxide dissolved in the sea-water, are mainly controlled by the combined action of several processes:

(a) direct exchange between the sea-water and the air above it,

(b) turbulent mixing with adjacent water layers,

(c) photosynthesis carried out by plants, mainly phytoplanktonic algae, and

(d) respiration and other biological and chemical processes.

Process (a) is acting in both ways across the sea surface. Thus oxygen enters the sea when consumption in respiratory processes is more important than production by photosynthesis but it is lost to the atmosphere when excess production by photosynthetic organisms takes place for the equilibrium to be re-established. Oil films or detergents dispersed in the surface layer may decrease the diffusion coefficient of oxygen through the surface of the water by as much as 20% but it may be doubled by strong wave action (Perkins, 1974).

Process (c) takes place only in those waters that have a good balance between the rate of supply of nutrients and the intensity of the incoming solar radiation within the adequate spectral range. Even in such cases another factor, vertical turbulence, may strongly depress this process in favour of process (b) by keeping the organisms for too long a time below the compensation depth at which the amount of oxygen produced by phytoplankton is exactly equal to the amount required for respiration. This compensation depth varies greatly with the time of the day, season, water transparency, etc., and may range from a few to more than one hundred metres. On the other hand, process (b) is the only one which actually supplies oxygen to the waters lying below the compensation depth.

Process (d) acts everywhere in the sea and is the one responsible for the general decrease in dissolved oxygen concentrations with depth in the world oceans as well as for some specific features found in certain regions such as the oxygen minimum layers or the anoxic basins. In fact it has been used for the estimation of the time span elapsed since a given water mass has moved away from the surface layers. The process is highly dependent on the temperature of the water and on the amounts of organic matter, dead as well as living, produced in the euphotic zone or discharged into the sea from land-based sources.

Surface sea-water in the Mediterranean is always nearly saturated with dissolved oxygen, that is, in equilibrium with the atmosphere above it. In the open waters of the Mediterranean as well as in coastal regions away from the major sources of pollutants, especially during summer time, the development of a strong thermocline at around 30 to 50 metres severely limits the supply of nutrients from below the thermocline into the surface layer and therefore process (c) is only of some importance between the thermocline and the compensation depth established at or near the 100 m depth due to the generally high transparency of the waters above. This fact produces a maximum oxygen layer between 50 and 75 m depth typical of the oligotrophic regions of the oceans, and more marked in the western than in the eastern basin since the latter has a much more limited nutrient availability.

3.5.1 Effects of eutrophication on the ecosystem and man

At any rate, oxygen deficiency is the most serious adverse consequence of eutrophication. However, the discharge or production of excess organic matter, especially in the particulate form, strongly affects the ecosystem and man in a number of different ways, e.g. producing abnormally high algal blooms of dinoflagellates known as red tides, increasing the turbidity of the water which limits the penetration of light to a thin surface layer, blanketing of the bottom sediments with a possibly anoxic layer that kills benthic organisms and can even affect demersal fish, or increasing the survival time of pathogenous Escherichia coli as a result of shading by phytoplankton (Golterman, 1970).

The self-purifying capacity of the water is a delicate balance between the quantity of oxygen made available from the atmosphere, the quantity produced by photosynthesis and the quantity used in the oxidation of the locally produced and discharged organic matter together with the currents and horizontal turbulent diffusion spreading the pollutants to a larger area. This balance is easily upset and when sewage is continuously discharged in excess of the capacity of self-purification into a coastal zone with restricted circulation, the zone rapidly becomes a nuisance, turbid and foul-smelling, and devoid of natural life. Such a nuisance can be prevented by limiting the quantity of organic matter and nutrients discharged well below the capacity for self-purification of the water body receiving the discharge.

Oxygen deficiency: This phenomenon develops from the increased respiratory demand of the saprobic micro-organisms digesting the excess organic matter discharged into the sea by crude or partially treated sewage effluents. Besides, the simultaneous discharge of nutrients promotes the production of plant material which contributes to the respiratory demand with increased amounts of detritus sinking to the bottom while oxygen produced by photosynthesis in the surface euphotic layer only, greatly reduced by turbidity, finds its way to the atmosphere and is lost to the system.

The oxygen cycle may then be broken into an oxygen-producing surface layer and an oxygen-consuming bottom layer with a transport of this element in the downwards direction severely limited by restricted diffusion due to strong temperature or salinity gradients. Once the cycle is broken, the oxidation of organic matter proceeds through anaerobic pathways. The processes are then characterized by the production of foul-smelling compounds and gases (H_2S, CH_4) and by a failure to complete oxidative process.

In the sediments underlying polluted waters a lowering of their oxygen content is experienced due to the high biological and chemical consumption rates. If waters above are highly polluted, sediments may become completely anoxic. Even unpolluted waters can produce local deficiencies in the sediments by the decomposition of the decaying organic matter. In Zostera beds and salt marshes, supersaturation of oxygen created by photosynthesis during the day, can give way to oxygen deficiency at night when plants no longer photosynthesize but continue to respire. Marked oxygen concentration gradients with depletion of oxygen at the bottom can occur in stagnant enclosed areas with high sills and vertical temperature or salinity-controlled stratification. Simultaneous to or following large algal blooms, when large amounts of decaying organic matter may consume all the oxygen present, sulphate-reducing bacteria, e.g. of the genus Desulfovibrio, flourish. These bacteria use sulphate as a hydrogen acceptor to produce H_2S. They are abundantly and widely distributed in the marine environment, especially in the sediments. Obligately anaerobes, although not killed they cannot reproduce in the presence of free oxygen. In the Black Sea there is no free oxygen below 2000 m depth and the H_2S in solution forms a toxic layer 1800 m thick. Similar conditions, due to natural causes, may arise seasonally or intermittently in some highly productive zones but they may also appear as a consequence of pollution as seems to be the case in the Baltic Sea where critical natural cicumstances have been enhanced by the man-made eutrophication.

Production of H_2S in the sediments may lead to lethal conditions for the fauna and flora in the overlying water. It also combines with the oxides of iron to form sulphides which colour the anaerobic layer black. The blackened sulphides containing sediments are of a widespread distribution but the sulphides formed in the anaerobic conditions are oxidized rapidly in the presence of oxygen. The depth at which this occurs indicates the depth to which significant amounts of oxygen penetrate either by diffusion processes or by the circulation of aerated water.

Mediterranean sediments have in general a low organic carbon content (figure 3.5.6) due to the low biological production of the overlying waters and the presence of high oxygen concentrations in the deeper waters except perhaps in the neighbourhood of the large rivers (Ebro, Rhône, Po and Nile) where sea-weed growths are common. Therefore, local oxygen deficiencies can very well be connected with eutrophicating zones due to the discharge of crude or treated effluents (see following sections).

Algal blooms (red tides): Abnormally high blooms of dinoflagellates may give rise to the phenomenon known as red tide. A variety of species is capable of producing large blooms which discolour the water but Prymnesium parvum, Peridinium foliaceum, Gymnodinium breve, Gonyaulax poliedra, G. Tamarensis and Exuviaella baltica are among the best-known species. All these organisms, when in high densities, are far from being beneficial due to the production of a neurotoxin which can be fatal to animals and even to man when consuming intoxicated shell-fish (Perkins, 1974), an effect called "ziguatera". Shell-fish become tainted by the toxin and enormous numbers of fish may die in the presence of such blooms. Spray from a red tide carried inland by an onshore wind can cause considerable respiratory distress among the more susceptible members of a human population, e.g. bronchitics. It is true that this phenomenon is observed mainly in the warm waters of the world; some truly spectacular red tides occur off the coasts of the Americas. However they are not confined to low latitudes and have been reported in the Mediterranean Sea (Lopez y Arté, 1971) when a large bloom made up of Noctiluca scintillans covered the coast of the Catalan Sea, at least from the French/Spanish border to the Ebro delta. Nutrient enrichment and high water stability are essential for their development. It is interesting to note that with the eutrophication of many lakes by sewage and other effluents, toxic blooms of blue-green algae are becoming more widespread (Perkins, 1974) and probably the same may apply to the sea.

Turbidity and other effects on the pelagic environment:
Phytoplanktonic organisms require sunlight as energy source for photosynthesis and therefore their growth is confined to the euphotic zone, from the surface of the water to the compensation depth. Consequently, this depth controls the volume of sea-water in which primary production can take place. Since water is an absorbing medium, propagation of light is subject to attenuation. Certain dossolved products from decomposition of organic matter, under the collective name of yellow substance, give rise to significant absorption which starts in the yellow and grows towards shorter wave-lengths. Large quantities of this substance are brought to the sea by north European rivers but it is also formed in the sea and therefore present in variable concentrations everywhere in the ocean (Jerlov, 1970). The particulate matter in the sea is also responsible for absorption as well as scattering. The former process is on the average more marked for the short-wave than for the long-wave and of the spectrum, whereas particule scattering is found to be virtually independent of wave-length.

The penetration of light into estuarine and coastal waters is, consequently, largely dependent on the turbidity which is in general greater, and therefore the depth of light penetration is smaller than that of the open sea. This turbidity, mainly due to the presence of sedimentary materials in suspension but also to autochtonous organisms rearing in the water, may arise from the following sources:

a) rivers and other waters discharged into the coastal zone;

b) transport of sediments from the open sea into the coastal zone;

c) re-working of sediments within the coastal zone, and

d) living and dead particulate biogenic material produced in the coastal waters.

The effects of turbidity and rapid absorption of light upon the photosynthetic processes which can take place in polluted waters is considerable. Clearly, the phytoplankton will receive sufficient light for this vital process in the top layer only, contributing little to primary production. Under these circumstances nutrients are not taken up in sufficient amounts and eutrophic waters will be spread far off-and along-shore by surface currents and horizontal diffusion, covering a larger zone of the coastal as well as open waters.

According to Pérès (1976), the consequences of eutrophication on the pelagic communities are:

a) Species selection in favour of the more tolerant ones in both the producers and the consumers components;

b) Population increase more important for phytoplankton than for zooplankton. Energy is stored in the primary producers component and cannot flow into the consumers component;

c) Decrease in species diversity, and

d) Absence of the higher level organisms in the trophic pyramid. For example: Clupeid fish, consumers of zooplankton, avoid the eutrophic areas.

Other effects of more direct concern to man are, through the increased primary productivity, the uptake of toxic metals which enter the trophic chain and sometimes follow direct pathways to man, such as in the case of filter-feeding sea-food absent in less productive areas, sometimes following more complex processes as with demersal fish, also used for consumption, taking up their food from organisms by burrowing into the diminishing sediments in which mobilization of metals takes place, instead of into oxidized sediments normally found in the Mediterranean Sea.

Effects on the benthic environment: These effects are no different from those taking place in the pelagic environment although, since the benthic populations are more stable, they reflect, rather, the cumulative action of the pollutants. Here too, the sinergestic action cannot be ignored, the more outstanding effects, according to Bellan (1976) being:

a) Pollution always begins with elimination of the species more characteristic of the unpolluted biocenosis;

b) Increase in eutrophication causes the progressive appearance, with a high monotony, of more tolerant, cosmopolitan species;

c) When pollution is especially high, there is a complete absence of macrobenthos;

d) The decrease of the species number may have several consequences of which the most important are:

  - Mass mortality of organisms when sudden changes in the biotic or abiotic conditions occur or when the pollution unexpectedly increases;

  - Slow reconstruction of the original communities once the environmental conditions go back to normal.

3.5.2 Sources of eutrophicating substances

Eutrophication causes an increase in the nutritional standard of the environment with respect to nitrogen (N) and phosphorus (P), regardless of the form these elements may take (Perkins, 1974). Following Liebig's Law of the Minimum, dissolved N and P in any of the forms present in the marine environment (ammonia, nitrite, nitrate, phosphate, organic N and P) are at the base of the trophic chain and control the over-all biological production of the sea, according to a generalized photosynthesis/respiration cycle, schematically represented by

$$\text{Nutrients + Inorganic C} \quad \overset{\text{light}}{\qquad\qquad} \quad \text{Organic C + Oxygen}$$

This law states that growth is limited by the factor present in minimal quantity which, in the sea, happens to be N unlike the situation in fresh water systems where P is generally the limiting nutrient. In order to assess the importance of eutrophication, the input, output and turnover rates of the eutrophicating substances (nutrients and oxidizable organic matter) must be estimated and therefore the sources, sinks and storage pools identified.

In the open sea, the most important reserve of inorganic N and P is by far the deep water. Although exchange with neighbouring waters by horizontal advection and diffusion takes place and input from the air above, as well as losses to the sediments buried below, may not be negligible when balancing the nutrient budget of a water column, vertical transport, through turbulent diffusion from the deep to the surface waters, largely controls the biological production. The ecological cycle in the open sea is completed by the regeneration of nutrients by living organisms and their mobilization from detrital particles carried out by micro-organisms breaking down the organic molecules both in the waters and the underlying sediments. However, very little, if anything, is known about the time taken by all the processes involved.

In coastal areas where deep waters cannot reach the euphotic zone, biological production depends entirely on alternative sources of nutrients. This seems to be the case in areas of wide continental shelf such as the south-eastern shores of the Levantine Sea, where nutrients are found only at a depth exceeding 300 m and remain unaffected by vertical mixing under extreme winter conditions (Oren, 1977), or in parts of the Aegean Sea (IBP, 1971) and off Castellon in the NW Mediterranean (Munoz y San Feliu, 1972). When no other sources of nutrients exist, their concentrations become undetectable and primary production is extremely low. However, these areas often have considerable discharges of nutrients and organic matter to the sea by rivers and urban or industrial effluents. The nutrient supply is then considerably higher than in the open sea and biological production keeps the ecosystem in a more eutrophic state of equilibrium. This is especially true in areas where wide shelves have their origin in sediments discharged by large rivers such as the Ebro and the Rhône in the western basin and the Po and the Nile in the eastern basin.

A budget for dissolved N and P has been established for the entire Mediterranean Sea by McGill (1969) taking into account, on the one hand, the input of nutrients through river run-off and from the Black Sea and, on the other, the output to the Atlantic Ocean through the Straits of Gibraltar. According to McGill, the amounts of N and P involved in his budget are such that the residence-time of the nutrients in the Mediterranean is in the order of 400 years with 2 million Tm of N and 200,000 Tm of P flowing every year with the deep Mediterranean water into the Atlantic Ocean of which about one quarter is contributed by rivers and the remainder by the surface Atlantic water flowing into the Mediterranean. MED POL (1977) has also reported on the input of nutrients from rivers and other land-based sources, following a different method which has produced somewhat higher figures than those reported by McGill (table 3.5.2), probably reflecting an improvement in the estimation rather than a general increase in nutrient supply since McGill made his report.

Some general remarks can be made in relation to the discharge of water and nutrients in the Mediterranean Sea. Most of the fresh water being discharged is from rivers, while municipal and industrial effluents contribute with a negligible 2% of the total run-off. However, about 25% of the N and 16% of the P originates in coastal urban and industrial agglomerations since, on the average, N and P concentrations are one order of magnitude higher in these waters than in river water. Eutrophication created by urban and industrial effluents is therefore basically different from that caused by river run-off. Fresh water discharged by large rivers strongly influence the local and sometimes the general circulation pattern. Both high primary production, promoted by the relatively high nutrient concentration, and low organic matter load, especially relative to the large amount of inorganic suspended solids, are spread by circulation into a large area creating only mild eutrophication. On the other

Table 3.5.2. Nutrient budget for the Mediterranean Sea

(all units Tm/a)

	McGill (1969)			MED POL (1977)		
	Vol	N	P	Vol	N	P
Input from A.O.	$22,995.10^9$	1288.10^3	142.10^3	-	-	-
Input from B.S.	378	5	18	-	-	-
Output to A.O.	21,735	1826	202	-	-	-
Output to B.S.	189	0.3	5	-	-	-
Net gain	$+1449.10^9$	-533.10^3	-47.10^3	-	-	-
From rivers	441.10^9	538.10^3	57.10^3	420.10^9	800.10^3	300.10^3
From other sources:						
Domestic	-	-	-	2	65	30
Industrial	-	-	-	6	110	22
Agricultural	-	-	-	?	25	5
Total gain	441.10^9	538.10^3	57.10^3	430.10^9	1000.10^3	357.10^3

hand, hydrodynamic effects of effluents, due to their small water contribution, can hardly be distinguished other than by the appearance of surface "plumes", if the discharge is made at the surface, or small upwelling "cones", if it is at depth. Therefore these discharges tend to concentrate the organic matter and the nutrients in a narrow eutrophicated stretch along the shores of the highly polluted regions.

Sources of eutrophicating substances are unevenly distributed around the Mediterranean region. Figure 3.5.7 shows the location of the rivers flowing into the Mediterranean and figure 3.5.8 the population distribution along the shores. The western basin receives 35% of the total water run-off while the Adriatic Sea receives 38% and the remainder of the eastern basin 27%. The northern shores receive 91% of the water while the southern shores only 9%. As far as nutrients and organic matter are concerned, 55 to 65% of the total is discharged into the western basin with a population of 55%; 20 to 25% into the Adriatic with a population of only 8%, and 10 to 25% into the eastern basin with a population of about 37%. The northern shores discharge 90% of the eutrophicating substances with 65% of the population while the southern shores discharge only 10% with a population of 35% (see table 3.5.3).

More specific information is available for the Rhône (Coste, 1974), the Po (FAO, 1974), the Nile (Halim, 1960) and some of the smaller rivers flowing into the Adriatic Sea (Scaccini-Cicatelli et al., 1972; Scaccini-Cicatelli, 1973). Table 3.5.4 gives the monthly flow of water and nitrate N for the Rhône during 1968. According to Coste, the amounts discharged every year by the river are 53,700 Tm of N and 4,800 Tm of P, (the latter well below the estimate made by FAO (1974) of 10,200 Tm of P) promoting a supplementary growth of the phytoplankton population of 30 - 45 gC/m^2 per year, in a dilution area of about 2000 square miles, equivalent to about half the primary production of the water column in the neighbouring regions. This author concludes that the over-all primary production in the dilution area is therefore 50% higher than in nearby waters. This conclusion might however be challenged by the assertion of the fact that the 50 m thick surface layer in the area influenced by the fresh water (salinity less than 37.8 ppt) has, according to Coste, a much higher stability and therefore lower local transport of nutrients from the deep water than the other zones. Other important conclusions are that the atomic ratio N/P in the Rhône water is roughly the same (25.6) as the one given by McGill (1965) for the Ligurian Sea, that therefore no disequilibrium is produced and that, differing from other cases, no loss of nutrients has been detected when the fresh water is mixed with sea-water.

According to Halim (1960), the amount of P (and of Si-no data is given for N) flowing with the 30 Km^3 of Nile water was, before the building of the Asswan Dam, just under 6,000 Tm (286,000 Tm of Si), in agreement with FAO's estimate, the observation period being confined

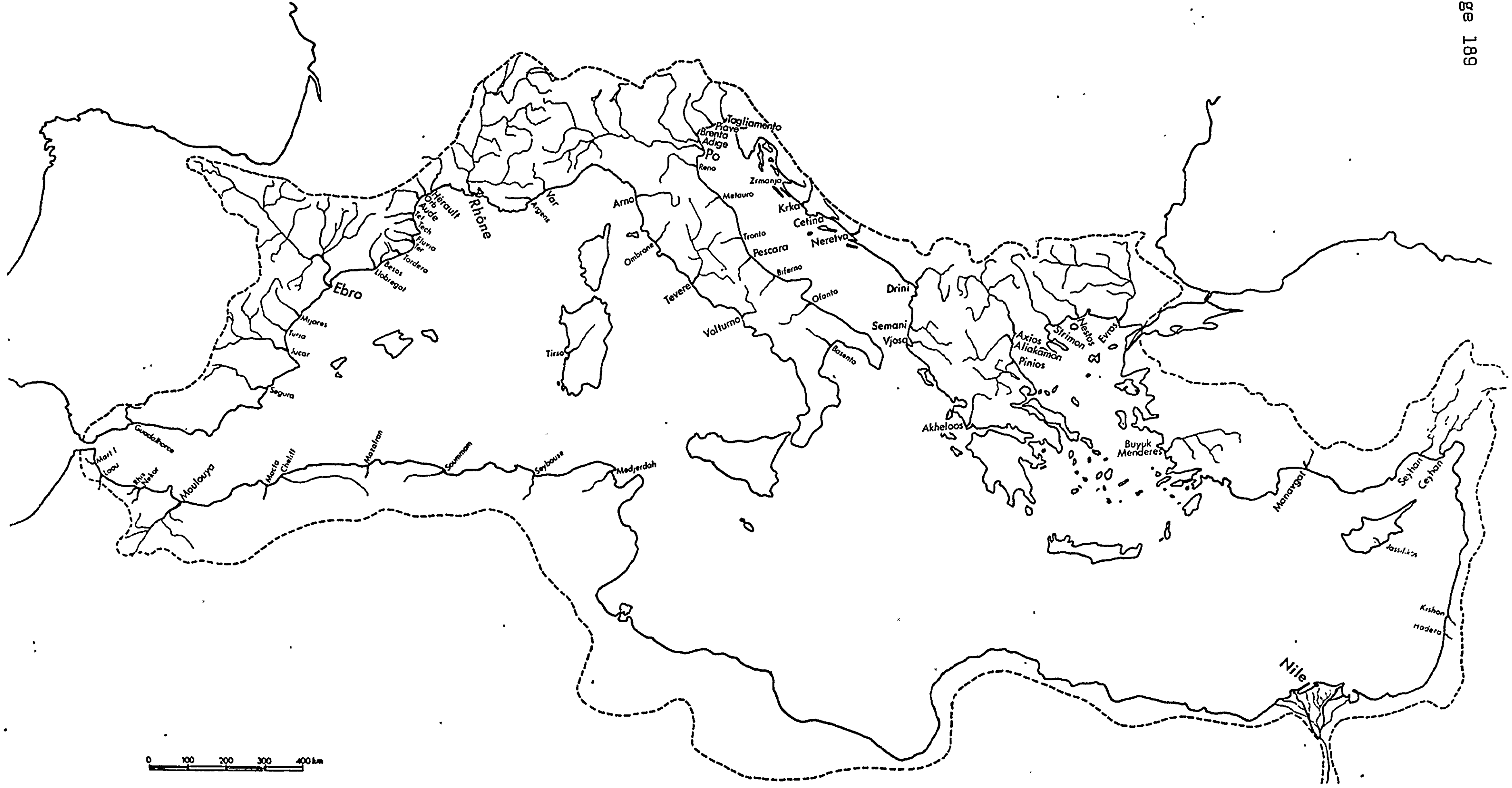

Fig. 3.5.7. Principal rivers flowing into the Mediterranean

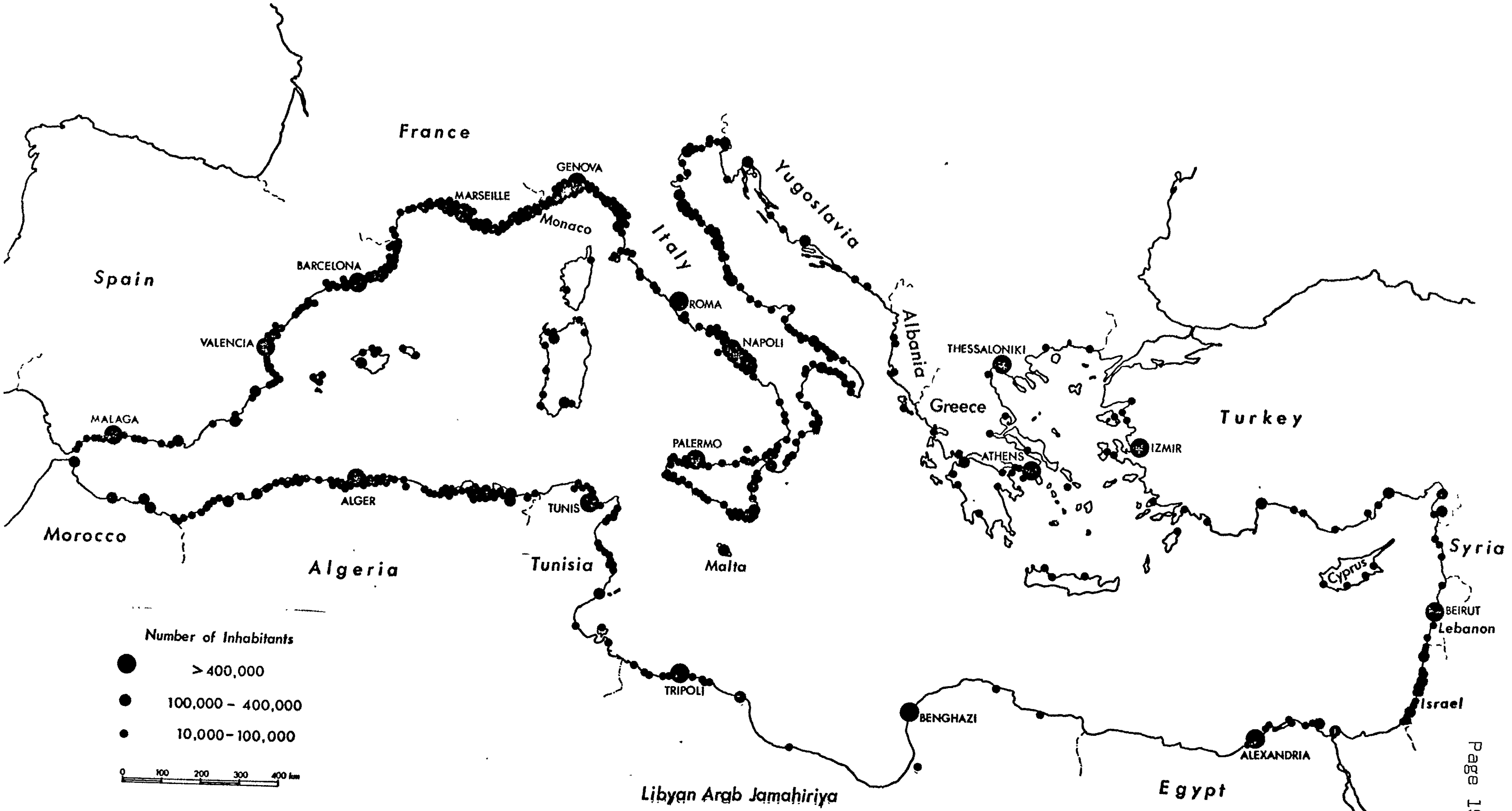

Fig. 3.5.8 Population distribution along the shores of the Mediterranean (MED X project).

Table 3.5.3. Nutrient input in the various basins of the Mediterranean

(from MED POL)

	Vol %	N %	P %	BOD %	COD %	Popul %
Western Basin (Areas I, II,III and IV)	35	61	66	55	55	55
Adriatic Sea (Area V)	38	25	23	22	24	8
Eastern Basin (Areas VI, VII, VIII, IX, and X)	27	14	11	23	21	37
North Shore (Areas II, IV, V, VI, VIII and IX)	91	90	90	90	90	65
South Shore (Areas I, III, VII and X)	9	10	10	10	10	35

Table 3.5.4. Amounts of nutrients discharged by the river Rhône

(from Coste, 1974)

Period	Mean flow m^3/sec	Nitrate-N ppm	Phosphate-P (no monthly measurements)
January	2,451	1.54	
February	2,324	1.44	
March	1,667	1.19	
April	1,738	0.91	
May	1,682	0.77	
June	1,320	0.77	
July	1,073	0.63	
August	1,473	0.63	
September	2,536	0.56	
October	1,848	0.63	
November	2,155	0.84	
December	1,735	1.05	
Total Tm/an	$57.1.10^9$	$5.37.10^4$	$4.8.10^3$ (*)

(*) FAO's estimate for phosphate was $10.2.10^3$ Tm/an (FAO, 1974) to four months (August to November) during the flood season. However, he considers this to be a minimum estimate since a large amount of nutrient containing organic matter in different forms is also carried down to the sea. This discharge is immediately followed by massive outbursts of diatoms producing an exceedingly dense phytoplankton crop in the waters surrounding the stream. River water with a high nutrient content extended beyond 10 km from the mouth but nutrient-exhausted waters were observed in the vicinity of the plume in the zone where the phytoplankton bloom started. This observation might be used to modify the conclusions arrived at by Coste in relation to the area actually being influenced by the high phytoplankton production. While the effect of low salinity may extend to a large region, the nutrients are exhausted by algal uptake in a much smaller zone and the sinking of organic matter dispersed in the river water takes place only in a reduced, highly eutrophic area.

In her studies on the two small rivers Metauro and Arzilla flowing from the Apennines into the western Adriatic Sea, Scaccini-Cicatelli has focused on the concentrations of P and of several forms of N in the river water, as well as on the atomic ratio N/P assuming that a ratio of 20 is the optimum for an equilibrated ecosystem. Table 3.5.5 can be taken as an example of the yearly fluctuations and long-term trend in the nutrient load of these rivers discharged in the coastal zone. The main conclusion is that these rivers, relatively poor in P as is the Adriatic surface water most of the time, contribute in a very direct way to the fertilization of the coastal waters and bottom of which the outstanding productivity is well known. However, the main causal factor for the fertility of this region is the discharge by the Po, by far the largest river in the entire Mediterranean with its 54 km^3 of water flowing every year. Taking into consideration the capacity of the water for self-purification, the 11 million inhabitant equivalents of the population and industrial activities of its lower catchment area alone (Modena, Ferrara, Bologna, Ravenna) contribute to an amount of P estimated (FAO, 1974) at 6,400 Tm and that of BOD at 151,200 Tm, in agreement with other sources of information.

The diffusion of the Po water has been extensively studied by Grancini and Cescon (1971), among others, with the following conclusions:

- The general transport is along the shore towards the south although strongly influenced by tides.

- There is an off-shore zone in which the pollutants tend to accumulate under tide-induced periodic contributions of river water.

- Horizontal diffusion is limited by a front at the boundary between the unpolluted, unstratified open-sea water and the highly polluted, stratified river water.

Table 3.5.5. Average concentration of phosphate-P and several forms of N in two small Italian rivers

(from Scaccini-Cicatelli, 1973)

	Metauro (flow 20 m^3/sec)				Arzilla			
	1967	1968	1969	Average	1967	1968	1969	Average
$P\text{-}PO_4$	4.53	7.44	10.26	7.41	7.99	50.81	19.64	26.15
$N\text{-}NH_3$	58.39	80.97	64.86	68.07	52.81	108.14	77.44	79.46
$N\text{-}NO_2$	5.01	28.36	9.81	14.39	24.63	22.94	38.98	28.85
$N\text{-}NO_3$	507.57	301.58	374.28	394.48	1,051.44	631.22	820.67	834.44
N tot.	570.97	410.91	448.95	476.94	1,128.88	762.30	937.09	942.75
N/P	127	56	43	64	141	15	48	36

- Vertical diffusion is strongly hindered by water stability with important seasonal effects. In summer a 50 cm thick fresh water layer forms at the surface without being mixed with the underlying marine water.

3.5.3 Present level of eutrophication in the Mediterranean Sea

The Mediterranean Sea has long been known as an impoverished area with a low nutrient level insufficient to support a large biological production (McGill, 1961). However, the primary production of the Mediterranean is perfectly comparable to that of the adjacent area in the Atlantic Ocean (FAO, 1972) and ranges from about 50 to 200 g C/m^2 an, corresponding to the third and fourth categories in a scale from 1 (low) to 5 (high) which might be applied to the entire world ocean (figure 3.5.9). Sournia (1972) has compiled the primary productivity studies carried out around the Mediterranean and from his review we have summarized the available data (table 3.5.6) basically in agreement with the previous figures. Although no single study covers the entire region, seasonal and spatial fluctuations are by far more important than the scattering produced by the various methods used.

Vertical distribution of primary productivity is highly heterogeneous as it is everywhere else in the oceans, but seasonal changes constitute the most important feature of the Mediterranean waters. Two complex processes control the productivity of the Mediterranean:

- nutrient limitation by highly stratified surface waters that makes vertical transport of nutrients extremely difficult. This situation is typified by summer conditions;

- light limitation by extremely and uniformly vertical waters resulting in a short time spent by phytoplanktonic organisms in the euphotic zone, swept upwards as they are by vertical movements of the water. This situation is typical of winter conditions especially in the northern half of the Mediterranean.

As a result, surface nutrient concentrations in winter, especially in the western basin, may be as high as the ones in the deep waters while phytoplankton biomass is kept at a very low level (Coste and Minas, 1967; Cruzado and Kelley, 1973). On the other hand, nutrient concentrations are barely discernible in the surface layers in summer, while phytoplankton biomass is limited to a thin layer btween the bottom of the thermocline and the compensation depth, where nutrients and light are hardly sufficient for the development of the algae that give rise to an oxygen maximum typical of the poorest regions in the world ocean (Minas, 1970).

Table 3.5.6 Summary of primary production levels in various areas of the Mediterranean

(g C/m^2 an)

Location	Production	Location	Production
NW Mediterranean		Adriatic Sea	
Castellon	23 - 85	Eastern Adriatic:	
Barcelona	76 - 85	Open waters	40 - 90
Banyuls	86 - 142	Bay waters	103 - 235
Golfe du Lion	78	Venice Lagoon	42 - 105
Rhône	100		19 - 126
Marseilles	60 - 87	Rovinj	56 - 100
Nice	24 - 83	Kastela	27 - 60
		Stoncica Bay	49 - 201
SW Mediterranean			
Atlantic water	40	Ionian Sea	
		Taranto	130 - 170
		Aegean Sea	
		Saronikos	44 - 71

The transitions from one situation to the other take place in spring and late autumn and represent the most productive seasons for the entire Mediterranean. The transition from the light-limited.winter conditions to the nutrient-limited summer conditions is extremely rapid in most areas especially in those more influenced by the appearance of less dense Atlantic water and/or river run-off which tend to stabilize the water column. Besides, transient factors such as strong winds may depress the process of stabilization of the thermocline (or rather of the pycnocline) thus the productive cycle shows a highly variable trend with notable eruptions of phytoplankton production of a very short duration which make the over-all biological production seem rather less when estimated by the usual methods.

No comprehensive survey of nutrient concentrations has ever been conducted for the entire Mediterranean Sea although a number of surveys in several parts of the region and various time series have been carried out especially in the coastal waters. Available observations show large geographical variations and a general decline in concentration as one goes eastwards (McGill, 1965). Based on data gathered during a series of expeditions to various Mediterranean zones, McGill has produced probably the most comprehensive background document on the geographical distribution of nutrients (phosphate P, nitrate N and silicate Si) in the region (figure 3.5.10) and come to the conclusion that no single factor can be considered as the predominating cause of the low nutrient concentrations observed, the major portion of nutrients being supplied to the surface water by mixing and biological regeneration. Several observations should however be taken into consideration:

- Concentrations of nitrate N and phosphate P increase from the Levantine Sea to the Alboran Sea through the Ionian Sea and the western basin in spite of the existence of a nutrient sink in the Straits of Gibraltar.

- The lowest concentrations of both nutrients occur in the Aegean Sea and the Adriatic Sea, in spite of the latter receiving the largest amount of nutrients from land-based sources (table 3.5.7).

- Atomic ratios N/P are extremely low in the Adriatic and Aegean Seas (findings at variance with those of Scaccini-Cicatelli (1967)) increasing towards the main body of the eastern basin. They are still higher in the western basin and even higher than in the Atlantic Ocean (table 3.5.8).

- Important amounts of ammonia found in surface waters of the Adriatic Sea (and of the Aegean passages) suggest a rapid biological regeneration of nutrients at shallow depths which might account for the relatively high primary production of this sea.

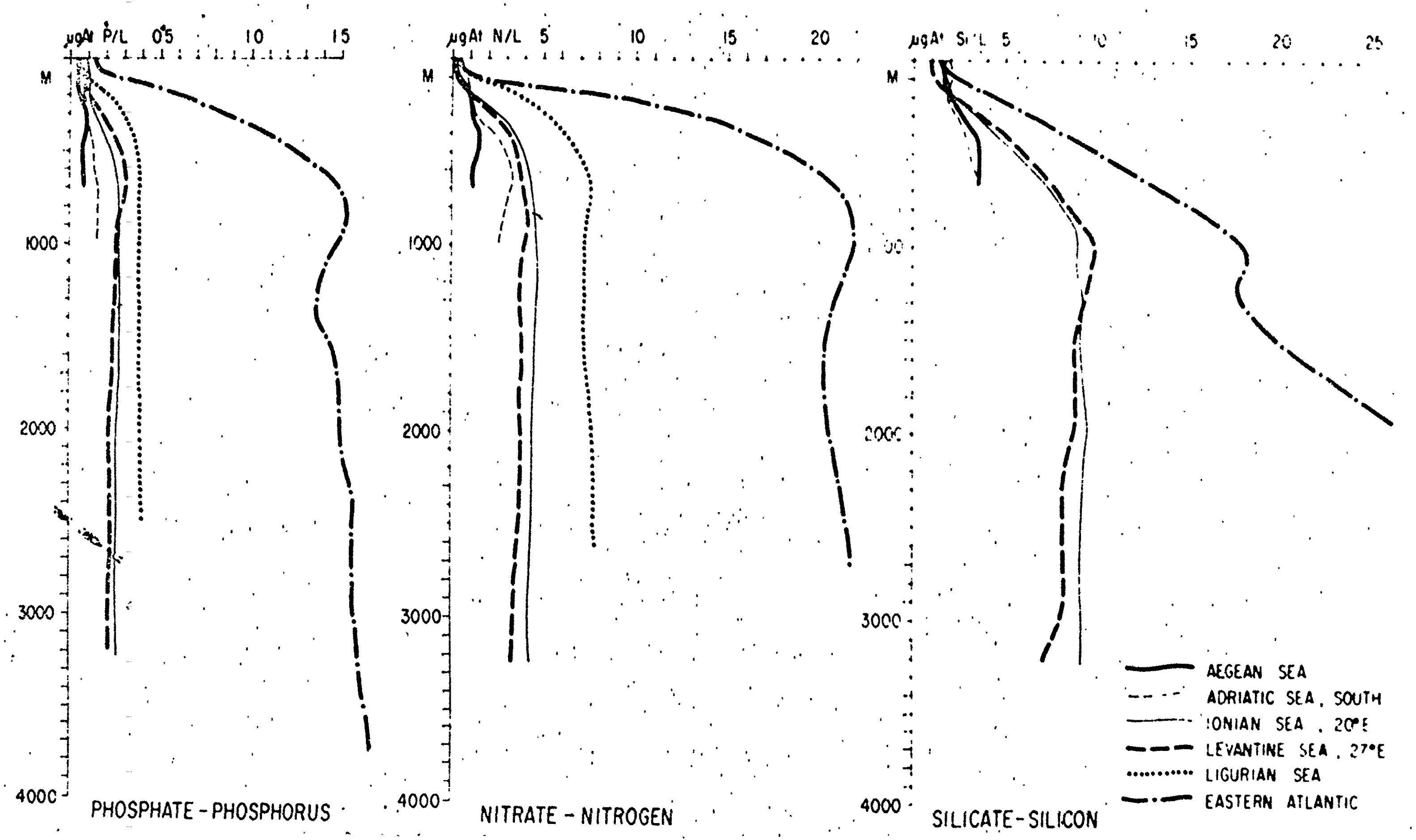

Fig. 3.5.10 - Summary of the concentration changes in the different areas of the Mediterranean Sea compared with available data from the eastern Atlantic Ocean. (McGill, 1965)

Table 3.5.7 The variation in nutrient concentrations in the Mediterranean Sea and the world ocean, expressed as factors of increase over the level in the Aegean Sea

(from McGill 1965)

	PO_4	NO_3	SiO_3
Aegean Sea	1	1	1
Adriatic Sea	2	2	1
Ionian Sea	3	3	3
Levantine Sea	3	3	3
Ligurian Sea	4	4	-
Alboran Sea	8	7	-
East Atlantic Ocean	12	12	8-12+
Indian and Pacific Ocean	24	24	60+

Table 3.5.8 Ratio by atoms of the nutrient concentrations in various areas of the Mediterranean.

(from McGill 1965)

	Si/P	N/P
Aegean Sea	2	2
Aegean Passages		
West	13	6
Central	8	9
East	23	15
Levantine Sea	26	14
Adriatic Sea		
North	8	1
South	16	18
Stn of Otranto	25	21
Ionian Sea		
38° N	32	20
20° E	30	18
Ligurian Sea		23

In order to keep track of the eutrophic areas one has to go back to the sources of nutrients all around the Mediterranean Sea. Large towns and rivers are the main sources and it is in this vicinity therefore, that eutrophication should be suspected. The crescent from Barcelona to Naples, the northern Adriatic and the shores from Beirut to Alexandria are the zones that appear to be more critically affected by the problem. Studies exist for some of the areas, from west to east:

Area I

Cities		Rivers	
Oran	465,000		
Nador	501,000		
Malaga	400,000		
Total	2,690,000	Total	120 m^3/sec

No data available from this area although the nutrient level here is one of the highest in the Mediterranean due to the extremely turbulent hydrographic regime influenced by the strong winds (Levante, Poniente, Terral) and the currents flowing past the Straits of Gibraltar.

Area II

Cities		Rivers	
Valencia	714,000	Ebro	550 m^3/sec
Barcelona	1,745,000	Rhône	1,712 "
Marseilles	916,000	Arno	103 "
Nice	359,000		
Genoa	804,000		
Total	8,870,000	Total	2,730 m^3/sec

Surface concentrations of nitrate and nitrite N off Barcelona (0 - 5 miles) range from 0 to 142 ug-at NO_3-N/l and 0 to 32 ug-at NO_2-N/l while chlorophyll ranges from 0 to 25 mg/m^3 and BOD from 30 to 1,200 mgO_2/l (Castellvi <u>et al</u>., 1977). Off-shore concentrations are never above 0.5 ug-at NO_3-N/l and 2 mg Ghl/m^3 decreasing in general shorewards (Salat <u>et al</u>., 1977). Therefore the coastal strip of eutrophic waters is restricted to about 5 miles.

According to Blanc and Leveau (1970) highly eutrophic waters exist in one coastal area near the Rhône mouth (Fos-sur-Mer) and in a coastal lagoon (Etang de Berre). The reported nutrient concentrations range from 1.4 to 6.1 ug-at PO_4-P/l and 0.7 to 29 ug-at NO_3-N/l in the Fos area and 0.7 to 2.2 ug-at PO_4-P/l and 0.2 to 11 ug-at NO_3-N/l in the Etang de Berre zone while chlorophyll concentrations range from 3.6 to 19.7 mg Chl/m^3 at Fos and 2.5 to 8.7 mg Chl/m^3 in the Etang de Berre. This high algal density seems to depress photosynthesis by the comparative obscurity created by its own shadow.

Area III

Cities		Rivers	
Algiers	1,269,000		
Total	4,439,000	Total	107 m^3/sec

No data available in this area although eutrophication of the zone near Algiers should not be excluded.

Area IV

Cities		Rivers	
Rome	2,874,000	Tevere	234 m^3/sec
Naples	1,221,000		
Palermo	666,000		
Tunis	874,000		
Total	8,131,000	Total	388 m^3/sec

No scientific papers describing eutrophication studies in this area are available although pollution problems around the Rome/Tevere zone and in the Gulf of Naples are well known.

Area V

Cities		Rivers	
Venice	365,000	Po	1,550 m^3/sec
Trieste	270,000	Adige	231 "
Bari	380,000	Neretva	355 "
		Drini	342 "
		Semani	113 "
		Vjose	182 "
Total	2,984,000	Total	3,365 "

This area has been relatively well studied and, in comparison with other Eastern Mediterranean fertilization potentials, that of the Adriatic Sea and especially the North Adriatic is extremely high. The phosphate concentrations in various parts of the Adriatic (see also table 3.5.7) according to Stirn (1972) are:

Depth	ug-at PO_4-P/l N. Adriatic	M. Adriatic	Otranto	Ionian
0	2.4	1.3	0.8	0.7
20	2.4	1.3	-	-
50	-	1.3	0.8	-
200	-	-	1.2	0.8
500	-	-	1.3	0.8

In the neighbourhood of Rovinj (Banjole Island) and in three off-shore stations, phosphate concentrations at several depths, during the years 1967 and 1968, according to Ilic (1972), ranged as follows:

Year	Banjole Is.	5 n.m.	11 n.m.	20 n.m.
1967	0.03-0.09	0.01-0.10	-	0.00-0.11
1968	0.02-0.12	-	0.02-0.14	0.01-0.13

These are rather low concentrations if compared with Stirn's data, and this is probably due to the general anti-clockwise circulation bringing to this area water from the Middle Adriatic with lower nutrient contents unlike the western shores where Scaccini-Cicatelli (1967) has reported, for the mouth of the Po river, values ranging from 0.3 to 1 ug-at PO_4-P/l and 5 to 10 ug-at NO_3-N/l with an atomic ratio N/P of 7. These concentrations decrease southwards to indistinguishable levels and show their minimum values in winter-time. Eutrophication in the neighbourhood of the Po and Adige is important as it probably is along the eastern shores near the Neretva and Drini, although no data are available for these areas.

Area VI

Cities		Rivers	
Catania	399,000	Akheloss	167 m^3/sec
Total	1,883,000	Total	180 "

No data available from this area.

Area VII

Cities		Rivers
Tripoli	670,000	
Benghazi	400,000	
Total	2,904,000	

No data available from this area.

Area VIII

Cities		Rivers	
Athens	2,540,000	Pinios	102 m^3/sec
Thessaloniki	557,000	Alikamon	133 "
Ismir	858,000	Axios	163 "
		Strimon	111 "
		Nestos	100 "
		Evros	311 "
		Buyuk Menderes	100 "
Total	4,584,000	Total	1,020 m^3/sec

According to Ignatiades and Becacos-Konthos (1969) nutrient concentrations in the surface waters of the Bay of Saronikos range from 0 to 0.7 ug-at PO_4-P/l and 0 to 1.7 ug-at NO_3-N/l while in the deeper water (100 m) they never reach values above 0.19 ug-at PO_4-P/l and 1.0 ug-at NO_3-N/l often lower than the surface values. Atomic ratios N/P of 0.7 to 11 with an average of 7 (in contrast with 2 given by McGill, 1969) suggest a poor phosphate supply to the area. A more geographically detailed study of the Bay of Saronikos by Becacos-Konthos and Dugdale (1971) and by Dugdale et al., (1972) shows clear indications that highly eutrophic waters discharged at the head of the Bay produce a marked increase in the phytoplankton density and nutrient concentrations:

	PO_4	NO_3	NO_2
Calm wind	0.2-1.4	0-2.0	0-0.9
Southerly wind	0-3.2	0-2.5	-

According to the authors, the eutrophicating effect of the Keratsini outfall (Athens-Piraeus sewage system) could be easily discerned as far as Aegina Island.

Area IX

Cities		Rivers	
		Manavgat	129 m^3/sec
		Seyhan	188 "
		Ceyhan	230 "
Total	1,320,000	Total	547 m^3/sec

No data available for this area.

Area X

Cities		Rivers	
Alexandria	2,382,000	Nile	500 m^3/sec
Port-Said	310,000		
Tel-Aviv	384,000		
Beirut	939,000		
Total	5,388,000	Total	500 m^3/sec

The eutrophicating effect of the Nile waters has been studied by Emara et al., (1973) in the neighbourhood of the mouth and by Saad (1972) in a brackish-water lake (Lake Mariut). Phosphate concentrations near Egyptian shores show a pronounced increase (0.20 ug-at PO_4-P/l) relative to the off-shore waters (0.04 ug-at PO_4-P/l) especially during summer and autumn. However, with the recent regulation of the Nile flow all through the year, important changes should be expected.

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4. CONCLUSIONS

Good intentions are not enough when insight into the true nature and extent of the problems involved is lacking. Therefore neither over-optimistic enthusiasm nor doomsday pessimism about the future of the Mediterranean will help anybody in programming an effective control of pollution, if it is based on "feelings" rather than on hard scientific facts.

There is no doubt about it: the Mediterranean is far from its pristine condition. But one must admit that pollution did exist on its shores long ago in historic times. The canals of Venice, the coastal waters off Alexandria, the Golden Horn of Istanbul, and many other places must have been public health hazards centuries ago as they are today. Yet it seems that the gradual changes are taking a qualitatively new and ugly turn and that the vast but limited waste-receiving capacity of the Mediterranean is being surpassed in ever increasing coastal areas.

To the man using these coastal waters for recreation, fishing and other activities it should be a slight consolation for him to know that the Mediterranean as a whole can still be considered as a healthy ecosystem which is not doomed to die in the next few decades, as some would like us to believe.

Clean coastal waters are the best guarantee for safeguarding the Mediterranean as an integrated ecosystem. It is therefore heartening that during the last ten yearsor so high priority has been assigned to aspirations to live life for its own sake and that man's activities are no longer exclusively inspired by the urge to master nature.