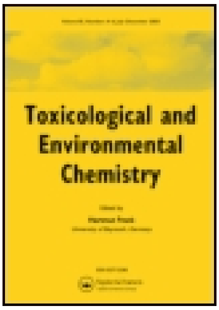

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TRANSPORT OF DISSOLVED/DISPERSED PETROLEUM HYDROCARBONS IN THE NORTHEASTERN MEDITERRANEAN

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The distribution and transportation of Dissolved/Dispersed Petroleum Hydrocarbons (DDPH) were investigated in the Northern Levantine together with the physical dynamics of the region. It was clearly observed that the characteristic meso-scale eddies formed in the area strongly affect the distribution of this pollutant. A recent example of cruises which was performed in March 1989, covered relatively large scale are in the Eastern Mediterranean and the chemistry studies coupled with the physical data for this time period. In the present study additionally the Chlorophyll-a was *in situ* measured spectrofluorometrically and this data correlated with the DDPH data in order to search the origin of hydrocarbons examined: biogenic or nonbiogenic.

INTRODUCTION

Mediterranean is one of the most oil-polluted areas of the world; since 0.5–1.0 million tons/y petroleum enter the sea (Le Lourd, 1977). The reason for this is quite clear; the countries surrounding Mediterranean especially in the eastern and southern parts are oil-producing countries. Thus the oil pollution by the normal operations of tankers flushing oil tanks at sea, other ships clearing fuel tanks and bilges, operations of refineries and petrochemical plants, sewage out falls carrying automotive and other industrial waste (concentrated on the European coasts) is considerably high in this semi-enclosed sea. Figure 1 shows the main production zones and transport routes for oil in the Mediterranean. The presence of permissible oil discharging area (Figure 1) and increased tanker traffic has resulted in the accumulation of DDPH's in especially certain areas in the Eastern Mediterranean.

The data presented and discussed in this paper is the results of analysis of the sea water samples for DDPH collected during the cruise of R/V BİLİM in March 1989. Sampling area scanned approximately $2.22 \times 10^5\,km^2$ which included Cilician, Antalya and Rhodes Basins (Figure 2). The region has been extensively studied recently in terms of petroleum pollution and our knowledge about the region is well documented.[1,6,14,15] On the other hand physical oceanography and physical parameters responsible for the transport and dispersion of pollutants in the marine environment and especially in the Northern Levantine have been investigated by Ünlüata[17] and Özsoy.[11]

The presence of two crude oil pipeline terminals, two fertilizer complexes, one

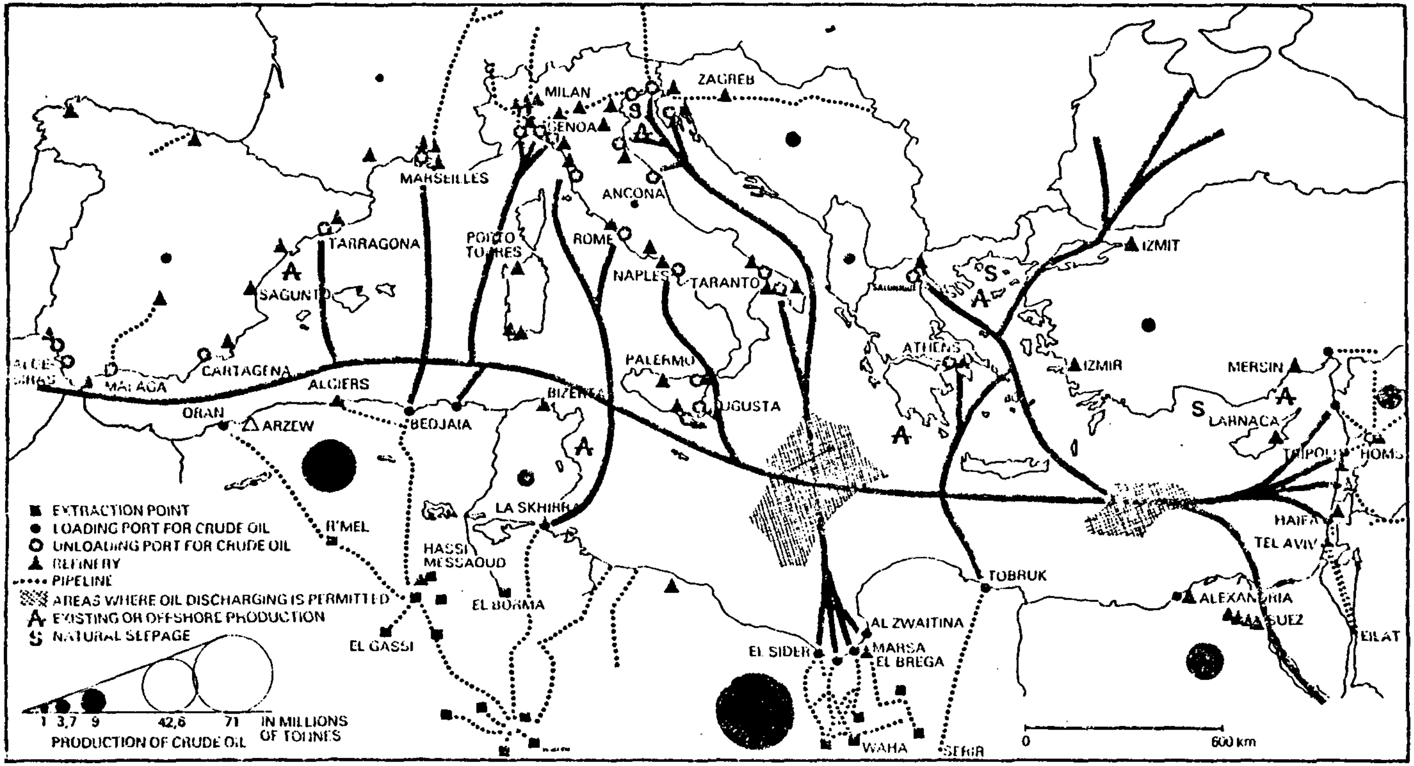

Figure 1 Production and transport of oil in the Mediterranean Sea (After Le Lourd, 1977).

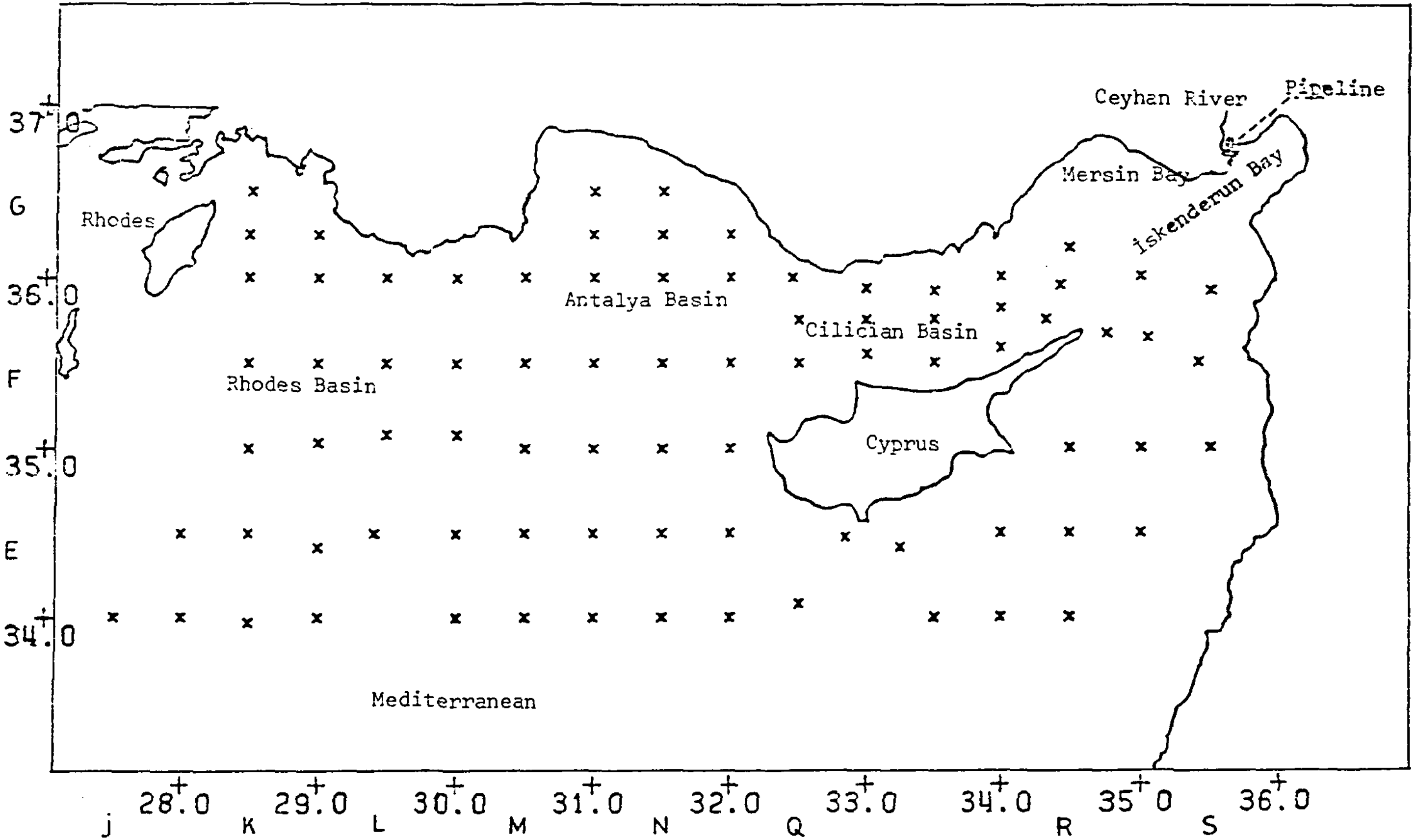

Figure 2 Positions of the stations occupied during the cruise of March 1989.

Table 1 The concentration of DDPH in the Northern Levantine Basin

Location	*Conc. range* (μg/l)	*Source*
Turkish Coastal Waters	0.02–40	Balkaş *et al.* (1982)
Cilician Basin	6	Saydam *et al.* (1984)
Southwest of Mersin	1.5	Saydam *et al.* (1984)
İskenderun Bay	7	Saydam *et al.* (1984)
Whole Northern Levantine	0.05–2.5	Kiliç 1986

iron and steel complex and many other industries and a very busy harbour and a city of İskenderun are located on the coasts of İskenderun Bay causing the Bay to be oil polluted. An accidental oil pollution was experienced in the Bay in April 1982 and about 8000 tons of crude oil entered the Bay via Ceyhan River. Another sensitive region in the area studied in terms of petroleum pollution is Mersin Bay. A refinery, a fertilizer factory, numerous industrial complexes and a busy harbour and a city of Mersin are located around the Bay. Some examples of the previous DDPH data are presented in Table 1.

However hydrocarbons are being produced by organisms in the euphotic zone[3,21,22] reported that on an average at least 60% of the total hydrocarbons in the samples of Bermuda coastal waters found were clearly biogenic. This large amount of biogenic material may contribute significantly to any sample which has been taken to see the impact of petroleum examined. Therefore its differentiation from petroleum hydrocarbons is of great significance and should be taken into consideration. Many of these biogenic compounds contain numerous conjugated double bonds whose fluorescence properties are largely unknown and those compounds may give false values for any method based purely on the fluorescence of the sample. For this purpose chlorophyll-a was measured by *in situ* fluorometer and the results were compared with the DDPH data in the present study. Physical aspects were also discussed in order to understand the events more clearly.

MATERIAL AND METHODS

Sea water samples were collected as far as possible from the effect of ship and other contaminants. Samples were taken into 2.51 amberlite bottles directly from 1 m below the surface and the depth of maximum chlorophyll-a. Sampling, preservation and analysis of dissolved and dispersed petroleum hydrocarbons (DDPH) of the water samples were carried out with the method described in Intergovernmental Oceanographic Commission Manual and Guides No. 13.[16]

Measurement of DDPH was carried out with a Turner Model 430 Spectrofluorometer. Analyses was performed at 360 nm emission and 310 nm excitation wavelengths with a band width of 15 nm. Standard used was Chrysene. All of the chemicals used throughout the work were spectrophotometric grade and blanks were performed for each set of measurements. Raman scattering and quenching tests were done with the methods explained in IOC M&G No. 13. A drawback of the applied method is the fact that there is no possibility of distinguishing biogenic and non biogenic hydrocarbons, however the method is rapid and very convenient for routine analysis.

For the detection of chlorophyll-a in field *in situ* Fluorometer Model Q-200 was used. The fluorometer consists of an underwater unit and a deck panel. Underwater unit contains of a Xenon discharge lamp which is electronically synchronized to the highly sensitive detector. The filter used in the instrument is coloured glass filter in combination with narrow band interference filter. The instrument is fitted with depth transducer as well.

RESULTS AND DISCUSSION

The distribution and dispersion of pollutants in the sea is influenced by physical, chemical and biological transfer processes. In order to understand the distribution of DDPH in the Northern Levantine, first of all the physical characteristics of the region were briefly reviewed.

One of the most important water masses found in the Eastern Mediterranean (EM) is the Levantine Intermediate Water (LIW) and the formation has been linked to the evaporative losses of heat and buoyancy and mixing in the Northern Levantine Basin (NLB).[18] The process includes cooling and increased salinity of surface waters in winter, generating sinking limited to intermediate depths and outflows toward the Atlantic via the Straits of Sicily. LIW is formed continuously throughout the year or that is formed in winter, but released slowly and steadily during the whole year.[5] Ovchinnikov[10] relates LIW formation to the doming of cold, low salinity waters at the center of the cyclonic gyres, which then become colder and gain salinity under the influence of winter conditions. Consequently, the new water type undergoes radial, almost iso-pycnal sinking at the periphery and is arrested at intermediate depths. It is therefore natural to find LIW mainly at the centers of anticyclonic eddies, at the periphery of cylonic gyres or between the cyclonic eddies and the coast. This type of physical system causes the transportation of water masses together with the pollutants and the accumulation of pollutants at certain places. An important consequence of the studies of[10,12] is that they strongly link LIW formation to mesoscale eddies.

The second important water mass in the EM is the Atlantic Water (AW) which enters from the Gibraltar strait to balance the mass deficit of the Mediterranean. It generally follows the north African cost[7] *en route* to the EM with its salinity and depth range increasing eastwards.

A basin-wide (EM) cyclonic mean circulation following the mainland coasts of the Levantine has long been established as the dominant current system[7,18] and further studies have shown numerous cyclonic and anticyclonic sub-basin scale gyres within this general circulation.[9] Ovchinnikov[9] indicates that the intermediate depth circulation essentially follows that of the surface and the intensities of the gyre diminish with depth, some disappearing completely at greater depths.

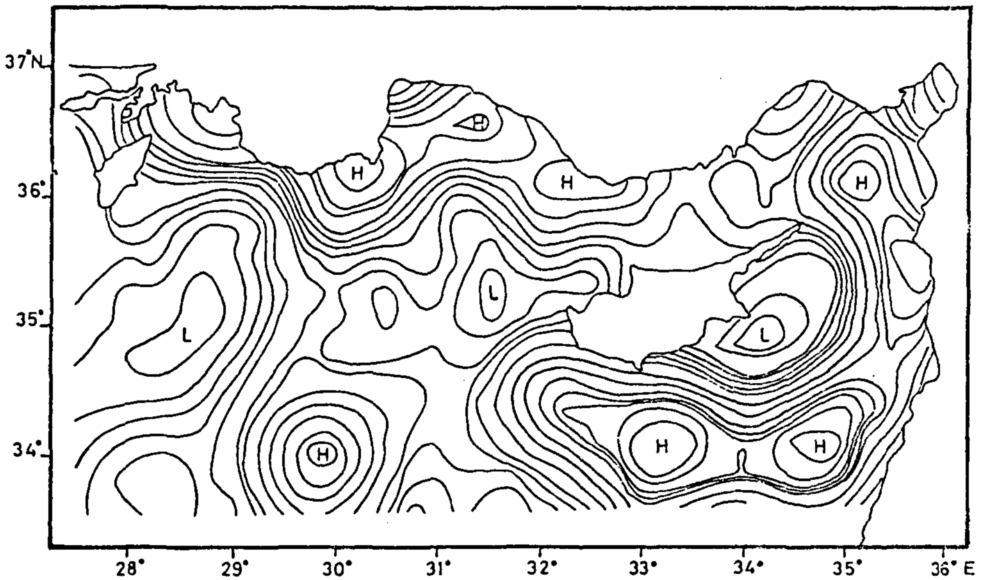

Figure 3 Surface circulation patterns in the Northern Levantine Basin (March 1989). Cyclonic and anticylonic systems are presented with "L" and "H" respectively.

The main sub-basin circulations defined in the EM are the quasi-permanent relatively large scale Rhodes cyclonic gyre, the Mersa Matruh anticyclonic gyre which is located southern part of Rhodes gyre, an anticyclonic gyre off İsraeli coasts, small scale cyclonic and anticyclonic gyre systems in Antalya Basin, in Cilician Basin and off İskenderun Bay.[9,11,12]

Figure 3 shows an example of the circulation patterns in the Northern Levantine Basin observed in March, 1989 cruise by the influence of these main gyre systems. The Rhodes gyre is a well known persistent feature covering a large area centered upon the Rhodes Basin. At its center a cold dome with uniform properties indicates permanent upwelling. In this time of period it seems there is an extension of the Rhodes gyre west of Cyprus. There is also a small scale cyclonic eddy system to the west of Cyprus. The anticyclonic eddies in the Northern Levantine seem to be trapped between the cyclonic circulation and the coast examples being the eddies in Antalya Bay and off İskenderum Bay (Figure 3). The extension of Mersa Matruh anticyclonic gyre was also observed just at southern parts of Rhodes gyre and the anticyclonic system is persistent off Israeli coast (Figure 3).

The surface distribution of Dissolved/Dispersed Petroleum Hydrocarbons (DDPH) is exhibited in Figure 4 and when one considers the circulation patterns in the same region (Figure 3) the eddies seem to affect the dispersion and distribution of this pollutant. The main striking structure here is the accumulation of DDPH at the northern borders of Rhodes cyclonic gyre with the anticyclonic

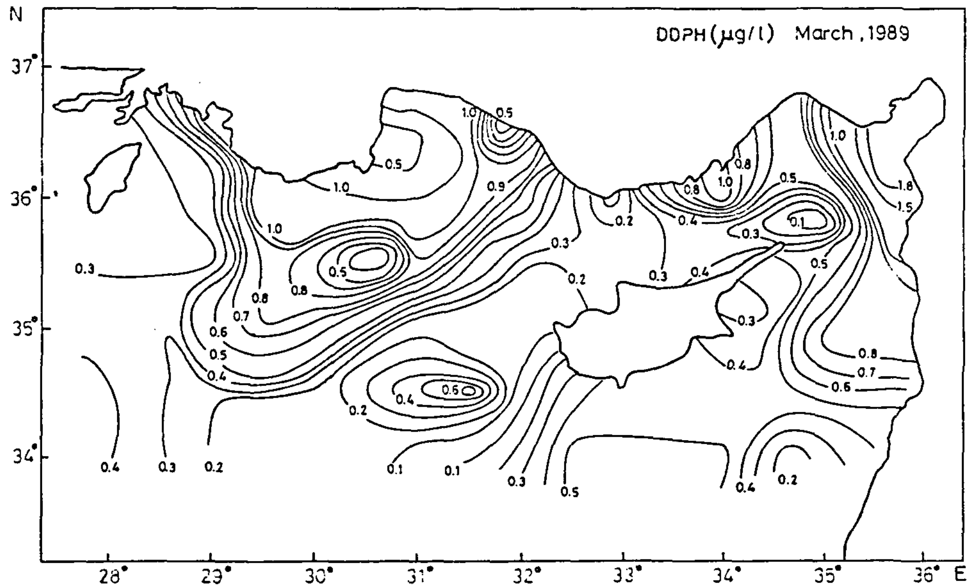

Figure 4 Distribution of Dissolved/Dispersed Petroleum Hydrocarbons (DDPH) in the Northern Levantine Surface Waters (March 1989) (Conc. unit: μg/l).

gyres in Antalya Bay. The same type of behavior was observed in the eastern part of Northern Levantine, the DDPH's were trapped between cyclonic and anticyclonic eddies or/and at the peripheries of the cyclonic gyres. Relatively high concentration values of DDPH were observed especiallyy in İskenderun and Mersin Bays where the area is under the effect of land-based sources. Definitely the presence of pipeline terminal, loading and unloading crowded ports, a refinery and of other industrial complexes make the area to be heavily oil-polluted. In this time period the DDPH concentration ranged in between 0.0–1.8 μg/l in the Northern Levantine excluding the source stations.

Not all hydrocarbons in the sea are derived from pollution; recently-formed hydrocarbons produced by living organisms and contribute the significant amount of total hydrocarbons.[3] The hydrocarbons in crude oil are very different in structure from those normally found in healthy unpolluted organisms. According to Zsolnay[23] petroleum hydrocarbons measured in the 6.9–25.8 μg/l range in the Mediterranean, considerable amounts of biologically produced hydrocarbon material were also present (0.8–22.8 μg/l). This data corresponds the 11.6–88.4 range as percentages. Thus chlorophyll-a data indicating the level of standing stock was collected for the same time period. Relative *in situ* chlorophyll-a fluoresence maxima were plotted on Northern Levantine map and presented in Figure 5a. The distribution of the depth of maximum chlorophyll-a is given in Figure 5b. As is seen from the figure and as previously investigated the deep chlorophyll-a maxima is a common feature in the Eastern Mediterranean.[2,13,19] The reason for this is the possible aggregation of phytoplankton cells within the

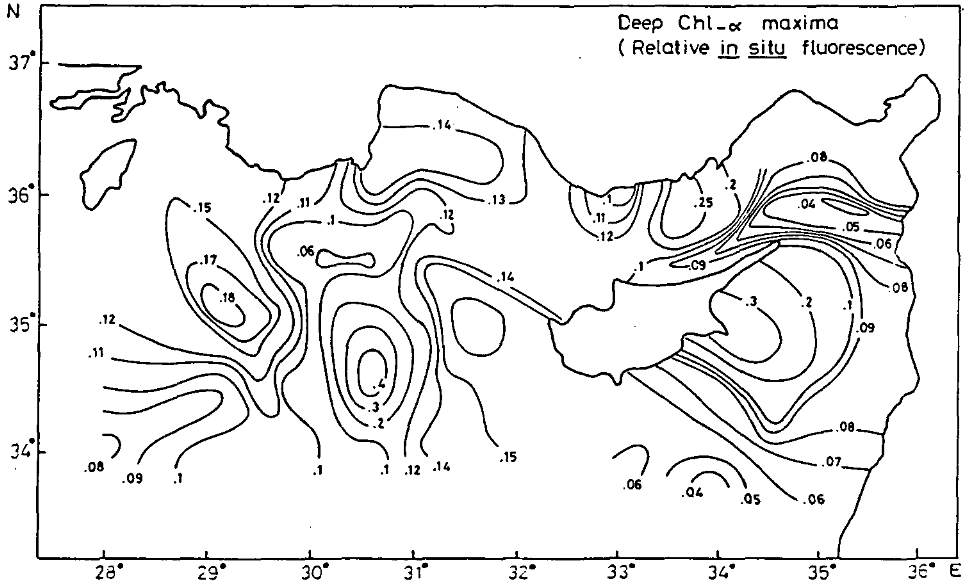

Figure 5a Relative maximum fluorescence intensities due to chlorophyll-a measured by *in situ* fluorometer at depths illustrated in Figure 5b (March 1989).

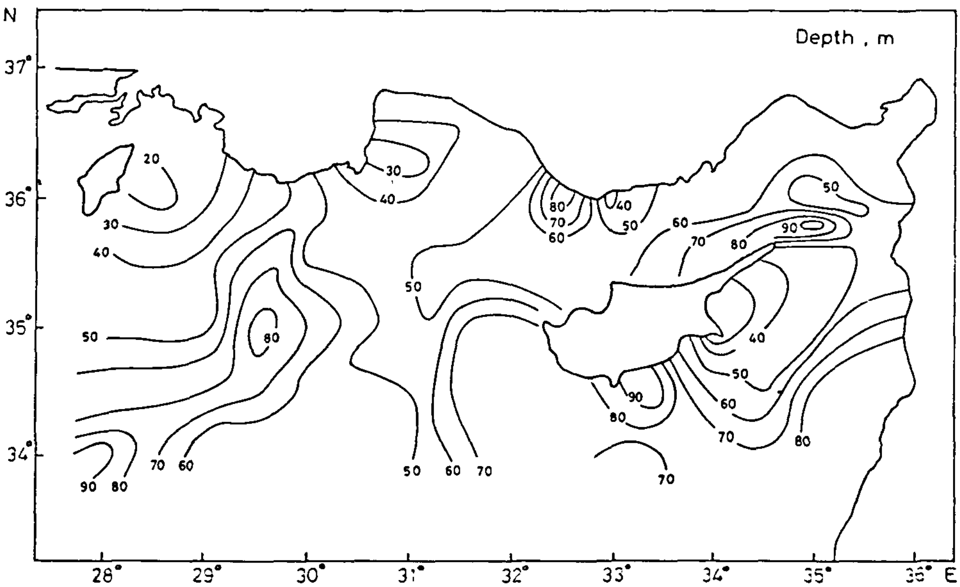

Figure 5b Depth (m) of maximum chlorophyll-a (March 1989).

Table 2 DDPH concentration at depths of maximum chlorophyll-a

Station	*Depth (m)*	*DDPH (μg/l)*	*Relative max Chl-a fluorescence*
G00K30 (in the Rhodes gyre)	60	0.33	0.15
F30P00 (periphery of the extension of Rhodes gyre)	50	0.00	—
F30N00 (in the Rhodes gyre	60	0.34	0.14
G00N00 (in the extension of Rhodes gyre)	60	0.62	0.11

nutricline due to increased buoyancy. The poorness of the euphotic zone in terms of nutrient elements encourages the primary producers to inhabit deep waters. The euphotic zone in the EM is relatively deep and photosynthetically active planktons prefer to inhabit the deeper levels of the euphotic zone. Ultra phytoplanktons are responsible for photosynthetic activity and they are more numerous towards the bottom of the euphotic zone or in deep chlorophyll-a maxima as deep as 100–120 m. Distributions of phytoplankton population (chlorophyll-a) and the physical dynamics of the water masses are also in agreement. It is so clear that when the nutricline rises up at the central parts of the cyclonic systems by local upwelling the depth of maximum chlorophyll-a could be observed at around same that with the nutricline. At the peripheries of the cyclones and at the centers of anticyclonic systems the depth of chlorophyll-α maxima lowers as deep as 80–90 m (Figure 5b). On the other hand maximum fluorescence intensities due to chlorophyll-a could be observed at the central parts of cyclonic gyres e.g. Rhodes cyclonic gyre, and lower values at the peripheries and at the central parts of anticyclonic systems (Figure 5a). In other words the habitation of phytoplankton is strongly affected by physical dynamics of the environment as is observed in the DDPH example.

Rhodes Basin in general and especially the offshore areas are not under the direct effect of land based sources. Thus the only mechanisims for the measurements of pollutant is the transfer and transportation of water masses in this region. The region therefore is so convenient to get information about the origin of hydrocarbons measured spectrofluorometrically. For this purpose sea water samples from the depths of maximum chlorophyll-α were extracted for the hydrocarbon content as shown in Table 2. In spite of insufficient data considerable high quantities of DDPH's were measured at the depth of maximum chlorophyll-a.

The vertical transport of oil pollutants down to these depth could physically be impossible since the water masses are locally upwelled in the Rhodes gyre thus the measured DDPH is not petroleum hydrocarbons; it is the fluorescence caused by

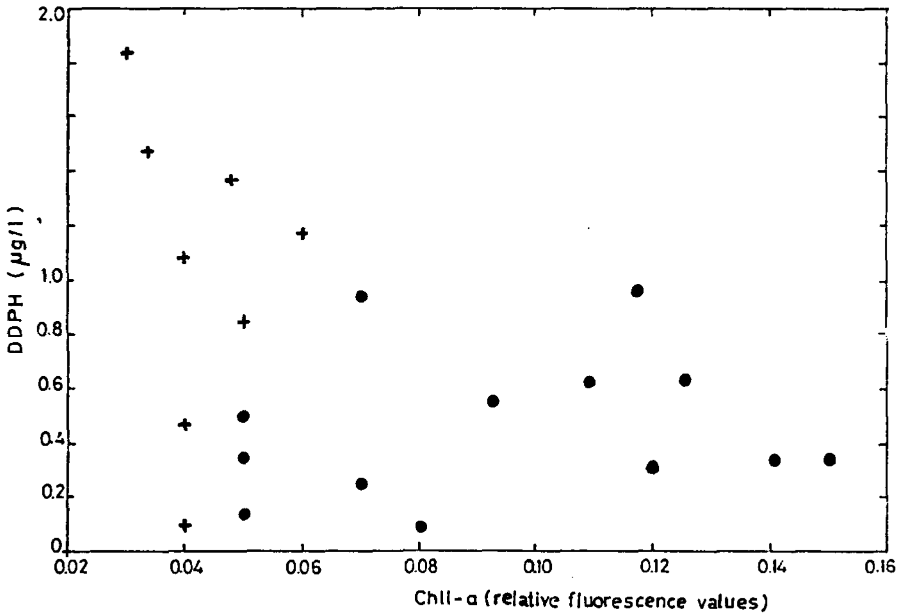

Figure 6 Chlorophyll-a versus Dissolved Dispersed Petroleum Hydrocarbons (DDPH) (March 1989).
+ İskenderun Bay
● Rhodes Basin.

biogenic origin hydrocarbons. In İskenderum Bay where the oil pollution is strong, it is difficult to make conclusion about the origin of hydrocarbons with such insufficient data and/or the complexity of the region. However, Figure 6 gives little information about the phenomenon and it seems chlorophyll-a is distributed homogeneously and there is oil pollution in the İskenderun Bay but there is approximately direct proportionality between chlorophyll-a and DDPH in Rhodes Basin where the processes are undisturbed by man's activities.

CONCLUSION

The distribution of pollutants and natural constituents is strongly affected by the physical dynamics of the area. This is well observed in only one cruise to Northern Levantine where two relevant parameters were analyzed at the same time period.

It seems that there is a significant production of hydrocarbon by phytoplankton which is measured as total hydrocarbon or DDPH by spectrofluorometer. A good correlation exists between petroleum hydrocarbon and chlorophyll-a in local upwelling area of Rhodes Basin, needs further investigation.

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