

different basins, including the control basin (untreated oil), were the location for hypertrophization phenomena including intense proliferation of macroscopic algae.

Discussion and Conclusion

Under the conditions of a controlled ecosystem characterized by the absence of permanent stirring resulting from wave action as well as the absence of a dilution of products and organisms, the disappearance of fuel-oil slicks is slow. It should be pointed out that these investigations began during the winter at temperatures of 11°C which are not the most favorable for the degradation of hydrocarbons (Atlas & Bartha, 1972) and that the experimental location is not normally contaminated by petroleum products and hence is not very rich in microorganisms capable of degrading hydrocarbons (Le Petit *et al.*, 1970).

Without going into the mechanisms involved, it appears that slicks treated by the dispersant agents being investigated (Corexit 9527, Hydrogamosol LT, OSR LT 126) disappear more quickly than untreated slicks. Four months after the first treatment, visual observation revealed only traces of hydrocarbons on the surface of the treated basins.

Under the conditions of the project the three dispersant agents produced an increase in the aerobic heterotrophic bacterial population numbers. This increase was considerably greater than what was observed in the untreated oil slick. The causes of the rise may be multiple, e.g. using different petroleum constituents as a source of carbon and energy by the population fraction capable of degrading such compounds; using the dispersant or its solvent in a competitive way or by another fraction of the microflora. In both cases, proliferation of a bacterial population suitable for degrading petroleum products would occur. The possibility also exists that petroleum products or dispersants eliminate the predator organisms which attack bacteria (cilia, flagellates and zooplankton) and limit bacterial populations in natural environments. In this case the ordinary bacterial population could proliferate by using the cadavers of these organisms as a source of carbon and energy.

With regard to the bacterial biomass, treatment by a dispersant agent is beneficial. However, our solely quantitative investigation did not define to what extent the structure of the original bacterial population is affected when the numbers increase. It is hardly probable that all the bacterial taxa present vary exactly the same way. Indeed, Mulkins-Phillips & Stewart (1974) have shown the selective effects of four agents on different bacterial genera. The successive periods of rapid degradation and stabilization for fuel-oil slicks suggests that variation occurs in the structure of bacterial populations and in particular in species capable of participating in the degradation of hydrocarbons.

The role of an eventual variation in the amounts of nutritive salts present, linked to a microbial activity in water and sediments, must not be eliminated among the possible causes of this succession of activity and stabilization phases.

A more thorough investigation including the qualitative variation of bacterial populations suited to the degradation of hydrocarbons, and also including the effects of inorganic elements on the rate of degradation, is planned for these experimental ecosystems which appear to be well suited for such research.

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Magnetic Monitoring of Marine Particulate Pollution in the Elefsis Gulf, Greece

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Measurements of magnetic susceptibility (χ) and saturation isothermal remanent magnetization (SIRM) on both filtered particulates and sediment samples provide a cheap,

rapid and non-destructive method of particulate pollution monitoring in marine environments where ferrimagnetic iron oxides are important components of the discharge from

industrial or urban complexes. The value of this approach is illustrated by reference to results obtained from the Elefsis Gulf, Greece, where the major source of particulate metal pollution is an iron and steel works discharging waste into a settling lagoon connected to the waters of the Gulf.

This report describes a simple, cheap, rapid and non-destructive method of marine particulate pollution monitoring applicable to situations where magnetic oxides of iron are major constituents of the pollutant. The value of the technique is illustrated by means of a summary of the preliminary results obtained from its application in the Elefsis Gulf. The Gulf is a shallow, almost enclosed embayment of the East Mediterranean close to the main areas of industrial development associated with Athens (Fig. 1). Further description of the location, the circulation and chemical parameters in the water, particulates and sediments is given in Scoullou (1973, 1974) and in Scoullou & Riley (in press). The major point source of particulates identified in the present survey is an iron and steel works near the North Eastern corner of the Gulf, established from 1925 onwards and first brought into production in 1948 using scrap iron in electric arc furnaces. The first blast furnace has been in operation since 1963 and the second since 1972 with a total production of ca. 800 000 tonnes of pig iron per annum. The factory complex also includes a cokery, steel making and oxygen plants, a rolling mill and port facilities.

Figure 1 plots the location of sixteen sample stations from which monthly samples of particulates were taken on Millipore membrane filters of $0.45 \mu\text{m}$ at depth of 0, 10, 20 and 30 m during the period March 1977 to February 1978 inclusive. The water volumes sampled ranged from 1.5 to 10.5 l, and the dry weight of total particulates varied from 2

to 40 mg. Also plotted are seventeen localities from which sediment cores up to 1 m long were taken using a pneumatic Mackereth (1969) minicorer. This method of sediment sampling using transparent Perspex core tubes normally preserves an undisturbed mud/water interface and avoids effectively any metal contamination of the samples. Each core was sliced horizontally into subsamples of either 10 mm or 20 mm depth range. All the filter samples and slices of sediment were dried at 50°C to a constant weight and measured using the magnetic techniques outlined below. The filter samples and a proportion of the sediment samples have been digested with HNO_3 and $\text{HNO}_3\text{-HF}$ respectively then analysed for total Fe using an Atomic Absorption Spectrophotometer (Instrumentation Laboratory Mod. 351).

Magnetic Parameters

Thompson *et al.* (1975), and Oldfield *et al.* (1978a,b) have shown that in lake sediments and peats, magnetic susceptibility (χ) and saturation isothermal remanent magnetization (SIRM) are often roughly proportional to each other and, where this is the case, either or both can be used to estimate the volume of ferrimagnetic minerals present. The dominant source of ferrimagnetic minerals in the atmosphere at the present day has been shown by Doyle *et al.* (1976) and by Oldfield *et al.* (1978a) to be magnetic spherules resulting from industrial and domestic combustion processes. Several additional studies (Oldfield *et al.*, in prep.) have confirmed that the spatial distribution and down profile concentration of ferrimagnetic oxides in peat accumulated above the groundwater table (hence reflecting solely atmospheric input) can only be explained in terms of a recent 19th and 20th Century origin. In the case of

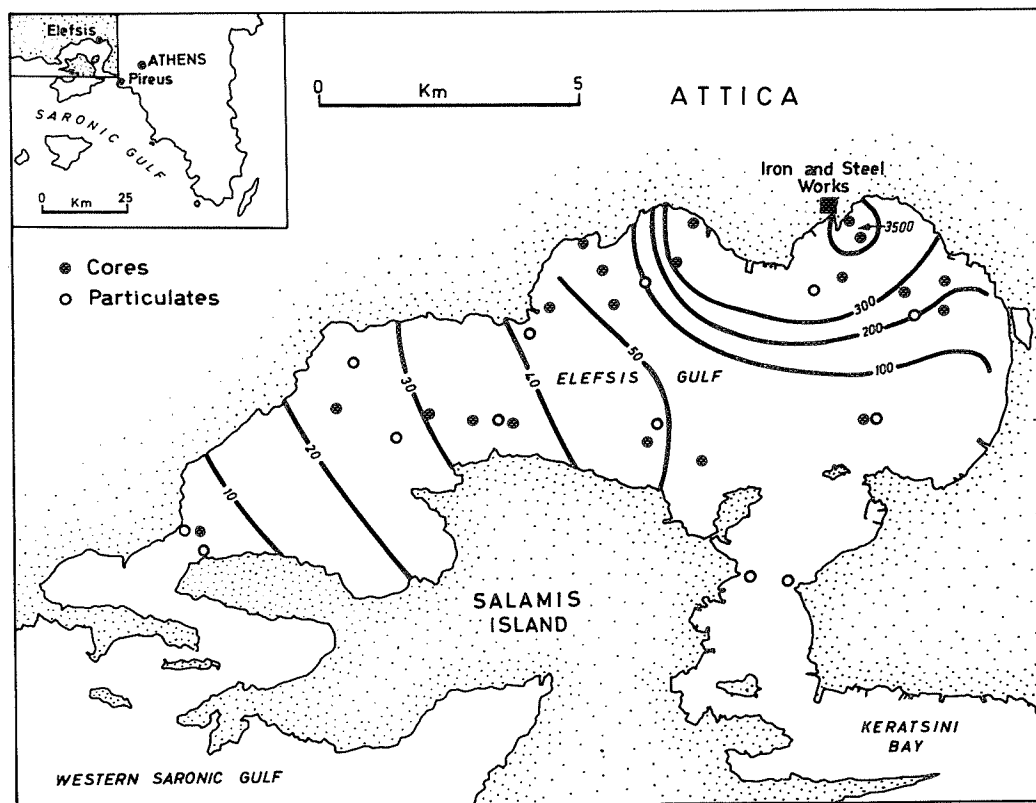


Fig. 1 Elefsis Gulf. Location Map with sites of sediment coring and particulate sampling plotted. The contours refer to contemporary surface sediment values for specific magnetic susceptibility ($10^{-6} \text{ G Oe}^{-1} \text{ cm}^3 \text{ g}^{-1}$).

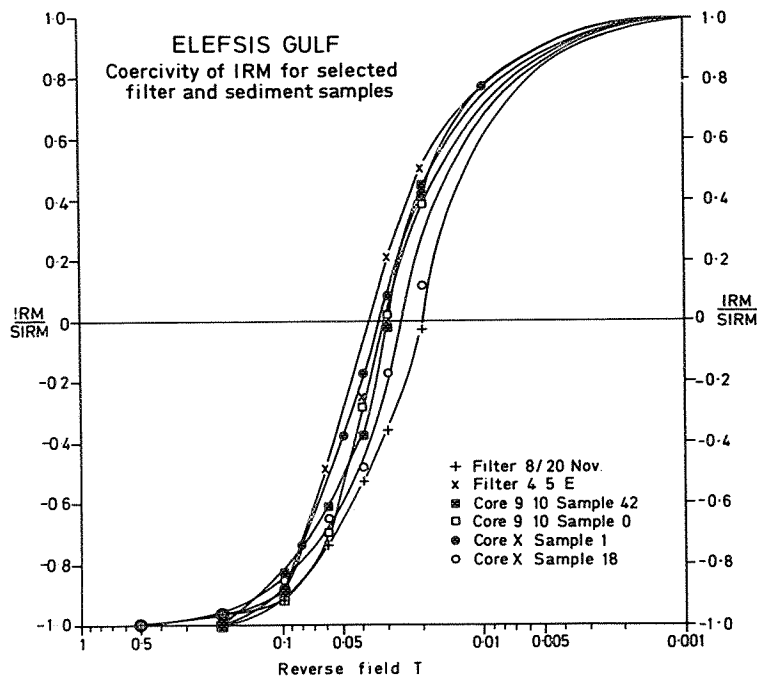


Fig. 2 Coercivity of saturation isothermal remanent magnetization (B_{CR}) spectra for magnetically extreme core and filter samples. Saturation isothermal remanent magnetization is normalized to 1.0. The point at which each curve intersects the horizontal zero line is the coercive field which can then be read off the logarithmic scale in Tesla (= 10000 Gauss) below. Coercive fields between 0.02 and 0.04 T are characteristic of relatively coarse grained magnetite. Complete or almost complete resaturation of each sample in a reverse field of 0.2 T indicates poverty in fine-grained haematite in all cases.

measurements on peat in the S. Pennines close to Sheffield, and in S.E. Finland, steel manufacture can be directly implicated in the generation of very high spherule concentrations. In the present case, iron oxides also enter the water directly through effluent discharge from various of the industrial processes as well as by natural run-off from the factory site. The present study uses both χ and SIRM as estimates of magnetic oxide content and B_{CR} as a rough indicator of magnetic mineralogy. Definitions of these parameters together with a full description of the methods and units of measurement used are given in the Appendix to Oldfield *et al.* (1978b).

Magnetic Measurements

Measurements of χ was carried out using a low-field susceptibility bridge circuit similar to that described by Molyneux & Thompson (1973). SIRM was determined by first placing samples in a 'saturating' magnetic field usually of 1 T (10 kOe) at room temperature and then measuring the magnetic moment induced in, and retained by, the sample after removal to zero field. A computerised slow-speed spinner magnetometer (Molyneux, 1971) was used for this remnance measurement.

Whole-core scanning of χ can be carried out at the rate of up to ca 10 cores per hour with the results obtainable within minutes in the form of numerical and graphic printout. Single sample χ measurements can be carried out at the rate of several hundred measurements per hour either on dried samples of known weight or samples of constant volume (normally *ca.* 10 ml). SIRM measurements can be completed at the rate of ca 2 per minute by using an electro-magnet and magnetometer in adjacent rooms. All the methods of measurement can be completed rapidly before other studies commence; they are completely non-destructive and there are very few subsequent types of analysis which they preclude.

Once measurements of SIRM have been completed, the coercivity of IRM (B_{CR}) can be determined by placing the sample in a series of increasing reverse fields, usually from 0.01 T (100 Oe) upwards, and measuring the resultant coercivity spectra obtained are roughly diagnostic of the magnetic mineral assemblage present in the sample (Dunlop, 1972).

Results

Figure 2 plots IRM against the logarithm of backfield for two filter samples and four sediment samples from the Elefsis Gulf. The strong parallelism between the curves points to a broadly similar magnetic mineral assemblage in the samples. Total saturation in a reverse field of 0.2 T and near total saturation at 0.1 T confirm the low anti-ferromagnetic haematite content and the dominance of ferri-magnetic spinel-type cubic oxides in the samples measured. The range of coercive fields between 0.02 T and 0.04 T indicates dominance of the magnetic minerals by relatively coarse grained magnetite. Recent sediment samples from the Gulf on which both χ and SIRM were measured gave low and constant SIRM/ χ values of 80 to 100. From the above it may be concluded that a relatively homogeneous magnetic mineral assemblage is present throughout and that 'magnetite' is the dominant magnetic mineral in both the filter papers and the recent sediments. In view of these inferences, it is reasonable to use both χ and SIRM as rough indices of the concentration of magnetic minerals in the samples.

Figure 1 plots the spatial distribution of sediment surface values of χ in contour form and confirms the dominance of the point source at the iron and steel works. Figure 3 shows down core variations in χ in several cores taken close to the industrial site. Core X was taken only 0.3 km from the artificial lagoon which receives the plant's effluents, the others at distances varying from 1 to 3 km. The recent nature

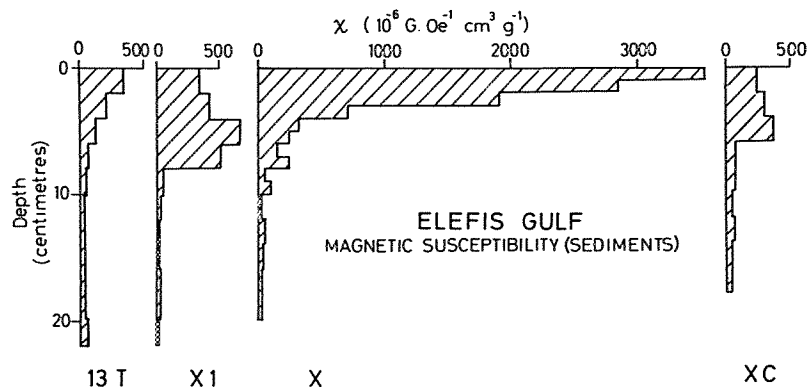


Fig. 3 Down-core variations in specific susceptibility for four cores close to the N.E. Corner of the Elefsis Gulf. χ is plotted as $10^{-6} \text{ G Oe}^{-1} \text{ cm}^3 \text{ g}^{-1}$.

of the peak χ values is clearly indicated. Figure 4 plots SIRM vs total iron in filter paper samples for the month of January. This was shown by means of chlorophyll *a* determination to be the period of minimum phytoplankton biomass. A strong linear relationship emerges suggesting that careful calibration and use of this parameter in the Elefsis Gulf may provide a rapid index of total particulate iron concentrations.

Conclusions

Measurements of magnetic susceptibility (χ) saturation isothermal remanent magnetization (SIRM) and coercivity of IRM (B_{CR}) provide a cheap, simple, safe, rapid, non-destructive basis for monitoring important aspects of marine particulate pollution where the main point sources include industrial complexes or iron ore loading/unloading facilities (cf. Boney, 1978) likely to generate

either directly, or through combustion processes, high concentrations of magnetic iron oxides, the methods are applicable to both sediment samples and filtrates and can be used on samples with dry weights as low as $2 \times 10^{-3} \text{ g}$. They have many advantages over routine methods of analysis not least of which are very considerable savings in time and the non-destructive nature of the techniques employed. Where, as in the Elefsis Gulf, magnetic forms of iron from anthropogenic sources form a roughly constant and probably high proportion of the total iron input, χ and IRM measurements (once calibrated by selected total iron determination) can be used to estimate total particulate iron concentrations in both the water and the sediment columns. They may also provide a very useful method for studying bottom circulation and particulate dispersion associated with several types of industrial and municipal discharge. Since, in many cases, a very high iron concentration is also associated with the presence of other, hazardous metals,

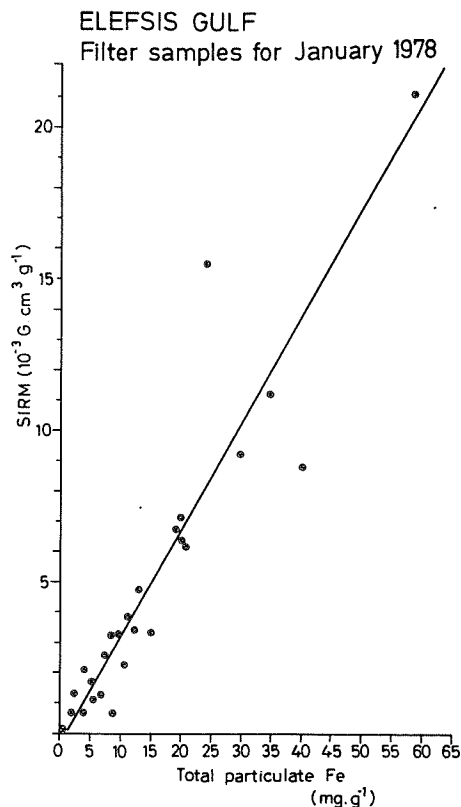


Fig. 4 Saturation isothermal remanent magnetization (SIRM) versus total particulate iron in filter samples for January 1978.

both in particulate and dissolved forms, the present approach could contribute to methods of preliminary assessment in a wide range of long term metal monitoring projects.

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Extractable Organics and Hydrocarbons in the Mediterranean Sea

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The level of tanker shipments in the Mediterranean is relatively high, being approximately 8 million barrels per day in 1972 and 1975 (Lloyds, 1972, 1975). This represents an important proportion of world-wide shipments which in 1972–1975 were approximately 30 million barrels daily. Because of the tanker traffic and the Suez Canal opening in June 1975, there was particular interest in obtaining hydrocarbon baseline data prior to changed conditions caused by this event. In response, the present study was carried out in the latter half of 1975 when 0–1 m and –5 m samples were collected along the tanker routes; Augusta, Sicily/Gibraltar; Augusta/Alexandria, and Augusta/Tunis. Total dispersed extractable organics (lipids) and nonvolatile hydrocarbons (C_{14+}) were measured.

Hydrocarbons were found to be complex mixtures of normal and isoparaffins, cycloparaffins and aromatics. Surface water showed a persistent pattern of *n*-paraffins of carbon numbers 16, 17, 18, and 19, with a preponderance of the C_{17} and C_{19} 's. Presence of these compounds and low concentrations of aromatics indicate that an important proportion of the hydrocarbons were of biogenic origin.

In other previous studies, Jardas & Munjko (1972) measured extractable organics off Vis Island in the Adriatic Sea. This is essentially coastal water which was found to contain extractable organics of 2.7 ppm at the surface and 1.2 pp, at –5 m. In the case of Jardas & Munjko and in our own study, extractable organics include all lipids, such as hydrocarbons, esters, fatty acids and alcohols. Marty & Saliot (1976) collected surface film and subsurface samples that were subsequently analysed for dissolved and particulate hydrocarbons. Of particular interest to this study are their measurements for water at

2 m and 50 m from approximately 80–130 km off Nice. Respective total hydrocarbon contents of 45 and 6 $\mu\text{g l}^{-1}$ (ppb) were found with 90% being in a dissolved state.

A previous study by this laboratory (Monaghan *et al.*, 1973) included the measurement of extractable organics and nonvolatile hydrocarbons in samples collected during two LNG tanker voyages between Brega, Libya, and Las Spezia, Italy. Findings of this study are presented for comparative purposes.

Sampling and Analysis

Before being delivered to the ship, the sampling gear, including glassware, pails and other equipment, was thoroughly rinsed with carbon tetrachloride and dried. On board ship, this apparatus was kept in an oil-free location. Details of sampling are described elsewhere (Brown *et al.*, 1975) but numerous precautions are taken to eliminate contamination while the sample is collected and during extraction of the water with carbon tetrachloride. In order to accurately gauge and correct for contamination in samples, sample blanks are taken daily. During this study, 18 blanks (9 deck, 9 engine room) were taken. Mean concentrations of 3.9 and 0.9 ppb were observed for extractable organics and nonvolatile hydrocarbons, respectively. One of the 18 blanks showed serious contamination in that its concentration even exceeded that of actual samples.

All samples were collected off the 4000 dwt. tanker *Esso Nordica* as she travelled the Mediterranean Sea carrying a cargo of lube oil base stock and ballast. In sampling from a moving tanker, water was scooped with a bucket from the surface whereas a subsurface sample was