FOREWORD

Marine contamination by petroleum, whether by natural seepage or by spills from ships at sea, by accidents in harbour or at offshore installations or by atmospheric or terrigenous input is by no means a new or rare phenomenon. In recent years however, the problems have been highlighted not only by the increased utilisation and marine transport of oil but also by a number of spectacular accidents which have raised questions about possible effects on the ecosystem. A number of detailed studies have been carried out in an attempt to answer these questions. The demands for such knowledge have been further increased by the various questions raised as a result of expansion of offshore exploration and exploitation for oil, particularly in environments hostile to these operations, in regions as far apart as the northern North Sea and the coast of Alaska.

Consequently, diverse aspects of the problem are being studied in several parts of the world by chemists and biologists who are often asking the same questions but using different approaches and sometimes producing conflicting views. Against this background, it seemed timely therefore to bring together a group of scientists from university, industry and government, actively engaged in such work, to examine and discuss common problems relevant to petroleum hydrocarbon contamination of the marine ecosystem and so a Workshop was sponsored by the International Council for the Exploration of the Sea, and held in Scotland at Aberdeen in September 1975.

The Workshop considered methodology, occurrence and fate in the environment, and effects on the ecosystem of petroleum hydrocarbons in the sea. Most of the papers presented and updated where necessary, are brought together in the present volume together with an edited version of the recorded discussion that followed each session. Of necessity, the reportage of the discussion is very brief although the proportion of time available for discussion compared favourably with that set aside for formal presentation of the papers. In preparing the discussion reports, the editors were assisted in particular by Dr R. Hardy, Dr R. Johnston, Mr P. R. Mackie and Dr I. C. White, and by comments from several contributors.

No attempt was made to produce specific recommendations but a study of the papers in this volume does give a clear indication of several lines of research which must be followed up before an adequate understanding can be reached of the effects of petroleum in the sea and it is evident that widespread monitoring operations will be fully effective only when the basis of our knowledge has been thus extended.

A list of participants to the workshop may be found in Appendix I.

A. D. McIntyre
K. J. Whittle

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SORPTION OF BENZENE ON PARTICULATE MATERIAL IN SEA WATER

Adam Zsolnay
Bermuda Biological Station for Research, St. George's West, Bermuda

The sorption of benzene on particulate material occurring naturally in sea water before, during and after a plankton bloom was studied. Sorption was significant, ranging from 4·8 to 28·4 μg benzene sorbed per mg of particulate material. The greatest amount of sorption took place during the plankton bloom, when the number of particles was also greatest. At other times the relationships between the amount of benzene sorbed, the amount of particulate material present and the degree of biological activity were not clear.

INTRODUCTION

A large amount of the material that is produced by the phytoplankton is excreted in a non-particulate form (Anderson and Zeutschel, 1970; Thomas, 1971; Wallen and Green, 1971; Chung, 1972). Since these organisms are capable of producing hydrocarbons (Clark and Blumer, 1967, Blumer et al, 1970; Blumer et al, 1971; Youngblood et al, 1971; Zsolnay, 1973; Zsolnay, 1975), one would expect an accumulation of these compounds in the upper hydrosphere unless a mechanism exists which transports them to the lower hydrosphere and to the sediment. One such possible mechanism is the sorption of the hydrocarbon on the particulate material, which then sinks to the sediment. This same mechanism could also transport hydrocarbons from petroleum pollution and spread them throughout the water column and to the sediment.

It has been shown that this sorption can occur with DDT (Pierce et al, 1974), with fatty acids (Suess, 1970; Meyers and Quinn, 1971), and with some hydrocarbons (Meyers and Quinn, 1973). All these studies, however, were done either on pure minerals or on materials from sediment that had been artificially added to sea water or to a saline solution. Although these studies provide valuable evidence that hydrocarbons and other weakly polar compounds sorbe on material that may be present in the sea, they do not take into consideration the enormous variety of the particulate material that is present in the hydrosphere, containing items such as faecal pellets, dead and living organisms, clay minerals, silicates, etc. Furthermore, the non-biogenic material can often have a surface coating of organic material, such as was found by Hamilton and Greenfield (1965) and by Suess (1973). This surface coating quite possibly has a major influence on the ability of a particle to sorbe additional organic material. This study was undertaken to determine whether or not a hydrocarbon, such as benzene, could be sorbed on the particulate material that is naturally present in the sea. It was also hoped to establish whether hydrocarbons sorbe particularly well on the large amount of "fresh" biogenic particulate material that is created during a plankton bloom.

METHODS

Surface water samples were taken from Kiel Bight before the spring plankton bloom, during it, and one week, two weeks, one month and two months after it. To each sample, 11 mg/litre of ^{14}C labelled benzene were added. The benzene had an activity of 1 μCi/ml. After mechanical stirring for 24 hours (50 to 70 rpm), 1 litre aliquots were vacuum filtered through a Nucleopore filter (pore size, 0·4 μm). Afterwards the filters were rinsed by drawing untreated sea water through them. Each filter was then extracted with toluene (5 ml) in an ultrasonic bath for 15 min, and the radioactivity of the extract determined on a Betascint BS 5000 scintillation counter.

A major difficulty was that some of the benzene which was sorbed on the particulate material, would sorbe on the filter. This made the use of blanks essential. It was found in a separate study that the Nucleopore filters used would sorbe no additional benzene after distilled water containing radioactive benzene (0·5 litre, 11 mg/litre) had been filtered through them. Therefore blanks were run by filtering in addition 0·5 litre aliquots from the sea water sample containing the radioactive benzene. Measurement of these aliquots showed the amount of benzene that sorbed on the filter itself and the amount that sorbed on particulate material in 0·5 litre of sea water. The filters through which 1 litre had been filtered contained the benzene sorbed on the filter and the amount that was sorbed on the particulate material from 1 litre. By subtracting the two values and multiplying by two, the amount of benzene sorbed on the particulate material from 1 litre of sea water was determined. Although the amount of benzene sorbed on the filters was relatively small (no more than 20 % of the amount on the particulate material), it varied considerably. Therefore to obtain statistically meaningful results, it was necessary to filter a fairly large number (about 11) of both the 0·5 and 1 litre aliquots from each sample.

A previous attempt had been made to separate the particulate material with a high speed centrifuge. This would have eliminated the difficulties associated with filtration. Unfortunately this proved to be impractical. Despite lengthy centrifugation times, the particulate material was easily disturbed when the centrifuge tube was handled.

The weight of the particulate material was determined by filtering three 1 litre aliquots with moderate vacuum through Nucleopore filters (pore size 0·4 µm) that had previously been heated to 50° and weighed. The filters were then heated at 50° until dry and reweighed.

RESULTS AND DISCUSSION

The average amount of benzene sorbed on particulate material, the average amount of particulate material and their ratios per litre of sea water are given in Table 34. In all cases a *t*-test showed that the average amount sorbed was significantly greater than zero, when a probability value of 0·05 or less was used as a criterion of significance.

Benzene was used in this study because of its relatively good solubility in water (McAuliffe, 1966). In this way, amounts could be realistically weighed and added directly without the need for additional organic solvents that might have changed the surface potentials on the particles. The fact that it was in true solution prevented this rather large amount of hydrocarbon material from forming an emulsion. There is a definite danger that an emulsion would have been retained on the filter in the same way that particles are. The amount of benzene used was far in excess of the amounts that would be present under non-pollution conditions, but in this preliminary study, the sole intent was to see if sorption can occur. No attempt was made to determine whether or not an adsorption isotherm would fit the data.

One can conclude that under the conditions described benzene does sorbe on the particulate material occurring naturally in sea water. Since most other hydrocarbons are considerably more hydrophobic than benzene, it is reasonable to believe that they would sorbe more readily. Once these hydrocarbons are on particles, they are readily available both to the food chain and for transport to the sediment. This result strengthens the rationale for using filter feeding organisms for pollution monitoring purposes. This rationale is that hydrocarbon pollution, whether acute or chronic, will sorbe on the particulate material which will then be filtered out by the filter feeders.

Table 34. Average amount of benzene sorbed on particulate material, average amount of particulate material and their ratio per litre of sea water

Date of sample		Number of samples	Benzene sorbed on part. mat. with s. d. of mean (µg/l)	Particulate material (mg/l)	Ratio benzene, sorbed/part. mat. (µg/mg)
15 Dec	1973	12	19·74 ± 8·84	1·49	13·3
26 Mar	1974	10	91·24 ± 14·6	3·34	27·3
19 Apr	1974	11	29·02 ± 4·42	1·61	18·0
25 Apr	1974	12	15·96 ± 2·08	0·93	17·2
15 May	1974	10	12·20 ± 3·30	0·43	28·4
13 Jun	1974	12	6·52 ± 2·42	1·36	4·8

The greatest amount of sorption occurred at the end of March, which is when the plankton bloom took place. This was also the time when the greatest amount of particulate material was present. As the bloom aged, the amount of sorption continuously decreased. As a result one would be tempted to conclude that benzene sorbes especially well on freshly created biogenic material, except that the December value, measured during a period of low biological activity, shows about the same sorption as the April one, from a period of relatively high biological activity. Furthermore, the amount of benzene sorbed is not purely a function of the amount of particulate material present. This can be seen from the fact that the benzene sorbed/particulate material ratio does not stay constant (Table 34). An analysis of variance confirms this, at the 0·01 probability level. In addition, one can see that the amount of particulate material increases sharply between May and June, while the amount of benzene sorbed shows a significant drop. In conclusion, benzene sorbes to a significant degree on the particulate material occurring naturally in the sea, but the extent of this sorption is controlled by factors more complicated than either the amount of particulate material present or the extent to which biological activity is going on.

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