Copyright ©

Aus dem Institut für Meereskunde an der Universität Kiel

Preliminary Study of the Dissolved Hydrocarbons and Hydrocarbons on Particulate Material in the Gotland Deep of the Baltic

von Adam Zsolnay

Vorläufige Untersuchung des gelösten Kohlenwasserstoffgehaltes und des Kohlenwasserstoffgehaltes des partikulären Materials im Gotland Tief (Ostsee) Zusammenfassung: Die Kohlenwasserstoffbestimmungen in natürlichen Gewässern, entweder mit dem gaschromatischen oder dem Infrarot-Verfahren, haben einige schwerwiegende Nachteile. Daher wurde ein spezielles Verfahren entwickelt: Das mit organischem Lösungsmittel extrahierte Material wurde dünnschichtchromatographisch auf einer sehr kurzen Platte getrennt, die mit 10% $AgNO_3$ Kieselgel überzogen war. Als Laufmittel wurde Hexan benutzt. In der Nähe der Front waren gesättigte und einkernige Kohlenwasserstoffe. Ein Versuch, die ungesättigten Kohlenwasserstoffe zu bestimmen, war erfolglos, da diese sich nicht von Verbindungen, die nicht Kohlenwasserstoffe waren, trennen ließen. Das die Kohlenwasserstoffe enthaltende Kieselgel wurde abgekratzt, mit Hexan eluiert, und die Kohlenwasserstoffe in einem CHN-Analysator bestimmt. Es konnten noch Mengen bis zu 1 µg gemessen werden. Im Gotland Tief wurden gelöste Kohlenwasserstoffe und ebenfalls in partikulärer Substanz bestimmt. Der durchschnittliche Wert für gelöste, nicht olefinische Kohlenwasserstoffe für alle Tiefen betrug 57,2±4,2 µg C/l, was 1,5% des gesamten, gelösten organischen Kohlenstoffs entspricht. Der durchschnittliche Wert für nicht-olefinische Kohlenwasserstoffe in partikulärer Substanz für alle Tiefen betrug 1,1±0,75 µg C/l; das entspricht 0,8% des gesamten partikulären organischen Kohlenstoffs. Das Verhältnis von partikulärem, nicht-olefinischen Kohlenwasserstoff-C zu gesamt partikulärem organischem Kohlenstoff hatte bei 110 m Tiefe ein Maximum und bei 10 m ein Minimum erreicht. Der Kohlenwasserstoffgehalt hatte keinen Einfluß auf das C_{org}/N Verhältnis in partikulärer Substanz.

Summary: The quantitative determination of hydrocarbons in nature with either gaschromatography or infrared has several major drawbacks. Therefore a special method was developed. The material obtained by extraction with non-polar solvent was separated on a very short thin layer plate of 10% $AgNO_3$ silica gel with hexane as the solvent. The saturated and benzyl hydrocarbons were found near the front, separated from non-hydrocarbon material. An attempt to separate the unsaturated hydrocarbons from non-hydrocarbon material was unsuccessful. The silica gel containing the hydrocarbons was eluted with hexane, and the hydrocarbons were determined in a CHN analyzer. Amounts as small as 1 µg could be determined.

Dissolved hydrocarbons and hydrocarbons within particulate matter were determined in the Gotland Deep, a Baltic Basin. An average value of 57.2±4.2 µg C/l as non olefinic, dissolved hydrocarbon was determined, which is about 1,5% of the total dissolved organic carbon. The average of non-olefinic hydrocarbon on particulate material was 1.1±0.75 µg C/l, which is equivalent to 0.8% of the total particulate organic carbon. The ratio of particulate, non-olefinic hydrocarbon to total, particulate organic carbon was the highest at 110 m and lowest at 10 m. The hydrocarbon content had no significant influence on the C_{org}/N ratios of the particulate material.

Introduction:

There have been numerous studies of the hydrocarbons in sediments (Blumer et al., 1970; Bray and Evans, 1961; Clark and Blumer, 1967; Evans et al., 1957; Hunt, 1961; van Hoeven et al., 1969; Kvenvolden, 1966; Meinschein, 1961, 1965, 1969; Oro et al., 1965 Oro and Nooner, 1967; Robinson et al., 1965; Stevens et al., 1956; Zsolnay, this issue), however outside of one or two measurements of the hydrocarbons in polluted waters (Blumer et al., 1970), the author is unfamiliar with any determinations of hydrocarbon contents in marine waters. The reason for this probably due to the fact that their concentration is very low, and their inertness makes them relatively hard to detect.

This inertness, however, makes them of interest both in the study of carbon cycles in nature (Meinschein, 1969) and in the fact that they are pollutants (Blumer, 1969; Blumer et al., 1970). An attempt was made to measure the background values of olefinic and of saturated and aromatic hydrocarbons as a function of depth in a deep Baltic basin. Since the amounts were so small and all the hydrocarbons, not just the linear ones, were to be determined a new experimental technique had to be developed.

Method

The previous methods for the determining of hydrocarbon content in the aquatic environment have generally been by means of a gas-liquid chromatograph or by the use of infrared spectra. In both cases the samples are usually extracted with an unpolar solvent and then purified on a column to separate the hydrocarbons from any other weakly or non-polar substance that might have been present in the sample. With gas-liquid chromatography the purified extract containing the hydrocarbons is then injected into the gas-liquid chromatograph and as each compound comes through the column a peak is created. The heigh of each peak varies proportionally with the amount of each compound that was injected. One difficulty is that there are innumerable hydrocarbons which have about the same retention time and as a result they do not form individual peaks but rather a broad buckle. To give a chromatogramme like this a total quantitative value is rather difficult. The second difficulty is that in order to have any hope of having all the hydrocarbon come off the column, it is necessary to let the gas-liquid chromatograph run up to an hour. Even then all the material might still not have come off, and any that does come off during the isotherm phase will become less and less distinct. In short although gas-liquid chromatography is very good for the study of linear hydrocarbon patterns, it is not truely suitable when rapid determinations of background hadrocarbon content is desired.

A rapid method for obtaining total hydrocarbon content is possible with infrared spectrometry. Here the extracted and purified sample is studied by an IR spectrometer and the values in a specific range are compared to a standard (Carlberg and Skarstedt, 1970). The first difficulty is that the method has a lower limit of detection of 0.05 mg/l which is too low for routine marine studies. The second difficulty is the selection of the proper standard. This according to Carlberg and Skarstedt (1970) results in an accuracy of only ± 26%.

The method used here was organic solvent extraction, followed by purification with thin layer chromatography. Thin layer chromatography was prefered in this phase of the research over column chromatography, since it enabled one to observe more readily the separation of the various compounds. The part of the TLC plate containing the hydrocarbons was then scrapped off, and the amount of hydrocarbon on it was determined by burning in a CNH analyzer.

In order to measure the dissolved hydrocarbons, one liter of filtered sea water was shaken with 15 ml. of hexane (MERCK uvasol grade) for 15 minutes in a separatory funnel, which was afterwards allowed to stand for 10 minutes. The hexane phase including a small amount of the top aqueous phase was then run into a centrifuge glass, which was then placed under vacuum in a desiccator until the volume was reduced by about half. The aqueous phase was then removed by means of a long thin pipette, and the solution was further concentrated until the volume was about 0.5 ml. This was then carefully applied to a TLC plate 1.5 cm wide with a 0.25 mm thick layer of silica gel with 10% $AgNO_3$. The solvent used was pure hexane (MERCK uvasol grade), and the front was allowed to advance 5 cm. The top 1.5 cm was then scrapped off and placed into a small scintered glass filter. The organic material was eluated off with 0.7 ml of pure hexane, which was allowed to drip into a test tube containing a glass fiber filter that had previously been cleaned by being heated to 500° C overnight. The test tube was placed briefly in a desiccator under vacuum to evaporate the hexane. The filter was then removed and burned in a CHN analyzer and the results were obtained as hydrocarbon carbon. Amounts as small as 1 µg C can be readily determined on the analyzer.

Repeated extraction of the same sea water sample showed that 85% of the dissolved hydrocarbons that were extractable were extracted with the first 15 ml of hexane. Tests with standards showed that saturated linear hydrocarbons, isoprenoid hydrocarbons such as pristane, and alkyl benzenes were to be found within 1.5 cm of the front, while olefinic hydrocarbons, naphtalene, chloresterol, and esters of fatty acids remained further than 1.5 cm away from the front. Although chlorinated pesticides were not tested, one can assume that their concentration is in normal non-polluted water much lower (Ahling and Jensen, 1970) than that of the hydrocarbons. Therefore with this test one obtains the concentration of what here will be called the non-olefinic hydrocarbons consisting of saturated hydrocarbons and hydrocarbons with only one aromatic ring. It was also hoped to measure the total hydrocarbons by running an aliquot sample on silica gel without silver nitrate. This way the olefinic hydrocarbons could be determined by substracting the non-olefinic hydrocarbons from the total hydrocarbons. In reality however, non hydrocarbon material such as phytol could not be fully separated from the hydrocarbons when silver nitrate was absent from the silica gel. In addition highly unsaturated hydrocarbon material such as β-carotene did not move sufficiently rapidly with the hexane solvent.

The hydrocarbon content of the particulate material was determined as follows. The particulate material was filtered out of the sea water with a Whatman GF/C glass phase filter that had been cleaned by heating overnight. The filter was dried at room temperature in a desiccator. Afterwards it was placed in a centrifuge glass containing 4 ml of 5 : 3 (v : v) methanol-hexane (all solvents MERCK uvasol grade) and placed in an ultrasonic extractor for 15 minutes. The methanol and hexane were then divided into two phases by the addition of 0.25 ml of twice distilled water, and the entire contents were again placed in an ultrasonic field for 15 more minutes. The centrifuge tube was then removed and centrifuged. Afterwards the hexane layer was removed by means of a pipette and treated in the same way as the material obtained by liquid-liquid extraction above. Repeated extractions of the same particulate material showed that 68% of the non-olefinic hydrocarbons were extracted with a single extraction. The reason that the extraction from particulate material is more difficult than the extraction from the sea water is most likely due to the fact that the hydrocarbons can be absorbed within clay matrices (Weiss, 1969). Another reason could be the hydrocarbon absorption within humic acid material (Ogner and Schnitzer, 1970).

The standard deviation of the methods were obtained by making multiple determinations from the same homogeneous sample.

In addition the particulate organic carbon and C_{org}/N ratios were determined by means of the CHN analyzer. Here the filters were pretreated with 1% HCl solution in order to remove any carbonate that might have been present. They were then dried in a desiccator overnight and burned directly in the analyzer.

Samples

It was hoped to have samples from four different stations in the Gotland Deep so that the general distribution of hydrocarbons in this basin might be determined, however, stormy weather enabled only two stations to be made. They were station 15 A at 57°20'N, 20°03'E and station S 3 at 57°13'N and 20°04'E. Both stations had a depth of 230 m, and were made during the September cruise 1970 of the R. V. "ALKOR". Up to 6 l of water were collected at each depth and filtered through 2.5 cm diameter Whatman GFC glass phase filter pairs. In each case the uppermost filter of the pair was used as the experimental while the bottom filter was used as the control when organic particulate carbon or particulate hydrocarbon were determined. Since the amount of water that could be filtered through any one filter pair was limited, three filter pairs were usually used. Through the first one only 1 liter was filtered and, it was used to determine organic particulate carbon. Then 2.5 liters were filtered through each of two other filter pairs, however, a maximum of only 1.5 liters of 10 m water could be filtered through one filter pair. The filters from any one depth, that were not used for the particulate organic carbon determinations, were analyzed together for the hydrocarbon content by the method decribed above. The control filters were anylyzed in the same way, and their values were substracted from the experimental ones. One liter of the filtered sea water was analyzed for dissolved hydrocarbons.

Conclusions

The conclusions can all be seen in Table 1. By non-olefinic hydrocarbon is meant saturated hydrocarbons and aromatic hydrocarbons containing no more than one ring. The values after a ± indicate the standard deviation of the measuerement.

Table 1

		Particular Material		Dissolved Material
Depth Meters	Total C_{org} µg/l	C_{org}/N (Atoms)	Non-olefinic hydrocarbon Carbon µg/l	Non-olefinic hydrocarbon Carbon µg/l
Station 15A				
20	229.2	6.92	0.9 ± 0.75	48.0 ± 4.2
70	75.9	10.03	1.0 ± 0.50	58.0 ± 4.2
110	98.1	7.68	2.3 ± 1.20	57.5 ± 4.2
150	72.7	8.06	1.0 ± 1.00	58.5 ± 4.2
200	88.0	10.19	0.5 ± 0.75	64.0 ± 4.2
Station S 3				
10	450.1	10.70	1.0 ± 0.75	
90	92.3	7.62	1.0 ± 0.60	
110	103.9	6.58	1.7 ± 1.20	
150	94.8	7.05	0.8 ± 0.60	
200	97.0	6.72	0.8 ± 1.33	

Discussion

The particulate hydrocarbon values are most likely on the low side, since the extraction procedure was not capable of readily extracting all the hydrocarbons present. In addition the standard deviation was very high when compared to the size of the values. Therefore, any conclusions drawn have to be of a rather tentative nature. The average amount of particulate non-olefinic hydrocarbon carbon to total particulate organic carbon was 0.8%. At both stations the highest particulate non-olefinic hydrocarbon/organic carbon ratio was to be found at 110 m (Table 2). The lowest ratio was found to be at the 10 m level. This at first might be considered to be surprising unless one considers the fact that olefinic hydrocarbons were not measured. Organisms are much more likely to have olefinic hydrocarbons than saturated ones, and they have a great many labile organic

Table 2

Depths Meters	% non-olefinic hydrocarbon carbon of total organic carbon in particular material
Station 15 A	
10	0.4
70	1.3
110	2.3
150	1.4
200	0.6
Station S 3	
10	0.2
90	1.4
110	1.6
150	0.8
200	0.8

compounds, which disappear at lower depths and therefore enable the more stable hydrocarbons to make up a greater percentage of the total organic carbon as one goes below the euphotic zone.

The dissolved hydrocarbon values are considerably larger than the particulate hydrocarbon ones. Since dissolved organic carbon was not determined, it is not possible to see how the dissolved, non-olefinic hadrocarbon/organic carbon ratio varies with depth. However, if one takes the average dissolved organic carbon value of 3.7 mg/l that EHRHARDT (1968) found in the Gotland Deep one has an average dissolved, non-olefinic hydrocarbon/organic carbon content of 1.5%. One would expect that hydrocarbons, being strong waterphobes, would have a larger hydrocarbon/organic carbon ratio for particulate material than for dissolved material, but this is here not the case. The hydrocarbon content had no significant influence on the C_{org}/N ratios of the particulate material.

The method used here is felt to be superior to either the gasliquid chromatographic or infrared one for the determination of background hydrocarbon values in natural waters. One serious weakness is the fact that olefinic hydrocarbons were not detectable. Another is the fact that standard deviation was so high. However, at present, research is going on in this laboratory in order to overcome these difficulties and to make the preparations more rapid and less cumbersome, therefore, this report is to be considered as preliminary, but due to the lack of information on the hydrocarbon content in natural waters, it was decided to make the results to date known.

The technical assistance of Mr. Jürgen Heinemann is here gratefully acknowledged. This work was financed by the German Research Association (Deutsche Forschungsgemeinschaft).

Bibliography

AHLING, B. and S. JENSEN (1970): Reversed liquid-liquid partition in determination of polychlorinated biphenyl (PCB) and chlorinated pesticides in water. Analyt. Chem. 42, 1483—1486.

BLUMER, M. (1969): Oil pollution of the ocean. "Oil on the Sea", D. P. Hoult, Editor, Plenun Press.

Blumer, M., G. Souza, and J. Sass (1970): Hydrocarbon pollution of edible shellfish by an oil spill. Mar. Biol. **5**, 195—202.

Bray, E. E., and E. D. Evans (1961): Distribution of n-paraffins as a clue to recognition of source beds. Geochim. cosmochim. **22**, 2—15.

Carlberg, S. R. and C. Bo Skarstedt (1970): Determination of small amounts of non-polar hydrocarbons (oil) in sea water. Meddelande från Havsfiskelaboratoriet. **96**, 10 pp.

Clark, R. C. jr. and M. Blumer (1967): Distribution of n-paraffins in marine organisms and sediments. Limnol. Oceanogr. **12**, 79—90.

Ehrhardt, M. (1969): The particulate organic carbon and nitrogen and the dissolved organic carbon in the Gotland Deep in May 1968. Kieler Meeresforsch. **25**, 71—80.

Evans, E. D., G. S. Kenny, W. G. Meinschein, and E. E. Bray (1957): Distribution of n-paraffins and separation of saturated hydrocarbons from recent marine sediments. Analyt. Chem. **29**, 1858—1861.

Van Hoeven, W., J. R. Maxwell, and M. Calvin (1969): Fatty acids and hydrocarbons as evidence of life process in ancient sediments and crude oils. Geochim. cosmochim. **33**, 877—881.

Hunt, J. M. (1961): Distribution of hydrocarbons in sedimentary rock. Geochim. cosmochim. **22**, 37.

Kvenvolden, K. A. (1966): Evidence for transformations of normal fatty acids in sediments. In Advance in Organic Geochemistry, G. D. Hobson and G. C. Speers, Editors, Pergamon Press, Lond.

Meinschein, W. G. (1961): Significance of hydrocarbons in sediments and petroleum. Geochim. cosmochim. **22**, 58—64.

Meinschein, W. G. (1965): Soudan Formation: organic extracts of early Precambrian rocks. Science **150**, 601—605.

Meinschein, W. G. (1969): Hydrocarbons-saturated, unsaturated and aromatic. In: Organic Geochemistry, G. Eglinton and M. T. J. Murphy, Editors, Springer-Verlag, Berlin, New York. pp 330—373.

Ogner G. and M. Schnitzer (1970): The occurrence of alkanes in fulvic acid, a soil fraction. Geochim. cosmochim, **34**, 921—928.

Oro, J., D. W. Nooner, A. Zlatkis, S. A. Wikström, and E. S. Barghoorn (1965): Hydrocarbons of biological origin in sediments about two billion years old. Science **148**, 77—79.

Oro, J., D. W. Nooner (1967): Aliphatic hydrocarbons in Precambrian rocks. Nature **213**, 1082.

Robinson, W. E., J. J. Cummings, and G. U. Dineen (1965): Changes in Green River oil-shale paraffins with depth. Geochim. cosmochim. **29**, 249—258.

Stevens, N. P., E. E. Bray, and E. D. Evans (1956): Hydrocarbons in sediments of Gulf of Mexico. Bull. Amer. Assoc. Petrol. Geol. **40**, 975—983.

Weiss A. (1969): Organic derivatives of clay minerals, zeolites, and related minerals. In: Organic Geochimstry, G. Eglinton and M. T. J. Murlhy, Editors, Springer-Verlag, Berlin, New York. pp. 737—781.