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by Hubert Hellmann

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Determination of Paraffins in Waters

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- Results of IR Spectroscopy and Gas Chromatography -

by Hubert Hellmann

As main constituents of mineral oils, paraffins are indicators of water pollution; at the same time, however, they are products of the metabolism of living things, in particular of micro-organisms and of the phytoplankton. The resulting consequences with respect to the estimation of oil contamination are described and a number of examples is given.

1. INTRODUCTION

Paraffins are the major component of many raw oils and important refined products, for example, the fuel oil EL^{*)}. The analysis of methyl and methylene groups of which the paraffins are composed can therefore serve as proof of mineral oil contamination in the event of accidental oil spills - this includes ground and surface waters.

On the other hand, it is known that micro-organisms and plankton produce paraffins in the course of their metabolism. At the latest, these will be released to the water phase when these materials die off, and possibly they will be released before that. According to WASSOJEWITSCH (1), for example,

*) In the following, the paraffins are also called hydrocarbons.

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bacteria and plankton annually synthesize 500,000 tonnes of hydrocarbons in the Black Sea.

If one bears in mind that the above micro-organisms not only produce (2,3) but also biochemically decompose hydrocarbons, and that one or the other process is subject to seasonal variations - quite apart from other effects - the usefulness of paraffin analysis for estimating mineral oil contamination becomes a problem, in our opinion. This is not to say that paraffins are unsuitable as mineral oil indicators, merely that the determination of the paraffin concentration in a water sample is not sufficient by itself. Rather, the so-called background has to be known. By background we mean those hydrocarbon concentrations present in the environment without the artificial addition of mineral oils.

The determination of this background is not easy, even for ground waters, and it does not necessarily give unambiguous results directly.

In flowing waters with variable discharge and variable sewage loads (without mineral oils!), it is to be expected that the background will not only depend on the parameters mentioned above, but also on the time of year, the sample location, the water temperature and others.

The determination of the background therefore usually presents a difficult problem.

As far as our own work is concerned, we tried to analyse the hydrocarbons in the Rhine at Koblenz with respect to their origin. At the same time, it was possible to include a large number of drinking water wells in this study. The method of analysis itself is discussed in the Appendix.

HYDROCARBONS IN THE RHINE AT KOBLENZ

2.1. Characteristics of the Sample Location

The water samples were taken from the river at the 590.3 km marker on the left bank of the Rhine. This point lies approximately 590 km below the exit of the Rhine from Lake Constance, that is approximately 160 km below the mouth of the Neckar River and approximately 100 km below the mouth of the river Main. For the analysis of the measured results, it is important to realize that the Rhine accepts considerable amounts of sewage near Basle (150 river km), Mannheim (mouth of the Neckar river) and Mainz (mouth of the river Main). Ships travel the Rhine from Basle onwards, and this traffic increases from Mannheim onwards. The section of the river from Mainz to Koblenz is known as a tourist region, because there is much turbulence in the water (mountainous region) and there are no significant disposals of sewage into the river. The mean monthly flow rate of the Rhine at the sample point lies between about 1200 m³/s and 1800 m³/s.

2.2 Hydrocarbon Concentration as a Function of Discharge

Figure 1 shows the hydrocarbon concentrations in Rhine river water that were measured recently for various discharge rates, i.e., from 1968 to 1970. These measurements covered a discharge range from 600 to over 4000 m³/s. In our opinion, it is significant that strong and rapidly changing variations in the discharge occurred mainly in conjunction with rain falls in the medium high mountains, while slower increases and decreases in the discharge were connected with melting snow in the high mountains. As a rule, the largest changes are to be expected in winter and spring.

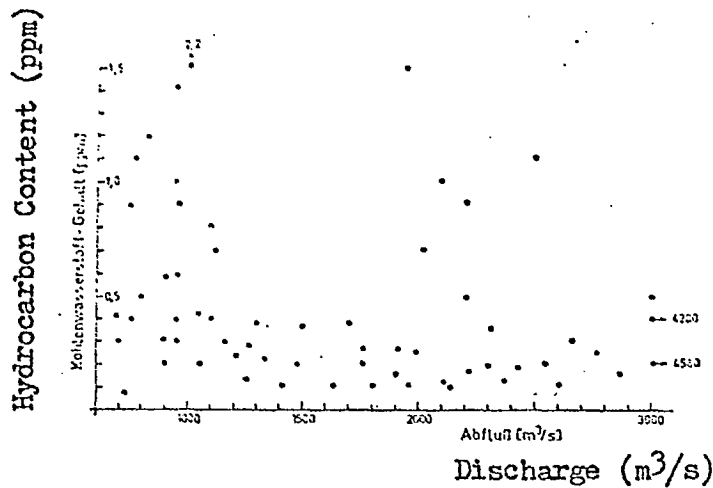


Figure 1. Hydrocarbon content in Rhine water 1968/70 in relation to discharge

It may be seen from figure 1, as well as from (4) and (5), that the hydrocarbon concentrations range from 0.1 to 2.5 mg/l, and that they occasionally reach 8 mg/l. The concentration is fairly uniform (0.1-0.4 mg/l) over a wide region of discharge; however, even at high water (4200 m³/s) it is still 0.2 to 0.4 mg/l, therefore it doesn't drop off below 0.2 mg/l.

At low water, there is a large increase at times; however, the large scatter in the hydrocarbon concentrations of samples taken from equal flows and also taken at the same time of day is more characteristic. Above all, a considerably greater than average hydrocarbon concentration is observed for a rapidly increasing flow rate in the river; it just as quickly drops back down to a smaller value.

From this it may be seen that a relationship between the concentration and discharge may only be evident under certain conditions. In particular, high variations in concentration for the same discharge, high concentrations during rapid increases in flow, and the peak values occurring occasionally

all indicate that mineral oil contaminations are superimposed on the hydrocarbons already present in the river. For very high flows ($> 3000 \text{ m}^3/\text{s}$), the effect of added man-made hydrocarbons should be negligible. The origin of the "residual concentration" of hydrocarbons still remaining will be discussed in more detail in section 2.4.

2.3 Hydrocarbon Concentration as a Function of the Time of Year

Up till now, we were only able to use the first months of 1971 for determining the suspected influence of seasonal biochemical processes on the hydrocarbon content of Rhine river water. Largely this was because for several months the water flow remained almost constant (see figure 2) - it was equivalent to that of mean low water and was therefore eliminated as a variable in determining its effect on the hydrocarbon content.

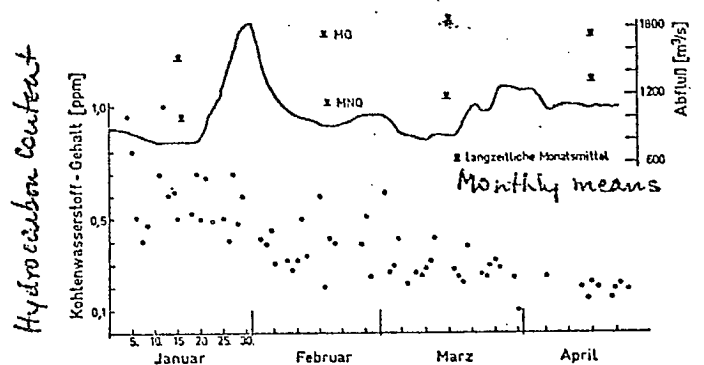


Figure 2. Hydrocarbon Content in Rhine Water, January - April 1971

It may be seen from figure 2, that the hydrocarbon concentration lies between 0.1 and 1.0 mg/l. The minor role played by the water flow in the large changes in concentration is quite evident here. It is worth noting the range of variation of the measured values in consecutive months: January, 0.4-1.0; February, 0.2-0.6; March, 0.2-0.4 and April, 0.1-0.3 mg/l. -It is easy to

recognize the decreasing trend of the hydrocarbon concentration from January (mean value of 0.6 mg/l) to March (0.3 mg/l) and April (0.2 mg/l). The same decrease in concentration was observed for the total extract (with respect to CCl_4 as extraction agent) in the months from January to April, 1971.

A detailed discussion of the causes of this decreasing trend in hydrocarbon concentration seen in this single series of measurements is naturally not going to be very rewarding. Nevertheless, there are some indications that biochemical processes (decomposition of oil) become increasingly more significant in the period from January to April.

Seasonal variations in the hydrocarbon concentrations of ground waters were also observed (6).

The results described in sections 2.2 and 2.3 primarily point to the necessity of continuing with these studies, and to also perhaps include other parameters so that the role of biochemical processes may be explained completely.

2.4 Hydrocarbon Concentrations in Suspended Solids

The numerical data given in figures 1 and 2 refer to the total hydrocarbon content in a liter of water, i.e. the totally dissolved part plus the part attached to suspended solids.

Although the water flow corresponding to a certain dissolved hydrocarbon concentration suffices as a reference point, the suspended solid content (which is determined at the same time) should also be given when hydrocarbons are absorbed in suspended solids or bound to them in some other way (see below). It is known (see also (7)), that the flow of suspended solids increases with increasing discharge. Apart from some special cases, which we will not consider

here, the relationship between drainage and suspended solid flow is given by the equation

$$S = a \cdot Q^b \quad (1)$$

where S = suspended solid flow in g/cm^3 , and Q = discharge in m^3/s .

For the inorganic component of the suspended solids of the Rhine near Koblenz, the constants a and b had the following values in 1967/1968:

$$\begin{aligned} a &= 4.1 \times 10^{-4} \\ b &= 1.44 \end{aligned}$$

For the organic component we obtained

$$\begin{aligned} a &= 2.3 \times 10^{-2} \\ b &= 0.70. \end{aligned}$$

As a result, then, the following equation applies to the suspended solids:

$$S = 4.1 \times 10^{-4} Q^{1.44} + 2.3 \times 10^{-2} Q^{0.70} \quad (2)$$

The hydrocarbon concentration obtained from the suspended solids after settling and filtration had the following relationship to the suspended solid flow:

$$C_s = 68.6 \times S^{-0.99} \quad (3)$$

where C_s is the hydrocarbon concentration in mg per g of suspended solids, and S is the suspended solid flow in g/m^3 .

The hydrocarbon concentration in the water is therefore

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$$\begin{aligned} C_s &= 68.6 \times S^{-0.99} \quad (4) \\ C_w &\approx 68.6 \end{aligned}$$

where C_w is the hydrocarbon concentration in units of mg/m^3 water.

The hydrocarbon concentration fixed in the suspended solids is therefore 70 micrograms per liter, and it is seen to be virtually independent of the discharge. The hydrocarbon load flowing down river each second is proportional to the discharge, and therefore increases with it. For average flow rates, it is 105 kg/s or roughly 10 t/day at Koblenz.

As far as deciding the origin of the hydrocarbons attached to the suspended solids ^{*)} is concerned, we consider it significant that the hydrocarbon load changes with the discharge analogous to the solid load, and that even in waters free of mineral oil the hydrocarbon concentration of the sediments is in close correlation to the amount of organic material in the sediment. The comparison of the undissolved hydrocarbon concentrations found in the Rhine at Koblenz with numerical values obtained from unaffected water sediments leads us to conclude that we are dealing with the natural background here. Occasionally one can observe higher hydrocarbon concentrations - with respect to the suspended solids - and ~~for~~ these can simply be interpreted as being caused by mineral oil contamination. We did not find a preferential absorption of mineral oils in the suspended solids of the Rhine; we did not expect it either, because on the one hand the hydrocarbons from smaller oil contamination accidents appear in the dissolved form to by far the greatest extent, and on the other hand the concentration of suspended solids in flowing waters is normally too small to effect significant absorption of the oil.

*) The method of sample preparation that was used presumably did not enable all the hydrocarbon content to be detected, since complete destruction of the cell walls, particularly those of diatoms, can only be achieved with special techniques (for example, ultrasonics). The measured values might be a little low.

3. HYDROCARBONS IN GROUND WATERS*)

The same arguments that were presented for the background in flowing waters apply to ground waters, however, with some modifications. Even though the variations in discharge do not have to be considered here in the sense in which they were for flowing waters, there are still a number of other parameters which make definite determinations no less difficult than for flowing waters. For instance, the following parameters now become significant: the geological structure carrying the ground water, the type of ground and its utilization, permeability of the various ground layers, depth of the sample point, vegetation period and many others.

Experience so far has been based on water samples taken from public water works and ground water observation tubes. These show that the hydrocarbon concentration rarely exceeds 0.1 mg/l or more. It is not yet possible to assign values to the actual background component from natural sources and to the component corresponding to man-made additions.

4. GAS CHROMATOGRAPHY RESULTS

The surface and ground water results presented in sections 2 and 3 were obtained by means of IR spectroscopy. We are dealing only with data on concentrations. The most important results are as follows:

- The hydrocarbon concentration in the Rhine at Koblenz lies between 0.2 and 1.0 mg/l for most of the time. Higher concentrations are only observed for short periods of time.

*) A detailed report on the experimental results is being prepared.

- Pronounced variations in the measured results with respect to the time of day indicate mineral oil contamination.
- There is evidence of considerable biochemical decomposition.
- A relatively small fraction of the total hydrocarbon concentration is attached to solids.
- The hydrocarbon concentration was predominantly below 0.1 mg/l in ground waters that were sampled.

Gas chromatography gives more extensive information in the sense that it can identify the paraffins present in the water samples. Figure 3 shows a typical spectrum. It shows that the concentration of n-paraffins (straight chains) is much greater than that of the iso-paraffins (branched chains) and naphthalene, as is also the case for mineral oils. The series more or less starts with decane (C_{10}) and ends with triacontane (C_{30}). It usually peaks at two maxima, one at $C_{14} - C_{17}$ and the other at $C_{24} - C_{26}$. In the following, we consider only the n-paraffins, and even so only those whose concentration does not fall below about 5 % of the most abundant compound - this will be dictated by the full scale deflection of the recorder. Figure 4 gives some typical results in schematic form.

Spectrum 1 shows the paraffin distribution of all the water samples from January to February 1971. The distribution always shows two maxima at C_{17} and C_{26} , and two boiling regions can be recognized. The lower boiling region covers the paraffins from C_{13} to C_{22} , and the higher boiling region from about C_{20} to over C_{30} . The last one is represented a little more strongly in the spectrum.

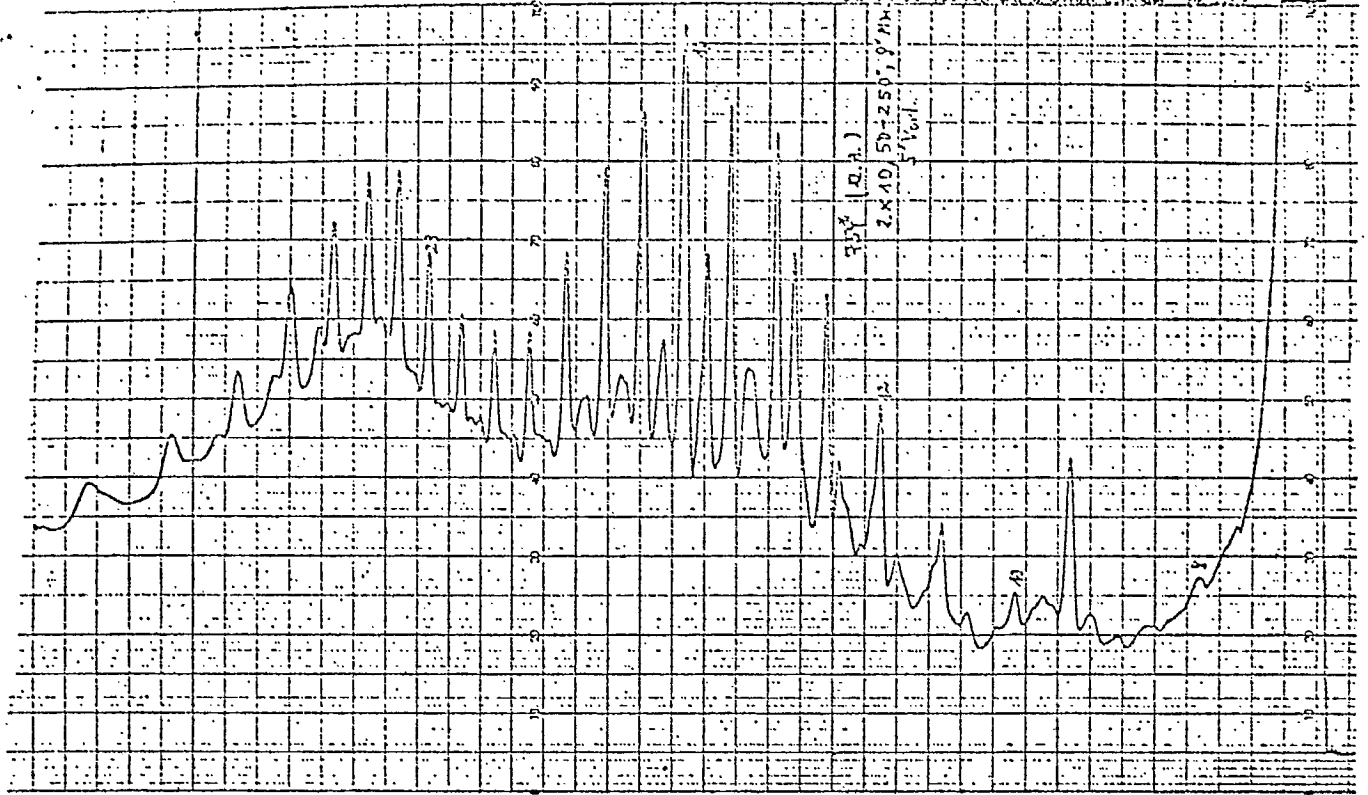


Fig 3.

Gas chromatogram of paraffin fraction of a Rhine water extract

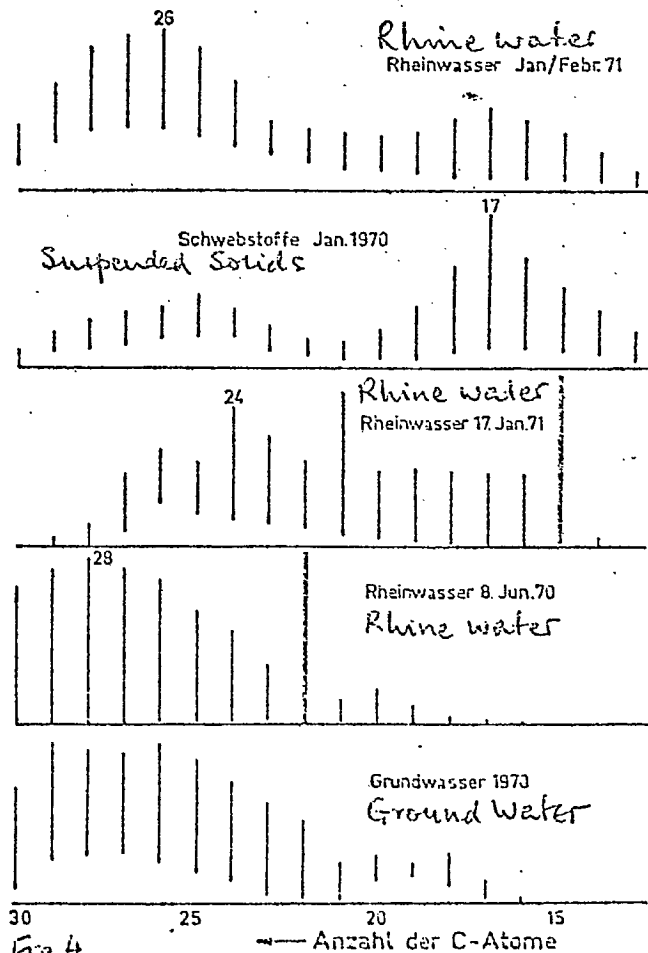


Fig 4

Abb. 4 Verteilung von Normal-Paraffinen in Gewässern
Distribution of n-paraffins in waters

Spectrum 2 shows the paraffin distribution of a suspended solid sample taken on 8. 1. 1970. Two maxima can be seen at C₁₇ (very large) and C₂₅ (very small). The centre of the paraffin distribution is definitely in the lower boiling region. Completely opposite to this is the paraffin distribution found in a water sample (10 l water including suspended solids) taken on 17. 1. 1971. An unusually strong maximum is present at C₁₅, and there are additional strong maxima at C₂₁ and C₂₄. The paraffins from C₁₆ to C₂₀ are about equal in intensity. One gets the impression that the primary spectrum similar to spectra 1 and 2 has been doped with additional paraffins at C₁₅ and C₂₁.

The paraffins in spectrum 4 taken on the 8. 6. 1970 are quite different again. Its centre point lies in the high boiling region (C₂₀ to C₄₀). A remarkably strong maximum at C₂₂ is followed by a maximum at C₂₈ in the series. There are relatively few paraffin components below C₂₀.

Spectrum 5 is the only representative of ground water paraffin distributions. It was determined from 100 ground water samples at just as many locations. There is a surprising similarity with spectrum 4. Again the paraffins are mainly distributed over the higher boiling region from C₂₀ onwards with not very clearly defined maxima at C₂₆ and C₂₉.

To summarize the above results, one may say:

- The n-paraffin distribution of water and suspended solid samples as a rule is composed of two boiling regions ranging from approximately 180° - 350° and 350° - 400° C, and they are characterized by maxima at C₁₅ - C₁₇ and C₂₅ - C₂₆.
- Rhine water samples tend to indicate low boiling paraffins in the p.1/ winter (December - January), and high boiling paraffins in the

summer. In the intervening months, the paraffin distribution shifts from the low boiling region to the high boiling region.

- The sampled ground waters had a paraffin distribution which corresponded to the summer characteristics of Rhine water.
- In the Rhine, deviations from the so-called "norms" are only observed rarely and for short periods of time.

SUMMARY

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Summary

The examination of water samples taken from the Rhine near Koblenz during the years 1968-1971 shows that hydrocarbon concentrations as well as the distribution of the paraffins are subject to more or less characteristic changes in time. For example, seasonal biochemical processes overlie the influence of the flow rate, and the naturally formed hydrocarbons overlap the ones that have been added artificially. Findings indicate that the hydrocarbon disintegration taking place in the Rhine river in spring is much more pronounced than the one noted in winter. In the same way, the main trend in the distribution of paraffins shifts from the low-boiling paraffines (C₁₀-C₂₀) to the high-boiling ones (C₂₀-C₄₀). At present, the quantity of hydrocarbons artificially added within the framework of this dynamic process cannot be determined exactly because the background itself changes continuously.

Groundwaters carry their own, specific problems in respect of the hydrocarbon contents. The latter are much lower than in the case of the examined Rhine water. The hydrocarbon distribution is limited to the high-boiling fraction and resembles the summer characteristic of the Rhine water problem.

Appendix

25 ml CCl₄ were used per liter of water in the extraction; the polar substances contained in the extract were separated in a column loaded with Al₂O₃. The IR determination was made in an IR tube of 10 mm diameter (9). For further details of this, see (8).

For the gas chromatographic analysis, the paraffins were first separated from the aromatic substances on a thin-layer plate coated with silica gel, hexane being used as a solvent. The paraffins were then separated in a gas chromatograph with the aid of a separating column (silicon rubber). The separation was carried out over the temperature region from 50 to 280° C, with a temperature rate increase of 8° C per minute (10), (11).

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- (10) Gas Chromatograph, Model 900 of the same Company, separating column 67 S, 20.58, solvent CCl₄, Recording by FID, nitrogen carrier gas.
- (11) I am grateful to Mrs. M. Holeczek of the Federal Institute of Water Science for the analytical determinations.

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