Large scale experiments on groundwater pollution by oil spills- interim results

Introduction

A description of groundwater pollution by oil spills was presented [1, 2] in 1972, 1973, together with an announcement of large scale experiments.

As illustrated by fig. 1 of reference 1, the pollution is confined to a groundwater channel of limited width and over a limited depth interval. Within the aquifer the polluted stream will run side by side with unpolluted water without mixing with it to any worthwhile extent. Where a polluted stream — in many cases, after years of

PROF. IR. D. N. DIETZ
TH Delft,
afdeling der Mijnbouwkunde

travel — ends up in a well or a drain, unpolluted water will also enter the well or drain from other directions and from other depth intervals. In real cases pollution will therefore only be observed in a much diluted form. Our experiments were aimed at singling out the undiluted, polluted water, leading of course to higher concentrations of pollutants and higher taste numbers than will ever be observed in practice. These tests involve twelve large sand columns, which were put into operation in 1974.

All columns, except two control tests, contained a layer of oil polluted sand on top of the groundwater bearing part of the sand in such a way as could have been caused by an oil spill (fig. 1). These columns, buried in natural outdoors conditions, were subject to the natural seasonal weather conditions. The downward velocity of the groundwater is governed by the rainfall

and under the local conditions this velocity is about 1 m/year on the average. It is therefore roughly equivalent to express chemical changes in the groundwater per year travel time or per meter travel distance.

From the groundwater in these columns large samples were extracted at five depth levels and these samples were analysed in great detail. The table presents four such analyses, of which there will ultimately be 216. The methods of analysis, some of them specially developed for the purpose, have recently been described by de Vos, Bridié and Herzberg [3].

The tests are planned to run for 3 years, some of them will be extended for an additional 3 years. A full study of the results will take several years more. Presently available observations over more than two years, however, warrant an interim publication.

Fig. 1 - Sandcolumn with oil polluted layer and connections to sample groundwater.

Equipment

The sandcolumns, contained in concrete walls are 2 x 2 m² wide. Thus, the natural infiltration caused by rainfall minus evaporation is sufficiently large, so that the withdrawal of the numerous 10 liter water samples, being less than 5 % of the main stream, causes only a minor disturbance.

The pancake of polluted sand, high in the column, was created by the addition of some 10 % saturation of light fuel oil. Light fuel oil was chosen, because its components are not so light that they evaporate easily nor so heavy that they hardly dissolve in water. Light fuel oil was therefore considered to offer the severest test. For some experiments we used an artificial fuel oil, a mixture of only 4 representative pure components. This should give us a better chance to keep track of all components and their partly oxidized products.

The outlet at the bottom of each column is regulated by an overflow pipe. The water-level in the column is varied stepwise: at the high winterlevel the oil pancake is submerged, at the lower summerlevel the ground air has access to the pancake.

Chemistry

Aerobic - anaerobic

Rainwater carries free oxygen is solution. In summertime ground air can also supply free oxygen.

Immediately below the oil pancake the ground-water was always found to be without any measurable concentration of free oxygen. Obviously aerobic conditious can only prevail in the top of the oil pancake. Anaerobic conditions exist in the lower part of the pancake and also in the groundwater column underneath. This conclusion confirms the findings of earlier investigations [4, 5].
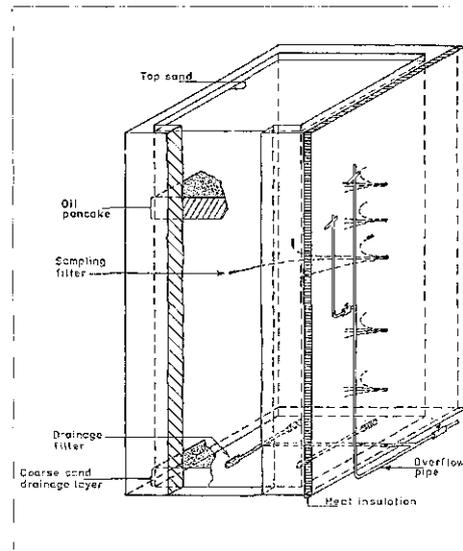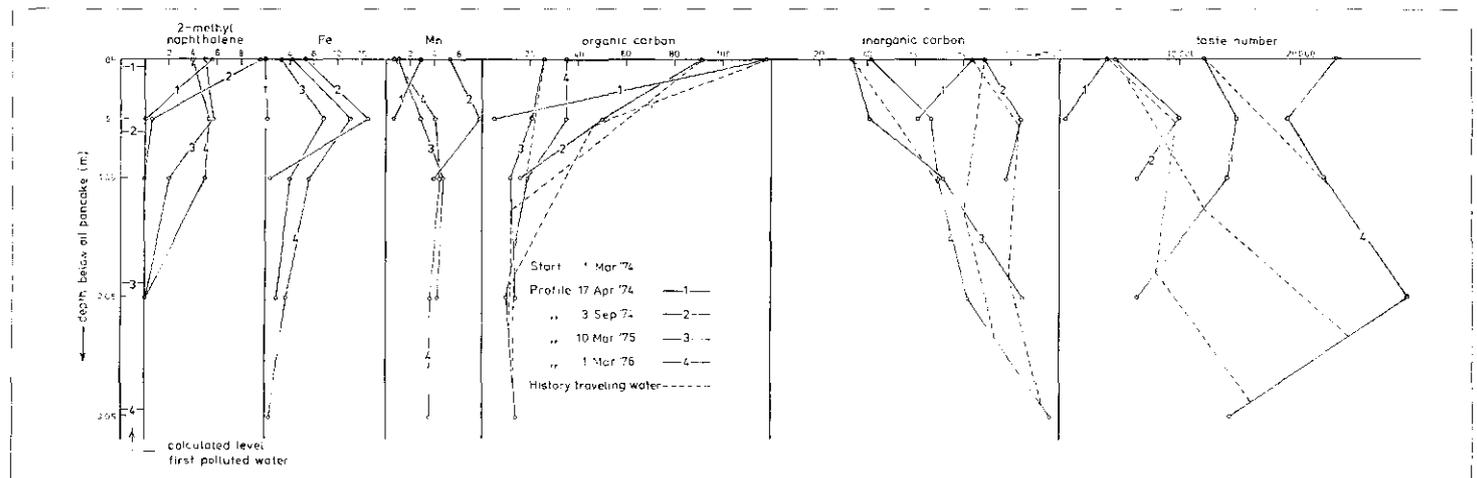
Fig. 2 - Concentrations and taste in groundwater polluted by a 4-component fuel oil.

Oil components dissolved in groundwater

The behaviour of a single oilcomponent can best be studied from the results of one of the tests with synthetic mixture, of which only 2-methylnaphthalene is significantly soluble in water.

The rainwater percolating through the oil pancake with its large contact area receives an equilibrium concentration, which from fig. 2 we observe to be some 5 to 10 ppm 2-methylaphthalene. From small scale tests it was determined that about 3 times as much is adsorbed on the sandgrains as is dissolved in the water. This should cause a chromatographic retardation by a factor of about 4. Although somewhat obscured by several disturbances, this retardation is still noticeable.

As adsorption on the sandgrains increases less than proportional with the concentration in the groundwater, the area under a concentration curve should be more than proportional to the total amount of 2-methylnaphthalene present underneath the pancake. The amount removed from the pancake at equilibrium concentration should be proportional to the amount of water percolated. We find however, that compared with the accumulated percolation, the area under the curves grows at a diminishing rate, which can only be explained if more and more of the 2-methylnaphthalene is broken down.

Organic carbon

The natural sand contains organic material, such as easily recognizable plant-roots. In an unpolluted control test the groundwater contained some organic carbon, 5 ppm at the top, 9 ppm at the bottom (fig. 3). This appearance of soluble organic compounds must be caused by oxidative processes. Free oxygen concentration is undetectably low and anaerobic oxidation can be deduced from the presence of up to 2 ppm iron and up to 2.5 ppm manganese.

Returning our attention to fig. 2, concerning a polluted column, we observe iron contents up to 17 ppm and manganese contents up to 8 ppm. Compared with the control test there is an increased anaerobic activity.

Most remarkable in fig, 2, however, are the organic carbon contents. These are much higher than the organic carbon in the control test plus the carbon from dissolved hydrocarbons. The extra organic carbon can only belong to oxidized products from the hydrocarbons in the oil pancake and this oxidation has already been indicated as aerobic in the top and anaerobic in the bottom part of the pancake.

We must conclude that the dissolution of the original hydrocarbons from the pancake is only a minor effect and that much more hydrocarbons are removed from the pancake by incomplete oxidation to more soluble products. In the detailed chemical analyses many such products are found, mainly carboxylic acids and phenols. These compounds are fairly soluble, therefore no significant chromatographic retardation is to be expected.

It was already established that such hydrocarbons as are in solution do disappear and they may be expected to be incompletely oxidized similarly. This, however, should not alter total organic carbon content. From fig. 2 we see a very strong reduction of organic carbon with time and depth. At the lower levels, where the water has covered distances of 2 and 3 m, the organic carbon is only slightly above that of the control test. After traveling with the groundwater for some 2 years most of it has disappeared.

Inorganic carbon

In the control test (fig. 3) the inorganic carbon content increases with depth from about 50 to 80 ppm. These concentrations should be caused by an exchange with the soil material and by the oxidation of organic matter.

In an oil polluted column the inorganic carbon content reaches a higher level with depth, in fig. 2 up to some 110 ppm. As the inorganic carbon goes up, the organic carbon goes down. The organic compounds, mostly products of incomplete oxidation of hydrocarbons, are apparently further oxidized to inorganic material. A detailed study of the stepwise oxidation of single compounds has yet to be made.

Cell count

It is recognised that the processes are of a bio-chemical nature, but much remains unknown about the organisms that are active. Many types of organisms will be attached to the sand body. They will hardly be found in the watersamples and can only be evaluated after completion of the tests by destructive investigation of the sand-columns.

Some organisms do appear in the water and although the cell count does certainly not tell the full story, it does represent biological activity and it correlates to some extent with the intensity of the chemical changes.
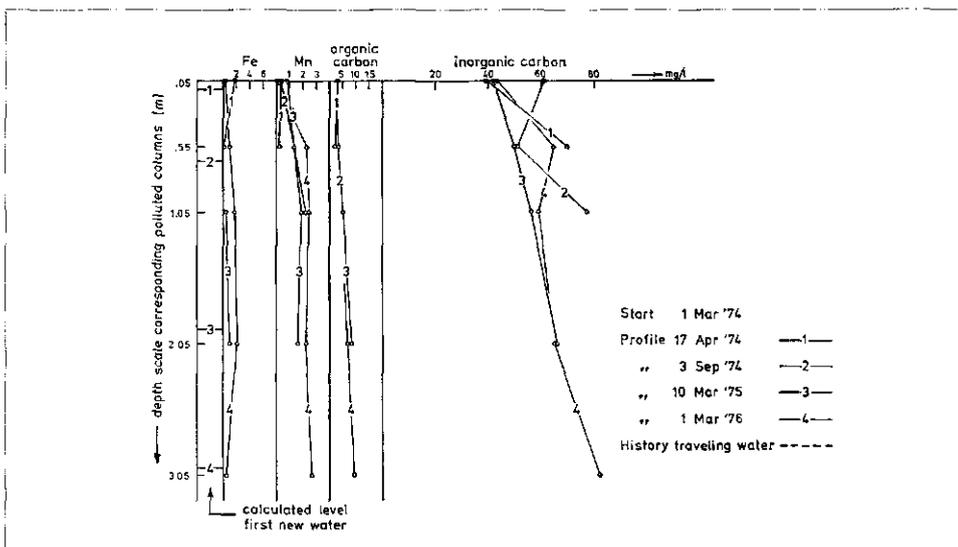
Taste number

For the purpose of drinking water supply the taste of the groundwater is of primary importance. In how far the taste can be removed by the usual purification methods remains to be investigated.

The human taste can be very sensitive, in some cases well below detection level by chemical analysis. The sensitivity of taste varies very widely from one organic compound to another: a spoonful of well purified medicinal oil (paraffine oil) may be swallowed almost readily, but many compounds cause a disagreable taste in solutions with concentrations down to from 1 ppm to 1 ppb.

We can hardly expect the taste of our untreated, polluted groundwatersamples to be better than that of unpolluted groundwater, regardless of the taste of the latter. For the determination of taste under these circumstances we used groundwater from corresponding levels in the control test, both as a dilutant and as a basis of comparison.

Fig. 3 - Concentrations in unpolluted control test.

It is very hard to correlate the taste numbers of the lysimetersamples with the chemical water analyses. For the first two years the taste numbers went up rapidly to a level of the order of 20,000. During that period, most of the hydrocarbons disappeared and the partly oxidized products, representing the bulk of the organic carbon, were reduced considerably. In very general terms we can conclude, that in the course of time an increasing taste number is caused by a decreasing concentration of pollutants and that in the course of the degradation, compounds become predominant that are more and more objectionable per unit weight. From field experience we know qualitatively that after sufficient travel time the taste number goes down. We had not expected that this reduction is postponed to the final stage of decay.

In one exceptional test such a reduction is already observed in the second year (fig. 4). From values of 20,000 to 40,000 the taste number went down to about 10,000. This might be encouraging, but it cannot yet be considered significant, because in that same period the taste numbers in a duplicate test (not shown) — where reactions had for some reason a sowewhat slower start — were still rising to about 14,000.

Observations after longer travel times are required.

Probably the most important information, yet to be obtained, concerns the taste of the groundwater after is has been subjected to a standard treatment by a large scale drinking water supply installation. The treatment can be simulated by semi-continuous operation of a semi-technical sized plant. The required quantity of groundwater can only be obtained by complete drainage of a sandcolumn, when that column is being abandoned after several years of percolation and sampling.

Fertilizing experiments

Some lysimeters were continuously fertilized in such a way, that the percolating water would start with a constant concentration of fertilizer.

Main ingredient was sodium nitrate (NaNO₃) to obtain an initial concentration of 1 gr/liter in the water. At a net rainfall of 40 cm/year this would correspond with 659 kg/ha . year (588 lbs/acre . year) of nitrogen. On its way down in the sand-column, most of the nitrate is used up, predominantly during the warm summer-months. Nitrogen-containing organic compounds are found in higher concentrations than in the non-fertilized tests.
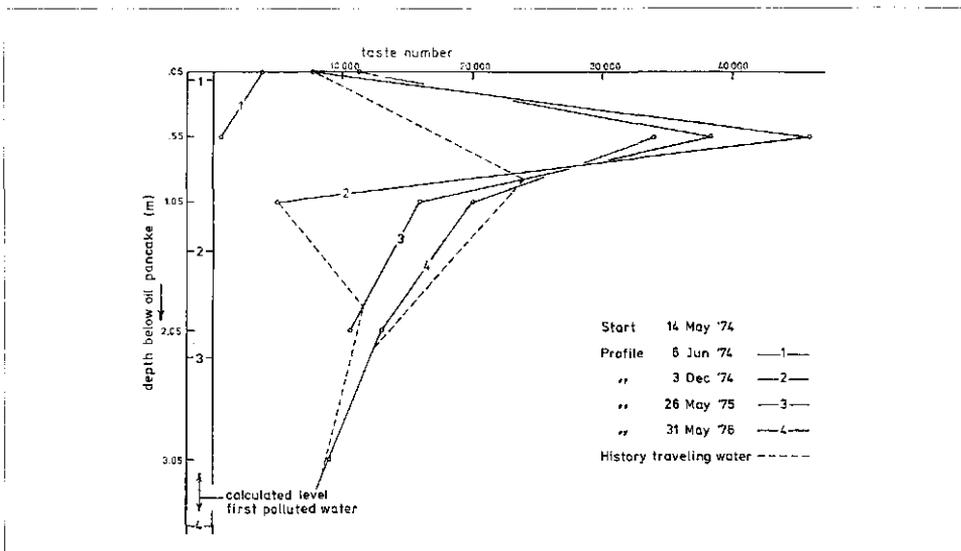

Fig. 4 - Early decline in taste of groundwater polluted by a commercial fuel oil.

TABLE - Sample set of analyses.

Sampling date: 10 Mar 75 (after one year operation)
Lysimeter no. 8
Oil: mixture of 4 pure components
Fertilization: none
Rainfall: natural

Sampling level in cm below	oil pancake	5	55	105	205
pH		7.0	7.1	7.0	7.0
Dissolved oxygen	mg/l	0.2	0.2	0.2	0.3
Cell count (Aerobic)	ml⁻¹	3,500	450	200	1,300
Taste number		11,300	20,000	12,600	5,300
Inorganic carbon	mg/l	32	40	63	106
Organic carbon	mg/l	20(18)	16(14)	15(14)	16(21)
Hydrocarbons	mg/l	9.1	6.5	3.7	n.d.
2-methylnaphtalene	mg/l	7.8	6.5	3.7	n.d.
Trans Decalin	mg/l	0.28	n.d.	n.d.	n.d.
Cis Decalin	mg/l	0.22	n.d.	n.d.	n.d.
Heptamethylnonane	mg/l	n.d.	n.d.	n.d.	n.d.
Hexadecane	mg/l	n.d.	n.d.	n.d.	n.d.
Chem. oxygen demand	mg/l	40	45	35	45
Fe	mg/l	3.2	6.8	3.4	1.2
Mn	mg/l	2.0	2.5	3.3	3.3
Conductivity (20 °C)	μS/cm	416	375	481	746
Nitrate (NO3)	mg/l	n.d.	n.d.	n.d.	n.d.
Nitrate (NO2)	mg/l	n.d.	n.d.	n.d.	n.d.
Ammonia (NH3)	mg/l	0.2	0.6	0.07	0.2
Phosphate (PO4)	mg/l	0.25	0.8	0.15	0.12
Phenolics	mg/l	0.03	0.2	0.2	0.4
Hydroxy Decalin	mg/l	0.03	0.07	0.04	n.d.
Decalone	mg/l	0.08		0.07	0.06
Trans β-Decalone	mg/l	0.18	0.31	0.21	0.04
Cis β-Decalone	mg/l	0.10		0.10	0.04
Dihydroxy Decalin	mg/l	n.d.	n.d.	n.d.	n.d.
Decalin Dione	mg/l	n.d.	n.d.	n.d.	n.d.
Hydroxy Decalon	mg/l	n.d.	n.d.	n.d.	n.d.
Bicyclo (4.4.0) Dec-1-ene, 3-one	mg/l	0.02	0.04	0.04	n.d.
6-methyl coumarin	mg/l	n.d.	n.d.	n.d.	n.d.
Rest neutrals	mg/l	3.4	0.3	1.5	0.2
4-methyl salicylic acid	mg/l	3.5	2.4	0.1	0.1
2-naphthoic acid	mg/l	1.8	1.7	1.1	0.02
1,2-dihydro, 1,2-dihydroxy 7-naphthoic acid	mg/l	n.d.	n.d.	n.d.	0.04
Rest carboxylic acids	mg/l	2	1	1	5

n.d. = not detectable

The nitrate enhances the oxidation of hydrocarbons to soluble oxygen-containing organic compounds, but also the ultimate decay of these compounds to inorganic carbon compounds. The net influence of the nitrate on the organic carbon content can be either way.

The fertilizer also contained some potassium orthophosphate (KH_2PO_4 and K_2HPO_4) aimed at an initial concentration of 0.1 gr/liter. This has no effect and impressions are that the phosphate is precipitated in a very early stage by the presence of calcium.

Main conclusions

Previous studies have established that spilled oil will settle at residual saturation in a 'pancake' on top of the groundwater (the groundwaterlevel at the time of the spill). The fraction of the rainfall within a water catchment area that feeds the groundwater via the pancake will originate a narrow stream of polluted groundwater within the total groundwaterflow. The natural decay of the unmitigated pollution has been studied as it will occur in this narrow stream. The dilution of the ensuing water by the unpolluted main stream into wells or drains is a matter of simple arithmetic per individual case and is not discussed.

Our experiments have shown:

Rainfall, percolating through the pancake on its way to the groundwaterbody will dissolve oil components to concentrations of 1 to 10 ppm (slightly less if expressed as organic carbon content) depending on solubilities.

Hydrocarbons in the pancake are subject to aerobic and anaerobic oxidation. The oxidized products are sufficiently soluble and bring the organic carbon content of the water up to roughly 50 ppm, depending on the nature of the oil and on the prevailing temperature.

Organic carbon content, mainly due to these oxygen-containing organic compounds, is reduced by anaerobic oxidation to a fraction of 0.5 to 0.1 after a travel time of two years. At the same time, inorganic carbon content goes up, demonstrating a significant rate of ultimate decay of the pollutants.

In spite of this decay the taste numbers rise to about 20,000. Except in one lysimeter, they have not yet shown signs of going down. One can only conclude that, in the last stages of stepwise oxidation, small concentrations of the most obnoxious compounds prevail.

No barrier to ultimate decay of the

pollutants having been observed, the taste numbers should ultimately come down, but they will do so only in the very last stage.

This stage is now expected to fall beyond the originally planned 3 years duration of the tests.

As taste of groundwater, destined for drinking water, is by far the most important property, plans are being developed to extend the period of observation.

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The analyses are being carried out by the Royal Dutch Shell Laboratory in Amsterdam.

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Agenda