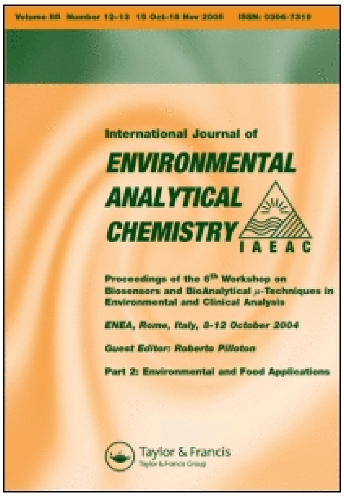

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Chromatographic Investigations of the Behaviour of Dichlobenil and 2,4,5-T in Water During Slow Sand Filtration†

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In this study the behaviour of the herbicides dichlobenil and 2,4,5-T during slow sand filtration of surface water was investigated. Slow sand filtration is applied to artificial groundwater recharging of Ruhrwater. The herbicides were added into the Ruhrwater supply of a pilot plant. The quantitative determination of dichlobenil, 2,4,5-T and their metabolites was performed by high pressure liquid chromatography. Sample preparation and analysis were simplified either by direct injection of the filtered water sample into a liquid chromatograph or by using a column switching system consisting of a short precolumn as enrichment column and an analytical column—this was used when working in the ppb range. With dichlobenil a partial elimination by adsorption and degradation was observed. The elimination rate of 2,4,5-T was very low, only app. 10% of the added amount; no degradation product was observed.

KEY WORDS: HPLC, herbicides, slow sand filtration, trace enrichment, column switching.

INTRODUCTION

Slow sand filtration is a frequently used method in artificial ground water recharge. During this process surface water flows through a filter containing layers of sand and gravel and is thereby biologically and mechanically cleaned. As the use of agrochemicals especially of herbicides is increasing, the danger of contamination of surface water e.g. by

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leaching is given. Therefore it is important to get more knowledge about the behaviour of these substances during the slow sand filtration process. In this study we have investigated the two herbicides dichlobenil (2,6-dichlorobenzonitrile) and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid). There have been some investigations about their behaviour during the underground passage but no investigations concerning slow sand filtration for artificial ground water recharge.[1,2,3]

The concentrations used were in the range of amounts which have been found in surface waters. Dichlobenil—besides other application purposes—was also used against weed infestation in ditches, ponds and lakes in the F.R.G. in 1981. The normal amount of application corresponds to a concentration of 1 mg/l in surface water.[4] Therefore the dosage in the ground water pilot plant was performed with a concentration of 0.5 mg/l. Struif *et al.* have found concentrations of 2,4,5-T in lakes and rivers up to 40 ppb.[5]

In our study we have chosen a concentration of about 14 ppb in river water (river Ruhr). The identification and quantitative determination of the herbicides were performed by HPLC. The analytical method should enable the separation of the active ingredient as well as possible metabolites in a reasonable time to analyse a lot of samples directly after sampling. Therefore we have simplified the sample preparation by either using direct injection (after filtration of Ruhrwater) or, in the ppb-range, by on-line trace enrichment on a short precolumn with subsequent column switching to the analytical column.

EXPERIMENTAL

Apparatus

A HPLC system Hewlett-Packard 1084 B with variable UV detector (Hewlett-Packard, Böblingen, F.R.G.) was used for the determination of dichlobenil concentrations ranging from 100 to 500 μg/l by direct injection of water samples. The determination of trace amounts of herbicides and metabolites in the ppb range was done by a column switching system with a short enrichment column and analytical column. The columns were switched in an on-line mode by a Rheodyne valve (type 7120).

Two high pressure pumps M 6000 A (Waters Ass., Königstein, F.R.G.) and a variable UV detector SF 770 (Kratos; Karlsruhe, F.R.G.) were used. The quantitative evaluation was done with an integrator HP 3385 A. As analytical columns steel columns with dimensions of 120 mm × 4.6 mm, 80 mm × 4.6 mm and of 145 mm × 4.0 mm were used (Knauer, Berlin and Merck, Darmstadt, F.R.G.). Knauer steel columns of 40 mm × 4.6 mm were used as enrichment columns. All columns were packed with good reproducibility with LiChrosorb RP 18 or RP 8, 5 μm (Merck).[6] Filtration of water samples was performed by a 20 ml glass syringe connected to a Swinny filter holder (stainless steel) with a membrane aqueous filter (0.45 μm pore size) (both Millipore, Neu-Isenburg, F.R.G.).

Reagents

All solvents for chromatography were of analytical grade purity. Methanol for residue analysis and bidistilled water was used for the mobile phases. HPLC-water (Baker, Merck) was used for reconditioning and flushing the enrichment columns and as solvent for the external standards.

To avoid disturbance by impurities or formulation agents analytical grade herbicides (98% purity, Ega, Steinheim, F.R.G.) were added into the pilot plant. For external standards herbicides of at least 99% purity (Ehrensdorfer, Augsburg, F.R.G.) were available. Tetrabutylammonium hydrogen sulfate (Ega) for ion-pair chromatography and sodiumhydroxide-borate buffer pH 9 and pH 11 (Merck) were used.

Methods

1) *Development of an analytical method to determine dichlobenil and 2,4,5-T in surface water (Ruhr Water)*

If the concentration of dichlobenil is higher than 100 μg/l, a separation of interfering substances in Ruhrwater as well as a quantitative determination is possible by simply direct injection of the filtered water sample into a liquid chromatograph. No other sample clean-up steps than filtration are necessary. The only requirements are the UV-detection at 210 nm (absorption maximum of dichlobenil) as well as a suitable transparency of the mobile phase at this wave length (e.g. methanol LiChrosolv). Figure 1 shows a typical chromatogram of a Ruhrwater sample with a concentration of 500 μg/l. Dichlobenil—with a retention time shorter than 4 minutes—is well separated from other unknown substances. Sample filtration was performed with a 20 ml all glass syringe connected to a Swinny-filter-holder, discarding the first 10 ml. For quantitative calculations we have chosen the method of external standard by using a standard solution of similar concentration in HPLC-water. In Table I the relative standard deviations obtained by this method at various concentrations are given. The calibration curve is linear in this concentration range. When measuring samples with concentrations below 100 μg/l the relative standard deviation increases to 10% and higher. Therefore in case of low concentrations enrichment and column switching is recommended. This method is already described for some other compounds.[7–10]

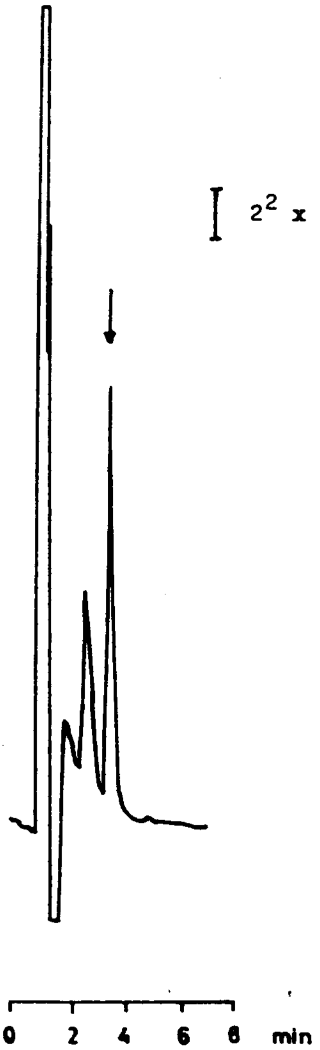

FIGURE 1 Chromatogram of dichlobenil, direct injection of 20 μl prefiltersupernatant (0.5 mg/l); apparatus: Hewlett-Packard 1084 B; column: LiChrosorb RP 18 5 μm, 145 × 4.0 mm i.d.; mobile phase: Methanol-water 70:30 v/v; flow: 1.0 ml × min^{-1}; detection: UV 210 nm; sample preparation: filtration of water sample (0.45 μm aqueous filter).

TABLE I

Relative standard deviations for the determination of dichlobenil at various concentrations by direct injection

Solvent	H_2O (bidist.)			Ruhrwater		
Injection volume	20 µl			20 µl		
Dichlobenil concentration (µg/l)	500	330	230	173	116	95
Rel. standard deviation (%)	2.2	1.4	3.8	6.2	9.5	12.0

Trace analysis in the ppb-range of dichlobenil and its metabolites as well as of 2,4,5-T was performed by column switching. A short precolumn was used as enrichment column which could be switched to the analytical column in an on-line-mode. A schematic diagram of the enrichment operation and the analytical determination is shown in Figure 2. Sample filtration was performed as described above. To obtain peaks with a small band width one should add tetrabutylammonium hydrogen sulfate (TBAHS) to samples which may contain carboxylic—or phenoxycarboxylic acids (TBAHS-concentration 0.0175 mol/l). This should also be added to the water, which is used for reconditioning and for flushing of the pump and the precolumn after enrichment and after an analytical determination (each time 4 ml) as well as to the mobile phase (same concentration as above). Instead of tetrabutylammonium hydrogen sulfate, sodium hydroxide borate buffer was used for the determination of 2,6-dichlorobenzamide. In this case 1 ml buffer pH 9 or alternatively 0.1 ml buffer pH 11 was added to 10 ml sample volume, giving a final pH of app. 8.5. Standard solutions were treated in the same way. To avoid alkaline hydrolysis of dichlobenil giving too high values for 2,6-dichlorobenzamide, the analysis should be performed immediately after addition of the buffer.[11]

Figures 3–6 show typical chromatograms of these determinations. With the described method there were no losses by break through effects during enrichment. This was proved first by the linearity of the calibration curves as well as by comparison with direct injection of 20 µl of some absolute amounts of herbicides showing recoveries of 99 ± 1%.

In Table II the relative standard deviations are given for several samples.

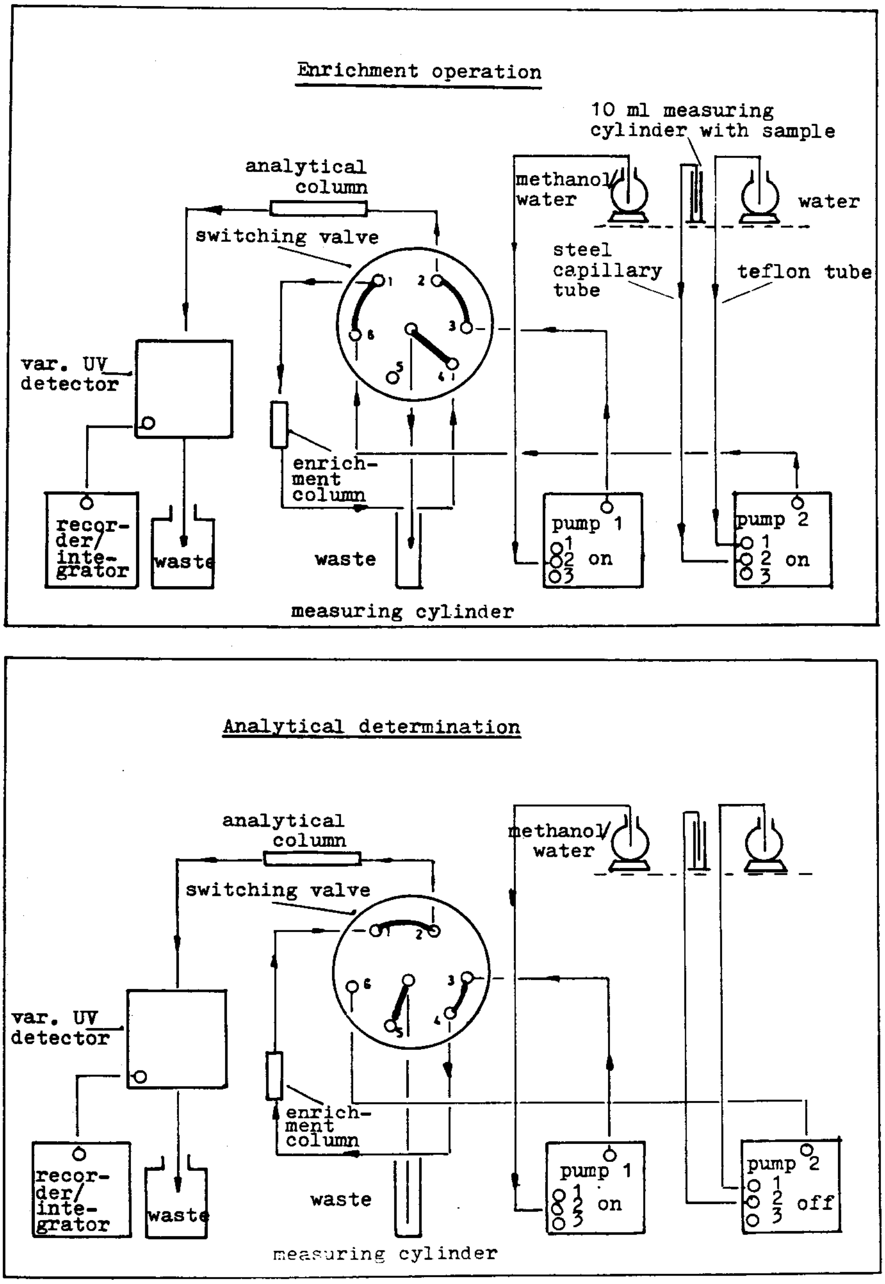

FIGURE 2 Scheme of apparatus used for trace analysis of herbicides in water samples by enrichment and column switching.

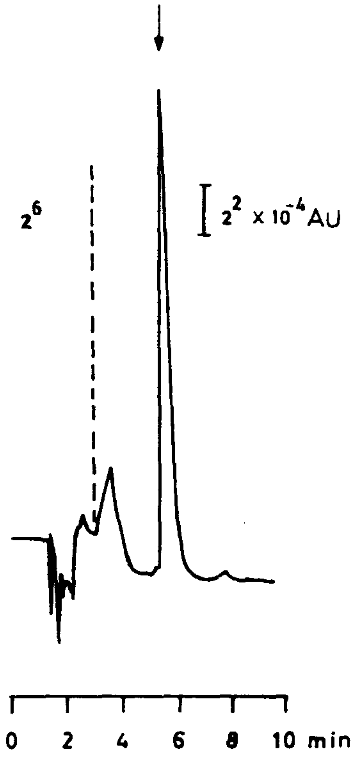

FIGURE 3 Chromatogram of dichlobenil, concentration from 2 ml mainfilter-discharge (59 μg/l); apparatus: column switching technique with 2 Waters pumps 6000 A; columns: enrichment column LiChrosorb RP 18 5 μm 40 mm × 4.6 mm i.d., analytical column LiChrosorb RP 18 5 μm 125 mm × 4.0 mm i.d.; mobile phase: Methanol-water 65:35 v/v; flow: 1.0 ml × min^{-1}; detection: UV 210 nm; sample preparation: filtration of water sample (0.45 μm aqueous filter).

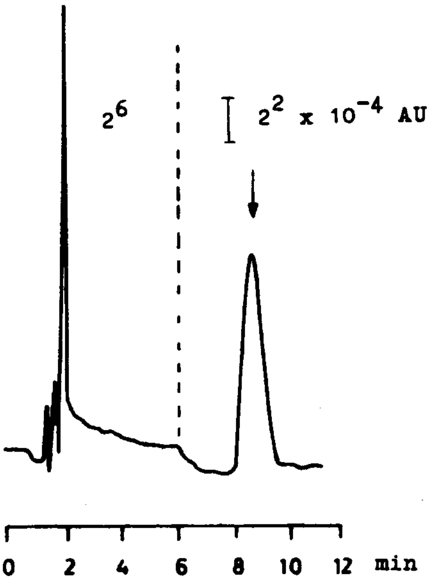

FIGURE 4 Chromatogram of 2,6-dichlorobenzamide, concentration from 5 ml mainfilter discharge (19.2 μg/l); mobile phase: Methanol-water 20:80 v/v; sample preparation: sodiumhydroxide-borate buffer was added to the filtered water sample (final pH app. 8.5); apparatus, columns, flow, detection: conditions as in Figure 3.

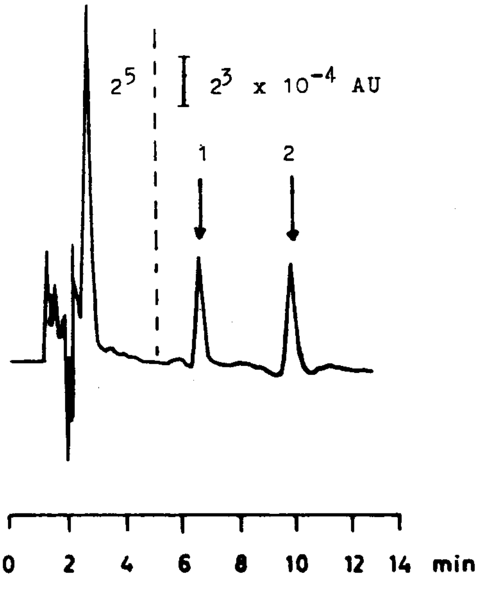

FIGURE 5 Chromatogram of 2,6-dichlorobenzoic acid (1) and 3,5-dichloro-4-hydroxybenzoic acid (2), concentration from 5 ml aqueous solution (10.0 μg/l); mobile phase: Methanol-water 45:55 v/v + tetrabutylammonium hydrogen sulfate (0.0175 mol/l); apparatus, columns, flow, detection: conditions as in Figure 3.

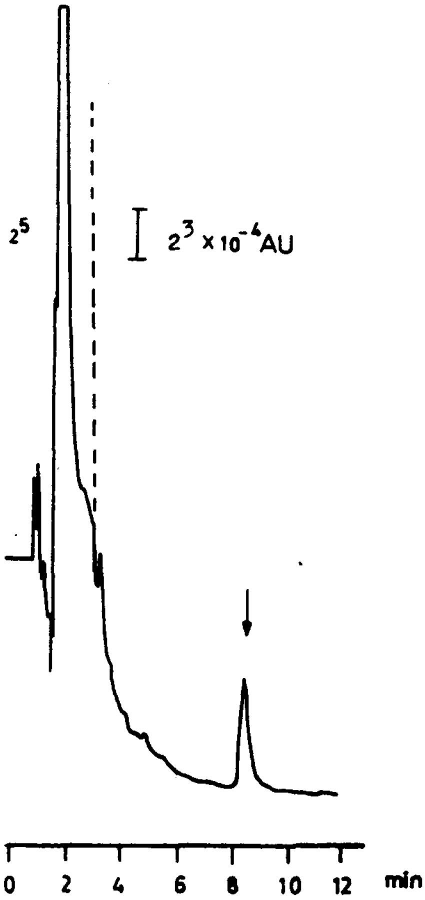

FIGURE 6 Chromatogram of 2,4,5-T, concentration from 5 ml prefiltersupernatant (8.7 µg/l); columns: enrichment column LiChrosorb RP 18 5 µm 40 mm × 4.6 mm i.d., analytical column LiChrosorb RP 8 5 µm 80 mm × 4.6 mm i.d.; mobile phase: Methanol-water 56:44 v/v + tetrabutylammonium hydrogen sulfate (0.0175 mol/l); sample prepration: tetrabutylammonium hydrogen sulfate was added to the filtered water sample (0.0175 mol/l); apparatus, flow, detection: conditions as in Figure 3.

TABLE II

Relative standard deviations for the determination of several substrates at various concentrations by enrichment and column switching

Substrate	2,6-dichlorobenzonitrile		2,6-dichlorobenzamide		2,6-dichlorobenzoic acid	3,5-dichloro-4-hydroxybenzoic acid	2,4,5-T	
Solvent	H_2O^a	Ruhrwater	H_2O^a	Ruhrwater	H_2O^a	H_2O^a	H_2O^a	Ruhrwater
Enrichment volume (ml)	1	2	5	5	5	5	5	5
Concentration (μg/l)	100	46	25	22	10	10	15	12
Rel. standard deviation (%)	3.1	1.1	2.5	4.2	1.9	2.1	1.6	2.1

[a] Bidistilled water.

2) *Application of the methods to investigate the behaviour of dichlobenil and 2,4,5-T during slow sand filtration*

Three slow sand filter basins of the groundwater pilot plant of the Institut für Wasserforschung GmbH, Dortmund (F.R.G.) were used for our investigations. One of these basins was used as a control to detect interfering substances in the Ruhrwater. Figure 7 shows a cross sectional drawing of a slow sand filter pilot plant consisting of a prefilter- and a mainfilter-basin. The infiltration speed was 10 cm/hour during the period of experiments. After a normal operation period of about ten weeks for getting natural conditions aqueous solutions of herbicides were added directly into the riverwater supply of the prefilter by a pump.

A solution of dichlobenil was added for 60 hours so that the concentration in the prefiltersupernatant was app. 500 μg/l; after this time the dosage of the herbicide and the Ruhrwater supply was stopped and for 68 days a circulation of water in the slow sand filter unit was started by a dipped pump connected to the main filter outlet.

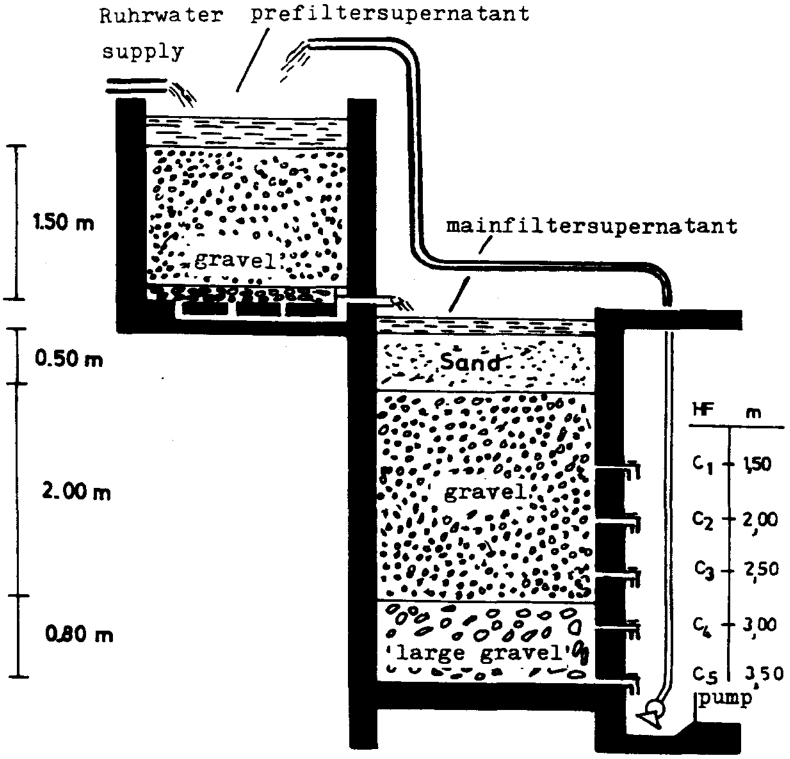

FIGURE 7 Cross sectional drawing of the pilot plant.

Insignificant losses of water by evaporation were replaced by Ruhrwater from time to time. After the end of circulation the Ruhrwater supply was opened again and the dichlobenil concentration in the mainfilter outlet was controlled daily for further 14 days ("recovery phase"). 2,4,5-T in aqueous solution was added for 9 days into a second slow sand filter plant so that the concentration in the prefiltersupernatant was 13–14 μg/l. After the end of the addition phase the determination of the 2,4,5-T concentration was continued for 6 days at the 5 different sampling sites of the pilot plant.

Sampling was done daily during dosing phase and recovery phase of the slow sand filter basins.

RESULTS AND DISCUSSION

Figure 8 shows the concentrations of 2,4,5-T which were determined at 5 different sampling sites of the pilot plant.

140 hours after the start of the 2,4,5-T addition phase the concentration in the prefiltersupernatant decreased from 13 to app. 9 μg/l. This was caused by a short electricity breakdown of the dosing pump.

As the results show, only a limited elimination of 2,4,5-T was found, mainly in the prefilter (app. 10% of the added amount). A large amount of algae was found in the prefilter supernatant—this would probably account for the loss of 2,4,5-T (the algae were clearly swollen). Checking the concentration during the recovery phase of the slow sand filter shows values above the detection limits only up to 66 hours after the end of the dosing phase. This experiment gave no hint for a microbial degradation[12] or for an evident elimination by adsorption on the sand layer of the mainfilter. Figure 9 shows the concentrations of dichlobenil during the additions phase at 4 different sampling sites of the slow sand filter basin.

After 60 hours the concentration of Dichlobenil in the outlet of the mainfilter approximately reached that of the prefilter supernatant. The time for complete breaking through of 2,4,5-T was only 30 hours, in a tracer study with a NaCl-solution it was only 27 hours.

This longer period for complete breaking through of dichlobenil indicated—in comparison to the tracer study with NaCl and the addition phase of 2,4,5-T an adsorption of dichlobenil. Figure 10 shows the concentration of dichlobenil in the main filter outlet during the "recovery phase" of the slow sand filter basin after the end of circulation. A slow desorption was observed.

After the end of the experiment the sand of the main filter was extracted by steam distillation.

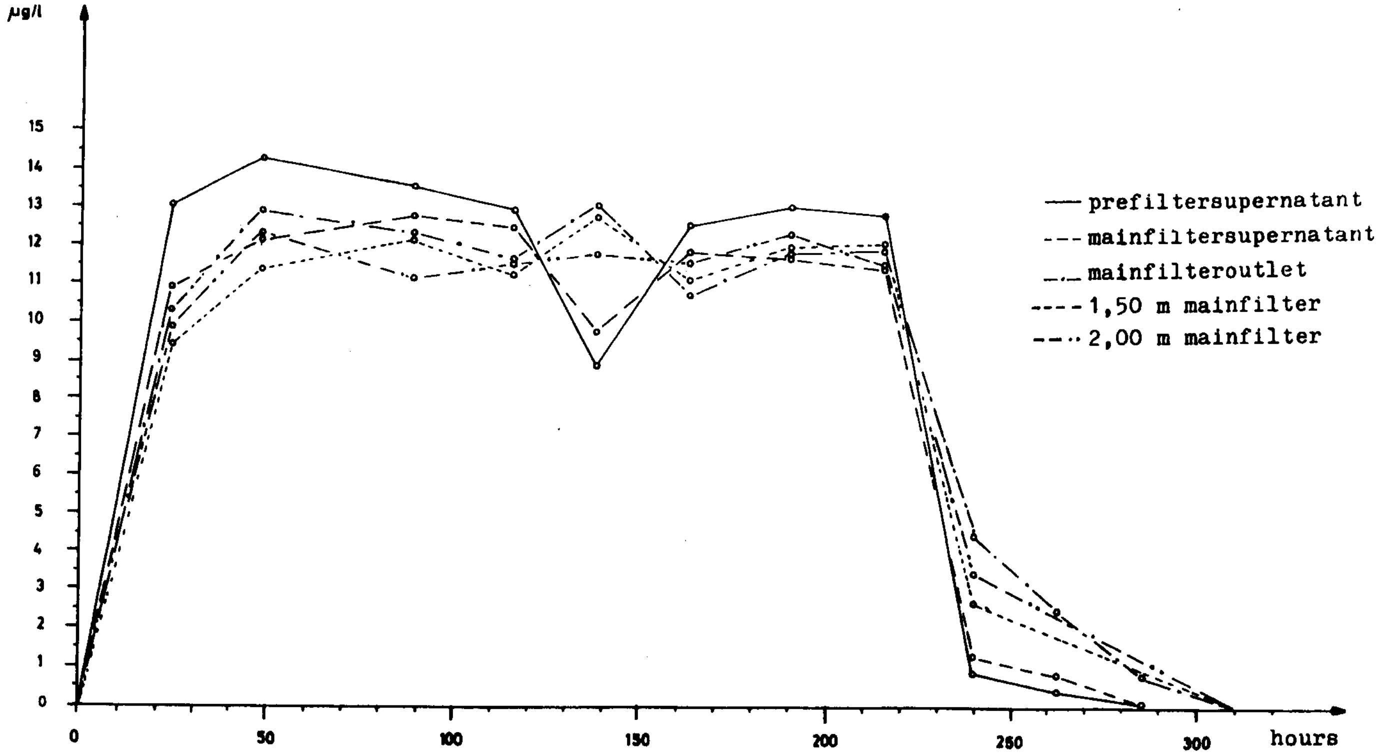

FIGURE 8 Behaviour of 2,4,5-T during passage through the slow sand filter.

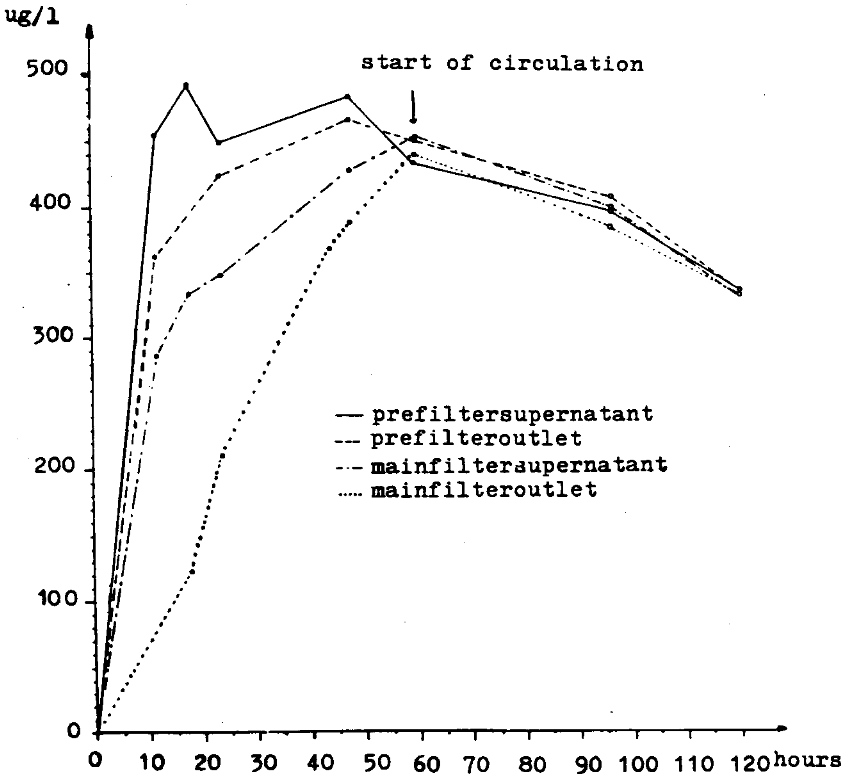

FIGURE 9 Addition phase of dichlobenil into a slow sand filter.

The condensate was subjected to the enrichment procedure and 0.027 ppm dichlobenil were found; so an adsorption of dichlobenil into sand was proved. The concentration course of dichlobenil in the mainfilteroutlet during the complete phase of the experiment (addition phase, circulation and recovery phase) is shown in Figure 11.

In the conventional method for artificial groundwater recharge of Ruhrwater a circulation is not used. In this study we have used a circulation phase so that if an elimination of dichlobenil would occur it becomes more evident. Further on the formation of degradation products can be studied more easily because they will appear in higher concentrations.

A reduction of dichlobenil by adsorption and degradation of approximately 90% of the original concentration was found after 68 days of circulation of Ruhrwater in the slow sand filter. Little losses of

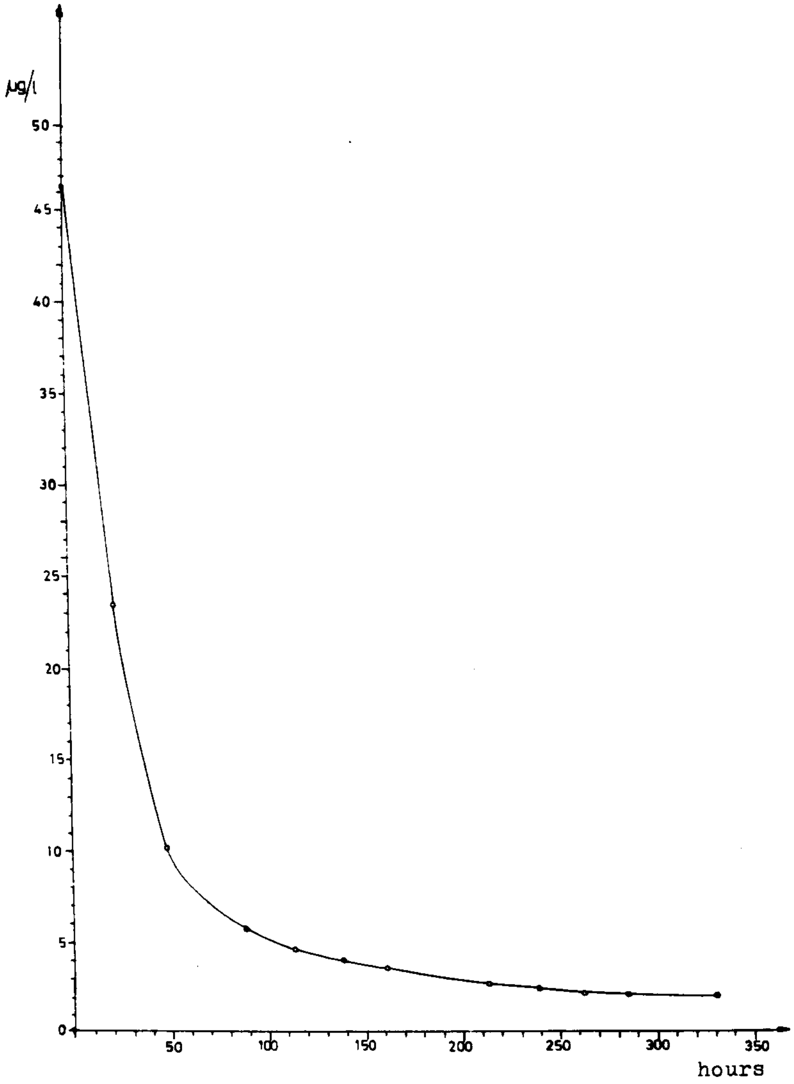

FIGURE 10 Desorption phase of dichlobenil after the end of circulation.

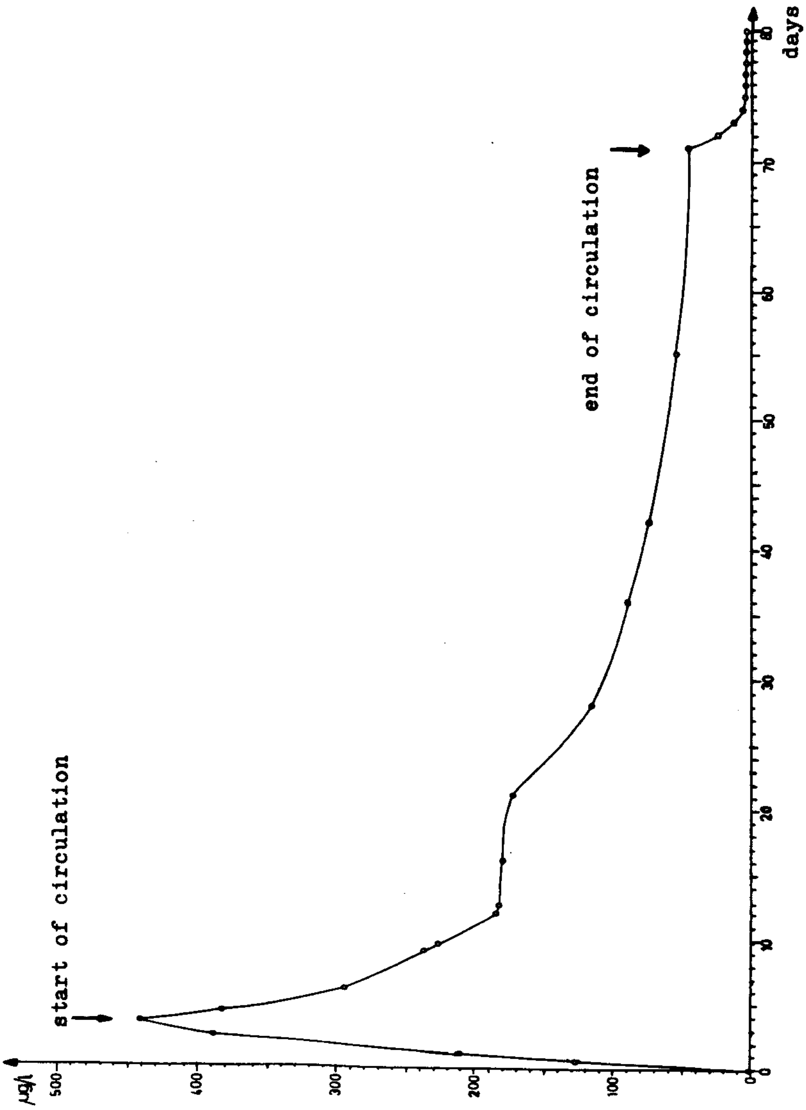

FIGURE 11 Behaviour of dichlobenil during addition phase, circulation and desorption phase in a slow sand filter.

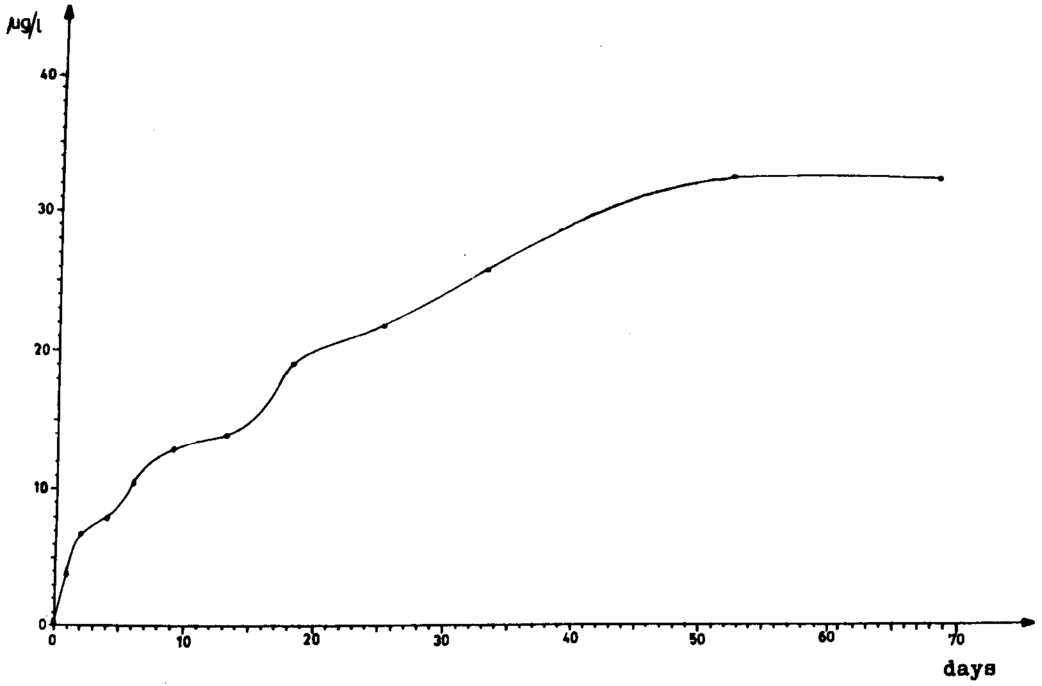

FIGURE 12 Formation of 2,6-dichlobenzamide from dichlobenil during circulation in a slow sand filter.

substrate by evaporation during circulation could be possible, as dichlobenil is a relatively volatile substrate (vapour pressure at 20°C: 5.5×10^{-4} torr).[12,13]

The approximately constant concentration of dichlobenil between the twelfth and twenty-first day corresponds with a decrease in the number of bacteria and a little rate of metabolism (see Figure 12) during this period. The number of bacteria increased later (by adaptation), also did the formation of 2,6-dichlorobenzamide. The formation of 2,6-dichlorobenzamide from dichlobenil during circulation shows Figure 12. 2,6-dichlorobenzamide was the only degradation product of dichlobenil that was detected during the period of the experiment.[12,13]

CONCLUSIONS

Only a limited elimination of 2,4,5-T and dichlobenil during slow sand filtration was observed. Dichlobenil was partially adsorbed and degradated. The only degradation product, formed from dichlobenil, was 2,6-dichlorobenzamide. The rate of elimination of 2,4,5-T was only 10%. No degradation product of 2,4,5-T was observed.

The enrichment procedure from water samples by precolumnconcentration and column switching has proved to be a rapid and sensitive method. Trace analysis with height recoveries of the relative volatile herbicide dichlobenil, its metabolites and the very polar phenoxycarboxylic acid 2,4,5-T is well possible.

Acknowledgement

We wish to thank Dr. K. H. Schmidt (Head of the Institut für Wasserforschung, Dortmund) for giving us the possibility to use slow sand filter basins and the "Land Nordrhein-Westfalen" for the financial support of these investigations.

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