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BEHAVIOUR OF DISINFECTANTS (CHLOROPHENOLS) DURING UNDERGROUND PASSAGE

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ABSTRACT

Infiltration processes with three chlorophenols (2-chlorophenol, 2.4-dichlorophenol, 3-methyl-4-chlorophenol) were investigated. In the activated carbon-sand filter system used, both adsorption and biodegradation processes were observed. More than 95 % of the chlorophenols injected could be eliminated.

INTRODUCTION

In the Federal Republic of Germany, 90 % of the drinking water are obtained from aquifers (ref. 1). Therefore knowledge of the behaviour of potential groundwater pollutants becomes increasingly important (ref. 2-4). Among other compounds in last years especially chlorinated organics, including chlorophenols which are used as disinfectants, have received special interest.

The European Community passed the drinking water regulations in July 1980 with remarkably low limits for phenols (0.5 µg/l) and chlorinated pesticides (0.1 µg/l per substance). In the Ruhr Region, where bankfiltration and artificial groundwater recharge were used as traditional purification steps, concentrations in the range of ng/l up to µg/l could be detected in the raw water (ref. 5).

It was obviously nessesary to investigate the concentrations and elimination rates of these compounds in groundwater and in drinkingwater, respectively. The results obtained as well as supplementary half-technical pilot studies are reported elsewhere (ref. 6-7). Based on these measurements, further information was gathered concerning the transport and fate of chlorophenols during the infiltration processes. The results are presented in this paper.

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EXPERIMENTAL PROCEDURES

Column experiments

For simulation of mechanical and biological prefiltration of the Dortmunder Stadtwerke AG, glass columns with 60 cm length and 15 cm i.d. were filled with gravel and charged with Ruhr water. The prefiltered water was introduced into the main filters for which also glass-columns of 15 cm i.d. and 140 cm length were used. In contrast to the technical practice in Dortmund, the filter body consisted of an additional 10 cm layer of granulated activated carbon (Merck 2514, BET 800 m^2/g, penetration coefficient K_f 1.4×10^{-2} m/s), followed by 100 cm of sand filling (Rheinen Süd, BET 1.19 m^2/g, K_f 7.8×10^{-4} m/s). The velocity of the filtration process was kept at 84 cm/h. By assumption of 30 % porosity, the effective velocity was 288.5 cm/h.

2-chlorophenol, 2.4-dichlorophenol, and 3-methyl-4-chlorophenol were injected at the prefilter outlet to obtain good mixture. The concentration was 1.4 mg/l of each substance in the infiltrated water.

Samples were collected every 12 hours at the Ruhr water inlet, in the supernatant water of the main filter, at the activated carbon outlet, and in the sand filter effluent.

Analytical measurements

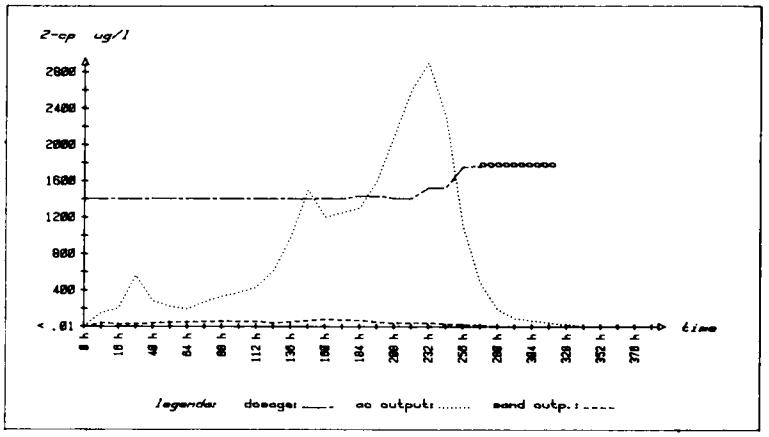
For analytical determination of the phenol concentrations, samples of 100 ml were used. Only in the sand filter effluent 2000 ml samples were taken. After acidification to pH 2 the extraction and derivatisation was performed according to Krijgsman (ref. 8). Gas chromatographic determination with capillary glass columns (0.25 mm i.d., 25 m length, Carbowax 20 M) and FID-detection gave detection limits of 0.2 and 0.03 µg/l, respectively.

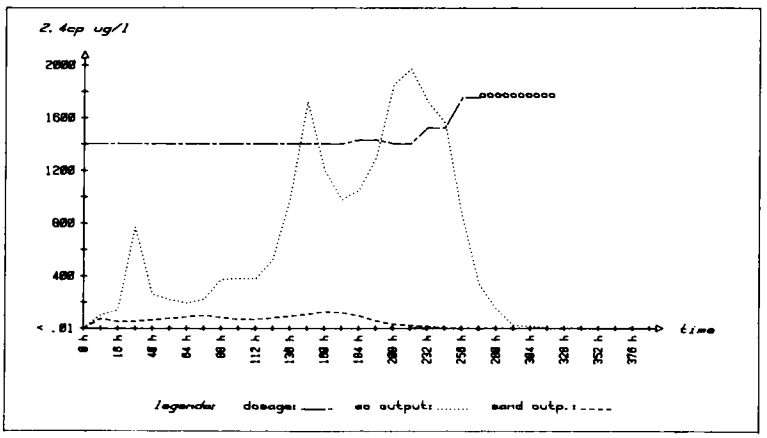
Every 24 hours additional samples for chemical and bacteriological water analysis were collected and examined according to German standard procedures (DEV).

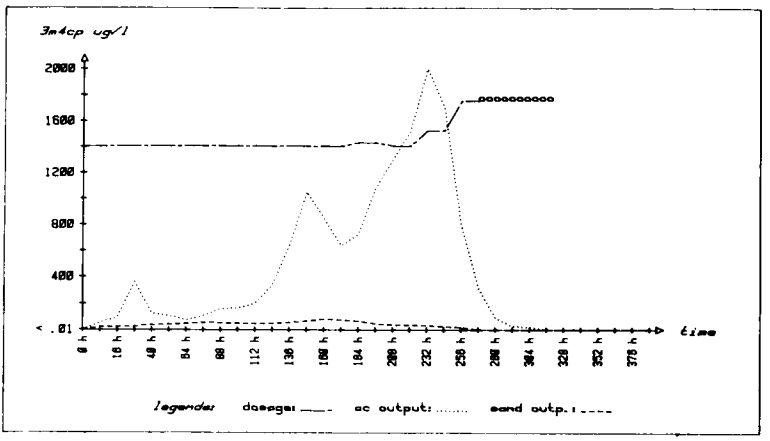
RESULTS

The total observation period was 410 hours. Within the first 196 hours phenols were injected with 1.4 mg/l and within the following 72 hours with 1.8 mg/l. After 328 hours, that was three days after termination of dosage, the detection limit at all samling points was reached without later re-increase. Figures 1-3 show the time-dependent concentrations curves of dosage, carbon- and sand effluent. In the carbon effluent, the concentration for all phenols rose slowly to 600 µg/l within the first 124 hours. Then a rapid breakthrough

Fig. 1 - 3. Concentration curves depending from time for 2-chlorophenol, 2.4-dichlorophenol, and 3-methyl-4-chlorophenol.







followed in one day. The concentration increase up to 2800 µg/l for 2-chlorophenol seems to be induced by the rather high concentration in the supernatant water. Before dosage ended, a rapid concentration decrease was observed. In the sand filter effluent remarkably low concentrations occured throughout the whole period, with 2.4-dichlorophenol showing the highest values.

During the whole time the chemical and bacteriological parameters did not change significantly.

The fractional breakthrough data allow a better comparison of the behaviour of the three substances. For 2-chlorophenol the complete breakthrough in the carbon layer could be detected after 184 hours, for 3-methyl-4-chlorophenol some ten hours later. No complete breakthrough was observed for 2.4-dichlorophenol (Fig. 4).

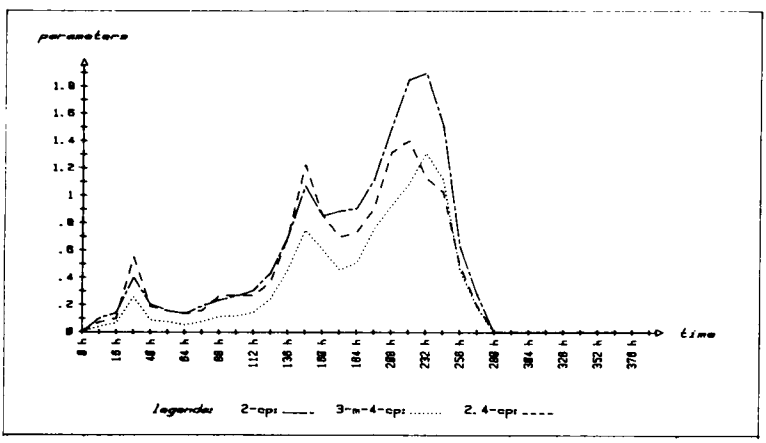


Fig. 4.Fractional breakthrough in the carbon layer

Therefore the concentration decrease begins first for this compound, though the dosage rose at the same time.

The data given indicate a typical dispersion and adsorption pattern with following biodegradation.

Taking the effluent concentration of the activated carbon as initial dosage for the sand filter, an immediate breakthrough occurs with a maximum concentration response after 64 hours with no significant adsorption. At this point only 40 % of the 3-methyl-4-chlorophenol input were removed by the sand filter. For 2.4-dichlorophenol it was 50 % and about 70 % for 2-chlorophenol. Than a smooth biodegradation follows.

It can be seen, that the adsorption effect of the upper layer overlaps with the early beginning of biodegradation in the sand filter. The concentration increase by breakthrough in the carbon layer is subsequently suppressed while passing the sand. This is obviously a result of biological degradation, but this process was not examined in detail because of its complexity.

Figure 5 indicates the rates of substances retained by the whole filter system relative to dosage concentrations. In no case more than 10 % of the input concentration were transported with the effluent. A slow rise up to maximum values at 172 hours is followed by a decrease, which comes to its end after 256 until 280 hours.

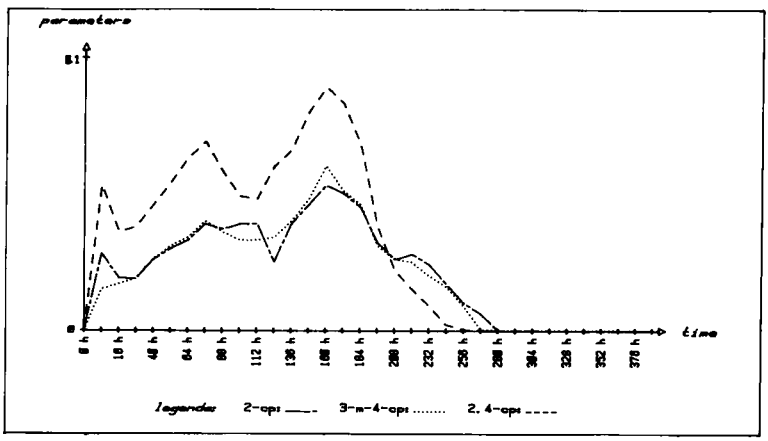


Fig. 5. Fractional breakthrough in the whole filter system

The amount of phenols retained within the filter can be calculated by integrating the breakthrough curves as a function of the cumulativly injected water volume. The results for the calculated amounts are given in table 1.

TABLE 1
Retained amounts of chlorophenols in carbon, sand in relation to carbon effluent, and in the whole filter system

substance	dosage (mg)	carbon (mg)	(%)	sand (mg)	(%)	carbon and sand (mg)	(%)
2-chloroph.	5641	1801	32	3667	96	5468	97
2.4-chloroph.	5641	2297	41	3090	92	5387	96
3-metyl-4-chlor.	5641	3248	58	2192	92	5440	96

DISCUSSION

Chlorophenols are water soluble organic compounds. Therefore only insufficient elimination by adsorption processes on soils can be expected. Adsorption isotherms from slow-sand-filter materials with Freundlich k-values in the range of 10-5 to 10-7 confirm this assumption. Also former half technical studies show an immediate breakthrough of chlorophenols through the whole filterbody. In this case the simulated slow-sand-filter with underground passage shows neither elimination by adsorption nor biodegradation.

Results from field studies in the area of the Dortmunder Stadtwerke AG indicate a higher amount of 2-chlorophenol and others in the groundwater compared with infiltrated water. Some phenols were found to be transformation products from substances with higher moleculare weight (ref. 9). This is why a concentration increase of phenols from raw water to groundwater can occur.

Therefore the following hypothesis can be postulated:

1. In soil elements with filter velocities up to 1 m/h no adsorption takes place because of the high water solubility of the investigated phenols.
2. Phenols can be formed by degradation of high molecular weight substances or transformation of chlorobenzenes.
3. In adapted biological systems such as the filter system presented here, complete degradation can occur under favourable conditions.

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