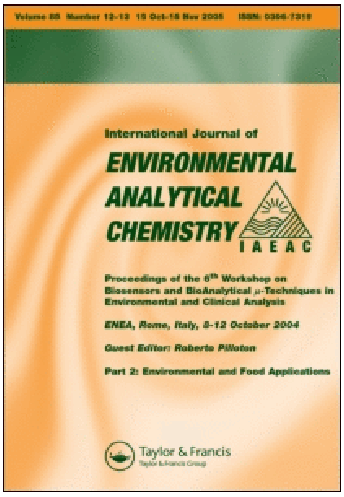

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J. Hrubec[a]; G. den Engelsman[a]; A. C. De Groot[a]; R. S. Den Hartog[a]
[a] National Institute of Public Health and Environmental Protection (RIVM), BA Bilthoven, The Netherlands

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BEHAVIOUR OF ORGANIC MICROPOLLUTANTS DURING GROUNDWATER RECHARGE

J. HRUBEC, G. den ENGELSMAN, A. C. DE GROOT
and R. S. DEN HARTOG

*National Institute of Public Health and Environmental Protection (RIVM), PO Box 1,
3720 BA Bilthoven, The Netherlands*

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Pilot plant studies were conducted to investigate the behaviour of organic micropollutants (OM) during artificial ground water recharge of pretreated river Rhine water in the dune areas. The behaviour of the studied OM was mostly affected by biological anaerobic processes. The rate of these processes correlated with the redox potential, which was primarily controlled by the biologically unstabilised organic matter of the recharge aquifer. Under anaerobic conditions ($E_h \sim +150$ mV) a substantial or complete transformation of a number of halogenated C_1-C_3 aliphatics, nitro- and chloronitrobenzenes was found at temperatures higher than 5° C. At lower temperatures a lower degree of the degradation and the formation of some potentially hazardous reaction products (dichloromethane, bromochloromethane, chloroanilines) has been observed. Furthermore the studies revealed a substantial retardation of the transformation rate at low concentration levels of some studied compounds (toluene, dichlorobenzenes, EDTA). Aerobic processes led to a significant elimination of brominated trihalomethanes, some phenoxy pesticides and NTA.

KEY WORDS: Groundwater recharge, organic micropollutants, halogenated compounds, nitrobenzenes, pesticides.

INTRODUCTION

In the Netherlands approximately one third of the nation's drinking water supply is derived from surface water. The most important sources are the rivers Rhine and Meuse. To tide over periods of accidental pollution of river water and to egalise fluctuations in river water quality storage is necessary. The storage takes place in open reservoirs or by means of underground storage in the dunes along the North Sea coast.

In the first step of a typical treatment system the river water is pretreated by coagulation and filtration to remove suspended solids and phosphates. The goal of the pretreatment is to prevent clogging of the recharge surfaces and to limit eutrophication of the water in recharge basins and channels. The pretreated water is then recharged via open channels and basins. The retention time of water in the aquifer is in the order of several months. The recharge is characterised by suboxic or slightly anaerobic environments in the sandy aquifer, which has mostly a low content of organic material. The abstracted water after the recharge, containing residues of odor and taste compounds, iron, manganese and ammonium is posttreated by a system of processes, including softening, aeration, dosing of powdered activated carbon and by slow sand filtration.

The dunes are regarded as a unique area of great national importance. During the last decades a growing resistance to water recharge has been risen due to adverse ecological effects. From the point of view of the national drinking water supply, however dune recharge is regarded as one of the most reliable treatment systems available.

To obtain more information on the role of the dune recharge by the water quality improvement and especially on the removal of potential toxic organic micropollutants (OM) a number of field[1] laboratory[2,3], and pilot plant[5–7] studies have been conducted in the last decade.

The pilot plant studies carried out in 1982–92 consisted of three experimental series. In the first series (1982–1983) the fate of inorganic constituents, heavy metals, trihalomethanes and some organic sum parameters (adsorbable, extrahable and volatile organic halogens: AOX, EOX, VOX) were studied. Some data on individual OM and on the changes of the mutagenic activity were obtained also. Due to the fact, that the recharge water was chlorinated only during summer season (water temperature > 10°C) the results of this series gave only an incomplete picture of the fate of halogenated compounds.

The main objective of the second (1984–86) and third (1988–92) series was to evaluate the effects of the influence of the soil composition, seasonal temperature variations and the redox potential on the behaviour of selected individual OM. To obtain information on the influence of low water temperature on the behaviour of halogenated compounds the recharge water was chlorinated in the second series during 18 months, including two winter seasons.

In this paper the results of all three series are reviewed.

EXPERIMENTAL

Pilot plant

The pilot plant, located in the recharge area of the Amsterdam Water Works, consisted of three tanks, 6.5 m high, 2 m in diameter.

- Tank I was filled with a clean dune sand with a low content of organic matter (0.04% organic carbon).
- Tank II contained contaminated dune sand with a higher content of incompletely stabilised organic matter (0.76% OC). This organic matter is formed by decay of the algae on other organisms in the water and the bottom of the recharge basins.
- Tank III contained a clean river sand, which was mixed with peat, i.e. a highly stabilised organic material (0.22% OC).

The sand in the tanks was replaced before the start of all three series.

The recharge water was Rhine water pretreated by coagulation and filtration. During some periods of the study the recharge water was chlorinated.

Table 1 Influent/effluent data for redox sensitive macroparameters in 1990–1991 (mean values, N = 24).

Parameter (mg/l)	*Influent*	*Effluent* *Tank I*	*Tank II*	*Tank III*
O_2	7.8	5.5	0	0.3
E_h (mV)	550	380	150	280
$NO_3^- - N$	3.6	3.4	0.1	2.1
SO_4^-	72	72	67	69
Fe	0.02	0.04	0.6	0.02
Mn	0.01	0.01	0.2	0.1

The recharge rate was 0.1 m/day and the residence time of the water in the sand bed was approximately 15 days.

The differences in conditions during the recharge in the individual tanks are characterised by the data on the changes of redox sensitive macroparameters (Table 1). The table reveals, that the recharge in Tank I took place under aerobic conditions, Tank II under anaerobic conditions characterized by complete denitrification and in Tank III were suboxic conditions (partial denitrification).

The slow sand filtration studies were conducted in tanks, 2 m high, 1 m in diameter. the sandbed depth was 1 m and the filtration rate 0.2 m/hr.

The recharge and filtration plants are described in detail elsewhere[5,7].

Studied compounds

The studied OM had been predominantly selected from the "Black ann Grey Lists" of the EEC[8] and from thė compounds frequently identified in the river Rhine. The main studied groups of OM are listed in Table 2.

Analysis

The concentration, separations and identification procedures used in the studies have been reported in detail elsewhere: AOX[9], volatile and nonvolatile halogenated compounds and pesticides[10–13], NTA and EDTA[13].

Table 2 Groups of studied organic micropollutants.

—Adsorbable organic halogen (AOX)
—Trihalomethanes (THM's)
—Other C_1-C_3 chlorinated aliphatics
—Volatile aromatics
—Chlorobenzenes
—Nitrobenzenes
—Chloroanilines
—Pesticides
—Synthetic chelators (NTA, EDTA)

The sampling scheme was designed to account for retention time of water in the tanks. Details of the sampling regime are outlined elsewhere[5,6]. The frequency of the sampling for most of the volatile OM was once or twice per two weeks and for the nonvolatile one or two times a month.

The sampling for the OM analyses began six months after the start of the recharge series to avoid the influence of adaptation, resp. acclimatization period of the biological degradation processes on the results.

RESULTS AND DISCUSSION

Halogenated compounds

The majority of the studied OM in the recharge water consisted of chlorinated and brominated compounds, which can be divided in two subgroups:

- compounds present in the river Rhine water as result of waste discharges into the river
- compounds formed during chlorination of the recharge water (AOX and THM's).

The halogenated compounds formed by chlorination of the recharge water exhibited the most pronounced behaviour during the recharge. These compounds were present in the recharge water in relatively high concentrations and therefore evaluation of their behaviour was easier than of the other OM.

AOX and THM's

The mean values of the AOX concentrations in the influent and effluent water during the periods with and without chlorination of the recharge water are presented in Table 3. The table reveals, that while the removal in T I and T III was approximately at the same level during the both periods (50%), the removal in T II (tank with the lowest redox potential) during the chlorination period was substantially higher (75%). These results suggest that the halogenated compounds formed by the chlorination of the river water could be degradated more easily than the halogenated compounds of industrial origin, present in the river water.

The effect of the recharge on degradation of THM's during the period with the chlorination of the recharge water is demonstrated in Table 4. The table indicates nearly complete

Table 3 Removal of AOX during periods with and without chlorination of recharge water (mean values).

	Influent concentr. (µg/l)	*Removal effect (%)*		
		Tank I	*Tank II*	*Tank III*
Period I (N = 37) (no chlorination)	44	50	36	34
Period II (N = 44) (chlorination)	180	49	75	54

Table 4 Removal of trihalomethanes during chlorination of the recharge water (mean values, N= 45).

Compound	*Influent concentr. (μg/l)*	*Removal effect (%)*		
		Tank I	*Tank II*	*Tank III*
$CHCl_3$	5.5	27	95	55
$CHCl_2Br$	10.5	48	99	64
$CHClBr_2$	13.5	91	99	75
$CHBr_3$	5.2	87	99	84

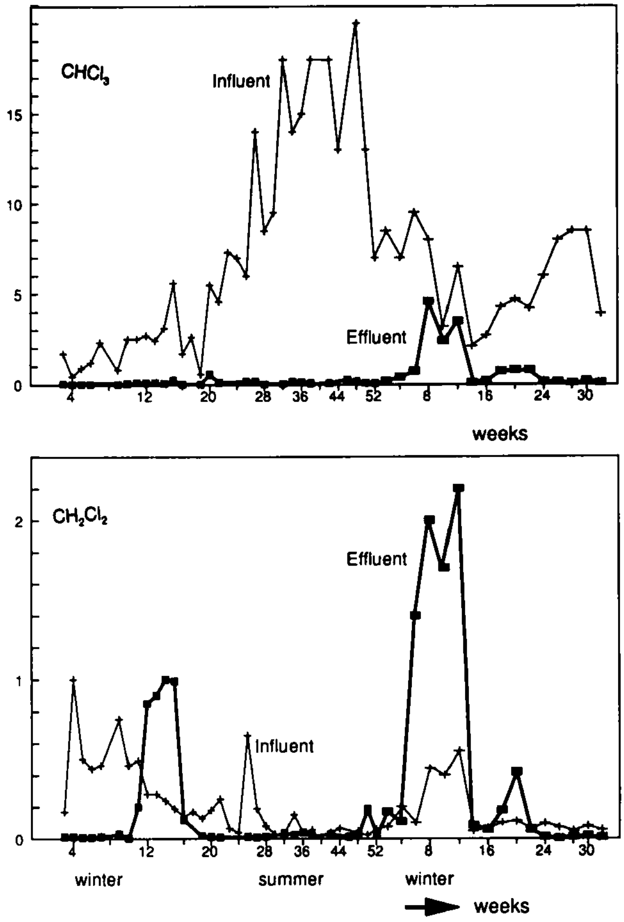

Figure 1 Influent/effluent concentrations versus time for $CHCl_3$ and CH_2Cl_2 in Tank II during recharge of chlorinated water.

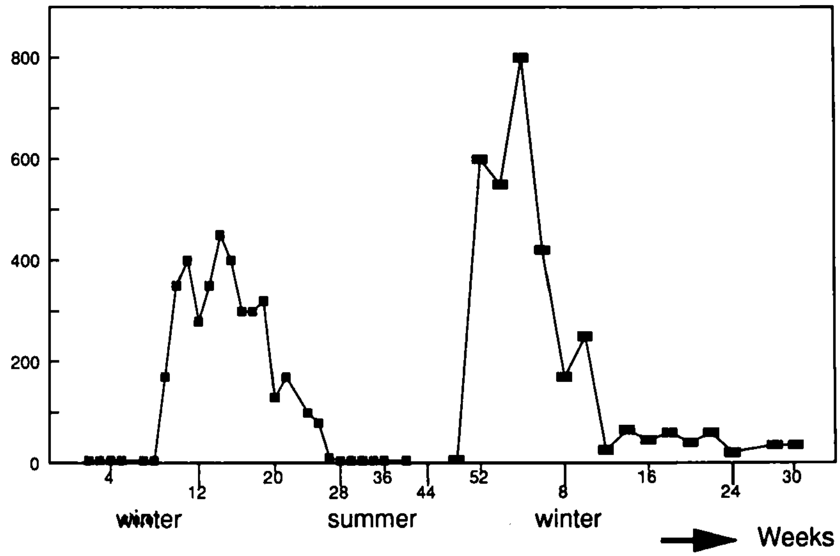

Figure 2 Effluent concentrations versus time for CH_2ClBr in Tank III during recharge of chlorinated water (all influent concentrations below detection limit).

removal of all THM's in T II. In the other tanks only highly brominated THM's were substantially transformed. The observed higher degree of THM's transformation at low redox potential agrees with the results of the dune recharge field studies[1] and the laboratory studies of Bouwer and McCarty[14,15].

The degradation of highly brominated THM's under aerobic conditions in T I can be explained by abiotic hydrolysis[15].

The course of the influent/effluent concentrations of tri- and dichloromethane in T II and of bromochloromethane in T III during a one and half year run, are presented in Figures 1 and 2. The figures demonstrate a clear increase of the effluent concentrations of dihalomethanes during the periods of lower temperatures and a retardation in the degradation of trichloromethane during the second winter the experimental run, when the temperatures declined below 5°C. These data confirm that the mechanism anaerobic degradation of halogenated aliphatics is based on sequential dehalogenation[16–18].

The observed negative influence of the winter temperatures on the degradation of THM under anaerobic conditions can be explained as a cumulative effect of a common temperature dependence of the chemical reactions and of a retardation of the biological activity in the tanks resulting in an increase of the redox potential.

Other chlorinated aliphatics

The removal effects of the recharge for other chlorinated aliphatics than THM's are presented in Table 5.

Table 5 Removal of other C_1-C_3 chloroaliphatics (N = 39–45, mean values).

Compound	*Influent concentr. (ng/l)*	*Removal effect (%)*		
		Tank I	*Tank II*	*Tank III*
CCl_4	22	N.S.*	77	44
CH_2Cl-CH_2Cl	242	N.S.	69	N.S.
CCl_3-CH_3	35	N.S.	86	26
$CHCl$=CCl_2	47	N.S.	53	N.S.
CCl_2=CCl_2	85	N.S.	81	N.S.
CH_2Cl-$CHCl$-CH_3	29	N.S.	24	N.S.

*Statistically no significant change at 95% level

The table indicates that in aerobic Tank I no statistically significant changes took place of any of the studied compounds. This observation is in agreement with a number of references[19–21], suggesting resistance of chlorinated aliphatics to aerobic biodegradation. In anaerobic Tank II all studied C_1–C_2 chlorinated aliphatics with the exception of trichloroethene were effectively transformed. A low degradation effect of trichloroethene could be explained by partial dechlorination of tetrachlorethane, which was present in the recharge water in relatively high concentrations. The formation of tri- from tetrachlorethane by anaerobic degradation has been reported from studies of Vogel and McCarty[16] and Barrio-Lage *et al.*[17]

Chlorobenzenes (CB's)

From the analyzed CB only dichlorobenzenes (DCB's) and 1,2,4-trichlorobenzene were found in sufficiently high concentrations to evaluate their behaviour.

The removal of DCB's based on the data from the entire study as presented in Table 6 suggests a quite effective removal of DCB's in Tanks II and III. However, as illustrated in Figure 3, an effective removal of 1,2-DCB in Tank II was achieved only at the start phase of the recharge. It seems reasonable to suppose that the fate of 1,2-DCB at the beginning phase of the recharge was controlled by the adsorption and that the time run of the effluent concentrations in Figure 3, represents an adsorption breakthrough curve. If the strong concentration fluctuations is taking into account, than the measured breakthrough time seems to agree reasonably well with those calculated by the adsorption model reported by Karickoff *et al.*[23]. Figure 3 illustrates also general complications, which were met by interpretation of the analytical data of some other OM groups, such as chloroethers, organic phosphates and phtalates, caused by the strong fluctuations of the concentrations at a very low level.

According to Table 6 no removal of the studied CB's took place in Tank I. This finding seems to contradict some references[3,24,25], and our study on biodegradation of OM during slow sand filtration[7], according to which especially 1,2- and 1,4-DCB's are easily biodegradable under aerobic conditions. A possible explanation of these contradictions can be the

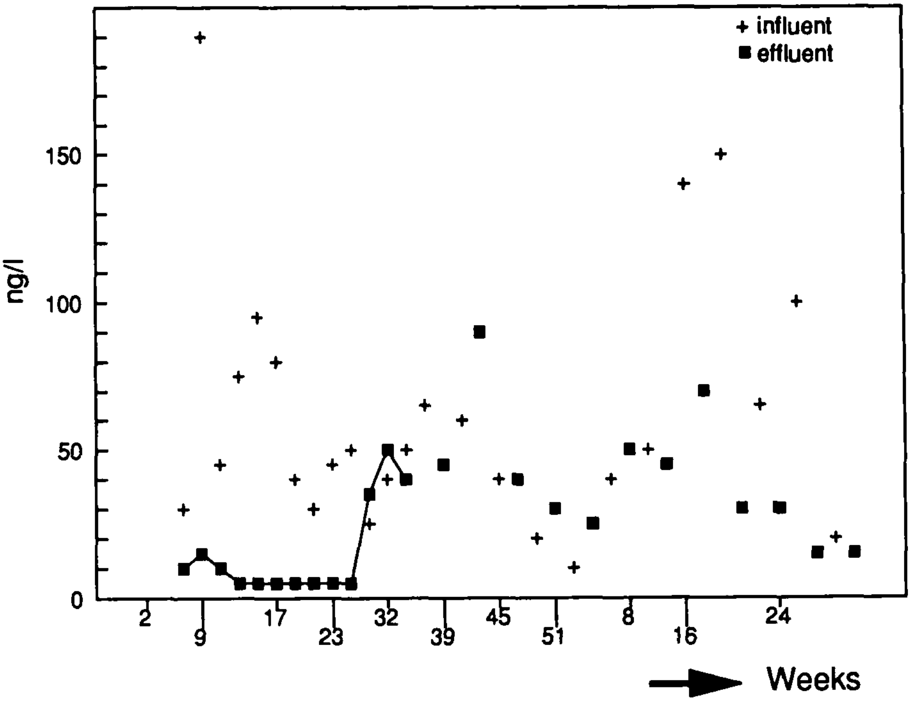

Figure 3 Influent/effluent concentrations versus time for 1,2-dichlorobenzene in Tank II.

Table 6 Removal of substituted benzenes (N = 26, mean values).

Compound	*Influent concentr. (ng/l)*	*Removal effect (%)*		
		Tank I	*Tank II*	*Tank III*
1,2-Dichlorobenzene	38	N.S.*	70	30
1,3-Dichlorobenzene	7	N.S.	70	55
1,4-Dichlorobenzene	21	N.S.	80	65
1,2,4-Trichlorobenzene	15	N.S.	87	80
Nitrobenzene	79	32	97	63
2-Nitrotoluene	90	40	96	55
3-Nitrotoluene	24	N.S.	92	66
4-Nitrotoluene	9	N.S.	66	66
2-Chloronitrobenzene	98	38	98	75
3-Chloronitrobenzene	22	36	91	73
4-Chloronitrobenzene	26	54	93	77
2-Chloroaniline	12	40	−280	−120
2,4-Dichloroaniline	9	N.S.	N.S.	N.S.
2,5;2,6-Dichloroaniline	7	N.S.	N.S.	N.S.

*Statistically no significant change at 95% level

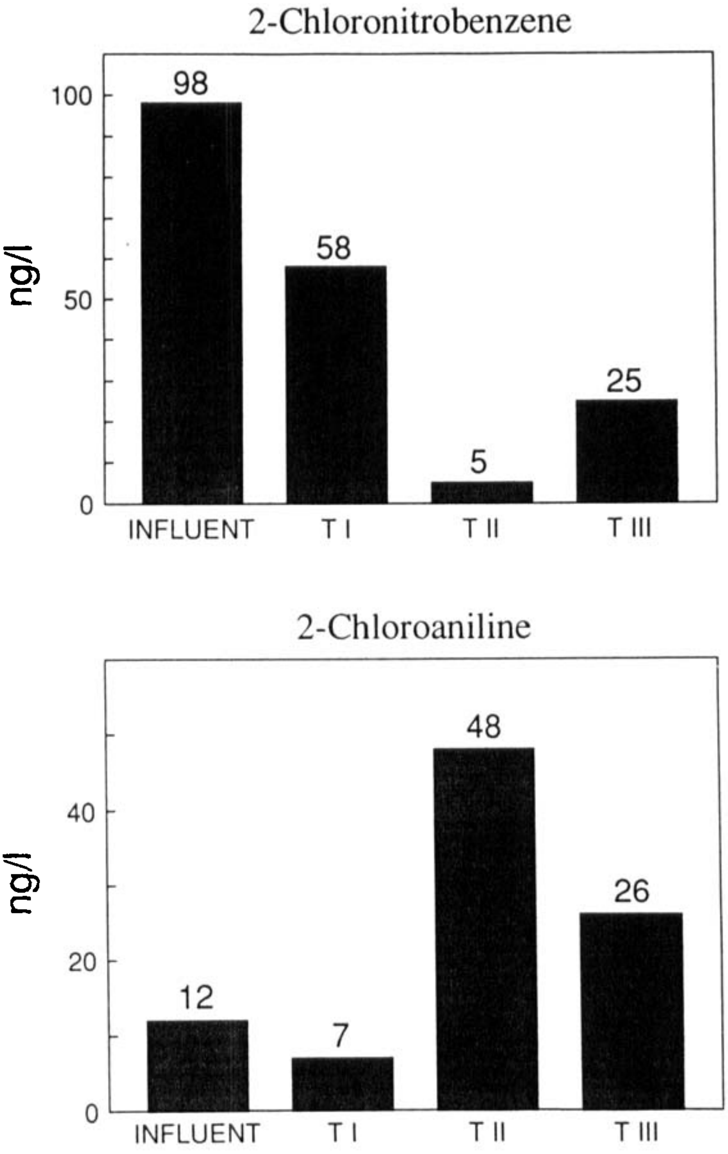

Figure 4 Influent/effluent concentrations for 2-chloronitrobenzene and 2-chloroaniline (mean values).

very low concentrations of CB's in the influent water of the tanks (max. in the order of tens of ng/l), while the results of the studies mentioned in the forgoing references are related to concentration ranges of µg/l.

Nitrobenzenes (NB's), chloronitrobenzenes(CNB's)

The data on the behaviour of the substituted benzenes presented in Table 6 reveal a slight degradation of the studied NB's and CNB's in aerobic Tank I and nearly complete degradation in anaerobic Tank II. From the results of the analyses during the winter seasons (not shown) no negative influence of low water temperature on degradation of NB's and CNB's in this tank could be detected.

An important side-effect of the anaerobic degradation of CNB's was the transformation of 2-chloronitrobenzene to 2-chloroaniline in Tank II (Figure 4). Due to the fact that CA's could posses a higher health risk than CNB's and because the sequential transformation of CA could result in the formation of even more dangerous chloroazobenzenes[22] the potential formation of CA's should be considered as one of the negative aspects associated with anaerobic recharge.

Volatile aromatics

From the analyzed volatile aromatic hydrocarbons only benzene and toluene were regularly present in the recharge water in concentrations above the detection limit (5 ng/l). In none of the tanks a statistically significant change of benzene, present in recharge water in concentrations between 20–30 ng/l, was found.

The data on the removal of toluene in the periods with low and high influent concentrations are presented in Figure 5. The differences in the effects suggest that the removal was quite strongly concentration dependent.

Biodegradation of benzene and methylbenzenes at higher concentrations under aerobic and denitrification conditions has been reported from a number of field studies on riverbank and dune recharge[1,26,27].

Pesticides

To obtain more information on behaviour of pesticides in the whole drinking water treatment system including dune recharge an additional study was performed to investigate the fate of the pesticides, which are frequently found in the river Rhine water, during slow sand filtration. This strictly aerobic biological process is used, as mentioned before, in the postreatment of the recharged water.

The study revealed that by this process, in spite of the high water percolation rate compared with recharge (approxim. 0.2 m/hr) and very short retention time of the water in the filter (in a range of several hours), some biodegradable pesticides could be effectively transformed (Table 7). The study also confirmed that by the degradation of the phenoxy herbicides chlorophenols can be formed. Chlorophenols, regarding drinking water quality requirements, are considered as harmful pollutants due to their very low taste and odor threshold concentrations.

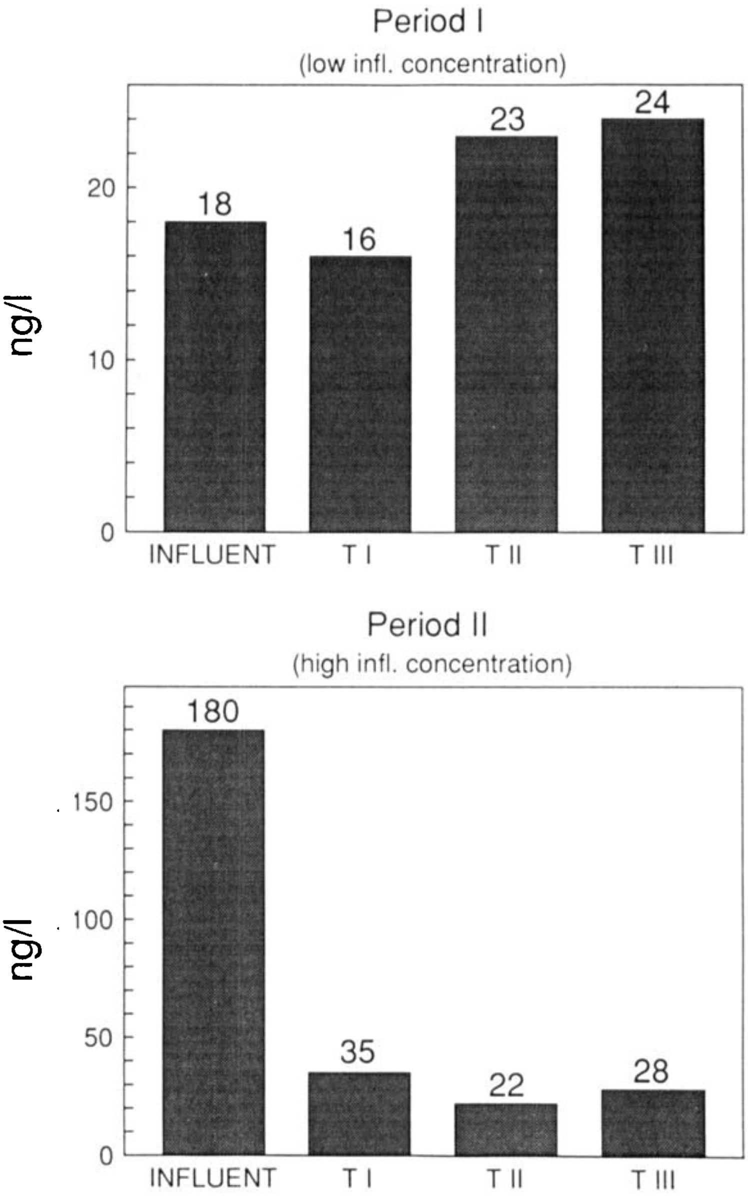

Figure 5 Influent/effluent concentrations for toluene in periodes with low and high influent concentrations (mean values).

Table 7 Transformation of pesticides and chlorophenols during slow sand filtration (N = 8, mean values).

Compound	*Influent concentr. (ng/l)*	*Removal effect (%)*
Atrazine	610	N.S.*
Bentazon	690	N.S.
2.4-D	850	87
MCPA	790	90
MCPP	520	> 90
2,4,5-T	650	70
TCA	2000	50
2,4-dichlorophenol	31	N.S.
2-methyl-4-chlorophenol	< 5	N.S.
2,4,5-trichlorophenol	24	−350

*Statistically no significant change at 95% level

Synthetic chelators

The result of the studies, focused on nitrilotriacetic acid (NTA) and ethylenediaminotetracetic acid (EDTA) confirmed rapid biodegradation of NTA under the condition of the recharge[3]. Even by temperatures below 5 °C and under anaerobic conditions at concentrations up to 2 mg NTA/l a complete removal during the recharge was achieved.

EDTA, as expected, appeared to be entirely nondegradable under suboxic and anaerobic conditions in T II and T III. In T I partial removal was found. The removal appeared to be significantly affected by the level of the influent concentrations and by temperature (Table 8). Concentration dependence of EDTA degradation by biological drinking water treatment, including river bank recharge was already reported by Dietz[28].

From Table 8 and from the information about effect of river bank recharge along the river Glatt in Switzerland[29] and field data from the dune recharge[30], it follows that at the typical EDTA concentrations in the river Rhine water (in the order of several tens µg/l), no appreciable removal by the dune recharge can be expected.

Table 8 Relationship between EDTA removal in Tank I and influent concentrations and temperature (N = 16–26 per period).

EDTA Influent concentr. (µg/l)	*Removal effect (%)*	
	Temperature > 10°C	*Temperature < 10°C*
520	60	27
90	33	16
8	—**	N.S.*

*Statistically no significant change at 95% level
**Not enough data

CONCLUSIONS

– Biological anaerobic degradation appears to be the dominant transformation process during the recharge for the majority of the studied halogenated and nitro-OM.
– The rate of these anaerobic processes by the recharge of water with low concentrations of dissolved organic matter was predominantly determined by the content of unstabilised organic material in the aquifer. This material substitutes the primary substrate and controls the intensity of biological processes and the level of the redox potential.
– Anaerobic dehalogenation and denitrification resulted especially at winter temperatures, in formation of potentially hazardous transformation products, such as dihalomethanes and chloroanilines.
– Remedy of this negative effect and far reaching removal might be achieved by combination with aerobic processes (slow sand filtration) or by the use of effective separation process (adsorption on activated carbon) during the posttreatment of the recharged water.
– The results of the pilot plant studies are generally in good agreement with the field data.

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