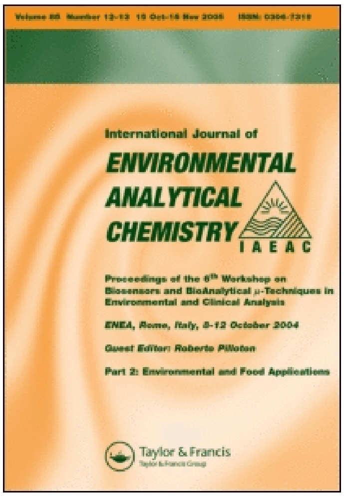

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C. Skark[a]; P. Obermann[b]
[a] Institut für Wasserforschung GmbH Dortmund, Schwerte, FRG [b] Ruhr-Universität Bochum, Institut für Geologie, Bochum, Germany

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TRANSPORT OF PESTICIDES UNDER AQUIFER CONDITIONS

C. SKARK* and P. OBERMANN†

**Institut für Wasserforschung GmbH Dortmund, Zum Kellerbach 46, 58239 Schwerte, FRG; †Ruhr-Universität Bochum, Institut für Geologie, Universitätssraße 150, 44801 Bochum, Germany*

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Pesticide transport was determined in a quarternary coarse grained aquifer which was characterized by low organic carbon content. Water spiked with the pesticides atrazine, chlortoluron, isoproturon, simazine and terbuthylazine and chloride salt as conservative tracer, was injected in the aquifer. Mean residence times (MRT) of pesticides were generally 1.5 to 3 times higher than the MRT of the tracer. Sediment retention capacity calculated from experimental data yielded generally small values below 250 ng/kg sediment. Retardation characteristics were in the order of magnitude expected from literature data on organic carbon/water partition coefficients. Transport of pesticides was due to convection and dispersion whereas adsorption and degradation was low.

KEY WORDS: s-Triazines, phenyl ureas, groundwater, solute transport, retardation properties, organic carbon/water partition coefficient.

INTRODUCTION

Pesticides are detected in groundwater of the Federal Republic of Germany (FRG) although pesticides may only be applicated according to the legal constraints in the FRG, provided that the substance properties do not imply groundwater hazard. In 1989, 31 active substances or their metabolites were found in groundwater of the old states of FRG[1]. The concentrations of 13 substances were exceeding the limit values of 0.1 µg/l for a single pesticide in drinking water. In Northrhine-Westphalia the following substances were found: atrazine (18%), desethylatrazine, simazine, chlortoluron (7%), bromacile, isoproturon, diuron, methabenzthiazuron, propazine, and metolachlor (0.8%; enumerated in descending frequency of detection;[2]). A similar spectre of parameters and a similar distribution of frequency were determined in evaluating reports of states and waterworks in the FRG[3]. The occurrence of pesticides is a severe problem for the drinking-water-supply and makes it necessary to survey transport behaviour of pesticides in the saturated zone.

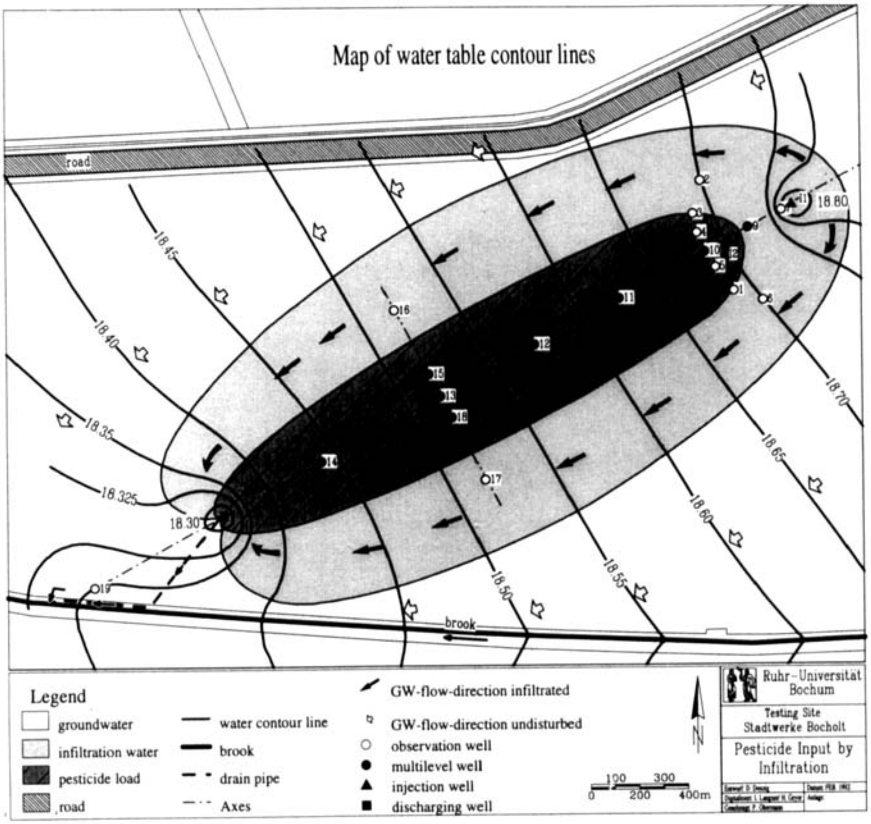

Figure 1 Testing site

EXPERIMENTAL

Description of the testing site

Water, spiked with the triazines atrazine, simazine, terbuthylazine and the phenyl ureas chlortoluron and isoproturon (concentration 1µg/l for each substance) and chloride as a conservative tracer, was continuously infiltrated in the saturated zone of a quarternary, sand-gravel aquifer in Bocholt, Northrhine-Westphalia, FRG, under controlled hydraulic conditions (Figure 1;[4,5]). The site was not precontaminated with pesticides. Water-samples were taken after flow distances of 10 m and 50 m by multi-level-wells to examine pesticide and tracer concentration.

Analytical methods

The pesticide content of water samples was analysed by HPLC with a diode-array-detection after solid-phase extraction with RP-C18-material and elution with acetonitrile[6]. The chromatographic conditions were gradient elution with acetonitrile/water in presence of ammonium acetate on Hypersil ODS (3 μm). s-Triazines and metabolites were detected at a wavelength of 230 nm, phenyl ureas at 245 nm. Quantitative detection limits were 50 ng/l.

The sediment fraction smaller than 2 mm was analysed to determine mineral and clay mineral composition, carbon and nitrogen content and cation exchange capacity (CEC). Mineral and clay mineral studies were carried out by X-ray-diffraction. Organic carbon content was calculated from the difference of total carbon and anorganic carbon content analysed by coulometric titration after pyrolytic digestion or digestion with perchloric acid respectively[7]. Nitrogen content was determined after pyrolytic digestion and chemoluminiscence detection of nitrogen-dioxide[8]. Cation exchange capacity was calculated from the results of an exchange sequence[9], in which the first step was cation exchange on the solid phase by 0,5 M ammonium chloride at pH 7 (saturated by calcium-carbonate) followed by second exchange step by 1 M potassium chloride at pH 2. The ammonium concentration in the second step solution was considered as CEC.

Characterization of sediment and hydraulic condition

In stratigraphy of the testing site tertiary, very low transmissive clay, Dingdener Glimmerton (DGT), is overlayed by 8 m middle-pleistocene fluviatile terrace-sediments, Untere Mittelterrasse (UMT), which are dominated by gravel (Figure 2; averaged median = 4.7 mm). These sediments are covered by further 10 m sand-dominated, young-pleistocene river terrace sequence, Niederterrasse (NT, averaged median = 1.3 mm). The uppermost sequence in the profile is built up by holocene sands and silts. The rock paragenese is dominated by quartz containing up to 10 wt.-% feldspars and subordinately phyllosilicates and calcite. The examination of the clay mineral composition yields an average amount 72 wt.-% illite-smectite in UMT and subordinated parts of chlorite and kaolinite. The aquifer material was characterized by low content of Corg (mean = 213 mg/kg in dry material < 2 mm in UMT; in NT mean = 386 mg/kg) as can often be found in quaternary porous aquifers. The mean cation exchange capacity in the UMT hit the order magnitude of low calcareous sands with a value of 0.6 mmol(eq)/100 g in dry material < 2 mm[10]. Content of nitrogen in the sediments of UMT could be determined between 13 mg/kg and 27 mg/kg in dry material < 2 mm, which was assumed to be bound organically, as no nitrate or very little amounts of ammonium were found in water extracts.

Geometric means of the coefficient of hydraulic conductivity (kf-values) yielded in UMT $3.5*10^{-3}$m/s and $2.9*10^{-4}$ m/s in NT. Flow conditions during the experiment were quasi-stationary. The apparent flow velocities were determined between 0.7 m/d and 1.9 m/d.

Transport behaviour of pesticides in groundwater

Evaluation method To assess transport of chemicals in groundwater, both convective and dispersive transport as well as adsorption- and decay-processes have to be enumerated. In empirical procedures the retardation of non-conservative substances could be estimated by

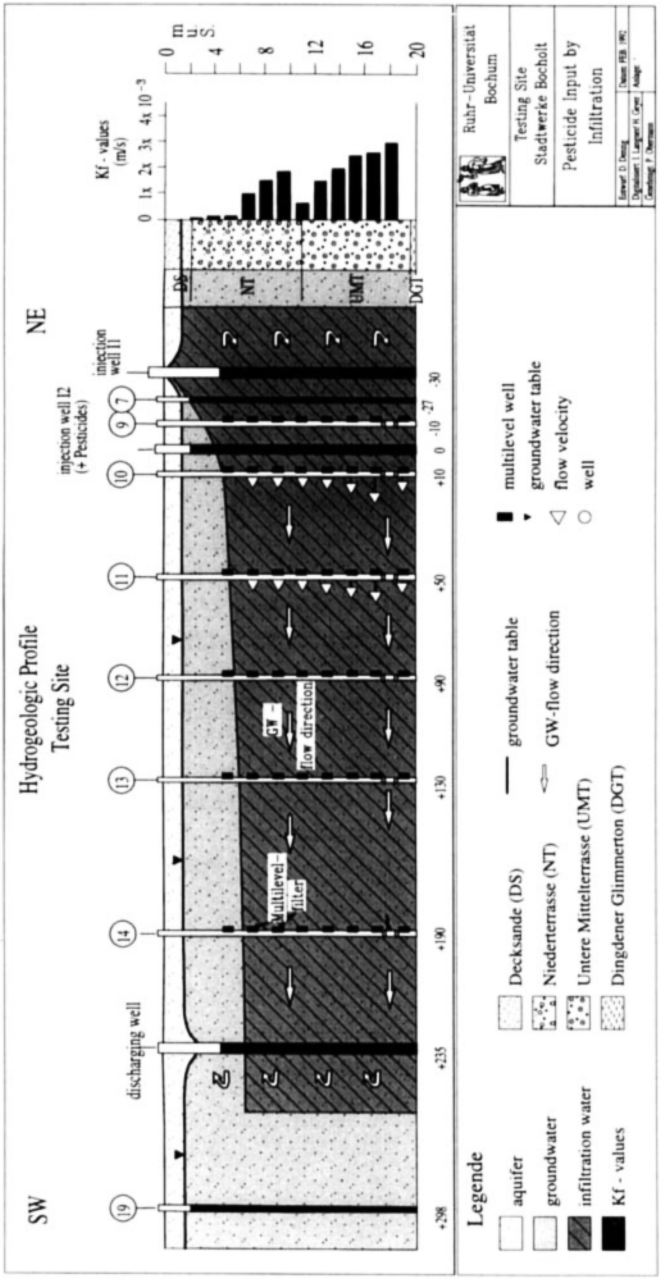

Figure 2 Cross section of the testing site

calculating a mean residence time (MRT) from the time-concentration function[11,12] and comparing the result with the MRT of a conservative tracer. While the tracer concentration is determined by convective and dispersive transport and therefore the time-concentration function reproduces the water-movement, a delay of the non-conservative substance may appear due to adsorption and decay. The relative residence time appears as a relation of the MRT of the conservative and the non-conservative substance to have a measure for the retardation. A specific retention capacity of the sediment can then be obtained under the assumption that retardation is due to adsorption.

RESULTS AND DISCUSSION

After 84 days and 10 m flow distance the mean residence times of pesticides were mostly 1.5 to 3 times higher than MRT of the conservative tracer (Figure 3). Only in 14 m depth some higher relative residence times were found. The evaluation of data for a flow distance of 50 m and a time-interval of 175 days revealed a similar retardation of pesticides. In

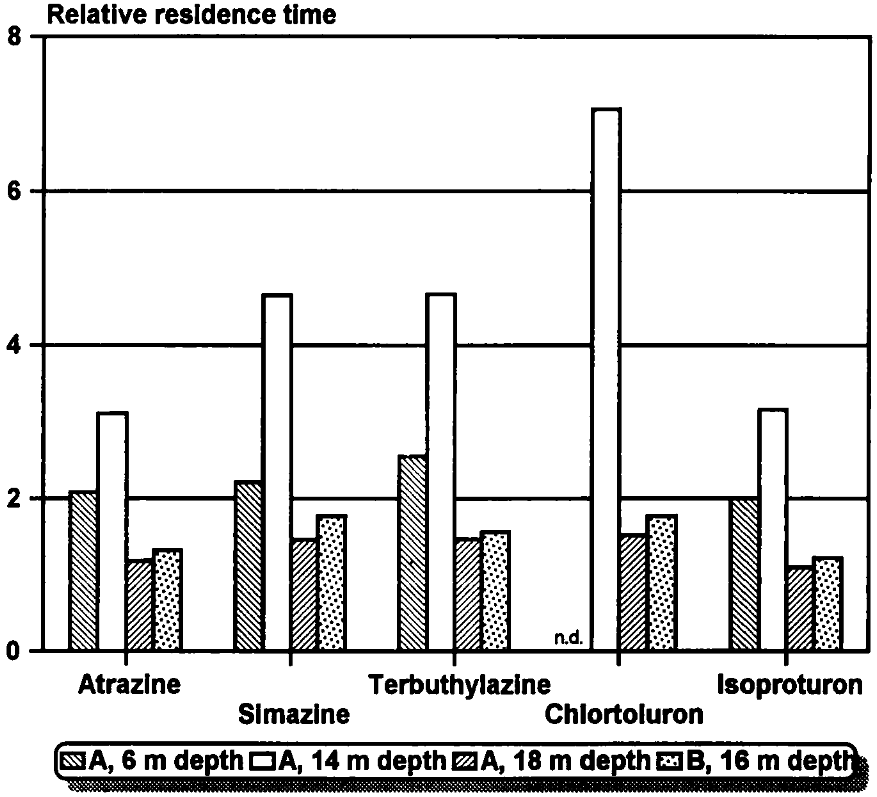

Figure 3 Relative residence times in several depths
A = flow distance 10 m; B = flow distance 50 m; n.d. = not determinable

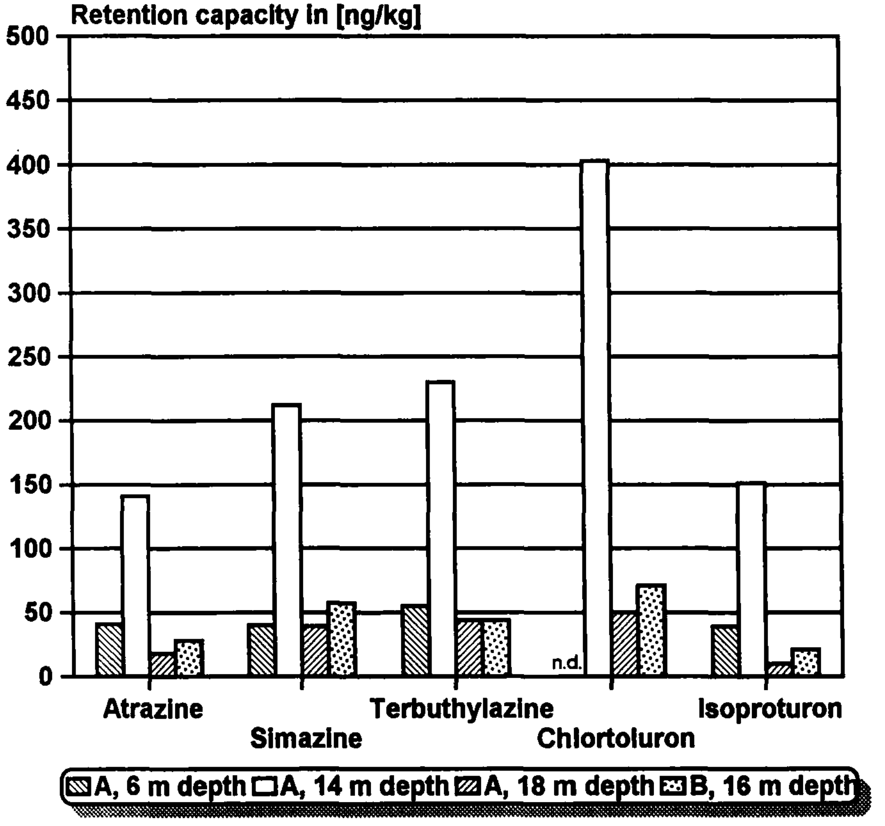

Figure 4 Retention capacity in several depths
A = flow distance 10 m; B = flow distance 50 m; n.d. = not determinable

laboratory- and field-experiments on transport behaviour of triazines other research groups determined similar residence times[13,14,15]. The mobility of pesticides in the Bocholt field experiment decreased in the following sequence:

isoproturon ≥ atrazine > simazine ≥ terbuthylazine > chlortoluron

A calculation of retention capacity yielded mostly small values between 40 ng/kg and 200 ng/kg active substance/kg sediment (Figure 4, Table 1). Only for chlortoluron a higher retention capacity was obtained at 14 m depth and a flow distance of 10 m.

In a semi-quantitative mass balance over 175 days 70% to 90% of infiltrated pesticides were transported convectively or dispersively (Figure 5). Smaller amounts were adsorbed at the sediment (5%). An amount of about 2% had not yet passed the 50 m flow distance at the end of the balance time interval. The remaining part was supposed to be degraded biologically or chemically which corresponds to a "half-life-time" of more than one year

Table 1 Retardation properties in several depths
A = flow distance 10 m; B = flow distance 50 m; n.d. = not determinable

	A, 6 m depth		*A, 14 m depth*		*A, 18 m depth*		*B, 16 m depth*		*Mean*
Substance	*RRT 1) [-]*	*RC 2) [ng/kg]*	*RRT 1) [-]*	*RC 2) [ng/kg]*	*RRT 1) [-]*	*RC 2) [ng/kg]*	*RRT 1) [-]*	*RC 2) 3) [ng/kg]*	*lg(Koc)*
Atrazine	2,1	41	3,1	141	1,2	18	1,3	28	2,65
Chlortoluron	n.d.	n.d	7,1	403	1,5	50	1,8	71	3,14
Isoproturon	2	39	3,2	151	1,1	10	1,2	21	2,61
Simazine	2,2	40	4,7	212	1,5	39	1,8	57	2,93
Terbuthylazine	2,6	55	4,7	230	1,5	44	1,6	44	2,92

1) rounded values; RRT = MRT(pesticide)/MRT(tracer)
2) calculated from exact values; RC = Ci(pesticide)*(RRT-1) * n/[rho*(1-n)]
3) mean calculated from Koc-values of all depths and of all flow distances

A	flow distance 10 m	MRT	mean residence time in [d]
B	flow distance 50 m	Ci	mean infiltration concentration in [ng/l]
RRT	relative residence time	n	effective porosity
RC	retention capacity	rho	grain density in [kg/dm^3]
Koc	organic carbon/water partition coefficient	n.d.	not determinable

under the assumption of a first-order decay reaction. Under these conditions a cumulative concentration increase in the groundwater could not be excluded. Whether any decay reaction took place in reality is doubtful, as the microbial degradation-products of atrazine (desethylatrazine and desisopropylatrazine) could not be detected at any phase of the experiment.

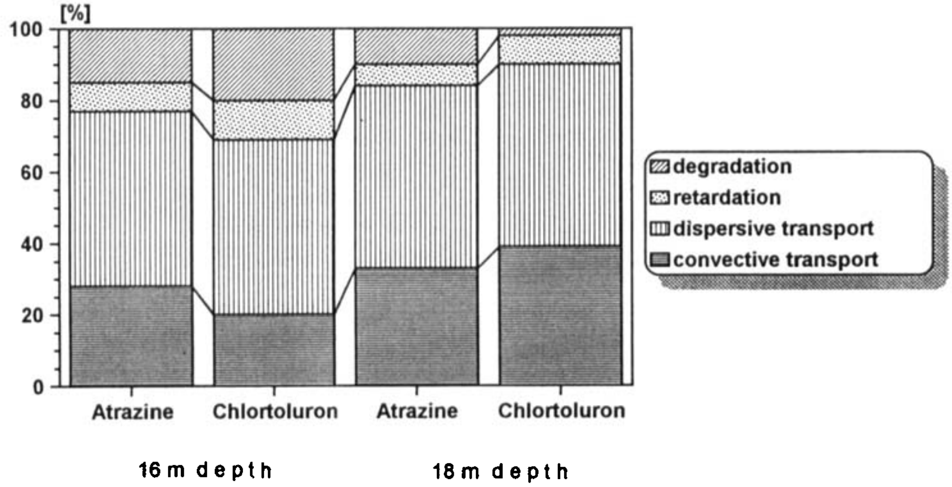

Figure 5 Semi-quantitative mass balance
convective transport = recovery of substance
dispersive transport = calculated from recovery of conservative tracer
retardation = adsorption and storage on the flow distance
degradation = remaining rest

In a second experimental phase the concentration of two substances atrazine and chlortoluron was increased to 4μg/l for each substance in the infiltration water, while the concentration of the other substances was retained. The mean residence times of the substances infiltrated with higher concentration decreased from 38% up to 67% in comparison to the first experimental phase. So a precontaminated sediment yields a noticeable smaller transport retardation of organic substances in the water.

Risk assessment

The transport behaviour of the pesticides varied with depth, but the differences in retardation were small and widely neglectable in risk assessment under groundwater conditions. Thus in risk assessment physicochemical properties of the particular substance should be considered. One of the indicators of adsorption tendency of organic substance is the partition coefficient between water and organic carbon (Koc). Calculating the expected retardation characteristics from Koc-data of literature[16] for the tested pesticides a comparison with experimental data will show that these hit the same order of magnitude except a deviation for chlortoluron (Figure 6). Thus substance characterizing values from literature could give a first assessment of transport behaviour and of the resulting risk.

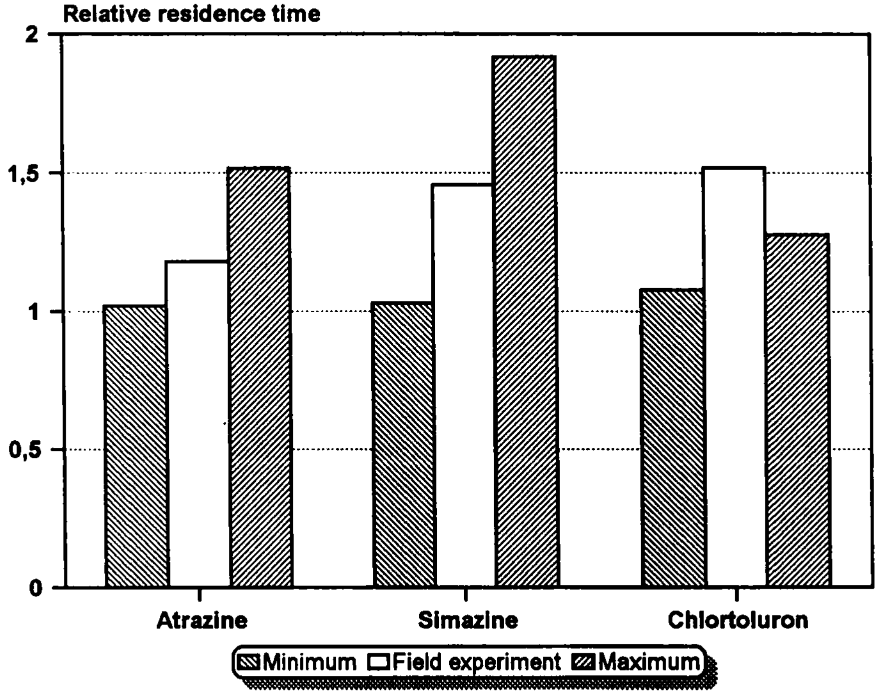

Figure 6 Relative residence times calculated on literature data of organic carbon/water partition coefficients (Minimum, Maximum; [16]) and averaged from the field experiment

CONCLUSION

Once pesticides have reached groundwater, their transport is mainly influenced by convection and dispersion. This is due to different physicochemical conditions in the saturated zone and the sediment of the most porous aquifers compared to the unsaturated zone and the soil. Lower microbial population and activity decrease degradation processes. Coarse-grained, transmissive sediments of productive aquifers are deposited under fluvio-glacial conditions which result in generally low content of sorption-active substances like clay minerals or organic matter in the sedimentary matrix. This content is much lower than in the surface-near weathering-zone. So adsorption plays a subordinated role as retardation moment as well.

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