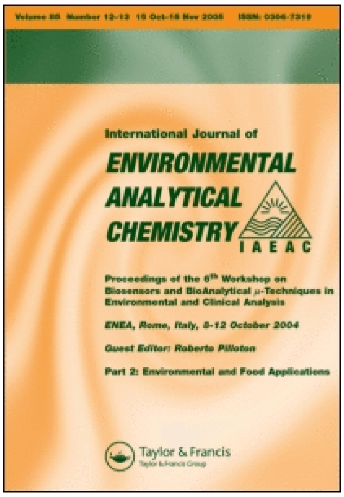

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BEHAVIOUR OF PHENOXYACETIC ACIDS DURING UNDERGROUND PASSAGE WITH DIFFERENT REDOX ZONES

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The behaviour of the three phenoxyacetic acid herbicides 2,4-D, 2,4,5-T and MCPA during underground passage and bankfiltration was tested in a model system consisting of laboratory filter columns filled with natural underground materials. Different redox environments were reproduced by operating the filters with natural aerobic and anaerobic groundwater. In the presence of oxygen, biodegradation of the three herbicides started after a lag phase. Under sulfate reducing conditions, no degradation could be observed. To assess the factors that may influence microbial degradation in the anaerobic environment, the concentration of herbicides, the time and the nutrient content were varied, but this did not increase degradation. The maximum retention of the herbicides in the filters was 30%, mainly due to adsorption to the filter material.

KEY WORDS: Underground passage, phenoxyacetic acids, biodegradation, anaerobic

INTRODUCTION

The phenoxyacetic acids are used as herbicides worldwide since 1940s. Their fate in soil and water has been thoroughly investigated, especially for 2,4-D, 2,4,5-T and MCPA as the most important representatives of the group[1,2]. 2,4-D and MCPA are known to be biodegraded rapidly in aerobic environments while 2,4,5-T-degradation needs a longer adaptation. Recently it has been shown that phenoxyacetic acids are also degraded in methanogenic environments like contaminated aquifers[3,4]. Information on their behaviour under sulfate or nitrate reducing conditions is lacking.

In water catchment areas where groundwater is recharged artificially or by bankfiltration often a typical succession of redox zones is found (Figure 1). When surface water with degradable organic compounds infiltrates into the underground, the available oxygen is depleted by microbial activities and nitrate, manganese, iron and sulfate are used as electron acceptors. In the infiltrating water decreasing concentrations of nitrate and sulfate are found as well as increasing ones of ammonium, iron and manganese. Also the microbial population changes in number, species and activity. Consequently changing redox conditions affect the degradation of pollutants.

To investigate the influence of the redox conditions and especially of sulfate reducing ones on the behaviour of phenoxyacetic acids, different underground environments were reproduced in a model system. Laboratory filter columns filled with two underground materials were operated with either aerobic groundwater or anaerobic groundwater from

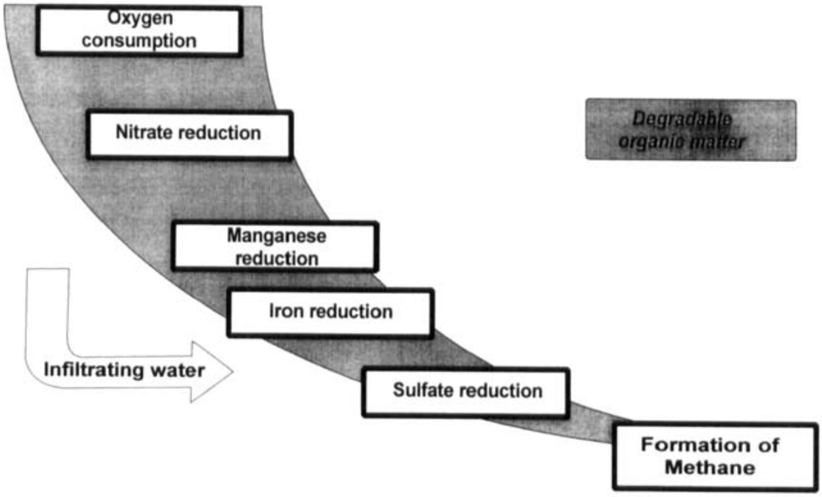

Figure 1 Succession of redox zones during underground passage.

a sulfate reducing site of bankfiltration. Their characteristic parameters are shown in Table 1. Previous experiences have proved that the pilot plant is suitable to reproduce the natural conditions[5].

The three herbicides 2,4-D, 2,4,5-T and MCPA were added continuously to the influents of aerobic and anaerobic filters and their concentrations in the effluents measured. The substrate concentration, the nutrient content and the time for the experiments were varied to assess their influence on degradation.

METHODS AND MATERIALS

The pilot plant

The pilot plant consists of laboratory filters of 1 m (i.d. 22 cm) and a reservoir (Figure 2). The aerobic water is led directly to the filters, while the anaerobic groundwater first passes a reservoir, which is filled with gravel coated with iron and manganese, to

Table 1 Characteristics of aerobic and anaerobic groundwater from the Ruhr valley

Parameter	*aerobic*	*anaerobic*
Flow velocity (m/d)	1 – 50	0.1 – 2
Oxygen (mg/l)	4 – 7	< 0,2
Nitrate (mg/l)	10 – 20	< 0.1
Nitrite (mg/l)	< 0.02	< 0.02
Ammonium (mg/l)	< 0.01 - 0.05	5 – 11
Sulfate (mg/l)	40 – 50	< 0.1 – 2
Iron (mg/l)	0.01 – 0.3	5 – 30
Manganese (mg/l)	0.001 – 0.004	0.4 – 7

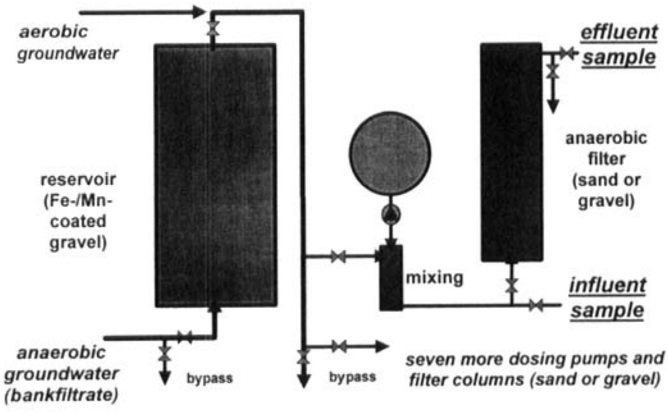

Figure 2 Scheme of the pilot plant.

stabilize the redox situation. Filters and reservoir are operated in an upward flow to guarantee homogenous, reproducible, hydraulic conditions, and, when working anaerobically, to prevent the entrance of oxygen.

The average flow velocity is adjusted to 1.2 m per day. This is in the range of the typical slow flow velocities found in sites of bankfiltration.

Experimental design

By operating the filters with different types of groundwater, aerobic and sulfate reducing environments could be created.

The filters contained gravel from the river Ruhr or sand from slow sand filters to simulate two extreme different underground situations. Herbicide concentrations of 50,200,500 µg/l were applied. The time of the experiments was extended to up to six weeks to allow a microbial adaptation. The influence of phosphate and a supplementary carbon source was determined by addition of 0.5 mg/l phosphate-P or sodium acetate (1 mg/l organic C).

The filters had been operated aerobically or anaerobically for several weeks to establish a stable redox situation before the test substances were added continuously to the filter influents.

Samples were analyzed for the phenoxyacetic acids daily and for nitrate, nitrite, ammonium and sulfate every two days. The latter served as a control for the stability of the redox situation.

Chemical analyses

The determination of the phenoxyacetic acids was performed following a method described as a draft for German Standard Methods (DIN-Entwurf 38407, Teil 13) with gas chromatographic separation and mass selective detection. Sample preparation was slightly changed according to the special requirements of the anaerobic groundwater. 1 l of the acidified sample (pH<2) was spiked with an internal standard (30 µl 2,4,5-

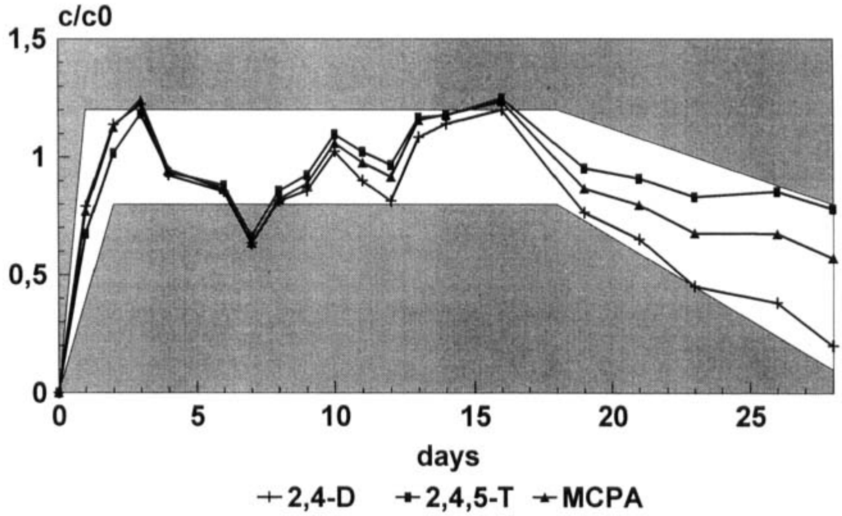

Figure 3 Aerobic sand filter with 200 µg/l 2,4-D, 2,4,5-T and MCPA (relative concentrations).

Trichlorophenoxypropionic acid, c=5 µg/µl) and percolated through a C_{18}-cartridge, that was dried with N_2 afterwards. The phenoxyacetic acids were eluated with 2 x 2 ml of acetone and esterfied with 5 ml of methanol-sulfuric acid (4.5+0.5 ml). After extraction with hexane the compounds were separated by gas chromatography with a DB 5 column and detected by a mass selective detector. Nitrate, nitrite, sulfate and ammonium analyses were done by German Standard Methods (DEV/DIN).

RESULTS

Adsorption and biodegradation are the main mechanisms to reduce the concentration of an organic substance passing a filter. Sorption is often the most important process until equilibrium is reached. Biodegradation in many cases starts after a lag phase, which may differ in length. Rate and extent of both processes depend on the properties of the compound and the environmental conditions.

Figure 3 shows the relative concentrations observed in an aerobic sand filter supplemented with 200 µg/l 2,4-D, 2,4,5-T and MCPA. After two days, the concentrations in the effluent reached the influent ones. The relative concentrations remained almost constant for 2 to 3 weeks except for analytical variations. After about three weeks, phenoxyacetic acids concentration began to decrease probably due to microbial degradation. At the end of the experiment, 2,4-D was degraded to about 20% of the added concentration and MCPA to about 60%. For 2,4,5-T only a slight reduction was observed.

The influence of the redox range on degradation is obvious from Figure 4 which shows an experiment with a sulfate reducing sand filter. Sorption to the filtermaterial appeared to be more effective and a complete breakthrough could be observed only after 6 days against 2–3 days under aerobic conditions. The effluent concentrations remained almost as the influent ones. No degradation of the test substances could be detected even after six weeks.

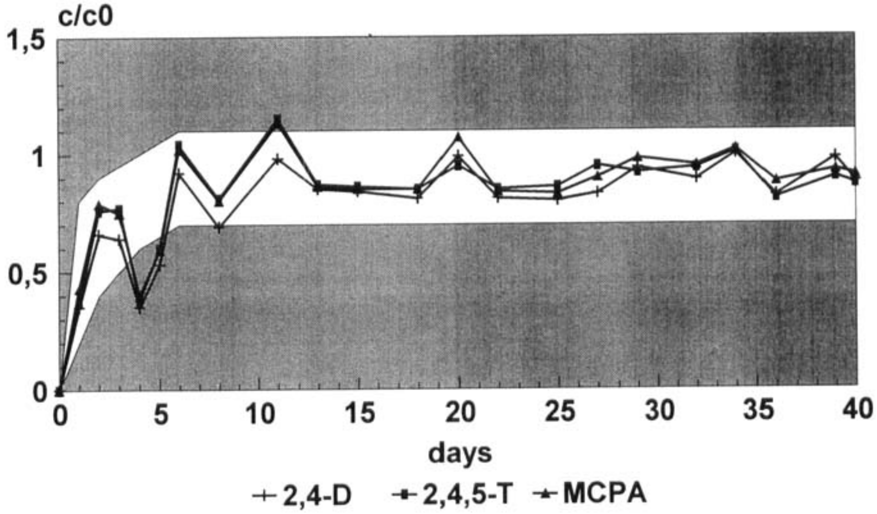

Figure 4 Anaerobic sand filter with 200 µg/l 2,4-D, 2,4,5-T and MCPA (relative concentrations).

To determine the influence of substrate concentration experiments were done with higher (500 µg/l) and lower (50 µg/l) concentrations of the test substances for four weeks.

Figure 5 shows the results of these experiments as mass balances for the different concentrations added and the two filter materials. Percentage retention in the filters was calculated from the amounts of in- and output. A maximum of about 30% retention could be observed at 500 µg/l.

Based on the relative concentration curves it could be concluded that most of the retention in the filters was caused by sorption to the filtermaterial.

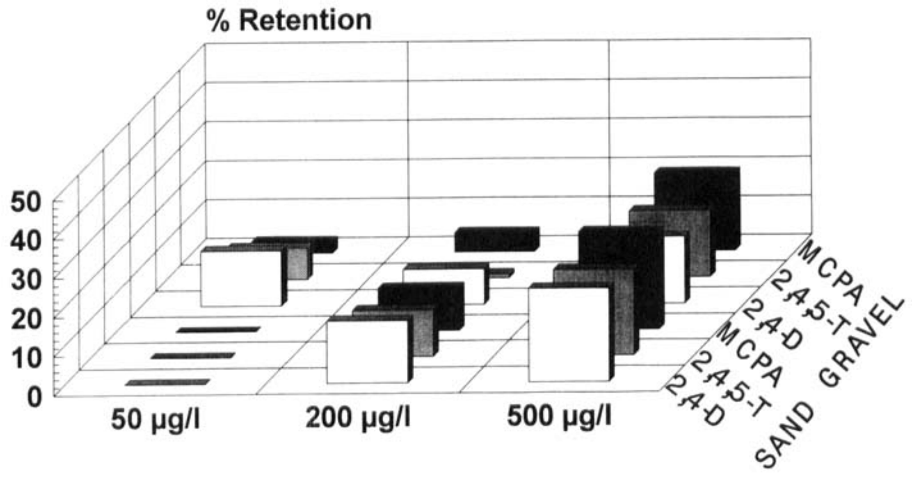

Figure 5 Percentage retention of 50, 200 and 500 µg/l 2,4-D, 2,4,5-T and MCPA in sand gravel filters after 4 weeks.

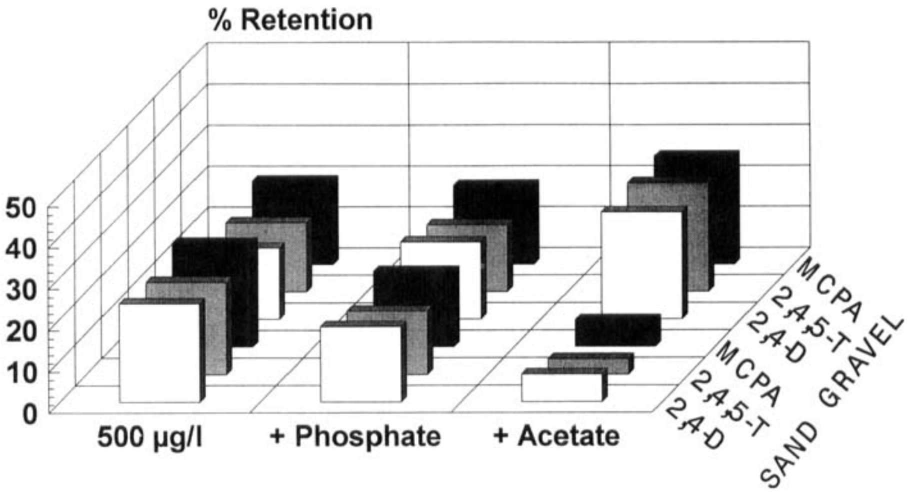

Figure 6 Percentage retention of 500 µg/l 2,4-D, 2,4,5-T and MCPA in sand gravel filters with additional phosphate and acetate after 4 weeks.

No decisive difference was observed between the sand and gravel filled filters. For the sand filters a correlation between concentration and percentage retention was seen.

The anaerobic groundwater contains only small amounts of nutrients and the microbial population is very low. To promote microbial processes, phosphate (0.5 mg/l phosphate-P) or sodium acetate (1 mg/l organic C) were added to the filters together with 500 µg/l of the three herbicides.

The mass balances calculated from these experiments are shown in Figure 6 which compares filters with herbicides only to those with nutrients added. Hardly any increased retention could be induced by nutrient addition. With phosphate almost no difference could be observed, while additional acetate did result in a slightly better reduction in the gravel filter and more remarkable, a lesser one in the corresponding sand filter.

DISCUSSION

The three herbicides could be metabolized after a lag phase of three weeks in an aerobic sand filter in the order 2,4-D>MCPA>2,4,5-T.

Under sulfate reducing conditions the three phenoxyacetic acids were almost persistent. Other investigations in a methanogenic aquifer have shown that phenoxyacetic acids were degraded with a dehalogenation as the first step[6,7,8]. This process was inhibited by high concentrations of sulfate (2000 mg/l). For other compounds dehalogenation was also found under sulfate reducing conditions[9,10]. In our anaerobic groundwater only very small amounts of sulfate are present (<0.1 – 2 mg/l), but no dehalogenation could be observed.

Acknowledgements

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