Treatment of Chlorinated Hydrocarbons Contaminated Groundwater in Constructed Wetlands –

Process Characterisation in Small Scale Experimental Systems

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Monochlorobenzene (MCB) and perchloroethene (PCE) are persistent groundwater contaminants worldwide.
Several studies confirmed that MCB and PCE are degradable through microbial activities but under different conditions. MCB degradation by bacteria usually occurs under aerobic conditions and is usually persistent in the anoxic environment. Unlike MCB, PCE is persistent under aerobic condition, because the initial step of PCE dechlorination can take place only when oxygen is absent; whereas the further dechlorination of its daughter product trichloroethene (TCE) is possible under both aerobic and anaerobic conditions. Therefore, the conditions for biodegradation of MCB and PCE are primarily very different.
A systematic investigation on only MCB removal by a pilot scale horizontal subsurface flow constructed wetland system in Bitterfeld (Germany) has already been conducted in the past.

The objective of this diploma work was to investigate the removal conditions after PCE, as a second compound which needs different redox conditions than MCB, was added to the inflow water. The characterization of the fate of the two contaminants in the wetlands, their spatial and temporal gradients and the occurrence of their metabolites, were main research aspects. Microbial contaminant degradation should be proven with the help of carbon stable isotope fractionation analysis.

The two experimental constructed wetlands had a dimension of 6 m (length) × 1 m (width) × 0.5 m (depth). One wetland (bed) was planted with common reed (*Phragmites australis*) and the other bed was left unplanted (control). Both beds were filled with the local aquifer material. Each soil bulk was 5 m long, followed by a free water compartment up to the outflow. The wetlands were supplied with the local groundwater containing MCB, the main organic contaminant to which PCE was added. An average flow rate of 4.37 l/h, corresponding a hydraulic retention time of approximately 6 days, was realized. The water level was maintained at 40 cm in both wetlands (about 10 cm below the soil surface) and in their free water compartments.

The experimental wetlands showed a high efficiency in removing both organic contaminants from the pore water concomitantly. Only less than 50 % of MCB and 10 % of PCE were left in the outflow water, and the average removal rate of contaminants in the planted wetland was 10-30 % higher than in the unplanted wetland. It confirms that constructed wetlands can effectively remove chlorinated hydrocarbons (even if they need very different redox conditions for their microbial degradation) as contaminants. Particularly the presence of plants enhanced the contaminants removal. In this study, the removal of MCB showed a horizontal profile different from that of the year 2005, i.e., there was not a clear gradient of MCB reduction along the flow path, instead, a more homogenous removal along the flow path was observed after a sharp reduction of MCB concentration from inflow to 0.5 m. Such a different pattern was partly due to the long period of extreme high temperature in the year 2006, which led to overwhelming anoxic

conditions in the soil filter that may not favour aerobic degradation of MCB. Furthermore, this strong reduction of concentrations may also be attributed to volatilization due to the new pressure conditions when the groundwater arrives from a 20 m deep well and enters into both wetlands.
Taken the highly volatile nature of MCB into account, it is concluded that phyto-/volatilisation was the dominant process in MCB removal. At the same time, carbon isotope fractionation analysis for MCB did not provide positive evidence to MCB biodegradation, which opposes the result from the year 2005; however, this pathway cannot be excluded. Apart from the extreme weather conditions, the addition of the new compound PCE may also lead to the unexpected results in this study. Its metabolites VC and DCE are very toxic to organisms, and the microorganisms that degrade PCE may interact with MCB degrading bacteria in unpredictable ways. More research is needed to clarify the new conditions.
Different from MCB removal, PCE was removed gradually along the flow path. Respectively 90 % and 75 % of PCE was already removed from pore water at the first two meters in the planted and unplanted beds. On the one hand, the sharp decrease of PCE concentration in the wetland reflected the process that PCE was quickly distributed throughout the wetland as a new compound; and on the other hand, the strong absorption capacity of the organic matters to the chlorinated solvents like PCE and the enhanced phyto/-volatilisation process could also contribute to the removal of PCE from pore water. The $^{12}C/^{13}C$ isotope fractionation and the occurrence of metabolites of PCE reductive dechlorination clearly proved the occurrence of anaerobic biodegradation. The isotope shift of PCE showed a maximal value of 3.1±0.3 ‰. Furthermore, the high correlation between PCE concentration decrease and the isotope signature enrichment indicated that biodegradation played a crucial role in the PCE removal.
Geochemical parameters were used to characterize the diverse processes in the wetlands. The very low DO concentration suggested the dominant anoxic condition in the wetland, which may favour the anaerobic microbial degradation of PCE. The strong iron(II)-mobilization in both beds indicates that iron(III) may be used as an electron acceptor when oxygen is absent. However, due to the heterogeneity of the rhizosphere, sulphate-reducing and denitrifying bacteria could also co-exist actively in the wetlands.

More research in quantifying the importance of the main removal processes in the wetlands with the help of stable isotope tracers are needed in order to optimise the treatment in the system. So, based on stable isotope fractionation techniques, further investigations are needed to analyze whether biodegradation by plants also takes place in the wetlands. Lab experiments in micro- or meso- scale wetlands should be carried out in order to identify the unclear factors which hinder the biodegradation of chlorobenzene, and to assess the use of iron(III) and sulphate as electron acceptors for contaminant degradation by the microorganisms.