

Constructed wetland treatment of groundwater contaminated by chlorinated volatile organic compounds

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Abstract

Chlorinated volatile organic compounds (VOC) such as monochlorobenzene (MCB), dichlorobenzenes (DCBs) and perchloroethene (PCE) are among the most widespread groundwater pollutants worldwide. Chlorinated VOC contaminated groundwater causes environmental hazards particularly when it discharges into rivers and river floodplains. Constructed wetlands (CW) represent a promising cost-efficient technology to prevent the contamination of surface waters. In the presented study, the removal efficiency and the seasonality of removal, the relevance of various removal pathways and the influence of planting were determined for CW treatment of chlorinated benzenes contaminated groundwater in the temperate climate zone. In addition, the simultaneous treatment of microbially oxidizable and reducible chlorinated VOC (MCB and PCE) and the optimization of CW treatment by adaptation of operation conditions were investigated. Removal of MCB, DCBs and PCE from groundwater was studied in the field and laboratory, using pilot-scale horizontal sub-surface flow (HSSF) CW and rhizosphere model reactors.

A comprehensive pilot-scale study was carried out on the removal of MCB, 1,2-DCB and 1,4-DCB from groundwater in a HSSF CW. Treatment of MCB and 1,4-DCB was efficient, in particular in the upper filter layer, while 1,2-DCB was not considerably removed. Load removal efficiencies amounted to 59-65% ($2327\text{--}3179\ \mu\text{mol m}^{-2}\text{ d}^{-1}$) for MCB and 59-69% ($27\text{--}35\ \mu\text{mol m}^{-2}\text{ d}^{-1}$) for 1,4-DCB in the summer period. The removal of chlorobenzenes was significantly enhanced by the presence of plants (*Phragmites australis*). Modelling of removal processes demonstrated that plants play an important role in MCB removal due to root oxygen release, intensification of water table fluctuations and direct uptake. The application of stable isotope methods and conventional microbiological methods provided evidence for both aerobic and anaerobic microbial MCB degradation. Model calculations confirmed the high potential of oxidative microbial MCB degradation in the system. In contrast, emission measurements indicated that surface volatilization was a minor removal process. Simultaneous treatment of MCB and PCE in the pilot-scale HSSF CW required a long adaptation period, as was evident from the development of PCE and metabolite concentration patterns, and was efficient 2.5 years after operation started. After adaptation, complete removal of 10-15 μM PCE was achieved, and outflow concentrations of chlorinated metabolites were negligible. Ethene production and detection of *Dehalococcoides* sp. indicated complete PCE dechlorination. Up to 100% of the PCE inflow load ($1250\pm 260\ \mu\text{mol d}^{-1}$) were dechlorinated on a filter passage of 1 m, and a maximum of 30% was recovered as ethene. Thus, HSSF CW are a promising approach for the remediation of groundwater contaminated by mixtures of highly and lowly chlorinated VOC.

Technical optimization approaches to MCB and PCE treatment in CW by application of different treatment conditions were explored in macro-gradient free rhizosphere model reactors. MCB removal was very efficient (>99%) under low carbon load (overall oxic) and moderate carbon load (overall reducing) conditions. Higher loads of easily degradable carbon resulted in lower removal efficiencies of 72-96%. Under low carbon load and high carbon

load conditions, 79-87% of PCE loads were eliminated, but no microbial reductive dechlorination activity was detected. Thus, plant uptake and volatilization were considered as important removal processes for PCE. Under fluctuating moderate carbon load conditions, reductive dechlorination was initiated and minimum 10% of PCE inflow loads were dechlorinated. To conclude, moderate additional organic carbon loads enable both MCB and PCE removal processes, indicating a good optimization potential for CW treatment of mixed groundwater contaminations.



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