Abstract

Permeable reactive barriers (PRBs) are one of the innovative technologies being used for *in situ* passive and sustainable remediation of groundwater contaminated with diverse substances including chlorinated solvents, e.g. trichloroethylene (TCE) and tetrachloroethylene (PCE). As the contamination plume passively migrates under the influence of the natural hydraulic gradient, the contaminants react with the reactive materials emplaced in a zone perpendicular to groundwater flow leading to either their transformation to less harmful compounds, or fixation/sorption. To date, zero-valent iron (ZVI) is the most worldwide used reactive material for the removal of chlorinated solvents from groundwater. Although significant removal efficiencies have been demonstrated, the formation of mineral precipitates may limit the long-term performance of the PRB with ZVI by decreasing its reactivity and permeability. Remediation of groundwater contaminated with chlorinated solvents using PRBs with alternative reactive materials is not fully recognized and its comprehensive solution requires development of a methodical approach. This work was aimed to demonstrate that low-cost reactive materials, such as compost and brown coal waste may be an effective alternative to treat groundwater contaminated with TCE to overcome the problems that ZVI possesses.

The site selected as a case study is located in S-E Poland in the vicinity of Nowa Deba. TCE has been detected in the Quaternary aquifer and some wells of the waterworks with concentrations up to 6130 µg/L, exceeding Polish standards for drinking water and giving to the aquifer a “poor” chemical status. It is anticipated that the PRB with compost and brown coal waste mixture may allow to meet both: groundwater and drinking water standards. Feasibility study proved that the site conditions are favourable for installation of the PRB to reduce TCE concentrations to target values. There are no underground structures or geological features that may impede the installation of the barrier, or interfere with the trenching or excavations. Additionally, stratigraphy of the aquifer with a low-permeability clay layer at the bottom makes barrier installation optimal to prevent contaminant underflow. However, the aquifer depth is a constraint that may require expensive construction methods. Groundwater velocity is considered manageable, but since it is high, it can signify an increase in construction costs of a barrier due to higher thickness required to achieve the desired residence time of contaminated plume within the active zone.

Through an extensive literature review candidate materials were identified including: brown coal (waste), compost (commercially available), diatomaceous earth (waste from a brewery), mulch (grass clippings) and zeolite (clinoptilolite). They were selected based on availability, low costs, and suspected or proven ability to remove TCE via biotic or abiotic processes. The material mixtures comprised: compost-brown coal, zeolite-compost, compost-mulch and mulch-diatomaceous earth. They were assumed to increase the general removal efficiencies due to the combination of various removal processes, improved hydraulic performance of the system and accelerated removal rates. Laboratory batch and column tests were conducted to select effective reactive materials to be placed instead of ZVI in a PRB to treat TCE-contaminated groundwater. Results of batch tests indicate that brown coal was the most effective with a removal efficiency of 97%, followed by compost (86%) and the brown coal-

compost mixture (86%). Although the addition of compost to brown coal did not result in higher removal efficiency, it increased the hydraulic conductivity and showed the potential to simultaneously reduce the TCE concentration in groundwater by two processes: sorption and biodegradation. However, biodegradation, needs to be further investigated to ensure the complete dechlorination of TCE into ethane to avoid the accumulation of its daughter products like dichloroethylene (cis-DCE) and vinyl chloride (VC). Considering the results of column experiments, breakthrough curves showed that brown coal was the most efficient in removing TCE from groundwater followed by the brown coal-compost mixture. In addition, the determined hydraulic conductivity (K) for brown coal was two orders of magnitude lower than for compost. The addition of compost to brown coal increased the K value by one order of magnitude due to different particle sizes of the materials, which is beneficial from the PRB design viewpoint. Finally, the retardation factors (R_f) of TCE for brown coal and the brown coal-compost mixture were almost three times higher than for compost alone.

The selected brown coal-compost mixture was further tested in a pilot-scale installation to evaluate under field conditions the efficiency of a proposed PRB to remove TCE (109 μg/L) from contaminated groundwater. Three stainless steel boxes (1.2 × 0.5 × 0.5 m) with the brown coal-compost mixture at three different mixing ratios of 1:1, 1:3, and 1:5 (by volume) were installed at the premises of the waterworks affected by the TCE plume to simulate the PRB. Contaminated groundwater was pumped into the system at a flow rate of 3.6 L/h. Residence times in the boxes were of: 25, 20, 10 hours, respectively. Effluent samples were analyzed for TCE, cis-DCE, VC and ethane. During the 198-day experimental period TCE concentrations in groundwater decreased below ≤1.1 μg/L, i.e. much lower than both: groundwater and drinking water standards in Poland. After 16 days the concentrations of cis-1,2-DCE were recorded indicating possible TCE reductive dechlorination. However, complete transformation of TCE into non-toxic byproducts was not evidenced during the time of experiments, indicating that reductive dechlorination slowed down or stopped at DCE and designed residence times were not long enough to allow the complete dechlorination process.

A 3-D groundwater transport numerical model developed for the studied area using the software - Visual MODFLOW was applied to aid the design of PRB with brown-coal and compost mixture to treat TCE contaminated groundwater at the premises of waterworks. The modeling results allowed to: (i) estimate the groundwater flow changes as influenced by diverse PRB systems (continuous wall and funnel and gate), and propose the optimum configuration, length and thickness of the PRB; (ii) evaluate the effect of decreasing hydraulic conductivity of the reactive materials over time and its impact on key design parameters, such as: capture zone, residence time and discharge rate; (iii) select the location of downgradient monitoring wells to assess the PRB performance. Simulation results suggested that the most effective barrier configuration comprises the funnel and one gate (total length of 1310 m and 3 m thick). The costs of PRB installation at the studied site are high due the depth of aquifer that requires costly excavation methods and the estimated barrier’s length. Comparing the costs for different PRB configurations, it can be concluded that the barrier with one gate is the less expensive alternative. This, along with the analysis of the capture zone, leads to the conclusion that such configuration is cost-effective for the studied site.