



Assessing biodegradation of chlorinated aliphatic hydrocarbons in a river sediment by conservative and reactive isotope tracers (^2H , ^{18}O , ^{13}C)

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This study is part of the joint project SEDBARCAH, which investigates the intrinsic capacity of microbial communities in eutrophic river sediments as natural biobarriers against the release of chlorinated aliphatic hydrocarbons (CAHs) from polluted ground water into surface water. The study site is located in an industrial area in Vilvoorde (Belgium) and characterized by heavily CAH-contaminated groundwater, which infiltrates the sediments of the eutrophic river Zenne.

The stable isotopic compositions ($\delta^2\text{H}$, $\delta^{18}\text{O}$) of ground water, interstitial water, and Zenne surface water were used as conservative tracers to distinguish between river sediment zones, which are characterized by (i) ground water influx and exfiltration and (ii) river water infiltration and mixing between ground and surface water. Interstitial water was sampled in 3 longitudinal river sediment profiles in up to 3 depths in a 45 m long section of the Zenne. The $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -data show that ground water and Zenne surface water are isotopically clearly distinct. Interstitial water mostly exhibits $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -values identical or close to ground water, indicating influx of ground water into the sediments and exfiltration into the surface water at these positions. However, at several sampling positions and depths $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -values of interstitial water approaches or attains those of Zenne surface water. This testifies to surface water infiltration into the river sediments and mixing with ascending groundwater. These findings thus reflect the existence of small- to mid-scale hydraulic

heterogeneities in the sediment and/or differences in the basal river flow velocities, which led to the establishment of zones of rapid as well as slow or even suppressed discharge of CAH-contaminated ground water into the Zenne surface water.

At present, the CAH-pollution in the ground and interstitial water consists of vinyl chloride (VC), *cis*-1,2-dichloroethene (*cis*-DCE), and 1,1-dichloroethane (1,1-DCA). No CAHs could be detected in the surface water. The $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -results show that some interstitial water samples with very low CAH-concentrations are derived from zones of surface water infiltration. Here, $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -values close or identical to surface water indicates that river water was able to infiltrate the sediment, suppress ground water exfiltration, and dilute the CAH-bearing ground water to variable extents. Largely independent of their respective CAH-concentrations ([VC] up to $\sim 1600 \mu\text{g/L}$), most interstitial water samples are derived from a spatially rather broad zone of groundwater influx and exfiltration, as indicated by $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -values approaching those of ground water.

In the vast majority of interstitial water samples, the concentrations and carbon isotopic compositions ($\delta^{13}\text{C}$) of VC and *cis*-DCE exhibit a highly significant correlation. In the overall dataset, $\delta^{13}\text{C}$ of VC and *cis*-DCE ranges from -28.5 to 37.2 ‰, and -12.6 to 5.0 ‰, respectively. In samples where both VC and coexisting *cis*-DCE could be analysed isotopically, *cis*-DCE is markedly enriched in ^{13}C relative to VC. These findings provide clear evidence for sequential biodegradation of both *cis*-DCE and VC by reductive dechlorination in most positions in the Zenne sediments. Very low $\delta^{13}\text{C}$ -values of VC (~ -20 to -29 ‰) occur in the rather broad zone of ground water influx and exfiltration. This finding suggests a rapid transition of the CAHs through the river sediments into the surface water, which results in a lack of sufficient time for effective biodegradation in the sediments. Here, the bulk of CAHs enter the Zenne water and are diluted to concentrations below detection limit. A few samples, however, show VC-concentrations that are (much) lower than expected based on their $\delta^{13}\text{C}$ -values. These samples are characterized by $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -values close to those of surface water. This strongly suggests that here VC-concentrations are (significantly) affected by dilution with infiltrating surface water, in addition to biodegradation. The capacity of the microbial communities of the Zenne sediments as natural biobarriers against the release of CAHs into the surface water is hence significantly determined by the hydraulic conditions in and at the river sediment.