Assessing chlorinated ethene degradation in a large scale contaminant plume by dual carbon–chlorine isotope analysis and quantitative PCR

The fate of chlorinated ethenes in a large contaminant plume originating from a tetrachloroethene (PCE) source in a sandy aquifer in Denmark was investigated using novel methods including compound-specific carbon and chlorine isotope analysis and quantitative real-time polymerase chain reaction (qPCR) methods targeting Dehalococcoides sp. and vcrA genes. Redox conditions were characterized as well based on concentrations of dissolved redox sensitive compounds and sulfur isotopes in SO4 2−. In the first 400 m downgradient of the source, the plume was confined to the upper 20m of the aquifer. Further downgradient it widened in vertical direction due to diverging groundwater flow reaching a depth of up to 50 m. As the plume dipped downward and moved away from the source, O2 and NO3 − decreased to below detection levels, while dissolved Fe2+ and SO4 2− increased above detectable concentrations, likely due to pyrite oxidation as confirmed by the depleted sulfur isotope signature of SO4 2−. In the same zone, PCE and trichloroethene (TCE) disappeared and cis- 1,2-dichloroethene (cDCE) became the dominant chlorinated ethene. PCE and TCE were likely transformed by reductive dechlorination rather than abiotic reduction by pyrite as indicated by the formation of cDCE and stable carbon isotope data. TCE and cDCE showed carbon isotope trends typical for reductive dechlorination with an initial depletion of 13C in the daughter products followed by an enrichment of 13C as degradation proceeded. At 1000 m downgradient of the source, cDCE was the dominant chlorinated ethene and had reached the source δ13C value confirming that cDCE was not affected by abiotic or biotic degradation. Further downgradient (up to 1900 m), cDCE became enriched in 13C by up to 8‰demonstrating its further transformation while vinylchloride (VC) concentrations remained low (b1 μg/L) and ethene was not observed. The correlated shift of carbon and chlorine isotope ratios of cDCE by 8 and 3.9‰, respectively, the detection of Dehalococcoides sp genes, and strongly reducing conditions in this zone provide strong evidence for reductive dechlorination of cDCE. The significant enrichment of 13C in VC indicates that VC was transformed further, although the mechanism could not be determined. The transformation of cDCE was the rate limiting step as no accumulation of VC occurred. In summary, the study demonstrates that carbon–chlorine isotope analysis and qPCR combined with traditional approaches can be used to gain detailed insight into the processes that control the fate of chlorinated ethenes in large scale plumes.