



Evaluating potential chlorinated methanes degradation mechanisms and treatments in interception trenches filled with concrete-based construction wastes

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A complex mixture of chlorinated organic compounds is located in an unconfined carbonated bedrock aquifer with low permeability in a former industrial area next to Barcelona (NE Spain). The site exhibited an especially high complexity due to the presence of multiple contaminant sources, wide variety of pollutants (mainly chlorinated ethenes but also chlorinated methanes) and unknown system of fractures (Palau et al., 2014). Interception trenches were installed in the place of the removed pollution sources and were filled with construction wastes with the aim of retaining and treating the accumulated contaminated recharge water before reaching the aquifer. Recycled concrete-based aggregates from a construction and demolition waste recycling plant were used to maintain alkaline conditions in the water accumulated in the trenches (pH 11.6±0.3) and thus induce chloroform (CF) degradation by alkaline hydrolysis. An efficacy of around 30-40% CF degradation in the interception trenches was calculated from the significant and reproducible CF carbon isotopic fractionation (-53±3‰ obtained in batch experiments (Torrentó et al., 2014). Surprisingly, although hydrolysis of carbon tetrachloride (CT) is extremely slow, a significant CT carbon isotopic enrichment was also observed in the trenches. The laboratory experiments verified the low capability of concrete to hydrolyze the CT and showed the high adsorption of CT on the concrete particles (73% after 50 days) with invariability in its $\delta^{13}\text{C}$ values. Therefore, the significant CT isotopic fractionation observed in the interception trenches could point out the occurrence of other degradation processes distinct than alkaline hydrolysis. Geochemical speciation modelling using the code PHREEQC showed that water collected at the trenches is supersaturated with respect to several iron oxy-hydroxides and therefore, CT degradation processes related to these iron minerals cannot be discarded. In addition, the combination of alkaline conditions in the trenches with in situ chemical oxidation (ISCO), which would be able to remove the rest of the accompanying pollutants, is proposed and merits evaluation. Preliminary batch experiments were performed to evaluate the feasibility of different chemical oxidation reactions (permanganate, persulphate, hydrogen peroxide and Fenton) on the complex contaminated recharge water which were, in general, more effective for degrading the chlorinated ethenes than for the chlorinated methanes (Torrentó et al. EGU 2012).

Therefore, this study seeks to improve the understanding of CF and CT degradation mechanisms/processes that are going on in the interception trenches as well as to select between the two most effective chemical oxidation remediation treatments (persulphate and permanganate) taking into account their efficiency respect the chlorinated methanes removal, the generated acute toxicity and the applicability of the carbon isotopic fractionation as an indicator of the effectiveness of the future in situ remediation.

Additionally, ongoing batch experiments are expected to elucidate if CT is undergoing abiotic reductive dechlorination by Fe-bearing minerals such as hydrophobic green rust (Ayala-Luis et al., 2012) which transform CT into non-chlorinated substances such as formic acid and carbon monoxide. This unstable iron compound might be formed in the interception trenches during chloride induced corrosion of iron mineral phases present in the concrete-based construction wastes (Sagoe-Crentsil and Glasser, 1993). The role of other minerals like iron oxy-hydroxides, carbonates or sulphides cannot be discarded at all. The potential of $\delta^{13}\text{C}$ values to assess the efficiency of this abiotic CT degradation reaction will be also evaluated.

References

Ayala-Luis, K.; Cooper, N.; Bender C. and Hansen. H. (2012) Efficient dechlorination of carbon tetrachloride by hydrophobic green rust intercalated with dodecanoate anions. *Environmental Science & Technology* 46, 3390-3397.

Palau, J.; Marchesi, M.: Chambon, J.: Aravena, R.; Canals, A.; Binning, P. J., Bjerg P. L.; Otero, N.; Soler, A. (2014) Multi-isotope (carbon and chlorine) analysis for fingerprinting and site characterization at a fractured bedrock

aquifer contaminated by chlorinated ethenes. *Science of the Total Environment* 475, 61–70.

Sagoe-Crentsil, K.K.; Glasser, F.P. (1993) "Green Rust", Iron Solubility and the Role of Chloride in the Corrosion of Steel at High pH," *Cement and Concrete Research*, 23(4), 785–91.

Torrentó, C., Audí-Miró, C., Marchesi, M., Otero, N. and Soler, A. (2012) Comparison of four oxidation processes for the treatment of water contaminated with a mixture of chlorinated volatile organic compounds. *EGU General Assembly 2012*. Vienna. *Geophysical Research Abstracts*, 14: EGU2012-11310.

Torrentó, C.; Audí-Miró, C.; Bordeleau, G.; Marchesi, M.; Rosell, M.; Otero, N.; Soler, A. (2014) The use of alkaline hydrolysis as a novel strategy for chloroform remediation: the feasibility of using construction wastes and evaluation of carbon isotopic fractionation. *Environmental Science & Technology*, Just Accepted Manuscript (DOI: 10.1021/es403838t)