

Isotopic Fractionation as a Tool to Assess Degradation of Chlorinated Ethylenes by a Zero Valent Iron Barrier

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INTRODUCTION.

Chlorinated Aliphatic Hydrocarbons (CAH's) such as trichloroethene (TCE) are extensively used as industrial solvents in dry cleaning and metal degreasing processes. One of the most promising remediation techniques for CAH's in groundwater is their removal via abiotic reductive dechlorination using Zero Valent Iron (ZVI). This reaction can be performed in the field by installing a permeable reactive barrier (PRB) (Dayan et al., 1999; Prommer et al., 2008).

During reductive dechlorination of TCE by ZVI, TCE is affected by carbon isotope fractionation (Slater et al., 2002, Prommer et al., 2008). The carbon isotopic composition of residual TCE can be related to the amount of TCE degraded using the Rayleigh model (Prommer et al., 2008). Therefore, stable carbon isotopes analysis has been suggested as a valuable tool to evaluate the extent of degradation and, in consequence, to control the efficiency of the PRB in the field.

OBJECTIVES.

The present study was aimed at (i) determining the isotopic enrichment factor (ϵ) of TCE, which is necessary to estimate the extent of its transformation produced by a ZVI-PRB; and (ii) to study the degradation pathways of cis-DCE during the reaction with ZVI (i.e. hydrogenolysis to vinyl chloride (VC) and dichloroelimination to acetylene). Determination of degradation pathways is a necessary step prior to evaluate the production of toxic intermediates. For this purpose, batch experiments of TCE and cis-DCE were performed.

MATERIAL AND METHODS.

Two batch experiments were carried out in this study. Experiment-1 studied the

degradation of TCE and its isotopic fractionation during reductive dechlorination by ZVI. Experiment-2 studied the degradation of cis-DCE and its possible pathways during reductive dechlorination by ZVI. Both batch experiments were carried out per duplicate using 25 mL vials. The vials were filled with iron (2.5 ± 0.1 g) and the TCE or cis-DCE solution and closed immediately with screw caps with Teflon lined silicon septa and without headspace. The type of iron used in this study was cast iron, which is commonly used in field applications of PRBs (Slater et al., 2002). Control vials, which consisted of TCE or cis-DCE solutions without iron, were prepared along the experiments. The preparation of all the material took place inside an anaerobic chamber. Sample concentrations of both experiments were determined by headspace (HS) analysis using a FOCUS Gas Chromatograph coupled with a DSQ II Mass Spectrometer (GC-MS) (Thermo Fisher Scientific, Waltham, MA, USA). The low molecular weight byproducts from the cis-DCE degradation (ethene, ethane, methane) were semi-quantitatively determined by a gas chromatograph with a thermal conductivity detector (GC-TCD) (Hewlett Packard 5890). Carbon isotope ratios of the samples from Experiment-1 were determined by compound specific isotope analysis (CSIA) using headspace solid-phase microextraction (HS-SPME) and a GC-C-IRMS system consisting in a Thermo Scientific GC IsoLink gas chromatograph coupled to a Delta Plus isotope ratio mass spectrometer through a combustion interface. The method and equipment used are described in detail in Palau et al. (2007).

RESULTS.

The results obtained in Experiment-1 showed that TCE concentration was reduced up to 73% after 180 h, and in

Experiment-2 that 99% of the cis-DCE was reduced after 430 h. The neperian logarithm of both TCE and cis-DCE concentrations versus the remaining fraction was represented over time exhibiting a good correlation ($R^2 > 0.95$) and indicating that the rate of TCE and cis-DCE reduction by iron is a first order with respect to its concentration. The slope of the linear regression obtained represents the rate constant of the degradation processes (0.0065 h^{-1} for TCE and 0.0114 h^{-1} for cis-DCE).

The isotopic composition of the remaining TCE showed a significant enrichment in ^{13}C during the reaction, from -31 to -16‰ . In contrast, the isotopic composition of TCE ($\delta^{13}\text{C}$) in the control vials was approximately constant, with values between -30.9 and -31.4‰ (Fig. 1). TCE isotopic data were evaluated according to a Rayleigh regression not forced through the origin. A square regression of $\ln f$ vs $\ln((\delta^{13}\text{C-TCE}+1000)/(\delta^{13}\text{C-TCE}_0+1000))$ yields a slope of $\alpha-1$ (Fig. 2), where α corresponds to the isotope fractionation factor. The isotope fractionation factor ($\alpha = 0.9866$) was expressed as permil enrichment factor ($\epsilon = 1000(\alpha-1)$) obtaining a value of -13.4‰ .

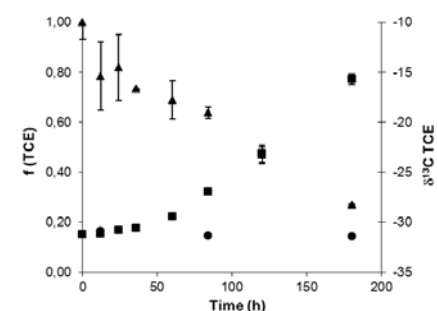


fig 1. Carbon isotope fractionation in the residual TCE during reductive dechlorination. Triangles and squares represent the TCE remaining fraction and its isotopic signature ($\delta^{13}\text{C}$) respectively, circles represent the control experiments.

palabras clave: Hierro Zero Valente, Barrera Permeable Reactiva, Fraccionamiento Isotópico, Etilenos Clorados, Factor de Enriquecimiento Isotópico.

key words: Zero Valent Iron, Permeable Reactive Barrier, Isotopic Fractionation, Chlorinated Ethylenes, Isotopic Enrichment Factor.

Regarding Experiment 2, the byproducts obtained from the reductive dechlorination of cis-DCE were: vinyl chloride (VC), ethene, ethane, methane and butene. VC concentration firstly increased up to 204 µg/L at 108 h and then dropped down to 14 µg/L after 430 h. A significant increase of ethene was also observed during cis-DCE reduction. Ethane also showed an important increase along the course of reaction, while methane and butene were detected in low amounts (Fig. 3).

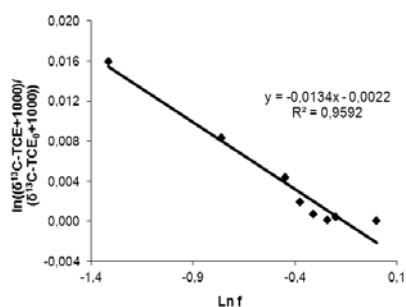


fig 2. Isotope values of residual TCE fraction in a double logarithmic plot over the respective remaining fractions.

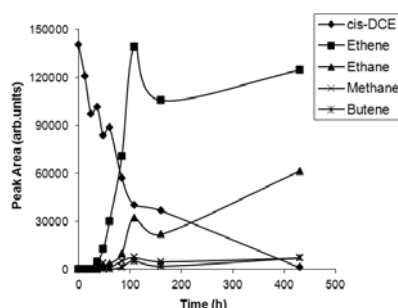


fig 3. Peak areas of cis-DCE and its byproducts over time (Experiment-2).

DISCUSSION.

The calculated K_{obs} for TCE (0.0065 h^{-1}) is within the range of literature values, from 0.0012 to 0.0091 h^{-1} for cast iron (Slater et al., 2002 and Dayan, et al., 1999). Recent TCE experiments conducted with the same cast iron showed higher K_{obs} values but near the upper part of the range (0.0138 and 0.0097 h^{-1}). In the case of cis-DCE the K_{obs} (0.0114 h^{-1}) is higher than the one obtained by Dayan et al. (1999), 0.0053 h^{-1} . As for Dayan et al. (1999), lower K_{obs} were observed in recent experiments for cis-DCE (0.0008 and 0.0006 h^{-1}). During cis-DCE degradation byproducts of the hydrogenolysis (vinyl chloride and ethene) and hydrogenation (ethane) pathway were detected. The concentration changes of VC during cis-

DCE reduction (see above) suggest a rapid transformation of VC to ethene after its production from cis-DCE. The relatively high concentration of ethene after a reaction time of 108 h supports this possibility. The absence of acetylene may be explained by the lower production from cis-DCE and its rapid degradation. This hypothesis is supported on the fact that butene, a possible acetylene byproduct, was detected in a low proportion. Then, ethene seems to be producing ethane because of its increasing presence in the samples.

Regarding the isotopic data, the isotopic composition of remaining TCE in Experiment-1 shows a significant enrichment in ^{13}C over time ($\epsilon = -13.4\text{‰}$) with an inverse relationship between remaining fraction and $\delta^{13}\text{C}_{TCE}$ (Fig. 1). This isotopic enrichment points out that the TCE concentration decrease in the reaction vials is mainly due to degradation by ZVI and not because of non-degradative processes such as volatilization or sorption. Deviation of four points at the beginning of the experiment that do not fall on the curve (Fig. 2) is characterized by a TCE concentration reduction without observing any isotopic fractionation, which typically occurs during non-degradative processes. Consequently, this fact could be associated to TCE sorption on iron particles, also observed on the kinetics of both experiments. Some authors (Dayan et al., 1999 and Slater et al., 2002) also showed similar isotopic deviations from the Rayleigh model curve. These authors indicated that these unfit of the data during early stages of the experiment could be related to non equilibrium partitioning of TCE between the iron, water and TCE.

The isotopic enrichment factor of TCE (-13.4‰) is within a wide range of literature ϵ values for the same reaction but with different types of ZVI and iron treatments (from -8.6 to -24.8‰) (Dayan et al. 1999 and Slater et al., 2002). In the recent experiments conducted with the same type of iron, there were obtained ϵ values of -14.7 and -14.1‰ . Slater et al. (2002) found similar ϵ values for three experiments with the same autoclaved cast iron but with different iron/water ratios: -16.8 , -15.2 and -15.8‰ . These experiments and the wide range found in literature would suggest that ZVI from distinct suppliers could produce different ϵ a

values. Therefore, in order to use the isotopic approach to evaluate accurately the extent of reductive dechlorination of TCE in the field, ϵ values should be determined previously from batch experiments.

CONCLUSIONS.

Significant degradation of both TCE and cis-DCE has been observed in this study, obtaining half lives of 106 and 84 hours, respectively. Reductive dechlorination byproducts of cis-DCE (vinyl chloride, ethene, ethane and butene) have been detected in Experiment-2. Also methane has been found. Both reported degradation pathways (hydrogenolysis to VC and dichloroelomination to acetylene) seem to be occurring, however, further investigation is necessary elucidate which is the most dominant pathway.

The isotopic composition of remaining TCE in Experiment-1 shows a significant enrichment in ^{13}C over time with an inverse relationship between concentration and $\delta^{13}\text{C}_{TCE}$ indicating the role of degradation by ZVI.

Results compared to bibliographic data and recent experiments point out that because of different ϵ values from distinct ZVI suppliers, ϵ values should be determined previously to field applications in order to evaluate accurately the real extent of reductive dechlorination of TCE that occurs in a PRB in the field by using the isotopic approach.

REFERENCES.

- Dayan, H., Abrajano, T., Sturchio, N.C., Winsor, L. (1999): Carbon isotopic fractionation during reductive dehalogenation of chlorinated ethenes by metallic iron. *Org Geochem*, **30**, 755-763.
- Palau, J., Soler, A., Teixidor, P., Aravena, R. (2007): Compound-specific carbon isotope analysis of volatile organic compounds in water using solid-phase microextraction. *Journal Chromatogr A*, **1163**, 260-268.
- Prommer, H, Aziz, L.H., Bolaño N., Taubald, H., Schüth, C. (2008): Modelling of geochemical and isotopic changes in a column experiment for degradation of TCE by zero-valent iron. *J Contam Hydrol.*, **97**, 13-26.
- Slater, G.F., Lollar, B.S., King, A., O'Hannesin, S. (2002): Isotopic fractionation during reductive dechlorination of trichloroethene by zero-valent iron: influence of surface treatment. *Chemosphere.*, **49**, 587-596.