Evaluating TCE Degradation in a ZVI- PRB Using Compound Specific Isotope Analysis

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ABSTRACT

A pilot-scale zero-valent iron (ZVI) Permeable Reactive Barrier (PRB) was installed at an industrial facility to treat a chlorinated Volatile Organic Compound (VOC) plume. Groundwater multilevel monitoring wells showed a decrease in VOC concentrations where high levels of total organic carbon (TOC) have been detected. The geochemical data indicated reducing conditions in the areas where VOC reduction was observed, suggesting that biotic processes could be a major mechanism of VOC degradation. Compound-Specific Isotope Analysis (CSIA) using carbon stable isotopes were used as a complementary tool for evaluating the contribution of abiotic and biotic processes to VOC trends in the vicinity of the PRB. The isotopic data showed enriched isotope values around the PRB compared to the isotope composition of the VOC source confirming that VOC degradation is occurring along the PRB. A batch experiment was performed to evaluate the site-specific abiotic isotopic fractionation patterns. Field isotopic trends were different from those obtained during the batch experiment. These differences in isotopic trends combined with changes in VOC concentrations and redox parameters indicated that biotic processes are the predominant pathways involved in degradation of VOCs in the vicinity of the PRB.

Key words: Permeable Reactive Barrier, zero-valent iron and Compound Specific Isotope Analysis.

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1 - INTRODUCTION

As part of a comprehensive remedial program adopted for an industrial facility, a pilot-scale ZVI-PRB was installed at the downgradient property boundary to prevent off-site migration. As part of the site-monitoring program, multilevel monitoring wells, located upgradient and downgradient from the PRB (Figure 1), were periodically sampled post-PRB installation for VOCs and inorganic compounds to evaluate long-term PRB performance. Data indicated an increase in Total Organic Carbon (TOC) accompanied by a concurrent decrease in terminal electron acceptors, suggesting that biotic processes could be acting as the main mechanisms for VOC degradation rather than the expected ZVI- driven abiotic processes.

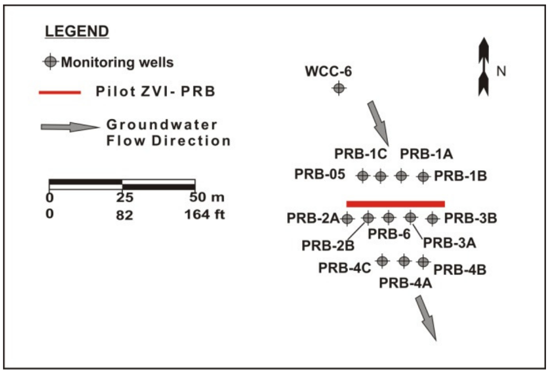

FIGURE 1: Site Layout – Monitoring wells location.

The main objective of this research was to evaluate the role of abiotic and biotic processes on VOCs reduction within the pilot PRB using a combined approach of VOCs and inorganic data evaluation and CSIA.

2 - MATERIAL AND METHODS

Groundwater samples were collected for the analysis of VOCs, dissolved gases, inorganic parameters and CSIA. A batch experiment was conducted in order to obtain the isotopic fractionation factor for the abiotic reduction of VOCs in site groundwater in the presence of ZVI at pre-determined time intervals.

3 - RESULTS AND DISCUSSION

TCE was the main compound present in the groundwater used in the experiment (19.2 mg/L). TCE tended to decrease after 12 hours as the abiotic reaction proceeded, generating by-products such as 1,2-cis-DCE, ethene and ethane (Figure 2A and B).

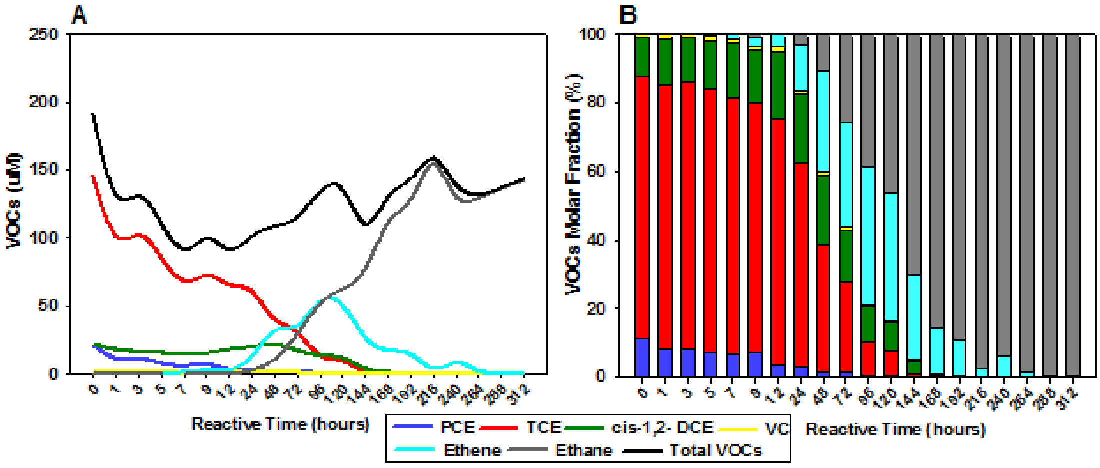

Figure 2: Batch experiment detail – A- VOC's concentrations over time and B- Molar Distribution over time.

Initially, during the first 12 hours of the experiment, no significant isotopic fractionation was observed for TCE, PCE and cis-1,2-DCE (Figure 3). After a period of 12 hours, a high ^{13}C enrichment of approximately 60‰ was observed for TCE during the experiment. This pattern is typical for the abiotic degradation of TCE. Also, an enrichment of δ^{13}C of cis-1,2 -DCE was also observed, following a parallel reaction to the TCE degradation, indicating that cis-1,2-DCE was also degraded . However, as shown in Figure 3, the δ^{13}C of cis-1,2 -DCE was always more depleted than the δ^{13}C of TCE signature over the entire experiment. This parallel pattern has been reported as being a typical trend observed during the abiotic reduction of TCE and cis-1,2-DCE (Elsner *et al*., 2008).

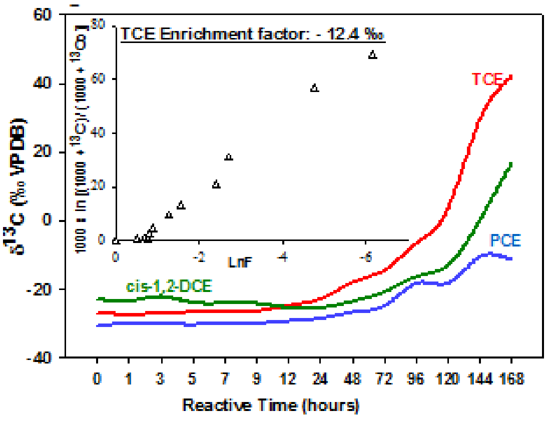

Figure 3: δ^{13}C Isotopic Fractionation during the abiotic experiment.

As shown in Figure 4A, TCE represents 8 to 35% of the total VOCs molar fraction for monitoring wells PRB-01B and PRB-02B. Monitoring well PRB-03B has also shown some evidence of TCE degradation, but to a lesser extent. The δ^{13}C data (Figure 4C) obtained in these wells showed an enrichment of the TCE and 1,2-cis-DCE isotope signatures, indicating that degradation of both compounds is occurring. Cis-1,2-DCE showed a much more enriched $\delta^{13}C$ signature than TCE.

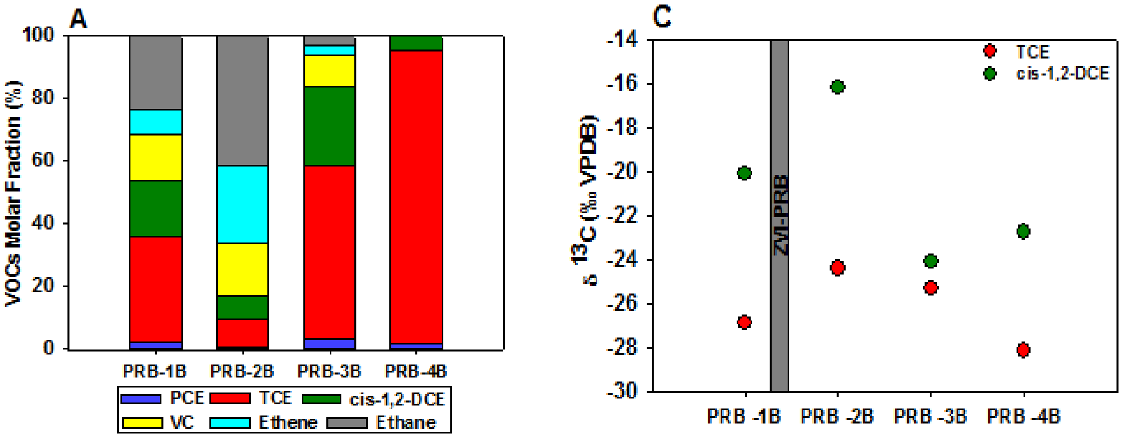

Figure 4: A- VOC's Molar Distribution and C- TCE and cis-1,2-DCE $\delta^{13}C$

Comparing batch and field results, it was seen that batch experiment showed that cis-1,2-DCE is always more depleted in 13C than TCE, following a parallel pattern. In contrast, during biodegradation, isotope signatures of sequential products are initially depleted compared to the reactants and can become more enriched as they degrade. In the field, the isotope signature of cis-1,2-DCE is consistently much more enriched than the TCE signature in the wells where typical daughter products are found. This type of pattern is very characteristic of microbial reductive dechlorination of TCE.

4 - CONCLUSIONS

The results indicated that significant biodegradation is likely to be occurring at the study site in addition to the expected abiotic degradation. It is suggested that high levels of TOC could have persisted in the local aquifer, maintaining high concentrations of electron donors over a long period of time and increasing the biodegradation capacity in the local aquifer in the vicinity of the PRB. CSIA field results, when compared to the expected site-specific abiotic pattern, have also shown strong evidence to support the role of biodegradation as a major process involved in the attenuation of TCE in the vicinity of the PRB.

5 - REFERENCES

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