Fingerprinting TCE Sources in a Sedimentary Bedrock Aquifer using Compound Specific Isotope Analysis.

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ABSTRACT

Chlorinated volatile organic compounds were detected in an industrial facility in the upper part of the underlying sedimentary fractured bedrock aquifer. Several monitoring wells installed at the site were sampled for VOC's, inorganic parameters and Compound Specific Isotope Analysis (CSIA). A deep municipal well, located approximately 500 meters southwest from the investigated site, was also included in this study. VOC's were detected in this well and neither the City nor the Ministry of the Environment of the Province of Ontario (MOE) has been able to determine the origin of these compounds. Groundwater for VOC's analysis and CSIA were therefore collected in the municipal well in order to evaluate the relationship between the Trichloroethene (TCE) detected in the municipal well and the TCE plume detected in the nearby industrial facility. The $\delta^{13}C$ values of TCE obtained in groundwater from the monitoring wells were 12 ‰ more depleted than $\delta^{13}C$ values obtained for the deep production well. These data and the VOC's composition indicate that there is no relationship between the TCE plume at the site and the TCE present in the water of the municipal well, suggesting that other potential regional TCE sources are likely to be present in the area.

Key words: TCE, Compound Specific Isotope Analysis, Fractured Bedrock Aquifer.

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1 - INTRODUCTION

Chlorinated solvents compounds such as Tricholorethene (TCE) are used in a very wide range of industrial processes. The inappropriate handling and disposal of these products associated to the low drinking water standards adopted by the Regulatory Environmental Agencies commonly lead to the occurrence of local impacts to the groundwater of regulatory concern. These impacts are normally associated to the formation of Volatile Organic Compounds (VOCs) dissolved plumes, which can be quite persistent if contaminants are present as Dense Non Aqueous Phase Liquids (DNAPL) or residual phase, acting as long-term contaminant sources. Normally, intensive site characterization is required in these areas in order to identify the sources of contamination and the fate and extent of these plumes in the groundwater system.

A detail site conceptual model is a key component of the progress toward cleanup of contaminated areas. Additionally, the identification of impacted areas is extremely important in source water protection and groundwater management studies, since drinking water wells can become exposed to these impacts, compromising the groundwater quality for drinking purposes.

In industrial areas, the investigation of contaminated aquifers is sometimes not easy to be successful achieved since different source areas of a same compound could exist associated to different industrial properties. In this scenario, comingled plumes can occur beneath multiple properties, creating difficulties in the delineation of individual plumes and in the definition of cleanup liabilities. The same situation also applies when contaminants eventually migrate towards a groundwater receptor and the origin of the compounds of concern cannot be determined.

Normally, in regional studies, the accessibility of data could be sometimes very restricted, since the access of properties is not always allowed. In these cases, a more regional groundwater study to evaluate contamination with multiple potential sources cannot be done using conventional methods. As proposed by van Warderdam *et al.*(1995) and USEPA (2008), Compound Specific Isotope Analysis (CSIA) is a promissory tool for fingerprinting sources of chlorinated compounds in groundwater. The ratio of stable isotopes comprising the chlorinated solvent molecule vary for different manufactures indicating that a same compound may have different isotopic signatures that can be used to distinguish contaminant sources in areas where multiple potential sources are found to occur (Figure 1).

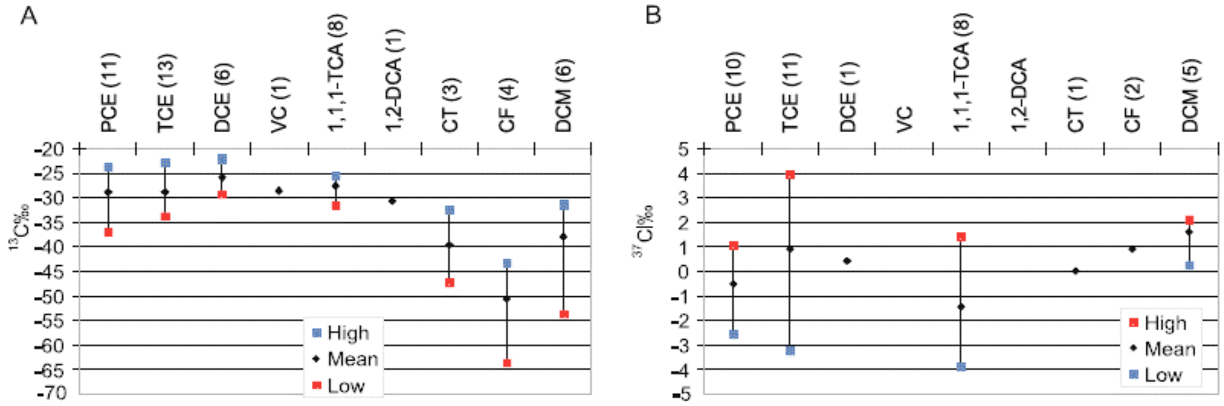

Figure 1. $\delta^{13}C$ (A) and $\delta^{37}Cl$ (B) for different manufactures and products (Modified from EPA, 2008).

1.1 - Objectives

The aim of this study is to evaluate the origin of the TCE detected in a municipal production well located in the vicinity of a TCE contaminated area applying Compound Specific Isotope Analysis.

2 - SITE BACKGROUND

The study site is located in the industrial north-western quadrant of the City of Guelph, Ontario, Canada (Figure 2). TCE has been used in the past as a degreaser and VOC's groundwater impacts associated to three different bedrock aquifer horizons (shallow, intermediate and deep) were identified beneath the property. In the early 1990s, the City of Guelph started an evaluation of the municipal groundwater resources and in 1993, VOC's (mainly TCE) were detected in the groundwater collected from the Smallfield municipal well, which consists in a 102 mbgs (meters below ground surface) open borehole. As a consequence of the presence of these compounds of concern within the local bedrock aquifer, the well was taken out of operation. Multiple potential sources of contamination are found to be potentially associated with this impact since several industries are located in the vicinity of the well. However, up to this point, neither the City of Guelph nor the MOE has been able to determine the origin of these compounds of concern.

2.1 - Site Hydrogeology

The local geology is comprised by a fractured grey dolostone associated with the Guelph and Amabel Formations, with a thickness of approximately 30-40m and 60-70m, overlaid by 3 to 5m of glacial till (Kennel, 2008). Beneath the area of study, three different aquifer horizons were recognized in the upper part of the Guelph Formation as a function of the depth below the bedrock surface and by the vertical contaminants distribution (shallow – from 0 to 4 m, intermediate – from 4 to 10 m and deep – from 10 to 16 m). The main groundwater flow is assumed to be associated to horizontal fractures, which comprises the main structural features of the bedrock. Horizontal hydraulic conductivities values range from 5.1 x 10^{-8} to 5.3 x10^{-3} m/s in some of the wells. Vertical fractures are less frequent but they also contribute to the existence of vertical groundwater flow within the shallow and deep portions of the bedrock.

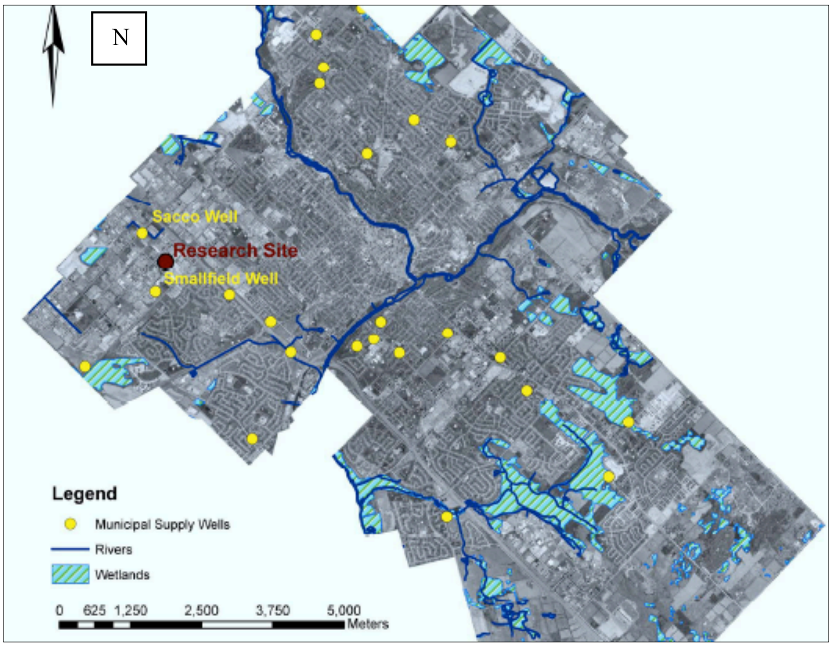

Figure 2. Site location (Modified from Kennel, J.M., 2008).

3 - MATERIAL AND METHODS

3.1 - Field Sampling

Groundwater sampling was conducted in August 2008. Groundwater collected in the monitoring wells were sampled using a peristaltic pump and analysed for selected VOC's, dissolved gases, major cations and anions, alkalinity, trace metals, Dissolved Organic Carbon (DOC), $\delta^{13}C$ of TCE and cis-1,2-DCE. Eight vertical grab groundwater samples were also collected for VOC's and ^{13}C of TCE analysis along the open borehole of the production well using a Canister Sampler in order to conduct a depth discrete vertical profile of the VOC's distribution and to fingerprint the isotopic composition of TCE in the local groundwater. All analyses were performed at the University of Waterloo, Ontario, Canada.

3.2 - CSIA Analytical Methods

The carbon isotope ratio of chlorinated compounds was determined using a gas chromatograph connected via a combustion interface to an isotope-ratio mass spectrometer. Carbon isotope ratios ($^{13}C/^{12}C$) are expressed in delta notation ($\delta^{13}C$) measured relative to the Vienna Peedee Belemnite (VPDB). The ^{13}C values are given using the delta notation defined as $\delta = (R_{sample}/R_{reference} - 1) \times 1000$, where R_{sample} and $R_{reference}$ are the carbon/chlorine isotope ratios of the aqueous sample and the respective standard. The precision for carbon isotope analysis is ± 0.5‰.

4 - RESULTS AND DISCUSSION

4.1 - Contaminant Distribution – Monitoring wells

TCE represents 95 to 100% of the molar fraction of total VOC's (Figure 3) at the source area. Downgradient from the source, the amount of cis-1,2-DCE increases indicating that biodegradation is occurring along the groundwater flow path. MW-19-III, located in the vicinity of the plume, has shown the larger TCE degradation (45% of the molar fraction of VOC's). Inorganic data also indicates that suitable geochemical conditions for TCE degradation exists in this area of the plume since sulfate reducing conditions are found to occur.

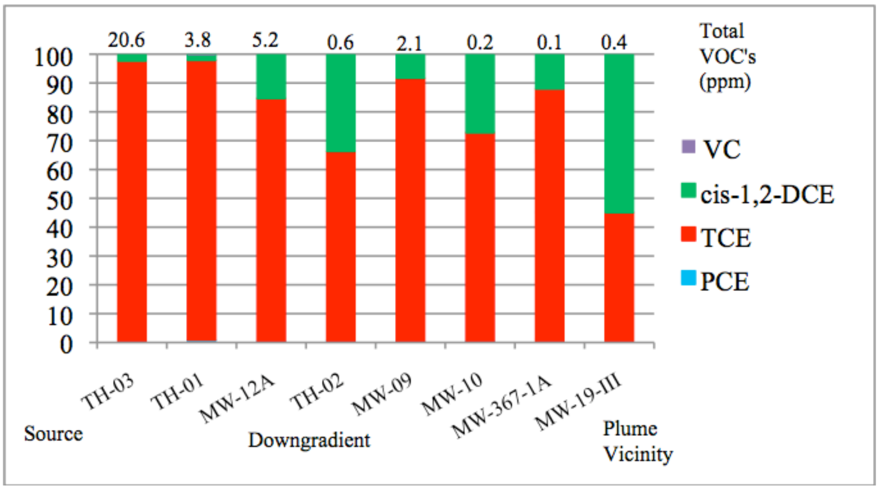

Figure 3. Molar Fraction of Total VOC's - Shallow Bedrock Aquifer.

4.2 - Fingerprinting TCE Source

The carbon isotope data showed a wide range in the $\delta\ ^{13}C$ values, which varies between -35.6‰ and -24.59‰ at the study site. The $\delta\ ^{13}C$ values of TCE from the Smallfield production well are around -23 %. Figure 4 presents the comparison between the shallow monitoring wells and the grab groundwater samples collected in the Smallfield production well. According to the results, a difference of approximately 12 ‰ was detected for the TCE δ^{13}C between the source area well (TH-3) at the site and the Smallfield production well.

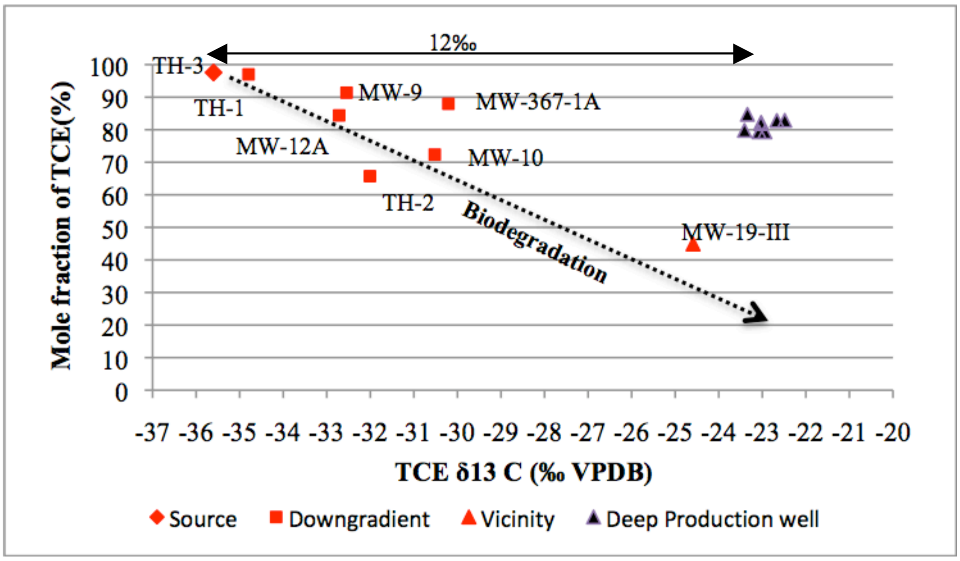

Figure 4. Comparison of the isotope fingerprint- shallow monitoring wells vs. production well.

It is well documented that biodegradation change the isotope composition of organic compounds toward more enriched isotope values (Hunkeler et al., 1999). Then, it would be possible to postulate that the isotope composition of the TCE from the production well could be explained by biodegradation of TCE present in the site source area. This hypothesis can be tested analyzing the expected δ^{13}C enrichment trend as a function of TCE biodegradation, as presented in Figure 4. According to the data, in order to achieve an enrichment of 12‰ in the TCE of the production well starting from the isotopic composition of the TCE at the site source area, the TCE in the production well should account by about 15 to 20% of the VOC's molar fraction. Since TCE represents about 80% molar of the total VOC's in this well, TCE in the production well cannot be linked to the TCE at the site source area.

5 - CONCLUSIONS

The results obtained in this study indicated that biodegradation is one of the processes attenuating the concentration of TCE along the flow system at the site. The carbon isotope and VOC's data have shown that the TCE detected in the Municipal well has a different origin than the TCE plume located beneath the studied area, indicating that other potential TCE sources are responsible for the TCE impact of the groundwater in the areas near the production well.

6 - REFERENCES

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