Natural Attenuation of Methylene Chloride in Salina Group Bedrock Groundwater

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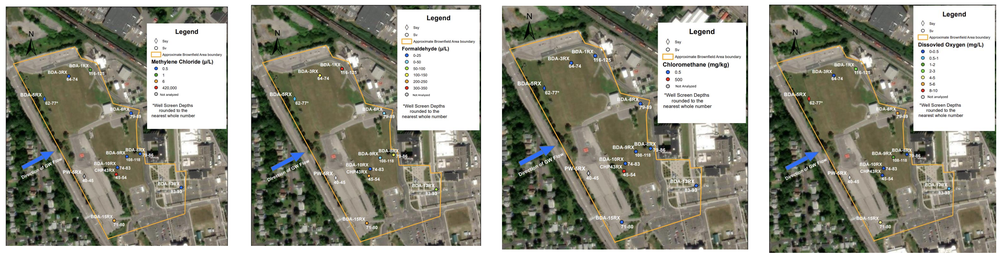
Abstract

The study area is a currently active manufacturing and environmental remediation site located in Onondaga County, New York. The site is affected by groundwater contamination from methylene chloride, an organic solvent used in the process of making Penicillin V. This study aims to determine if there may be natural attenuation processes (biotic or abiotic) occurring in the groundwater at this contamination site. The site is underlain by bedrock consisting of the Upper Silurian Syracuse and Vernon formations. Previously published studies of these formations showed that they primarily consist of siliciclastic (shale or mudstone), carbonate (dolostone), and sulfate (gypsum) lithologies (Leutze 1956) . To get a more complete geochemical characterization, samples from three bedrock outcrops of the Syracuse Formation were analyzed using powder X-Ray diffraction (XRD) and polarized light microscopy. Energy-dispersive spectrometry (EDS) geochemical data for the Syracuse and Vernon formations were also reviewed and included from a preexisting study (Fox et al. 2022). Biotic natural attenuation potential was evaluated by interpreting groundwater parameters in contaminated wells. In terms of abiotic natural attenuation (ANA), geochemical characterization suggests that ferroan dolomite may be a reactive mineral with the potential to facilitate ANA in both formations for certain contaminants, particularly tetrachloroethene (PCE) and trichloroethene (TCE). Evaluation of the potential for abiotic breakdown of methylene chloride was limited in this study by an apparent lack of previous research on this potential natural attenuation mechanism.

Results

Groundwater Parameters/Geochemistry



Maps showing the different groundwater parameters used in this study

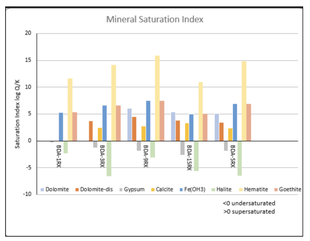
Summary

- Methylene chloride was highest in groundwater wells CHP43RX, BDA-1RX, and BDA-15RX
- Each of the contaminated wells had high concentrations of formaldehyde
- Only well CHP43RX had a significant concentration of chloromethane
- Well CHP43RX had the lowest dissolved oxygen <0.5, DO for BDA-1RX was between 2-3 and BDA-15RX was between 4-5
- Well CHP43RX and BDA-15RX had the highest pH ranging from 10-12, BDA-1RX had a pH of 9-10
- ORP for CHP43RX was -150 to -200, BDA-1RX was -50 to -100 and BDA-15RX was 0 to -50
- Collectively the field parameter and VOC contaminant distribution data suggest:
  - The primary source of methylene chloride in groundwater at the site is close to the location of well CHP43RX
  - Natural attenuation of methylene chloride is occurring based on the detection of known degradation products
- Evaluation of major cation and major anion data indicate that site groundwaters are consistent with Ca-SO4 and Na-Cl waters, which are consistent with bedrock lithology at the site.

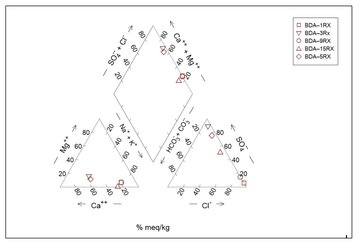
Syracuse and Vernon Formation Geochemistry

Summary of XRD Results

Major Minerals (>10 wt%)	Minor Minerals (<10 wt%)
Ferroan Dolomite $Ca(Mg,Fe^{2+})(CO_3)_2$	Calcite $Ca(CO_3)_2$
Gypsum $Ca(SO_4)\cdot 2(H_20)$	Quartz SiO_2



Dolomite, Dolomite-dis, Calcite, Fe(OH3) Hematite, and Goethite are supersaturated in the groundwater
Halite and Gypsum are undersaturated in groundwater



Deeper Wells BDA-15RX, BDA-9RX and BDA-1RX have Na-Cl waters. Shallower wells BDA-3RX and BDA-5RX have Ca-SO4 waters.

Iron (wt%)			
Syracuse Formation		Vernon Formation	
Max	5.0	Max	4.2
Min	<0.5	Min	1.5
Mean	1.6	Mean	2.9

Summary of EDS Data of the Syracuse and Vernon Formations

References

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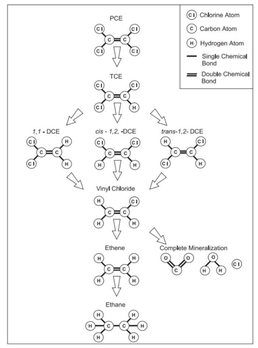
Wiedemeier, T. H., M. A. Swanson, D. E. Moutoux, E. K. Gordon, J T. Wilson*, B. H. Wilson*, D H. Kampbell*, P. E. Haas, R. N. Miller, J. E. Hansen, AND F. H. Chapelle. TECHNICAL PROTOCOL FOR EVALUATING NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUND WATER. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-98/128 (NTIS 99-130023), 1998.

Wright, J., Kirchner, V., Bernard, W., Ulrich, N., McLimans, C., Campa, M. F., Hazen, T., Macbeth, T., Marabello, D., McDermott, J., Mackelprang, R., Roth, K., & Lamendella, R. (2017, November 7). *Bacterial community dynamics in dichloromethane-contaminated groundwater undergoing natural attenuation*.

Methodology

Laboratory analytical techniques were used to provide a baseline geochemical characterization of the Syracuse and Vernon Formations. Three samples of the Syracuse formation were collected from Onondaga and Madison counties for geochemical characterization. Petrographic analysis was used to determine porosity, primary and secondary minerals, and grain size. Slides for petrographic analysis were used from pre-existing studies/research. Pre-existing slides were made from rock samples at the same outcrop sites used in this study. XRD was performed using a Brunker D2 diffractometer to determine mineral composition. EDS detector geochemical data for the Syracuse and Vernon formation were implemented from pre-existing research. To evaluate natural attenuation at the remediation site, readily available public information provided by the New York State Department of Environmental Conservation (NYSDEC) was utilized. Groundwater parameters from a December 2017 sampling date including pH, dissolved oxygen, oxidation reduction potential, chloromethane, and formaldehyde were mapped to evaluate the potential for natural attenuation. Sulfate is also typically used to help characterize natural attenuation; however, given the naturally high concentration of sulfate in the Syracuse and Vernon Formations, it was excluded from this study. The Geochemist's Workbench (GWB) Software was used to compute basic geochemical calculations of groundwater including mineral saturation index and water type. Due to a lack of data, groundwater parameters from a sampling event in 2018 were used. Analytes including sodium, potassium, alkalinity, sulfate, temperature, calcium, magnesium, manganese, specific conductivity were also used to characterize groundwater geochemistry at this site.

Pathways and Products



Process of reductive dechlorination (Wiedemeier et al. 1998)

Biological-Anerobic

Anaerobic degradation involves reductive dechlorination. Anaerobic microorganisms use chlorinated molecules as an electron acceptor. Through this process, chlorine atoms are sequentially removed from the contaminant molecule and replaced by hydrogen. In the case of dichloromethane, reductive dechlorination will remove a chlorine, and chloromethane will be produced as a result (Popek 2018).

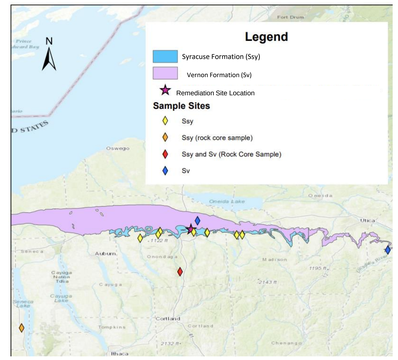
Biological-Aerobic

Aerobic degradation of dichloromethane by microorganisms is catalyzed by the enzyme DCM dehalogenase. Through this process, dichloromethane is converted into two molecules of HCL and formaldehyde (Wright 2017).

Abiotic

In most chlorinated solvents natural attenuation occurs through reductive dechlorination via reactive minerals. However, the rate and exact method of natural attenuation for methylene chloride is not well understood.

Sample Locations



Sample locations of rocks used for XRD and EDS analysis

Conclusions

- There is evidence that both aerobic and anaerobic natural attenuation has occurred in well CHP43RX.
  - The process of reductive dechlorination is demonstrated by the chloromethane concentration (produced by the breakdown of dichloromethane). As well as, the dissolved oxygen concentration (<0.5), and ORP (reductive pathways are most likely to occur in reducing conditions in groundwater).
  - High concentration of Formaldehyde in groundwater in well CHP43RX suggests that aerobic natural attenuation had occurred. Formaldehyde is a common product of aerobic degradation of dichloromethane. Aerobic natural attenuation is an oxygen consuming process. It is possible that DO decreased to the concentration it is currently at through aerobic natural attenuation.
  - In contaminated wells BDA-1RX and BDA-15RX, aerobic attenuation is most likely dominant. Formaldehyde concentrations, DO, as well as pH supports the conclusion that aerobic attenuation is occurring. The concentrations of chloromethane are not significant enough to conclude anaerobic attenuation is occurring, dissolved oxygen concentrations are also too high to support anaerobic attenuation (>0.5).
- Volumetrically ferroan dolomite is the primary mineral in the Vernon and Syracuse formation with the potential to facilitate ANA.
- Supersaturation of dolomite, goethite, and hematite suggest these minerals have the potential to precipitate in site groundwater and therefore have the potential to act as reactive iron minerals
- It cannot be concluded whether or not abiotic natural attenuation is occurring in the groundwater wells given the apparent limited amount of research regarding ANA of methylene chloride