Providing Additional Support for Monitored Natural Attenuation (MNA) by Including Abiotic Degradation of CVOCs

INTRODUCTION

Mass magnetic susceptibility measurements can provide useful information by providing a surrogate estimate of magnetite abundance therefore indicating potential for abiotic reactions. This fact sheet focuses on the collection of mass magnetic susceptibility data in aquifers with PVC monitoring wells, open boreholes, or soil borehole core data.

The following topics are discussed:

- Abiotic Degradation of Chlorinated Ethylenes by Magnetite;
- Occurrence and Importance of Magnetite in Aquifer Systems and Relationship with Mass Magnetic Susceptibility;
- Overview of Methods Used to Quantify Mass Magnetic Susceptibility;
- Using a Downhole Sonde to Measure Magnetic Susceptibility, and;
- Good Practice to Apply Data on Magnetic Susceptibility to Document Abiotic Degradation.

ABIOTIC DEGRADATION OF CHLORINATED ETHYLENES BY MAGNETITE

Abiotic degradation of chlorinated ethylenes in aquifer materials containing magnetite can be an important mechanism for natural attenuation. In contrast to anaerobic biodegradation, abiotic degradation by magnetite does not go through a sequential reductive dechlorination. That is, PCE is not degraded to produce TCE, TCE is not degraded to DCE, and DCE is not degraded to VC. As a consequence, degradation of chlorinated ethylenes by magnetite does not produce compounds that are on the list of USEPA MCLs. Instead, this degradation produces compounds that are not detected by EPA Method 8260.

At some sites, a cursory analysis of solute concentration data suggests that TCE is degrading to DCE, but further degradation of DCE has "stalled" because there is no evidence for production of VC or Ethene. However, when the monitoring data are evaluated using a computer model of the solute plume that properly accounts for dispersion, advection and sorption, it is necessary to have degradation of cDCE in the model to be able to calibrate the model to the field data.

This indicates that another degradation mechanism must be operating at the site. In many cases, this degradation can be attributed to degradation by magnetite. A relationship has been found between degradation rate constants and magnetic susceptibility associated with magnetite in aquifer sediment (Figure 1).

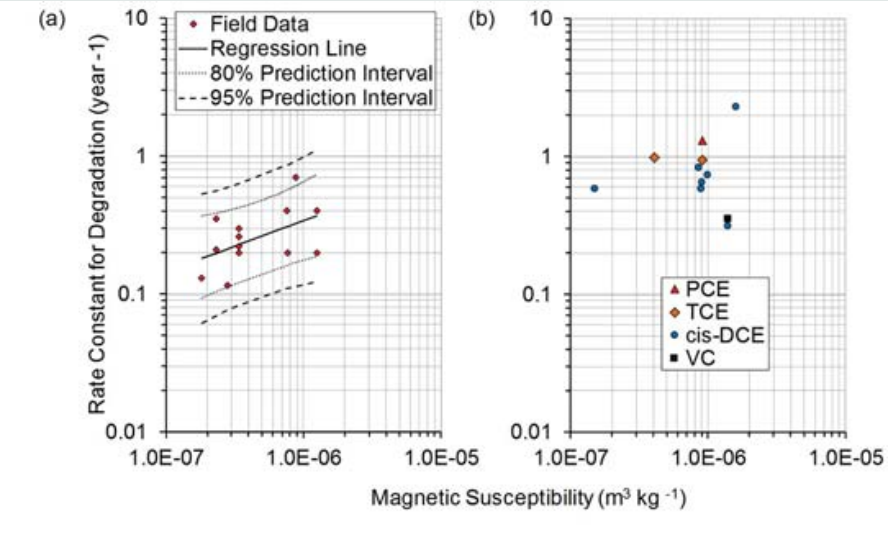

Figure 1: Relationship Between 1st Order Degradation Rate Constant for Degradation by Magnetite and Magnetic Susceptibility (a) Rate Constants at Field Scale (b) Rate Constants in Microcosms. From Wiedemeier et al. (2017).

RESOURCES

WWW.SERDP-ESTCP.ORG

Search for Projects ER-201129/ER-201129-201584

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/

Wiedemeier et al. 2017. Efficacy of an in-well sonde to determine magnetic susceptibility of aquifer sediment: Groundwater Monitoring and Remediation: DOI 10.1111/GWMR.12197

Disclaimer: This publication is intended to be informational and does not indicate endorsement of a particular product(s) or technology by the Department of Defense (DoD) or T.H. Wiedemeier & Associates, Inc. (THWA), nor should the contents be construed as reflecting the official policy or position of any of those Parties. Mention of specific product names, vendors or source of information, trademarks, or manufacturers is for informational purposes only and does not constitute an endorsement or recommendation by the DoD or THWA. Although every attempt is made to provide reliable and accurate information, the authors of this publication do not warrant or otherwise represent in any way the accuracy, adequacy, efficiency, or applicability of any product or technology discussed or mentioned herein, including the suitability of any product or technology for a particular purpose.

OCCURRENCE AND IMPORTANCE OF MAGNETITE IN AQUIFER SYSTEMS AND RELATIONSHIP WITH MASS MAGNETIC SUSCEPTIBILITY

Magnetite is a natural component of many aquifers. There is a direct correlation between the quantity of magnetic materials in aquifer sediments and their magnetic susceptibility (Figure 2; Canfield and Berner, 1987; Horneman et al., 2004). The relationship is linear over a range in values of two orders magnitude. However, there is significant variation from one sample to the next. The 95% prediction interval on the quantity of magnetic materials varies by a factor of 3.4 from the regression line. The magnetic susceptibility of aquifer sediment can be characterized with good sensitivity and at low cost.

Under ordinary circumstances the magnetic susceptibility of soil and sediment is dominated by magnetite. There is an important exception. Greigite (Fe_3S_4) can form in sediments with adequate sources of sulfide and iron (Roberts, 2015). The magnetic susceptibility of greigite can be as high 2.0E-04 m^3/kg (Dekkers et al., 2000), which brings it in the same range as magnetite. In sulfate-reducing aquifers, it is possible that greigite will produce magnetic susceptibility that can be confused for magnetite. This normally is not a problem, because in such aquifers, anaerobic biological reductive dechlorination usually is the predominant degradation mechanism.

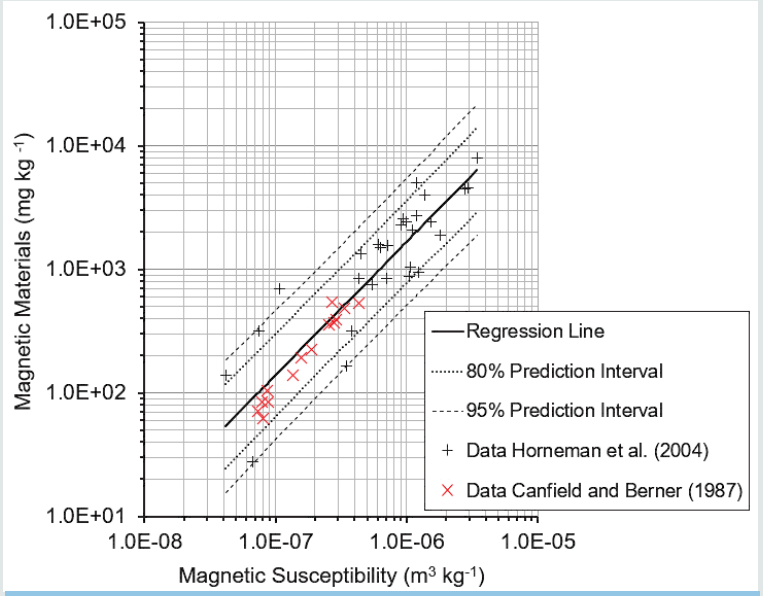

Figure 2: Relationship Between Magnetic Susceptibility of a Sediment and the Content of Magnetic Minerals. Redrawn from He et al. (2009).

OVERVIEW OF METHODS USED TO QUANTIFY MASS MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility can be measured by several methods, including:

- Collection of samples from borehole cores for analysis in an analytical laboratory using a mass magnetic susceptibility meter (Figure 3);
- Use of a downhole sonde (Figure 4) in an open borehole, and;
- Use of a downhole sonde in a non-metallic groundwater monitoring well.

As shown by Wiedemeier et al. (2017), both the mass magnetic susceptibility meter and the downhole sonde give similar results. However, the sonde provides many more data points over a given vertical interval, thus providing better aquifer coverage.

The choice of whether to use soil samples or a downhole sonde typically depends upon where a site is in the characterization process. For those sites where borehole drilling is complete, a downhole sonde in completed PVC monitoring wells may provide the only access to site-specific magnetic susceptibility data.

Figure 3: Barrington MS2 Magnetic Susceptibility System with the MS2BDetector Used to Analyze Rock and Sediment Samples.

Figure 4: Downhole Magnetic Susceptibility Sondes. The White Sonde is 125 cm (~49 inches) Long and Has a Diameter of 45 mm.

USING A DOWNHOLE SONDE TO MEASURE MAGNETIC SUSCEPTIBILITY

Borehole sondes used for magnetic susceptibility are based on electromagnetic induction. This principle is illustrated in Figure 5. A small transmitter coil is energized with an alternating current. This coil (Tx) generates an alternating magnetic field which is sensed by a nearby receiver coil (Rx). The magnetic susceptibility sonde has a finite depth of lateral penetration based on the spacing of the coils and the amount of energy used to induce the magnetic field. The receiver coil together with a capacitor bank and oscillator circuit produce an alternating magnetic field in the vicinity of the coil. Any magnetic material bought within the influence of this field brings about a reduction in the natural resonant frequency of the oscillator circuit. The magnetic susceptibility of the materials immediately around the borehole is proportional to the reduction in the natural resonant frequency. This is measured by a meter/data logger attached to the sonde (Figure 6).

One sonde that can be used is the W&R Instruments HM-453S (W&R-instruments, Brno, Czech Republic: http://www.wr-instruments.com/index.php). For the HM-453S, the Tx-Rx spacing is 25 cm. This equates to optimal readings being made at roughly 20 cm from the sonde, with the accuracy of the magnetic susceptibility measurements dropping off beyond this distance. Based on this, boreholes less than about 40 cm in diameter are optimal for the HM-453S. Magnetic susceptibility readings made in larger boreholes will not be as accurate as those made in smaller boreholes.

In addition to borehole diameter and well construction materials, the sonde is particularly sensitive to temperature. Therefore, the sonde must be lowered into the formation water and allowed to equilibrate for at least 15 minutes prior to calibration and subsequent use.

Figure 6: Winch Used to Lower and Raise Sonde and Matrix Data Logger. Data Logger is Connected to Computer via USBCable.

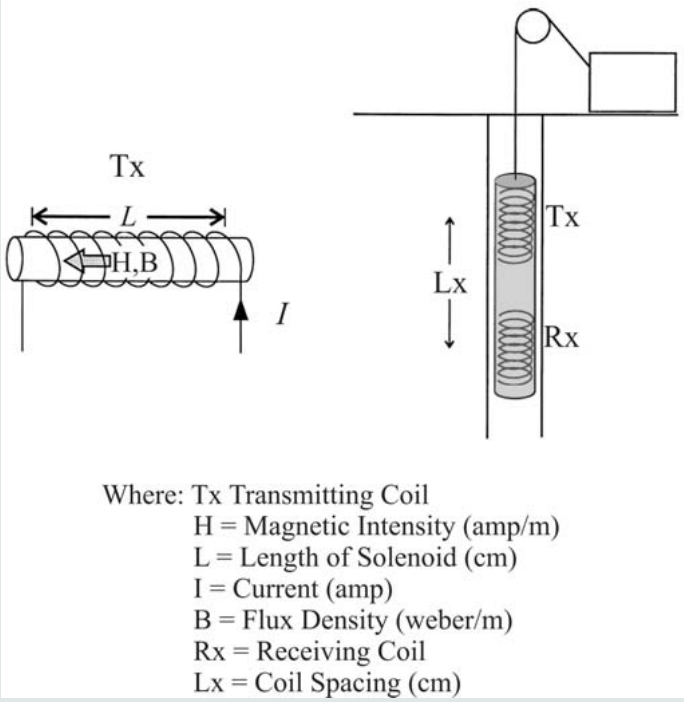

Figure 5: Theory for Mass Magnetic Susceptibility Probe. From McNeill et al. (1996).

The sonde reports volume magnetic susceptibility in SI units. The volume magnetic susceptibility values reported by the sonde need to be converted to mass magnetic susceptibility. This can be accomplished by dividing by an assumed bulk density for the aquifer material.

Assuming a porosity of 0.35 and a particle density of 2,650 kg/m^3, the bulk density is 1,700 kg/m^3. Following these assumptions, the working range of the HM-453S sonde extends from 4.12E-9 m /kg to 4.12E-5 m^3/kg.

The sonde should be recalibrated immediately prior to use in each monitoring well. One method to accomplish this is to first calibrate the sonde against air (avoid electromagnetic fields such as overhead power lines and metallic objects), which was taken to have a value of zero (0), and then against a standard. For the range of magnetic susceptibilities commonly found in common aquifer materials, a magnetic susceptibility of 2.94E-6 m^3 /kg is a good choice. During the validation project, for the HM-453S, the standard was contained in a holder that is positioned at a fixed location alongside the sonde. The response of the sonde was adjusted to match the value of the standard. The holder containing the standard was removed and the sonde was introduced into either 5.1 cm or 10.2 cm ID PVC groundwater monitoring wells using a Mount Sopris Instruments R-4200-1000-200 Mini Winch (Figure 6). Data from the sonde were recorded using the Mount Sopris Instruments R-5MXA-1000 Matrix Console (Figure 6). A reasonable rate for lowering the sonde seems to be about 10 feet per minute. The sonde does not need to be centered in the well or forced against the sidewall of the well/borehole.

EQUIPMENT NECESSARY TO USE THE DOWNHOLE SONDE

The components required to collect downhole data using a magnetic susceptibility sonde include:

1. Sonde with coaxial cable (Figure 4);
2. Tripod with pulley to guide the wireline cable with the sonde attached down the well (Figure 7);
3. Winch (Figures 6 and 7);
4. Data recorder to record and reduce data (Figure 6 and 8), and;
5. WellCAD or similar to analyze and display data.

GOOD PRACTICE FOR APPLYING DATA ON MAGNETIC SUSCEPTIBILITY TO UNDERSTAND ABIOTIC DEGRADATION

- Use magnetic susceptibility to provide a second line of evidence as defined by USEPA (1999) and validated in ESTCP Project ER201129 completed in 2015. Use magnetic susceptibility to evaluate if abiotic degradation by magnetite is a plausible explanation for a rate constant that is extracted from the monitoring data and the geological and hydrological properties of the site. Do not use magnetic susceptibility to estimate or predict a rate constant for degradation.
- If possible, the magnetic susceptibility data should be collected in the same wells that provide concentration data used to extract field-scale rate constants. In the BioPIC Tool, previously developed under ER2015129, the purpose of surveying a site for magnetic susceptibility is to evaluate a field-scale rate constant for abiotic degradation. The rate constant is extracted by analyzing monitoring data from several wells that lie along a transect in the direction of groundwater flow, as near to the plume centerline as possible. The rate constant represents that segment of the aquifer. Magnetic susceptibility measurements should be collected along the same segment of the aquifer.
- If information is available on the vertical distribution of hydraulic conductivity, or on the texture of unconsolidated porous media, use that information to filter the data on magnetic susceptibility, and take the mean of the data points that are associated with the regions that carry the major portion of groundwater flow.
- If the groundwater in the aquifer is sulfate reducing, do not use magnetic susceptibility as a line of evidence for abiotic degradation by magnetite, unless it can be shown that the magnetic susceptibility is associated with magnetite and not greigite. Greigite can be distinguished from magnetite by comparing total Sulfur and total Iron(II) in the sediment.
- Review the data provided by the sonde. Exclude from interpretation any data where there is a sharp transition to a very high magnetic susceptibility. These data may be associated with steel or iron in centralizers in the well, or with tools that might have been dropped into the borehole.

Figure 7: Sonde (already down hole) with Coaxial Cable Attached, Tripod, Winch, and Data Recorder. Computer Recording Data is on Left Side of Truck in Box to Protect From Sunlight.

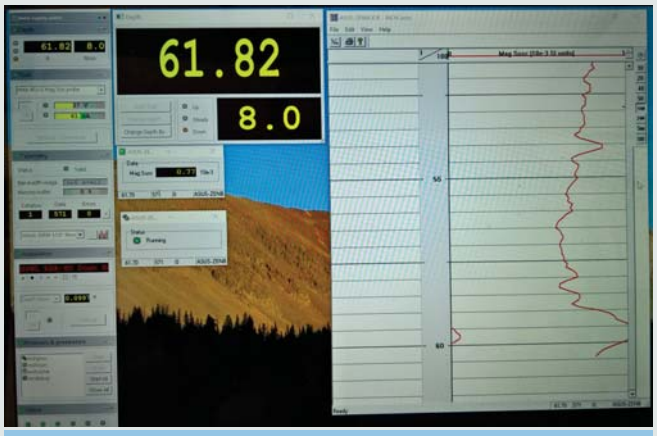

Figure 8: Real-Time Data Readout From Downhole Sonde.

REFERENCES

Canfield, D.E. and R.A. Berner. 1987. Dissolution and pyritization of magnetite in anoxic marine sediments. Geochimica et Cosmochimica Acta 51: 645-659.

Dekkers, M.J. et al. 2000. Magnetic properties of hydrothermally synthesized greigite (Fe3S4)—II. High- and low-temperature characteristics. Geophysical Journal International 141: 809-919.ESTCP. 2015.

He, Y., C. et al. 2009. Identification and Characterization Methods for Reactive Minerals Responsible for Natural Attenuation of Chlorinated Organic Compounds in Ground Water: US Environmental Protection Agency: EPA 600/R-09/115. Available at: http://nepis.epa.gov/Adobe/PDF/P1009POU.pdf.

Horneman, A., A. et al. 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part I: Evidence from sediment profiles. Geochimica et Cosmochimica Acta 68: 3459–3473.

McNeill, J. D. et al. 1996. Application of a borehole induction magnetic susceptibility logger to shallow lithological mapping: Journal of Environmental and Engineering Geophysics 1, no. B: 77-90.

Roberts, A.P. 2015. Magnetic mineral diagenesis. Earth-Science Reviews 151: 1-47.

Wiedemeier et al. 2017. Efficacy of an in-well sonde to determine magnetic susceptibility of aquifer sediment: Groundwater Monitoring and Remediation: DOI 10.1111/GWMR.12197