Understanding Magnetic Susceptibility

Culpepper et al. (2018) raises some basic questions about the role of magnetite in abiotic degradation of TCE in aquifers. They make the following statement:

> Taken together however, the existing literature and our findings provide no rigorous evidence that magnetite reduces PCE and TCE under anoxic conditions, and in fact, suggest that magnetite does not reduce PCE and TCE under a variety of conditions.

Notice that the first part of this claim is restricted to degradation under anoxic conditions. The most useful application of degradation of PCE or TCE by magnetite is MNA of relatively low concentrations of PCE or TCE in aerobic aquifers. The warning provided by Culpepper et al. (2018) does not apply to aerobic aquifers.

Culpepper et al. (2018) expands their concern with the following statement:

> The lack of compelling evidence for PCE and TCE reduction by magnetite raises important questions regarding whether magnetic susceptibility of aquifer sediments is a useful indicator for abiotic degradation of chlorinated ethenes by magnetite (Wiedemeier et al., 2017). Recent work has suggested that in situ magnetic susceptibility measurements might be used along with chlorinated ethene concentration decreases in monitoring wells as a line of evidence for the occurrence of natural attenuation by sediment magnetite in an aquifer (Wiedemeier et al., 2017). Our findings, however, suggest that magnetic susceptibility may not be a useful indicator for abiotic natural attenuation of chlorinated ethenes by reductive elimination.

This statement implies that materials assayed by magnetic susceptibility (magnetite) must consistently degrade TCE to be useful to evaluate monitored natural attenuation (MNA). This statement shows a misunderstanding on the part of Culpepper et al. (2018) of the logic used by U.S. EPA to evaluate MNA.

Magnetic susceptibility is useful to identify aquifer material where it is plausible that chlorinated ethylenes may be degraded through an abiotic reaction mechanism that involves magnetite. Other lines of evidence are necessary to establish the value of the rate constant for degradation in the plume of contamination at field scale, and to unequivocally associate the degradation rate constant with an abiotic mechanism in samples of aquifer material.

Appropriate use of magnetic susceptibility to evaluate MNA

The United States Environmental Protection Agency uses a three-tiered approach to evaluate MNA (U.S. EPA, 1999).

> (1) Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a groundwater plume, decreasing concentrations should not be solely the result of plume migration. In the case of inorganic contaminants, the primary attenuating mechanism should also be understood.)

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(2) *Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.*

(3) *Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).*

Unless U.S. EPA or the overseeing regulatory authority determines that historical data (Number 1 above) are of sufficient quality and duration to support a decision to use MNA, data characterizing the nature and rates of natural attenuation processes at the site (Number 2 above) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (Number 3 above) may also be necessary.

The EPA guidance was written before the contribution of abiotic processes to MNA was fully appreciated. However, the references to biological degradation processes can reasonably be extrapolated to abiotic processes. As required by U.S. EPA, the site must first demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. If the magnetite in an aquifer did not degrade TCE, and other mechanisms did not act on the TCE, there would be no clear and meaningful trend to evaluate. The role of magnetic susceptibility is to associate the documented degradation process with a mechanism for degradation.

ESTCP (2015) and Wiedemeier et al. (2017) express the first line of evidence for MNA as a first order rate constant for degradation of PCE, TCE, DCE or Vinyl Chloride that is necessary to calibrate a transport and fate model to the field data. As described in Wiedemeier et al. (2017):

Before selection of MNA as a site remedy, the U.S. EPA or other regulatory agencies typically will require two lines of evidence (U.S. EPA 1999). The first direct line of evidence requires data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. The second line of evidence, which generally is required, was designed to corroborate that degradation is occurring and is responsible for decreasing contaminant concentrations. If the field-scale rate constant for degradation can be explained by abiotic degradation by magnetite, then the U.S. EPA's second line of evidence for MNA has been provided.

ESTCP (2015) provides the second line of evidence by comparing the field scale rate constant and the average magnetic susceptibility of the aquifer sediment to the range of rate constants and magnetic susceptibilities from a series of laboratory microcosm studies published in He et al. (2009). As described in Wiedemeier et al. (2017):

An empirical relationship has been established between the mass magnetic susceptibility of aquifer sediment and the rate constant for degradation of PCE, TCE, cis -DCE, and VC in the sediment (ESTCP 2015). A worksheet is available that facilitates the evaluation of natural attenuation by abiotic degradation by magnetite (ESTCP 2015). The embedded file Magnetic Susceptibility.xlsx in the BioPIC Tool (ESTCP, Alexandria, VA) allows a user to evaluate abiotic degradation by magnetite at a new site by comparing the rate constant and magnetic susceptibility at the new site to the range of rate constants and magnetic susceptibilities of the benchmark sites that were compiled in ESTCP (2015).

The benchmarks provide a basis of comparison to determine if abiotic degradation by magnetite is a plausible explanation for the field scale rate constant for degradation. This is not the same as proving that magnetite is responsible for the degradation. The comparison is basically saying, "if the magnetite in the subject site behaves like magnetite in the benchmark sites, then abiotic degradation by magnetite can explain the observed field scale rate constant."

As described above, Culpepper et al. (2018) make the following statement:

> Taken together however, the existing literature and our findings … suggest that magnetite does not reduce PCE and TCE under a variety of conditions.

The authors of ESTCP (2015) and Wiedemeier et al. (2017) were aware of this fact. As reported in He et al. (2009), aquifer sediment from Site A at the Twin Cities Army Ammunition Plant (TCAAP) did not degrade PCE or TCE in the microcosm study at a rate faster than the loss of PCE or TCE from the container controls, even though the sediment had appreciable magnetic susceptibility. For some reason, the sediment did degrade *cis*-DCE. As a result, Wiedemeier et al. (2017) provides the following recommendations:

> Use magnetic susceptibility to provide a second line of evidence as defined by U.S. EPA (1999). Use magnetic susceptibility to evaluate whether 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.

The U.S. EPA provides for a third line of evidence if the second line evidence is not convincing to a regulator. The third line of evidence can be provided by performing a laboratory microcosm study of degradation of ^{14}C labeled TCE by sediment from the site. The degradation of the TCE is directly measured by the accumulation of the ^{14}C-label in the transformation products. The microcosm studies, as developed in David Freedman's laboratory at Clemson University, are described in Darlington et al. (2013) and Yu et al. (2018). The studies are commercially available through Microbial Insights, Inc.

Microcosm studies associating degradation of PCE, TCE and *cis*-DCE with magnetic materials in sediment from unconsolidated aquifers

Figure 1 presents data from conventional microcosm studies of abiotic degradation of PCE and TCE in aquifer sediment (Appendix B of He et al., 2009). The sediments were contained in 65-mL serum bottles with a Teflon®-faced butyl rubber septum that was sealed to the bottle with a crimp cap. In some microcosms the sediment was autoclaved to kill microorganisms in the sediment. These are referred to as "killed microcosms." If the sediment was not autoclaved the microcosms were referred to as "living microcosms." The "container controls" were serum bottles that contained sterile distilled water that was amended with the chlorinated ethylenes. The "container controls" accounted for loss of the organic compounds from the microcosms by diffusion into and through the septum.

The sediments labelled TCAAP Site 102 and TCAAP Site A are from the former Twin Cities Army Ammunition Plant near Arden Hills, MN. Baytown, MN is a few miles away. The aquifer sediments were glacial outwash sands. In four treatments constructed with aerobic aquifer material (Panels A, C, E and F), the rate of attenuation of PCE or TCE in sediment was greater than the rate of loss from the container controls. In two treatments constructed with anoxic sediment (Panels B and D), the rate of attenuation was not greater than the rate of loss in the controls.

Figure 2 presents data from conventional microcosms studies of abiotic degradation of *cis*-DCE in aquifer sediment (Ferrey et al., 2004; Appendix B of He et al., 2009). In addition to the sites in Minnesota, microcosms were constructed with sediment from the bed of Black Creek, which is immediately south of the Thermo-Chem site near Muskegon, MI.

In all the sediments, the rate of removal of *cis*-DCE in the sediments was greater than the rate of loss from the container control, regardless of whether they were oxic or anoxic when they were collected. This is true for the sediment where degradation of PCE and TCE were not detected (Panels E and F). The rate of degradation in sediment where the microorganisms were killed was very similar to the rate in sediment that was not sterilized, indicating that the removal was an abiotic process (compare Panel A to B, C to D and G to H).

The straight lines in the figures are a regression of the logarithm of the concentration of PCE or TCE on the time of incubation. The slope of the regression of the natural logarithm of concentration on time is the first-order rate constant for removal in the sediment. First-order rate constants for removal of PCE, TCE and *cis*-DCE in the sediments and the container controls is presented in Table 1.

Corespondance between the rate constants for removal in aquifer sediments and removal by synthetic magnetite

Degradation of PCE, TCE and *cis*-DCE occurs on the surface of the magnetite crystal (Lee and Batchelor, 2002). The rate constant should depend on the surface area of magnetite presented to a given volume of water. To allow direct comparisons of the performance of the magnetite, the rate constants for removal of PCE, TCE and *cis*-DCE in microcosm studies or laboratory reactors (in units of day^{-1}) are divided by the specific surface area of the magnetite in the water (m^2/L) to produce a surface area specific rate constant (L m^{-2} day^{-1}). The specific surface area is calculated by multiplying the mass of magnetite exposed to the water (g/L), by the specific surface area of the magnetite crystals (m^2/g). The surface area specific rate constants can be compared from one material to another and one study to another. The surface area specific rate constants are presented in Table 1.

The estimates of the surface area specific rate constants from the microcosm studies are expressed to two significant digits, but the certainty in these calculated values are probably much less. The quantity of magnetite was estimated from the magnetic susceptibility using formulas in He et al. (2009). The specific surface area of the magnetite in all the sediment samples was assumed to be the same as the specific surface area of magnetite in the TCAAP intermediate sample (row 10 in Table 1). Nevertheless, some relationships stand out when the area specific rate constants in the sediments are compared to the area specific rate constants for magnetite synthesized in the laboratory.

Lee and Batchelor (2002) provided the definitive study of rates of abiotic degradation of chlorinated ethylenes by magnetite synthesized in the laboratory. When Fe^{+2} was not added to the reaction, they found that the rate constants for PCE, TCE, *cis*-DCE and vinyl chloride were essentially the same, ranging from 8.38×10^{-7} to 5.64×10^{-7} L m^{-2} day^{-1}. If Fe^{+2} was added to the reaction mix, the rate constants for *cis*-DCE and vinyl chloride were an order of magnitude higher, 5.74×10^{-6} and 5.78×10^{-6} L m^{-2} day^{-1} respectively. The rate constant was sensitive to added Fe^{+2}, but not the particular chlorinated ethylene involved in the reaction.

Row 7 in Table 1 summarizes the range of values for the area specific rate constant for degradation of TCE in the experimental reactors constructed by Culpepper et al. (2018) when they added Fe^{+2} to the reactors. The median value of Culpepper et al. (2018) for degradation of TCE when Fe^{+2} is added to the reaction mix is in good agreement with the value from Lee and Batchelor (2002) for degradation of *cis*-DCE when Fe^{+2} is present in the reaction mix (Row 9). The lowest value for TCE degradation reported by Culpepper et al. (2018) is in good agreement to the value for TCE degradation reported by Lee and Batchelor (2002) when Fe^{+2} was not added to the reaction mix (Row 3), as well as the value for PCE degradation in the absence of added Fe^{+2} (Row 1), or the value for *cis*-DCE degradation in the absence of added Fe^{+2} (Row 8). Depending on the concentration of Fe^{+2} in the reaction mix, the values of the area specific rate constants vary by more than an order of magnitude, but the range of values in the study of Culpepper et al. (2018) encompass the range of values reported by Lee and Batchelor (2002). There is no identifiable systematic difference in the behavior of magnetite synthesized by Lee and Batchelor (2002) and Culpepper et al. (2018).

Similarly, there is no identifiable difference in the behavior of magnetite synthesized by Culpepper et al. (2018) and the removal of PCE, TCE and *cis*-DCE in sediments containing magnetic materials. The highest value of the rate constant from Culpepper et al. (2018) for degradation of TCE is in reasonable agreement to values for removal of PCE in sediment from TCAAP Site 102 (Row 2), TCE in sediment from TCAAP Site 102 (Row 4), TCE in sediment from Baytown, MN (Row 5), and *cis*-DCE in sediment from TCAAP intermediate (Row 10). The median value of the rate constant from Culpepper et al. (2018) for degradation of TCE in the presence of Fe^{+2} was in good agreement with values for removal of *cis*-DCE at the oxic sites (Rows 11, 12 and 13).

The magnetic materials in aquifer sediments described in Table 1 behaved more like synthetic magnetite that had been amended with Fe^{+2}. Culpepper et al. (2018) noted that their synthesized magnetite degraded TCE only when enough Fe^{+2} was added to cause the precipitation of $Fe(OH)2$ in the reaction mix. They then extrapolated this behavior to field scale.

> *However, in nearly all of our experiments the amount of Fe(II) added exceeds typical concentrations of Fe(II) in groundwater (typically <50 mg L^{-1} or 1 mM), … making the precipitation of ferrous hydroxide unlikely to be relevant to field conditions.*

At field scale, the concentration of Fe^{+2} in groundwater is a pool that turns over. It is likely that Fe^{+2} produced by biological iron reduction would be removed in part to form reactive surface-bound Fe^{+2} species on the magnetite in the aquifer sediment (Lee and Batchelor, 2002). Over time, the quantity of Fe^{+2} transferred to magnetite could be many times greater than the concentration in the groundwater at any particular time. The reactive surface-bound Fe^{+2} species on the magnetite in the aquifer sediment could have formed at any time in the past. The reactivity of the magnetic materials may not be related to the current concentration of Fe^{+2} in the groundwater.

Conclusion and summary

If there is sufficient magnetic susceptibility in aquifer sediment, it is possible that the magnetic materials in the aquifer sediment will carry out an abiotic degradation of PCE, TCE and *cis*-DCE. If the rate constants for the abiotic degradation are large enough, abiotic degradation can support the use of MNA as a remedy or part of the remedy at a site. However, the magnetic materials in the sediments of some aquifers are not reactive. As a result, magnetic susceptibility alone should not be used to estimate a rate constant for the natural abiotic degradation of PCE, TCE or *cis*-DCE. Following the guidance of U.S. EPA (1999), the rate constants should be extracted from an analysis of the monitoring data that describe the behavior of the plume of contamination at field scale. Following the logic of U.S. EPA (1999), magnetic susceptibility can be used as a second line of evidence to associate a field-scale rate constant for attenuation of PCE, TCE or *cis*-DCE attenuation with a plausible mechanism for the attenuation. If it is necessary to document that the plausible mechanism is actually operating at the site, we recommend applying U.S. EPA's third line of evidence, and doing a microcosm study on the aquifer material from the site. Microcosm studies that follow the accumulation of ^{14}C-labelled degradation products from ^{14}C-labelled TCE or *cis*-DCE are available through Microbial Insights, Inc.

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Table 1. Surface area specific rates of removal of PCE and TCE on magnetite.

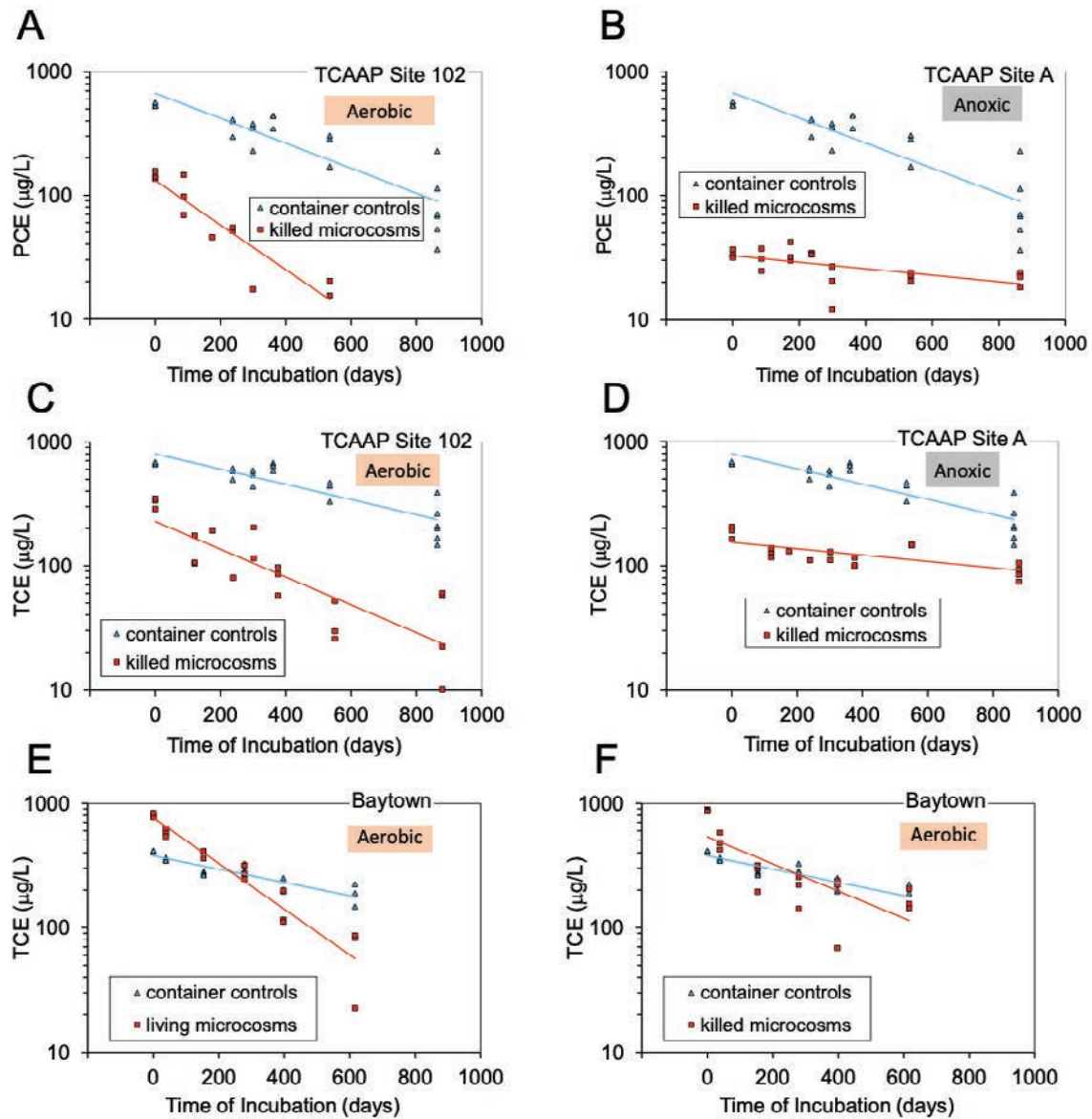| Reference	Source of Magnetite	First-Order Rate Constant ± 95% Conf. Interval **Microcosm** *Container Control* year^{-1}	Magnetite exposed to pore water g L^{-1}	Specific Surface Area Magnetite m^2 g^{-1}	k_{SA} Surface Area Specific Rate Constant for Transformation **Median** *Range* L m^{-2} day^{-1}
Removal of PCE					
Lee and Batchelor (2002)	Synthesized No added Fe^{2+}			57.2	0.56×10^{-6}
He et al. (2009)	TCAAP Site 102 *(Aerobic)*	**1.32 ± 0.45** *0.83 ± 0.23*	12	24	13×10^{-6}
Removal of TCE					
Lee and Batchelor (2002)	Synthesized No added Fe^{2+}		63	57.2	0.72×10^{-6}
He et al. (2009)	TCAAP Site 102 (oxic)	**0.95 ± 0.31** *0.51 ± 0.13*	12	24	9.0×10^{-6}
He et al. (2009)	Baytown (oxic)	**0.98 ± 0.49** *0.45 ± 0.11*	5.1	24	22×10^{-6}
Culpepper et al. (2018)	Synthesized No added Fe^{2+}		5 to 20	63	Not Detected
Culpepper et al. (2018)	Synthesized Plus Fe^{2+}		5	63	**4.3×10^{-6}** *0.4×10^{-6} to 15×10^{-6}*
Removal of cis-DCE					
Lee and Batchelor (2002)	Synthesized No added Fe^{2+}		63	57.2	0.56×10^{-6}
Lee and Batchelor (2002)	Synthesized Plus Fe^{2+}		63	57.2	5.7×10^{-6}
Ferrey et al. (2004)	TCAAP Intermediate (anoxic)	**2.29 ± 0.25** *0.071 ± 0.082*	22	24	12×10^{-6}
Ferrey et al. (2004)	TCAAP (oxic)	**0.31 ± 0.08** *0.071 ± 0.082*	41	24	1.8×10^{-6}
He et al. (2009)	TCAAP Site A (anoxic)	**0.73 ± 0.18** *0.21 ± 0.04*	29	24	2.9×10^{-6}
He et al. (2009)	TCAAP Site 102 (oxic)	**0.65 ± 0.20** *0.21 ± 0.04*	27	24	2.7×10^{-6}

Figure 2. Degradation of *cis*-DCE in sediment from unconsolidated sandy aquifers.