

Chemical Reductants for ISCR: The Potential for Improvement

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ABSTRACT: The abiotic reduction reactions that form the basis of in situ chemical reduction (ISCR) have been studied extensively, but there has been little effort to develop a unified understanding of what factors control ISCR performance. Some of the key factors are summarized here, with the ultimate goal of building a basis for rational design of better ISCR reductants.

INTRODUCTION

The fact that groundwater and sediment contaminants can be reduced by pathways that are abiotic (i.e., do not directly involve microorganisms) has been well documented in the literature for more than 30 years. Some of the early work on this has been reviewed (Tsukano 1986; Tratnyek et al. 1989; Wolfe et al. 1992), and since then there have been many academic studies of organic contaminant degradation reactions using model systems designed to represent the natural reductants that are most likely to be responsible for abiotic reduction reactions in soils, sediments, and groundwaters. These putative abiotic reductants are of three types: minerals that derive their reducing capacity from Fe^{II} [e.g., magnetite (Lee et al. 2002; Gorski et al. 2010), green rust (Erbs et al. 1999; O'Loughlin et al. 2004), goethite (Amonette et al. 2000; Elsner et al. 2004), and clays (Cervini-Silva et al. 2002; Elsner et al. 2004)] or S^{II} [e.g., mackinawite (Butler et al. 1999) and pyrite (Kriegman-King et al. 1994; Lee et al. 2002)] and redox-active moieties associated with natural organic matter [e.g., quinones (Tratnyek et al. 1989; Schwarzenbach et al. 1990; Uchimiya et al. 2009)].

Despite this background, most practitioners—and some researchers—have assumed that in situ abiotic reduction of contaminants (e.g., as a component of natural attenuation) in the environment is insignificant. Recently, however, several studies have characterized sites where a significant portion of contaminant degradation appears to be due to direct reaction with reducing mineral phases (Ferrey et al. 2004; Darlington et al. 2008), and these studies have renewed interest in the role that these phases might play in natural attenuation and the prospects for manipulating such systems to generate more or better reductants in situ (Becvar et al. 2008). An example of such a manipulation is the technology known as “in situ redox manipulation” [ISRM (Fruchter et al. 2000; Szecsody et al. 2004)], where dithionite (a soluble chemical reductant) is injected to reduce native ferric iron to produce adsorbed and structural ferrous iron, which is a fairly effective reducing agent for easily reduced contaminants (like chromate, carbon tetrachloride, and munitions compounds).

Coincident with the above developments, there has been rapid development of remediation technologies that involve emplacement of zero-valent iron (ZVI) to serve as the chemical reductant of contaminants (Tratnyek et al. 2003). This field has become fairly mature in recent years, and there is now considerable competition among vendors of ZVI for remediation applications. This has led to efforts to engineer better forms of

ZVI, or formulations of ZVI, and other enhancements. The first major strategy for enhancing ZVI performance involved bimetallic combinations of ZVI and catalytic metals like Pd or Ni (Grittini et al. 1995; Gui et al. 2003). More recently, more attention has been directed toward nano-sized zero-valent iron (nZVI), where the nano-size of the particles is intended to impart various properties that might enhance remediation performance (Tratnyek et al. 2006). Other approaches to engineering better reductants range from controlling metallurgical properties (Landis et al. 2001) to replacing Fe^0 with other metals like Zn^0 (Tratnyek et al. 2010).

Even more recently, recognition that all of the above chemical reductants form the basis for a fairly coherent family of remediation technologies—called “in situ chemical reduction” or ISCR (Brown et al. 2006; Brown 2008)—presents an opportunity to advance all forms of ISCR technologies by recognizing and utilizing some of the general properties of reductants that determine the strengths, weaknesses, similarities, and differences among the options. This paper reviews the general considerations that determine reductant reactivity, with the ultimate goal of addressing two key questions: (i) how can we make a priori predictions of how a particular reductant will perform in remediation of a particular contaminant, and (ii) can we make significant improvements in the chemical reductants that are currently available by rational design of new materials with optimal properties.

BACKGROUND

The chemical criteria that determine the feasibility of contaminant remediation by particular abiotic reductants include thermodynamic, mechanistic, and kinetic factors (Tratnyek et al. 2000). First, we try to clearly distinguish these three factors, and then we consider ways that they are interrelated.

Thermodynamic Criteria. Unlike some pathways for contaminant degradation (e.g., hydrolysis and oxidation), reduction reactions under environmental conditions span a wide range of free energy changes, from favorable to unfavorable. For the overall process to be favorable, the free energy of reaction must be negative, which requires that the sum of the oxidation potential of the reductant and the reduction potential of the reductate¹ be

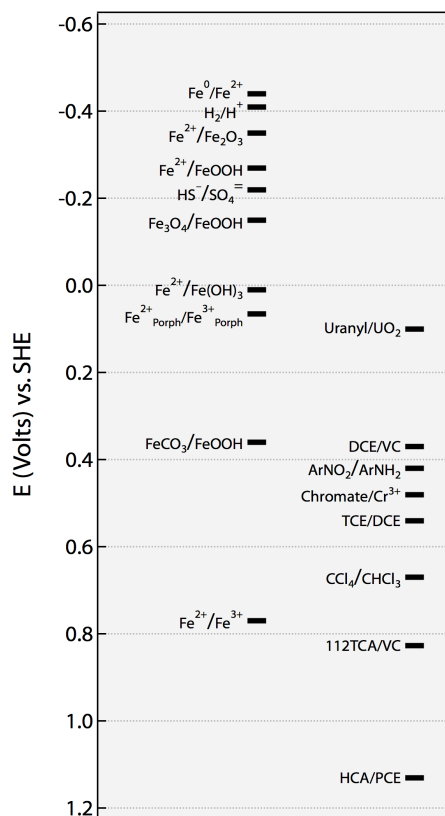


Figure 1. Redox ladder for ISCR reductants (left) vs. representative contaminants (right). Based on reduction potentials for pH 7 and 25 °C from Tratnyek et al. (2000)

¹ The term “reductate” was coined in Miehr et al. (2004) to represent the reactant that undergoes reduction, which in this case is a contaminant of concern. The reductate is also an oxidant, but the former term is more intuitive in contexts such as this.

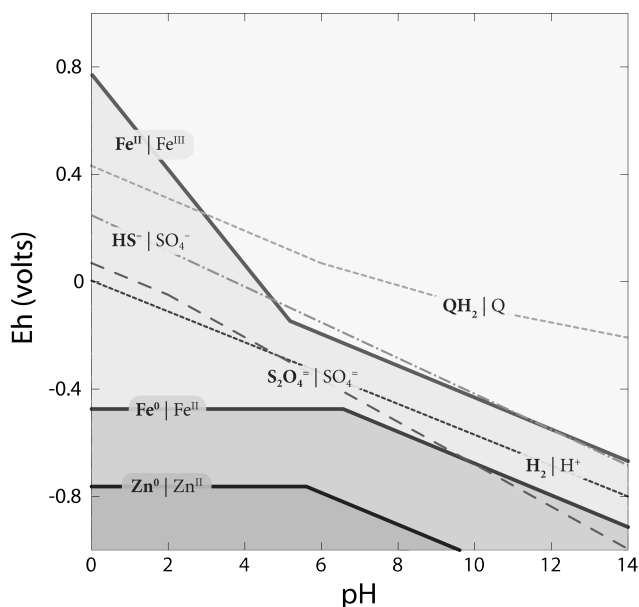


Figure 2. Eh-pH diagram for selected ISCR reductants. Only boundaries involving redox reactions are shown. QH₂|Q represents the redox couple for lawsone.

selected reductants. Of the reductants shown, Zn⁰ has by far the lowest potential, followed by Fe⁰. The Fe^{II} containing phases magnetite, green rust, mackinawite, and pyrite are grouped in the middle of the plot (shaded medium gray). Among the solution phase reductants shown, S₂O₄⁼ (dithionite), H₂, and HS⁻ all appear to be nearly as strong as the iron containing solids at pH > 7, even though the former group generally reacts less rapidly and more selectively with most reductates. At pH > 10, S₂O₄⁼ is effective for reducing Fe^{II} to Fe⁰ (Sun et al. 2008).

In addition to these inorganic reductants, there are naturally occurring organic reductants that could be included in this analysis. The data for this are available for simple organics that are putative natural reductants (Stone et al. 1993) and model compounds for the hydroquinone/quinone moieties associated with natural organic matter (Tratnyek et al. 2000; Nurmi et al. 2002). In Fig. 2, one quinone model compound has been included (lawsone) to show that these are relatively weak reductants.

Mechanistic Criteria. Most of the redox couples included in Figs. 1-2 correspond to half-reactions written as two-electron transfers between relatively stable reactants and products. However, assuming this fully represents the pathways and mechanisms that occur can be misleading. For example, Fig. 3 illustrates the numerous possible reaction steps that together made up the several pathways that result in degradation of CCl₄ under reducing conditions. Note that only one elementary step involves concerted two-electron transfer; whereas most steps involve single electron transfers or H atom transfers. The overall effect of competition between the elementary steps shown in Fig. 3 is branching between the two major pathways for product formation: one leading to CHCl₃ (which is still a contaminant) and the other to HCOOH, CO, and/or CH₄ (which are benign).

positive. In the redox ladder shown in Fig. 1, this condition applies for oxidation half-reactions on the left that lie above reduction half-reactions on the right. The figure shows that thermodynamically strong reductants like Fe⁰ are capable of affecting the whole range of contaminant reduction reactions, but milder reductants like mackinawite and green rust may cause only the most favorable contaminant reductions (e.g., dechlorination of HCA and CCl₄.)

The thermodynamics of many redox reactions are strongly dependent on pH, so comparison of putative or potential reductants is best done over the range of relevant pH's. Figure 2 shows Eh vs. pH for the half-reactions that control contaminant reduction by

Similar pathway/mechanism complications exist for other major types of reducible contaminants. The case with the greatest practical consequences is the competition between one- and two-electron dechlorination pathways for chlorinated ethenes (Arnold et al. 2000), where preference for the latter pathway is a major advantage of Fe^0 (and Zn^0) over other reductants. It is easy to rationalize this pattern in reactivity on the grounds that stronger reductants are more likely to push two electrons onto the reductate (before other atom transfer steps lead to hydrogenolysis), thereby favoring the reductive elimination products. However, other factors could also result in different patterns in reactivity.

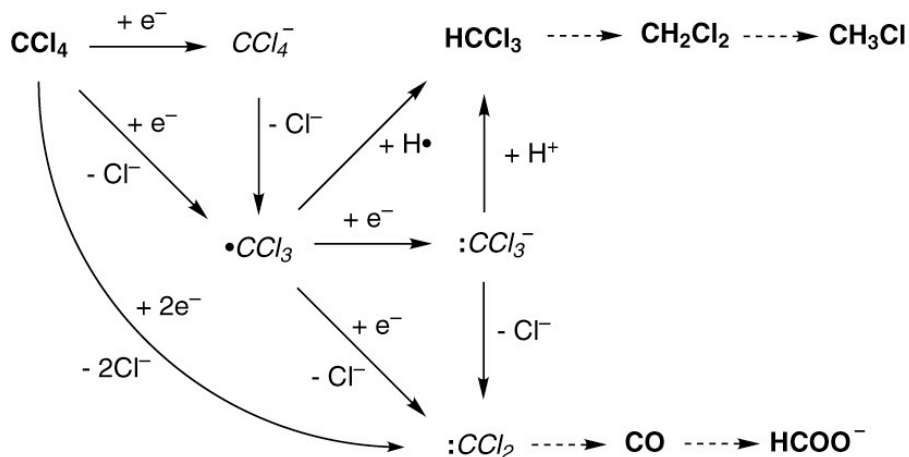


Figure 3. Possible elementary reaction steps contributing to reduction of CCl_4 , leading to hydrogenolysis products (upper right) or reductive elimination products (lower right). Details are discussed in Valiev et al. (2008).

Kinetic Criteria. Even for contaminant reduction reactions where the thermodynamic and mechanistic considerations are favorable, the kinetics of reaction can vary widely. Quantitative structure-activity relationships (QSARs) commonly are used to describe the relative reactivity of a homologous series of contaminants with a particular reductant (Tratnyek et al. 2003), but there have been very few efforts to develop QSAR type models for the kinetics of reactions between a series of reductants and particular reductates. A major obstacle to the latter is the difficulty in obtaining a readily measurable property that can be used to represent the relative reactivity of particulate materials such as granular Fe^0 .

One variation on the QSAR model that can—at least in principle—be used to describe the relative reactivity of heterogeneous environmental reductants involves “cross correlations” between rate constants measured on a set of reductants using two or more contaminant reduction reactions. This approach gave satisfactory QSARs for suspensions of anoxic sediment (Tratnyek et al. 2003) and useful qualitative relationships with a set of nine types of Fe^0 (Miehr et al. 2004). A subset of Miehr’s data set is replotted in Fig. 4, showing just the cross correlations for two pairs of reductates: TNT vs. TCE and chromate vs. TCE.

The first pair of contaminants shown in Fig. 4A are both uncharged organic contaminants that are readily reduced by Fe^0 (formally by electron transfer, but possibly

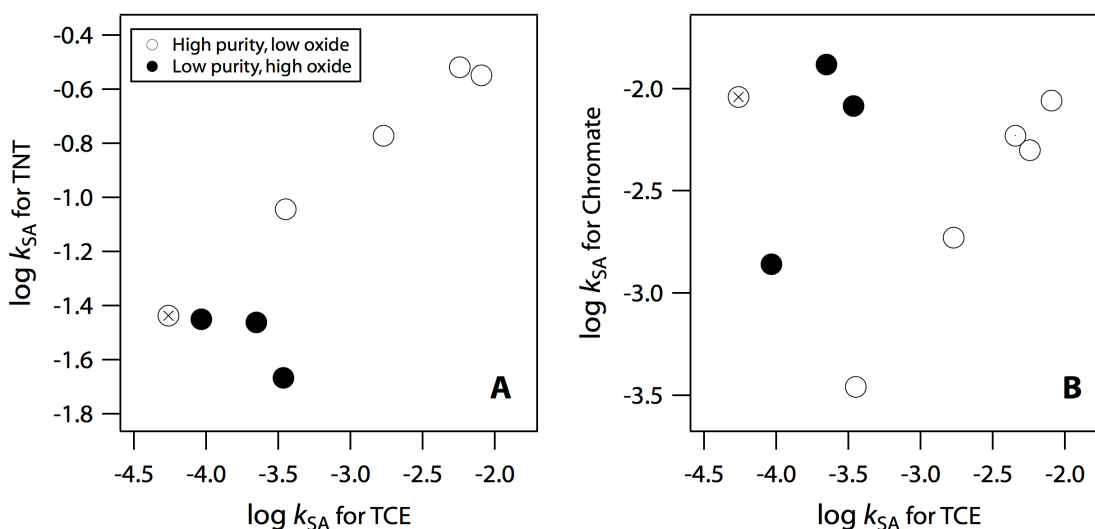


Figure 4. Cross-correlations between rate constants for reduction of selected contaminants (A: TNT vs. TCE, B: Chromate vs. TCE) by different types of granular Fe^0 (symbols). Data from Miehr et al. (2004).

by a mixture of reduction mechanisms analogous to the situation with CCl_4 illustrated in Fig. 3). The similarity between these two reductates presumably accounts for the observed correlation, with the clustering of the low-purity construction-grade materials at the low end of both axes presumably reflecting the passivation of these materials with oxides. Fig. 4B also shows the expected correlation between $\log k_{SA}$ for chromate and TCE, but only for the high-purity materials. The low purity types of Fe^0 remove chromate more rapidly, and appear as outliers. This reflects a difference in mechanism of contaminant removal (apparently there is significant adsorption of chromate without reduction), and illustrates the difficulty in formulating general models for predicting the kinetics of contaminant removal by heterogeneous reductants.

CONCLUSIONS

The above discussion illustrates some of the many obstacles to defining simple relationships between ISCR performance metrics (e.g., rate of contaminant disappearance) and properties of either contaminants or reductants. Making a priori predictions of reductant performance is particularly challenging, but will be essential to guide rationale design of improved treatment processes based on ISCR.

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REFERENCES

- Amonette, J. E., D. J. Workman, D. W. Kennedy, J. S. Fruchter and Y. A. Gorby. 2000. "Dechlorination of carbon tetrachloride by Fe(II) associated with goethite." *Environmental Science & Technology* 34(21): 4606-4613.

- Arnold, W. A. and A. L. Roberts. 2000. "Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles." *Environmental Science & Technology* 34(9): 1794-1805.
- Becvar, E., P. Evans, C. Lebron, H. Stroo, J. T. Wilson and R. Wymore (2008). *Workshop on In Situ Biogeochemical Transformation of Chlorinated Solvents*. Brooks City Base, TX, Air Force Center for Engineering and the Environment (AFCEE). Doc. No. AFD-080429-058.
- Brown, R. A. (2008). "Developments in in situ chemical reduction (ISCR) technology." *Proc. of the 6th International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, Paper C-066.
- Brown, R. A., R. L. Lewis, R. J. Fiacco, Jr. and M. C. Leahy (2006). "The technical basis for in situ chemical reduction (ISCR)." *Proc. of the 5th International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, d 04 ppr/1-d 04 ppr/8.
- Butler, E. C. and K. F. Hayes. 1999. "Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide." *Environmental Science & Technology* 33(12): 2021-2027.
- Cervini-Silva, J., R. A. Larson, J. Wu and J. W. Stucki. 2002. "Dechlorination of pentachloroethane by commercial Fe and ferruginous smectite." *Chemosphere* 47(9): 971-976.
- Darlington, R., L. Lehmicke, R. G. Andrachek and D. L. Freedman. 2008. "Biotic and abiotic anaerobic transformations of trichloroethene and cis-1,2-dichloroethene in fractured sandstone." *Environmental Science and Technology* 42(12): 4323-4330.
- Elsner, M., R. P. Schwarzenbach and S. B. Haderlein. 2004. "Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants." *Environmental Science and Technology* 38(3): 799-807.
- Erbs, M., H. C. B. Hansen and C. E. Olsen. 1999. "Reductive dechlorination of carbon tetrachloride using iron(II) iron(III) hydroxide sulfate (Green Rust)." *Environmental Science & Technology* 33(2): 307.
- Ferrey, M. L., R. T. Wilkin, R. G. Ford and J. T. Wilson. 2004. "Nonbiological removal of cis-dichloroethylene and 1,1-dichloroethylene in aquifer sediment containing magnetite." *Environmental Science and Technology* 38(6): 1746-1752.
- Fruchter, J. S., C. R. Cole, M. D. Williams, V. R. Vermeul, J. E. Amonette, J. E. Szecsody, J. D. Istok and M. D. Humphrey. 2000. "Creation of a subsurface permeable treatment zone for aqueous chromate contamination using in situ redox manipulation." *Ground Water Monitoring and Remediation* 20(2): 66-77.
- Gorski, C. A., J. T. Nurmi, P. G. Tratnyek, T. B. Hofstetter and M. M. Scherer. 2010. "Redox behavior of magnetite: Implications for contaminant reduction." *Environmental Science and Technology* 44(1): 55-60.
- Grittini, C., M. Malcomson, Q. Fernando and N. Korte. 1995. "Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system." *Environmental Science & Technology* 29(11): 2898-2900.
- Gui, L. and R. W. Gillham (2003). Preparation and regeneration of nickel-iron for reduction of organic contaminants. In: *Chlorinated Solvent and DNAPL Remediation: Innovative Strategies for Subsurface Cleanup*. Washington, DC, American Chemical Society. *ACS Symp. Ser. Vol. 837*, pp. 206-216.

- Kriegman-King, M. R. and M. Reinhard. 1994. "Transformation of carbon tetrachloride by pyrite in aqueous solution." *Environmental Science & Technology* 28(4): 692-700.
- Landis, R. L., R. W. Gillham, E. J. Reardon, R. Fagan, R. M. Focht and J. L. Vogan (2001). *An examination of zero-valent iron sources used in permeable reactive barriers*. International Containment & Remediation Technology Conference and Exhibition, Orlando, FL, Florida State University, Tallahassee.
- Lee, W. and B. Batchelor. 2002. "Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. pyrite and magnetite." *Environmental Science and Technology* 36(23): 5147-5154.
- Miehr, R., P. G. Tratnyek, J. Z. Bandstra, M. M. Scherer, M. Alowitz and E. J. Bylaska. 2004. "The diversity of contaminant reduction reactions by zero-valent iron: role of the reductate." *Environmental Science & Technology* 38(1): 139-147.
- Nurmi, J. T. and P. G. Tratnyek. 2002. "Electrochemical properties of natural organic matter (NOM), fractions of NOM, and model biogeochemical electron shuttles." *Environmental Science and Technology* 36(4): 617-624.
- O'Loughlin, E. J. and D. R. Burris. 2004. "Reduction of halogenated ethanes by green rust." *Environmental Toxicology and Chemistry* 23(1): 41-48.
- Schwarzenbach, R. P., R. Stierli, K. Lanz and J. Zeyer. 1990. "Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution." *Environmental Science & Technology* 24(10): 1566-1574.
- Stone, A. T., K. L. Godfredsen and B. Deng (1993). Sources and reactivity of reductants encountered in aquatic environments. In: *Chemistry of Aquatic Systems: Local and Global Perspectives*. Dordrecht, The Netherlands, Kluwer.
- Sun, Q., A. J. Feitz, J. Guan and T. D. Waite. 2008. "Comparison of the reactivity of nanosized zero-valent iron (nZVI) particles produced by borohydride and dithionite reduction of iron salts." *Nano* 3(5): 341-349.
- Szecsody, J. E., J. S. Fruchter, M. D. Williams, V. R. Vermeul and D. Sklarew. 2004. "In situ chemical reduction of aquifer sediments: enhancement of reactive iron phases and TCE dechlorination." *Environmental science and Technology* 38(17): 4656-63.
- Tratnyek, P. G. and R. L. Johnson. 2006. "Nanotechnologies for environmental cleanup." *NanoToday* 1(2): 44-48.
- Tratnyek, P. G. and D. L. Macalady. 1989. "Abiotic reduction of nitro aromatic pesticides in anaerobic laboratory systems." *Journal of Agricultural and Food Chemistry* 37(1): 248-254.
- Tratnyek, P. G. and D. L. Macalady (2000). Oxidation-reduction reactions in the aquatic environment. In: *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*. D. Mackay and R. S. Boethling (Eds.). Boca Raton, FL, Lewis, pp. 383-415.
- Tratnyek, P. G., A. J. Salter, J. T. Nurmi and V. Sarathy (2010). Environmental applications of zerovalent metals: Iron vs. zinc. In: *Nanoscale Materials in Chemistry: Environmental Applications*. L. E. Erickson, R. T. Koodali and R. M. Richards.), American Chemical Society, in press.
- Tratnyek, P. G., M. M. Scherer, T. J. Johnson and L. J. Matheson (2003). Permeable reactive barriers of iron and other zero-valent metals. In: *Chemical Degradation*

- Methods for Wastes and Pollutants: Environmental and Industrial Applications.*
M. A. Tarr (Ed.) New York, Marcel Dekker, pp. 371-421.
- Tratnyek, P. G., E. J. Weber and R. P. Schwarzenbach. 2003. "Quantitative structure-activity relationships (QSARs) for chemical reductions of organic contaminants." *Environmental Toxicology and Chemistry* 22(8): 1733-1742.
- Tsukano, Y. 1986. "Transformations of selected pesticides in flooded rice-field soils — A review." *Journal of Contaminant Hydrology* 1(1/2): 47-63.
- Uchimiya, M. and A. T. Stone. 2009. "Reversible redox chemistry of quinones: Impact on biogeochemical cycles." *Chemosphere* 77(4): 451-458.
- Valiev, M., E. Bylaska, M. Dupuis and P. G. Tratnyek. 2008. "Combined quantum mechanical and molecular mechanics studies of the electron transfer reactions involving carbon tetrachloride in solution." *Journal of Physical Chemistry, A* 112(12): 2713-2720.
- Wolfe, N. L. and D. L. Macalady. 1992. "New perspectives in aquatic redox chemistry: Abiotic transformations of pollutants in groundwater and sediments." *Journal of Contaminant Hydrology* 9(1/2): 17-34.