

FINAL REPORT

Emerging Core Concepts for Assessment and Enhancement of Abiotic Natural Attenuation of Groundwater Contaminants

SERDP Project ER-2620

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Paul Tratnyek
Richard Johnson
Ying Lan
Kei Inoue
Ania Pavitt
Graham O'Brien Johnson
Oregon Health & Science University

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4. LIST OF ACRONYMS

Acronym	Definition	Acronym	Definition
χ_m	Mass Specific Magnetic Susceptibility	MT, Mgt	Magnetite
χ_v	Volume Specific Magnetic Susceptibility	NACs	Nitro Aromatics
ANA	Abiotic Natural Attenuation	NB	Nitrobenzene
AOP	Advanced Oxidation Process	NOD	Natural Oxidant Demand
AQDS	Anthraquinone Disulfonate	NOM	Natural Organic Matter
BET	Surface Area by Gas Adsorption	NRD	Natural Reductant Demand
COC	Contaminant of Concern	nZVI	Nano Zero Valent Iron
CP	Chronopotentiometry	OCP	Open-Circuit Potential
CRP	Chemical Reactivity (Redox) Probe	PCE	Perchloroethylene
CT	Carbon Tetrachloride	PCNB	4-Cl-NB1-Chloro-4-Nitrobenzene
DNAN	2,4-Dinitroanisole	PCNB	Para-chloronitrobenzene
DTT	Dithiothreitol	PRB	Permeable Reactive Barrier
FeS	Iron Sulfide (Mackinawite)	RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
GT	Goethite	RMI	Reactive Mineral Intermediate
HER	Hydrogen Evolution Reaction	S-nZVI	Sulfidated Nano Zerovalent Iron
HT	Hematite	SCV	Staircase Cyclic Voltammetry
ISCO	In Situ Chemical Oxidation	ST	Siderite
ISCR	In Situ Chemical Reduction	SWV	Square-Wave Voltammetry
k_{obs}	Pseudo First Order Rate Constant	TCE	Trichloroethylene
k_M	Mass Normalized Rate Constant	TNT	2,4,6-Trinitrotoluene
k_{SA}	Surface Area Normalized Rate Constant	VC	Vinyl Chloride
LC	Lepidocrocite	WT	Wustite
MS	Magnetic Susceptibility	ZVI	Zero Valent Iron

5. KEYWORDS

Groundwater Remediation, In Situ Chemical Reduction (ISCR), Oxidation-Reduction (Redox), Magnetic Susceptibility, Standard Performance Metrics.

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7. ABSTRACT

Introduction and Objectives: It is now widely recognized that abiotic processes play an important role in the natural attenuation (NA) of groundwater contaminants, and this development has created demand for new and improved methods of measurement and/or enhancement of abiotic NA processes. The overall aim of this project was to develop several of these methods into “core concepts” that will help to form a foundation for field applications of abiotic NA, and related varieties of “in situ chemical reduction” (ISCR).

Technical Approach: The three methods developed under ER-2620 include (i) standardized and validated performance metrics, (ii) enhancement of performance by mediation or activation, and (iii) rigorous yet practical quantification of reductant demand. Each of these objectives was pursued through a combination conceptual model development, data mining, laboratory experiments, and modeling.

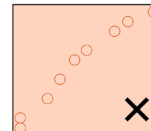
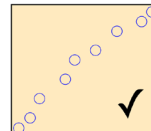
Results: With respect to performance metrics (i), the project demonstrated that simultaneous consideration of rate constants normalized to mass and surface area (k_M and k_{SA} , respectively) of the reducing mineral phase is sufficient to quantify some major effects, such as sulfidation of iron and iron oxides. However, k_M and k_{SA} are not easily applicable to field conditions. In principle, a field measurable parameter like magnetic susceptibility (MS) could serve as a surrogate for magnetite mass concentration, but magnetite does not appear to be directly responsible for contaminant reduction under most conditions.

With respect to mediation/activation (ii), it was determined that addition of most shuttle compounds (e.g., quinones) had limited benefits, but stimulating the formation of “reactive mineral intermediate” (RMI) phases by adding Fe(II) to iron oxides can greatly enhance rates of contaminant reduction. It was concluded that these RMIs may serve as mediators in ANA processes under in situ conditions.

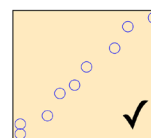
With respect to quantification of reductant demand (iii), a comprehensive conceptual model was developed with quantitative definitions of the efficiency and selectivity of contaminant reduction using sulfidation of (nano)zerovalent iron. These concepts should be applicable to other ISCR technologies and related ANA processes.

Benefits: The three core concepts developed in this project include protocols and metrics that should enable DOD site managers to perform more precise and quantitative assessment of the potential contributions of (enhanced) ANA in the remediation of sites contaminated with chlorinated solvents and munitions residues.

Rate
Constant



Fe(II) in
magnetite



Magnetic
Susceptibility

8. EXECUTIVE SUMMARY

Introduction: It is now widely recognized that abiotic processes play an important role in the natural attenuation (NA) of groundwater contaminants, and this development has created demand for new and improved methods of measurement and/or enhancement of abiotic NA processes. Most research towards this goal has approached the problem from the perspective defined by many years of work on biotic NA. However, the appeal of abiotic NA also stems from the success of chemical reduction technologies such as those involving zerovalent iron, dithionite, etc. These natural and engineered approaches to contaminant degradation share many fundamental aspects, so there are substantial benefits to treating them as a class of technologies, now known as “in situ chemical reduction” (ISCR). There is further synergy from recognizing the parallels between ISCR and in situ chemical oxidation (ISCO), which is somewhat more advanced in terms of full-scale commercial application.

The analogy between ISCO to ISCR was part of our rationale for structuring this project around important and fundamental “core” concepts that are relatively well established in the field of ISCO, but that are only emerging as key to ISCR including all aspects of abiotic NA. These core concepts involve (i) practical metrics of remediation performance, (ii) enhancement by activation and/or mediation, and (iii) consideration of natural reductant demand. **Performance metrics** that are rigorously defined and validated—such as the EE/O metric using in advanced oxidation processes—should provide a common basis for *methodologies* used to quantify and compare processes that result in abiotic NA. **Activation and/or mediation** are required for most ISCO technologies, and offer many possibilities for enhancing the performance of ISCR/ANA under field conditions, but have received little attention to date. **Reductant demand** is analogous to oxidant demand, but while the latter is widely used to assess suitability of ISCO to field sites, the former rarely incorporated in assessment of remedies based on ISCR or ANA.

Objectives: The overall objective of this project was advance the theory and practice of abiotic NA and ISCR by developing three core concepts that build on analogous concepts that are relatively well established in ISCO.

- The first concept involved “figures of merit” that can form the fundamental basis for rigorous comparison of all variations on ISCR-based remedies for contaminated groundwater. The corresponding objective was to evaluate the options for normalizing rate data on contaminant reduction to provide metrics with maximum generality while still being practical to apply to real ANA/ISCR situations.

- The second concept involved methods of enhancing abiotic NA by activation of chemical reductants and/or mediation of reaction between chemical reductants and contaminants. The corresponding objective was to evaluate options for enhancing ANA/ISCR performance by activation/mediation and identify those that are mostly like to be applicable to field-scale conditions.
- The third concept involved reductant demand, which reflects all of the processes that consume electrons under reducing conditions, of which contaminant reduction is only one. The corresponding objective was to develop a more complete conception model that relates demand, capacity, and selectivity of redox processes relevant to ANA/ISCR.

Technical Approach: The three concepts investigated in this study are strongly interrelated, but the relationships are more parallel than serial, so the approach taken to pursuing the corresponding objectives involved frequent cross-overs and the final allocation of results to objectives in this report is somewhat loosely defined. We think this is a desirable outcome because it is consistent with the overall objective of developing a comprehensive set of concepts and methods that advance the practice of ANA/ISCR.

All three objectives corresponding to the three core concepts featured in this project were all pursue with a similar approach: starting with critical analysis of prior work, then laboratory scale experimentation to fill data gaps, followed by correlation analysis to identify relationships among the data (new and old), and culminating in the development and application of models for prediction, upscaling, etc. More specifically, Objective 1 involved evaluation established performance metrics for other/related applications, collection of data for performance metric validation, and analysis of the data to identify normalization protocols that result in improved performance metric. Objective 2 involved identification of prospective enhancement strategies from a wide range of precedents, testing the most promising in controlled laboratory experiments, and evaluation of the prospects for upscaling. Objective 3 involved development protocols for measuring reductant demand, experimentally validating these protocol, and integration of reductant demand into conceptual models of abiotic NA processes.

Results and Discussion:

Objective 1, Performance Metrics: Work under this objective focused on determining the most useful ways of quantifying the performance of abiotic NA processes, including the “theoretical” model, essential data for parameterizing the model, and protocols for its application to field sites. Specifically, this involved extending the mass- and surface area-

normalization (k_M and k_{SA}) approach—which we developed for ZVI—to abiotic NA processes that involve reducing minerals such as iron oxides and sulfides.

Throughout work on this project, and several others before and on-going, we have been working to develop protocols for compiling and managing databases of results from kinetic studies of contaminant degradation. The overall strategy for this task was to build on, and improve on, that effort, while applying it to ISCR type contaminant degradation reactions. The result is tentatively named the “ISCR Kin” (or IscrKin) database. The current version of the ISCR Kin database includes two files on Google Drive: one for dehalogenation reactions and the other for nitro reduction reactions.

A large part of the data in the IscrKin was used in a review article on the effects of sulfidation on contaminant reduction by zerovalent iron [2]. We used that data in a meta-analysis of sulfidation effects that showed micro- and nano-sized ZVI can be more effective when modified with lower-valent forms of sulfur, including sulfide, dithionite, thiosulfate, and elemental sulfur. An example of this analysis is shown in **Figure 1**.

We also developed and experimental method for comparing the reactivity of pre-equilibrated nonstoichiometric magnetite to Fe(II) and instant sequential spikes of Fe(II) to nonstoichiometric magnetite during reduction of p-chloronitrobenzene (PCNB). This method utilized serial respikes or contaminants and reductants to more efficiently get both kinetic and capacity data for contaminant reduction while simultaneously characterizing the temporal evolution of the conditions (esp. the RMIs) that control the reduction rates. The results indicate that sequential spikes of freshly prepared dissolved Fe(II) increased the reductive capacity of magnetite, while magnetite that has pre-equilibrated with Fe(II) produced the fastest reaction.

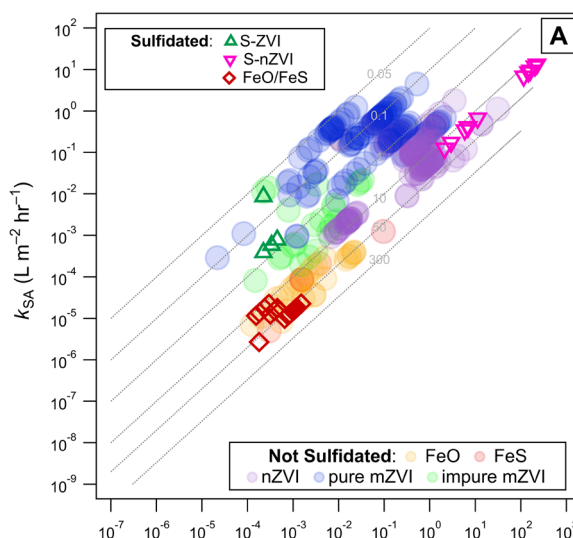


Figure 1. Meta-analysis of kinetic data for reduction of carbon tetrachloride by iron materials with and without sulfidation. For details see Figure 11.

Lately, magnetic susceptibility has gained renewed interests in environmental remediation. Because both magnetite and ZVI—the main contributors of abiotic remediation—are magnetic-bearing materials, and their magnetic susceptibility differ due to their compositions. Recently there is a vigorous discussion on applying magnetic susceptibility as a tool to identify the abundance of magnetite and/or ZVI in sediments in remediation sites. To clarify the relationship between MS measurements and conditions favor reductive abiotic natural attenuation, MS of various iron-based materials were compared and we tested for correlations between magnetic susceptibility and kinetic data for the reduction of nitro aromatic (model) contaminants. A major result is summarized in **Figure 2**, which shows that indicated χ_m of different iron materials follows the trend: granular ZVI > magnetite-maghemite > hematite > iron sulfides (bearing only little magnetism).

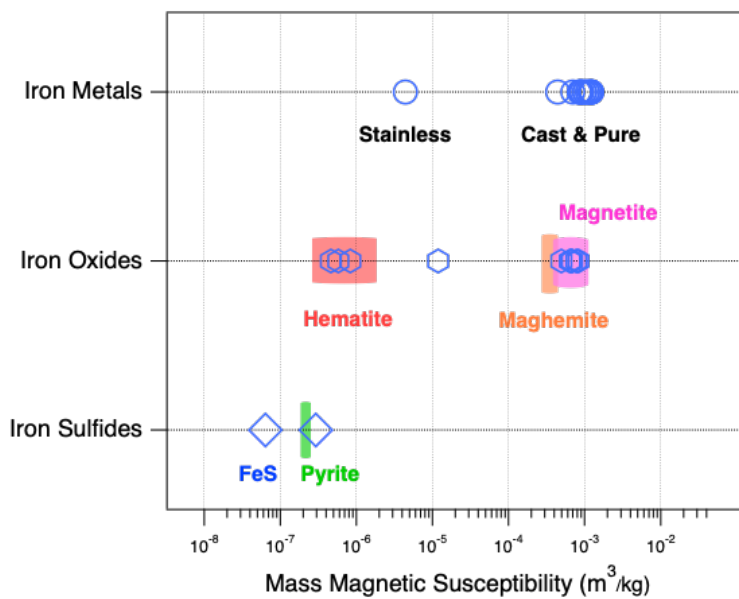


Figure 2. Mass magnetic susceptibility (χ_m) of iron-based materials; bars representing literature reported χ_m ranges of iron minerals from [1].

Objective 2, Activation/Mediation:

Under this objective, we began by focusing on quinone-type electron shuttles as prospective mediators of electron transfer that might cause increased rates of contaminant reduction under ANA/ISCR conditions. However, the result from preliminary experiments were not as promising as experiments by us and others that showed abiotic reduction rates can be greatly increase by addition of Fe(II) to iron minerals. This caused us to shift our focus to the reactive mineral intermediate (RMI) phases that form in iron oxide + Fe(II) systems and that appear to be responsible for most contaminant reduction. Many batch experiments were performed using combinations of iron oxides and Fe(II) with various dosing schemes. The results show that even nitro aromatic compounds (which are the most easily reduced contaminants of concern to DOD) are much more rapidly reduced by iron oxides after addition of enough Fe(II) to cause formation of RMIs.

Since there has been very little direct characterization of RMIs under in situ conditions, we used electrochemical methods that can be applied to essentially identical conditions as the batch experiments with nitro benzene. In order to observe the dynamics of RMI formation and its influence on the effective redox potential of iron oxide solids we titrated our medium with acid, base, or (mainly) $\text{Fe(II)}_{\text{aq}}$. This was done using zero-current single-electrode chronopotentiometry (CP) on a rotating glassy carbon disk electrode in suspensions of six reagent-grade iron oxides: goethite (GT), hematite (HT), lepidocrocite (LC), magnetite (MT), siderite (ST) and wustite (WT). The solution conditions were varied from Fe(II) concentrations that were below the available sites of the iron oxides to higher Fe(II) concentrations encountered in the environment. The open circuit potential (E_{OC}) measured by CP and pH (also measured in situ) were compared to

calculation from equilibrium speciation models and thermodynamic data. The results (e.g., **Figure 3**) suggest that most of the conditions tested yield similar limiting values of E_{OC} , which is consistent with the formation of a common RMI phase over time. Eventually, these results should help to define the relationship between RMI formation and rates of contaminant reduction, under laboratory and field conditions.

Objective 3, Reductant Demand: This task built on approaches taken in earlier work on “reduction (or reductive) capacity”, which is highly relevant but largely forgotten or neglected, and on relatively recent work concerning NOD, which is relatively well known to practitioners of ISCO but not as comprehensive or rigorous as it could be. Here (**Table 1**), we present a comprehensive and unifying framework for defining reductant (and oxidant) demand and related concepts such as capacity, with explicit mathematical definitions of each, and systematic consideration of “lumped in” and “factored out” variables. The framework represented by **Table 1** can be adapted to oxidation/ISCO.

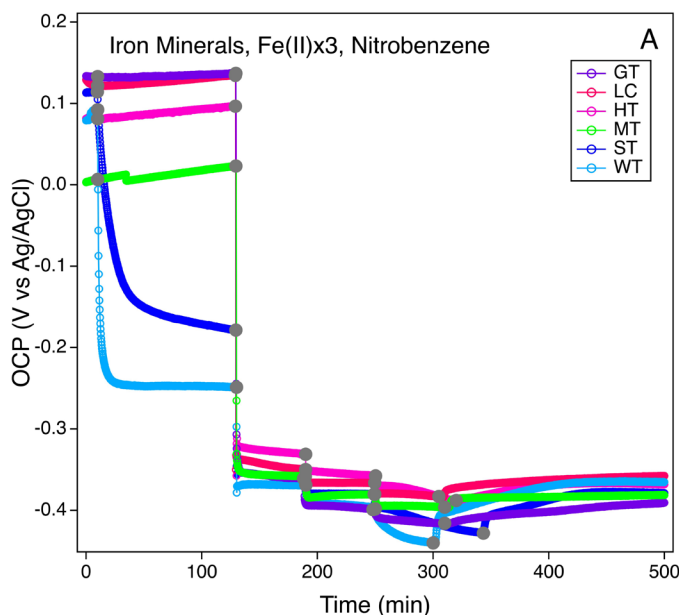


Figure 3. Open circuit potential vs. time of iron oxides with added Fe(II) or nitrobenzene. For details see Figure 34.

Table 1. Classification scheme to define the relationships between concepts involved in capacity and demand of reduction reactions. The quantitative definitions are intuitive, and are consistent with prior work, but we have not found them written out previously. The scheme can be applied to oxidations (NOD, etc.) by swapping the roles of oxidized and reduced species.

Qualitative Terminology	Oxidant (Ox _i = oxidized species i)	Reductant (Red _j = Reduced species j)	Quantitative Definition
Capacity = How much contaminant can I treat? (for specified amount of treatment)	CoC, Probe (Cr, TCE) - <i>measured</i>	Env. Matrix (Aquifer, GW, Soil) - <i>given</i>	Reductive Capacity (RC) $RC_{ox_i} = \frac{\Delta[Ox_i]^{t=end}}{[Red]}$
Demand = How much treatment do I need? (for specified amount of contaminant)	Env. Matrix (Aquifer, GW, Soil) - <i>given</i>	Treatment, Assay (ZVI) - <i>measured</i>	Reductant Demand (RD) $RD_{red_j} = \frac{\Delta[Red_j]^{t=end}}{[Ox]}$

During the course of this project, sulfidation emerged as one of the most promising, and practical, methods of enhancing the performance of ZVI and related ISCR technologies (cf. the discussion of Fe(II) as an enhancement under Objective 2). After a period of emphasis on the enhanced contaminant degradation rates that are sometimes seen with sulfidated iron-based reductants, we recognized that the greatest benefit of sulfidation was not increased rate of contaminant degradation, but rather in increased selectivity of reaction with contaminants over side reactions, and the resulting increase in efficiency. Communicating this insight to practitioners became an urgent priority for us, and this task provided an opportunity to pursue that goal. We instigated a collaboration with the others who had contributed the most on topic, and after extensive deliberation, our consensus was documented in a review paper in the themed issue on halocarbons in the environment for the journal *Environmental Science: Process & Impacts*. Key aspects of this paper [3], are summarized below.

Implications for Future Research and Benefits: The results of this project advanced the theory and practice of abiotic NA in three complementary areas. Metrics for performance that are rigorously defined and widely adopted will allow, for the first time, quantitative comparison of abiotic NA outcomes. Enhancement of abiotic NA by control of activation and/or mediation processes will make this approach more effective where it is already applicable and more flexible for application to a wider range of contaminated sites.

Reductant demand characterization will become as essential to evaluation of abiotic NR as oxidant demand characterization is currently for proposed applications of ISCO. The scope of this project emphasizes scenarios of groundwater contaminated with chlorinated solvents, primarily, and explosives compounds, secondarily, but the results apply to other media and contaminants where chemical reduction of contaminants can be important.

9. OBJECTIVES

The three core concepts that are the focus of this project align closely with the three specific objectives highlighted in SERDP SON No. ERSON-16-01, “Measurement and Enhancement of Abiotic Attenuation Processes in Groundwater”. First, performance metrics that are rigorously defined and validated provide a common basis for methodologies used to quantify and compare processes that result in abiotic NA. Second, activation and mediation are approaches to *enhancement* of abiotic NA processes with many variations that could be applicable to a wide range of contaminated site scenarios. Third, correctly assessing and meeting reductant demand is essential to minimizing the *uncertainties and risks* regarding the short- and long-term performance of remedies based on abiotic NA.

The three core concepts that corresponding objectives are:

- The first concept involved “figures of merit” that can form the fundamental basis for rigorous comparison of all variations on ISCR-based remedies for contaminated groundwater. The corresponding objective was to evaluate the options for normalizing rate data on contaminant reduction to provide metrics with maximum generality while still being practical to apply to real ANA/ISCR situations.
- The second concept involved methods of enhancing abiotic NA by activation of chemical reductants and/or mediation of reaction between chemical reductants and contaminants. The corresponding objective was to evaluate options for enhancing ANA/ISCR performance by activation/mediation and identify those that are mostly like to be applicable to field-scale conditions.
- The third concept involved reductant demand, which reflects all of the processes that consume electrons under reducing conditions, of which contaminant reduction is only one. The corresponding objective was to develop a more complete conception model that relates demand, capacity, and selectivity of redox processes relevant to ANA/ISCR.

The project sought to advance all three of these “emerging core concepts” with the net result of providing a more complete and coherent foundation for abiotic NA (and all other variations of ISCR). The scope emphasized scenarios of groundwater contaminated with chlorinated solvents, primarily, and explosives compounds, secondarily, but the results apply to other media and contaminants where chemical reduction of contaminants can be important.

10. BACKGROUND

10.1. Abiotic Natural Attenuation

Contaminant degradation by reduction reactions that are—more or less—abiotic has been well documented in the academic literature since at least the 1980's [4], but evidence that in situ abiotic reduction contributes significantly to natural attenuation was lacking. Recent studies, however, have demonstrated that there can be an abiotic component to natural attenuation, even for relatively recalcitrant contaminants like trichloroethylene (TCE) [5, 6]. This has led to renewed interest and research in contaminant reduction by iron and sulfide minerals, although much of this recent work is formulated as an outgrowth of prior work on biotic NA (e.g., ER-2530, ER-2532).

At the same time, remediation technologies based on strong chemical reductants like zerovalent iron (ZVI) and dithionite have been extensively studied and widely applied. This proliferation has led to a body of knowledge on abiotic contaminant degradation processes that are comparable in scope and highly complementary to that which has come from the perspective of biogeochemical natural attenuation. To take advantage of this synergy, we have argued the benefits of grouping natural and engineered abiotic attenuation into one class of groundwater treatment processes and that this class is what should be meant by the term “in situ chemical reduction” [7]. This inclusive definition of in situ chemical reduction (ISCR) has been a major theme in our technology transfer efforts over the last few years and seems to have taken hold as the consensus understanding among practitioners. This definition also helped to define the scope of our previous SERDP project (ER-2308) and the project described here.

While working to advance both basic and applied aspects of ISCR, we identified three major opportunities based on analogies to in situ chemical oxidation (ISCO). We described these as “emerging core concepts” because we believe that they will be highly influential and widely adopted once they are fully developed. Our confidence that they will be widely adopted was based, in part, on their close analogy to established core concepts in ISCO. We tested these ideas by using the “emerging core concepts” theme in quite a few well-attended presentations and the response was very strongly positive. For one of those presentations (a webinar on ISCR), we developed a figure to illustrate the relationships between possible core concepts and various remediation technologies related to ISCR. The figure is shown in **Figure 4**.

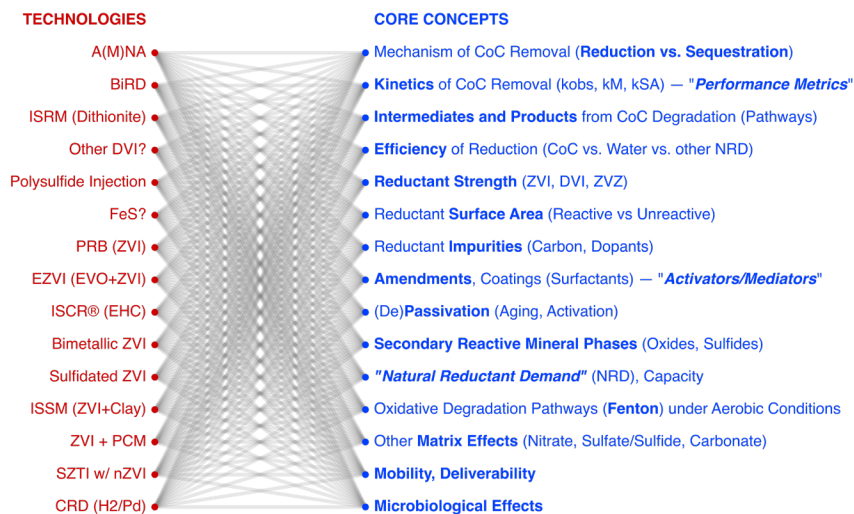


Figure 4. Summary of connections between the various remediation technologies that comprise ISCR and concepts that are high-level enough to be regarded as “core”. This version shows all combinations linked, to emphasize how broadly applicable core concepts can be. The original version of this figure was prepared for a webinar on ISCR presented on 9/2018 and hosted by Regenesi.

10.2. Standardization of Metrics for Remediation Performance

Of the core concepts summarized in Figure 4, the first one that we chose to emphasize concerns *standardized performance metrics*, such as the “figures-of-merit” developed by Bolton et al. [8, 9] for evaluating advanced oxidation processes (AOPs). Bolton derived his metrics (EE/O and EE/A) from fundamental chemical engineering theory, but in such a way that they are directly applicable to commercial applications of AOPs. They have been authorized as official standard methods [10] and now are widely used for comparisons among competing products for water treatment. Nothing of this caliber exists for any groundwater remediation process, but aspects of Bolton’s approach could be extended to ISCO and ISCR. We have tried to lay some of the foundation for an ISCR figure-of-merit through many years of work on kinetics of contaminant degradation by ZVI, starting with our seminal 1996 paper [11] that showed the most useful basis for comparison is based on the mass and surface area normalized rate constants, k_M and k_{SA} . More recently, we have been working with vendors of ZVI to define the most appropriate performance metric for selection among existing products or optimization of new formulations (Figure 5).

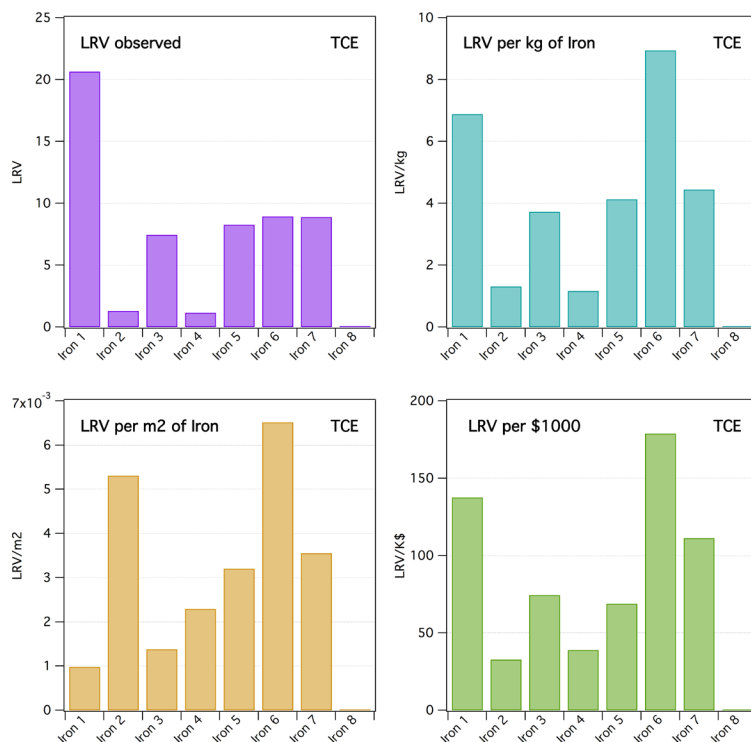


Figure 5. Example comparisons of different performance metrics (y-axis) vs. ZVI products (x-axis). LRV = log removal value (similar to “OoM” (9)).

In principal, all of these concepts can be extended to the processes involved in contaminant reduction by abiotic NA, although there are significant conceptual challenges that need to be addressed. Foremost among these is to validate and standardize protocols for normalizing COC degradation rates to environmental conditions. Recently, it has been suggested this can be done with magnetic susceptibility [6], but the evidence that this works (as currently practiced) is far from convincing. This and related issues were addressed in Objective 1, especially in Task 1.3.

10.3. Approaches to Enhancement of Abiotic Attenuation

The second core concept we choose to focus on was *enhancement by “activation” or “mediation”*. Activation is central to ISCO, where various activators are provided to enhance the formation of reactive oxygen species (esp. hydroxyl radical from iron-activated peroxide and sulfate radical from alkali-activated persulfate). Batchelor et al. [12] have shown that similar activation strategies (adding heat, light, etc.) can make more reducing species from reductants and named these combinations Advanced Reduction Processes (ARPs). An example ARP is the combination of sulfite and UV-light to

generate sulfite radical, which rapidly degrades vinyl chloride [13]. However, the specific formulations they have investigated mostly require irradiation with UV-light, so they probably are not suitable for in situ applications.

We recently showed that a weak magnetic field (WMF) can dramatically accelerate selenite removal by ZVI (**Figure 6**) [14], and we believe that the mechanism of this WMF effect will apply to other contaminants and reductants (i.e., magnetite). It is conceivable that the WMF effect could be used to enhance or restore the reactivity of a ZVI PRB or nZVI reactive treatment zone. Whether this effect is significant with passivated reducing minerals (e.g., Fe_3O_4 and FeS) has not been studied to date.

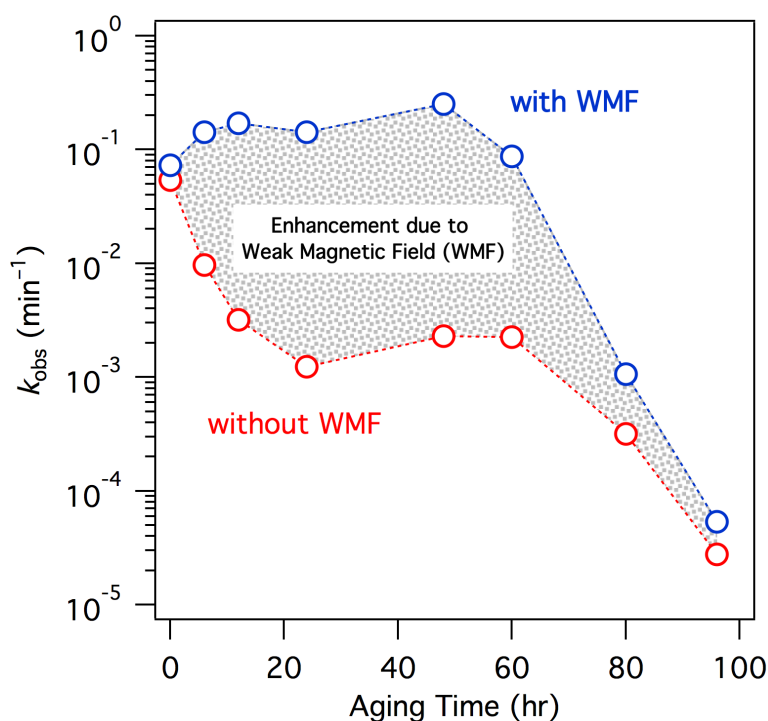


Figure 6. Example of enhanced contaminant removal by reductant activation: k_{obs} for selenium sequestration by nZVI w/ and w/o WMF. (12)

Another approach to enhancement involves electron-transfer mediators (a.k.a. “electron shuttles”) such as quinones, flavins, porphyrins, cobalamins, and corronoids. Many studies have shown that these mediators can accelerate contaminant reduction processes [e.g., 15, 16-19], but there has not yet been a concerted effort to evaluate these chemistries for enhancement of abiotic NA. Furthermore, most work on activation and mediation has focused only on the kinetics of contaminant degradation, thereby neglecting the possible benefits of redirecting contaminant degradation to pathways with

more desirable products. Efficient evaluation of the many possible variations on activation/mediation requires the systematic approach proposed as Objective 2.

10.4. Reductant Demand and Reductive Capacity

The third core concept featured in this project involves “*natural reductant demand*” (NRD), which is the ISCR analog of “natural oxidant demand” (NOD), the latter being well studied and widely applied for ISCO. In previous work [20], we have shown that NRD can play a significant role in limiting the delivery of nZVI into the subsurface, but the broader implications of NRD to other ISCR scenarios have yet to be considered.

We anticipated that most of the factors that make NOD difficult to define and quantify also apply to NRD. Specifically, both are operationally defined parameters that depend on the kinetics of competing reactions between multiple oxidants and reductants. Thomson et al. [21, 22] have described some of the higher-level interactions involving NOD, and our recent work with chemical redox probes under reducing conditions (for ER-2308) is producing evidence that these interactions might also apply to NRD. This is illustrated by **Figure 7**, which is based on data for one of our chemical redox probes, but generalized to show reduction of a moderately recalcitrant contaminant of concern (COC) like TCE. When nZVI dose is high and/or NRD is low and complete, TCE reduction should be relatively rapid; but at low nZVI dose and/or high NRD oxidation of Fe^0 to Fe^{II} leaves only Fe^{II} species to produce relatively slow and incomplete TCE degradation. A more easily reduced contaminant (e.g., RDX) would react more rapidly with weaker reductants, thereby shifting all the curves in **Figure 7** downward and providing a lesser apparent reductant demand and greater apparent capacity for reduction. This analysis was extended to conditions of fully passive abiotic NA (e.g., without nZVI) in Objective 3.

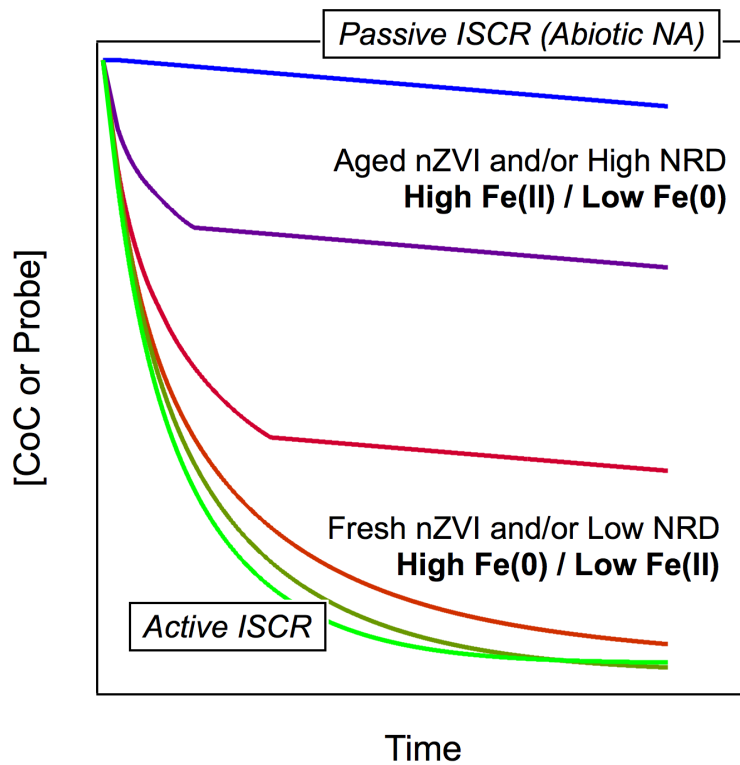


Figure 7. Illustration of operational factors that together determine reductant demand and, inversely, capacity to reduce contaminants. Adapted from data to be published in (21).

11. METHODS AND RESULTS

11.1. Core Concept 1—Performance Metrics

Work under this objective focused on determining the most useful ways of quantifying the performance of abiotic NA processes, including the “theoretical” model, essential data for parameterizing the model, and protocols for its application to field sites. Specifically, this involved extending the mass- and surface area- normalization (k_M and k_{SA}) approach—which we developed for ZVI—to abiotic NA processes that involve reducing minerals such as iron oxides and sulfides.

The scope of this objective was originally structured into three tasks, and the results presented below are arranged according to those tasks. However, there is overlap between the tasks, so the allocation of specific results among the task sections is influenced by other factors such as the chronology of publications that include these results.

11.1.1. Meta-Analysis of Rates of Chlorinated Contaminants (Task 1.1)

11.1.1.1. Planned/Approach (Compile and critically evaluate relevant prior work)

Building on the review of published data by He et al. [6], we proposed to expand the dataset to include a wider range of contaminants (including energetics), less well known or new studies, and a more extensive meta-data analysis for identifying and prioritizing data gaps (building on skills and tools from ER-1735). An illustration of this type of analysis is shown in **Figure 8**. This figure shows some of the trends that might be expected: e.g., that abiotic reduction rates would follow the trend nitro aromatics > chlorinated alkanes > chlorinated alkenes, and that faster reduction rates would be produced by the more strongly reducing mineral phases.

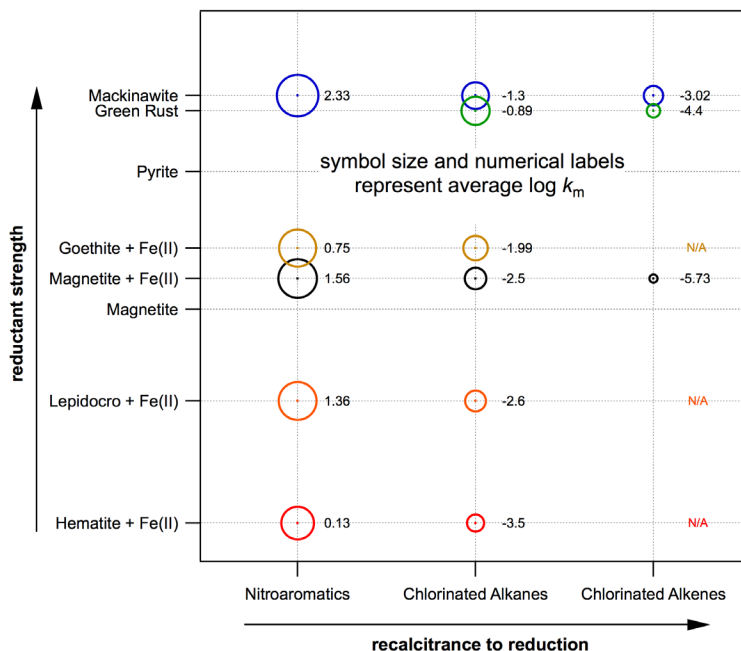


Figure 8. Summary of available kinetic data for contaminant reduction by mineral reductants. Number-labels are average values of rate constants normalized to mineral mass concentration (k_M). Adapted from a figure in Fan et al. (24)

However, more and better data are needed before this type of analysis can be completed. For example, **Figure 8** is based on first order disappearance rate constants normalized to total mass (concentration) of the solid phase, because that is the only relevant normalization that is almost always possible to perform. As expected, and noted below, it is difficult to do this with most published data because they are not accompanied by sufficient methodological detail to estimate more rigorous normalization metrics (such as to some estimate of reactive surface area). Furthermore, **Figure 8** does not include RDX, many chlorinated ethanes, and most chlorinated ethenes, because sufficient data for these important COCs were not yet available in the literature.

11.1.1.2. Comprehensive Online Database

Throughout work on this project, and several others before and on-going, we have been working to develop protocols for compiling and managing databases of results from kinetic studies of contaminant degradation. Our first major effort of this sort was for a SERDP project on in situ chemical oxidation (ER-1289), which resulted in the “ISCO Kin” (or IscoKin) database that is now published on-line at <https://zenodo.org/record/3736665> (DOI: 10.5281/zenodo.3736665). The overall strategy for this task was to build

on, and improve on, that effort, while applying it to ISCR type contaminant degradation reactions. The result is tentatively named the “ISCR Kin” (or IscrKin) database.

The IscoKin database was originally formatted as an Excel spreadsheet, which was exported to an SQL format database that could be searched from a form that was made available on the web. This time, for now, we have chosen to develop the IscrKin database as a “sheet” on Google Drive, where access can be viewed and edited by anyone that has been given access. We plan to continue with this approach until the database development reaches a stopping point that justifies taking a snapshot of the full contents and making them available to all (probably on Zenodo, as with the IscoKin database).

The current version of the ISCR Kin database includes two files on Google Drive: one for dehalogenation reactions and the other for nitro reduction reactions. Both sheets are very large, with many rows for each reported kinetic result (i.e., experiment) and many columns for the corresponding identifying information (Authors, Year, Reference, etc.), conditions (contaminant, reductant, concentrations, pH, etc.), and results (k_{obs} , k_{M} , k_{SA} , etc.). There are many anomalies that complicate the data management; such as cases where k_{obs} wasn’t reported but can be estimated from figures in the source, where the specific surface area of minerals used were not reported, but they are available in other publications; and where the original manuscript appears to contain errors.

It is not practical to include the whole IscrKin database in this report, but screen shots are included below to illustrate its current status (**Figure 9** and **Figure 10**).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1	Sort Num.	Data Num.	Data Source (Ref, Date, Page, Fig/Tab)	Original Source	Mineral Type	Mineral Source	Mineral Code	Grain Size (µm)	SSA (m ² /g)	SSA SD	SSA Source	Mineral Dose (g/L)	Fe (II) Dose (mM)	Fe (II) Dose (mM) Accumulated	Fe (II) Dose (mM) Stock / Mineral Dose	Fe (II) Dose (mM) Total Stock / Mineral Dose	Fe (II) Measured at the beginning of section (mM)	Fe (II) Measured at the end of section (mM)	Fe (II) Consumed (mM)	
2	10																			
3	11	K1	190122_Kal_E1_001_1	Kal	Fe(II) Cntrl		9						1	1.14						
4	K2	190122_Kal_E1_002_1	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	1	1.14	2.28	0.20						
5	13	K3	190129_Kal_E2_001_1	Kal	Lepidodocrite	Bayferrox	3		16.2	Fan16,TS1	0.500	1	1.14	2.28	0.14				2.54E-01	8.86E-01
6	14	K4	190201_Kal_E3_001_1	Kal	Fe(II) Cntrl		9						1	1.14					5.20E-01	6.14E-01
7	15	K5	190201_Kal_E3_002_1	Kal	Hematite	Bayferrox	1		14.2	Fan16,TS1	0.500	1	1.14	2.28	0.16	9.13E-01		5.48E-01	5.92E-01	
8	16	K6	190201_Kal_E3_002_2	Kal	Hematite	Bayferrox	1		14.2	Fan16,TS1	0.500	2	2.28	4.56	0.32	6.77E-01		1.08E+00	1.20E+00	
9	17	K7	190208_Kal_E4_001_1	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	0.5	0.56	1.11	0.10	4.15E-01		5.01E-02	5.10E-01	
10	18	K8	190208_Kal_E4_001_2	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	1	1.11	2.22	0.19	5.30E-01		2.51E-01	8.59E-01	
11	19	K9	190208_Kal_E4_002_1	Kal	Goethite	Bayferrox	2		14.9	Fan16,TS1	0.500	0.5	0.56	1.11	0.07	3.72E-01		1.29E-01	4.31E-01	
12	20	K10	190220_Kal_E5_001_1	Kal	Goethite	Bayferrox	2		14.9	Fan16,TS1	0.500	0.5	0.51	1.03	0.07	4.18E-01		1.43E-02	4.48E-01	
13	21	K11	190213_Kal_E5_001_2	Kal	Goethite	Bayferrox	2		14.9	Fan16,TS1	0.500	1	1.03	2.06	0.14	4.15E-01		2.61E-01	7.69E-01	
14	22	K12	190213_Kal_E5_002_1	Kal	Hematite	Bayferrox	1		14.2	Fan16,TS1	0.500	0.5	0.51	1.03	0.07	4.69E-01		3.12E-01	1.98E-01	
15	23	K13	190213_Kal_E5_002_2	Kal	Hematite	Bayferrox	1		14.2	Fan16,TS1	0.500	1	1.03	2.06	0.14	7.41E-01		3.40E-01	6.90E-01	
16	24	K14	190213_Kal_E5_003_1	Kal	Fe(II) Cntrl		9						0.5	0.51		4.62E-01		3.15E-01	1.95E-01	
17	25	K15	190213_Kal_E5_003_2	Kal	Fe(II) Cntrl		9						1	1.03		8.17E-01		2.18E-01	8.12E-01	
18	26	K16	190220_Kal_E6_001_1	Kal	Lepidodocrite	Bayferrox	3		16.2	Fan16,TS1	0.500	0.5	0.53	1.06	0.07	4.01E-01		1.79E-02	5.12E-01	
19	27	K17	190220_Kal_E6_002_1	Kal	Siderite	??	6						0.500	0.5	0.53	1.06		8.86E-02	4.40E-01	
20	28	K18	190220_Kal_E6_002_2	Kal	Siderite	??	6						0.500	1	1.06	2.11		5.80E-01	2.18E-01	
21	29	K19	190301_Kal_E7_001_1	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	0.25	0.28	0.56	0.05	2.04E-01		2.51E-02	2.55E-01	
22	30	K20	190301_Kal_E7_001_2	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	0.5	0.56	1.12	0.10	2.79E-01		8.24E-02	4.78E-01	
23	31	K21	190301_Kal_E7_001_3	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	0.75	0.84	1.69	0.15	3.44E-01		1.18E-01	7.22E-01	
24	32	K22	190301_Kal_E7_002_1	Kal	Goethite	Bayferrox	2		14.9	Fan16,TS1	0.500	0.25	0.28	0.56	0.04	2.40E-01		1.07E-02	2.69E-01	
25	33	K23	190301_Kal_E7_002_2	Kal	Goethite	Bayferrox	2		14.9	Fan16,TS1	0.500	0.5	0.56	1.12	0.08	2.30E-01		1.43E-02	5.44E-01	
26	34	K24	190308_Kal_E8_001_1	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	0.25	0.28	0.56	0.05	1.91E-01		5.01E-02	2.30E-01	
27	35	K25	190308_Kal_E8_001_2	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	0.5	0.56	1.12	0.10	3.83E-01		8.24E-02	4.78E-01	
28	36	K26	190308_Kal_E8_001_3	Kal	Magnetite	Bayferrox	5		11.6	Fan16,TS1	0.500	0.75	0.84	1.68	0.14	3.58E-01		1.29E-01	7.11E-01	
29	37	K27	190308_Kal_E8_002_1	Kal	Goethite	Bayferrox	2		14.9	Fan16,TS1	0.500	0.25	0.28	0.56	0.04	2.33E-01		1.07E-02	2.69E-01	
30	38	K28	190308_Kal_E8_002_2	Kal	Goethite	Bayferrox	2		14.9	Fan16,TS1	0.500	0.5	0.56	1.12	0.07	3.51E-01		1.07E-02	5.49E-01	

A	B	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	
1	Sort Num.	Data Num.	Fe(II) Consumed (mM)	Dose Number	Medium, Buffer	pH start	pH end	Equilib Time (hr)	RMI precip	CoC, CRP	CoC Code	[CoC]o (µM)	[CoC]o Fit (µM)	[CoC]o Fit (µM) SD	kobs* units?	kobs* units? SD	kobs* units	kobs* (1/hr)	kobs* SD	AM (L/hr/g)	AM SD	logKoa (L/hr/m ²)	ASA (L/hr/m ²)	ASA SD
2	10																							
3	11	K1		1.20	FeCl ₂ HEPES, NaCl	8	7.46	20	2	NB	1	100	103.79	6.11	3.795E+00	5.830E-01	1/hr	3.795E+00	5.830E-01					
4	K2			1.20	FeCl ₂ HEPES, NaCl	8	7.24	20	1	NB	1	100	98.456	6.72	8.291E+00	1.720E+00	1/hr	8.291E+00	1.720E+00	1.658E+01	3.440E+00	1.552E-01	1.430E+00	2.965E-01
5	13	K3	8.86E-01	1.20	FeCl ₂ HEPES, NaCl	8	6.91	20	2	NB	1	100	99.378	6.3	1.273E+01	1.930E+00	1/hr	1.273E+01	1.930E+00	2.545E+01	3.860E+00	1.962E-01	1.571E+00	2.383E-01
6	14	K4	8.14E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.39	20	2	NB	1	100	97.039	3.2	6.397E-01	8.520E-02	1/hr	6.397E-01	8.520E-02					
7	15	K5	5.92E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.35	20	2	NB	1	100	97.24	2.25	8.883E-01	6.700E-02	1/hr	8.883E-01	6.700E-02	1.737E+00	1.340E-01	-8.126E-01	1.223E-01	9.437E-03
8	16	K6	1.20E+00	2.00	FeCl ₂ HEPES, NaCl	8	7.33	20	2	NB	1	100			1.922E+00	5.280E-01	1/hr	1.922E+00	5.280E-01	3.844E+00	1.050E+00	-5.675E-01	2.707E-01	7.437E-02
9	17	K7	5.10E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.3	20	1	NB	1	100	97.749	6.25	2.109E+00	8.940E-01	1/hr	2.109E+00	8.940E-01	4.218E+00	1.388E+00	-4.333E-01	3.637E-01	1.197E-01
10	18	K8	8.59E-01	2.00	FeCl ₂ HEPES, NaCl	8	7.3	20	1	NB	1	100			1.258E+00	7.770E-02	1/hr	1.258E+00	7.770E-02	2.516E+00	1.554E-01	-6.637E-01	2.169E-01	1.340E-02
11	19	K9	4.31E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.5	20	2	NB	1	50	48.272	2.56	4.851E+00	6.170E-01	1/hr	4.851E+00	6.170E-01	7.702E+00	1.234E+00	-1.863E-01	6.511E-01	8.282E-02
12	20	K10	4.96E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.44	20	2	NB	1	100	96.891	6.62	4.854E+00	6.170E-01	1/hr	4.854E+00	6.170E-01	9.707E+00	1.634E+00	-1.861E-01	6.515E-01	1.097E-01
13	21	K11	7.60E-01	2.00	FeCl ₂ HEPES, NaCl	8	7.44	20	2	NB	1	100	W		3.952E+00	2.070E-01	1/hr	3.952E+00	2.070E-01	7.904E+00	4.140E-01	-2.753E-01	8.309E-01	2.779E-02
14	22	K12	1.98E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.43	20	2	NB	1	100	97.876	1.33	3.201E-01	3.010E-02	1/hr	3.201E-01	3.010E-02	6.401E-01	6.020E-02	-1.346E+00	4.508E-02	4.239E-03
15	23	K13	1.95E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.46	20	2	NB	1	100	100.42	2.22	3.344E-01	4.920E-02	1/hr	3.344E-01	4.920E-02	3.218E+00	3.200E-01	-8.447E-01	2.266E-01	2.254E-02
16	24	K14	8.12E-01	2.00	FeCl ₂ HEPES, NaCl	8	7.46	20	2	NB	1	100			4.480E+00	6.830E-01	1/hr	4.480E+00	6.830E-01					
17	25	K15	5.12E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.3	20	2	NB	1	100	99.269	4.06	8.168E+00	7.840E-01	1/hr	8.168E+00	7.840E-01	1.634E+01	1.598E+00	3.641E-03	1.008E+00	9.679E-02
18	26	K16	4.40E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.35	20	2	NB	1	100	98.197	5.31	2.672E+00	6.150E-01	1/hr	2.672E+00	6.150E-01	5.345E+00	1.230E+00			
19	27	K17	8.42E-01	2.00	FeCl ₂ HEPES, NaCl	8	7.35	20	2	NB	1	100			3.758E+00	7.880E-01	1/hr	3.758E+00	7.880E-01	7.515E+00	1.576E+00			
20	28	K18	2.55E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.51	20	1	NB	1	100	97.231	2.21	2.739E-01	1.050E-01	1/hr	2.739E-01	1.050E-01	5.478E-01	2.100E-01	-1.326E+00	4.722E-02	1.810E-02
21	29	K19	4.78E-01	2.00	FeCl ₂ HEPES, NaCl	8	7.51	20	1	NB	1	100			5.194E-01	3.960E-02	1/hr	5.194E-01	3.960E-02	1.029E+00	7.960E-02	-1.048E+00	8.359E-02	6.802E-03
22	30	K20	7.22E-01	3.00	FeCl ₂ HEPES, NaCl	8	7.51	20	1	NB	1	100			1.215E+00	5.230E-02	1/hr	1.215E+00	5.230E-02	2.429E+00	1.046E-01	-6.790E-01	2.094E-01	9.017E-03
23	31	K21	2.68E-01	1.20	FeCl ₂ HEPES, NaCl	8	7.52	20	2	NB	1	100	98.349	4.66	2.266E+00	5.210E-01	1/hr	2.266E+00	5.210E-01	4.532E+00	1.042E+00	-5.169E-01	3.042E-01	6.993E-02
24	32	K22	5.46E-01	2.00	FeCl ₂ HEPES, NaCl	8	7.52	20	2	NB	1	100			3.755E+00	7.570E-01	1/hr	3.755E+00	7.570E-01	7.510E+00	1.514E+00	-2.976E-01	5.040E-01	1.016E-01
25	33	K23	2.30E-01	1.00	FeCl ₂ HEPES, NaCl	8	7.67	0	1	NB	1	100	98.798	2.63	4.378E-01	1.310E-01	1/hr	4.378E-01	1.310E-01	8.756E-01	2.620E-01	-1.122E+00	7.548E-02	2.239E-02
26	34	K24	4.78E-01	2.00	FeCl ₂ HEPES, NaCl	8	7.67	0	1	NB	1	100			6.474E-01	3.770E-02	1/hr	6.474E-01	3.770E-02	1.295E+00	7.540E-02	-9.522E-01	1.119E-01	6.500E-03
27	35	K25	7.11E-01	3.00	FeCl ₂ HEPES, NaCl	8	7.67	0	1	NB	1	100			1.611E+00	6.110E-02	1/hr	1.611E+00	6.110E-02	3.222E+00	1.222E-01	-5.664E-01	2.777E-01	1.053E-02

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V
1	Sort by COC	Sort by Source	Sort by Exp.	Data Source (First/Senior Author)	Data Source (Year)	Data Source (Paper DOI)	Data Source (Page, Fig, Table)	Data Source (Original)	Material (Mineral) Category	Material (Mineral) Source, Type	Material (Mineral) Short Name	Material (Mineral) Notes	Material (Mineral) Grain Size (um)	Material SSA (m ² /g)	SSA (SD or 95% CI)	SSA Source	Mineral Dose (g/L)	Pretreatment (Aging) Conditions	Pretreatment (Aging) Time (hr)	Initial Reaction Medium (at t = 0)	pH t = 0	pH t = end
2	01	01	01	Amonette/Gorby	2000	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		5,000	HEPES @ pH 7	24	PIPES	6.90		
3	01	01	02	Amonette/Gorby	2000	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		5,000			PIPES	6.90		
4	01	01	03	Amonette/Gorby	2000	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		5,000			PIPES	6.90		
5	01	01	04	Amonette/Gorby	2001	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		5,000			PIPES	6.90		
6	01	01		Amonette/Gorby	2002	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		1,000			PIPES	7.00		
7	01	01		Amonette/Gorby	2003	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		2,000			PIPES	7.00		
8	01	01		Amonette/Gorby	2004	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		5,000			PIPES	7.00		
9	01	01		Amonette/Gorby	2005	10.1021/ed9913582			Fe2O3/Fe(OH)	G				55,000		10,000			PIPES	7.00		
10	01	02		Bulko/Tratnyek	1998	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
11	01	02		Bulko/Tratnyek	1999	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
12	01	02		Bulko/Tratnyek	2000	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
13	01	02		Bulko/Tratnyek	2001	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
14	01	02		Bulko/Tratnyek	2002	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
15	01	02		Bulko/Tratnyek	2003	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
16	01	02		Bulko/Tratnyek	2004	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
17	01	02		Bulko/Tratnyek	2005	[10.1021/jp9713113m]			Pure Fe(OH)	FL			0.019	83,330					Unbuffered			
18	01	02		Butterfayes	2000				Fe Sulfide	FS			0.050	10,000					TRIS and Tris-HCl	8.30		
19	01	03		Choi et al 2009	2009				FeS													
20	01	04		Danielsen/Hayes	2004				MG												10.00	
21	01	04		Danielsen/Hayes	2004				MG												9.50	
22	01	04		Danielsen/Hayes	2004				MG												9.00	
23	01	04		Danielsen/Hayes	2004				MG												8.50	
24	01	04		Danielsen/Hayes	2004				MG												8.00	
25	01	04		Danielsen/Hayes	2004				MG												7.50	
26	01	04		Danielsen/Hayes	2004				MG												7.00	
27	01	04		Danielsen/Hayes	2004				MG												6.50	
28	01	04		Danielsen/Hayes	2004				MG												6.00	
29	01	05		Danielsen et al, 2005					Fe3O4	MG				18,010		25,000			Unbuffered		7.00	
30	01	05		Danielsen et al, 2005					Fe3O4	MG				18,010		25,000			Buffered with Tris-d		8.30	
31	01	05		Danielsen et al, 2005					Fe3O4	MG				18,010		25,000			Buffered with Tris-H		8.30	
32	01	05		Danielsen et al, 2005					Fe3O4	MG				18,010		25,000			Buffered with TEA-d		8.30	
33	01	07		Owlin and Muller 1999					FeS													
34	01	07		Owlin and Muller 1999					FeS													
35	01	08		Doone et al, 2003					Other	SI				1,231		1,500			HEPES		8.30	

	A	B	C	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV
1	Sort by COC	Sort by Source	Sort by Exp.	COC, CRP	[Coc] SD Target (uM)	[Coc] SD from fit (uM)	[Coc] SD from fit (uM)	k(obs) (raw, units from RA)	k(obs) SD (raw, units from RA)	k(obs) SD (raw, units from RA)	k(obs) norm. units SD (1/hr)	k(M) norm. units SD (1/hr)	k(M) reported (L/h/m ²)	k(M) SD reported (L/h/m ²)	k(M) calc = k(M)/PP (L/h/m ²)	k(SA) SD reported (L/h/m ²)	k(SA) SD reported (L/h/m ²)	k(SA) calc = k(AQ)/PP (L/h/m ²)	Product (Primary)	Product (Yield)	Products (Secondary)
3	01	01	02	CT							2.500E-02		5.000E-03			9.090E-05					
4	01	01	03	CT							1.083E-01		2.166E-02			3.938E-04					
5	01	01	04	CT							1.083E-01		2.166E-02			3.938E-04					
6	01	01		CT							1.460E-02		1.460E-03			2.655E-04					
7	01	01		CT							3.330E-02		1.665E-02			3.027E-04					
8	01	01		CT							1.000E-01		2.000E-02			3.636E-04					
9	01	01		CT							1.750E-01		1.750E-02			3.182E-04					
10	01	02		CT							1.200E-01		1.440E-03			7.579E-02					
11	01	02		CT							2.200E-01		2.400E-03			1.263E-01					
12	01	02		CT							1.800E-01		2.160E-03			1.137E-01					
13	01	02		CT							6.400E-01		7.680E-03			4.042E-01					
14	01	02		CT							3.100E-01		3.720E-03			1.958E-01					
15	01	02		CT							6.100E-01		7.320E-03			3.853E-01					
16	01	02		CT							4.700E-01		5.640E-03			2.969E-01					
17	01	02		CT							5.200E-01		6.240E-03			3.284E-01					
18	01	02		CT							1.090E-01		1.090E-02			2.180E-01					
19	01	03		CT									3.687E-02								
20	01	04		CT																	
21	01	04		CT																	
22	01	04		CT																	
23	01	04		CT																	
24	01	04		CT																	
25	01	04		CT																	
26	01	04		CT																	
27	01	04		CT																	
28	01	04		CT																	
29	01	05		CT							3.200E-02		1.280E-03			7.110E-05					
30	01	05		CT							9.460E-02		3.784E-03			2.301E-04					
31	01	05		CT							3.920E-02		1.568E-03			8.710E-05					
32	01	05		CT							3.870E-02		1.548E-03			8.600E-05					
33	01	07		CT									6.107E-02								
34	01	07		CT									7.249E-02								
35	01	08		CT							5.320E-01		3.547E-01			2.881E-01					
36	01	09		CT							7.600E-03		2.585E-03			1.521E-04					

Figure 10. Screen shots of the IscrKin database for abiotic dechlorination data: (A) columns from the left, (B) columns from the right side of right. Current version contains 600+ entries (rows).

The current version of the database includes data only the most widely studied chlorinated solvents: carbon tetrachloride and trichloroethylene. Other chlorinated aliphatics can be added, be this was postponed because the effort would be very time consuming. Reductants represented range from iron oxides (e.g., goethite) with added Fe(II) to zerovalent iron. Data on sulfidic systems have not yet been added.

11.1.1.3. Performance Metrics vs. Effects of Sulfidation

Iron-based materials used in the degradation of chlorinated contaminants, especially micro- and nano-sized ZVI, can be more effective when modified with lower-valent forms of sulfur, including sulfide, dithionite, thiosulfate, and elemental sulfur. This sulfur modification of iron-based materials (or other metals, such as silver) is referred to as “sulfidation”. Sulfidation has recently attracted attention from both scientists and practitioners. Many studies have emphasized increased rates of contaminants removal via sulfidation. However, most of these conclusions are based on comparisons between controls and sulfidation effects under a narrow range of conditions, so the generality of such results merits further consideration. To address this, we have compiled most of the kinetic data that are currently available for reduction of chlorinated organics by iron-based reductants, and subjected them to the meta-analysis, which have been published in a review titled “Sulfidation of iron-based materials: A review of processes and implications for water treatment and remediation” [2].

By far, the majority of data available are for CT and TCE, which are summarized in the format of surface area normalized rate constant (k_{SA}) vs. mass normalized rate constant (k_M) in **Figure 11A** and **B**, respectively. For both contaminants, the available data obtained with sulfidated reductants are shown with open markers and solid circles are used for non-sulfidated iron-based materials (including nZVI, microscale ZVI of various purities, FeS, and iron oxides). For CT (**Figure 11A**), the data for sulfidated materials form clusters roughly coincident with data obtained with non-sulfidated forms of the same material, suggesting that sulfidation does not generally increase rates of CT degradation. In contrast, the TCE kinetic data (**Figure 11B**) show at least one order of magnitude increase in k_M and/or k_{SA} for sulfidated materials compared with their non-sulfidated analogs, and there is sufficient data to conclude that this enhancement probably applies over most conditions. For chromate (**Figure 11C**), sulfidation generally does not increase the rate of contaminant removal.

The contrasting effect of sulfidation on reduction rates of TCE and CT has been rationalized as a reflection of differences in dechlorinating species for these two contaminants. It was hypothesized that surface sulfur poisons the recombination of atomic hydrogen to form H_2 , thereby leaving more atomic hydrogen at the surface for TCE degradation [25]. This hypothesis is supported by data showing (i) no enhancement of CT reduction (which occurs predominantly by electron transfer) (ii) a similar enhancement of TCE degradation rates by adding another known poison for atomic hydrogen recombination (i.e., arsenic [26]), and (iii) the decrease in H_2 formation [25].

However, this hypothesis may be inconsistent with other data, such as the increasing TCE reduction rate by S-nZVI with increasing pH, which has been observed with both S-nZVI [27] and Fe/FeS [28]. This pH dependence is opposite that for H₂ formation by ZVI corrosion (and therefore, presumably, the availability of surface H, which is an intermediate in the formation of H₂). Furthermore, the observed pH dependence of TCE degradation by sulfidated nZVI is consistent with the pH effect observed with pure nanocrystalline FeS [29], but opposite to the trend with unmodified nZVI [30]. Prior studies on TCE degradation by pure FeS have noted that higher pH increases the negative charge of FeS surface, thereby providing increased driving force for electron transfer [29, 31]. These results favor an alternative hypothesis proposed by Rajajayavel et al. [27], that TCE reduction by S-nZVI occurs predominantly via FeS, which serves as a mediator of electron transfer from Fe(0) to FeS-sorbed contaminants. This also is consistent with the high electron conductivity of FeS [32], and the inhibited H₂ production from S-nZVI may simply be due to FeS blocking direct access of water to Fe(0) sites.

The operational variable that seems to have the greatest overall effect on the kinetics of contaminant reduction by sulfidated nZVI is the S/Fe ratio. For all contaminant types, sulfur sources, and sulfidation methods, contaminant reduction rates increase from low to moderate S/Fe ratios and then plateau or decrease at high S/Fe ratios.

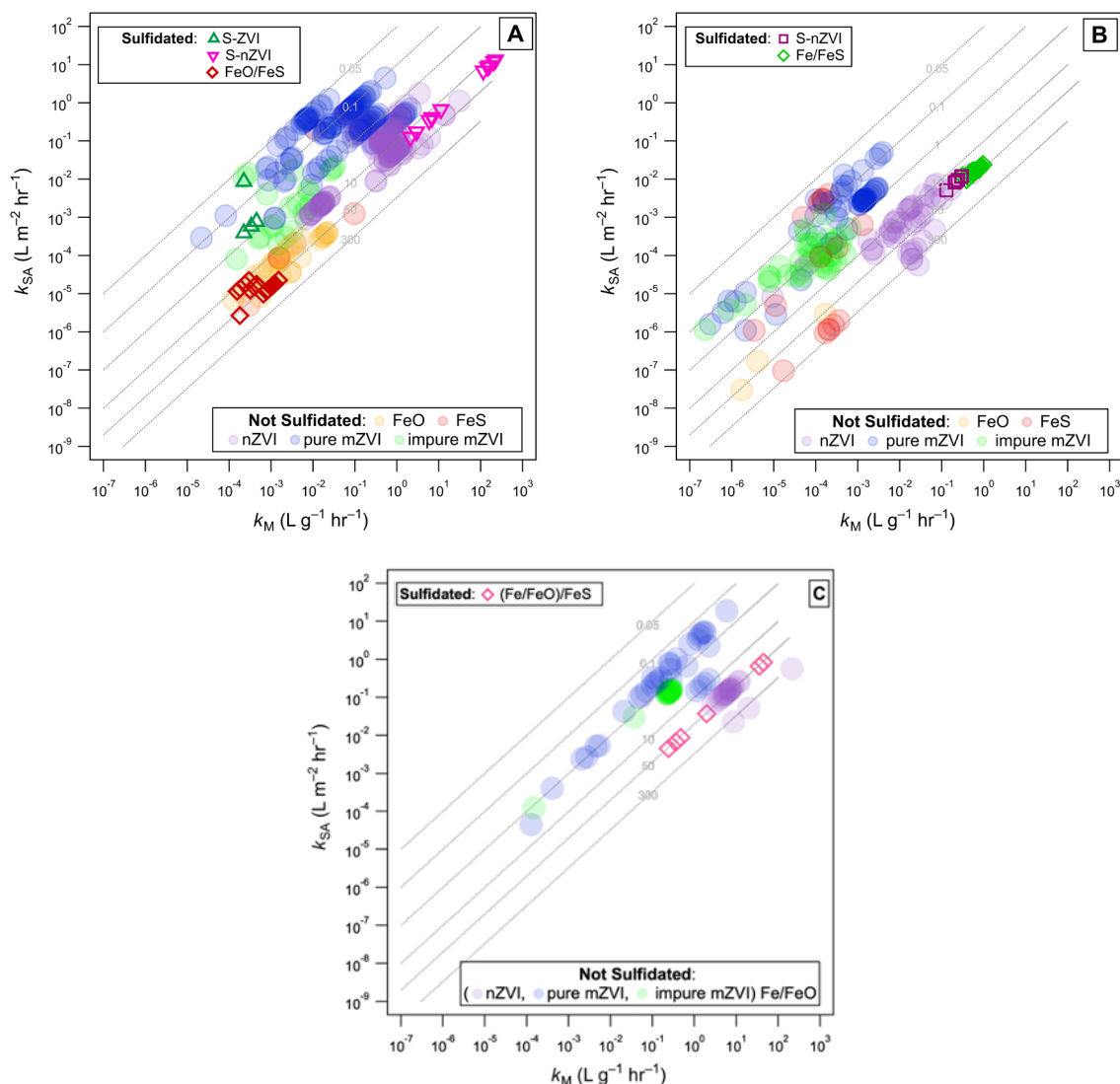


Figure 11. Comparison of rate constants for contaminant reduction by reducing materials with and without sulfidation [2]:(A) k_{SA} vs k_M plot for CT (331 k's); (B) k_{SA} vs k_M plot for TCE (189 k's); (C) k_{SA} vs k_M plot for chromate. The diagonal contours in (A), (B), and (C) represent specific surface areas used to calculate k_{SA} .

11.1.2. Model System Development (Task 1.2)

11.1.2.1. Planned/Approach (Methods for Filling Data Gaps)

To help fill the data gaps identified in Task 1.1, we performed controlled laboratory experiments using representative COCs and reducing materials. In most respects, the specific experimental and analytical protocols were similar to those that we have used in

many prior studies [e.g., 23, 24, 33, 34]. The new data from this task were combined with literature data compiled in Task 1.1 and the data set was analyzed for correlations, much as we did in a previous study of 8 COCs vs. 9 types of ZVI [35]. That study uncovered a reactivity pattern that is diagnostic for two modes of COC removal (reduction vs. adsorption). We hypothesize that such diagnostic patterns in reactivity would be found in this study: for example, between phases dominated by Fe(II) and those containing sulfide.

11.1.2.2. Model System Calibration and Validation

The first phase of work on this task involved exploratory batch experiments for calibration and validation of an efficient protocol for measuring the kinetics of (model) contaminant reduction under conditions with relevance to natural attenuation.

Iron Mineral Suspensions. Most experiments under Task 1.2 were done with suspensions of magnetite (Mgt) or iron sulfide (FeS). Magnetite and FeS were selected as representatives of the iron oxides and iron sulfides groups, respectively. They have distinctive reactivity towards groundwater contaminants, and therefore were used as model minerals. Magnetite was purchased from Sigma-Aldrich, and dissolved Fe(II) was added to magnetite suspensions to simulate conditions of ISCR. Iron sulfide was synthesized by mixing equal concentration and equal volume of FeCl₂ and Na₂S inside the anaerobic chamber [36], and washed using DI water and 0.1 M NaCl at least three times.

For batch experiments, all solutions are sparged with N₂ for at least 30 mins before being transferred into a N₂ filled anaerobic chamber with O₂ concentration less than 0.8 ppm. All solutions are equilibrated with the N₂ atmosphere for 1 hour while rigorously stirred on a stir plate. Two types of Fe(II) addition are employed, including “pre-exposure” of magnetite to dissolved Fe(II) by allowing solutions to equilibrate overnight, and “instant-exposure” of magnetite to dissolved Fe(II) that takes place during batch experiment (no equilibration).

Nitro Reduction Experiments. These experiments were performed in 60-mL serum vials sealed with septa and aluminum crimp caps. Reactors were filled with magnetite or FeS and pH buffer to achieve desired mineral loads inside the anaerobic chamber. Experiments were initiated by injection of a stock solutions of NACs. Reactors were then rotated for the duration of analysis. pH was controlled using MES buffer (pH 6), HEPES buffer (pH 7) and Trizma buffer (pH 8). At desired intervals, aliquots (0.7 mL) were

removed from the batch reactor, filtered using a Fisherbrand™ syringe filter (0.22 μm PTFE membrane) to a HPLC sample vial containing 5 μL 69%-72% perchloric acid.

NACs concentrations were analyzed by HPLC equipped with a Varian ProStar 210 solvent delivery module, a 410 autosampler, and a 330 photodiode array detector, with a Agilent ZORBAX Extend 80 Å C18 column (4.6 x 250 mm, 5 μm) at a detection wavelength of 230 nm, 276 nm, 276 nm, and 298 nm for TNT, PCNB, NB, and DNAN, respectively. The mobile phase consisted HPLC-grade methanol at either 40% or 50% in water, depending on the NACs analyzed, at a flow rate of 1 mL min⁻¹.

A previous study used chemical reactivity probes (CRPs) to characterize the thermodynamic and kinetic aspects of contaminant reduction by reducing iron minerals [37], and identified the data gaps in abiotic natural attenuation of chlorinated solvents and NACs. Therefore, for this task, we conducted controlled laboratory experiments using NACs (NB, PCNB, TNT, and DNAN) and natural iron minerals (magnetite and FeS) with the purpose of filling the data gaps. Combining the new and old data in **Figure 12** confirms the expected trend in abiotic reduction rates: nitro aromatics > chlorinated alkanes > chlorinated ethenes. Note, however, that there is no clear boundary between the contaminant groups. Instead, the k_M clusters overlap due to different mineral conditions, such as aging and availability of dissolved Fe(II), which strongly affected mineral reactivity.

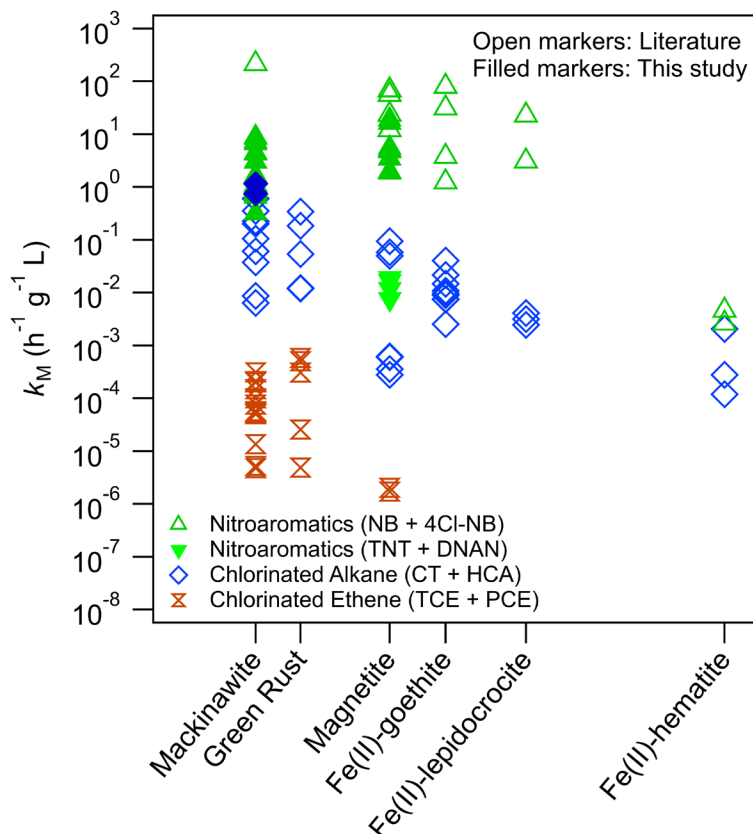


Figure 12. Mass-normalized reduction rate constants (k_M) of kinetic CRPs (including NACs and chlorinated alkanes) and chlorinated ethenes with various reducing iron minerals (open symbols: values reported in literature; solid symbols: measured value determined in this project). The literature data in this figure are from Fan et al. [38].

We also conducted experiments to compare the reactivity of pre-equilibrated nonstoichiometric magnetite to Fe(II) and instant sequential spikes of Fe(II) to nonstoichiometric magnetite during reduction of PCNB. This method utilized serial respikes or contaminants and reductants to more efficiently get both kinetic and capacity data for contaminant reduction while simultaneously characterizing the temporal evolution of the conditions (esp. the RMIs) that control the reduction rates. The results indicate that sequential spikes of freshly prepared dissolved Fe(II) increased the reductive capacity of magnetite (**Figure 13**), while magnetite that has pre-equilibrated with Fe(II) produced the fastest reaction.

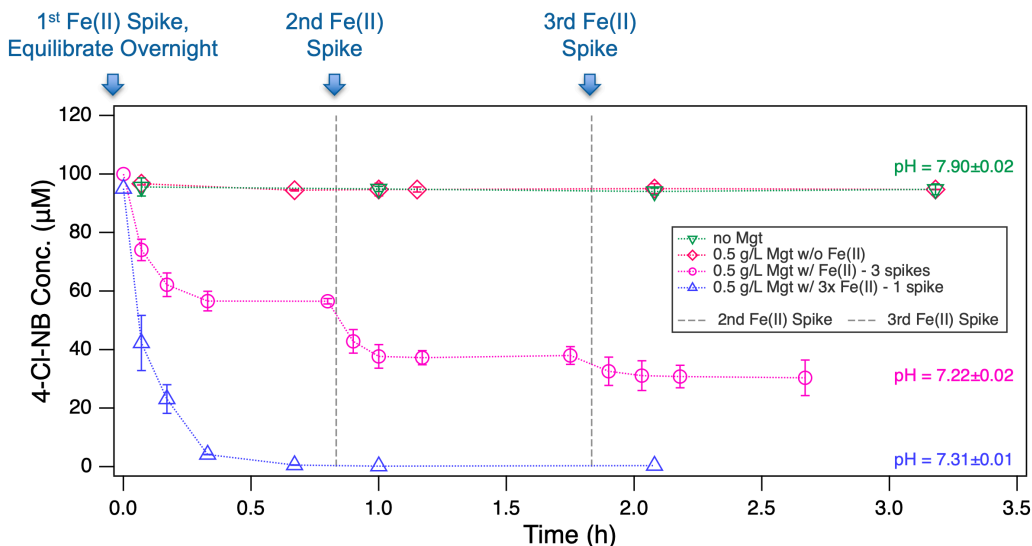


Figure 13. Demonstration of the experimental approach developed for use in this task, using reduction of PCNB (4-Chloronitrobenzen, p-nitrobenzene) using magnetite with an initial pH of 8. Two types of dissolved Fe(II) additions are employed: pre-equilibration of magnetite with dissolved Fe(II) overnight (first Fe(II) spike) and instant sequential spikes of dissolved Fe(II) during the experiment (second and third Fe(II) spikes).

11.1.2.3. Final method for measuring kinetics of abiotic reduction by iron minerals

The method developed as described in the previous section was further refined and finalized for use in an extensive study of the kinetics of nitro reduction by iron oxide minerals. The method is described in detail below:

Materials and Common Methods. All chemical reagents were ACS reagent grade and used as received without further purification. For all operations involving Fe(II) and CRPs, anaerobic conditions were maintained inside an anoxic chamber (MO-10-M from Vacuum Atmosphere Company) filled with 100% N₂ (O₂ < 1 ppm) at 22 ± 1 °C, unless otherwise mentioned.

Preparation of Mineral Suspensions. Goethite (GT), lepidocrocite (LP), magnetite (MT), and hematite (HT) were acquired from Bayferrox (Burgettstown, PA). These materials have been used in many prior studies of redox reactions involving iron oxides. Siderite and wüstite were acquired from Strem Chemicals (Newburyport, MA) and Alfa Aesar (Haverhill, MA) respectively. Ferrous ion (Fe(II)) stock solution was prepared using FeCl₂•4H₂O from Fisher Scientific (Hampton, NH) with > 99% purity. Various quantities of Fe(II) stock solution (~500 mM) were added to the anoxic mineral

suspensions with pH adjusted to 8.0 (or as noted) by 10 mM HEPES. The suspensions were transferred to 123 mL borosilicate clear glass serum bottle, which were then crimp sealed and placed on a rotator for equilibration (~20 h). After the equilibration, same amount of Fe(II) was “respiked” into the reactor roughly 1 h and 2 h after NAC was injected.

Kinetic Study of Reduction of NACs. Three NACs were selected for batch experiments: nitrobenzene (NB), 2,4-Dinitroanisole (DNAN), and 2-methyl-1,3,5-trinitrobenzene (TNT), which were acquired Sigma Aldrich, Alfa Aesar, and Chem Service. For all NACs, the reactions were carried out in 120 mL borosilicate clear glass serum bottles, crimp sealed with Viton septa, containing an initial concentration of ~50 uM or ~100 uM. The reactors were mixed on the rotator at 22 ± 1 °C. At each sample point, 1.0 mL mineral suspension was withdrawn after injecting the same volume of N₂ into the vial using a gastight plastic syringe, filtered with a 0.20 um filter, and placed into a vial containing 50 uL of 5.0 M hydroxylamine hydrochloride. Hydroxylamine hydrochloride quenched reaction and stabilized NACs, the nitroso intermediates, and amine products of the parent NAC compound concentrations (Klausen et al. 1995, Alessi et al. 2008). The samples were analyzed for disappearance of parent compounds for all NACs, and appearance of nitroso intermediate and amine product of NB by a high-performance liquid chromatography (HPLC) with a photo diode array detector.

Measurement of Fe(II) Concentration. Throughout reactions, Fe(II) concentrations were measured using the phenanthroline method [39] using ferrous ion reagent from Hach Company (Loveland, CO). At each sample point, 0.5 mL mineral suspension was withdrawn after injecting the same volume of N₂ into the vial using a gastight plastic syringe, filtered with a 0.20 um filter, and placed into a 20 mL screw cap vial containing a packet of ferrous ion reagent and 9.5 mL of anoxic DI water. After letting the vial sit for 4 minutes, the absorbance of the solution at 510 nm was measured using DR/2000 from Hach Company.

11.1.2.4. Results for nitro reduction with iron oxides + Fe(II)

A selection of the results of from experiments performed using the method described above are summarized below. In all cases, the figures represent a times series that included periodic addition (“spikes”) of Fe(II), the timing of which is indicated by the vertical dashed lines in the figures.

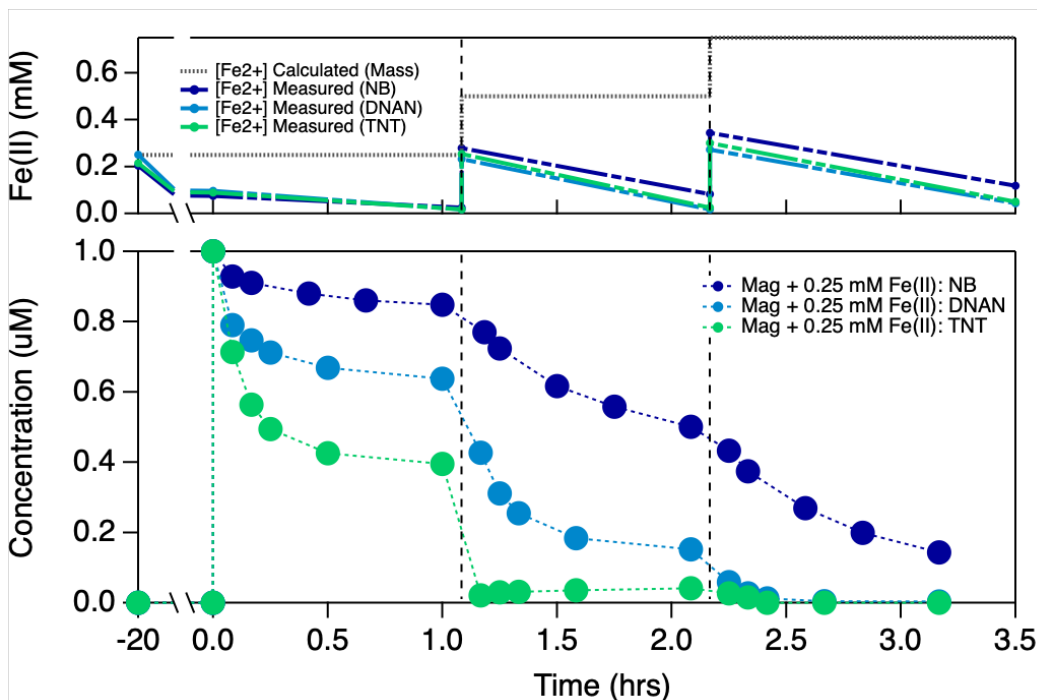


Figure 14. Reduction of NB, DNAN, and TNT by magnetite + Fe(II) suspensions. Experimental conditions: 0.5 g/L iron oxides, pH 8 10 mM HEPES buffer 20 h equilibration prior to addition of NACs, $[NACs]_0 = 100 \text{ uM}$ for NB and DNAN and 50 uM for TNT. Fe(II) respikes were calculated to add 0.25 mM Fe(II) in the reactor each time.

This figure shows that magnetite + Fe(II) suspensions reduced NB, DNAN, and TNT over several hours. The rate constants k_{obs} for NB, DNAN, and TNT were calculated for each sections of the reactions, which were always $k_{TNT} > k_{DNAN} > k_{NB}$. One of the advantages of measuring $[Fe(II)]$ in parallel was that it gave us an insight of how the plateaus happen. We can see that when the plateau develops, Fe(II) is also used up in the reactor, suggesting that Fe(II) could be the limiting component of the reduction.

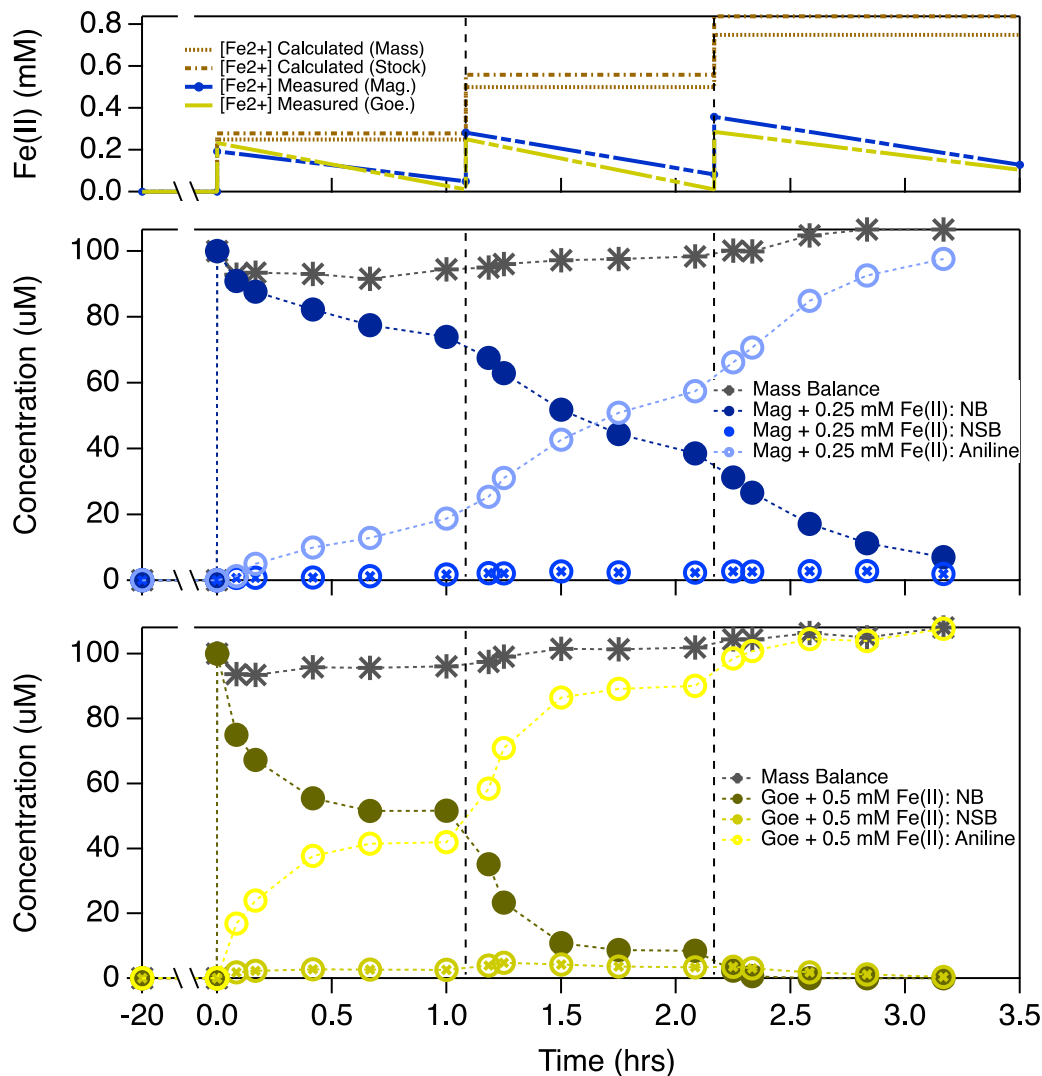


Figure 15. Reduction of NB to aniline by magnetite + Fe(II) and goethite + Fe(II) suspensions. Experimental conditions: 0.5 g/L iron oxides, pH 8 10 mM HEPES buffer, NO EQUILIBRATION prior to addition of NB, $[NB]_0 = 100 \text{ uM}$. Fe(II) respikes were calculated to add 0.25 mM Fe(II) in the reactor each time.

In this experiment, both of the reactors were not equilibrated prior to addition of NB, so the medium was not “aged” as it was in most other experiments. Despite of the lack of equilibration period, the traces of reduction of NB in both reactors were comparable to the ones with the ones obtained with aging, which were allowed to equilibrate for 20h prior to addition of NB. This result suggests relatively instantaneous formation of RMI in the reactor upon the addition of Fe(II).

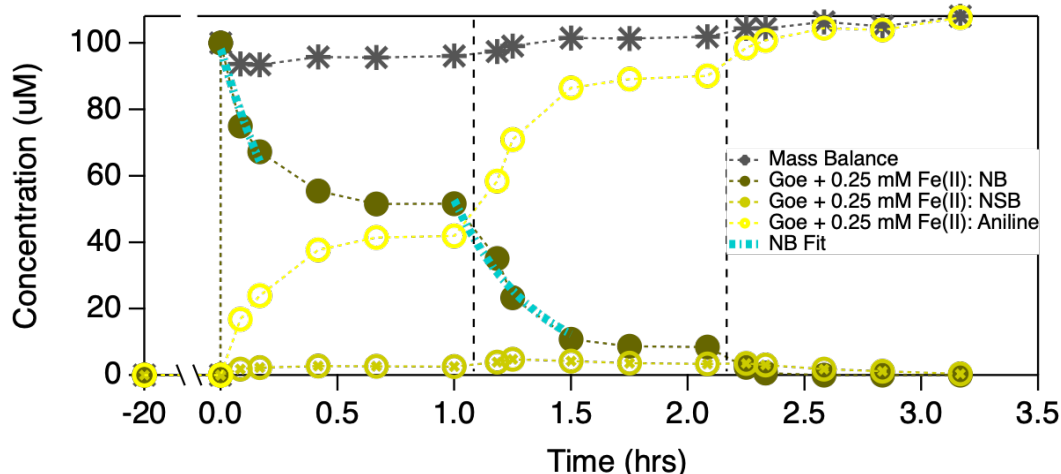


Figure 16 .Reduction of NB to aniline by magnetite + Fe(II) and goethite + Fe(II) suspensions. Experimental conditions: 0.5 g/L iron oxides, pH 8 10 mM HEPES buffer, no equilibration prior to addition of NB, [NB]₀ = 100 uM. Fe(II) respikes were calculated to add 0.25 mM Fe(II) in the reactor each time.

This batch is same condition as the batch in **Figure 15**, however, both of the reactors were not equilibrated prior to addition of NB. Despite of the lack of equilibration period, the traces of reduction of NB in both reactors were comparable to the ones with the ones that are shown in figure 7, which were allowed to equilibrate for 20h prior to addition of NB. This result suggests relatively instantaneous formation of RMI in the reactor upon the addition of Fe(II).

11.1.3. Evaluation of Normalization Methods (Task 1.3)

11.1.3.1. Planned/Approach (Normalization Methods)

This task focused on the most fundamental and challenging aspect of the development of quantitative performance metrics for abiotic NA processes, which is the selection of method for normalizing kinetic data to operational (field) conditions. A good normalization method needs to reflect the environmental variation in factors that actually control reduction rates, and yet be based on data that are relatively easy to acquire so they can be (or become) readily available.

For this purpose, total specific surface area is one obvious starting point, but since only a fraction of the surface area will be significantly reactive, we decided that this approach was insufficient. On the assumption that magnetite (Fe₃O₄) is the dominant phase responsible for abiotic NA, and from which it follows that it might prove useful to

normalize kinetic data to magnetic susceptibility [6]. Magnetic susceptibility (MS) is a parameter that is easily measured on small quantities of aquifer material when appropriate instrumentation is available. This approach is catching on quickly, and some commercial laboratories have been providing magnetic susceptibility measurements for use in treatability testing. However, the evidence that there is a correlation between dechlorination rates and magnetic susceptibility is weak, so this approach needs to be evaluated more rigorously. We planned to perform that analysis by measuring rates of reduction on a range of contaminants with a variety of well-characterized environmental materials and then subjecting the data to an statistical analysis for correlations.

While we expected the normalization of COC reduction rates to magnetic susceptibility will be somewhat successful over a limited range of controlled conditions, we hypothesize that this would not be sufficient for general purposes and that other, more comprehensive, normalization strategies will be necessary. For this purpose, we chose to focus on Fe(II) as the species controls formation of reactive intermediate (RMI) iron oxides phases. This approach is described in Section 11.2.2.3.

11.1.3.2. Magnetic susceptibility as normalization factor

Magnetic Susceptibility (MS, χ) is a measure of the magnetic properties of a material (either a pure phase or a mixture), which indicates whether a material is attracted into or repelled out of a magnetic field. Magnetic susceptibility can identify the magnetic-bearing materials that present in a sample but rapid and non-destructive means, thus has been widely used in environmental sample measurements. Magnetic susceptibility measurements have been used to detect anthropogenic pollutions and to identify areas that are worth more detailed investigations. Topsoil contains iron oxides and heavy metals originate from fossil fuels has higher magnetic measurements than uncontaminated areas [40, 41]. Lately, magnetic susceptibility has gained renewed interests in environmental remediation. Because both magnetite and ZVI—the main contributors of abiotic remediation—are magnetic-bearing materials, and their magnetic susceptibility differ due to their compositions. Recently there is a vigorous discussion on applying magnetic susceptibility as a tool to identify the abundance of magnetite and/or ZVI in sediments in remediation sites.

To clarify the relationship between MS measurements and conditions favor reductive abiotic natural attenuation, MS of various iron-based materials were compared and tested for correlations between magnetic susceptibility and kinetic data for the reduction of nitro

aromatic (model) contaminants. Our overall conceptual model and approach to this problem is summarized in **Figure 17**.

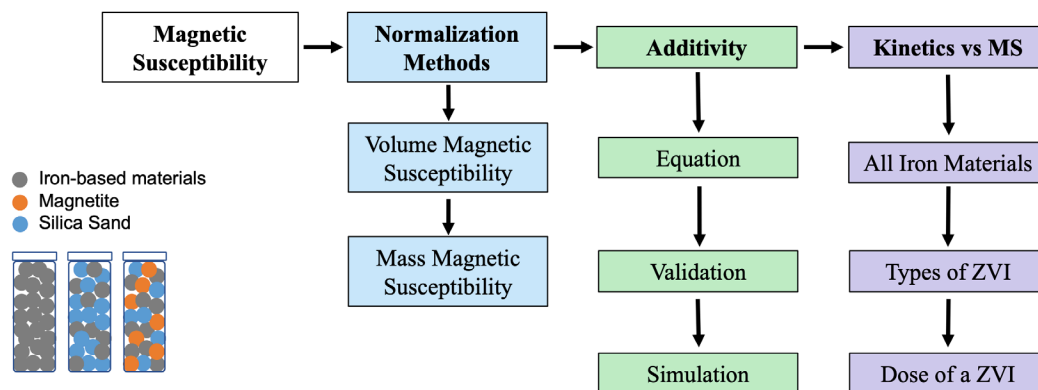


Figure 17. Rubric for evaluation of the relationship between magnetic susceptibility (MS) and rates of contaminant degradation.

Magnetic susceptibility was measured using Bartington MS3 Magnetic System (purchased for the project) equipped with a MS2G and/or a MS2B sensor. Mass specific magnetic susceptibility (χ_m) for Columbia River sediment samples was obtained using a MS2B sensor. For iron-based materials evaluation, volume specific magnetic susceptibility (χ_v) was obtained using a MS2G sensor, and was converted to mass specific magnetic susceptibility (χ_m), by dividing by the bulk density (ρ) of the sample:

$$\chi_m = \chi_v / \rho \quad (1)$$

Magnetite is a common natural component of sediments. Sediments from Columbia river (Portland, OR) were collected, oven dried, sieved, and isolated by magnetic separation. Results indicated χ_m correlates with magnetite weight percent (**Figure 18A**), and sediments with smaller particle sizes ($< 75 \mu\text{m}$, $75\text{-}147 \mu\text{m}$) have higher magnetite content (**Figure 18B**). This supports the possibility of using magnetic susceptibility to predict the magnetite content in sediments and soils.

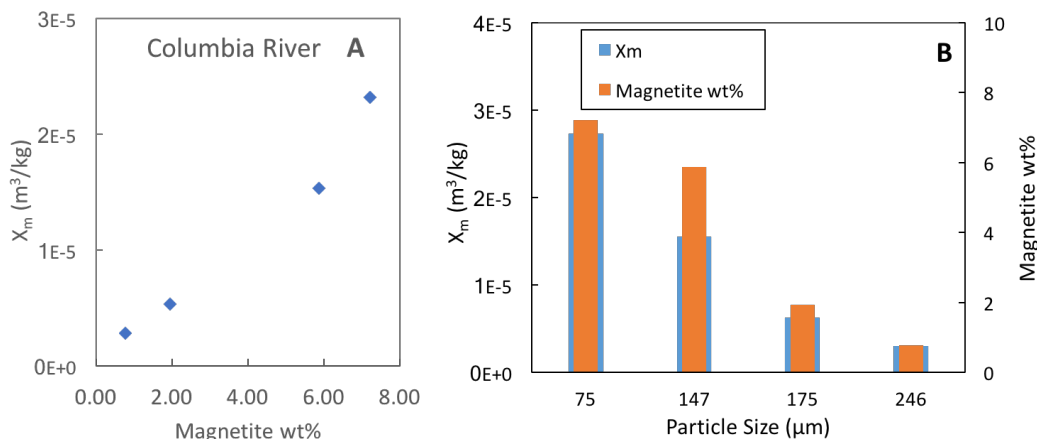


Figure 18. Relationship between (A) mass specific magnetic susceptibility (χ_m) and magnetite weight percent in Columbia river (Portland, OR) and (B) distribution of magnetite according to the sediment particle sizes.

To better understand the relationship between magnetic susceptibility and magnetic material content, commercial iron material (magnetite of different sizes, maghemite, and zero valent iron, which has a much higher magnetic moment) were tested. **Figure 18** indicated χ_m of different iron materials follows the trend: granular ZVI > magnetite/maghemite > hematite > iron sulfides (barring only little magnetism).

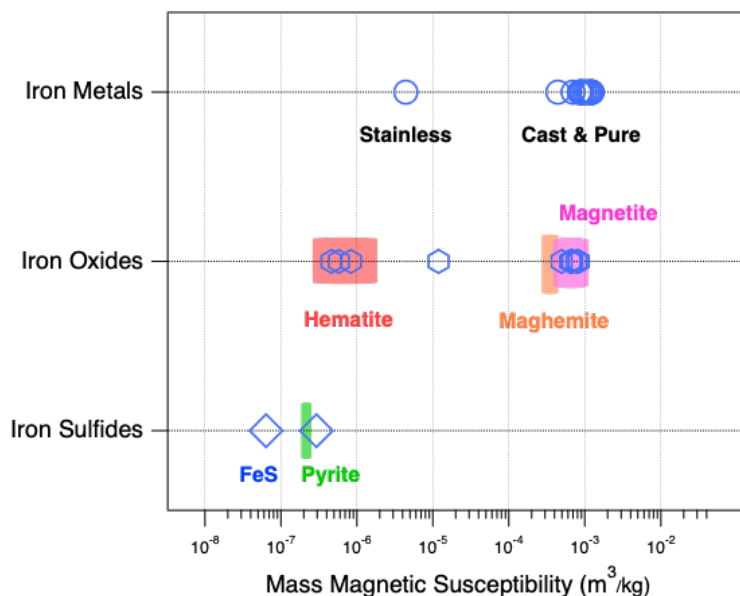


Figure 19. Mass magnetic susceptibility (χ_m) of iron-based materials; bars representing literature reported χ_m ranges of iron minerals [1].

While **Figure 18** is based on pure materials, mixtures of iron-based materials and non-magnetic materials, such as sands and clays, exist in natural and filed conditions. It's critical to understand the additivity of magnetic susceptibility. We proposed the additivity of magnetic susceptibility follows the equation:

$$\chi_{m,total} = \frac{\sum(\chi_{m,n} \times M_n)}{\sum M_n} \quad (2)$$

where χ_m is the mass specific magnetic susceptibility, M is the mass of the material.

Equation 2 is tested using both experiments (**Figure 20**) and computing simulation (**Figure 21**).

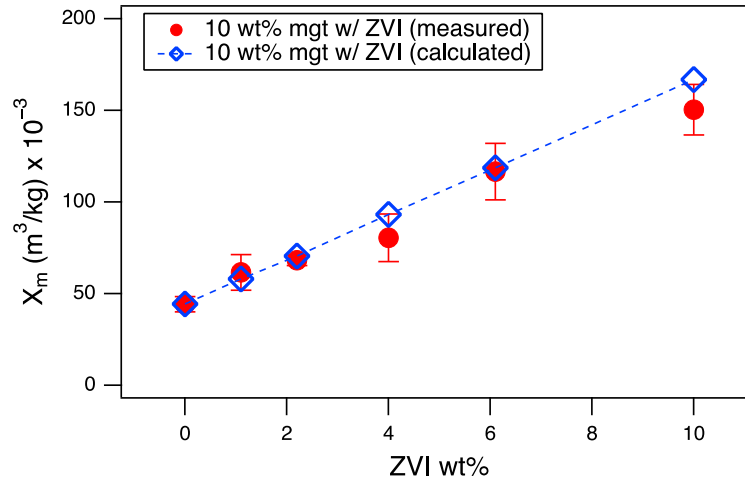


Figure 20. Additivity of mass magnetic susceptibility. Solid markers are measured χ_m using magnetite, ZVI and silica sands with different weight percent. Open markers are calculated χ_m using Equation 2. Calculated χ_m is consistent with measured χ_m .

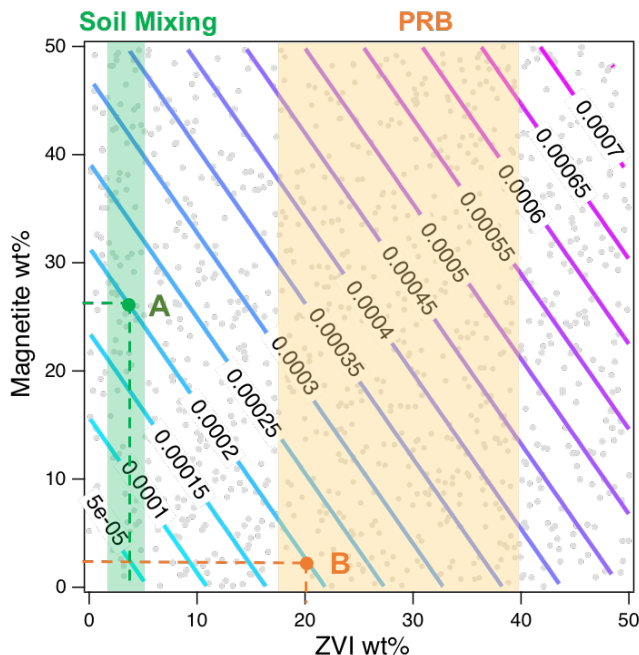


Figure 21. Additivity of mass magnetic susceptibility simulated by computer. The diagonal contours are $\chi_{m,\text{total}}$ calculated using different weight percent of ZVI and magnetite (both χ_m known). Site A and B share the same $\chi_{m,\text{total}}$, while site A represent soil mixing condition with a high magnetite and low ZVI content, and site B represent PRB condition with a low magnetite and high ZVI content

The results indicate when predicting the reduction ability of various materials using χ_m , it is important to take the iron-types into consideration. For example, sample A and B from **Figure 21** share the same χ_m , $2.0 \times 10^{-4} \text{ m}^3/\text{kg}$. The soil sample from Site A (soil mixing) is consist of 26% magnetite, 4% ZVI, and 70% non-magnetic materials, while the soil sample from Site B (PRB) is consist of 3% magnetite, 20% ZVI, and 77% non-magnetic materials. The TCE reduction rate would be quite different in these two sites. This suggests cross compare χ_m , total among remediation sites should not be encouraged.

Kinetic of iron materials of various χ_m was studied (**Figure 22**). No correlation was observed over full range of reductants while effects of pH and Fe(II) are more significant.

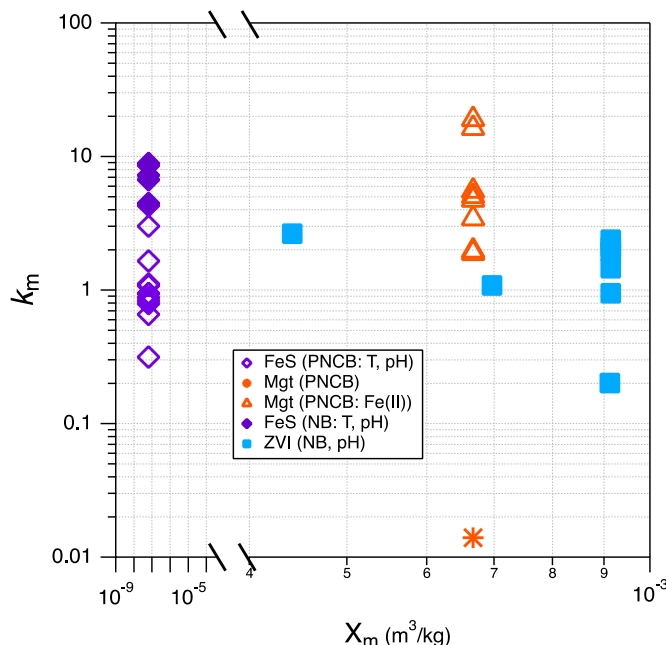


Figure 22. k_m vs. χ_m of multiple pure iron phases (reduction of nitro aromatics). Three types of iron materials were selected: FeS, magnetite, and ZVI, PNCB and NB were used as model contaminants. Fe(II) was added to improve the reactivity of magnetite.

These results indicate that if magnetic susceptibility is high, the system has the potential to abiotically reduce certain contaminants. Further conclusion will have to rely on additional information about the system's composition and environmental conditions. If the material contributes to the magnetic susceptibility is ZVI, the system has a high possibility that it can reduce contaminants via abiotic reduction. If the material contributes to the magnetic susceptibility is mainly magnetite, it's reducing capacity is largely determined by the stoichiometry of the magnetite, as well as the availability of dissolved Fe(II) in the system, neither of which can be predicted merely by magnetic susceptibility.

The lack of high magnetic susceptibility does not mean abiotic degradation is absent, because magnetic measurement does not detect iron sulfide minerals, which are strong reductants.

To further investigate the relationship between k_m and χ_m , we narrowed down the selection to multiple ZVIs (**Figure 23**) and one ZVI with different doses (**Figure 24**). No correlation was observed between χ_m and k_m of different types of ZVIs (**Figure 23**). Monotonic correlation was found between k_{obs} and χ_m of mixtures with different ZVI

content (**Figure 24**). These suggested χ_m may serve as a surrogate of ZVI content under controlled conditions.

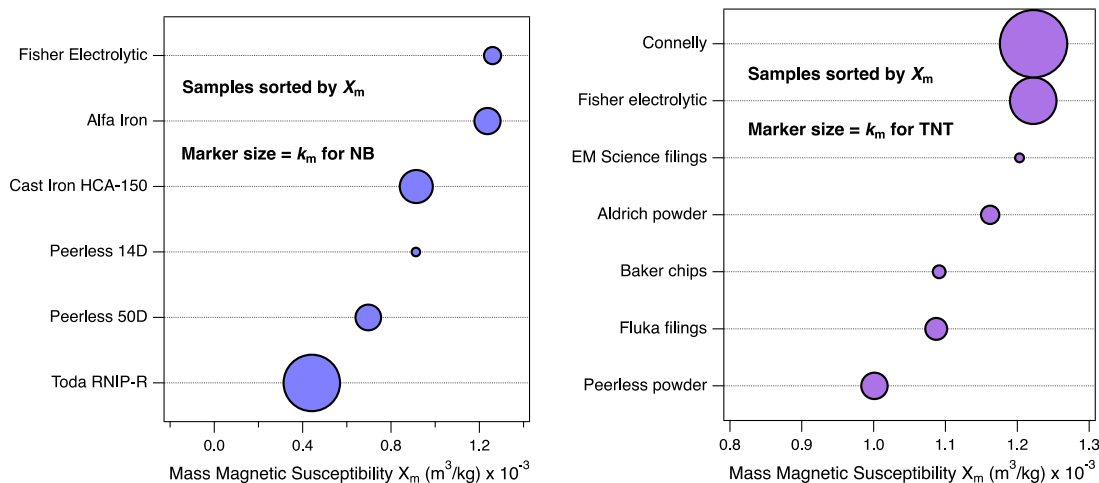


Figure 23. k_m vs. χ_m of multiple pure ZVI (reduction of nitro aromatics). TNT and NB were selected as model contaminants. Size of solid markers represents k_m for TNT and NB.

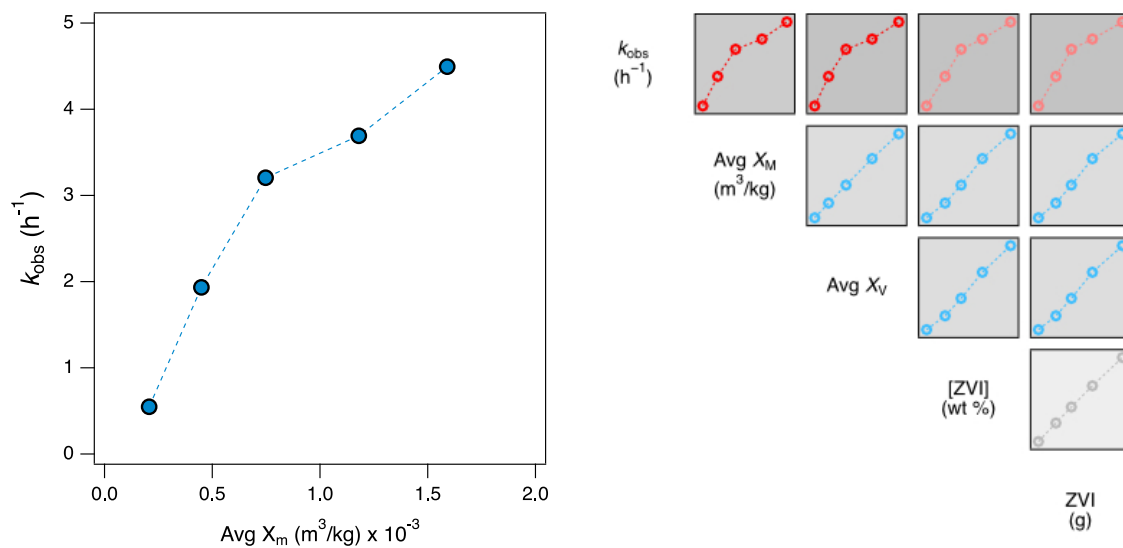


Figure 24. k_{obs} vs χ_m of mixtures of ZVI and silica sand. Variation of χ_m in one reaction system was achieved by mixing different ratios of ZVI and silica sand.

11.1.3.3. Fe(II) as a normalization factor

Over the time period of this project, multiple lines of evidence caused us to refocus our search for meaningful factors for rate constant normalization from magnetic susceptibility

to measures of Fe(II) available to activate iron oxides. Starting with observed/measured pseudo first-order rate constants (k_{obs}), mass-normalized k_{obs} (k_{M}), and surface-area normalized k_{obs} (k_{SA}), we considered further normalizing the k 's by various measures of Fe(II). The measures of Fe(II) tested were those that are operationally appropriate for batch experiments: added, dissolved, sorbed, and precipitated Fe(II).

Rather than start by defining and calculating new values of rate constants, we chose to focus on exploratory data visualization of the effect of the proposed normalization factors. These results are shown in **Figure 25** and **Figure 26**. In both of the figures, the criteria for identifying successful normalization is convergence of the data around a trend in the primary variable. Inspection of **Figure 25** does not show such a trend because each panel does not include the effect shown in the previous panel. These figures are effectively combined in **Figure 25** and it does suggest the anticipated trend (increasing k_{SA} with increasing Fe(II) for any combination of nitro compound and iron oxide).

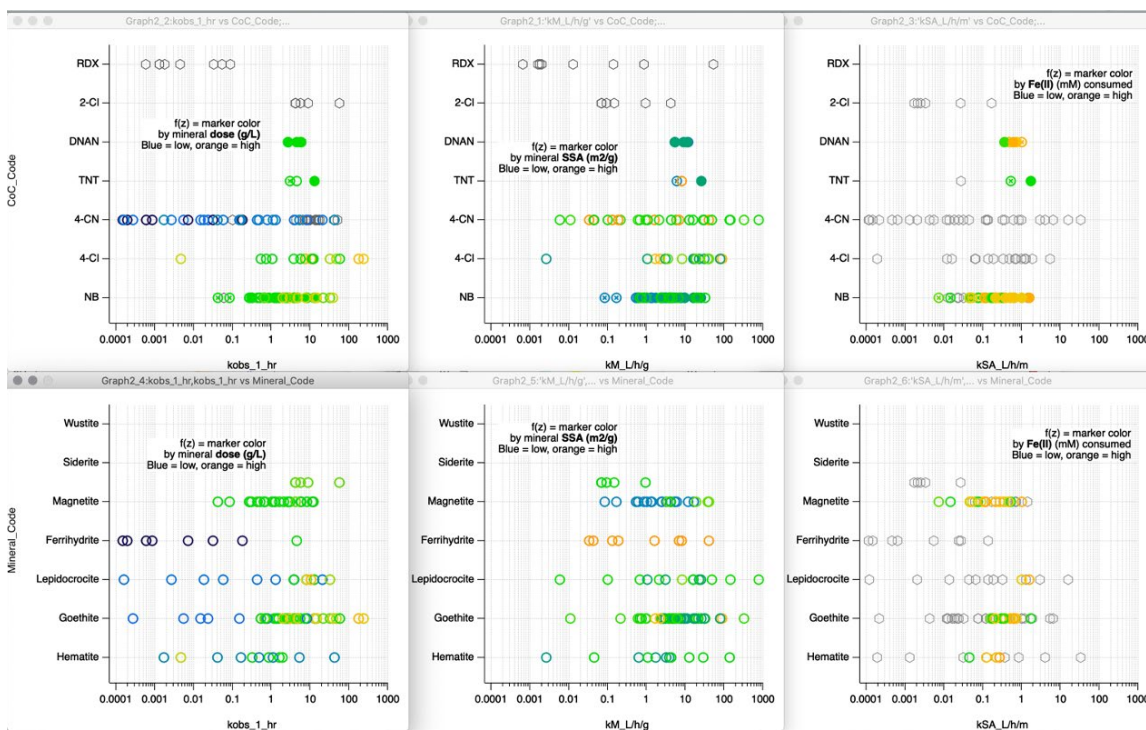


Figure 25. Preliminary exploratory analysis of rate constant data for reduction of 7 nitro compounds by 7 iron oxide minerals (with added Fe(II)). The top row shows nitro compounds on the y-axis and the bottom row shows Fe(II) minerals on the y-axis. In each column, the marker color represents the factor used in normalization of the k 's in the next column. The data in these figures are included in the database described in Section 11.1.1.2.

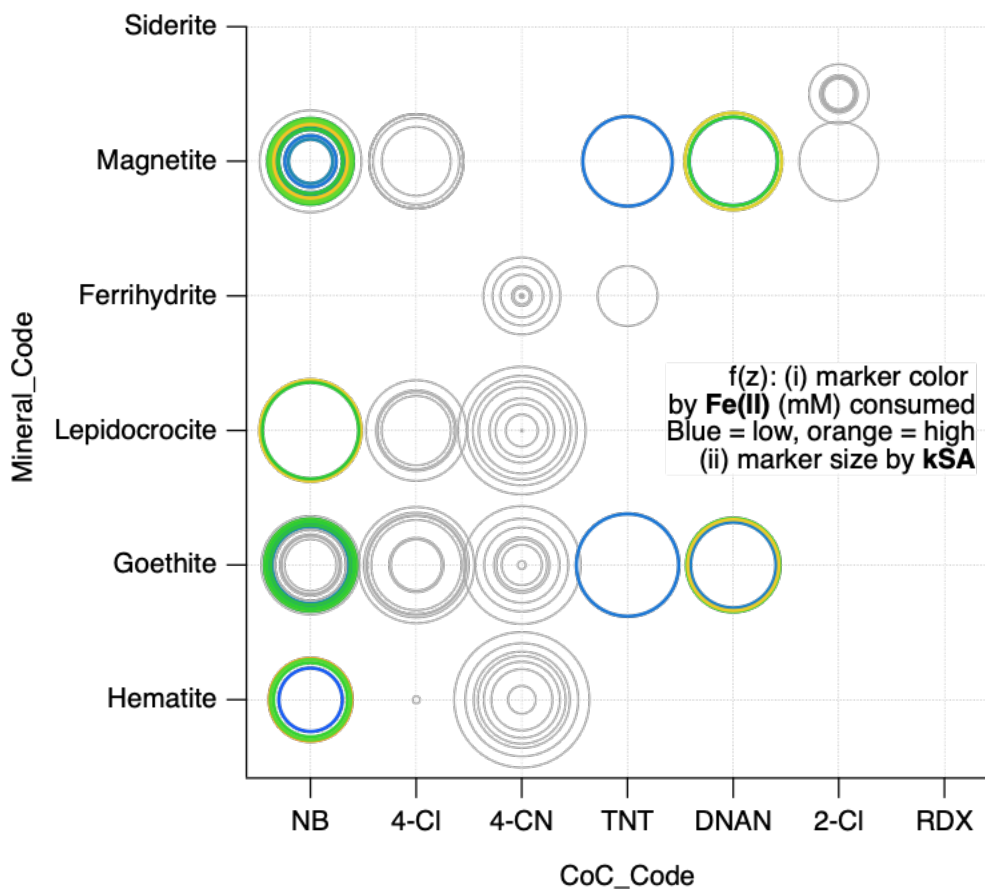


Figure 26. Alternative, 2-D representation of the data in Figure 25, with iron oxide minerals on the y-axis, nitro compounds on the x-axis, Fe(II) dose represented by the color, and k_{SA} represented by the marker size. The expected trend is for color to progress from cool (blue, low Fe(II) dose) on small rings to hot (yellow, high Fe(II) dose) on high rings.

11.2. Core Concept 2—Activation/Mediation

This objective involved evaluation of methods for enhancing the performance of abiotic NA by manipulations that result in activation and/or catalysis of the contaminant reduction reaction. The focus was on *activation*, *mediation*, and *catalysis* methods of enhancement; not on new ways of creating reducing conditions, but rather on modifications that could make established or existing reductants more effective. Concepts and specific candidates for enhancement were drawn from the extensive academic literature on activation and mediation (e.g., references in **Table 2** below), so the emphasis of this task was on assessing their potential applicability under realistic conditions of abiotic NA.

11.2.1. Evaluate activators and mediators for enhancing abiotic natural attention (Task 2.1)

11.2.1.1. Planned/Approach (Evaluation of Mediator/Enhancement options)

In this task, we began by surveying the full range of activators and mediators that might have application to enhancement of abiotic natural attenuation pathways. At this stage, we will define our scope broadly, to ensure that no candidates are excluded prematurely. **Table 2** provides a summary of the range of activators/mediators that we plan to include. A few others that were added, such as the flavonoid menaquinone, which is a common plant derived polyphenolic compound with redox shuttle properties.

Most ETMs fall into four classes of environmentally relevant compounds: flavins, porphyrins, siderophores, and quinones. Flavins are tricyclic rings derived from isalloxazine. The flavin moiety forms flavin adenine dinucleotide, flavin mononucleotide, and is present as a group in flavoproteins, which are all important in biological systems. Flavins have also been investigated in environmental systems, including in the remediation of organic pollutants, such as chlorinated ethylenes and carbon tetrachloride [42, 43]. Porphyrins are macromolecular cyclic ligands that bind metals. Geoporphyrins or petroporphyrins are a type of porphyrin obtained from fossils and make up the most plentiful porphyrins on earth [44]. Porphyrins form the active center in haemoglobin and chlorophyll. Porphyrins, like flavins, are important and ubiquitous in biological systems. Porphyrin enzymes have shown the ability to degrade organic contaminants, such as nitroaromatics [45]. Siderophores are iron chelating compounds that are excreted by microorganisms to help sequester iron. Siderophores enhance redox reactions of Fe^{2+} with nitroaromatic compounds, suggesting that

siderophores could also aid in attenuation of other contaminants of concern [46]. Quinones are oxidized versions of aromatic molecules, such as phenols and catechols. They are ubiquitous in the environment, as many dyes are quinone derivatives. Quinones are common in biological systems and serve in electron transport of photosynthesis and aerobic respiration. Quinones are also thought to make up the redox active groups in natural organic matter (NOM).

A few points of elaboration on the candidate activator/mediators given in **Table 2**: The photoactivation of chemical reductants that has been described in several recent papers by Batchelor et al. [12, 13, 47] clearly has potential for *ex situ* applications, but this was not part of the scope of this project. However, some of the chemistry induced by photoactivation (homolysis to generate radicals) could arise from other activation methods, especially heat, which we planned to address in Task 2.2 (but changed our focus to Fe(II), as described in Section 11.2.2.3?).

Most work on chemical mediators of contaminant reduction reactions has focused on natural biogeochemical processes, especially those involving natural organic matter (NOM) and microbially-produced extracellular redox shuttles. Surprisingly, this work has put little emphasis on active/engineered remediation strategies, and this opportunity appears to have been largely overlooked by consultants and vendors currently pursuing abiotic NA (or other forms of ISCR). In this project, we initially focused on mediators that have proven to increase reduction rates in the lab, are not very strongly adsorbed, are biologically compatible, and are commercially available at reasonable cost.

Table 2. Summary of activators and mediators to be considered in Task 2.1.

Activators/Mediators	Principle	Practice	References
Physical Activators			
Heat	Homolysis of dithionite to SO ₂ radicals	Unrecognized role in In Situ Redox Manipulation ¹	[48]
Light (Advanced Reduction Processes)	Makes strongly reducing radicals, as in AOPs	Applications of ARPs under development ²	[12, 13, 47, 49]
Weak Magnetic Field	WMF gradients depassivate Fe ⁰ (and maybe Fe ₃ O ₄)	Field applications to PRBs under investigation ³	[14, 50-54]
Chemical Mediators			
Coronoids (Porphyrins, Vitamin B ₁₂)	Reversible electron transfer mediators (shuttle)	Field tested [55], and increasingly added to EVO ⁴	[56-61]
Flavins (Riboflavin)	Quasi-reversible electron transfer mediators (shuttle)	Not field tested, but “feed grade” riboflavin is available ⁵	[62-64]
Quinones (Juglone, AQDS, NOM)	Reversible electron transfer mediators (shuttle)	Research not translated to field yet, but Juglone is abundant ⁶	[18, 65-67]
Fe ^{II} w/ ligand stabilization	Ligand stabilization to control precipitation or adsorption	Analogous to Fe ^{II} stabilization for ISCO, not for ISCR yet ⁷	[46, 68-74]

¹ Jim Szecsody, personal communication; ² Bill Batchelor, personal communication; ³ X. Guan, personal communication. ⁴ Bill Newmann, personal communication; ⁵ Feed grade riboflavin advertised online for ca. \$50/kg; ⁶ Extracts are available from Walnut bark; ⁷ Dick Brown, personal communication.

11.2.1.2. Summary of preliminary mediator selection results

In the second part of Task 2.1, we tried to go beyond the qualitative considerations summarized in **Table 2** and provide more quantitative analysis of the potential enhancements to remediation performance provided by the various activators and mediators. For this, we used some of the theoretical and conceptual tools for performance metrics that were developed in Objective 1. The best example of this are the plots shown in **Figure 27** and **Figure 28**, which are in what we call $\pm R$ format. This helps to visualize the relative degree of enhancement (or inhibition) of contaminant degradation rates by plotting rates constants measured with enhancements against rates constants determined without enhancements. This requires that the data be organized in pairs with treatment and without (i.e., controls) under otherwise comparable conditions. But, in other respects, the format is very flexible in the types of data it can accommodate. In addition to allowing multiple different treatments (corresponding to the legends in **Figure 27** and **Figure 28**), the axes can include rate constants of different types (k_{obs} , k_{m} , k_{SA} , etc.) because the units cancel. The two figures show that degree of enhancement by various

treatment varies greatly with secondary operational factors, but generally a promising R falls in the range of 5-50.

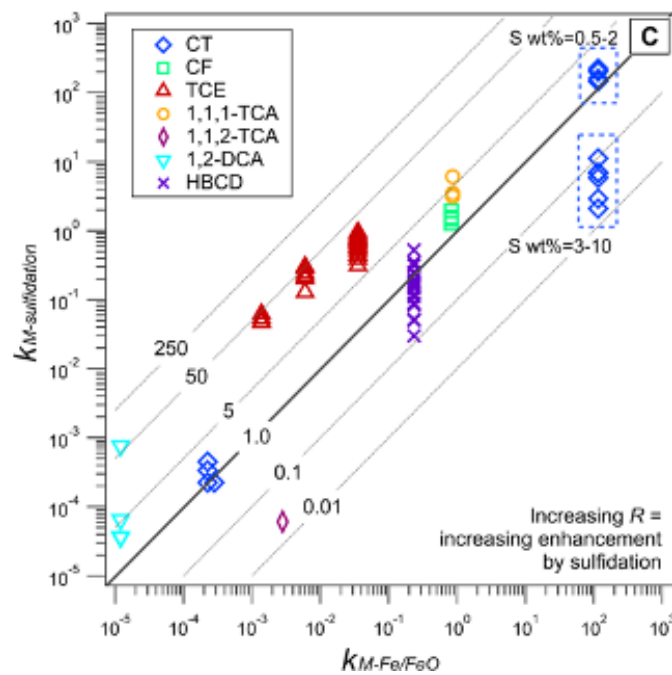


Figure 27. Comparison of rate constants for contaminant reduction by reducing materials with and without sulfidation: k_M with sulfidation vs k_M without (95 k's from 8 refs^{14, 16-18, 43, 82, 86, 143}). The diagonal contours represent the relative effect of treatment (R). [75]

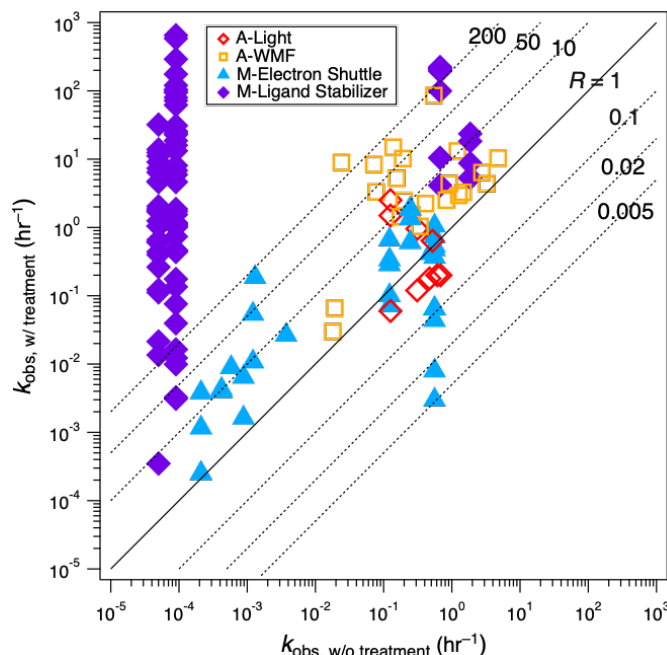


Figure 28. Comparison of rate constants for contaminant reduction of mixed contaminants by reducing materials with and without activators and mediators. Contaminants include chlorinated solvents (CT, PCE, VC, etc.), munition compounds (PCNB, RDX, etc.) and metals (Cu(II) and Se(IV)). Activators include light and weak magnetic field, mediators include electron shuttles (i.e., riboflavin, organic matters) and ligand stabilizer (i.e., Tiron) [14, 46, 54, 63, 68, 74, 76].

11.2.2. Test and calibrate activation/mediation effects (Task 2.2)

11.2.2.1. Planned/Approach (to testing)

Focusing on the most promising candidates and most important data gaps identified in Task 2.1, we performed some preliminary bench tests using experimental and analytical protocols similar to those we have used in many prior studies (e.g., [23, 24, 33, 34]. Initially, we thought that riboflavin was the most promising candidate mediator for further study. It had already been shown that riboflavin can greatly increase rates of contaminant reduction in laboratory tests [63, 64], so we planned to quantify this effect using the reductants most relevant to abiotic NA (e.g., Fe_3O_4 , FeS , etc.) and conditions more representative of field sites.

In parallel with testing for mediator enhancement of contaminant reduction rates, we performed electrochemical characterization of mediator redox properties. Mediators are commonly used in electrochemistry to improve electron transfer between redox centers in

solutes like proteins and the working electrode [77]. An ideal mediator is fully reversible, meaning fast electron transfer with no side reactions, has a well-known redox potential under the relevant experimental conditions, and reacts with known proton and electron stoichiometry, which are readily determined with electrochemical methods.

11.2.2.2. Experimental Exploration of Activation Effects – Shuttles

Our preliminary batch experiments with riboflavin were not very promising, so we moved on first to quinones and then later to Fe(II) amendment. In this experiment, AQDS was added as a shuttle (**Figure 29**). The reduction was observed in every reactor but only if AQDS was NOT present. In reactor 2, 3, and 4, upon the addition of AQDS, the reactions seem to terminate immediately. This raises the question of whether magnetite + Fe(II) can reduce AQDS or not. Another thing to notice is the plateauing that happens in all of the batches.

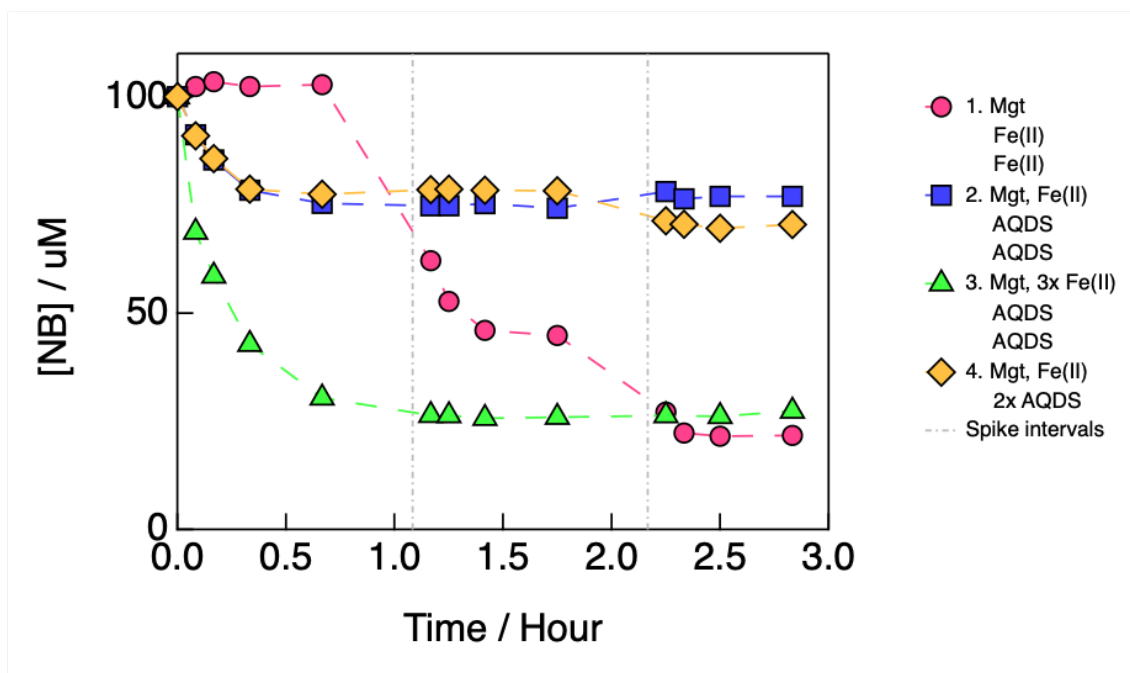


Figure 30. A graph of NB concentration at each time point. Each reaction was carried out in a 50 mL clear crimp-top vial. Each reactor contained 0.5 g/L of magnetite and 50 mL of 10 mM Trizma buffer pH adjusted to 8.0. After the initial spike (-12 hr) each reactor was allowed to equilibrate overnight on rotator before injection of nitrobenzene at $t = 0$ hr. Reactor 1 (Red circle) was equilibrate overnight without any spikes, then re-spiked with 1.0 mM aqueous Fe(II) solution at $t = 1.08$ and 2.16 hr. Reactor 2 (Blue square) was equilibrated with a spike of 1.0 mM aqueous Fe(II) solution at $t = -12$ hr, then re-spiked with 75 μ M aqueous AQDS solution at $t = 1.08$ and 2.16 hr. Reactor 3 (Green triangle)

was equilibrated with a spike of 3.0 mM aqueous Fe(II) solution at $t = -12$ h, then re-spiked with 75 μ M aqueous AQDS solution at $t = 1.08$ and 2.16 hr. Reactor 4 (Orange diamond) was equilibrated with a spike of 1.0 mM aqueous Fe(II) solution at $t = -12$ hr, then re-spiked with 150 μ M aqueous AQDS solution at $t = 1.08$ hr.

The model quinones were considered as candidates for mediators include several that were known to be well-behaved ETMs from prior studies of their electrochemistry [78-82]. Of the seven model compounds we tested (**Figure 21**), six were derivatives of ortho- or para-naphthoquinones and one was a para-anthraquinone. These quinones were further distinguished by hydroxyl, alkyl, or sulfonate substituents. An example of the resulting SCV and SWV data (for Juglone) can be seen in **Figure 22**. In all cases, the model compounds gave SCVs and SWVs that are typical of reversible quinone-hydroquinone couples in aprotic solvents [83-86]. In such cases, SCVs typically exhibit anodic and cathodic peaks that differ by $59/n$ mV, where n is the number of electrons transferred in the reaction, and the ratio of anodic to cathodic peak currents should be ~ 1 [87]. Also, the corresponding SWV peak potential should be the average of potentials of the anodic and cathodic SCV peaks (i.e., $(E_{pa} + E_{pc})/2$). The primary reason for selection these particular model quinones was to provide a baseline of electrochemical behavior to compare with more complicated systems such as NOM, which is prevalent in the environment and would already be present in most in-situ remediations.

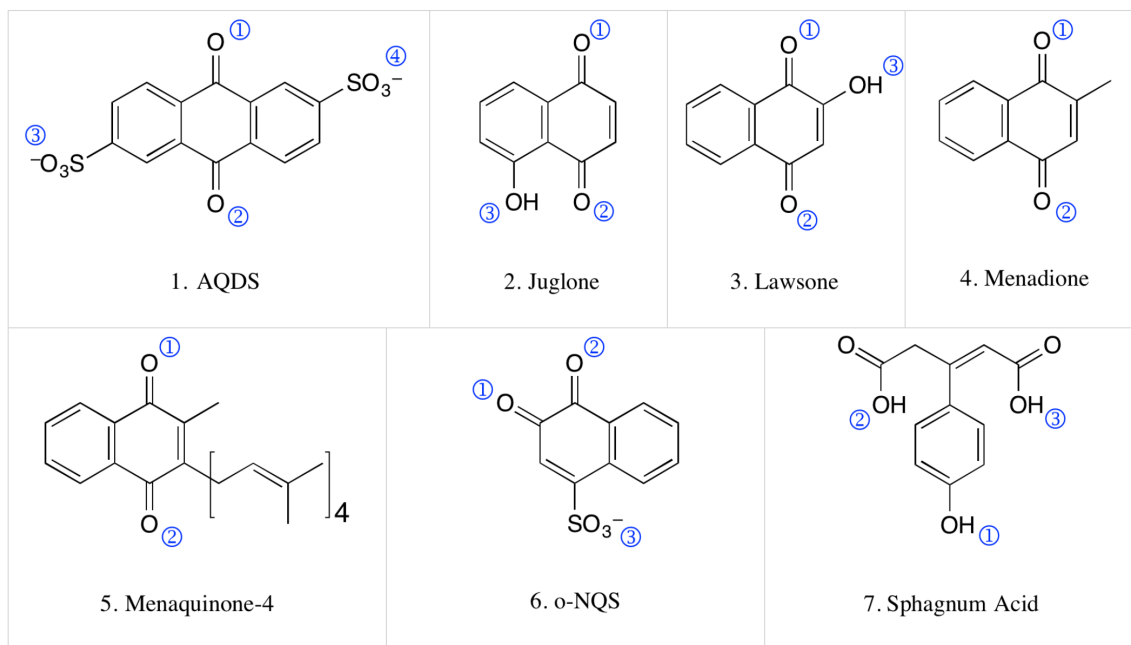


Figure 31. Chemical structures of model quinonoid mediators (electron shuttles) used in electrochemical experiments. Numbers refer to pK_a 's in Table S3 of Pavitt et al. [88].

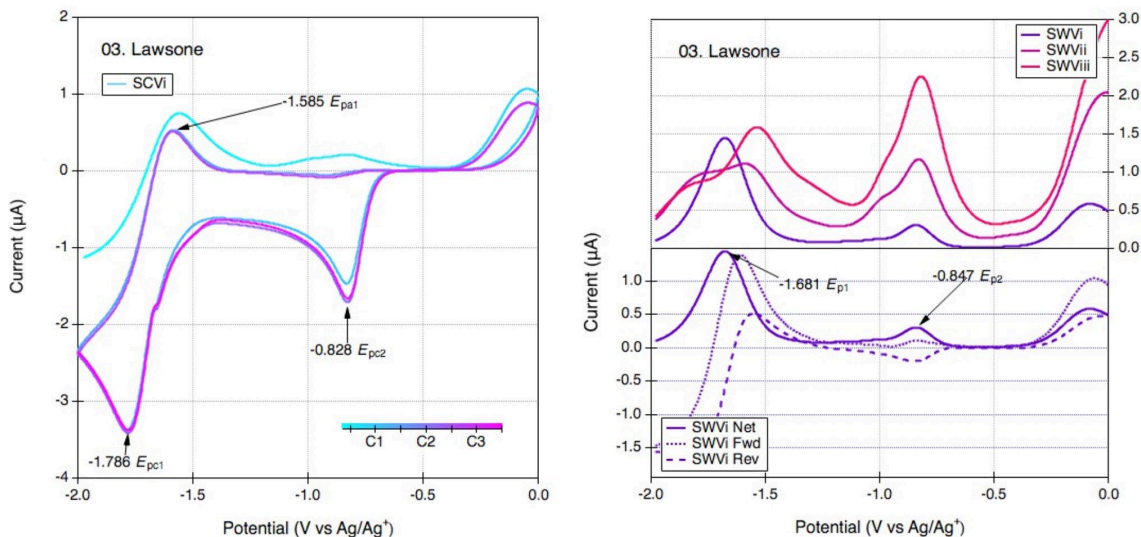


Figure 32. Primary SCV (left) and SWV (right) data for Juglone, a model quinone: Varying scan rate identified by *i*, *ii*, and *iii*. Conditions: 1.5 mM of model compound in 0.1 M TBAFP in DMSO, 1.6 mm Pt working electrode, Pt coil counter electrode and a Ag/Ag⁺ reference electrode filled with 0.1 M TBAFP and 0.005 M AgNO₃ in DMSO. Scan rate: SWVi and SCVi 25 mV s⁻¹, SWVii 125 mV s⁻¹, SWViii 225 mV s⁻¹. Step size 2 mV, amplitude 25 mV. From Pavitt et al. [88] supporting information.

11.2.2.3. Experimental Exploration of Activation Effects - RMIs

Electrochemical methods are very well suited to real-time and in situ characterization of redox-active species, with temporal resolution that can range from seconds to weeks or more. In order to explore the dynamics of RMI formation and its influence on the effective redox potential of iron oxide solids we titrated our medium with acid, base, or (mainly) Fe(II)_{aq}. This was done using zero-current single-electrode chronopotentiometry (CP) [89] on a rotating glassy carbon disk electrode in suspensions of six reagent-grade iron oxides: goethite (GT), hematite (HT), lepidocrocite (LC), magnetite (MT), siderite (ST) and wustite (WT). The minerals were selected to include Fe(III) oxides (GT, HT, LC), Fe(II) oxides (ST, WT), and mixed Fe(II)/Fe(III) oxides (MT). The solution conditions were varied from Fe(II) concentrations that were below the available sites of the iron oxides to higher Fe(II) concentrations encountered in the environment. The open circuit potential (E_{OC}) measured by CP and pH (also measured in situ) were compared to calculation from equilibrium speciation models and thermodynamic data. The results suggest that most of the conditions tested yield similar limiting values of E_{OC} , which is consistent with the formation of a common RMI phase over time. Eventually, these

results should help to define the relationship between RMI formation and rates of contaminant reduction, under laboratory and field conditions.

CP measurements were made using a potentiostat (Metrohm Autolab PGSTAT30), or (Vernier electrode amplifier) in a two-electrode cell (Gamry Instruments, EuroCell), pictured below, **Figure 33A**. The working electrode was a 3 mm diameter glassy carbon rotating disk electrode (Pine Research Instrumentation) at 2000 rpm (**Figure 33B**, post run) and the reference electrode was Ag/AgCl (BASi) filled with 3.0 M KCl encased in a fritted (Gamry, porous glass frit) bridge tube filled with 10 mM NaCl (and sometimes 10 mM HEPES). All potentials are reported vs. the Ag/AgCl reference electrode.

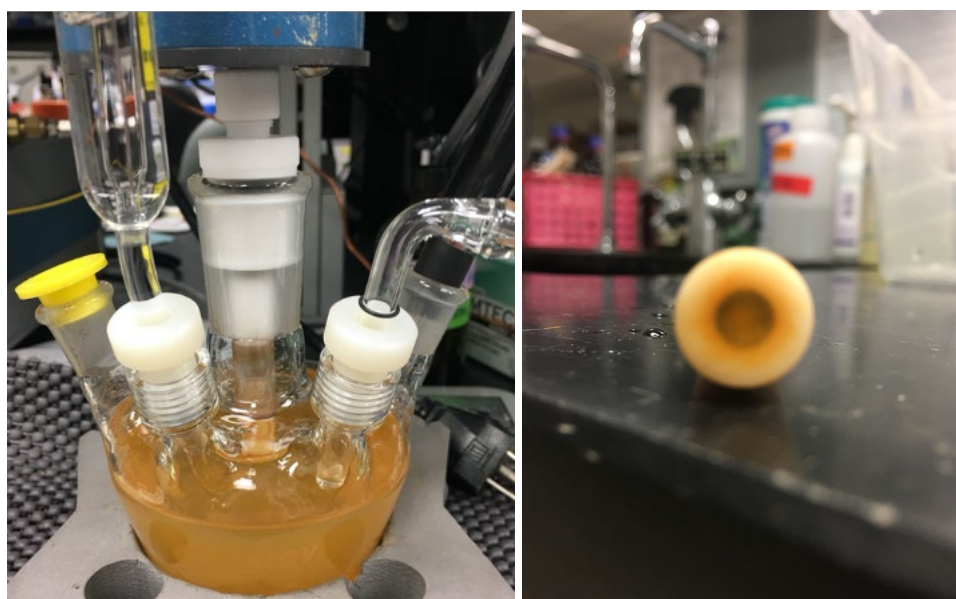


Figure 33. Electrochemical cell of (left) lepidocrocite and (right) the glassy carbon working electrode post run with a thin, deposited lepidocrocite film. Conditions: 10 mM NaCl, 0.5 g/L iron oxide, 0.25 mM doses (x3) of Fe(II), 3 mm glassy carbon rotating disk electrode at 2000 rpm, 3.0 M KCl Ag/AgCl reference electrode encased in a fritted bridge tube filled with 10 mM NaCl, pH adjusted with NaOH.

Before each set of electrochemical measurements, the working electrode was polished using 1.0, 0.3, and 0.05 μm MicroPolish Alumina (Buehler), rinsed with DI water in between each polish, then sonicated for 10 min, and rinsed again with DI water. The electrochemical cell was prepared by adding 200 mL of 10 mM NaCl (and 10 mM HEPES when required), and purging for 60 min with N_2 (ultra-high purity) using a copper catalyst oxygen filter and PEEK tubing, purging of the cell headspace was continued during the experiments.

Solution conditions were a dilute system to mimic environmental conditions and consisted of the following: 10 mM NaCl, 0.5, or 1.0 g/L of iron oxide, additions each of 0.25 mM Fe(II) (except in a few cases where we used site calculated Fe(II)) in the form of FeCl₂, and when used, 10 mM HEPES, and 10 μ M electrochemical mediators. Additions of Fe(II) were done using a dry FeCl₂ powder, this ensured a more accurate measurement of Fe(II) and prevented oxidation of the stock solution. A few times a stock solution was used and spectrophotometric measurements revealed an approximate 10% oxidation daily. Starting pH was 8, and was adjusted by titrating with NaOH and HCl. After deaeration, the OCP run was started and a background collected for 5 min, or a background scan was performed for SCV and SWV. This was followed by adding a 20 mL solution of IO in 10 mM NaCl (and 10 mM HEPES when required) that had previously equilibrated in the glovebox ~24 hrs. After approximately 60-90 minutes doses of FeCl₂ were added every 20-30 minutes.

To ensure anoxic conditions the following procedures were maintained. All powders (iron oxides, FeCl₂), all solutions (DI water, electrolyte), and all dispensing equipment (syringes, needles etc.) were stored in an anaerobic chamber (>0.1 ppm O₂) for a minimum of three days prior to use. Approximately 24 hours before an experiment was performed, 20 mL of electrolyte was added to the iron oxide and was left stirring on a mechanical roller. It was then transferred from the glove box to the benchtop electrochemical cell using a syringe. To ensure that no oxidation occurred during transfer from the glove box to the bench top and also for the duration of our OCP runs, 5,5-indigodisulfonic acid sodium salt (indigo carmine) was used as a test solution. Indigo carmine undergoes a distinct color change upon oxidation. Oxidation of indigo carmine was noted well past the time frame of our experiments.

Our first set of experiments were done in a buffered system, where we monitored OCP over several hours for six different minerals (GT, HT, LC, MT, ST, WT), **Figure 34**. Open circuit potential vs. time of iron oxides and Fe(II) 0.25 mM (A) and by site availability (B). Grey dots indicate addition of iron oxide, Fe(II). Conditions: 10 mM NaCl, 10 mM HEPES, 0.5 g/L iron oxide, 0.25 mM doses of Fe(II) x 3 (A), or by site availability (B), 3 mm glassy carbon rotating disk electrode at 2000 rpm, 3.0 M KCl Ag/AgCl reference electrode encased in a fritted bridge tube filled with 10 mM NaCl and 10 mM HEPES.. As expected the OCP for the three Fe(III) minerals (GT, HT, LC) were similar amongst each other and more positive than for the Fe(II) minerals (ST, WT), with the mixed Fe(II)/Fe(III) mineral (MT) falling somewhere in the middle. Fe(II) was then added to the system decreasing the OCP significantly. Interestingly, the OCP decrease

was not parallel amongst all of the minerals, but instead reached similar plateau values (E_{OC} limiting). That is, ST had the smallest difference (~ 120 mV), while GT had the largest difference in OCP (~ 500 mV), but all the minerals decreased in value to approximately -330 to -370 mV. The second and third additions of Fe(II) resulted in much smaller potential decreases ~ 20 - 30 mV (each addition of Fe(II) was 0.25 mM).

We thought maybe the reason for the smaller subsequent drops was due to site saturation after the first Fe(II) addition, so we calculated the sites available per mineral. We used calculations made by our lab using BET to obtain sizes of four minerals (GT, HT, LC, MT), and literature values for estimated sites per square area [90, 91]. These calculations gave us a high and a low estimate for sites available per square area of mineral. We then used the lowest number for the low end (2 sites/nm²) and added an appropriate amount of Fe(II) for our first dose, that corresponded to $\sim 50\%$ coverage of the available sites. This time, ST decreased ~ 87 mV while GT decreased ~ 380 mV

Figure 34B. The decrease for ST resulted in a 33 mV difference for a seventeen fold difference in Fe(II) molarity (0.25 to 0.015 mM). For GT, the OCP decrease was 120 mV lower for a similar difference in molarity of Fe(II) (0.25 to 0.014 mM). The second and third dose of Fe(II) was well over $\sim 130\%$ of the low estimate and $\sim 160\%$ of the high estimate (22 sites/nm²) respectively. The second and third Fe(II) doses resulted in decreases in OCP ~ 100 mV for GT, and HT (Fe(III) minerals), LC was anomalous with a second dose decrease of ~ 10 mV, but the third Fe(II) dose, OCP decrease was similar to the other Fe(III) minerals, ~ 90 mV.

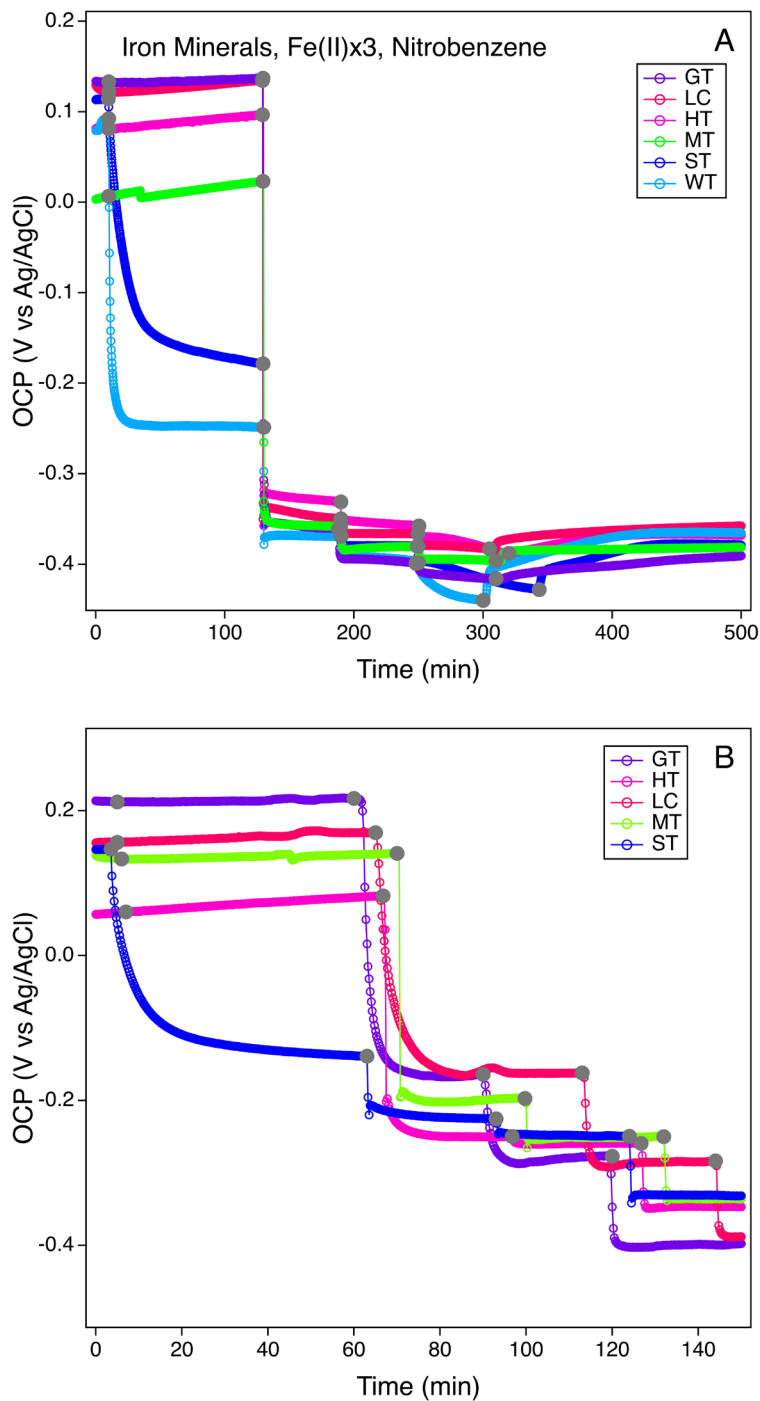


Figure 34. Open circuit potential vs. time of iron oxides and Fe(II) 0.25 mM (A) and by site availability (B). Grey dots indicate addition of iron oxide, Fe(II). Conditions: 10 mM NaCl, 10 mM HEPES, 0.5 g/L iron oxide, 0.25 mM doses of Fe(II) x 3 (A), or by site availability (B), 3 mm glassy carbon rotating disk electrode at 2000 rpm, 3.0 M KCl Ag/AgCl reference electrode encased in a fritted bridge tube filled with 10 mM NaCl and 10 mM HEPES.

For MT and ST the second and third Fe(II) doses resulted in OCP decreases of ~50 and 90 mV and ~25 and 80 mV respectively.

In general, the minerals that did not have structural Fe(II) had significantly larger decreases in OCP for the second Fe(II) dose, while the third and largest Fe(II) dose was similar amongst all minerals. There was still a large difference in OCP decreases between the first dose and the second and third doses of Fe(II) using surface site calculations. This could be further evidence that surface site availability does not explain Fe(II) uptake. Classic surface complexation modeling has not described iron oxide and Fe(II) behavior adequately, with uptake possibly having more to do with structure defects, or aggregations state [92, 93]. Others have demonstrated that uptake of Fe(II) with MT had to do with MT stoichiometry [94], as evidenced in our data by the Fe(III) oxides having much larger OCP decreases than the Fe(II) oxides. Uptake of Fe(II) by GT continued after apparent saturation [95], and others reported a two-stage process, an initial rapid uptake of Fe(II) followed by slower uptake [93, 96, 97]. It was also shown that as Fe(II) concentration increased, the exchange of Fe(II) with HT decreased, with the highest exchange happening at an Fe(II) concentration of 0.5 mM [98]. All of these behaviors could manifest in a large OCP decrease followed by a smaller decrease that is seen in our data.

During experiments in the buffered solution we noticed that the pH increased when Fe(II) was added (actually decreased then increased instantaneously). This behavior was contrary to what we expected, so we chose three representative minerals (GT, MT, ST), chosen due to differences in structural iron content and monitored OCP and pH simultaneously, **Figure 35** without using a buffer. When Fe(II) was added to the solution, the pH decreased as expected, with ST decreasing about half the value of MT and GT. This possibly confirms that structural Fe(III) plays a role in Fe(II) uptake. As already discussed, this is followed by electron transfer, Fe(II) desorption and formation of Fe(OH)₂ thereby releasing protons and driving down the pH. This happens instantaneously as evidenced by the steep decrease. After this initial decrease, the pH of MT and ST remain level, but GT pH starts increasing immediately. OH⁻ release is primarily due to ligand exchange, or ternary surface complexation (ref), but further probing would be required to assess which, or if either are the cause.

The OCP decreases in the unbuffered system are much smaller than the very large decreases we saw in the buffered solutions, there are also differences in behavior between the three minerals. For GT, the OCP decreases consist of a series of small steps toward more cathodic potentials, as the pH is adjusted to the starting pH before additions of

Fe(II). After the pH adjustment the OCP has dropped around 480 mV, around the same value as the buffered solutions (~490 mV), except in the buffered solution the OCP value was lower (-360 buffered, -260 unbuffered), this is also true for MT and ST. For MT the steps are not so uniform as for GT. In MT after the first potential decrease levels off, NaOH is added and the OCP decreases immediately and rebounds fairly quickly, the second NaOH addition produces the same result.

The third NaOH addition the OCP decreases less quickly and does not rebound, but follows a slight upward trend. Overall, the OCP decrease is larger in the unbuffered solution versus the buffered (435, 380 mV). For ST the OCP is well behaved as it is for GT, after Fe(II) addition and NaOH adjustments the OCP is lowered. For all three minerals the 2nd and 3rd additions of Fe(II) do not decrease in potential until NaOH is added.

We also monitored OCP and pH of aqueous Fe(II) **Figure 35**. The pH decrease for Fe(II) without an iron oxide was similar to that for ST/Fe(II), the pH decrease was quite small compared to GT/Fe(II) and MT/Fe(II). Once again reinforcing that structural Fe(III) is the driving force of Fe(II) uptake [99]. The OCP trends for Fe(II) aqueous are also similar to ST/Fe(II), although Fe(II) only decreases to approximately -350 mV and ST/Fe(II) decreases to -235 mV. This could be additional evidence for Fe(II) not getting oxidized unless a mineral is present [100]. While it is important to obtain OCP data, so that correlations with degradation rates could be made for better predictions of systems, it is valuable to keep in mind that correlations are only half the story. It has been shown that correlations between iron oxide suspensions and degradation rates no longer applied when an iron oxide was doped with a cation [101]. Because enhancement of degradation rates have been attributed to whatever species form once Fe(II) sorbs onto the iron oxide, it was equally important to identify those species.

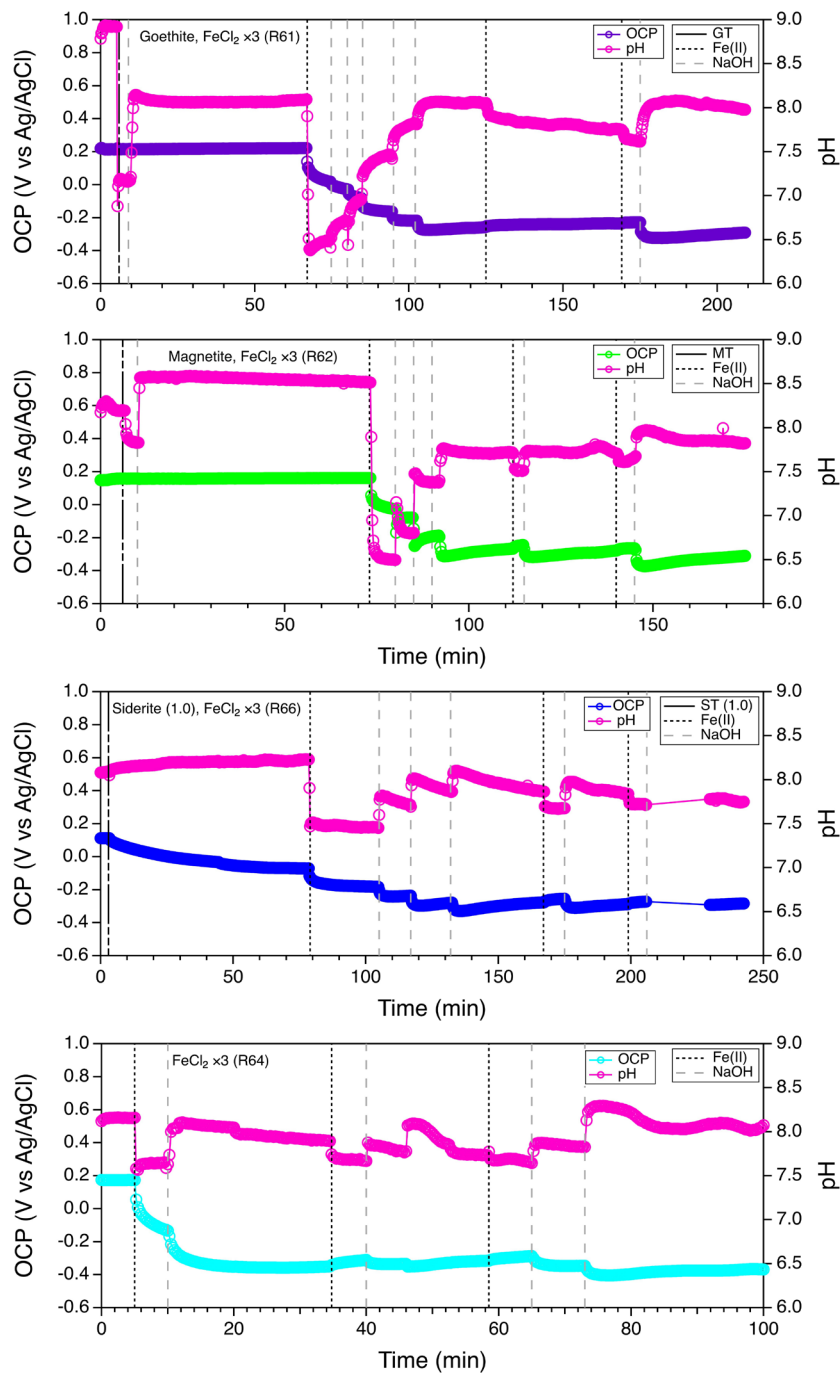


Figure 35. Open circuit and pH vs. time for three representative iron oxides (GT, MT, ST) and Fe(II). Vertical lines indicate addition of Fe(II) or pH adjustments using NaOH. Conditions: 10 mM NaCl, 0.5 g/L iron oxide, 0.25 mM doses of Fe(II) x 3, 3 mm glassy carbon rotating disk electrode at 2000 rpm, 3.0 M KCl Ag/AgCl reference electrode encased in a fritted bridge tube filled with 10 mM NaCl.

We used thermodynamic calculations to compare to our experimental data. For the experimental data we plotted OCP vs. pH in unbuffered solutions for three representative minerals with Fe(II) added and Fe(II) alone **Figure 36**. The color gradient represents passage of time, lightest being the first addition of Fe(II) and darkest being the end of the run, ~30 min after the third addition of Fe(II). For the thermodynamic calculations we used Geochemist's Workbench 12. We used React to predict the species expected to form under our experimental conditions. From React we extracted activities with changing pH, which were subsequently used in equilibrium equations obtained from Rxn. We did not include the exhaustive list of all species formed, only the ones that were close in values to our system.

For our Fe(II) only system (**Figure 36A**) our experimental values match thermodynamic values exactly. For the systems that include minerals (**Figure 36B-D**), our experimental values either lie above, or between the lines of the thermodynamic values. This is somewhat to be expected as the system with Fe(II) only is not complicated by the iron oxides. In this system, the data falls on the line for the Fe(II)/Fe(OH)_{3(ppd)} couple, indicating that Fe(II) is in equilibrium with a precipitated ferric hydroxide. This is also consistent with the pH values dropping as Fe(II) is added to the system (**Figure 35**).

For the systems with iron oxides none of the data fall directly on a theoretical line and for magnetite the experimental data is higher than any of the computed lines. It is possible that the goethite and siderite systems whose data fall in between the computed lines indicate a mixed potential of two, or more of the species listed. Magnetite differs slightly than the other two minerals in that its lattice is composed of Fe(II) and Fe(III) species. Stoichiometric magnetite is magnetite whose ratio of Fe(II) to Fe(III) is 0.5. The thermodynamic values assume this ratio and therefore it is expected that magnetite that is slightly more oxidized (has more Fe(III) in the lattice than predicted) would have higher OCP values. Previous work from our lab has shown that the magnetite used for our experiments was non-stoichiometric and gave higher OCP values than stoichiometric magnetite [102].

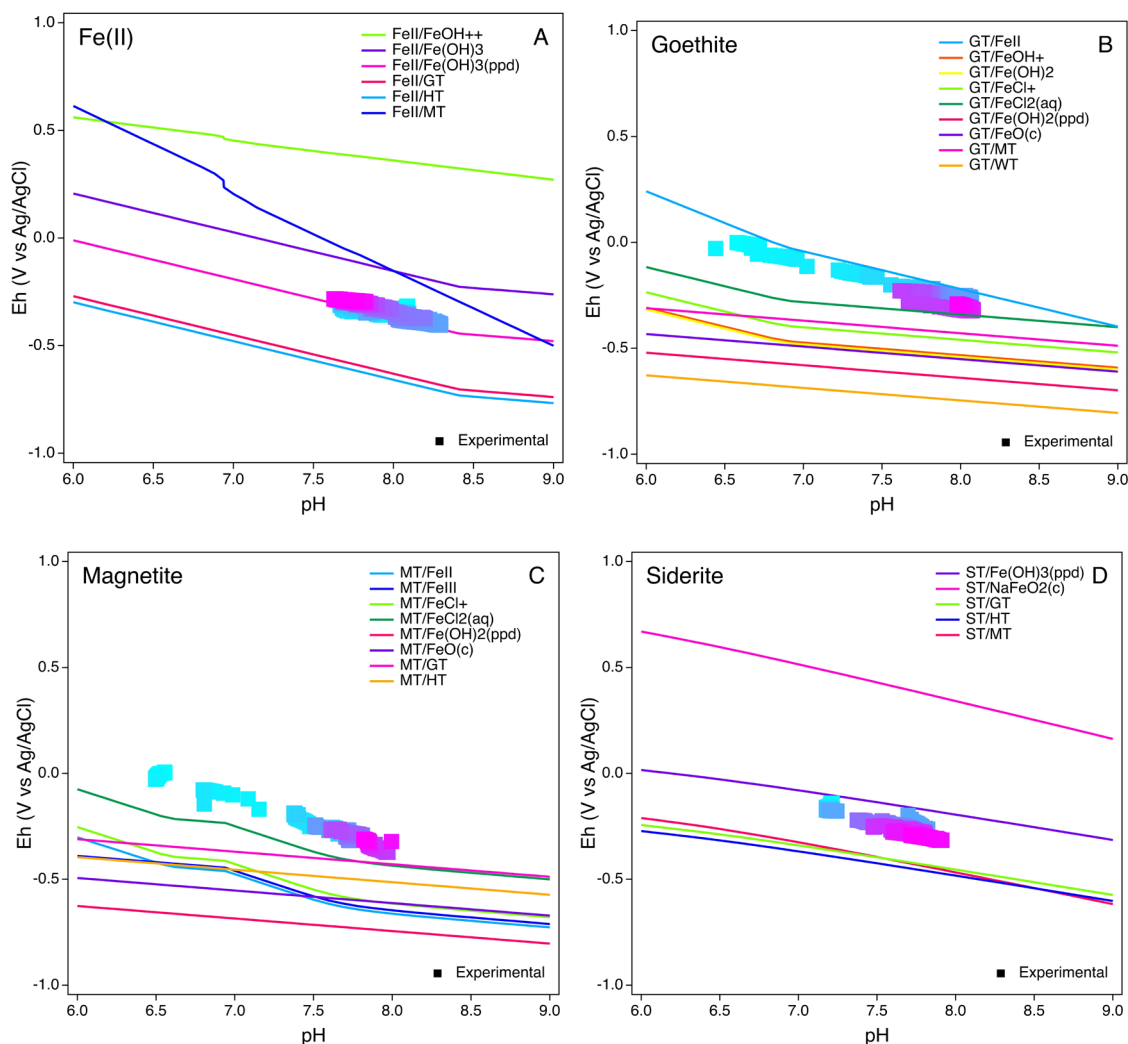


Figure 36. Experimental and computed Eh vs. pH values for Fe(II) (A), Goethite (B), Magnetite (C), and Siderite (D). Experimental conditions: 10 mM NaCl, 0.5 g/L iron oxide, 3 additions of 0.25 mM Fe(II), 3 mm glassy carbon rotating disk electrode at 2000 rpm, 3.0 M KCl Ag/AgCl reference electrode encased in a fritted bridge tube filled with 10 mM NaCl. Computed values were obtained using GWB12 React and Rxn. Equations can be found in Pavitt et al. (in prep). Redox couples are not written in the standard format, but written in terms of main species used in the calculations listed first.

Besides mixed potential it could be that we are recording only the beginning of the RMI phase. Other parameters that could cause higher OCP values are the time scale of the experiment. Our study was performed over the time scale of hours, whereas studies that were performed over days have shown that OCP decreases with time. For example, it was shown that initially the OCP of goethite and Fe(II) matched the thermodynamic data of amorphous Fe(OH)₃, but after 61 days it matched a more stable phase, possibly lepidocrocite, or maghemite [103]. The GT/Fe(II) predicted equilibrium was not achieved within the 61 days of the experiment, consistent with others whose data also plotted above the thermodynamic GT/Fe(II) values [104]. What we are seeing in our data is the initial phase of RMI formation, but this phase is dynamic and will change over time depressing the OCP further until it possibly matches the GT/Fe(II) couple. This may or may not happen however, as studies have shown a variety of effects for adding Fe(II) to mineral substrates, from growth of only the parent mineral when Fe(II) is added [93, 105], to a variety of unknown Fe(III) products, but only if the mineral had structural Fe(II) [100], to formation of secondary minerals only after contaminant reduction [106].

Other less dynamic parameters to consider are the slope of the line. The slope for our system did not change regardless of the mineral used. Slope changes have been shown in iron oxide Fe(II) systems and even slope reversals (negative to positive) [107]. Slope could potentially be used as a predictor of the types of species that could form over time. For example, in our system we had 28 different aqueous species and several minerals, which could be narrowed down by matching the thermodynamically predicted slopes to our experimental slopes. Furthermore, as already mentioned it is expected that over time the OCP will decrease so possibly over longer time periods our siderite system could match the thermodynamic values for the ST/GT, ST/HT or ST/MT and our Fe(II) only system could match the values for Fe(II)/GT or Fe(II)/HT.

11.2.3. Evaluate prospects for up-scaling to field sites (Task 2.3)

11.2.3.1. Planned/Approach (to upscaling)

While Task 2.2 was designed to determine which, if any, approaches to enhancing abiotic NT processes have promise under controlled conditions (laboratory batch and column experiments), there are many additional factors that must be considered to determine if an enhancement strategy will be useful in full-scale field applications. Ideally, the performance metrics developed under Objective 1 should be used to make the evaluation under this task as quantitative as possible. However, technology transfer to field

conditions involves other involves other considerations in addition to rates of contaminant reduction. One of the most important, is the *capacity* for contaminant reduction, which is the core concept that is featured in Objective 3, so the results under this task are integrated into the next section.

11.3. Core Concept 3—Reductant Demand

This objective was selected to address the limitations to the overall performance of abiotic NA (and other forms of ISCR) due to reactions that compete with COC degradation (i.e., NRD). The scope of NRD effects that could be important include reactions with water (in the case of ZVI only), dissolved solutes, organic matter, and solid/mineral phases.

11.3.1. Develop a conceptual model and quantitative protocols for assessing the NRD aspects of abiotic NA (Task 3.1)

This task built on approaches taken in earlier work on “reduction (or reductive) capacity” [108-110], which is highly relevant but largely forgotten or neglected, and on relatively recent work concerning NOD [21, 111-113], which is relatively well known to practitioners of ISCO but not as comprehensive or rigorous as it could be. Here (**Table 3**), we present a comprehensive and unifying framework for defining reductant (and oxidant) demand and related concepts such as capacity, with explicit mathematical definitions of each, and systematic consideration of “lumped in” and “factored out” variables. The framework represented by **Table 3** can be adapted to oxidation/ISCO.

Table 3. Classification scheme to define the relationships between concepts involved in capacity and demand of reduction reactions. The quantitative definitions are intuitive, and are consistent with prior work, but we have not found them written out previously.

The scheme can be applied to oxidations (NOD, etc.) by swapping the roles of oxidized and reduced species.

Qualitative Terminology	Oxidant (Ox _i = oxidized species i)	Reductant (Red _j = Reduced species j)	Quantitative Definition
Capacity = How much contaminant can I treat? (for specified amount of treatment)	CoC, Probe (Cr, TCE) - <i>measured</i>	Env. Matrix (Aquifer, GW, Soil) - <i>given</i>	Reductive Capacity (RC) $RC_{ox_i} = \frac{\Delta[Ox_i]^{t=end}}{[Red]}$
Demand = How much treatment do I need? (for specified amount of contaminant)	Env. Matrix (Aquifer, GW, Soil) - <i>given</i>	Treatment, Assay (ZVI) - <i>measured</i>	Reductant Demand (RD) $RD_{red_j} = \frac{\Delta[Red_j]^{t=end}}{[Ox]}$

Most of the previously proposed assays for capacity/demand related properties were developed without the benefit of the conceptual model represented by **Table 3**, so the relationship between the results obtained by the various assays has been unclear. In the proposal for this project, we demonstrated this using the scheme shown in **Table 4**, which is now quite old, and therefore outdated, as well as being largely unknown to the current practitioner community. We evaluated more recent approaches, such as that taken by Lee and Batchelor [109, 110], who proposed assays based on oxidants that are also contaminants (chromate and TCE). We also identified and tested a novel approach to assaying from reductive capacity using dithiothreitol, which is described below.

Table 4. Methods that may be employed for estimating oxidative capacity for soil materials, reproduced from Table 6.3 in [114]. These methods for “oxidative capacity”

represent reductant demand. The references cited in the table are: [108, 115-119]. The source of this table includes another table for reductive capacity (oxidant demand).

Method	Source	Comments
Cr(II)	(Barcelona and Holm, 1991a) (Barcelona and Holm, 1991b) (Barcelona and Holm, 1992)	Most aggressive but oxygen-free atmosphere recommended; high estimate
Digestion with Ti(III)-EDTA	(Ryan and Gschwend, 1991)	Developed for extraction of Fe oxides; applicability limited to iron oxide dominated solids
Titration/digestion with dithionite solution	(Loeppert and Inskeep, 1996) (Williams et al., 2000)	Valid for only specific remedial technology; targets Fe oxides
Exposure to treatment reagent	Not Documented	Case specific evaluation; requires preliminary research and development effort
Estimate based on mineralogy	Not Documented	No consensus values for reference minerals; unreliable value

11.3.2. Experimental calibration and validation of the models developed in Task 3.1. (Task 3.2)

Early in this project, we identified one completely novel alternative approach for testing: dithiothreitol (DTT). This reductant has been used extensively in the atmospheric and toxicology literatures to measure “oxidative potential” (equivalent to reductant demand) of fluids believed to cause oxidative stress, including atmospheric aerosols [120-122]. DTT is a commercially-available mild reductant, with well characterized redox chemistry (e.g., with quinones, such as in natural organic matter), no adverse biological effects, and easy analytical methods. Our preliminary experiments with DTT and iron minerals were somewhat promising, but other results under this objective (see below) seemed likely to be more impactful, so the DTT work was not developed significantly and the results are not shown here.

Our work on other assays for redox capacity evolved to become more central to the objectives of ER-2621, which we were working on concurrently with this project, so most of the results of this task are incorporated into the report on that project.

11.3.3. Integrate the results of 3.1 and 3.2—along with performance metrics from Objective 1—to develop predictive quantitative models for the effectiveness of natural and enhanced abiotic NA. (Task 3.3)

During the course of this project, sulfidation emerged as one of the most promising, and practical, methods of enhancing the performance of ZVI and related ISCR technologies (cf. the discussion of Fe(II) as an enhancement under Objective 2). After a period of emphasis on the enhanced contaminant degradation rates that are sometimes seen with sulfidated iron-based reductants, we recognized that the greatest benefit of sulfidation was not increased rate of contaminant degradation, but rather in increased selectivity of reaction with contaminants over side reactions, and the resulting increase in efficiency. Communicating this insight to practitioners became an urgent priority for us, and this task provided an opportunity to pursue that goal. We instigated a collaboration with the others who had contributed the most on topic, and after extensive deliberation, our consensus was documented in a review paper in the themed issue on halocarbons in the environment for the journal *Environmental Science: Process & Impacts*. Key aspects of this paper [3], are summarized below.

Definitions: In He et al. [3], the term “efficiency” is used in the precise technical sense (i.e., the relative quantity of inputs to outputs in a process[123]), rather than the common but casual and not entirely accurate use of the term as a synonym for rate of contaminant removal (e.g., “removal efficiency” [124] and “degradation efficiency” [125]). For the particular system of organohalide reduction by ZVI, the general definition of efficiency we use is the relative quantity of electrons transferred from ZVI to each of the competing product formation reactions. Given that ZVI is a rather strong reductant that can drive redox reactions with a variety of natural oxidants, including water, other (co)contaminants (esp. nitrate and heavy metals), and dissolved oxygen, efficiencies can also be defined for each individual process, or for groups of processes such as reactions with all non-contaminant oxidants (i.e., natural reductant demand, NRD). All of these types of efficiencies correspond to the Type II defined in a recent study [126] and were the primary focus of this He et al. [3].

Additional types of efficiency arise because the ZVI used in groundwater remediation is a particulate material with variable composition and availability for reaction with solution species (e.g., nano-scale ZVI that may react fully while mm-scale ZVI can passivate before all of the Fe(0) is oxidized). These efficiencies were classified as Type I in Qin et al. [126], and also are addressed in this analysis. Furthermore, it has been

suggested that branching among pathways of degradation product formation (e.g., via hydrogenolysis vs. reductive elimination) might be classified as an efficiency (Type III in Qin et al. [126]), but these are best expressed as product “yields” [127-130], and are only addressed in this review as examples of “selectivity”. Insofar as all of these types of efficiencies involve accounting for the redistribution of electrons with a system of redox reactions, they should be interrelated, and clarifying some of these relationships was a major goal of He et al. [3].

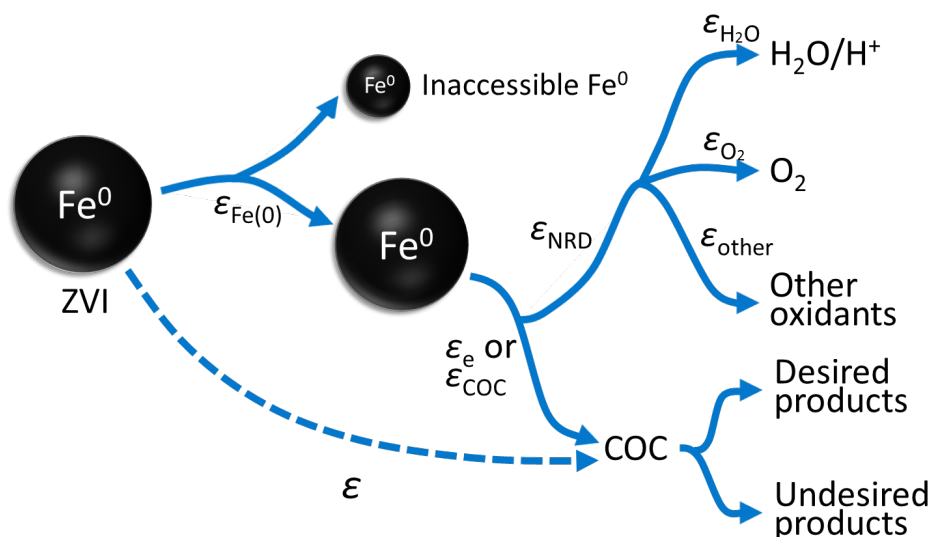


Figure 37. Summary of the relationship between particle efficiency (ϵ), efficiency of Fe(0) utilization ($\epsilon_{\text{Fe}(0)}$), electron efficiency (ϵ_e or EE) of contaminant reduction, and electron efficiency of NRD (e.g., H₂O, O₂, and other oxidants) reduction (ϵ_{NRD}). Earlier versions of this conceptual model can be found in Qin et al. [131].

Classification of Efficiencies. The overall relationship between types of efficiencies involved in contaminant degradation by ZVI is summarized in **Figure 37**. The first type of efficiency to consider is the fraction of Fe(0) that is available for reaction in the time frame relevant for remediation (months to years). The fraction of Fe(0) associated with ZVI that is available for oxidation (by contaminants and non-target species combined) has been referred to as the “utilization ratio” or “efficiency of Fe(0) utilization” [131, 132]. This quantity ($\epsilon_{\text{Fe}(0)}$) is defined by eqn (3).

$$\epsilon_{\text{Fe}(0)} = \frac{M_{\text{Fe}(0),\text{initial}} - M_{\text{Fe}(0),\text{final}}}{M_{\text{Fe}(0),\text{initial}}} \quad (3)$$

where $M_{\text{Fe}(0),\text{initial}}$ and $M_{\text{Fe}(0),\text{final}}$ are the initial molar quantity of Fe^0 and the final quantity of Fe^0 at the end of the particle's reactive lifetime. In this case, particle lifetime is operationally defined by complete loss of reactivity for dechlorination, which differs from the endpoint used for some of the other efficiencies defined below. For larger ZVI particles, such as microscale ZVI (mZVI) or construction-grade ZVI, low $\varepsilon_{\text{Fe}(0)}$ values should be common because accumulation of the iron oxide products of $\text{Fe}(0)$ oxidation result in complete passivation before the $\text{Fe}(0)$ at the particle core reacts.

The electrons released by accessible $\text{Fe}(0)$ (as defined by $\varepsilon_{\text{Fe}(0)}$) can be utilized to reduce the primary COC or the other oxidants such as H_2O , dissolved oxygen, nitrate, or non-target co-contaminants. The efficiency of electron utilization for contaminant reduction relative to all of the reduction reactions has been termed electron efficiency (ε_e or EE), whereas the electron efficiencies of reactions with H_2O , O_2 , and other oxidants can be expressed as $\varepsilon_{\text{H}_2\text{O}}$, ε_{O_2} , and $\varepsilon_{\text{other}}$, respectively. The sum of efficiencies of reduction processes involving these non-target species that are responsible for natural reductant demand is defined here as ε_{NRD} .

As indicated by **Figure 37**, the overall efficiency by which ZVI reduces COCs—which was termed “particle efficiency (ε)” by Liu et al. [133]—is the product of $\text{Fe}(0)$ utilization efficiency ($\varepsilon_{\text{Fe}(0)}$) and electron efficiency (ε_e) at the end of particle reactive lifetime (i.e., $\varepsilon = \varepsilon_{\text{Fe}(0)} \times \varepsilon_e$). Therefore, if the Fe^0 is fully consumed (i.e., $\varepsilon_{\text{Fe}(0)} = 1$), then ε is equal to ε_e .

Determination of Electron Efficiency. Electron efficiency (ε_e) is the fraction of total electrons from ZVI oxidation that are used in reduction of COCs (in this review, dichlorination of organohalides). As shown in **Figure 37**, and discussed further below, the branching between ε_e and ε_{NRD} reflects competition between (and selectivity for) oxidants for the electrons donated by Fe^0 . It should be noted that, in some cases, this representation may not describe the actual reaction pathway or mechanism. For example, nZVI synthesized by the borohydride reduction method (i.e., Fe/B) was found to give a high electron efficiency (92%), despite formation of H_2 gas from the reduction of water [133]. This result was shown to arise because the H_2 generated was used to dechlorinate TCE via hydrodehalogenation catalyzed by amorphous iron [134]. This implies that reduction of water and TCE dechlorination can involve sequential as well as parallel processes, even though the accounting used here (and in general, so far) treats all of the electrons used to reduce H_2O as part of NRD. This simplification does not affect the approaches to quantification of ε_e that are discussed below, although it must be

considered when interpreting ε_e data as evidence regarding contaminant degradation mechanisms, as explained below.

The quantitative definition of ε_e , which usually is expressed as a percentage, is given in eqn (4):

$$\varepsilon_e = \frac{N_e}{N_t} \quad (4)$$

where N_e is the quantity of electrons utilized for reduction of the COC and N_t is the total quantity of electrons provided by oxidation of Fe(0). In this definition, each N is described as a quantity of “electrons” because that is the most convenient and general basis for accounting the extent of redox reactions. As noted above, however, this does not necessarily imply these reactions occur (only) by electron transfer mechanisms, because various atom-transfer reactions can also contribute to redox reactions. In previous work [135], we have tried to accommodate this issue by using the more general term “reducing equivalents”, but that is not continued in this work for simplicity and consistency with the majority of other work on this topic. Also, for modified ZVI, and in particular sulfidated ZVI, electrons from iron sulfide are not considered here because dechlorination of organohalides (e.g., TCE) by FeS is typically much slower than dechlorination by sulfidated ZVI.

Factors effecting electron efficiency. The three types of electron efficiencies described above are affected by factors that can be intrinsic or extrinsic. The intrinsic factors relate mainly to the physical and chemical properties of the ZVI (e.g., particle size, crystallinity, surface area, hydrophobicity, or dopants), whereas the extrinsic factors include many environmental system variables, such as water pH, target contaminant concentration, and the presence of non-target reducible co-contaminants. These effects on ε_e can be further complicated by changes in the system over time as reactions proceed. To provide a quantitative basis for comparison and interpretation of the how particle properties and environmental conditions affect efficiency, we have summarized the available data in **Figure 38**. The figure illustrates some of the effects that these factors have on efficiency and these are discussed in detail in He et al. [3].

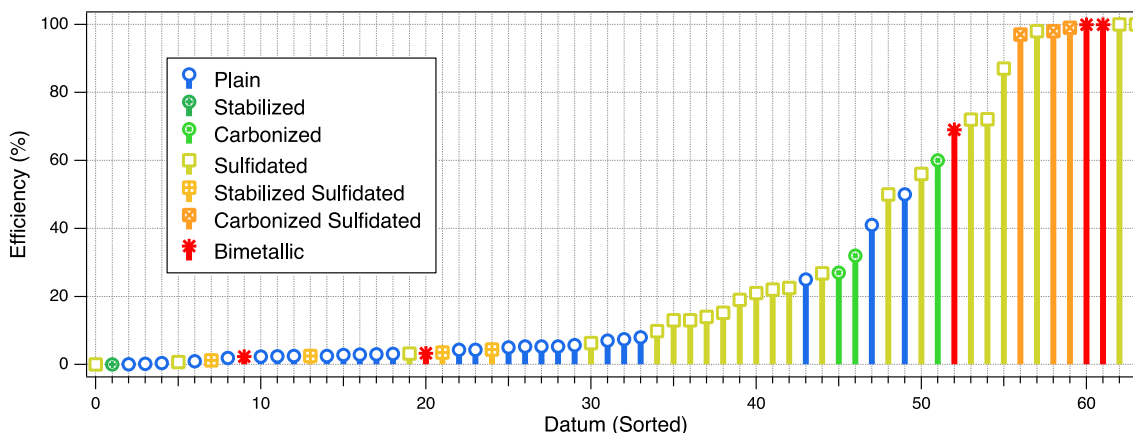


Figure 38. Summary of published efficiency data from studies of contaminant reduction by ZVI. For each experiment, all types of efficiencies that were reported are plotted at one position on the datum axis, which was sorted by increasing value of ε_e . Some of the main factors that affect efficiency are represented in the figure by marker type and color. The data and meta-data compiled for this analysis are given as SI in [3].

Implications for ANA. The majority of this review focused on TCE dechlorination by ZVI because that system is so widely studied that a considerable quantity of research on efficiency and selectivity aspects is now available. In many respects, it is a good model system for developing general concepts regarding efficiency and selectivity that should apply to other systems. For example, the strength of ZVI as a reductant means that several “input” reactions will be in competition (with TCE, H_2O , nitrate, etc.) and these reactions lead to several competing “output” reactions (formation of dechlorination products, iron oxides, etc.). Taken together in various combinations, the system exhibits a variety of efficiencies and selectivities that should be applicable to other environmental processes.

The efficiency and selectivity concepts developed in this review for TCE certainly will be applicable to other contaminants that are degraded by ZVI. For other chlorinated solvents (carbon tetrachloride, 1,1,1-trichloroethane, 1,2,3-trichloropropane, etc.) the only limitation is the lack of data, but this may be alleviated by studies forthcoming in the near future. For other organic contaminants (energetics like 2,4,6-trinitrotoluene and nitro-group containing pesticides like parathion; azo dyes, etc.) [136, 137], all of the concepts and definitions developed here will be applicable, although the specifics of their application may vary. For example, nitro reduction by ZVI generally is faster compared with dechlorination, and consumes 6 electrons to form fully reduced amino products, so it might outcompete other reduction processes resulting in higher electron efficiencies.

Similar generalizations should apply to the removal of metals, metalloids, and other inorganic contaminants (e.g., chlorine residual) and some of these were addressed above as competitors with TCE for reaction with ZVI.

Another possible extension of the efficiency and selectivity concepts developed here is to related treatment or remediation processes that do not involve ZVI. A compelling example of this is contaminant reduction with metals that are even more strongly reducing than ZVI, namely, zero-valent zinc (ZVZ) [138-141] and zero-valent magnesium (ZVMg) [142-144]. The reduction of water by ZVZ and ZVMg is much more favorable than ZVI, so HER is likely to compete more strongly with contaminants for electrons from the metal, making efficiency and selectivity even greater issues for practical applications of these reductants. In some respects, ZVZ (and probably also ZVMg) is an even better examples of how operational factors influence efficiency and selectivity because passivation of these metals can be much more complete than with ZVI, so rates of contaminant and water reduction, and the associated electron efficiencies, are likely to vary greatly with conditions that affect the passivation of these metals. This, in turn, could result in treatment processes that are effective, or ineffective, in ways that are not yet known.

Beyond engineered water treatment systems, there should even be applications of efficiency/selectivity concepts to the natural biogeochemical redox processes that contribute to the fate of contaminants. Lately, the effect of these processes has been termed abiotic natural attenuation (ANA), and there is considerable recent and on-going research to delineate the scope and core concepts of ANA [145-147]. The literature on ANA is not mature enough to include detailed, quantitative studies of efficiency and selectivity, but the concepts certainly are applicable. For example, if TCE dechlorination in an anoxic aquifer includes abiotic reduction by iron oxides and sulfides, and these phases are present in finite quantities, then the efficiency by which these phases provide electrons for dechlorination will determine if there is capacity in the system to achieve treatment goals. In one respect, iron oxide/sulfide systems are much simpler than ZVI systems because the former generally does not reduce water, so there is no significant HER no matter what other side reactions involved. On the other hand, the iron oxide/sulfide systems are more complex because they can be formed by in situ biogeochemical processes, whereas the ZVI system is limited by the quantity of the reagent provided.

12. OVERALL CONCLUSIONS AND IMPLICATIONS

The original design of this project around “core concepts” that are relatively well established in ISCO, but should have direct application to ISCR and ANA, proved to be good framework for pursuing the priority objectives of SERDP’s SON. At the same time, it allowed flexibility to adapt to developments in the field that were not fully anticipated when the project was conceived.

One example of this evolution is the use of magnetic susceptibility (MS) as a predictor of contaminant reduction rates by iron minerals. Reassessing this was an original priority of the project (within Objective 1), but it soon became evident from our early results—and evidence from other sources—that MS would not be very useful in the kind of general performance metrics we sought to develop. During the same time-period, evidence was mounting that added and/or dissolved Fe(II) was essential to obtaining significant reactivity between iron minerals and chlorinated solvents. This lead us to refocus our search for performance metrics to those that incorporated the effect of Fe(II). Also during the time-period of this project, sulfidation become one of the most studied variations on ISCR technologies, so some of this task was refocused on evaluating how to quantify the degree of sulfidation of iron-based materials.

Another transition that took place during this project involved the search for enhancements (Objective 2). We begin by focusing on organic electron transfer mediators (ETMs) like quinones and riboflavin, which seemed to have potential as amendments for enhancing ANA or ISCR performance. But, developments (again) within and outside this project, led us to refocus on the effect of Fe(II) phases that precipitate under conditions of ANA/ISCR, resulting in what we named (during this project) as “reactive mineral intermediates (RMIs). We added to the mounting evidence that RMIs can greatly enhance contaminant reduction rates, and field-scale applications of this idea are already starting to appear. This RMI idea is widely applicable—e.g., it could be useful in explaining the result of various “biogeochemical” remediation technologies—and we expect this will become a prominent area of research and technology development, in the near future.

The widespread interest in effects of sulfidation—especially on ZVI, but increasingly on the iron oxides involved in ANA—also caused us to expand the focus of Objective 3 from reductant demand to include the very closely related concepts of efficiency and selectivity of contaminant reduction. These concepts were developed using sulfidation of ZVI as the treatment process, because there is far more data on ZVI that is suitable for this analysis. The results show clearly that efficiency, selectivity, capacity, and demand

are closely related; how they are best defined and quantified, and why they are just as important to the overall success of ANA/ISCR remedies as rates of contaminant reduction.

The core concepts developed within this project that appear to be having the most impact are (i) enhancement of ANA/ISCR through reactions involving RMIs, and (ii) performance metrics for efficiency and selectivity. There is on-going work on both of these, on both their fundamental and applied aspects. In addition, this project received one of SERDP's 2019 Project of the Year awards because its findings have helped to establish quantitative protocols that can be used by DoD site managers to advance the design of enhanced natural attenuation technologies.

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14. APPENDICES

14.1. Supporting Data

No supporting information is provided here. However, several of the publications from this work have extensive supporting information, which can be found with the main manuscript via the publisher's website.

14.2. List of Scientific/Technical Publications

Peer-Reviewed:

- Torralba-Sanchez, T. L., E. J. Bylaska, A. Salter-Blanc, J., D. E. Meisenheimer, M. A. Lyon, and P. G. Tratnyek (2020) Reduction of 1,2,3-trichloropropane (TCP): Pathways and mechanisms from computational chemistry calculations. *Environ. Sci. Proc. Impacts* 22(3): 606-616.
- Qin, H., X. Guan, and P. G. Tratnyek (2019) Effects of sulfidation and nitrate on the reduction of N-nitrosodimethylamine (NDMA) by zerovalent iron. *Environ. Sci. Technol.* 53(16): 9744-9754.
- Kocur, C. M. D., D. Fan, P. G. Tratnyek, and R. L. Johnson (2019) Predicting abiotic reduction rates using cryogenically collected soil cores and mediated reduction potential measurements. *Environ. Sci. Technol. Lett.* 7(1): 20-26.
- Qin, H., X. Guan, J. Z. Bandstra, R. L. Johnson, and P. G. Tratnyek (2018) Modeling the kinetics of hydrogen formation by zerovalent iron: Effects of sulfidation on micro- and nano-scale particles. *Environ. Sci. Technol.* 52(23): 13887-13896.
- He, F., L. Gong, D. Fan, P. G. Tratnyek, and G. V. Lowry (2020) Quantifying the efficiency and selectivity of organohalide dechlorination by zerovalent iron. *Environ. Sci. Proc. Impacts* 22(3): 528-542.

In Preparation (largely written, but not yet submitted):

- Pavitt, A. S., and P. G. Tratnyek. 2020. Electrochemical characterization of reactive mineral intermediates (RMIs) from Fe(II) amended iron oxides. *Environ. Sci. Technol.*: in prep.
- Cai, S., B. Chen, X. Qiu, J. Li, P. Tratnyek, and F. He. 2020. Solid-solid sulfidation of zero valent iron by elemental sulfur in aqueous phase for enhanced dechlorination of trichloroethene. *Environ. Sci. Technol.*: in prep.
- Park, J., J. Z. Bandstra, P. G. Tratnyek, O. R. Harvey, J. Bae, M. J. Kwon, J. S. Ahn, C.-M. Chon, and G. Lee. 2020. Modeling the role of pH in contaminant sequestration by zerovalent metals: Chromate vs. zerovalent magnesium. *Environ. Sci. Technol.*: in prep.

14.3. Other Supporting Materials

No other supporting materials provided.

14.4. Outreach, Training, Other Technology Transfer

14.4.1. Short Courses and Webinars

- Webinar on In Situ Chemical Reduction (ISCR) hosted by Regenesys, 9/20/2018.
 - This event was very widely advertised and had hundred attendees. The presentation featured prominently the “core concepts” theme, and many of the results, of this project.
 - <http://www2.regenesys.com/paul-tratnyek-ohsu-webinar>
 - <https://youtu.be/IEjuwGrUpTs>
- Webinar on In Situ Chemical Reduction (ISCR) hosted by Tersus, 6/21/2018.
 - Presented by project postdoc Ying Lan
 - <https://www.gotostage.com/channel/100000000000620917/recording/29e5eaf654834975907f9c0e20676257/watch>

14.4.2. Workshops

- SERDP Workshop on Tools and Technologies Related to Chlorinated Solvents in Groundwater, 18-19 July 2018, Seattle, WA. Some ideas from this project figure prominently in this workshop’s final report.
- SERDP Workshop on Abiotic Degradation 9-10 October 2019, Minneapolis, MN. Presenter (on this project) and participant.

14.4.3. Conference Presentations (Keynote and Invited)

- American Chemical Society National Meeting, Spring 2020, Philadelphia, PA (Cancelled) “Reactive mineral phases from in situ biogeochemical processes: The key to abiotic natural attenuation?”
- Battelle Bioremediation Symposium, 15-18 April 2019, Baltimore, MD. “In Situ Chemical Reduction (ISCR): The Role of Reactive Mineral Intermediate Phases (RMIs) and Sulfidation”
- “New Tools” Talk at 2018 SERDP Symposium, 26-29 November 2018, Washington, DC. This presentation was a synthesis of many aspects of ER-2620. Available at:
 - <https://youtu.be/VzY3wTW9MV4>

- 11th International Symposium on Environmental Geochemistry, 7-10 August 2019, Beijing, China. “Emerging Core Concepts for In Situ Chemical Reduction and Abiotic Natural Attenuation”
- Battelle Chlorinated Conference 8-12 April 2018, Palm Springs, CA. Organizer of the session of ISCR.

14.4.4. Special Projects

- Instigator and lead organizer of a themed issue of the RSC journal Environmental Science: Processes & Impacts (ESPI) on the all aspects of the environmental fate, effects, and remediation of halogenated (semi)volatiles organic chemicals.
 - Recruited three co-editors: Elizabeth Edwards (U. Toronto) Biodegradation and Microbial Ecology, Sarah Blossom (U. Arkansas Med. Sci.) Epigenetics and Toxicology, Lucy Carpenter (U. York) Atmosphere/Ocean Chemistry
 - The resulting themed issue was published in March 2020, containing a wide range a paper relevant to ANA and ISCR. It is accessible from <http://rsc.li/halocarbons>.

14.4.5. Social Media

- In addition the the Zenodo Group site that we have been using for several years to make supplementary results from our work accessible permanently with open access, during this project we started a YouTube channel to archive video from our work, and continued to use LinkedIn to publicize all of the above the practitioner community.
 - <https://zenodo.org/communities/tratnyekgroup/>
 - https://www.youtube.com/results?search_query=paultratnyek
 - <https://www.linkedin.com/in/pgtratnyek/>