Reductive transformations of dichloroacetamide safeners: effects of agrochemical co-formulants and iron oxide + manganese oxide binary-mineral systems

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ENVIRONMENTAL SIGNIFICANCE STATEMENT

Dichloroacetamide safeners are an understudied class of emerging contaminants that can undergo reductive dechlorination to form monochlorinated products of potentially greater environmental mobility and toxicity. This study is the first to explore the effects of agrochemical co-formulants, including surfactants and an herbicide active ingredient, on thermal (non-photolytic) reactions of safeners. This investigation also explores the effects of commonly-overlooked variables such as buffer concentration, ionic strength, and reagent addition order on safener transformations in Fe(II)-amended mineral slurries. By examining how binary mixtures of the common soil minerals hematite and birnessite influence safener transformation under simulated iron-reducing conditions, this study advances our understanding of the environmental fate of safeners by more closely approximating the complexity of natural soils relative to single-mineral systems.

Reductive transformations of dichloroacetamide safeners: effects of agrochemical co-formulants and iron oxide + manganese oxide binary-mineral systems[†]

Allison N. Ricko,[a‡] *Andrew W. Psoras,*[a] *and John D. Sivey*[*abc]

[a] Environmental Science & Studies Program, Towson University, Towson, Maryland, United States

[b] Urban Environmental Biogeochemistry Laboratory, Towson University, Towson, Maryland, United States

[c] Department of Chemistry, Towson University, Towson, Maryland, United States

* Corresponding author: E-mail: jsivey@towson.edu; Tel: 1-410-704-6087

[†] Electronic supplementary information (ESI) available.

[‡] Current address: RXNT, Annapolis, Maryland, United States

ABSTRACT

The toxic effects of herbicides are often incompletely selective and can harm crops. Safeners are "inert" ingredients commonly added to herbicide formulations to protect crops from herbicide-induced injury. Dichloroacetamide safeners have been previously shown to undergo reductive dechlorination in anaerobic abiotic systems containing an iron (hydr)oxide mineral (goethite or hematite) amended with Fe(II). Manganese oxides (e.g., birnessite) are important redox-active species that frequently co-occur with iron (hydr)oxides, yet studies examining the effects of more than one mineral on transformations of environmental contaminants are rare. Herein, we investigate the reactivity of dichloroacetamide safeners benoxacor, furilazole, and dichlormid in binary-mineral, anaerobic systems containing Fe(II)-amended hematite and birnessite. As the molar ratio of Fe(II)-to-Mn(IV) oxide increased, the transformation rate of benoxacor and furilazole increased. The safener dichlormid did not transform appreciably over the sampling period (6 hours). The concentration of pH buffer ([MOPS] = 10 – 50 mM), ionic strength ([NaCl] = 10 – 200 mM), and order of solute addition (e.g., safener followed by Fe(II) or vice versa) do not appreciably affect transformation rates of the examined dichloroacetamide safeners in Fe(II) + hematite slurries. The presence of agrochemical co-formulants, including the herbicide *S*-metolachlor and three surfactants, in solutions containing $Cr(H_2O)_6^{2+}$ (as a model homogeneous reductant) also did not substantially influence rates of safener transformation. This study is among the first to examine laboratory systems of intermediate complexity (e.g., systems containing mixtures of agrochemical co-formulants or mineral phases) when assessing the environmental fate of emerging contaminants such as dichloroacetamide safeners.

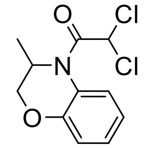
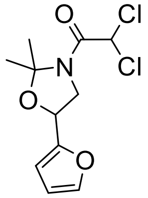
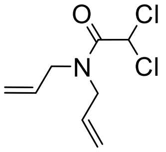
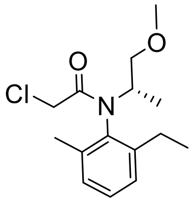
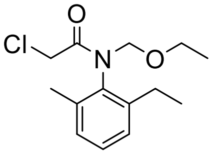
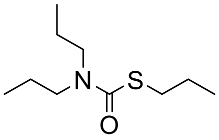
1. INTRODUCTION

Safeners are added to herbicide formulations to protect crops from the adverse effects of the active herbicide.[1-5] Safeners are referred to in the literature under a variety of additional names, including antidotes, antagonists, and protectants.[1] Safeners are applied in combination with herbicides as either a seed treatment or spray mixture.[1-5] Application as a spray mixture can occur before or after the crop plant has emerged from the soil.[2-5]

Dichloroacetamides are one of the most commonly used classes of safeners.[5] Dichloroacetamide safeners benoxacor, dichlormid, and furilazole are commonly paired with (mono)chloroacetamide and thiocarbamate herbicides (**Table 1**).[2-10] Benoxacor, for example, is paired with the chloroacetamide herbicide *S*-metolachlor in commercial formulations (e.g., Dual II Magnum®, Syngenta).[5,8] Dichlormid is commonly paired with the herbicide acetochlor (e.g., Surpass®, Dow AgroSciences), but can also be combined with other herbicides (e.g., vernolate).[2,5,8]

Chloroacetamide herbicides and their metabolites have been detected in surface water and groundwater,[11-14] suggesting that the associated safeners may also occur in these systems. Indeed, a recent study of Midwestern streams found at least one dichloroacetamide safener in 43% of samples analyzed, with maximum concentrations of 190 ng/L for benoxacor, 150 ng/L for furilazole, and 42 ng/L for dichlormid.[15] Chloroacetamide herbicides showed a positive correlation with safener concentration and were detected at maximum concentrations several orders of magnitude higher than the safener concentrations.[15] Safener detection coincided with corn planting seasons (April - May) and with storm events, implying overland transport into surface waters.[15] Additional studies determined that although safeners benoxacor and furilazole had lower solubility in water than some of their co-applied herbicides (**Table 1**),[7] column experiments suggest the likelihood that these safeners can leach into groundwater;[16] however, no groundwater occurrence studies have been reported to date.

Table 1. Structures and Properties of Dichloroacetamide Safeners and their Associated Herbicides.

		Water Solubility (mg/L) [a]	Boiling Point (°C) [b]	Log K_{ow} [a]
Dichloroacetamide Safeners				
	benoxacor	22 [c]	359.44	2.23 [c]
	furilazole	235 [c]	354.08	1.96 [c]
	dichlormid	1067 [b]	282.09	1.84 [d]
Chloroacetamide Herbicides				
	*S*-metolachlor	530 [e]	382.78	3.4 [f]
	acetochlor	223 [d]	378.17	3.03 [d]
Thiocarbamate Herbicide				
	vernolate	90 [d,g]	302.57	3.84 [d,g]

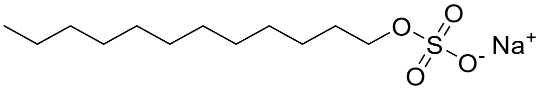
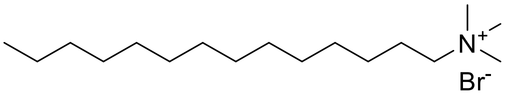
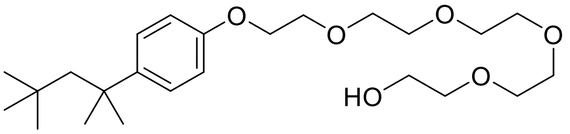
[a] Water solubility and LogKow values reported at 25 °C unless otherwise stated.
[b] Ref 6
[c] Ref 7
[d] Ref 8
[e] Ref 9
[f] Ref 10
[g] Reported at 20 °C

Safeners are classified as "inert" constituents in agrochemical formulations.[17] The (eco)toxicity of safeners toward non-target species has received rather limited attention in the peer-reviewed literature.[18-21] However, several environmental fate studies suggest that dichloroacetamide safeners can transform under environmentally relevant conditions into products (e.g., monochloroacetamides) that may be more biologically active (e.g., more susceptible to nucleophilic substitution) than the parent compounds.[17,22-24] Dichlormid was shown to transform via photolysis, hydrolysis, dealkylation, and dechlorination.[22] Benoxacor was found to photodegrade with a half-life of approximately 8 min under simulated sunlight, yielding a mixture of monochlorinated and dechlorinated products, while AD-76 and furilazole were more persistent.[23] In Fe(II)-amended suspensions containing either hematite or goethite, dichloroacetamide safeners can be reduced abiotically to monochlorinated products closely resembling active herbicides.[17] Rates of reductive dechlorination in Fe(II)-amended suspensions of hematite and goethite were strongly influenced by the identity of the *N*-substituents on the dichloroacetamides.[17] In the case of dichlormid, one transformation product was identified as the formerly-used herbicide *N,N*-diallyl-2-chloroacetamide (CDAA).[17] An additional simulated environmental subsurface study demonstrated dechlorination and sulfur substitution of AD-67, benoxacor, and dichlormid on the scale of hours facilitated by the presence of black carbon and polysulfides;[24] transformation products were of higher molecular weight, less polar, and (in some cases) polymerized.[24]

Agrochemicals are commonly applied as mixtures (formulations) of active + inert (or "other") ingredients. Examining chemical mixtures is important when assessing the fate of agrochemicals, as mixtures may impart synergistic and/or antagonistic effects.[25] For example, photodegradation rates of the herbicide metolachlor on quartz and in water were enhanced by the addition of the safener benoxacor, indicating a photosensitizing effect.[26] Studies have also examined the toxicity of herbicides and safeners on the bacterium *Vibrio fischeri*, finding that benoxacor held a lower inhibitory concentration 50% value than *S*-metolachlor alone or a combination of the two.[19] Additional tests on *Chironomus riparius* suggest toxic effects exerted by benoxacor and its monochlorinated analogue exceeded metolachlor alone.[18] While combined toxic effects are gaining attention, few studies have examined the transformations of safeners in the presence of co-formulants.

Surfactants are often co-formulated with herbicides to improve uptake into weeds (**Table 2**).[27-33] Surfactants can affect herbicides' physical properties (e.g., solubility and volatility), transformation rates, and adsorption onto soils.[28,31,32] Surfactants can either enhance or attenuate rates of herbicide transformation, depending on the specific surfactant + herbicide combination.[28,31,32] The effect of surfactants on adsorption also varies, depending on how the surfactant interacts with both the soil and the herbicide.[28] Whether or not surfactants can influence thermal (dark) reactions involving safeners has not been previously investigated.

Table 2. Structure and Properties of Some Surfactants Used in Herbicide Formulations. [a]

Surfactant	Class	CMC (mM) [b]	HLB [c]
 Sodium dodecyl sulfate (SDS)	Anionic	7 – 10	40
 Myristryltrimethylammonium bromide (MyTAB)	Cationic	4 – 5	n.a. [d]
 Triton® X-100	Nonionic	0.2 – 0.9	13.5

[a] Ref 31
[b] Critical micelle concentration (CMC) values are reported for 20-25 °C
[c] Hydrophile/lipophile balance (HLB)
[d] Data not available

Oxides of iron and manganese (e.g., hematite and birnessite, respectively) are abundant in a wide range of soil types and typically occur as clay-sized particles or as coatings on the surface of larger particles.[34,35] Selected properties of these minerals can be found in the **Electronic Supplementary Information** (**ESI, Table S1**). Manganese oxides, iron (hydr)oxides, and Fe(II) can co-occur in agricultural soils due to changing redox conditions as the soils shift from tilled (and aerated) to flooded (and anaerobic).[35,36] Manganese enrichment in the continental United States overlaps with agricultural regions where herbicides and safeners are applied in the highest quantities.[37-39] This overlap motivates our investigation of safener transformation in iron and manganese oxide mixed-mineral systems.

The presence of iron (hydr)oxides or manganese oxides alone is typically insufficient to facilitate redox reactions of agrochemicals.[40-43] The changing redox state of agricultural soils can, however, generate dissolved Fe(II),[35,36] which can adsorb onto some oxide minerals.[40,42,44]

Surface-bound Fe(II) on ferric (hydr)oxides is a stronger reducing agent than free Fe(II) in solution[40,43-45] and can promote electron transfer through the bulk crystal of minerals such as hematite.[46]

Fe(II) bound to surface (e.g., hydroxyl) sites on oxide minerals can serve as a reductant of environmental contaminants,[40,45,47-49] including agrochemicals,[17,41,50-52] in laboratory systems as well as in natural environments (e.g., soils[47] and aquifers[53]). The ability of Fe(II)-amended iron (hydr)oxide suspensions to effect reductive dechlorination of dichloroacetamide safeners has been reported,[17] but prior work has not examined these agrochemicals in systems containing manganese oxides. In systems containing Fe(II), birnessite [a Mn(IV) oxide] can oxidize Fe(II) to Fe(III), forming Fe(III) hydroxides and releasing dissolved Mn(II) into solution.[54-56] Under anaerobic conditions, the formation of dissolved Fe(II) along with dissolved Mn(II) and precipitation of Fe(III) hydroxides has been observed.[55] Though iron and manganese oxides have been investigated in single-mineral systems for their capacity to transform organic contaminants, this study examines binary-mineral systems to better represent complex natural soils.[57]

The goal of this study is to quantify the transformation rates of three dichloroacetamide safeners (benoxacor, dichlormid, and furilazole) in Fe(II)-amended hematite slurries and in homogeneous systems containing Cr(II) (i.e., $Cr(H_2O)_6^{2+}$). Specifically, we seek to: (1) determine the influence of herbicide and surfactant co-formulants on transformation rates in homogeneous systems containing aqueous Cr(II); and (2) identify effects of solution conditions (e.g., concentration of pH buffer and ionic strength), order of reagent addition, and the co-occurrence of the Mn(IV) oxide mineral birnessite on safener transformation rates Fe(II)-amended hematite slurries. Cr(II) was selected as a model reductant to permit reactivity investigations in homogenous systems (i.e., when the complicating effects of interfacial processes are negligible). This study is, to our knowledge, the first to examine the effects of mixed-mineral systems on the environmental fate of safeners and the first to explore the effects of co-formulants on reductive transformations of safeners.

2. METHODS

A comprehensive list of reagents, their purities, and vendor information can be found in **Table S2**. All aqueous solutions were prepared with deionized water purified with a Nanopure Analytical UV system (18 MΩ cm, Thermo Scientific). Stock solutions of $CrCl_2$ and $FeCl_2$ were standardized via UV-vis spectrophotometry before use (**Text S1** and **S2**).[58,59] The monochlorinated analogue of the safener benoxacor was synthesized for use in calibration standards (**Text S3** and **S4, Figure S1, S2**). Unless indicated otherwise, reagent concentrations were selected to facilitate determinations of reaction rate constants and do not necessarily represent concentrations anticipated in environmental systems.

2.1 Reaction Conditions.

All reactions examined herein were performed in 40-mL amber glass vials with Teflon-lined caps held at room temperature in an anaerobic chamber (3% H_2, 97% N_2 atmosphere bubbled through a 1-M sodium hydroxide solution to remove carbon dioxide). Water used for anaerobic experiments was purged with anaerobic chamber atmosphere before use. The total volume of all reaction solutions was 35 mL. Initial dichloroacetamide safener (benoxacor, dichlormid, or furilazole) concentrations in all reaction solutions was 20 μM, achieved via a methanolic spike at t = 0. These dichloroacetamide safeners have low air-water partition coefficients ($\log K_{aw} \leq -4.87$),[20] suggesting negligible partitioning into reactor headspace. Reactors were mixed continuously on a vial rotator, except when aliquots were removed for analysis.

Effects of Herbicide and Surfactant Co-Formulants. Reactions involving benoxacor and agrochemical co-formulants (surfactants and an herbicide) were performed in aqueous solutions of sulfuric acid (5.0 mM) amended with $CrCl_2$ (500 μM) as a reductant such that no solid phase was needed for the reaction to proceed. This approach permits the possible effects of co-formulants on homogeneous electron-transfer reactions to be interrogated directly.[17] Optimal surfactant effect for post-emergence spray applications typically occurs at a surfactant concentration of approximately 0.5 wt% in the mixture (equivalent to 17 mM for SDS, 15 mM for MyTAB, 8 mM for Triton® X-100)[30] while safeners typically occur at ~5 wt% (equivalent to 192 mM for benoxacor) in commercial emulsifiable concentrates, which generally undergo varying levels of dilution prior to field application.[20,24] These data informed our choice of surfactant concentrations, which ranged from 0 to 10 μM (i.e., [safener]/[surfactant] from 2 to 10), added as an aqueous spike of sodium dodecyl sulfate (SDS), myristryltrimethylammonium bromide (MyTAB), or Triton® X-100.

In a separate set of experiments, benoxacor was monitored in the presence of the herbicide *S*-metolachlor (no added surfactant). Concentrations of *S*-metolachlor ranged from 0 to 40 μM, added as a methanolic spike. Periodically over the course of each reaction, aliquots (0.500 mL) of reaction solutions were transferred to 4-mL glass vials pre-amended with 0.500 mL of 10 mM NaOH to quench the reaction. Analytes were extracted into 1.00 mL of toluene prior to analysis by gas chromatography (GC; see Section 2.2 below for analytical method details).

Effects of pH Buffer and Ionic Strength. Reactions to determine the effects of pH buffer concentration and ionic strength on transformation of benoxacor and furilazole (20 μM initial concentration, tested individually) were performed in an aqueous slurry of 10 g/L hematite (as Fe(III) oxide, Fe_2O_3) at pH 7.0. $FeCl_2$ was added as a concentrated aqueous spike to achieve an initial Fe(II) concentration of 5.0 mM. For reactions examining the influence of pH buffer concentration, the formal concentration of 3-morpholinopropane-1-sulfonic acid (MOPS) ranged from 10.0 to 50.0 mM, with the concentration of NaCl fixed at 50.0 mM. The influence of [MOPS] was examined to determine whether experimental artifacts arise from the use of MOPS to control the pH of mineral suspensions. For reactions performed as a function of ionic strength, the concentration of NaCl ranged from 10.0 to 200.0 mM, with the concentration of MOPS fixed at 30.0 mM. Reactions were initiated by adding a safener (methanolic spike) immediately following addition of Fe(II). Final methanol concentrations in slurries were ≤1 vol%. Slurry aliquots (1.00 mL) were obtained periodically during each reaction and were transferred to 2-mL plastic centrifuge tubes and immediately centrifuged (13,000 rpm for 10 min). Supernatant (~0.95 mL) was decanted into pre-weighed 4-mL glass vials and extracted into 2.00 mL of toluene (containing 10.2 μM of 2-chlorobenzonitrile as an internal standard) for analysis via GC. Volumes of supernatant and toluene added to the 4-mL vials were verified gravimetrically to ±0.01 mg (Mettler Toledo XA105).

Effects of Mixed-Mineral Systems. Mineral slurries were prepared in MOPS buffer solutions (30.0 mM, pH 7.0) containing 50.0 mM NaCl (to maintain constant ionic strength). Solids were fixed at 10 g/L (total solids loading) via addition of a concentrated slurry to achieve a mixture of 9 g/L hematite and 1 g/L birnessite. Fe(II) served as a reductant (2.0 to 22 mM) and was added to reactors as a concentrated aqueous spike of $FeCl_2$. Unless otherwise indicated, reactions were initiated by adding a safener (methanolic spike) immediately following addition of Fe(II). Selected experiments were performed to determine the effects of reagent addition by adding Fe(II) or Mn(IV) after amending reactors with a safener. Aliquots were obtained, centrifuged, and extracted into toluene as described above. Experiments examining the sorption of benoxacor, dichlormid, and furilazole onto hematite and birnessite are described in **Text S5**.

Experiments to examine the rate of Fe(II) oxidation by birnessite had a total solids loading of 1 g/L birnessite and an initial Fe(II) concentration of 6.0 mM, added as $FeCl_2$. Slurry samples (1.00 mL) were extracted using 9.0 mL of 1% HNO_3 to liberate solid-associated Fe(II). The sample solution was subsequently filtered with a 0.2 μm syringe filter (nylon membrane, Whatman) prior to analysis with UV-vis spectrophotometry (see Section 2.2 below).

Experiments examining the competitive adsorption of Fe(II) in the presence of Mn(II) included a total solids loading of 10 g/L as hematite. Fe(II) was added to reactors as $FeCl_2$ at either 1.5 or 3.0 mM. Mn(II) was added to reactors as $MnCl_2$ at either 1.5 or 3.0 mM. Accordingly, the Fe(II)/Mn(II) molar ratio ranged from 2:1 to 1:2. Samples (~2 mL) were filtered with a 0.2 μM nylon syringe filter prior to subsequent analyses of Fe(II) with UV-vis spectrophotometry. Mn(II) concentrations were not measured.

2.2 Analytical Methods

Instrumentation. Reactions monitoring the transformation (putatively reductive dechlorination) of safeners were analyzed via GC with either mass spectrometry (MS) or micro-electron capture (μECD) detection. Complete details of GC-MS and GC-μECD parameters can be found in the **ESI**, **Text S6**, including temperature program (**Table S3**), retention times (**Table S4**), limits of detection (**Text S7, Table S5, Figures S3, S4, S5**), analyte loss and extraction efficiencies (**Table S6, Text S8**, **Table S7**) and quantification of furilazole (**Text S9**, **Figure S6**, **Figure S7**). 2-Chlorobenzonitrile (CBN) was used as an internal standard (10.2 μM in toluene) for all GC analyses. Analysis of Fe(II) oxidation and adsorption, in the absence of safeners, was performed using a ferrozine indicator and an Agilent Cary 60 UV-visible spectrophotometer, following the method of Stookey.[59]

Rate Constant Determination. Rate constants for all reactions were determined by the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model for surface-mediated reaction kinetics. The LHHW model assumes that surface-mediated reactions proceed in three steps (eqs 1 – 3, assuming Fe(III) oxide as the solid):

$$>\mathrm{Fe^{III}{-}O{-}Fe^{II}} + \mathrm{i_{ox}\,(aq)} \rightleftharpoons\ >\mathrm{Fe^{III}{-}O{-}Fe^{II}}\ \text{---}\mathrm{i_{ox}} \qquad [1]$$

$$>\mathrm{Fe^{III}{-}O{-}Fe^{II}}\ \text{---}\mathrm{i_{ox}} \rightarrow\ >\mathrm{Fe^{III}{-}O{-}Fe^{III}}\ \text{---}\mathrm{i_{red}} \qquad [2]$$

$$>\mathrm{Fe^{III}{-}O{-}Fe^{III}}\ \text{---}\mathrm{i_{red}} \rightleftharpoons\ >\mathrm{Fe^{III}{-}O{-}Fe^{III}} + \mathrm{i_{red}\,(aq)} \qquad [3]$$

where $>\mathrm{Fe^{III}{-}O{-}Fe^{II}}$ represents Fe(II) adsorbed on the surface of Fe(III) oxide and $\mathrm{i_{ox}}$ and $\mathrm{i_{red}}$ represent the oxidized and reduced form of a dichloroacetamide, respectively. Under the assumption that the surface reaction (eq 2) is rate-limiting, the reaction rate is calculated by eq 4:

$$-\frac{\mathrm{d[i_{ox}]}}{\mathrm{dt}} = \frac{kK_{\mathrm{ox}}[\mathrm{Fe^{II}}]_{\mathrm{ads}}[\mathrm{i_{ox}}]}{1 + K_{\mathrm{ox}}[\mathrm{i_{ox}}] + K_{\mathrm{red}}[\mathrm{i_{red}}]} \qquad [4]$$

where k ($\mathrm{s^{-1}}$) is the rate constant for the surface reaction (eq 2); $[\mathrm{i_{ox}}]$ and $[\mathrm{i_{red}}]$ (mol/L) are the concentrations of oxidized and reduced analyte, respectively; $[\mathrm{Fe^{II}}]_{\mathrm{ads}}$ (mol/L) is the concentration of adsorbed Fe(II); and K_{ox} and K_{red} (L/mol) are the adsorption equilibrium constants for $\mathrm{i_{ox}}$ and $\mathrm{i_{red}}$, respectively. Previous work demonstrated that rates of reductive dechlorination of benoxacor in Fe(II)-amended goethite slurries were first-order in the initial concentration of benoxacor, consistent with the assumption that surface reaction is rate-determining.[17]

When dichloroacetamides and their reduction products exist predominantly in the dissolved (rather than the adsorbed) phase at equilibrium, then $(K_{\mathrm{ox}}[\mathrm{i_{ox}}] + K_{\mathrm{red}}[\mathrm{i_{red}}]) \ll 1$ and the denominator of eq 4 simplifies to 1.[17] When $[\mathrm{Fe^{II}}]_{\mathrm{ads}} >> [\mathrm{i_{ox}}]$ and $\mathrm{i_{ox}}$ is the only oxidizing agent of $\mathrm{Fe^{II}}$, $[\mathrm{Fe^{II}}]_{\mathrm{ads}}$ is anticipated to remain approximately constant throughout the reaction. Taken together, these two conditions permit eq 4 to simplify into a pseudo-first-order rate equation (eq 5):

$$-\frac{\mathrm{d}[\mathrm{i_{ox}}]}{\mathrm{dt}} = k_{\mathrm{obs}}[\mathrm{i_{ox}}] \qquad [5]$$

where k_{obs} ($\mathrm{s^{-1}}$) is a pseudo-first-order rate constant equal to $kK_{\mathrm{ox}}[\mathrm{Fe^{II}}]_{\mathrm{ads}}$. Integrating eq 5 yields:

$$\ln[\mathrm{i_{ox}}]_{\mathrm{t}} = -k_{\mathrm{obs}}\mathrm{t} + \ln[\mathrm{i_{ox}}]_0 \qquad [6]$$

where $[\mathrm{i_{ox}}]_{\mathrm{t}}$ is the concentration of the dissolved safener at time *t* and $[\mathrm{i_{ox}}]_0$ is the initial concentration of the dissolved safener. Eq 6 was used in conjunction with time course data to calculate k_{obs} values. Over the course of a reaction, the loss of the parent safener and (whenever feasible) the formation of the monochlorinated product were monitored**.** For most reactors, k_{obs} values were determined by analysis of a single reactor. In order to confirm reactor-to-reactor reproducibility, a set of four reactors was analyzed and showed high reproducibility (relative standard deviation of k_{obs} values of 4%). All statistical analyses discussed herein consisted of an F test, followed by a two-tailed Student's t test.

3. RESULTS AND DISCUSSION

3.1 Effects of Agrochemical Co-Formulants

The effects of agrochemical co-formulants on thermal (i.e., dark) transformations of dichloroacetamide safeners have not been previously studied. In order to determine the effects of co-formulants on the reduction of dichloroacetamide safeners, benoxacor was monitored over time in homogeneous systems amended with either an herbicide (*S*-metolachlor) or one of three surfactants (the anionic surfactant SDS, the cationic surfactant MyTAB, or the non-ionic surfactant Triton® X-100). Cr(II) was selected as the model reductant[17] to permit elucidation of the solution-phase effects of co-formulants on redox reactions involving benoxacor.

Effects of S*-Metolachlor on the Reductive Dechlorination of Benoxacor*. The loss of benoxacor in positive control reactors containing Cr(II) (but no added *S*-metolachlor) follows pseudo-first-order kinetics and generates monochloro-benoxacor as the only observed product (**Figure 1**), consistent with previous findings that Cr(II) is capable of promoting reductive dechlorination (hydrogenolysis) of dichloroacetamides.[17] The pseudo-first-order rate constant (k_{obs}) associated with the loss of benoxacor was not appreciably influenced by the presence of *S*-metolachlor at 8 – 32 μM (**Figure S8**). At an *S*-metolachlor concentration of 40.0 μM (**Figure S8**) a modest (12%) yet statistically significant decrease in k_{obs} was observed (Throughout this manuscript, statistical significance is defined as $p < 0.05$). These results suggest that dichloroacetamides are preferentially reduced in mixtures that also contain (mono)chloroacetamides, which agrees with previous studies showing that as the number of chlorine atoms increases from 1 to 3, hydrogenolysis rates of chloroacetamide (when present individually) also increase.[17] These findings also suggest that, at environmentally relevant concentrations of (di)chloroacetamides and reducing agents, the co-occurrence of a chloroacetamide herbicide is unlikely to substantially influence hydrogenolysis rates of dichloroacetamide safeners.

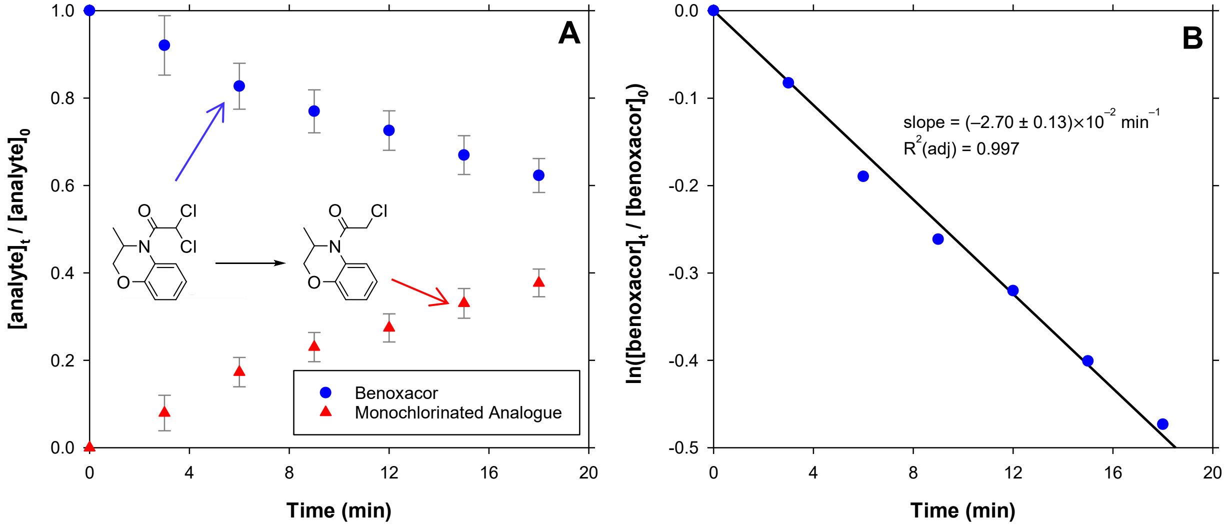


Figure 1. (A) Time course for the reduction of benoxacor into a monochlorinated analogue. **(B)** Natural log transformation of benoxacor, where the slope is equal to the observed reduction rate constant. Reactor conditions: $[\text{benoxacor}]_0 = 20$ µM, $[\text{Cr(II)}]_0 = 500$ µM, $[H_2SO_4] = 5.0$ mM. Error estimated represent 95% confidence intervals, calculated in (A) as t•u_x, where t is Student's t value and u_x is the standard uncertainty in x (n = 1 per time point).[60] Concentrations were normalized to the mass balance, assuming that $[\text{benoxacor}]_0 = [\text{benoxacor}]_t + [\text{monochloro benoxacor}]_t$.

Effects of Surfactants on the Reductive Dechlorination of Benoxacor. In the presence of SDS, MyTAB, and Triton® X-100, k_{obs} values corresponding to loss of benoxacor did not change appreciably as the concentration of surfactants changed (2 – 10 µM, **Figure S9**). Triton® X-100 (a neutral surfactant) did not significantly influence k_{obs} values relative to no-added surfactant controls. In the presence of SDS (anionic) and MyTAB (cationic), although k_{obs} values were largely unaffected by changes in surfactant concentration, k_{obs} values were significantly lower than in the absence of surfactant. In the presence of SDS, k_{obs} decreased by 18%, from 0.026 ± 0.002 s^{-1} (no SDS) to 0.0211 ± 0.0005 s^{-1} (average of all SDS levels). In the presence of MyTAB, k_{obs} was 0.0234 ± 0.0008 s^{-1}. While these minor differences are unlikely to have an impact on the environmental fate of benoxacor, they suggest that ionic surfactants may be capable of modestly inhibiting rates of electron transfer to dichloroacetamides in laboratory systems. Possible environmental effects of surfactants must also consider mobility differences (and synergies) between surfactants and dichloroacetamides in soil-water systems, which merits future investigation.

Effects of pH Buffer and Ionic Strength. In laboratory settings, experimental systems frequently incorporate pH buffers to control pH. This is particularly important for systems with a mineral phase that has a *circum*-neutral zero point of charge, as changes in the pH around this value can affect the net surface charge of the mineral. A change in mineral surface charge can strongly influence sorption, particularly for charged species in solution, like Fe(II).

MOPS is frequently used as a pH buffer in systems containing Fe(II) because of the low affinity of MOPS for metals.[61] Buchholz et al.[62] observed that increasing concentration of MOPS (1 – 50 mM) decreased reduction rates of CCl_4 in Fe(II)-amended goethite suspensions. Buchholz et al.[62] proposed that the MOPS effect in these systems resulted from competitive adsorption of MOPS on the goethite surface with concurrent release of adsorbed Fe(II).[62] In their previous examination of dichloroacetamide reduction in suspensions of Fe(II)-amended goethite and hematite, Sivey and Roberts[17] employed MOPS as a buffer (at 30 mM) but did not investigate the influence of MOPS concentration. In the Fe(II)-amended hematite systems containing dichloroacetamide safeners examined herein, no significant change in k_{obs} was evident as the concentration of MOPS varied from 10 to 50 mM (**Figure 2A**). The difference in results may be due to surface-sorbate interactions observed by Buchholz et al.[62] that are specific to CCl_4, goethite, or both.

Reactions examining the effect of ionic strength were prepared in the same manner as those for MOPS. In reactors containing varying concentrations of NaCl (10 – 200 mM), k_{obs} values associated with the loss of benoxacor and furilazole did not change appreciably (**Figure 2B**).

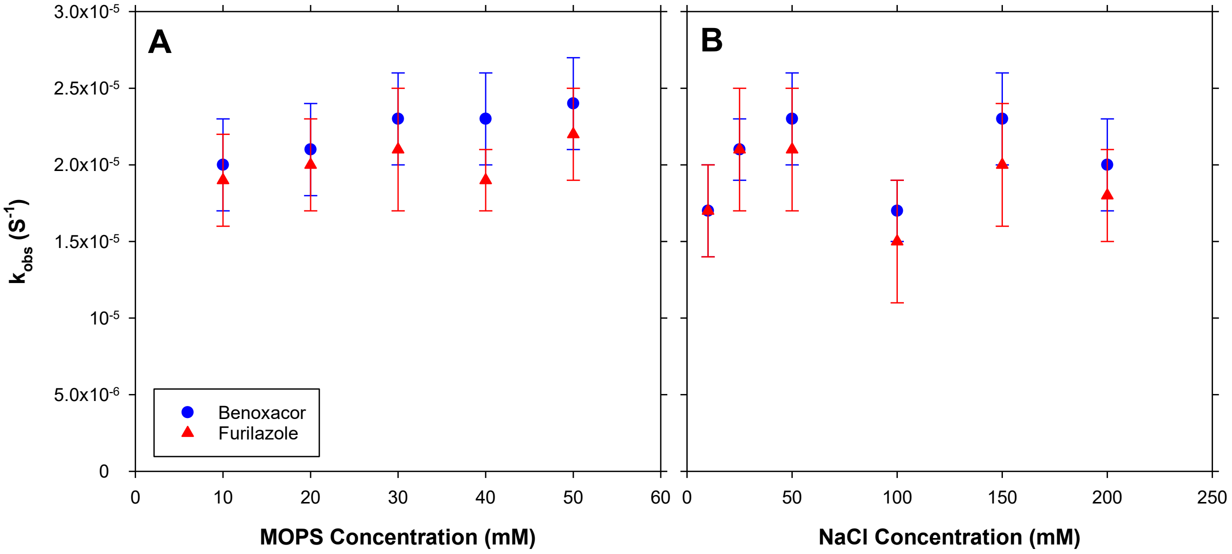


Figure 2. Observed pseudo-first-order rate constants (k_{obs}) for loss of benoxacor and furilazole in Fe(II)-amended hematite slurries as a function of the concentration of **(A)** MOPS and **(B)** NaCl. Frame A conditions: $[\text{benoxacor}]_0 = 20$ μM or $[\text{furilazole}]_0 = 20$ μM, $[FeCl_2]_0 = 5.0$ mM, [NaCl] = 50.0 mM, hematite loading = 10 g/L, pH 7.0. Frame B conditions: $[\text{benoxacor}]_0 = 20$ μM or $[\text{furilazole}]_0 = 20$ μM, $[Fe(II)]_0 = 5.0$ mM, [MOPS] = 30.0 mM, hematite loading = 10 g/L, pH 7.0. Error bars represent 95% confidence intervals associated with linear regressions of ln[safener] versus time plots (*n* typically equals 6) used to calculate k_{obs} values.

3.2 Control Experiments in Heterogeneous Systems.

Prior to examining the effects of binary (hematite + birnessite) mineral systems on transformations of dichloroacetamide safeners, control experiments were performed to determine the rate of Fe(II) oxidation by birnessite and the influence of Mn(II) (a reduction product of birnessite) on Fe(II) sorption in hematite slurries.

Oxidation of Fe(II) by birnessite (a Mn(IV) oxide) is thermodynamically favorable under environmentally-relevant pH/pE conditions and the anaerobic conditions examined herein.[35,36] To quantify the extent of Fe(II) oxidation in systems containing birnessite, reactions were performed in which oxidation of Fe(II) was monitored over ~4 h and an observed pseudo-first-order rate constant was determined. In the presence of 1 g/L birnessite at pH 7.0 and 6.0 mM Fe(II), the initial, aqueous Fe(II) concentration decreased by 40% after 4 h and was presumably oxidized to Fe(III) and/or adsorbed onto birnessite (**Figure S10**).

Oxidation of Fe(II) by birnessite results in the reduction of Mn(IV) to Mn(II). Therefore, the effects of Mn(II) on sorption of Fe(II) onto hematite was examined. Fe(II) adsorption was monitored in hematite slurries under conditions where the Mn(II)/Fe(II) molar ratio was 0, 0.5, 1.0, and 2.0 (**Figure S11**). In the absence of added Mn(II), 42% of the added Fe(II) was detected in the supernatant of the hematite slurries after an incubation time of 3 h, suggesting that 58% of the added Fe(II) was adsorbed. At Mn(II)/Fe(II) molar ratios of 0.5 and 1.0, the presence of Mn(II) did not have an appreciable effect on the extent of Fe(II) sorption. In systems with Mn(II)/Fe(II) = 2.0, the fraction of initial Fe(II) quantified in the aqueous phase decreased to 17%, suggesting that the presence of Mn(II) modestly enhanced the extent of Fe(II) sorption (e.g., via heteroaggregation) and/or that the added Mn(II) (as 99.9% $MnCl_2•(H_2O)_4$) introduced minor amounts of species (e.g., Mn(IV)) capable of oxidizing Fe(II).

3.3 Effects of Binary-Mineral Systems.

The effect of Mn(IV) oxides and the combined effects of Mn(IV) oxides and Fe(III) oxides on the reduction of dichloroacetamide safeners have not been studied previously. To determine the influence of Mn(IV) oxide on transformation rates of benoxacor, dichlormid, and furilazole, each safener was monitored (in separate slurries) in the presence of Fe(II)-amended birnessite, Fe(II)-amended hematite, and Fe(II)-amended binary-mineral systems (birnessite + hematite). The effect of reagent addition order was also determined by comparing the effect of adding the safener, Fe(II), or birnessite at t = 0.

Effect of the Mn(IV) Oxide Birnessite. Sorption of benoxacor onto hematite and birnessite resulted in approximately 20% of the added mass of benoxacor being associated with the solid phases (**Figure S12**). Sorption of dichlormid and furilazole onto both solids was imperceptible (i.e., mass adsorbed not significantly different than 0%). Mass distributions between solid and solution phases were not significantly different in hematite versus birnessite slurries. A previous investigation of dichloroacetamide sorption onto hematite also reported that partitioning to the solid phase was slight (<2% of the initial concentrations of dichloroacetamides added to the suspensions).[17] In the absence of natural organic matter, sorption of dichloroacetamides is likely influenced by nonspecific interactions (e.g., London dispersion forces) and by the hydrophobicity of the dichloroacetamides.[17]

In the presence of Fe(II)-amended birnessite with no added hematite, reduction rates of dichlormid, benoxacor, or furilazole were too slow to quantify after sampling over 6 h (data not shown). Fe(II) oxidation by birnessite has a half-life > 4 h in such slurries (**Figure S10**). Collectively, these findings suggest that Fe(II)-amended birnessite alone is insufficient to transform dichloroacetamides, despite the persistence of Fe(II) in such systems. A control reaction containing Fe(II) in the absence of a mineral phase did not show any discernible loss of Fe(II) over a 14-day period (data not shown), indicating that trace levels of oxygen in the anaerobic chamber were not sufficient to appreciably oxidize Fe(II).

In the slurries of Fe(II)-amended hematite + birnessite, no loss of dichlormid was observed over the period of observation (6 h); however, transformation rates of benoxacor and furilazole were sufficiently rapid to generally permit quantification of k_{obs} values (**Figure 3**). These observations are consistent with previous work,[17] which has shown that transformation of dichlormid is approximately an order of magnitude slower than that of benoxacor in Fe(II)-

amended hematite and goethite; furilazole was not evaluated in this prior work. These results also indicate that hematite is likely providing a reactive surface that facilitates electron transfer from Fe(II).[57]

In Fe(II)-amended binary-mineral systems, k_{obs} values for loss of benoxacor and furilazole were strongly influenced by the molar ratio of Fe(II)/Mn(IV) oxide (**Figure 3**). As the Fe(II)/Mn(IV) oxide ratio increased from 0.2 to 2.0, k_{obs} values for loss of benoxacor increased by a factor of 12 (**Figure 3**). As the Fe(II)/Mn(IV) oxide ratio increased from 0.2 to 1.0, k_{obs} values for loss of furilazole increased by a factor of 2. As Fe(II)/Mn(IV) oxide ratios increased from 1.0 to 2.0, k_{obs} values for loss of furilazole did not change appreciably (**Figure 3**).

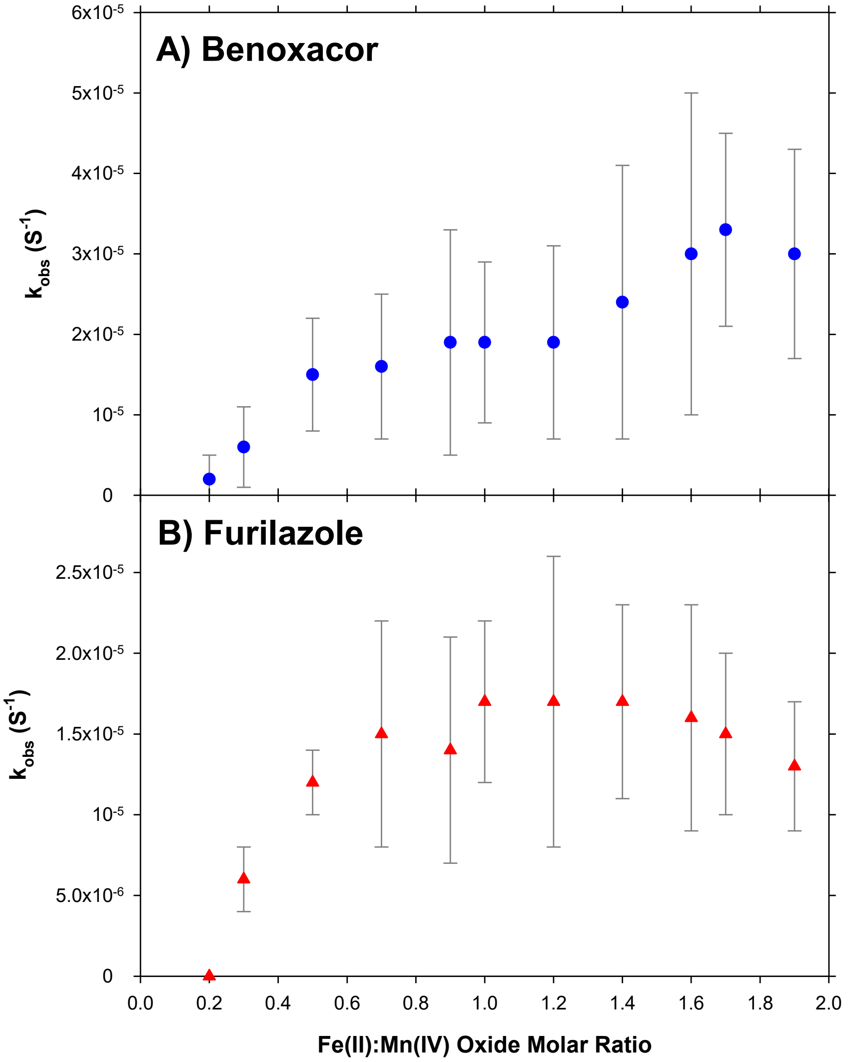


Figure 3. Observed reduction rate constant (k_{obs}) for **(A)** benoxacor and **(B)** furilazole with changing molar ratio of Fe(II) to Mn(IV) oxide. Reaction conditions: $[benoxacor]_0 = 20$ µM or $[furilazole]_0 = 20$ µM, hematite loading = 9 g/L, Mn(IV) oxide loading = 1 g/L, [MOPS] = 30.0 mM, [NaCl] = 50.0 mM, pH 7.0. Error bars represent 95% confidence intervals associated with linear regressions of ln[safener] versus time plots (n typically equals 6) used to calculate k_{obs} values.

A further experiment was performed with benoxacor to determine whether the change in k_{obs} values depicted in **Figure 3** resulted from oxidation of Fe(II) by Mn(IV) oxide. Duplicate reactions were performed for benoxacor in Fe(II)-amended hematite systems. After approximately 4 h of reaction time, 1 g/L of birnessite was added to one of the reactors, after which time the transformation of benoxacor slowed in this reactor relative to the no-added-birnessite system (**Figure 4**). At the time birnessite was added (t = 4 h), the fraction of the initially added benoxacor remaining in both reactors was approximately 82%. In the absence of birnessite, 56% of the remaining benoxacor had transformed by t = 50 h. In the reactor amended with birnessite, only

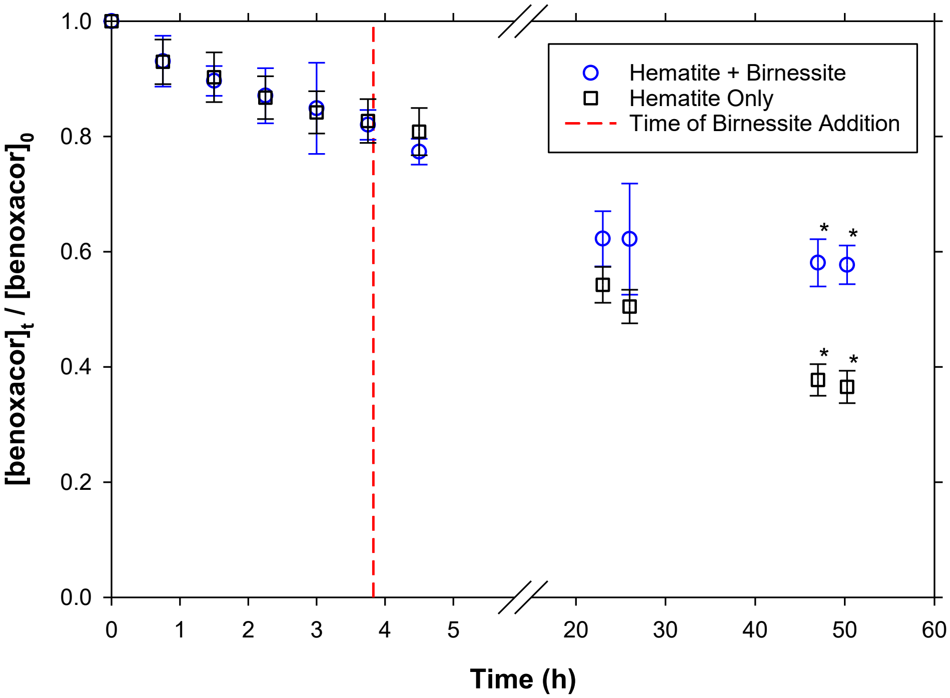


Figure 4. Comparison of the reduction of benoxacor in the absence of and after the addition of birnessite. Reactor conditions: hematite loading = 10 g/L, $[\mathrm{Fe(II)}]_0$ = 3.0 mM, $[\mathrm{benoxacor}]_0$ = 20 μM, [MOPS] = 30.0 mM, [NaCl] = 50.0 mM, pH 7.0. Dotted line indicates the addition of 1.2 g/L birnessite. Error bars represent 95% confidence intervals calculated as t•u_x, where t is Student's t value and u_x is the standard uncertainty in x (n = 1 per time point).[60] Hematite-only data are significantly different (at the 95% confidence level) than birnessite data at 47 h and 50 h (marked with asterisks *).

30% of the remaining benoxacor had transformed by t = 50 h. Natural agricultural soils contain between 0.10 and 0.74 wt% total manganese and between 1.4 and 2.8 wt% total iron.[63] On average, manganese makes up 10 – 30 wt% of the total iron + manganese loading.[63] In the binary-mineral system described in **Figure 4**, the added birnessite amounted to approximately 10 wt% of the total solids loading; a larger fraction of birnessite would likely be sufficient to effectively stop the reduction of benoxacor. These findings illustrate the importance of considering the effects of more than one mineral phase when seeking to better represent the redox chemistry of natural systems using laboratory experiments of intermediate complexity.

A previous study examining the oxidation of Fe(II) by birnessite at varying pH conditions concluded that the oxidation of Fe(II) at pH > 4 is controlled by reactions at the surface of birnessite.[64] As Fe(II) was oxidized, redox-active surface sites on birnessite minerals were exhausted, thereby slowing the Fe(II)-oxidation rate over time.[64] An additional study suggests that heteroaggregation can also block redox-active sites and thereby attenuate birnessite-mediated oxidation of Fe(II) in mixtures of MnO_2 and iron (hydr)oxides.[65] In our hematite + birnessite systems, heteroaggregation may also limit access of safeners to hematite-associated Fe(II), which (along with Fe(II) oxidation by Mn(IV)) could contribute to the decrease in reactivity observed upon addition of birnessite (**Figure 4**).

Effect of Reagent Addition Order. To determine effects of reagent addition order, the reduction of benoxacor was monitored in two sets of paired reactions: (1) adding Fe(II) last (i.e., at t = 0) compared to adding benoxacor last, and (2) adding birnessite last compared to adding benoxacor last (**Figure 5**). These two comparisons are designed to model environmental systems in which the safener is present (1) prior to anaerobic conditions being established and (2) prior to Mn(IV) oxide formation (e.g., via oxidation of Mn(II)).

The comparison of Fe(II) and benoxacor addition at t = 0 yielded similar results for the reduction of benoxacor (**Figure 5A**). Likewise, addition of Mn(IV) oxide at t = 0 yielded results that were not statistically different (based on Student's *t* test of k_{obs} values) from addition of the safener at t = 0 (**Figure 5B**). As addition order did not significantly affect the transformation rate of benoxacor, surface reaction (eq 2) likely represents the rate-limiting step in these systems. If, for example, the adsorption reaction (eq 1) were rate-limiting, a slower loss of the parent safener (benoxacor) should be observed when the safener (rather than Fe(II)) is added at t = 0.

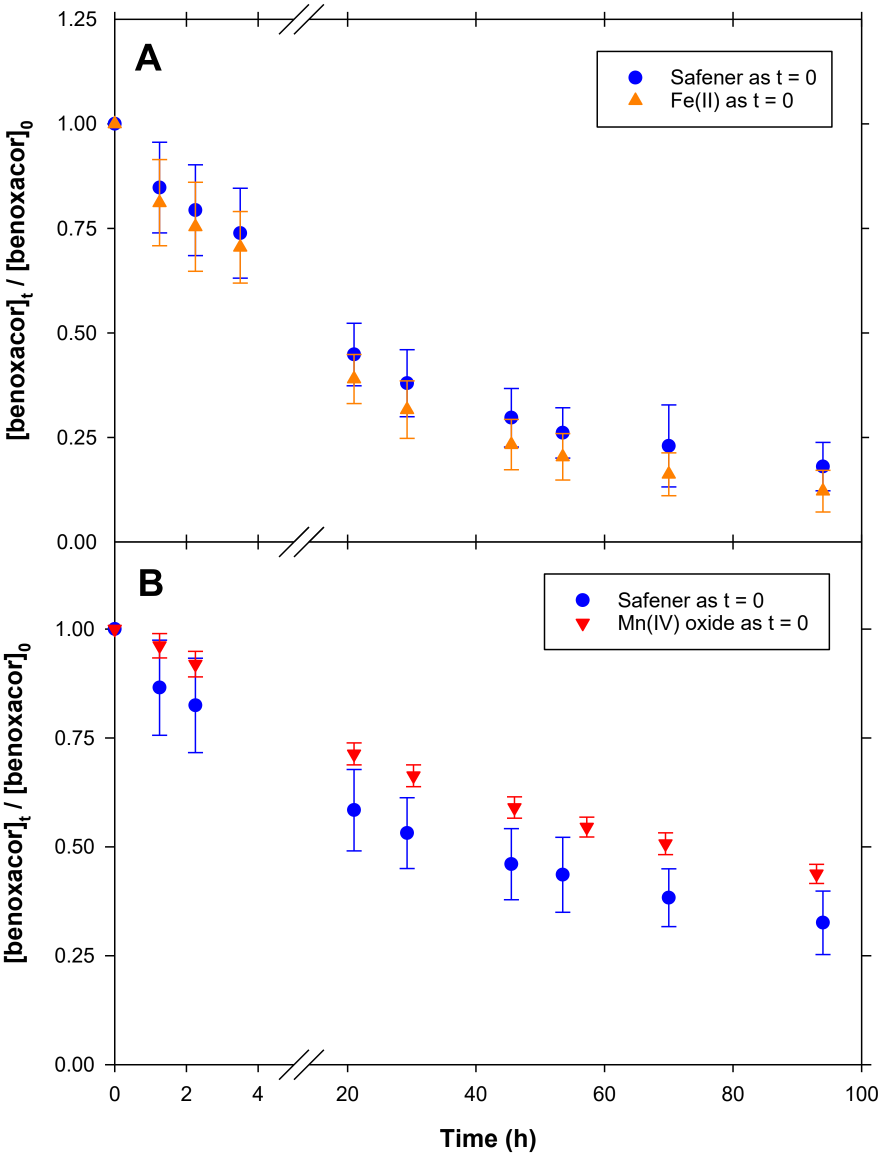


Figure 5. Comparison of benoxacor reduction as a function of order of reagent addition. Data shown in **(A)** compare the effects of adding the safener (benoxacor) or Fe(II) last (i.e., at t = 0). Data shown in **(B)** compare the effects of adding the safener or Mn(IV) oxide last (i.e., at t = 0). Frame A conditions: hematite loading = 10 g/L, $[Fe(II)]_0$ = 3.0 mM, $[benoxacor]_0$ = 20 µM, [MOPS] = 30.0 mM, [NaCl] = 50.0 mM, pH 7.0. Frame B conditions: hematite loading = 9.8 g/L, Mn(IV) oxide loading = 0.2 g/L, $[Fe(II)]_0$ = 3.0 mM, $[benoxacor]_0$ = 20 µM, [MOPS] = 30.0 mM, [NaCl] = 50.0 mM, pH 7.0. Error bars represent 95% confidence intervals calculated as t•u_x, where t is Student's t value and u_x is the standard uncertainty in x (n = 1 per time point).[60]

4. CONCLUSIONS

In this work, the herbicide *S*-metolachlor and surfactants SDS, MyTAB, and Triton® X-100 did not appreciably impact abiotic reductive dechlorination rate constants of dichloroacetamide safener benoxacor at commercially relevant formulation ratios in solutions with Cr(II) as a model homogeneous reductant. Various concentrations of MOPS buffer and NaCl (as an ionic strength adjustor) exerted no appreciable effect on the transformation rates of benoxacor or furilazole in Fe(II)-amended hematite systems. Dichlormid was the least reactive in these systems; no transformation was observed during the sampling period. Accordingly, dichlormid may be more persistent than benoxacor and furilazole under iron-reducing conditions.

The co-occurrence of birnessite and hematite in Fe(II)-amended slurries slowed rates of reductive dechlorination of benoxacor and furilazole relative to rates measured in the absence of birnessite. Fe(II)-amended slurries containing birnessite (but not hematite) did not result in any discernible transformation of dichloroacetamide safeners. Accordingly, Fe(II) adsorbed onto birnessite is insufficiently stable (toward oxidation by Mn(IV)) or insufficiently reactive (as a reducing agent) to facilitate reductive dechlorination of dichloroacetamide safeners under the conditions examined herein. Increasing the molar ratio of Fe(II)/Mn(IV) oxide caused the transformation rate of benoxacor and furilazole to increase by up to a factor of 12 and 2, respectively, highlighting the utility of multi-mineral systems in the effort to better represent environmental conditions in complex natural soils. Comparisons to Fe(II)-amended hematite slurries in the absence of birnessite revealed that the transformation rate of benoxacor slowed by approximately 50% when birnessite was added at environmentally-relevant Fe-to-Mn ratios. This reduction in transformation rates suggests the environmental persistence of dichloroacetamide safeners may be prolonged when Mn(IV) oxides co-occur with Fe(III) (hydr)oxides in soils and sediments.

Overall, our findings illustrate the complex interactions that can occur when safener-containing formulations encounter aqueous systems enriched in Fe(II), such as anaerobic (e.g., water-logged) soils, sediments, and aquifers.[47,53] Transformation of dichloroacetamide safeners into monochlorinated (and potentially bioactive) products can alter the environmental fate of safeners. To more fully understand the fate of dichloroacetamide safeners and their transformation products in environmental systems, future studies should examine the effects of natural organic matter, other Mn oxide minerals, and Mn-containing fertilizers on safener fate in soils and sediments. Future occurrence studies should also seek to quantify reductive dechlorination products of dichloroacetamide safeners in soils, surface water, and groundwater.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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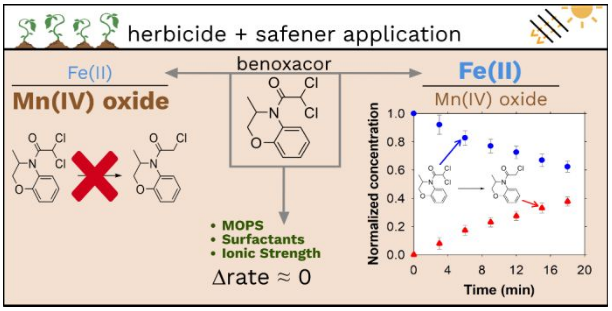

Abiotic redox transformation rates of dichloroacetamide safeners slow when birnessite is added to slurries of Fe(II)-amended hematite.