Electronic Supplementary Information

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

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Includes 21 pages, 7 tables, and 12 figures

Table S1. Properties of Common Oxide Minerals.[a]

Mineral	Chemical Formula	Oxidation State of Metal	Zero Point of Charge
Hematite	Fe_2O_3	+III	8
Birnessite	MnO_2	+IV	2

[a] All data obtained from ref 1

Table S2. List of Reagents, Their Purity, and Vendor.

Reagent	Purity	Vendor
2-chlorobenzonitrile	99%	Acros Organics
3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid, disodium salt hydrate	98+%	Acros Organics
3-morpholinopropane-1-sulfonic acid (MOPS)	≥99.5%	Sigma-Aldrich
acetochlor	96.8%	Sigma-Aldrich
acetonitrile	99.9%	Fisher Scientific
acetonitrile-D3 (CD$_3$CN)	99.8%	Cambridge Isotope Laboratories
benoxacor	99%	Sigma-Aldrich
chromium(II) chloride	99.9%	Acros Organics
dichlormid	>97%	Tokyo Chemical Industry
furilazole	99.9%	Sigma-Aldrich
iron powder, <10 micron	99.5%	Alfa Aesar
iron(II) chloride, anhydrous	99%	Acros Organics
iron(III) oxide	≥99%	Sigma-Aldrich
manganese(II) chloride tetrahydrate	99.9%	Alfa Aesar
manganese(IV) oxide	99.99+%	Acros Organics
methanol	99.9%	Fisher Scientific
myristyltrimethylammonium bromide	99%	Acros Organics
N,N-diallyl-2-chloroacetamide	96.5%	Chem Service
nitric acid	70%	Fisher Scientific
S-metolachlor	98.4%	Sigma-Aldrich
sodium acetate, anhydrous	99%	Alfa Aesar
sodium bicarbonate	99.7+%	Acros Organics
sodium bromide	99.5%	Acros Organics
sodium chloride	≥99%	Fisher Scientific
sodium chloride (high purity)	99.999%	Acros Organics
sodium dodecyl sulfate (aqueous)	20%	Fisher Scientific
sodium hydroxide (aqueous)	50%	Ricca Chemical Company
sodium hypochlorite (aqueous)	5.65 – 6%	Fisher Scientific
sodium nitrate	>99%	Acros Organics
sodium phosphate, dibasic	99+%	Acros Organics
sodium thiosulfate	≥98.0%	Fisher Scientific
sulfuric acid	≥95.0%	Fisher Scientific
toluene	≥99.5%	Fisher Scientific
Triton® X-100	electrophoresis grade	Fisher Scientific
vernolate	98.4%	Chem Service

Text S1. Preparation and Standardization of Aqueous Fe(II)

Fe(II) spiking solutions were prepared in an anaerobic chamber (3% H_2, 97% N_2) by dissolving $FeCl_2$ solid into 40 mL of 30.0 mM MOPS buffer with 50.0 mM NaCl. Fe(II) concentration in solution was standardized prior to each use via UV-vis spectrophotometry. UV-vis standardization followed Stookey[2] and used the disodium salt of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid (ferrozine) as an indicator for Fe(II). The $FeCl_2$ solution was filtered through a 0.2 μM syringe filter and 1.7 mL was combined with 0.6 mL of acetate buffer (1.0 M, pH 5.5) and 1.9 mL of ferrozine solution (2.0 M). The mixture was analyzed via UV-vis spectrophotometry at 562 nm ($\varepsilon = 20{,}735$ $M^{-1}cm^{-1}$)[3] and used within 24 hours of standardization.

Text S2. Reduction and Standardization of Aqueous Cr(II)

Cr(II) stock solutions were prepared following Sivey and Roberts.[3] Under anaerobic conditions (3% H_2, 97% N_2), in an Erlenmeyer flask, $CrCl_2$ and Fe(0) powder (<10 μm) were combined in 18 MΩ•cm water at a $CrCl_2$-to-Fe(0) molar ratio of 1:3. The solution was magnetically mixed at room temperature for approximately 12 hours to reduce any oxidized Cr species to Cr(II). After mixing, the solution was filtered through a 0.2 μm nylon syringe filter and the concentration of Cr(II) was determined using UV-vis spectrophotometry (714 nm, $\varepsilon = 5.6$ $M^{-1}cm^{-1}$).[4] Stock solutions were prepared by diluting the concentrated Cr(II) to 500 μM in 5.0 mM H_2SO_4. Stock solutions were used within 24 hours of standardization. Control experiments determined that the Fe(0) particles, in the absence of Cr(II), did not transform the dichloroacetamide safeners examined herein.

Text S3. Synthesis of Monochlorinated Analogue of Benoxacor

Synthesis reactions followed procedures outlined in Sivey and Roberts[3] with some modifications noted below. Acetonitrile (6 mL) was added to 18 MΩ•cm water (200 mL) in a 250-mL Erlenmeyer flask. Benoxacor (0.10 mmol) was added to the solution as a pure solid and dissolved via sonication. The solution was subsequently sparged with high purity N_2 and transferred to an anaerobic chamber (3% H_2, 97% N_2). After further sparging with chamber atmosphere, 1.0 mmol of $CrCl_2$ was added to the solution to serve as a reductant. The solution was magnetically mixed at room temperature for approximately 1.5 hours to obtain the maximum amount of monochlorinated analogue, without appreciable formation of the deschlorinated analogue (as determined by gas chromatography-mass spectrometry, GC-MS). To quench the reaction, the solution was removed from the anaerobic chamber and magnetically mixed to oxygenate the solution and oxidize any remaining Cr(II). Products were isolated via extraction into toluene and volatilization of the solvent under forced air.

Synthesis results were confirmed via GC-MS analysis and further characterized via proton nuclear magnetic resonance (^{1}H NMR), as described below in **Text S4**. The product was reconstituted in toluene for preparation of calibration standards.

Text S4. Characterization of Monochlorinated Analogue of Benoxacor

Characterization via ^{1}H NMR was carried out on a JEOL 400SS at 290 K and 399.78 MHz, using CD_3CN solvent. Chemical shifts for the monochlorinated analogue were compared to those reported for benoxacor in the literature.[5] Chemical shifts for benoxacor are: δ 1.22 (C9, d, 3H), 4.24 (C2, d, 2H), 4.69 (C3, b, 1H), 6.78 (C11, s, 1H), 6.9-7.0 (C7-8, c, 2H), 7.17 (C6, t, 1H), and 7.61 (C5, b, 1H).[5] For consistency, carbon atom numbering in the monochlorinated analogue matches those used by Miller, et al.[5] Chemical shifts for monochlorinated product are as follows (**Figure S1**): δ 1.15 (C9, b, 3H), 4.17 (C2, d, 2H), 4.33-4.40 (C3, 2d, 1H), 6.76 (C11, s, 2H), 6.89 (C6-8, t, 3H), and 7.07 (C5, t, 1H). Shifts at δ 1.90 and 2.14 correspond to CD_3CN and toluene, respectively; toluene is likely residual from the extraction step of the synthesis.

Analysis via GC-MS provided further information on the purity of the product. GC-MS methodology is described below in **Text S6**. No unidentifiable peaks were present on the GC-MS chromatogram (**Figure S2**) and the presence of the deschloro analogue was negligible. GC-MS analysis also allowed for quantification of the amount of parent compound present and calculation of the monochlorinated analogue concentration for preparation of calibration standards.
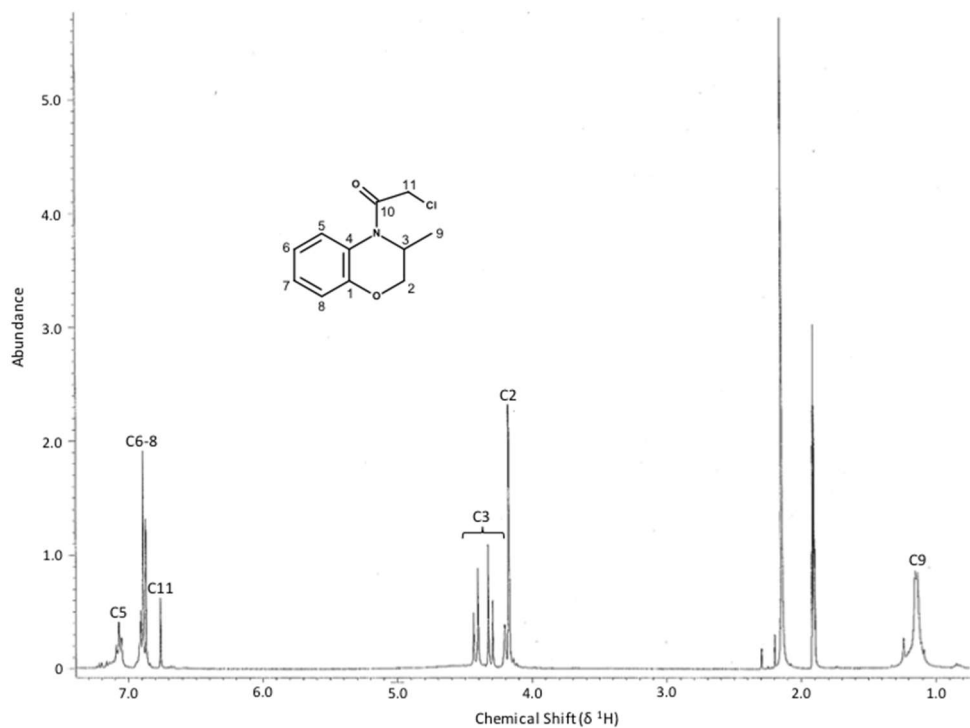
Figure S1. ^{1}H NMR spectrum for the monochlorinated analogue of benoxacor in CD$_3$CN. For consistency, carbon numbering follows that of Miller, et al.[4] Chemical shifts at δ 1.90 and 2.14 correspond to CH$_3$CN and toluene, respectively.
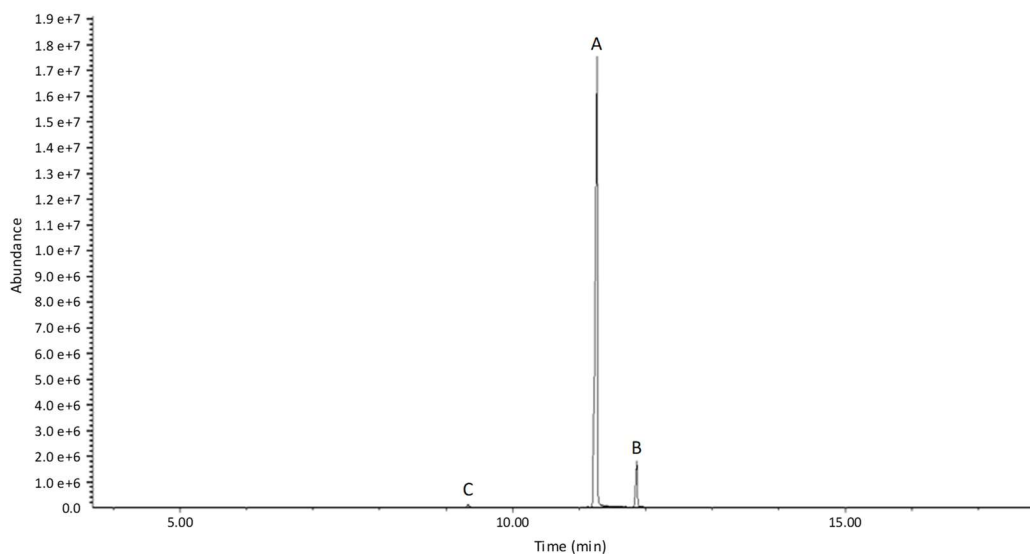

Figure S2. GC-MS chromatogram for the monochlorinated benoxacor synthesis product. Peak A corresponds to the monochlorinated analogue, peak B corresponds to benoxacor, and peak C corresponds to the deschloro analogue.

Text S5. Sorption of dichloroacetamide safeners to hematite and birnessite

Adsorption of the safeners benoxacor, dichlormid, and furilazole to Fe(III) oxide and Mn(IV) oxide was experimentally determined. Adsorption reactors were prepared at room temperature in 40-mL amber glass vials with Teflon-lined caps. Reactors contained 15 mL of aqueous slurry containing 10 g/L solids as either Fe(III) oxide or Mn(IV) oxide in 30.0 mM MOPS buffer at pH 7.0 with 50.0 mM NaCl. Benoxacor, dichlormid, or furilazole was added as a methanolic spike at 20 µM. Adsorption reactors were mixed continuously on a vial rotator for three days before aliquots were centrifuged (13,000 rpm, 10 min) and extracted into toluene for analysis via GC. Aliquots taken from adsorption reactors after 4 d confirmed that equilibrium between the aqueous and solid phases was reached within 3 d. The extent of sorption was quantified as the difference between added (initial) concentrations and concentrations measured in filtrates. The sorptive behavior of reduction products was not investigated; however, reductive dechlorination products of monochloroacetamides are anticipated to have a lesser affinity for the examined mineral phases due to their lower molar volume[3] and lower octanol-water partition coefficients (Table 1, main text) relative to dichloroacetamides.

Text S6. Instrument Parameters

GC analyses were performed on an Agilent 7890A GC with µECD and an Agilent 5975C MSD. Both µECD and MS detection used a single, splitless injection of 1 µL. Inlet temperature was 250 ^{0}C for µECD and 280 ^{0}C for MS detection. MS transfer line temperature was 280 ^{0}C. An Agilent DB-5MS+DG column (30 m length, 250 µm inner diameter, 0.25 µm film thickness) was used with both detectors. Carrier gas for both systems was He, with a flow rate of 2.0 and 1.0 mL/min for µECD and MS detection, respectively. Total run time for both the µECD and MS methods was 18.00 minutes. The temperature ramp program for both µECD and MS detection is given in **Table S3**. The retention times for µECD and the retention times and quantitation ions for MS detection are given in **Table S4**.

Table S3. GC Oven Temperature Program for Both µECD and MS Detection. Total Run Time Was 18.00 Minutes.

	Rate (^{0}C/min)	T (^{0}C)	Hold Time (min)
Initial	---	85	0.5
Ramp	12	280	1.25

Table S4. GC Retention Times for All Analytes with Both µECD and MS Detection, and Quantitation Ions Used with Selected Ion Monitoring (SIM) for MS Detection.

Analyte	µECD Retention Time (min)	MSD Retention Time (min)	Quantitation Ions (m/z) [a]
Internal Standard (CBN) [b]	5.41	5.12	137, 139
CDAA	6.58	6.31	173, 132
Dichlormid	7.24	7.05	207, 172
Vernolate [c]	n.a. [e]	7.95	203, 128
Monochlorinated Furilazole [d]	10.69	n.a. [e]	n.a. [e]
Furilazole [d]	11.02	n.a. [e]	n.a. [e]
Monochlorinated Benoxacor	11.39	11.27	225, 134
Benoxacor	11.99	11.87	259, 120
S-Metolachlor	13.03	12.96	283, 162

[a] Ions are listed with the monoisotopic molecular ion mass first, followed by the most abundant fragment ion with m/z greater than 100
[b] CBN = 2-chlorobenzonitrile
[c] Vernolate was not detected using µECD due to the lack of halogens
[d] Furilazole and the monochlorinated analogue were not analyzed via GC-MS
[e] Not determined

Text S7. Calibration, Limits of Detection, and Extraction Efficiencies

A linear calibration range of 0.3 – 16 µM was employed for all analytes. Peak separation with baseline resolution was observed for all analytes with both µECD and MSD (**Figures S3** and **S4**, respectively). For calibration curves, analyte detector response was normalized to that of the internal standard (2-chlorobenzonitrile, CBN). A typical calibration curve is shown in **Figure S5**, with corresponding instrumental limits of detection (LODs) and correlation coefficient (R^2) values given in **Table S5**.

Table S5. Limits of Detection (LODs) and Correlation Coefficients (R^2) Associated with Calibration Curves Shown in Figure S10.

Analyte	GC-µECD		GC-MS	
	LOD (µM)	R^2	LOD (µM)	R^2
benoxacor	1.2	0.9993	2	0.997
CDAA	0.9	0.9995	0.7	0.9997
dichlormid	1.4	0.9990	1.5	0.998
furilazole	1.3	0.9991	n.d. [a]	n.d. [a]
S-metolachlor	2	0.996	1.4	0.998
monochloro benoxacor	4	0.991	n.d. [a]	n.d. [a]
vernolate	n.d. [a]	n.d. [a]	1.8	0.998

[a] n.d. denotes not determined. Quantification of furilazole and the monochloro analogue of benoxacor were only performed by GC-µECD. Vernolate was not detected by GC-µECD, consistent with the absence of halogen atoms or other electronegative moieties.

For the GC measurements performed herein, instrumental LODs were calculated using eq S1[6]:

$$LOD = \frac{2ts_y}{m}\sqrt{\frac{1}{K}+\frac{1}{I\times J}+\frac{\bar{x}^2}{J\sum(x_i-\bar{x})^2}} \hspace{2cm} [S1]$$

where I is the number of calibration standards; J is the number of replicates of each standard; K is the number of replicates of the unknown; t is the Student's t, obtained from a one-tailed t-distribution with $(I\times J) - 2$ degrees of freedom; m is the slope of the calibration curve; s_y is the standard error of y for the calibration curve; and $\bar{x}$ is the mean concentration of the calibration standards.
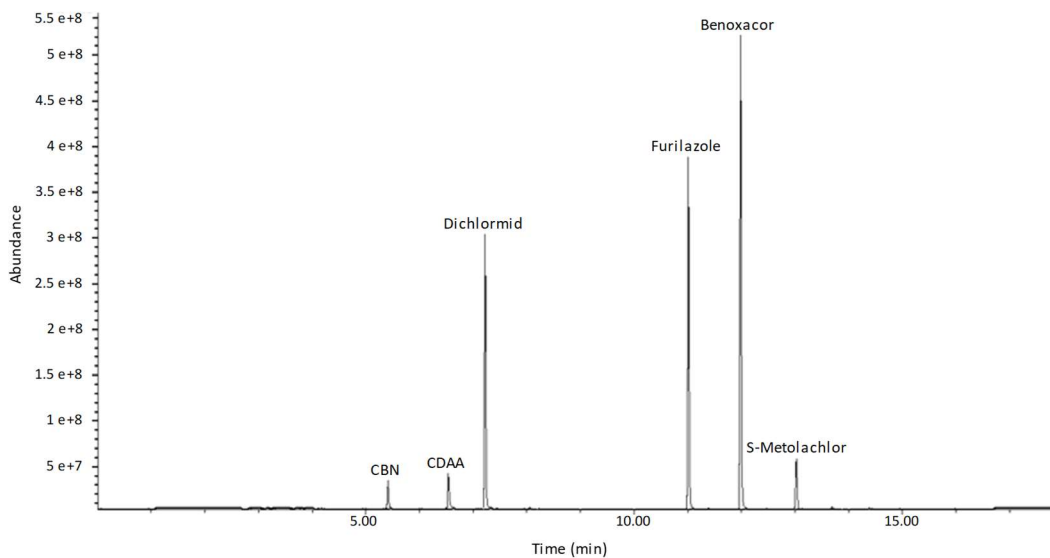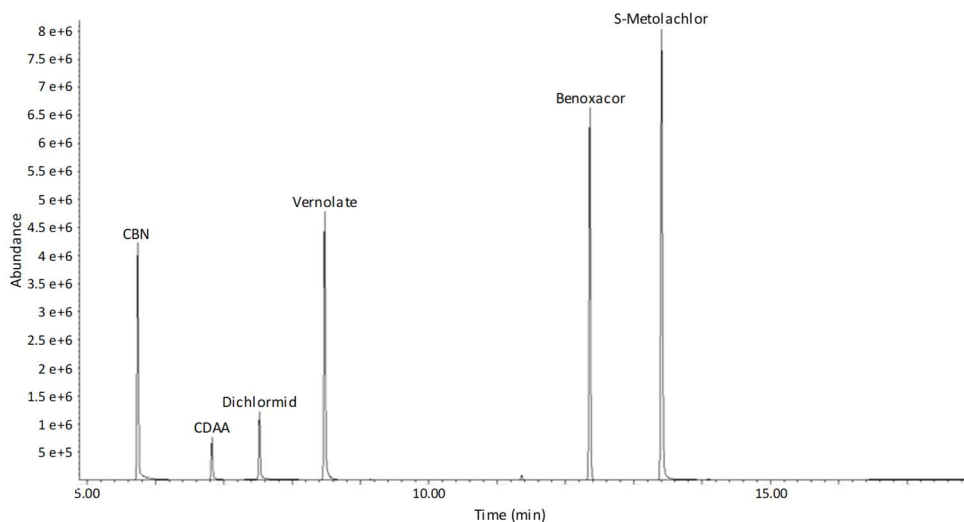
Figure S3. GC-μECD chromatogram of a calibration standard. All analytes are at approximately 16 μM, except for the internal standard (CBN, 10.2 μM). Peak separation and retention times are typical for all standards. The monochlorinated benoxacor analogue is not shown as it was calibrated with a separate set of standards; the monochlorinated furilazole analogue is also not shown as reference material was not available for this analyte (see Table S4 for retention times). Vernolate lacks halogen atoms and was not detected with μECD.

Figure S4. GC-MS chromatogram of a calibration standard. All analytes are at approximately 16 μM, except for the internal standard (CBN, 10.2 μM). Peak separation and retention times are typical for all standards. The monochlorinated analogue of benoxacor is not shown as it was calibrated with a separate set of standards (see Table S4 for retention time). Furilazole and its monochlorinated analogue are not shown as they were not analyzed using MS detection.
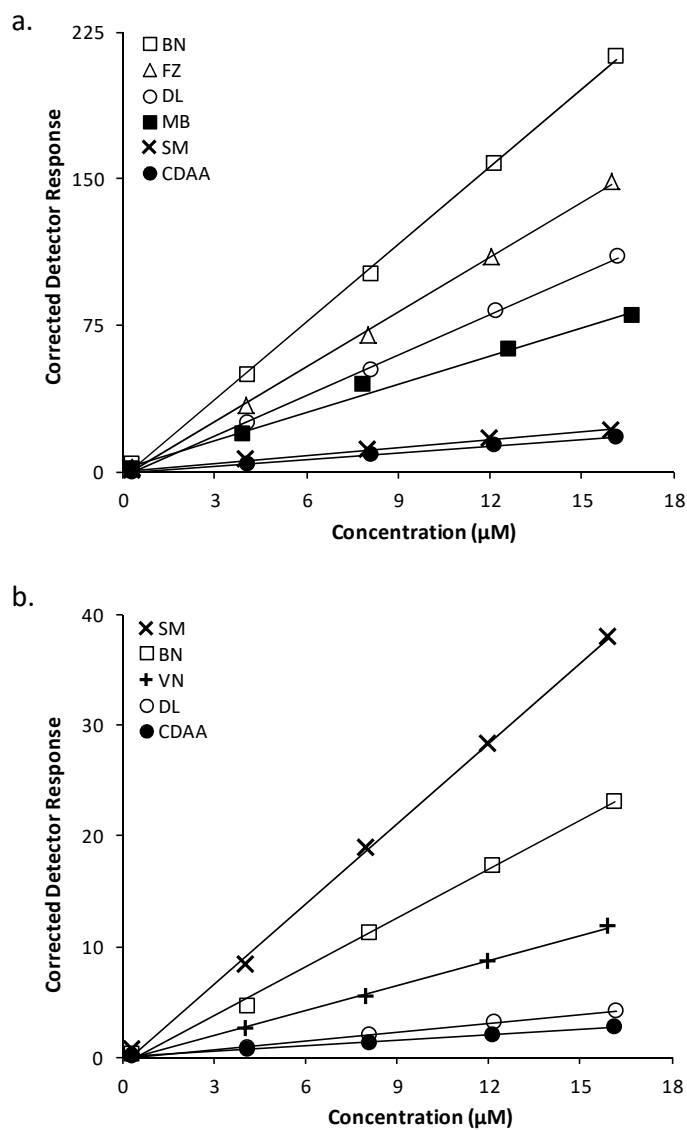
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Figure S5. Calibration curves for all analytes with **a.** μECD and **b.** MS detection. Detector response was normalized to the internal standard response for all analytes. Analytes are abbreviated as follows: benoxacor (BN), dichlormid (DL), furilazole (FZ), *S*-metolachlor (SM), monochlorinated benoxacor (MB), and vernolate (VN). Limits of detection (LODs) and correlation coefficient (R^2) values are given in Table S5.

To quantify analyte recovery following extraction into toluene, extraction efficiencies were experimentally determined for benoxacor, dichlormid, and furilazole, both alone and in the presence of surfactants. For extraction efficiencies in the absence of surfactants, aqueous solutions of analytes were prepared in 30.0 mM MOPS buffer at pH 7.0 with 50.0 mM NaCl. Analytes were added to the solution as a methanolic spike (7–14 µM). At room temperature in 4-mL amber glass vials with Teflon-lined caps, 1.0 mL of aqueous analyte solution was combined with either 1.0 or 2.0 mL of toluene and shaken vigorously by hand for approximately 20 seconds. After phase separation, the toluene layer was removed for analysis via GC. GC results were compared with the initial concentrations to obtain extraction efficiencies as a percentage of the amount of analyte in aqueous solution (**Table S6**). Recovery for each analyte was comparable between extractions using 1:1 and 2:1 toluene-to-aqueous volume ratios. Extraction efficiencies greater than 100% likely result from temporal variability in the relative detector response between the internal standard and analytes.

For extraction efficiencies in the presence of surfactants, aqueous solutions were prepared in the same manner as in the absence of surfactants, with either SDS, MyTAB, or Triton® X-100 present at 5 µM. Extractions with surfactants were performed following the same methods as described above, using only a 1:1 toluene-to-aqueous volume ratio and an aqueous safener concentration of 10 µM (**Table S6**).

Table S6. Extraction Efficiency for Safeners in the Absence and Presence of Surfactants at 5 μM. Values are Given as Percentages ± 95% Confidence Intervals.

Safener	Without Surfactant	SDS [a]	MyTAB [b]	Triton® X-100
Benoxacor	126 ± 8	140 ± 15	138 ± 12	159 ± 13
Dichlormid	121 ± 4	139 ± 11	135 ± 9	161 ± 9
Furilazole	100 ± 20	88 ± 12	85 ± 13	86 ± 13

[a] Sodium dodecyl sulfate (SDS)
[b] Myristryltrimethylammonium bromide (MyTAB)

Text S8. Recoveries Following Centrifugation

Recovery of analytes after centrifugation was quantified experimentally to determine potential loss to the surfaces of plastic centrifuge tubes. Aqueous solutions of the safeners benoxacor, dichlormid, and furilazole were prepared following the same methods as described above for determination of extraction efficiencies. At room temperature, 1.0 mL of aqueous solution was placed into plastic centrifuge tubes and centrifuged for 10 minutes at 13,000 rpm. After centrifugation, samples were extracted into 2.0 mL of toluene, following the method described above. A sample of aqueous solution, subjected to all steps except centrifugation, was analyzed as the control sample. Results from GC analyses were compared to the control sample to determine centrifugation recovery as a percentage of the amount of analyte originally present in the aqueous solution (**Table S7**). While recoveries were not significantly different than 100% for all three safeners, the uncertainty associated with the recovery of furilazole exceeded those of benoxacor and dichlormid.

Table S7. Centrifugation Percent Recovery for Safeners ± 95% Confidence Intervals.

Safener	Recovery (%)
Benoxacor	104 ± 9
Dichlormid	102 ± 8
Furilazole	90 ± 20

Text S9. Furilazole Product Quantification.

In order to account for the temporal variability in µECD response values, analyte concentrations were normalized to the mass balance (total concentration of parent dichloroacetamide and monochlorinated product). For furilazole, reference material was not available for its monochloro or deschloro analogue. We hypothesize that the transformation of

furilazole in the studied systems follows the reductive dechlorination previously observed[3] for benoxacor (**Figure S6**).
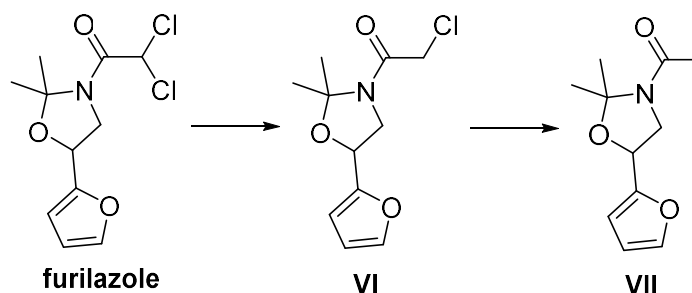

Figure S6. Postulated reductive dechlorination reaction for furilazole.

During GC analysis of furilazole reaction samples, a peak was observed in the chromatogram that was consistent with a monochlorinated analogue of furilazole (**Figure S7**). The peak consistently appeared at the same retention time (10.69 min) prior to furilazole (11.02 min). The peak area for the monochlorinated analogue consistently increased as that of furilazole decreased throughout a time course. In order to approximate a mass balance for reactions containing furilazole, the peak area of the assumed monochlorinated analogue was normalized to the internal standard using the following equation:

$$\text{Area}_{\text{MF,corrected}} = \frac{\text{Area}_{\text{MF}}}{\text{Area}_{\text{CBN}}} \times [\text{CBN}] \qquad \qquad [\text{S2}]$$

where $\text{Area}_{\text{MF,corrected}}$ (μM) is the corrected peak area of monochlorinated analogue of furilazole; Area_{MF} and Area_{CBN} (counts) are the peak areas of the monochlorinated analogue of furilazole and the internal standard, respectively; and [CBN] (μM) is the concentration of the internal standard.
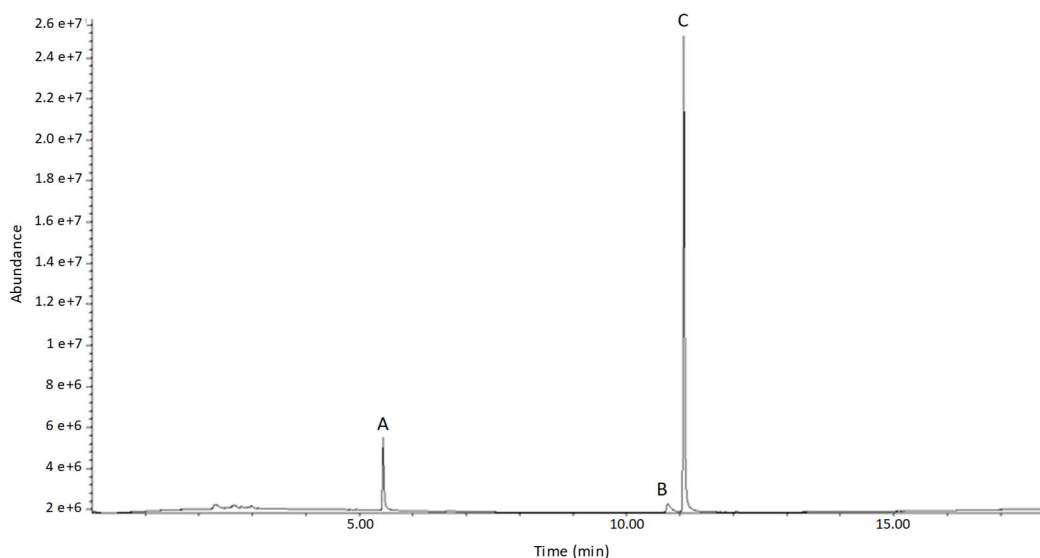
Figure S7. GC/μECD chromatogram from a reaction of furilazole with Fe(II)-amended hematite and birnessite after 5.5 hours. Peak A is the internal standard (CBN, 10.2 μM), peak B is assumed to be the monochlorinated analogue of furilazole, and peak C is furilazole. Reactor conditions: $[furilazole]_0 = 20$ μM, $[Fe(II)]_0 = 18$ μM, Fe(III) oxide loading = 9 g/L, Mn(IV) oxide loading = 1 g/L.
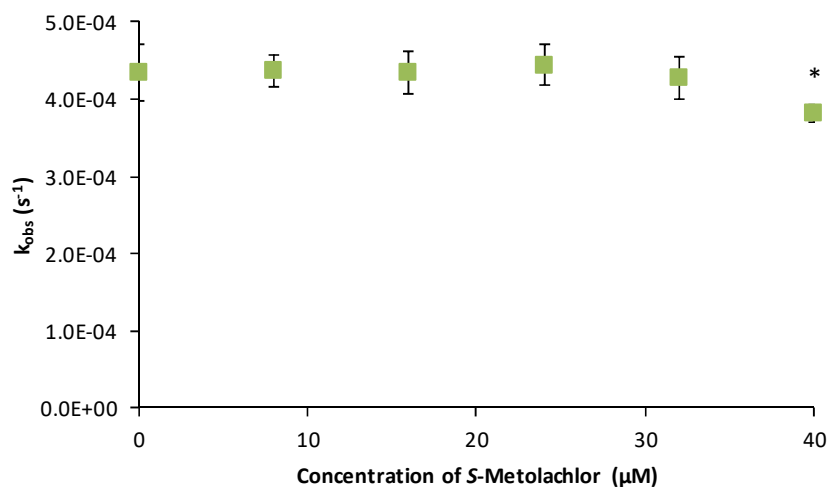

Figure S8. Observed reduction rate constant (k_{obs}) for benoxacor as a function of the concentration of the herbicide, *S*-metolachlor. Reaction conditions: $[benoxacor]_0 = 20$ μM, $[Cr(II)]_0 = 500$ μM, $[H_2SO_4] = 5.0$ mM, $[S\text{-metolachlor}]_0 = 0 - 40$ μM. Error bars represent 95% confidence intervals associated with linear regressions of ln[safener] versus time plots (*n* typically equals 6) used to calculate k_{obs} values. The rate constant at [*S*-metolachlor] = 40.0 μM (indicated with asterisk) is statistically different (at the 95% confidence level) from those at lower concentrations of *S*-metolachlor.
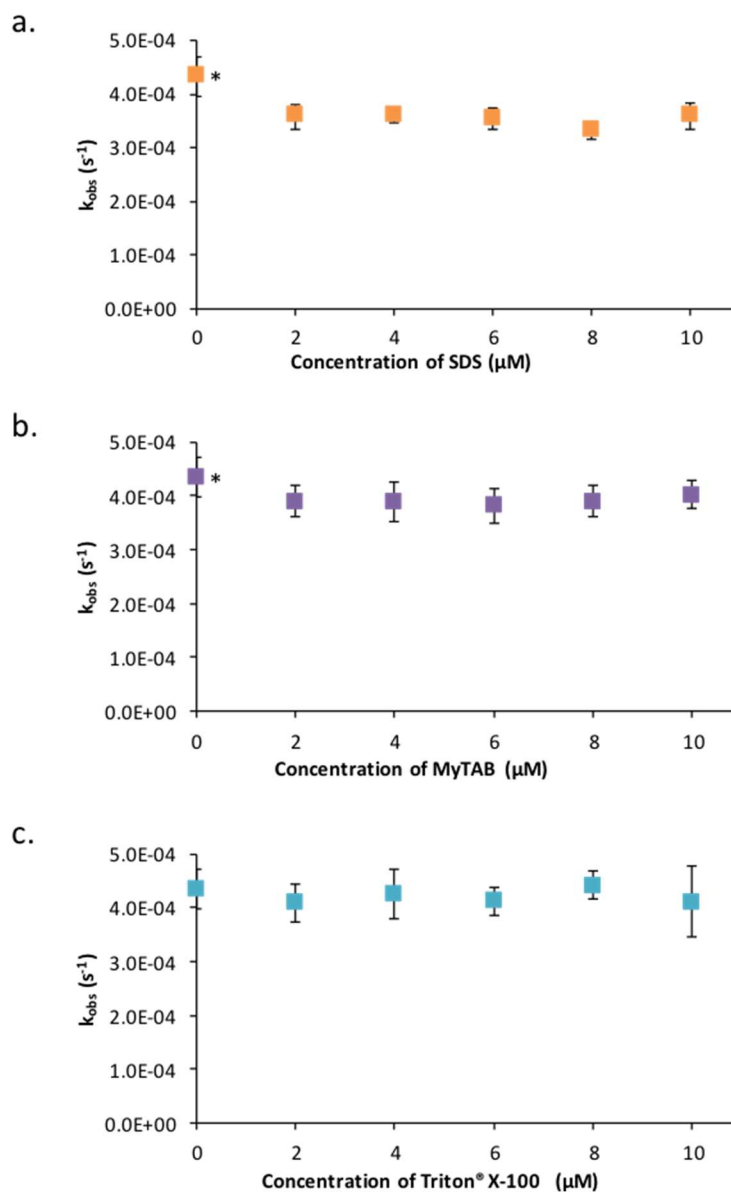
Figure S9. Observed transformation rate constant (k_{obs}) for reductive dechlorination of benoxacor with changing concentration of **a.** sodium dodecyl sulfate (SDS), **b.** myristryltrimethylammonium bromide (MyTAB), and **c.** Triton$^®$ X-100. Reaction conditions: [benoxacor]$_0$ = 20 μM, [Cr(II)]$_0$ = 500 μM, [H$_2$SO$_4$] = 5.0 mM. Surfactant concentration ranged from 0 – 10 μM. 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. For SDS and MyTAB, the rate constant with no surfactant present (indicated with asterisks) is significantly different (at the 95% confidence level) than those in the presence of added surfactant.
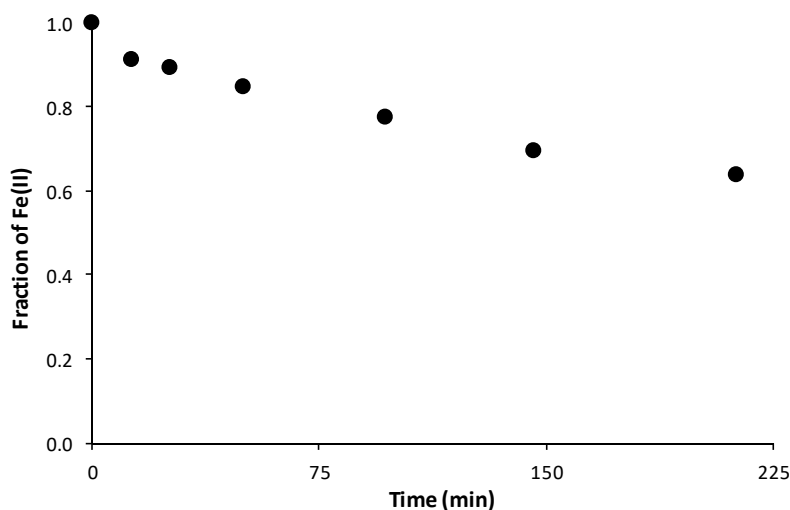
Figure S10. Fraction of initial, aqueous Fe(II) detected in slurries of birnessite (a Mn(IV) oxide) as a function of time. Reactor conditions: Birnessite loading = 1 g/L, $[Fe(II)]_0$ = 6.0 mM, [MOPS] = 30.0 mM, [NaCl] = 50.0 mM, pH 7.0.
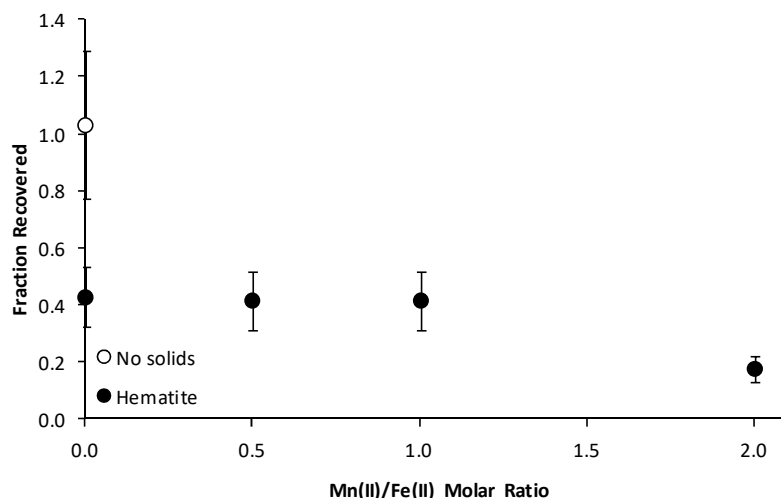

Figure S11. Fraction of aqueous Fe(II) recovered (calculated as $[Fe(II)]_t/[Fe(II)]_0$) as a function of Mn(II)/Fe(II) molar ratio. Reactor conditions: [MOPS] = 30.0 mM, [NaCl] = 50.0 mM, pH 7.0, incubation time = 3 h. In systems amended with solids, the hematite loading was 10 g/L. To achieve Mn(II)/Fe(II) molar ratios > 0, $[Mn(II)]_0$ and $[Fe(II)]_0$ were either 1.5 mM or 3.0 mM. For Mn(II)/Fe(II) molar ratios equal to 0, no Mn(II) was added and $[Fe(II)]_0$ = 6.0 mM. Error bars represent 95% confidence intervals calculated as $t \cdot u_x$, where t is Student's t value and u_x is the standard uncertainty in x (n = 1 per time point).[6]
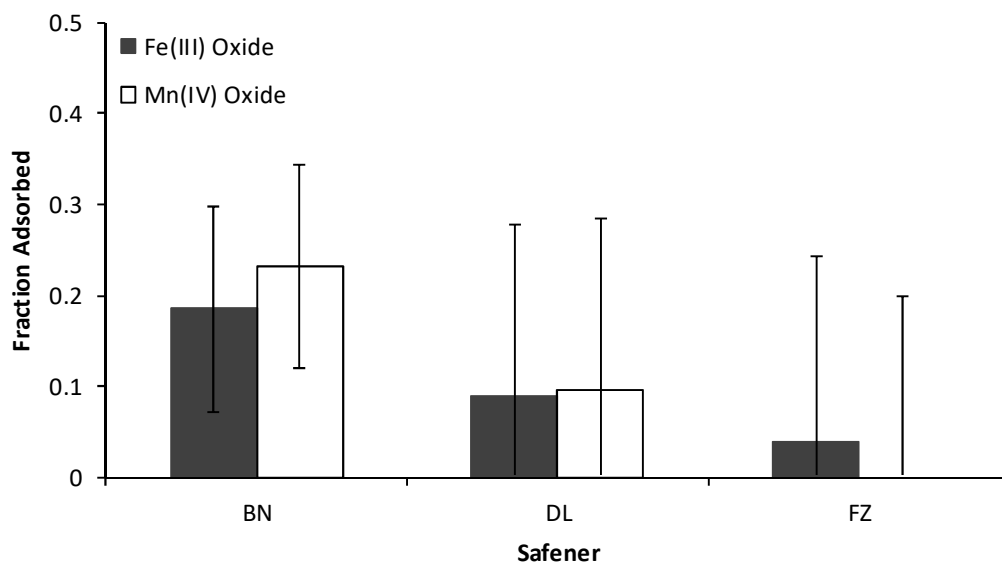
Figure S12. Adsorption of safeners benoxacor (BN), dichlormid (DL), and furilazole (FZ) to Fe(III) oxide (hematite) and Mn(IV) oxide (birnessite). Furilazole and dichlormid adsorption to both solids is not significantly different from zero. Adsorption of benoxacor is not significantly different between Fe(III) oxide and Mn(IV) oxide. Error bars represent 95% confidence intervals calculated as $t \cdot u_x$, where t is Student's t value and u_x is the standard uncertainty in x (n = 1 per time point).[6] Experimental conditions: solids loading = 10 g/L of hematite or birnessite, [MOPS] = 30.0 mM, [NaCl] = 50.0 mM, pH 7.0, [safener]$_0$ = 20 μM, incubation time = 3 d.

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