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Remediating dinoseb-contaminated soil with zerovalent iron

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ABSTRACT

Dinoseb, a dinitroherbicide, was once commonly used in aerial crop dusting of agronomic crops in the western United States. Widespread use combined with improper disposal practices at rural air strips has contaminated numerous sites. Our objective was to determine if zerovalent iron (Fe^0) could remediate dinoseb-contaminated soil. This was accomplished by conducting a series of batch experiments where we first determined if Fe^0 could remove dinoseb in aqueous solutions, then in contaminated soil slurries, and finally, in unsaturated soil microcosms (25 °C, θ_g = 0.30 kg H_2O kg^{-1}). Results showed quantitative dinoseb removal in the presence of Fe^0 in all three media (aqueous solutions, soil slurries, moist soils) and that removal increased by including either ferrous or aluminum sulfate with the iron treatment. Incubating contaminated soils with Fe^0 or Fe^0 plus salts ($FeSO_4$ or $Al_2(SO_4)_3$) resulted in 100% removal of dinoseb within 7 d. Liquid chromatography/mass spectrometry (LC/MS) analysis of degradation products showed the transformations imposed by the iron treatments were reduction of one or both nitro groups to amino groups. These amino degradation products were further transformed to quinonimine and benzoquinone and did not persist. These results support the use of zerovalent iron for on-site treatment of dinoseb-contaminated soil.

1. Introduction

Dinoseb (2-*sec*-butyl-4-6-dinitrophenol) is an extremely toxic phenolic herbicide that was once widely used for the selective control of grass and broadleaf weeds in several crops grown in the United States [1–3]. From a chemical perspective, dinoseb is classified as a dinitroherbicide and contains two electron-withdrawing nitro groups on its benzene ring. This chemical structure impedes electrophillic attack and makes dinoseb recalcitrant to soil microorganism under aerobic conditions [3]. Although dinoseb has not been documented to accumulate in soil when applied at labeled rates [4], high soil concentrations, resulting from improper disposal, can persist in the environment for many years [5–6]. This situation was especially prevalent at rural air strips where dinoseb was commonly used in crop dusting activities and unused product or rinsate was disposed directly to soil. The phenolic form of dinoseb is slightly soluble in water (52 mg l^{-1}) and only moderately sorbed (K_{oc} = 124 l kg^{-1}) by most soils [3,7]. Thus, the recalcitrance and relative mobility of dinoseb make it a prime candidate to contaminate ground or surface water.

Exposure to dinoseb can cause serious health hazards, especially to lungs and eyes [8]. Direct skin contact may cause irritation, yellow stains, burns, and dermatitis [8]. Moreover, dinoseb is a potential teratogen [9] and in 1986, the United States Environmental Protection Agency (USEPA) issued an emergency suspension of dinoseb in the USA due to the significant risk of birth defects and other adverse health effects [10]. Because dinoseb is toxic and persistent, technology efforts are needed to remediate existing dinoseb-contaminated soils. Previous research has documented excellent successes in remediating dinoseb-contaminated soils at the laboratory and field scale using a bioremediation scheme [1,2]. Much of this work originated from Stevens et al. [11,12], who observed that anaerobic cultures were capable of metabolizing dinoseb to acetate and CO_2.

Under reducing conditions, many contaminants can be degraded through reductive reactions. Considerable research has shown that reducing or removing electron-withdrawing moieties from parent structures generally results in more biodegradable products [13–15]. Kaake et al. [4] observed that dinoseb degradation involved nitro group reduction to amino groups followed by replacement with hydroxyl groups. The first demonstration of dinoseb degradation by a pure microbial culture, *Clostridium bifermentans* (KMR-1) was conducted by Hammill and Crawford [16]. They found that dinoseb was successfully degraded (>99% degradation) by KMR-1 within 96 h. However, KMR-1 could not utilize dinoseb as a sole car-

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bon or energy source, and degradation occurred via cometabolism in the presence of a fermentable carbon source.

When soils contain high contaminant concentrations, the toxicity of some chemicals may greatly reduce microbial transformation rates and hinder in situ bioremediation. Stevens et al. [12] tested the ability of the natural microbiota of several Idaho soils to degrade dinoseb and observed that some soils were capable of transforming dinoseb but in the presence of nitrate and high dinoseb concentrations, dinoseb degradation was inhibited in most soils.

One way of overcoming toxicity problems associated with highly contaminated soils is to employ an abiotic approach, such as using zerovalent iron (Fe^0) to chemically transform the contaminant. Previous research supports Fe^0 as a remedial treatment for many hazardous compounds including several pesticides, such as: metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl ethyl) acetamide] [17], alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide] [18], dicamba (3,6-dichloro-O-anisic acid) [19], DDT [(1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane] [20], and 2,6-dinitroaniline herbicides [21]. While much of the earlier research with zerovalent iron was tailored to demonstrating contaminant transformations in aqueous media under anaerobic conditions, other efforts have successfully used zerovalent iron to treat contaminant soil or sediment, with some experiments performed under microaerophillic conditions [22–25].

Possible contaminant removal mechanisms in the Fe^0–H_2O system include reduction (via surface contact or corrosion products), adsorption, precipitation, co-precipitation [26,27] and under some conditions and for certain contaminants, oxidative transformations [28,29]. At near neutral pH, iron corrosion yields an obstructive oxide film of corrosion products that influence contaminant adsorption, diffusion rates and long-term corrosion. Considerable research on Fe^0–H_2O systems has shown that in addition to the two major redox couples (Fe^{II}/Fe^0, $E^0 = -0.44$ V and Fe^{III}/Fe^{II}, $E^0 = 0.77$ V), adsorbed or structural Fe^{II} (structural Fe^{III}/Fe^{II}, $E^0 = -0.34$ to -0.65 V) can be more powerful in reducing contaminants than the Fe^0 surface [27]. Therefore, abiotic reduction in Fe^0–H_2O system will not necessarily be mediated by electrons from the iron metal [27].

To exploit the reduction potential of the Fe^0–H_2O system, use of zerovalent iron is generally implemented under fully anoxic conditions because the presence of oxygen is expected to lower the efficiency of the process by competing with the target contaminants [29], accelerating iron aging (passivation), and cause loss of reactivity [30]. Examples exist, however, where destruction kinetics of certain contaminants by Fe^0 have been accelerated by exposure to air, again lending credence to the fact that direct reduction by the iron surface is not always the main removal mechanism. Tratnyek et al. [31] observed a higher rate of CCl_4 degradation by Fe^0 in an air-purged system ($t_{1/2}$ = 48 min) than in a nitrogen-purged ($t_{1/2}$ = 3.5 h) or oxygen-purged environments ($t_{1/2}$ = 111 h). Satapanjaru et al. [17] found that Fe^0-mediated destruction of metolachlor was faster in batch reactors shaken under aerobic than anaerobic conditions and contributed this increase to the formation and facilitating effects of green rusts, mixed Fe(II)–Fe(III) hydroxides with interlayer anions that impart a greenish-blue color. Joo et al. [28] also observed that the herbicide molinate (*S*-ethyl azepane-1-carbothioate) was much more readily transformed by Fe^0 when shaken in the presence of air than when purged with N_2. These observations lend credence to using zerovalent iron in microaerophillic environments, such as those that might be encountered in treating soils.

Our objective was to use zerovalent iron to remediate a soil from a rural air strip that was contaminated with dinoseb. We report laboratory observations demonstrating the capacity of Fe^0 to reduce dinoseb in aqueous solution and soil slurry, and then demonstrate the effectiveness of Fe^0 to decrease dinoseb concentration in static, unsaturated soil microcosms.

2. Materials and methods

2.1. Materials

An analytical standard of dinoseb (2-sec-butyl-4,6-dinitrophenol) was purchased from Chem Service (West Chester, PA). Ferrous sulfate [$FeSO_4 \cdot 7H_2O$], and aluminum sulfate [$Al_2(SO_4)_3$] were purchased from Aldrich Chemical Co. (Milwaukee, WI). The iron powder used was Aggregate 60D obtained from Peerless Metal Powders (Detroit, MI). A typical size gradation for this iron using a 5 min RO-TAP sieve shaker was as follows: 23% 180 μm, 15% 150 μm, 16% 115 μm, 26% 75 μm, 13% 45 μm, and 7% <45 μm. Given this distribution, we calculate that the average diameter of the zerovalent iron was ~111 μm. The surface area of the iron source used in this study was measured by gas adsorption with the Brunauer, Emmet and Teller theory and determined to be 3.85 $m^2\ kg^{-1}$ (Micromeritics, Norcross, GA). We acknowledge that measured surface area does not account for the dynamic nature of the oxide film formation that occurs during corrosion in aqueous solutions. Dinoseb-contaminated soil was collected from the Coalinga Airport in Fresno County, CA.

2.2. Solution experiments

Aqueous phase experiments were conducted to determine the efficacy of zerovalent iron to degrade dinoseb. The initial dinoseb concentration was 30 mg l^{-1} (0.166 mM) and prepared in deionized water. Batch procedures included treating 100 ml of aqueous dinoseb with 0.25 g, 0.5 g, and 1.0 g of iron powder in 250-ml Erlenmeyer flasks. These iron loadings correspond to 0.25%, 0.5%, and 1% on a weight per volume basis (w/v) or 2.5 g l^{-1} (44.77 mM), 5 g l^{-1} (89.53 mM), and 10 g l^{-1} (179.06 mM). The initial surface area of these iron loadings were 0.00965 $m^2\ l^{-1}$ (0.25% Fe^0), 0.01925 $m^2\ l^{-1}$ (0.5%), and 0.0385 $m^2\ l^{-1}$ (1%).

Flasks were covered with Parafilm M (American National Can, Chicago, IL) and agitated on an Gryrotory shaker (G-10, New Brunswick Scientific Company, New Brunswick, NJ) at 140 revolutions min^{-1} at ambient temperature. All treatments were conduced in triplicate. At preselected times, 1 ml aliquots were removed and transferred to 1.7-ml polypropylene microcentrifuge tubes and centrifuged at 13,000 × *g* for 10 min. Temporal changes in dinoseb concentration were measured by high performance liquid chromatography (HPLC) (procedure described below).

We also determined the capacity of ferrous sulfate to enhance dinoseb removal by zerovalent iron. Batch procedures included treating 100 ml of 30 mg l^{-1} (0.166 mM) aqueous dinoseb with 0.25% (w/v) of iron powder in 250-ml Erlenmeyer flasks. Flasks were covered and agitated on an orbital shaker at ambient temperature. After 9 h of treating dinoseb with Fe^0 alone, 0.5 g of $FeSO_4$ was added in the dinoseb–iron–water system. Changes in dinoseb concentration were measured by HPLC at preselected times.

Another experiment compared the effect of ferrous and aluminum sulfate salts on dinoseb destruction by zerovalent iron. Aqueous dinoseb (30 mg l^{-1}) was treated with 0.5% (w/v) Fe^0 and equal concentrations of $FeSO_4$, or $Al_2(SO_4)_3$ [0.2%, w/v]. All treatments were conducted in triplicate. Because both salts have an acidifying effect on the iron–water mixture and may partially explain the enhanced destruction rates observed, we differentiated the effects of the salts and pH by controlling pH with a Metrohm pH Stat (Model 718, Brinkmann Instruments, Westbury, NY). In these experiments we kept the pH alkaline (ambient pH of Fe^0–H_2O mix-

ture) and treated dinoseb (17 mg l^{-1}; 0.09 mM) with Fe^0 (0.5%, w/v), Fe^0 + $Al_2(SO_4)_3$ (0.2%, w/v), and a control (alkaline pH).

2.3. Dinoseb and degradation product analysis

Dinoseb concentrations were determined by high performance liquid chromatography by injecting 20 μL of sample into a 4.6- by 250-mm Keystone NA column (ThermoHypersil-Keystone, Bellefonte, PA) connected to a Shimadzu (Kyoto, Japan) photodiode array detector with quantification at 220 nm. The mobile phase was 50:50 CH_3CN and water at flow rate of 1 ml min^{-1}. Typical retention time of dinoseb was 8 min.

Dinoseb transformation products were detected and tentatively identified using liquid chromatography–mass spectrometry (LC/MS). Separation and source conditions are similar to the method published for RDX and nitroso degradation products [32]. A 2.1- by 250-mm BetaBasic C-18 column (ThermoHypersil-Keystone) was used for separation on a Waters 2695 HPLC interfaced to a LCQ Classic ion trap mass spectrometer with electrospray ionization (Thermo Electron Corporation, San Jose, CA). Mobile phase consisted of 70:30 methanol:0.1% ammonium formate in water at 0.2 ml min^{-1}. Spray source conditions for ion detection were as follows—spray voltage: 5.25 V, capillary temperature: 150 °C, capillary voltage: −20 V, Tube Lens: 10 V, Sheath Gas: 75 and Aux Gas: 9 (arbitrary units).

2.4. Soil analysis

Dinoseb was extracted from 5 g soil in 50-ml Teflon centrifuge tubes by adding 20 ml CH_3CN and shaking overnight (>8 h) on a reciprocal shaker at ambient temperature. The tubes were then centrifuged at 5000 × *g* for 10 min and 1.5 ml of supernatant was removed and microcentrifuged at 13,000 × *g* for an additional 10 min. After centrifuging, 1 ml of supernatant was transferred to HPLC vial for dinoseb analysis. The extractions were conducted in triplicate.

Standard soil nutrient, soil texture, soil pH, organic matter, and cation exchange capacity (CEC) (Table 1) were conducted by Midwest Laboratories, Inc. (Omaha, NE).

2.5. Soil slurry experiments

Soil slurry was prepared by shaking dinoseb-contmainated soil with water. This was accomplished by combining 5 g soil with 20 ml of water (1:4, w/v) for 24 h in a 50-ml Teflon tube. Treatments included 1%, 3%, and 5% (w/v) zerovalent iron and a control. Experiments were conducted in triplicate at room temperature. All experimental units were continuously agitated on a reciprocal shaker during treatment. At preselected times, residual dinoseb in soil slurry was extracted by shaking the soil with CH_3CN for 12 h.

Table 1
Physical–chemical characteristics of dinoseb-contaminated soil.

Soil property	Unit	Value
Soil pH (1:1, soil:water)		8.3
Organic matter	%	0.6
Cation exchange capacity	meq kg^{-1}	145
Ca	mg kg^{-1}	2295
Mg	mg kg^{-1}	310
K	mg kg^{-1}	179
Fe	mg kg^{-1}	16
Mn	mg kg^{-1}	11
Cu	mg kg^{-1}	1.2
Sand	%	54
Silt	%	34
Clay	%	12

Dinoseb concentrations in the CH_3CN-extracts were determined by HPLC.

2.6. Soil incubation experiments

Batch studies with dinoseb-contaminated soil were subsequently conducted to determine optimum concentrations needed for efficient dinoseb removal by zerovalent iron, with and without ferrous or aluminum sulfate salts, in static soil microcosms. This was accomplished by incubating 20 g (air dry) soil with 1%, 3%, or 5% zerovalent iron (w/w) in 50-ml Teflon centrifuge tubes at 30 °C and a soil water content of 0.3 kg kg^{-1}. Aluminum sulfate addition was 1% (w/w) [0.2 g $Al_2(SO_4)_3$ to 20 g dinoseb-contaminated soil]. Ferrous sulfate additions were 1%, 3% or 5% (w/w) [0.2–1 g $FeSO_4$ to 20 g dinoseb-contaminated soil]. Sacrificial samplings were obtained after soils had been incubated for 3 and 7 d. Following the incubation, the soil was extracted with 25 ml of CH_3CN and analyzed by HPLC.

3. Results and discussion

3.1. Solution experiments

By treating an aqueous solution of dinoseb (30 mg l^{-1}) with varying masses of Fe^0, we found that maximum dinoseb removal (>90% within 12 h) occurred following treatment with 1% Fe^0 (w/v). Lower Fe^0 concentrations resulted in a decrease in dinoseb concentrations of 60% (0.5% Fe^0) and 30% (0.25% Fe^0) within 12 h (Fig. 1). HPLC analysis confirmed dinoseb transformations as evidenced by temporal decreases in dinoseb and corresponding increases in degradation products (see Section 3.3, dinoseb degradation products). HPLC analysis of acetonitrile extracts of the reacted iron indicated that no residual dinoseb was associated with the Fe^0. However, adsorption of dinoseb transformation products (that were not acetonitrile-extractable) and co-precipitation were removal mechanisms. The development of an oxide film is characteristic of aqueous iron corrosion and this film controls the rate of mass transfer of contaminant between the water phase and Fe^0 surface. Because oxide film growth is a dynamic process, contaminants may co-precipitate with iron oxides or hydroxides [27]. Co-precipitation has been documented to occur with heavy metals and natural and dissolved organic matter [33–37]. Using ^{14}C-labeled TNT (2,4,6-trinitrotoluene, 0.31 mM), Hundal et al. [13] showed that 1% Fe^0 (w/v) removed all TNT from solution within 8 h and 98% of the ^{14}C within 24 h. Through a series of sequential extractions, they

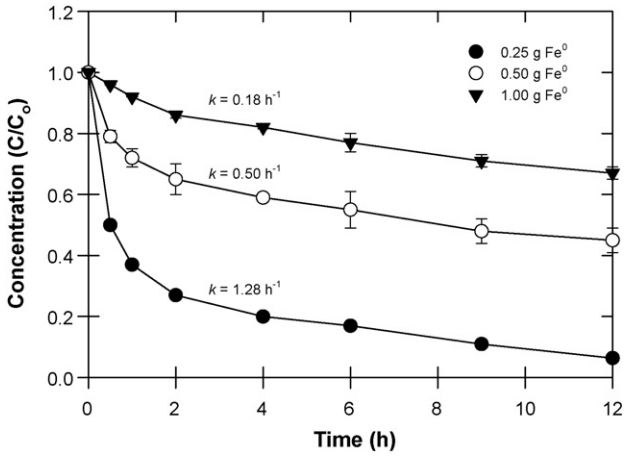

Fig. 1. Changes in aqueous dinoseb concentrations following treatment with varying Fe^0 masses (g per 100 ml). Initial dinoseb concentration was 30 mg l^{-1}. Bars on symbols represent standard deviations, where absent, bars fall within symbols.

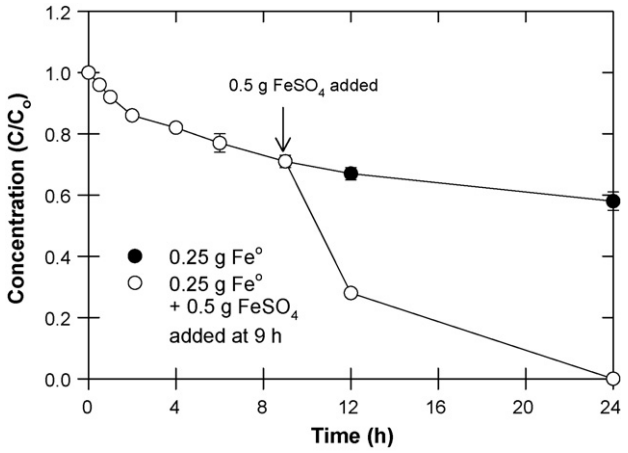

Fig. 2. Effect of adding $FeSO_4$ at 9 h on changes in aqueous dinoseb concentrations during treatment with Fe^0. Experimental units were 100 ml of dinoseb solution (30 mg l^{-1}) treated with 0.25 g Fe^0. Bars on symbols represent standard deviations, where absent, bars fall within symbols.

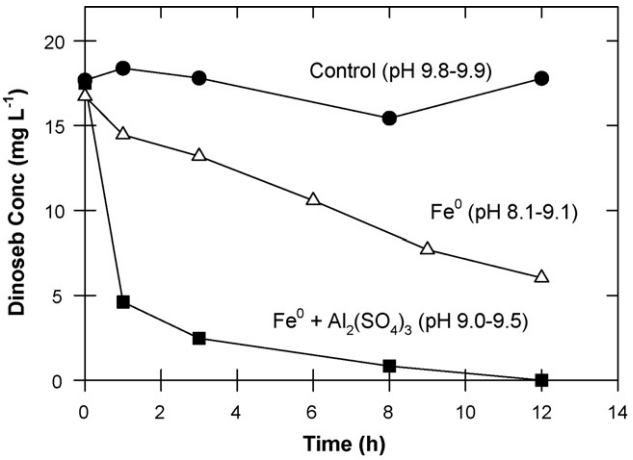

Fig. 4. Transformation of dinoseb under alkaline pH by Fe^0, $Fe^0 + Al_2(SO_4)_3$ and a control treatment.

found that <1% of the ^{14}C was extractable with acetonitrile and ~37% remained unextractable. Given the TNT and dinoseb are structurally similar (and both form amino degradation products), adsorption of transformed dinoseb and co-precipitation are likely the dominant removal mechanisms. Monitoring pH during this batch experiment showed that the aqueous mixture was acidic (pH ~4.5) prior to adding iron. After adding the iron, the pH of the solution increased rapidly to between 8.1 and 9.5. This pH would facilitate the formation of iron corrosion products and also promote co-precipitation of dinoseb.

Previous research has shown that small additions of ferrous or aluminum sulfate salts can greatly accelerate contaminant transformations by zerovalent iron [17, 22, 38, 39]. Treating 100 ml of dinoseb solution with 0.25 g Fe^0 resulted in a loss of ~70% within 12 h. However, when 0.5 g of $FeSO_4$ was added to the batch reactor after 9 h, complete removal was observed by 24 h (Fig. 2). Likewise, when either 0.2 g $FeSO_4$ or $Al_2(SO_4)_3$ were initially combined with 0.5 g Fe^0, complete transformation of dinoseb was observed within 6 h (Fig. 3). Monitoring the pH during these experiments showed that the salt additions counteracted the alkaline pH created by the corroding iron. Specifically, the alkaline pH of the iron and dinoseb solution (pH 8.1–9.5) decreased to pH 3–4 after adding the aluminum or ferrous sulfate. While we documented that some dinoseb transformation can occur under acidic conditions (up to 58% at pH < 4.2 after several days), the accelerated transformation of dinoseb within 6 h by the Fe^0 + salts (Fig. 3) cannot be explained by acid hydrolysis alone. To further demonstrate this point, we used a pH stat to keep the pH alkaline and compared dinoseb transformations by Fe^0, $Fe^0 + Al_2(SO_4)_3$, and a control. Results confirmed that dinoseb was stable under alkaline pH (Control, Fig. 4) and that adding aluminum sulfate with zerovalent iron, even when maintained in an alkaline pH, enhanced the transformation rate of dinoseb over Fe^0 alone (Fig. 4).

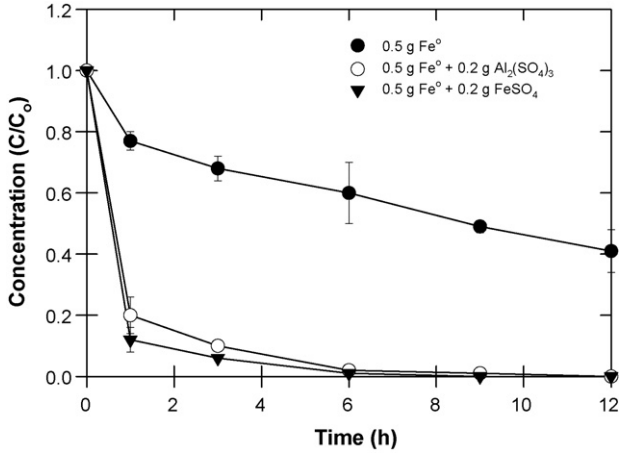

Fig. 3. Effects of iron and aluminum salts on transformation of dinoseb by zerovalent iron under unbuffered conditions.

Detailed discussions on how aluminum sulfate or other salts can accelerate the reductive transformation by iron have been previously described [17,22,38,39,40]. In brief, the presence of aluminum during iron corrosion facilitates the release of Fe(II), which when bound by iron hydroxides, plays an important role in the transformation of redox sensitive compounds [41]. Moreover, under the reducing and pH conditions imposed by the iron, sulfate promotes the formation of green rust II [$Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot nH_2O$] [42], which is also a strong reductant. Kim et al. [40] also showed that the adding halide ions with zerovalent iron significantly increased the removal of TNT (which is structurally similar to dinoseb) from solution. These solution experiments confirmed that Fe^0 plus ferrous or aluminum sulfate salts can readily transform dinoseb in aqueous solutions.

3.2. Dinoseb degradation products

The reaction products of dinoseb and zerovalent iron were detected in aqueous solution and tentatively identified by LC/MS. Operating in negative ion detection mode, we observed HPLC peaks for compounds with mass spectra consistent with $[M-1]^-$ ions corresponding to the reduction of one (m/z = 209, Fig. 5F) or both (m/z = 179, Fig. 5E) of dinoseb's nitro groups to amines. Proposed structures consistent with $[M-1]^-$ ions with m/z = 209 would be 6-amino-2-*sec*-butyl-4-nitrophenol or 4-amino-2-*sec*-butyl-6-nitrophenol and for m/z = 179, 2,4-diamino-6-*sec*-butylphenol. Temporal sampling indicated that the amino degradation products were transitory and decreased in concentration with time. Production of amino degradation products from nitroaromatic via zerovalent iron treatment is not uncommon. Keum and Li [21] studied the reduction of 11 nitroaromatic pesticides with zerovalent iron powder and using GC/MS verified that reduction of nitro to amino was a dominant reaction for all tested compounds. Although there has been concern over the human toxicity of aromatic amines, amino compounds are generally believed to be more biodegradable than the parent nitro compounds in aerobic environments. One way of determining whether the byproducts of the iron treat-

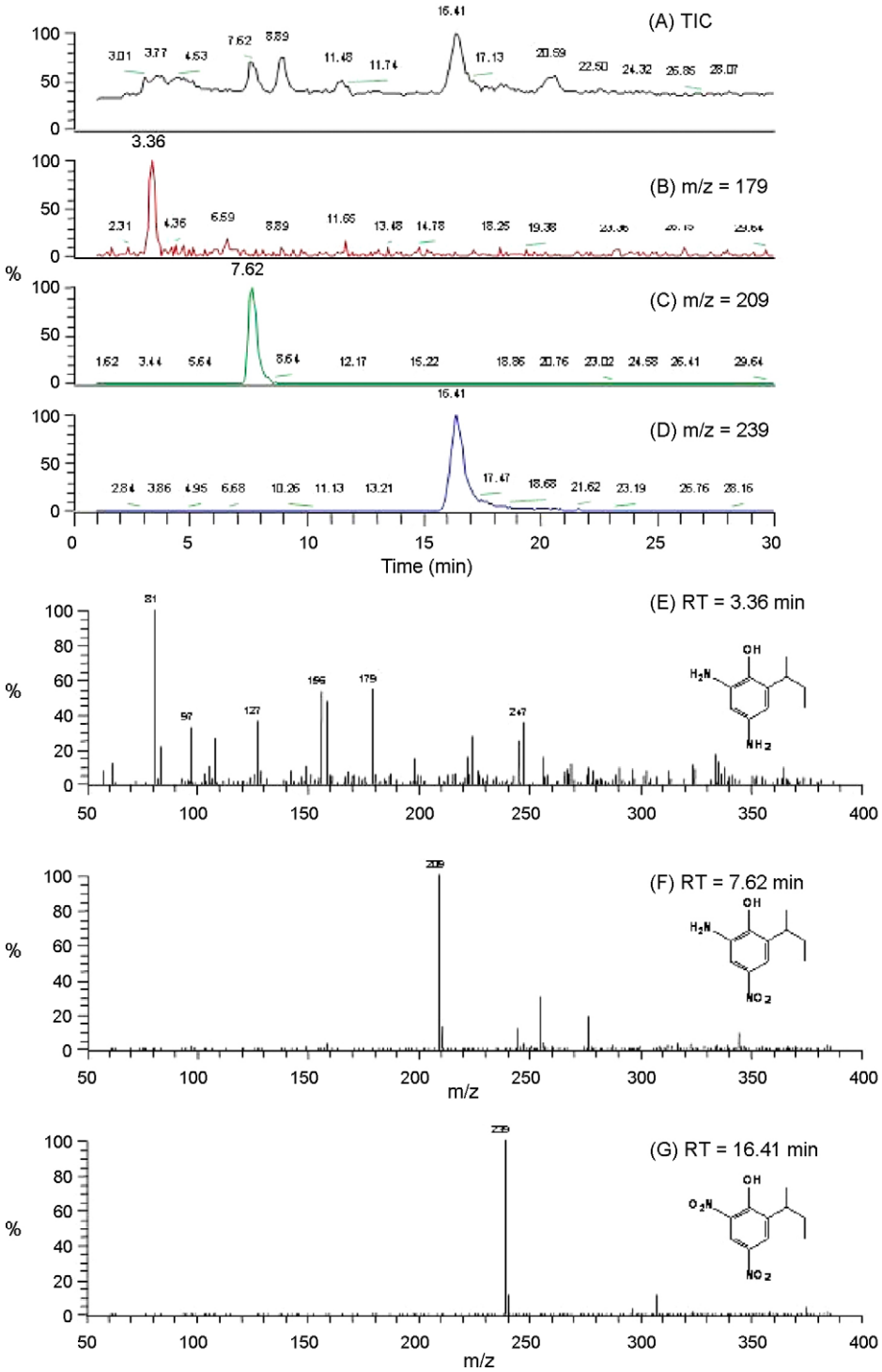

Fig. 5. LC/MS analysis of Fe^0-treated dinoseb using negative ion mode: (A) total ion chromatograph and selective ion monitoring (B–D); (E) mass spectra of 3.36 min peak; (F) mass spectra of 7.62 min peak; (G) mass spectra of dinoseb peak (16.41 min peak).

ment are biodegradable is to use ^{14}C-labeled compounds and then measure $^{14}CO_2$ production as a product of microbial respiration. Using such an approach, Hundal et al. [13] found that Fe^0-treated TNT (2,4,6-trinitrotoluene), which was also transformed into amino degradation products, was more biodegradable than untreated TNT.

Because the amino degradation products of dinoseb were transitory and did not persist in the Fe^0 treatments, additional products were likely produced. Using a microbial approach, research by Kaake et al. [4] provided detail analysis of dinoseb degradation under reducing conditions. Their results indicate that following reduction of dinoseb's nitro groups to amino groups, quinonimines (4-amino-6-*sec*-butyl-1,2-quinonimine, 2-amino-6-*sec*-butyl-1,4-quinonimine) followed by benzoquinones (4-amino-6-*sec*-butyl-1,2-benzoquinone, 2-amino-6-*sec*-butyl-1,4-benzoquinone) also formed prior to hydroxylation. Interestingly, our analysis using positive ion mode in LC/MS (Fig. 6) also showed HPLC peaks with mass spectra consistent with the $[M+1]^+$ ions of the two quinonimine (m/z = 179, Fig. 6D) and benzoquinone (m/z = 180, Fig. 6E) structures. The broadness of the m/z = 179 peak (RT = 4.42 min) in the ion chromatogram suggests that both quinonimine tautomers are present

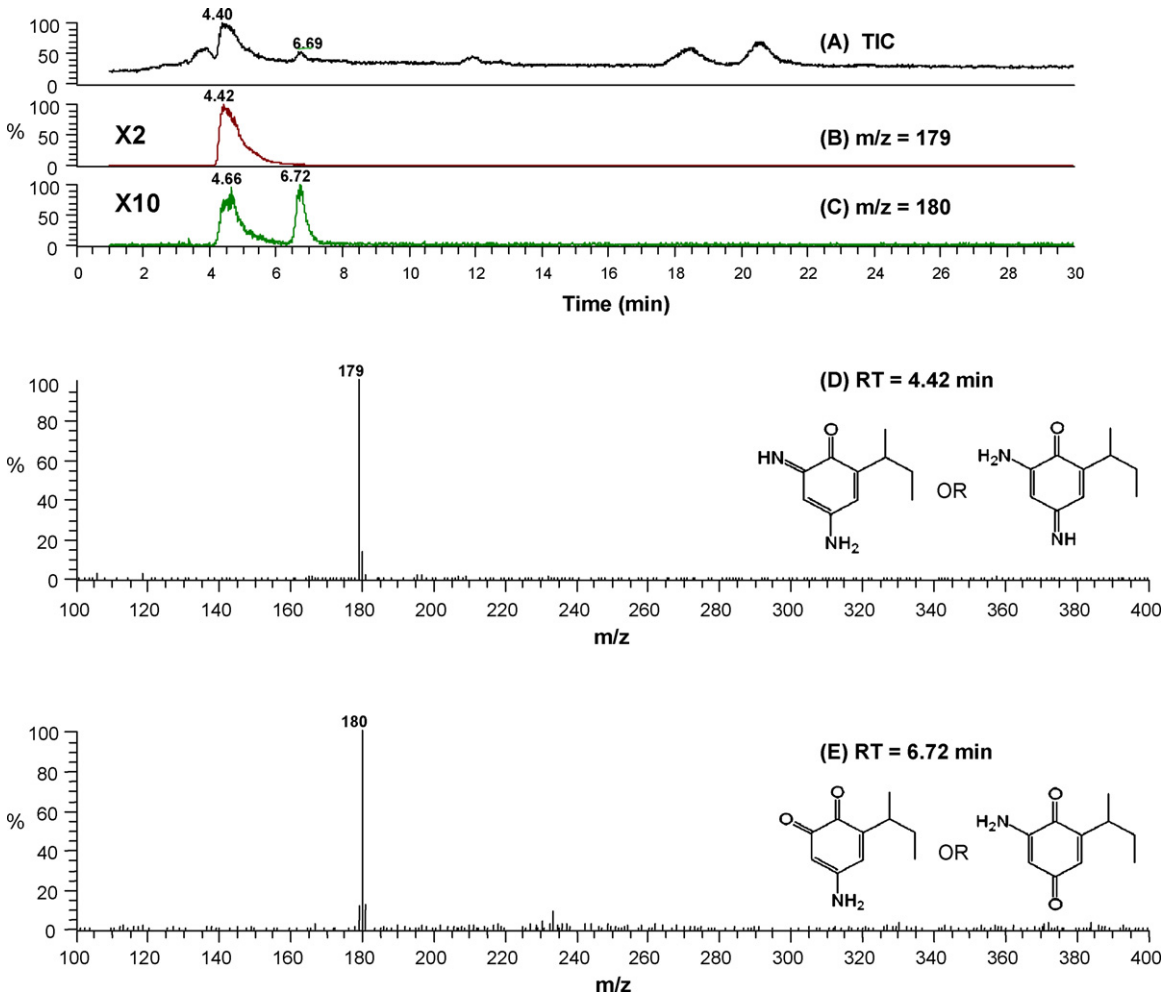

Fig. 6. LC/MS analysis of Fe^0-treated dinoseb using positive ion mode: (A) total ion chromatograph and selective ion monitoring (B–C); (D) mass spectra of 4.42 min peak; (E) mass spectra of 6.72 min peak.

and in equilibrium but are not chromatographically resolved. The isomeric form of the isomer comprising the benzoquinone peak (RT = 6.72 min) is unknown.

For the quinonimine and benzoquinone to form abiotically, oxidation of the reduced dinoseb species (i.e., 2,4-diamino-6-*sec*-butylphenol) would need to occur. Given that the batch reactors were exposed to air, some dissolved O_2 would be present to interact with the dinoseb products as well as the Fe^0 and iron oxides. Certain classes of compounds like phenols and aromatic amines can be oxidized in soil solutions by dissolved oxygen and these reactions are often accelerated by oxide surfaces that act as catalysts [43]. Manganese and iron oxide surfaces have been shown to catalyze amine oxidations by O_2 [43]. Thus, the reaction of 2,4-diamino-6-*sec*-butylphenol with dissolved O_2 and/or iron oxides provide possible oxidation pathways. In our Fe^0–H_2O reactors however, dissolved O_2 would likely preferentially react with zerovalent iron and the Fe^{II} present in the oxide films until the iron surface was passivated. Before complete passivation occurs, however, the interaction of zerovalent iron with O_2 can result in the oxidation of some organic compounds via a free radical reaction.

Joo et al. [28,29] showed molinate, benzoic acid, phenol, o-hydroxybenzoic acid, and aniline were oxidized by zerovalent iron (nano-scale and commercial sources) when used in the presence of oxygen. This occurred by the reaction of O_2 and Fe^0 to produce H_2O_2, which then reacted with Fe(II) to produce •OH. Using a similar approach, an alternative oxidation route would be for 2,4-diamino-6-*sec*-butylphenol to be transformed by •OH in several steps to a quinonimine is also proposed (Fig. 7). The oxidation could be initiated by removal of an electron from an amine group by the •OH, leading to a resonance stabilized radical cation. Hydrogen atom (•H) abstraction from a hydroxyl group would complete the two-electron oxidation, providing a quinonimine cation (Fig. 7A). Under the acidic conditions induced by the added $FeSO_4$, the quinonimine would undergo imine hydrolysis to produce a benzoquinone (Fig. 7B).

3.3. Soil slurry experiments

Soils from the Coalinga airport (Fresno County, CA) were passed through a 2-mm sieve and sent to Midwest Laboratory (Omaha, NE) for general chemical and physical analyses. Results indicated that the soil pH was alkaline; texture was classified as a sandy loam with very low organic matter (0.6%) (Table 1). HPLC analysis of acetonitrile extracts from soil indicated that the dinoseb concentration ranged between 140 and 250 mg kg^{-1}. This concentration range is consistent with the environmental investigation results initially conducted at the Coalinga Airport [44].

Mixing dinoseb-contaminated soil with water and treating with various concentrations of zerovalent iron revealed that the Fe^0 was still effective in transforming dinoseb in the presence of the contaminated soil (Fig. 8). A comparison of the "Fe^0 only" versus "$Fe^0 + Al_2(SO_4)_3$" treatment showed that the added $Al_2(SO_4)_3$ increased initial destruction within the first hour but both treat-

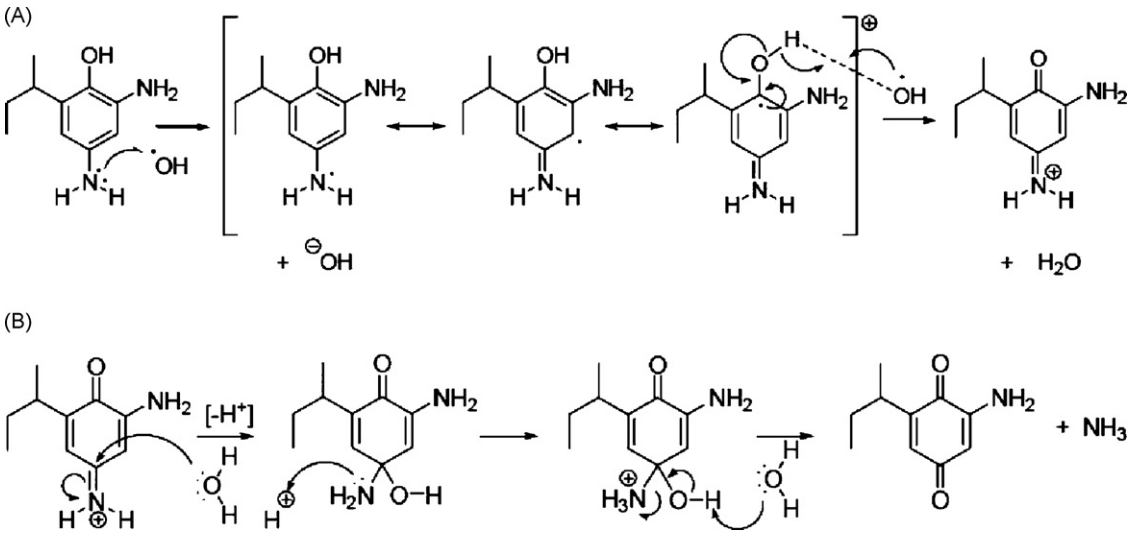

Fig. 7. Proposed pathways for (A) oxidation of 2,4-diamino-6-*sec*-butylphenol via hydroxyl radical and (B) hydrolysis of product quinonimine to quinone and ammonia.

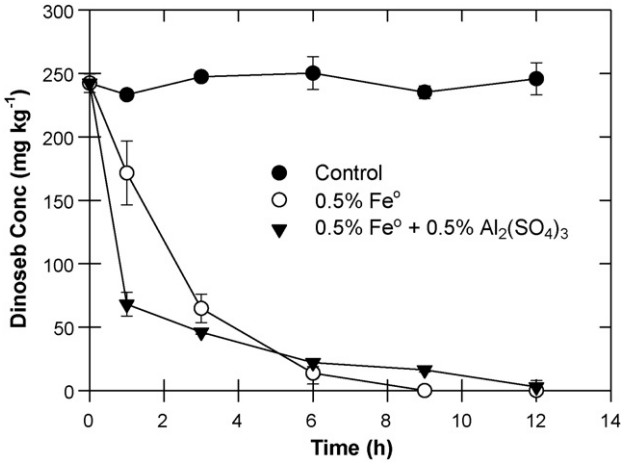

Fig. 8. Changes in dinoseb concentrations following treating soil slurry (1:5, dinoseb-contaminated soil:water) with 0.5% Fe^0 with and without $Al_2(SO_4)_3$.

ments were successful in transforming all the dinoseb within 12 h (Fig. 8).

3.4. Soil incubation experiments

Experiments with aqueous solutions and soil slurries support the potential of using zerovalent iron to remove dinoseb in the contaminated soil from the Coalinga airport. We acknowledge that the constant agitation used in our batch experiments disrupted oxide formation and was dissimilar to the static treatment soils would receive under field conditions either in situ or ex situ in windrows. Noubactep [26,27,45] has documented extensively the need for non-disturbed experiments to be run with Fe^0 so as to document and better characterize the progression of oxide formation and co-precipitation reactions that would occur under static conditions.

To treat large volumes of contaminated soil under field-scale conditions, it would be beneficial to treat the soil in situ or ex situ in windrows at soil water contents below field capacity so that leaching is minimized. Incubating dinoseb-contaminated soil with a variety of amendments showed that all iron concentrations were able to transform dinoseb. Using 5% Fe^0, no extractable dinoseb was observed after 3 d of incubation (Table 2). When only 1% (w/w) Fe^0 plus 1% $Al_2(SO_4)_3$ was used, all dinoseb was transformed within 7 d. Even the use of $FeSO_4$ alone was able to transform dinoseb but as evidenced by results obtained at days 3 and 7, the effect of $FeSO_4$ was short-lived and not sustainable (i.e., no difference in results between days 3 and 7, Table 2).

Results using zerovalent iron on the dinoseb-contaminated soil are encouraging. Past field-scale treatments of pesticide-contaminated soil have used up to 5% (w/w) iron [22]. Zerovalent iron is one of the major input costs to treatment, so being able use a lower dose (i.e., 1% Fe^0 rather than 5%) would make this treatment significantly less expensive and much more competitive with other

Table 2
Extractable dinoseb concentrations and pH following static incubations with Fe^0 and salts.

Treatment[a]	Soil pH			Extractable dinoseb (mg kg^{-1})		
	T = 0 d	T = 3 d	T = 7 d	T = 0 d	T = 3 d	T = 7 d
Control (initial)	8.01(0.24)[b]			147.89(16.04)		
1% Fe^0		7.96(0.63)	8.01(0.07)		15.57(2.36)	0
3% Fe^0		7.81(0.36)	7.41(0.15)		6.46(1.07)	0
5% Fe^0		7.94(0.24)	7.52(0.36)		0	0
1% Fe^0 + 1% $Al_2(SO_4)_3$		6.16(0.29)	6.22(0.19)		1.54(0.98)	0
3% Fe^0 + 1% $Al_2(SO_4)_3$		5.95(0.41)	6.04(0.73)		0.2(0.09)	0
5% Fe^0 + 1% $Al_2(SO_4)_3$		5.93(0.43)	6.12(0.16)		0	0
1% Fe^0 + 5% $FeSO_4$		6.09(0.32)	6.16(0.07)		0	0
1% $FeSO_4$		6.85(0.63)	5.02(0.38)		57.16(7.93)	55.16(10.66)
3% $FeSO_4$		6.02(0.12)	5.11(0.21)		16.73(2.15)	14.23(3.41)
5% $FeSO_4$		4.98(0.67)	4.99(0.44)		5.56(1.51)	4.96(0.09)

[a] All treatment percentages (%) are a soil weight basis (w/w).
[b] Sample standard deviation.

remedial options. Although factoring in labor, capital outlays, and equipment depreciation is complicated, listing chemical expenditures per mass of soil treated is relatively straightforward. Assuming the dinoseb-contaminated soil was treated with either 1% (w/w) Fe^0 or 1% Fe^0 and 1% $Al_2(SO_4)_3$ and using current prices (minus shipping) of $725 per ton of Aggregate 60D Fe^0 (Peerless Metal Powders, Detroit, MI) and $0.86 per lb for $Al_2(SO_4)_3$ (AgValley Cooperative, Edison, NE) both delivered in 50 lb bags, the input costs for treating 1 cubic yard (0.765 m^3) of contaminated soil (weighing 2360 lbs or 1070 kg assuming a bulk density of 1.4 g cm^3), would be $8.26 for zerovalent iron, $20.30 for $Al_2(SO_4)_3$, or $28.56 if both Fe^0 and $Al_2(SO_4)_3$ were used. Additional costs would need to be factored in for field supplies, analytical sampling, and soil mixing, which is often price-quoted on the volume of soil treated [22].

Although individual State regulations may vary, pesticide spills are usually handled in one of the two ways. The contaminated soil is excavated and shipped to a certified landfill or the contaminated soil is reapplied to farmland at labeled rates. When contaminated soils also contain banned or toxic chemicals, a third option of incineration may also be considered. Given that dinoseb has been banned and cannot be reapplied to farmland, the results from these treatability studies support the use of zerovalent iron as a possible on-site treatment of dinoseb-contaminated soil.

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