

# DDT, DDD, and DDE Dechlorination by Zero-Valent Iron

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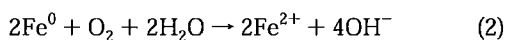
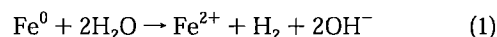
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Traditionally, destruction of DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] for environmental remediation required high-energy processes such as incineration. Here, the capability of powdered zero-valent iron to dechlorinate DDT and related compounds at room temperature was investigated. Specifically, DDT, DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane], and DDE [2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene] transformation by powdered zero-valent iron in buffered anaerobic aqueous solution was studied at 20 °C, with and without the presence of nonionic surfactant Triton X-114. The iron was successful at dechlorinating DDT, DDD, and DDE. The rates of dechlorination of DDT and DDE were independent of the amount of iron, with or without surfactant. The rates with surfactant present were much higher than without. Initial first-order transformation rates for DDT, DDD, and DDE were determined. For example, the initial first-order rate of DDT dechlorination was  $1.7 \pm 0.4$  and  $3.0 \pm 0.8 \text{ day}^{-1}$  or, normalized by the specific iron surface area,  $0.016 \pm 0.004$  and  $0.029 \pm 0.008 \text{ L m}^{-2} \text{ h}^{-1}$ , without and with surfactant, respectively. A mechanistic model was constructed that qualitatively fit the observed kinetic data, indicating that the rate of dechlorination of the solid-phase (crystalline) reactants was limited by the rate of dissolution into the aqueous phase.

## Introduction

Zero-valent iron can drive the dechlorination of chlorinated aliphatics and aromatics. Many chlorinated aliphatics (1-6) such as tetrachloroethene, trichloroethene, carbon tetrachloride, and chloroform can be dechlorinated reductively by zero-valent iron at room temperatures and pressures. The chlorinated aromatics (polychlorinated biphenyls) have been completely dechlorinated to biphenyl using zero-valent iron at elevated temperatures (7).

Some aspects of the mechanism of dechlorination by iron are understood. Zero-valent iron can reduce redox-reactive species including water (eq 1) and oxygen (eq 2) (1):



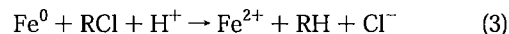
In the presence of water, alkyl chloride is reduced in a

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thermodynamically favored reaction (eq 3) (1):



Recent work has shown that the rates of dechlorination of chlorinated solvents (3, 5, 6) and of reduction of nitroaromatic compounds (8) by zero-valent iron are proportional to the specific iron surface area (surface area per unit reactor volume). These results imply that the reduction reactions occur by electron transfer at the iron surface.

DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] was a widely used pesticide, banned in the United States in 1972, but continues to be used in some countries. DDT is listed as a priority pollutant by the U.S. Environmental Protection Agency, and many DDT-contaminated sites are on the Superfund National Priority List. Effective destructive technologies for the treatment of DDT-contaminated sites other than incineration are lacking. Most DDT-contaminated sites are also co-contaminated with DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] and DDE [2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene], both as impurities in DDT and as products of natural DDT transformation. DDD and DDE are also classified as priority pollutants and are also extremely stable in the environment.

Reductively dechlorination of DDT can occur when coupled to the oxidation of metals. Biological systems catalyze reductive dechlorination of DDT using metal-coenzyme complexes where cations of iron or cobalt are oxidized in the reaction (9-11). The abiotic dechlorination of DDT was observed in the presence of cooking utensils at 100 °C and was attributed to zero-valent iron in the utensils (12). No previous work describing the use of zero-valent iron to remediate DDT contamination at room temperature was found in the peer-reviewed literature.

This study focused on DDT, DDD, and DDE transformation by zero-valent iron in aqueous systems. Each molecule of DDT, DDD, and DDE has two aryl chlorines and three, two, and two alkyl chlorines, respectively (Figure 1). The effectiveness of zero-valent iron in alkyl dechlorination shown in literature indicated a potential for dechlorination of the alkyl group on the DDT-related compounds. DDT, DDD, and DDE have water solubilities of  $3 \mu\text{g/L}$  ( $0.008 \mu\text{M}$ ) (25 °C),  $160 \mu\text{g/L}$  ( $0.5 \mu\text{M}$ ) (24 °C), and  $40 \mu\text{g/L}$  ( $0.11 \mu\text{M}$ ) (20 °C), respectively (13). These low solubilities may limit the interaction of these chemicals with zero-valent (solid phase) iron.

The influence of nonionic surfactant Triton X-114 on the rate of transformation was also studied. Triton X-114, an alkylphenol ethoxylate, greatly increases the apparent solubility of DDT to  $800 \mu\text{g/L}$  using  $200 \text{ mg/L}$  of surfactant (14) and enhances the apparent rate of anaerobic biological dechlorination of DDT (11). The critical micelle concentration of Triton X-114 in water at 25 °C is  $110 \text{ mg/L}$  (14).

The objective of this study was to determine the feasibility of using zero-valent iron and surfactant to dechlorinate the priority pollutants DDT, DDD, and DDE. Feasibility was measured as the initial rate of dechlorination of the parent species and the extent of dechlorination of DDT, DDD, and DDE.

## Experimental Procedures

**Batch Experimental Procedures.** Test reactors were 40-mL glass vials with Teflon-lined septum caps. Uncapped reactors were filled under anaerobic conditions by continuously flushing with nitrogen. Iron powder (0.3-3 g) was preweighed in test reactors. Then, the reactors were filled with 20 mL of deoxygenated buffer solution, the target compound (DDT or

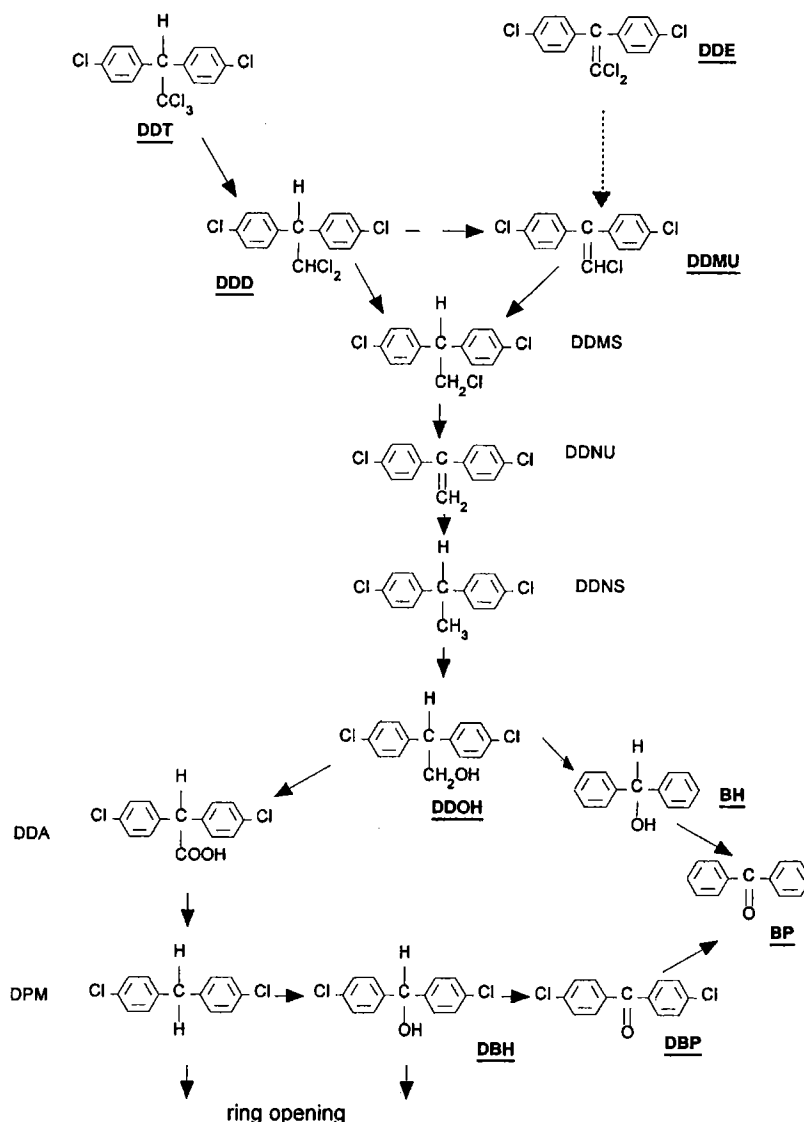


FIGURE 1. Proposed pathway of anaerobic reductive metabolism of DDT in microorganisms (from ref 15, modified according to ref 16). An underlined acronym (e.g., DDT) implies that the chemical was measured in this study. The dechlorination path of DDE to DDMU was added here based on well-known biotic and abiotic transformation of chlorinated ethenes.

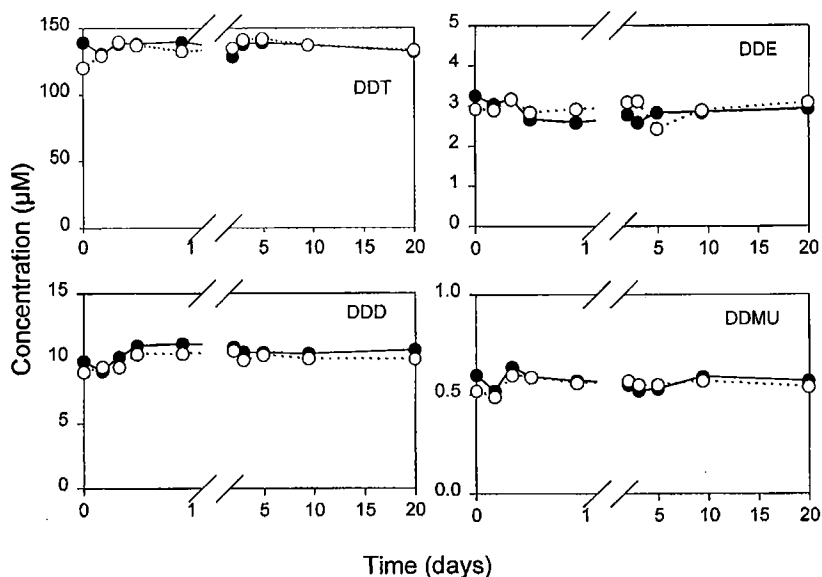


FIGURE 2. Transformation of DDT and its impurities (DDD, DDE, and DDMU) in reactors without iron and in reactors with iron and NaOH. These reactors are negative controls run to measure effectiveness of sample extraction: (●) no iron; (○) 50 g/L iron with 25 mM NaOH.

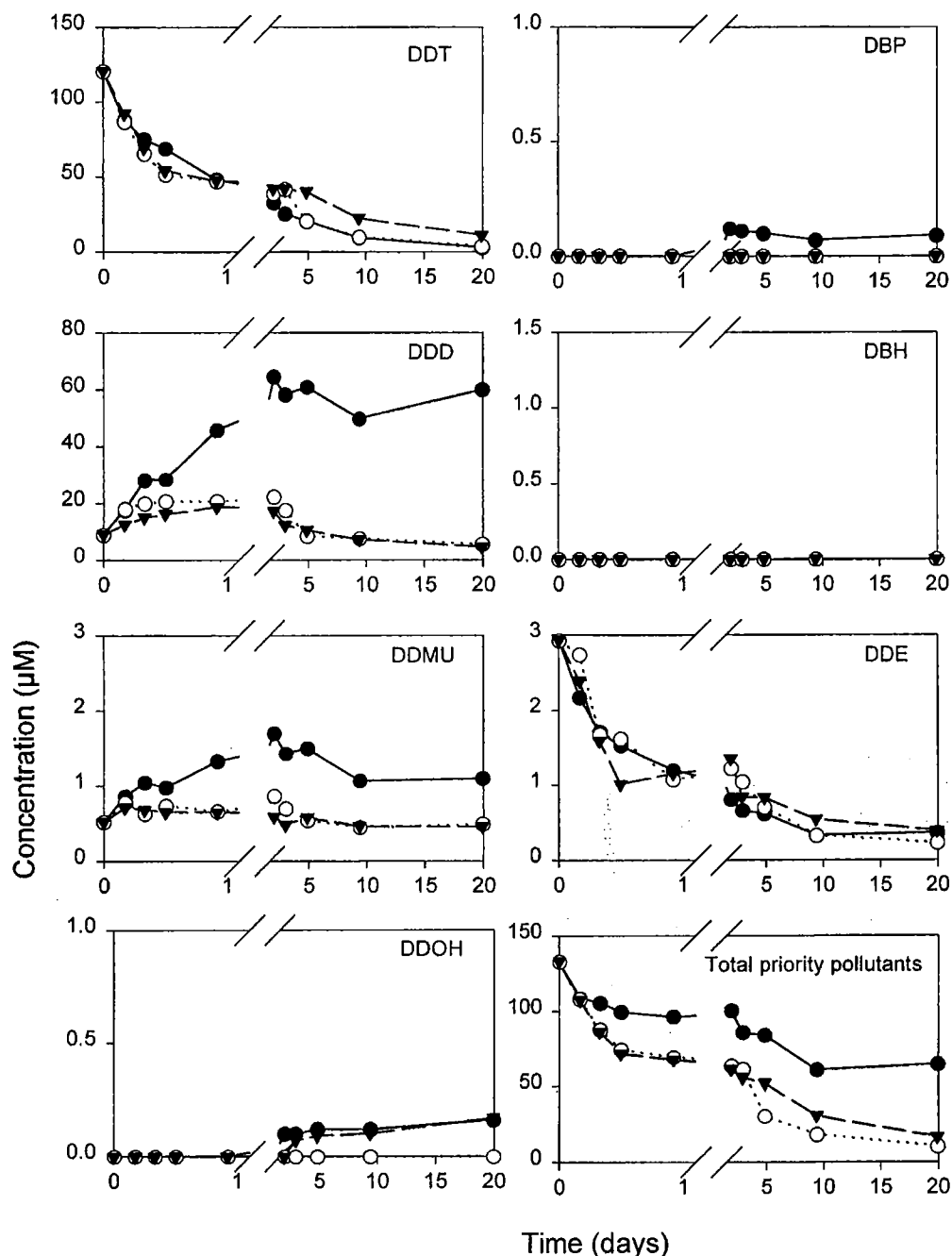


FIGURE 3. Transformation of DDT and related chemicals for various initial amounts of zero-valent iron: (●) 15 g/L iron; (○) 50 g/L iron; (▼) 150 g/L iron.

DDD dissolved in acetone), and, if required, Triton X-114 surfactant at 250 mg/L. The buffer solution was 20 mM MOPS [3-(*N*-morpholino)propanesulfonic acid] with initial pH adjusted to 7 and deoxygenated by purging with  $N_2$  gas for 1 h. Two 6-mm glass beads were added to improve the mixing in reactors spiked with DDT and DDD. The closed reactors were mixed by a rotary shaker at 130 rpm at  $20 \pm 0.5$  °C. Control reactors without iron or with iron and 25mM NaOH (to quench the reaction, see eq 3) were established to monitor the extraction efficiency. An appropriate number of equivalent reactors were established to allow duplicate reactors to be sacrificed at each sampling time.

#### Extraction for Measurement of DDT and Byproducts.

Extraction was performed *in situ*, i.e., in the sacrificed test reactors. The extractant included 0.5 mL of 1 M NaOH, 10 mL of toluene, and 0.5 mL of ethanol. NaOH was included to quench the dechlorination reaction (eq 3). Following addition of the solvents and NaOH, the reactors were closed

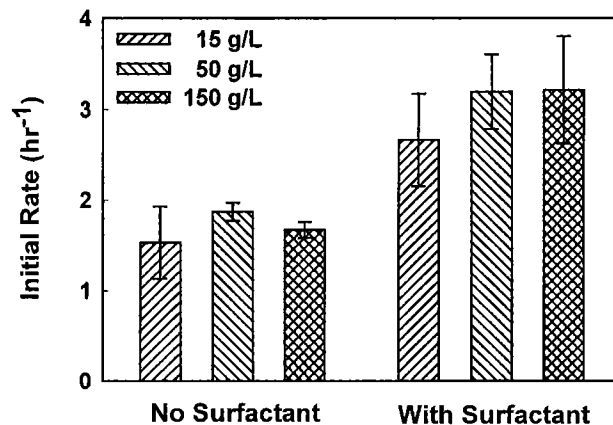


FIGURE 4. Calculated initial first-order transformation rates of DDT, without and with Triton X-114 surfactant, at the zero-valent iron levels noted. Error bars are 95% confidence limits.

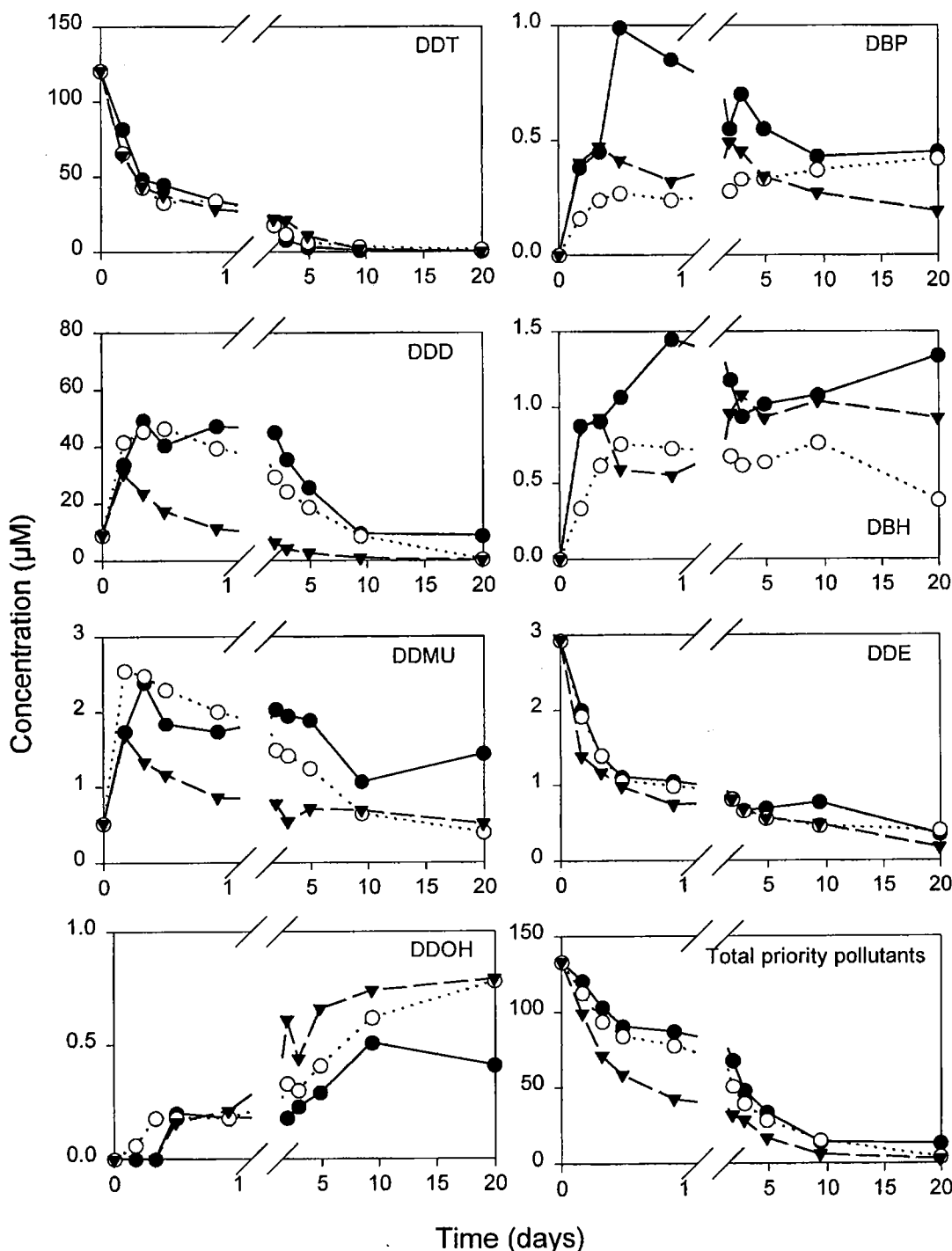


FIGURE 5. Transformation of DDT and related compounds with 250 mg/L surfactant Triton X-114 and various amounts of zero-valent iron: (●) 15 g/L iron; (○) 50 g/L iron; (▼) 150 g/L iron.

and mixed for 1 h by the same rotary shaker at 20 °C. Bottles were then centrifuged, and the solvent phase portion was taken for analysis.

To test the efficacy of this extraction method, two types of control reactors were established: reactors with no iron and reactors with iron and NaOH. The controls were spiked with DDT, were run for the entire length of the experiment, and were sampled at the same time as the active reactors. The iron with NaOH reactors were established to determine if NaOH could quench the dechlorination reaction. The no-iron control reactors were set up to determine if the presence of iron influenced the extraction efficiency.

Figure 2 shows the results of these control tests. Concentrations of DDT and its impurities (DDD, DDE, and

DDMU) did not change significantly during the 20-day test, indicating that NaOH was a good quenching reagent to use during sample extractions and that iron had no measurable influence on the extractability of the chlorinated compounds. Similar results were found from control reactors where DDD was used as the parent compound (Figure 7).

**Measurement of DDT and Byproducts.** DDT and its intermediates were measured with a gas chromatograph (Hewlett Packard, Model HP5890II), equipped a flame ionization detector (FID), an autosampler (HP7673), and a 30-m fused silica capillary column (Supelco SPB-1, 0.32 mm internal diameter, 1 μm film). Helium was the carrier gas with a flow rate of 1.1 mL/min; nitrogen was the makeup gas. Injection was carried out in splitless mode. Injection port

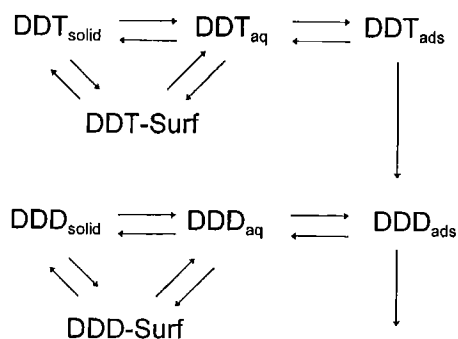


FIGURE 6. Proposed scheme of the important processes involved in DDT and DDD dechlorination by zero-valent iron. Subscripts solid, aq, and ads imply the chemical is crystalline, dissolved in the aqueous phase, or adsorbed to the iron surface, respectively. X-Surf implies that chemical X is associated with surfactant and surfactant micelles.

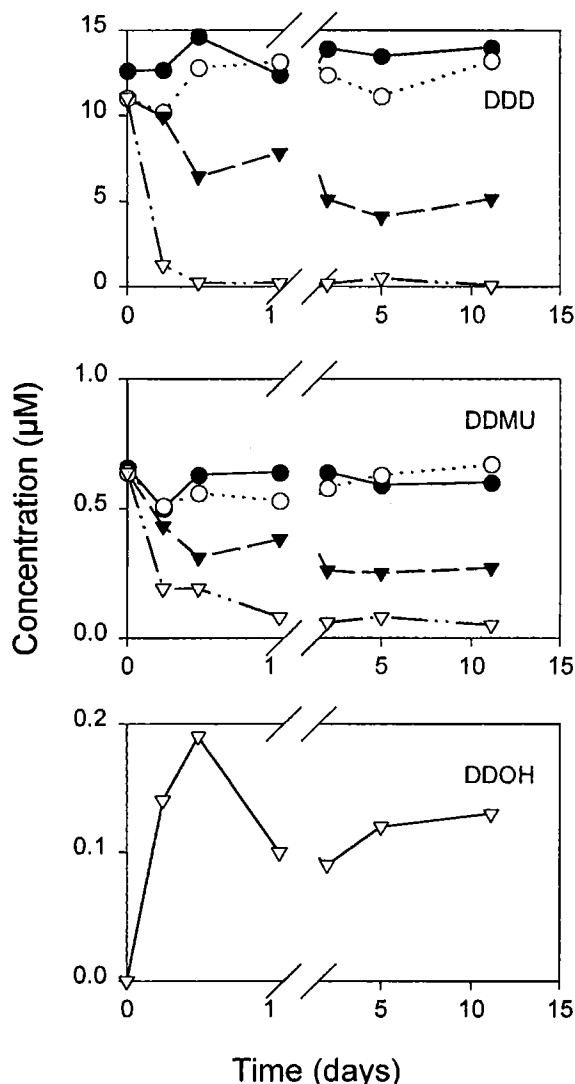


FIGURE 7. Transformation of DDD and related compounds for initial DDD concentration of 15.6 mM and for various other initial conditions: (●) no iron; (○) 50 g/L iron with 25 mM NaOH; (▼) 50 g/L iron; (▽) 50 g/L iron with 250 mg/L Triton X-114.

and detector temperatures were 250 and 300 °C, respectively. The column temperature was programmed to ramp from 85 °C (5 min hold) to 150 °C (7 min hold) at a rate of 30 °C/min, then ramp to 154 °C (4 min hold) at a rate of 1 °C/min, and finally ramp to 290 °C (8 min hold) at a rate of 5 °C/min.

The choice of which DDT transformation products to measure was determined from the known DDT reductive

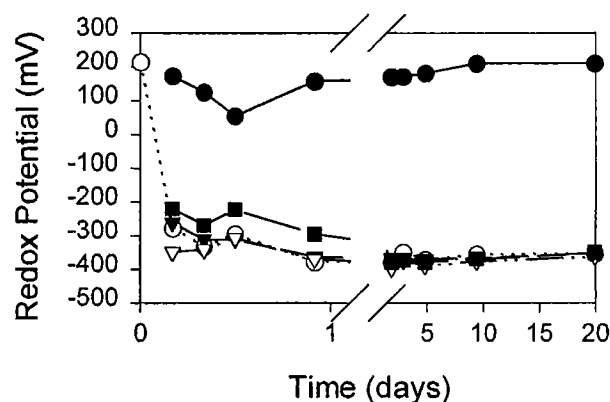


FIGURE 8. Oxidation-reduction potential (relative to the standard hydrogen electrode) measured in reactors with various initial conditions: (●) 50 g/L iron with 25 mM NaOH; (○) 15 g/L iron; (▼) 50 g/L iron; (▽) 50 g/L iron; (■) 50 g/L iron with 250 mg/L Triton X-114.

biotransformation pathway (Figure 1) and from the commercial availability of the compounds for use as GC standards. DDT, DDD, DDE, DDMU[1-chloro-2,2-bis(*p*-chlorophenyl)-ethylene], DDOH [2,2-bis(*p*-chlorophenyl)ethanol], DBH (dichlorobenzhydrol), and DBP (dichlorobenzophenone) concentrations were measured and are reported. DPM (dichlorodiphenylmethane), DM (diphenylmethane), BP (benzophenone), and BH (benzhydrol) were measured but not detected in any samples.

The sum of the measured molar concentrations of DDT, DDD, and DDE, defined as total priority pollutants, is also presented. Because DDT, DDD, and DDE are the only compounds in the known transformation pathway that are U.S. EPA priority pollutants, a drop in total priority pollutants with time indicates the overall success of the remediation process.

The concentration reported are an average of the duplicate measurements. Duplicate concentrations were consistent with relative percent differences typically less than 15%.

**Measurement of Oxidation-Reduction Potential.** Oxidation-reduction potential was measured with a Corning redox combination electrode (Pt/Ag/AgCl). The electrode was fitted with a test reactor cap and septum so that it could be placed into the test reactor, and the reactor was closed during measurement. The reading at 2 min without mixing was used as the measurement. For presentation here, the oxidation-reduction potential values were converted to a standard hydrogen electrode (SHE) reference by adding +222 mV to the mV reading obtained vs the Ag/AgCl reference used experimentally.

**Chemicals.** The electrolytically produced zero-valent iron (size < 100 mesh, 99%+ total iron), toluene, and ethanol were purchased from Fisher Scientific Co. (Pittsburgh, PA). The specific surface area of this zero-valent iron product was previously determined (3) to be 0.287 m<sup>2</sup>/g. Surfactant Triton X-114, DDT, DDD, DDE, DDOH, DBP, DBH, DM, BH and BP were purchased from Aldrich Chemical Co. (St. Louis, MO); DDMU and DDA were purchased from Crescent Chemical Co. (Hauppauge, NY); and MOPS was purchased from Sigma Chemical Co. (St. Louis, MO).

## Results and Discussion

The observed dechlorination kinetics discussed below do not necessarily represent the intrinsic kinetics because other factors may influence the apparent rate of dechlorination such as the dissolution rate of crystalline DDT. The concentrations reported are total reactor concentrations, i.e., the total mass of compound extracted from the reactor divided by the aqueous volume.

**DDT Transformation Experiment.** In these reactors, DDT was spiked as the primary parent compound at 120 μM (43

mg/L). DDD and DDE were present at  $t = 0$  as impurities in the DDT at 7.5% and 2.4% (mol/mol), respectively. Figure 3 shows that zero-valent iron successfully transformed DDT with over 90% of the original mass removed within 20 days. The figure shows almost equivalent DDT transformation patterns for all three levels of iron tested. No significantly large portion of the data set could be satisfactorily fit to a simple rate model (zero order, first order, or Langmuir). Nevertheless, a first-order degradation curve fit to the first 8 h of data (the first three data points) yielded the initial first-order rates for each level of iron (Figure 4). Clearly, the effect of increasing the mass of iron (i.e., the specific surface area of iron) in the reactors on the reaction rate was insignificant.

The independence of the DDT transformation rate on the specific iron surface area indicates that the transformation rate was limited by the mass transfer of DDT, either from slow dissolution of crystalline DDT or by poor mixing in the reactors. Since the rate of mixing (not quantified) was much faster than the apparent dechlorination rate, it is hypothesized that the rate of dissolution of DDT limits the observed rate.

This hypothesis is supported by the results shown in Figure 5. Here, in the presence of surfactant Triton X-114, the rate of transformation of DDT was faster than without surfactant and was also independent of specific iron surface area. Figure 4 shows the calculated initial first-order transformation rate of DDT in the presence of surfactant at the various iron levels. Averaging the rates across iron levels yield DDT first-order transformation rates of  $1.7 \pm 0.4$  and  $3.0 \pm 0.8 \text{ day}^{-1}$ , without and with surfactant, respectively, where the errors are 95% confidence limits. For comparison to other published data, these rates can be normalized by the specific iron surface area. Since the rate is not a function of the specific surface area, the lowest level of iron may be used for the normalization. The specific surface area for 15 g/L iron of this zero-valent iron formulation is  $4.3 \text{ m}^2/\text{L}$  yielding specific first-order rates of  $0.016 \pm 0.004$  and  $0.029 \pm 0.008 \text{ L m}^{-2} \text{ h}^{-1}$ , without and with surfactant, respectively. These specific rates are within a factor of 3 of the specific rates quoted elsewhere for various chlorinated ethanes (5). Note that since the rates observed here are limited by mass transfer, the intrinsic dechlorination rates are likely to be much faster.

DDD is the product of the reductive dechlorination of DDT (Figure 1) and is present initially as an impurity of the DDT formulation. The dynamics of the DDD concentrations varied greatly with the amount of iron and surfactant (Figures 3 and 5). Since the dechlorination rate of DDT (i.e., the production rate of DDD) was virtually independent of iron level, the dechlorination rate of DDD must be dependent on the specific iron surface area.

Figure 6, adapted from Bizzigotti et al. (6), shows a simple schematic model of the various processes competing in the dechlorination of DDT and DDD. The data above suggest that the dissolution of crystalline DDT into the aqueous phase is slow relative to adsorption to iron and to dechlorination. The presence of surfactant increases the apparent rate of dechlorination. Thus, surfactant appears to speed the transfer of DDT from the solid phase to the aqueous phase, i.e., the rate of transfer from DDT solid to surfactant micelles to the aqueous phase appears to be faster than direct dissolution into the aqueous phase.

The scheme in Figure 6 also assists in understanding the DDD concentration dynamics in Figures 3 and 5. Because the amount of DDD present at  $t = 0$  is relatively small, most of the DDD present is generated by dechlorination of DDT. A molecule of DDD formed on the iron surface can feed either into the next dechlorination reaction on the surface or can desorb into the aqueous phase. In the surfactant-free test, the DDD data in Figure 3 suggest that at the lowest iron level (15 g/L) the intrinsic DDD dechlorination rate was slower than the desorption rate resulting in DDD accumulation in the aqueous phase as crystals of DDD. Once in the crystalline

form, subsequent dechlorination of DDD would likely be limited by the rate of dissolution, as was the rate of dechlorination of DDT. At the higher levels of iron (50 and 150 g/L), the data suggest that the intrinsic dechlorination reaction was faster than the rate of desorption yielding little DDD accumulation. In the tests using surfactant (Figure 5), it seems that the two lowest levels of iron did not provide a reaction rate fast enough to avoid significant accumulation of DDD as crystals or partitioned into surfactant micelles. However, at the highest level of iron, little DDD accumulated, suggesting that the dechlorination rate was faster than desorption.

DDE, an impurity in the DDT formulation, was transformed by zero-valent iron as a parent chemical (Figure 1). As with DDT, the initial first-order rates were statistically independent of the specific iron surface area. The first order rates averaged across the iron levels were  $1.6 \pm 0.6$  and  $2.6 \pm 1.2 \text{ day}^{-1}$ , without and with surfactant, respectively. The specific iron surface area normalized rates were  $0.016 \pm 0.006$  and  $0.025 \pm 0.012 \text{ L m}^{-2} \text{ h}^{-1}$ , respectively, very similar to the rates for DDT. The DDE data suggests that DDE behaves very similar to DDT in that the rates of dechlorination of both compounds appear to be limited by the rate of dissolution.

The dynamics of DDMU, DDOH, DBH, and DBP, the other products of the dechlorination of DDT, showed some dependence on the iron level. Without surfactant present, the compounds were observed in low concentrations when they were not below detection limit. The behavior of these compounds fits the scheme discussed above for DDD, namely, surface area dependent apparent rates because the compounds were produced at the iron surface. Somewhat higher concentrations of the dechlorination products DDMU, DDOH, DBH, and DBP were observed with surfactant present corresponding to lower residual concentrations of DDT and DDD. However, the levels of these dechlorination products remained insignificant relative to the initial DDT concentration.

Total priority pollutants, i.e., the sum of DDT, DDD, and DDE concentrations, is a measure of the success of zero-valent iron in converting these regulated chemicals into non-regulated chemicals (Figures 3 and 5). For the greatest level of iron (150 g/L), the percent loss of total priority pollutants was 93% and >99%, without and with surfactant, respectively, indicating that zero-valent iron can be a very effective means of remediating DDT-contaminated media.

**DDD Transformation Experiment.** Since DDD was a product not the parent species in the DDT transformation experiment above, a simple test using DDD at 11.0–12.6  $\mu\text{M}$  (3.5–4.0 mg/L) as the parent compound, with and without surfactant, at 50 g/L iron was conducted to determine the rate of dechlorination of DDD. DDMU was present at  $t = 0$  as an impurity in the DDD at 5.8% (mol/mol). Figure 7 shows the dynamics of DDD and DDMU dechlorination. Zero-valent iron was successful in transforming DDD and DDMU with DDOH as the only product observed. Initial first-order rates of DDD dechlorination were  $0.95 \pm 0.66$  and  $8.0 \pm 0.8 \text{ day}^{-1}$ , without and with surfactant, respectively. DDMU is a potential product of the dechlorination of DDD. However, since DDMU never increased, apparently DDD was transformed to DDMS and onto other products (Figure 1). No transformations were observed in reactors lacking iron or with addition of NaOH to quench the reaction.

The initial first-order rates of disappearance of DDMU were  $1.5 \pm 0.2$  and  $2.9 \pm 2.4 \text{ day}^{-1}$ , without and with surfactant, respectively. Since the kinetics as a function iron level were not investigated in this test, the influence of iron level is not known. However, because DDD and DDMU were introduced into the reactors as solids, it is likely that the observed rates of dechlorination for DDD and DDMU were limited by dissolution rate, as discussed above.

**Other Results.** Despite buffering, the pH increased with time in all the reactors containing iron. In most reactors, the pH increased to nearly 8 within 1 day and finished in the range of 8–8.3. The oxidation–reduction potential decreased rapidly from a level of +200 mV vs SHE to less than –300 mV vs SHE within several hours and remained low for the duration of the experiment (Figure 7). The amount of iron and the addition of Triton X-114 had no significant effect on the oxidation–reduction potential. In reactors to which NaOH was added, oxidation–reduction potential remained above 0 mV vs SHE at all times and above +150 mV vs SHE most of the time.

During the test, a black-colored film developed on the reactor Teflon septa. The film was extracted *in situ* with the other components in the bottle. The film was detachable by sonication, but not all detached film was solubilized in 1% HCl solution.

### Acknowledgments

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### Literature Cited

- (1) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, *28*, 2045–2053.
- (2) Schreier, C. G.; Reinhard, M. *Chemosphere* **1994**, *29*, 1743–1753.
- (3) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32* (6), 958–967.
- (4) Orth, W. S.; Gillham, R. W. *Environ. Sci. Technol.* **1996**, *30*, 66–71.
- (5) Johnson, T. L.; Scherer, M. W.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, *30*, 2634–2640.
- (6) Bizzigotti, G. O.; Reynolds, D. A.; Kueper, B. H. *Environ. Sci. Technol.* **1997**, *31*, 472–478.
- (7) Chuang, F. W.; Larson, R. A.; Wessman, M. S. *Environ. Sci. Technol.* **1995**, *29*, 2460–2463.
- (8) Agrawal, A.; Tratnyek, P. G. *Environ. Sci. Technol.* **1997**, *31*, 153–160.
- (9) Barry, J. D.; Stotter, D. A. *Chemosphere* **1977**, *6*, 783–787.
- (10) Essac, R. G.; Matsumura, F. *Pharm. Ther.* **1980**, *9*, 1–26.
- (11) You, G.; Sayles, G. D.; Kupferle, M. J.; Kim, I. S.; Bishop, P. L. *Chemosphere* **1996**, *32*, 2269–2284.
- (12) DeLoach, H. K.; Hemphill, D. D. *J. Assoc. Off. Anal. Chem.* **1971**, *54* (6), 1352–1356.
- (13) *Treatability Database*, Revision 5.0; U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory: Cincinnati, OH.
- (14) Kile, E. D.; Chiou, C. T. *Environ. Sci. Technol.* **1989**, *23*, 832–838.
- (15) Lal, R.; Saxena, D. M. *Microbiol. Rev.* **1982**, *46*, 95–127.
- (16) *Microbial Decomposition of Chlorinated Aromatic Compounds: 1986*; U.S. Environmental Protection Agency, Office of Research and Development, U.S. Government Printing Office: Washington, DC, 1986; EPA/600/2-86/090; pp 138–145.

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