

Abiotic transformation of DDT in aqueous solutions

Erica F. Pirnie, Jeffrey W. Talley *, Lakhwinder S. Hundal

Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick Hall, University of Notre Dame, Notre Dame, IN 46556, United States

Received 11 November 2005; received in revised form 3 March 2006; accepted 22 March 2006

Available online 6 May 2006

Abstract

Significant concentrations of chlorinated pesticides such as 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) and its two main transformation products, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (DDE) are still present in soil and sediment systems more than 30 years after DDT use was banned in the United States. DDT enters waterways via the runoff from industrial point sources, agricultural lands and atmospheric deposition. We evaluated zero-valent iron (Fe^0), ferrous sulfide (FeS), as well as combining them with hydrogen peroxide (H_2O_2) as viable treatment technologies for degrading DDT in an aqueous solution. Treatment of DDT with Fe^0 and FeS resulted in approximately 88% and 56% transformation of DDT within 150 h, respectively. DDE production was insignificant in all systems. The DDT removal was slower with FeS than with Fe^0 , but the amounts of DDD and DDE produced did not exceed baseline. Treatment with a 1:1 mixture of Fe^0 – FeS removed about 95% of the added mass of DDT within 4 days and generated significant amounts of DDD and minor amounts of DDMU. When small amounts of H_2O_2 were introduced halfway through the Fe^0 and FeS treatment times, the mass of DDT decreased by 87% and 96%, respectively, within 2 days. Our results demonstrate that mixtures of Fe^0 – FeS in combination with H_2O_2 can be used for rapid and efficient removal of DDT from aqueous solutions.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Zero-valent iron; Ferrous-sulfide; Triton X-114; DDD; DDE; DDMU

1. Introduction

DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) was used extensively for pest control in agriculture and forestry worldwide (Foreman and Gates, 1997; Nowell et al., 1999). The use of DDT was banned on agricultural soils in the United States in 1972 (Sayles et al., 1997; Nowell et al., 1999) and in some parts of Europe by the late 1970s (Foght et al., 2001). High concentrations of DDT and its transformation products DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane) and DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene) continue to be found in soils and sediments at many locations (Nowell et al., 1999). Both DDE and DDD existed as impurities in commercial DDT formulations but can also be formed through the environmental transformation of

DDT (Sayles et al., 1997; Quensen and Mueller, 1998; Foght et al., 2001). DDT and some of its transformation products, especially the (–) enantiomers of *o,p'* isomers are shown to be estrogenically active (Garrison et al., 2000). It is reported to be a potential endocrine disruptor in both avian and mammalian systems, resulting in eggshell thinning, impaired male reproductive ability, and interference with sex hormones (Kupfer, 1975; McBlain, 1987; Kelce et al., 1995; Foreman and Gates, 1997; Garrison et al., 2000). The US Environmental Protection Agency has classified DDT, DDD and DDE as priority pollutants (Sayles et al., 1997; Foght et al., 2001).

DDT enters rivers and streams mainly through industrial point sources, runoff from agricultural fields and from atmospheric deposition due to volatilization (Nowell et al., 1999; Schwarzbauer et al., 2001; Binelli and Provini, 2003). DDT, DDD and DDE are strongly retained by soils, sediments, and biota lipids due to their low aqueous solubility

* Corresponding author. Tel.: +1 574 631 5164; fax: +1 574 631 9236.
E-mail address: jtalley1@nd.edu (J.W. Talley).

Table 1
Results of DDT transformation in various treatments

Treatment	Time	DDT transformed (% recovered from aqueous phase) ^a	Metabolites produced, μg		
			DDD	DDE	DDMU
Fe ⁰	150 h	88 ± 12 (61)	406 ± 50	16.0 ± 0.9	85 ± 6
FeS	150 h	56 ± 3 (46)	19 ± 2	2 ± 4	0.0
Fe ⁰ :FeS mix ^b	4 days	95.0 ± 0.4 (41)	360 ± 7	15 ± 17	27.0 ± 0.3
Fe ⁰ :FeS mix ^c	4 days	85 ± 8 (67)	351 ± 49	5 ± 5	34 ± 4
Fe ⁰ -H ₂ O ₂	2 days				
@ 0 time ^d		97.0 ± 0.5 (45)	164 ± 10	27 ± 6	0.0
@ 1/2 time ^e		87 ± 1 (40)	195.0 ± 0.4	0.0	61 ± 5
FeS-H ₂ O ₂	2 days				
@ 0 time ^d		66 ± 1 (34)	7.0 ± 0.6	0.0	0.0
@ 1/2 time ^e		96.0 ± 0.4 (4)	0.0	0.0	0.0
Fe ⁰ :FeS-H ₂ O ₂	2 days				
@ 0 time ^d		95.0 ± 0.4 (35)	194 ± 52	8 ± 2	55 ± 7
@ 1/2 time ^e		89 ± 5 (32)	145 ± 70	0.0	42 ± 22
Fe ⁰ -Triton X-114	16 days	98.0 ± 0.7 (75)	262 ± 19	101 ± 8	185 ± 18
FeS-Triton X-114	16 days	44 ± 3 (78)	107 ± 12	28.0 ± 0.9	0.0
Fe ⁰ :FeS mix-Triton X-114	8 h	99.0 ± 0.5 (82)	382 ± 13	21 ± 2	35 ± 1

^a Percent of total amount (approximately 800 μg) of DDT added.

^b 1:1 mixture (375 mg each) of abiotic agents.

^c 1:0.13 mixture (750 mg Fe⁰ to 100 mg of FeS or CaO₂).

^d Hydrogen peroxide (0.5 ml of 50% strength) was added at the beginning of the reaction.

^e Hydrogen peroxide (0.5 ml of 50% strength) was added after half of the total reaction time had elapsed.

(3, 40 and 160 $\mu\text{g l}^{-1}$, respectively) and high octanol–water partitioning coefficients ($\text{Log } K_{\text{OW}} = 6.36, 5.69$ and 6.02 , respectively). Sediments and benthic fauna may act as sinks for DDT, DDD and DDE (hereafter collectively referred to as DDX) and thus these compounds are extremely persistent in the environment (Heberer and Dünnebier, 1999). Concentrations of DDT in sediments vary greatly, from 3 to 8100 $\mu\text{g/kg}$ (Schwarzbauer et al., 2001; Wade et al., 2002). The half-life of DDX depends upon soil and sediment conditions with reported values ranging from 3 to 30 years (Dimond and Owen, 1996). In areas where dredging of these contaminated sediments is necessary to keep waterways open, resuspension of DDT in the dredging flux is a very real concern.

Abiotic reductive dechlorination of DDT was first reported about three decades ago by DeLoach (1971) in the presence of cooking utensils made of iron. Transformation of DDT in the soil–iron redox systems has also been observed (Glass, 1972). Gillham and O'Hannesin (1994) as well as Matheson and Tratnyek (1994) reported the reductive dehalogenation of a variety of chlorinated compounds in the presence of zero-valent iron (Fe⁰). Sayles et al. (1997) reported that Fe⁰ could successfully dechlorinate DDT in a buffered-aqueous solution. Greater than 90% of the total mass of added DDT (120 $\mu\text{mol l}^{-1}$) was removed within 20 days and similar rates of removal were observed for both DDD and DDE (Sayles et al., 1997). They further observed that the rate of DDT removal was independent of the surface area of Fe⁰, but the rate of DDD removal was limited by mass transfer to the Fe⁰ surface due to poor aqueous solubility of DDD (Sayles et al., 1997). It was observed that the rate of DDX removal by Fe⁰ doubled in the presence of Triton X-114 surfactant.

This was attributed to the greater mass transfer of DDX due to the apparent enhancement of its solubility in the surfactant micelles. It is well documented that reductive dechlorination by Fe⁰ is a surface mediated process and requires a direct contact between the substrate and the metal surface (Matheson and Tratnyek, 1994; Weber, 1996).

This study examined several combinations of abiotic techniques to transform DDX. It expanded previous work done with the abiotic transformation of DDX (Sayles et al., 1997) in that it explored various abiotic systems in an unbuffered state. Fe⁰, (FeS) and mixture of Fe⁰ and FeS were used in combination with hydrogen peroxide (H₂O₂) and Triton X-114 surfactant for abiotic transformation of DDT (Table 1). The work with Triton X-114 expanded previous work (Sayles et al., 1997) done with the surfactant by using an unbuffered system with the Triton present well below the critical micelle count. All of the experiments were conducted in non-buffered systems (without altering the pH and redox conditions), to more closely simulate natural aquatic environments.

2. Experimental section

2.1. Chemicals

Electrolytic iron powder (Fe⁰, 100 mesh); iron sulfide (FeS); calcium chloride (CaCl₂); chromatography grade hexane, acetone, toluene, and ethanol were obtained from Fisher Scientific (Fair Lawn, NJ). DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane); DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane) and DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene) were obtained from Sigma

(Milwaukee, WI) and were used without further purification. Triton X-114 was obtained from Aldrich (Aldrich Chemical Company, Milwaukee, WI) and ethyl alcohol 200 proof was obtained from Spectrum (Spectrum Quality Products, New Brunswick, NJ).

2.2. Redox potential

Reactants for these experiments were chosen because their potential to reduce/oxidize DDT and its metabolites and their stability in the environment (comparisons between more stable and less stable forms). Standard electrode potentials (volts) given by Bratsch (1989) for half-reactions in water at 298.15 K were used to estimate reactions and associate by-products. E° for the following half-reactions are: $\text{Fe}^{2+}/\text{Fe(c)}$, -0.44 , $\text{Fe}^{3+}/\text{Fe}^{2+}$, 0.771 , H_2O_2 , H^+/OH , 0.96 , H_2O , $\text{Sg(c)}/\text{S}^{2-}$, -0.57 . It was anticipated that H_2O_2 would result in the most complete transformation of DDT and its metabolites, as the free radicals formed during transformation should scavenge everything available. Matheson and Tratnyek (1994) showed that Fe^0 has a greater redox potential and will transform faster at pH 7 than the reaction of Fe^{2+} to Fe^{3+} suggesting that Fe^0 should further transformation more than FeS . Sayles et al. (1997) showed that the amount of Fe^0 and the addition of Triton X-114 had no significant effect on the redox potential of their systems. Varying the amount of metals and the addition of surfactant should not have a detrimental effect on the ability of reactants to transform DDT and its metabolites, although the solubility of DDT, due to the addition of surfactant, should increase the ability of the reactants to transform it.

2.3. Treatment procedures

Stock solutions of DDT, DDD and DDE (5 mM each) were prepared in chromatography-grade acetone. CaCl_2 (0.01 M) was prepared in distilled deionized water and was used as an unbuffered background electrolyte for all aqueous solution experiments. For experiments using Triton X-114, a 70 mg l^{-1} solution was made in Milli-Q water and used without any electrolyte. Glass vials (16 ml capacity) with Teflon-lined septa caps were used as reaction vials with about 0.75 g of Fe^0 or FeS being added to each vial. Then 8 ml of 0.01 M CaCl_2 or Triton X-114 solutions was added to the every vial. Reaction vials were spiked with 450 μl of DDT stock solution to achieve $100 \mu\text{g ml}^{-1}$ (150 μM) DDT per vial (compared to 43 mg l^{-1} spike used by Sayles et al., 1997). The concentration of DDT in solution was purposely higher than that found in natural systems as this was a screening test to identify different chemical mixtures that could transform DDT in aqueous solutions. Reaction vials were tightly sealed with Teflon-lined screw caps to prevent any loss of solution. To ensure proper sealing, Teflon tape was applied to the threads of the reaction vials before screwing on the caps. To minimize the influence of diffusion on the DDT removal rate, vials

were mixed continuously in the dark using a rotary shaker. Controls (without addition of any abiotic agent, i.e., Fe^0 or FeS) were also prepared to account for any possible loss of DDT due to interactions with reactor vials or caps. Sufficient numbers of reaction vials were used to allow for six vials (three for control and three for treatment) to be sacrificed for each sampling time. The triplicate samples were averaged and used to determine standard deviations, which are represented by error bars on all graphs.

At predetermined time intervals (0, 5, 15, 25, 30 min and 1, 2, 3, 4, 5, 6, 8, 24, 48, 96, 192, 384 and 720 h), reaction vials were removed from the shaker and 5 ml of chromatography grade hexane was added to each vial. After 2 h of mixing, reaction vials were removed from the shaker and placed on a counter top in an upright position for about 5 min to achieve complete phase separation. Approximately, 1 ml aliquots from the hexane phase were removed in 2 ml amber borosilicate glass vials; the vials were immediately sealed and later analyzed for DDT and its transformation products using gas chromatography.

For experiments using a Triton X-114 surfactant, an extraction method previously described by Sayles et al. (1997) was used, where 0.5 ml ethanol, 0.5 ml NaOH, and 5 ml toluene were added to each vial and the reaction vials shaken for 4 h until the aqueous phase was clear. The amount of DDT transformed by the abiotic treatments was calculated from the difference in concentrations between the controls and the treatment reaction vials. Similar experiments were conducted to determine the rates of DDE and DDD removal from the aqueous solutions.

2.4. Measurement of DDT, DDE and DDD

A Hewlett Packard 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and an autosampler (HP7673) was used for DDT, DDE and DDD analyses. The GC capillary column (HP-5, 30 m \times 0.32 mm, 0.25- μm film thickness) was obtained from Agilent Technologies. Ultra high purity helium (flow rate of 2.5 ml min^{-1}) and nitrogen were used as the carrier and makeup gas, respectively. The sample injection volume was 3 μl splitless for samples without surfactant and the injector temperature was set to 275 $^\circ\text{C}$. The oven temperature was ramped from 150 $^\circ\text{C}$ to 154 $^\circ\text{C}$ @ 5 $^\circ\text{C min}^{-1}$ and 154 $^\circ\text{C}$ to 290 $^\circ\text{C}$ @ 25 $^\circ\text{C min}^{-1}$ (hold for 0.5 min) for non-surfactant treatments. For samples with surfactant, the injection volume was 2 μl splitless; the oven temperature was ramped from 150 $^\circ\text{C}$ to 154 $^\circ\text{C}$ @ 5 $^\circ\text{C}$ (hold for 1 min), and 154 $^\circ\text{C}$ to 290 $^\circ\text{C}$ (hold for 4.26 min). The detector temperature was maintained at 290 $^\circ\text{C}$. This method was determined experimentally for most efficient elution of DDT and its metabolites in a hexane supernatant. Standards of DDT, DDE and DDD (1–450 μM) were prepared by diluting the stock (5 mM) solutions in chromatography-grade acetone for constructing calibration curves, which were used to determine DDT, DDE and DDD concentrations.

3. Results and discussion

3.1. DDT transformation by Fe^0 and FeS

The kinetics of DDT transformation by Fe^0 and FeS are shown in Figs. 1 and 2. Approximately, 88% and 56% of the added DDT was removed within 150 h of treatment with Fe^0 and FeS , respectively (Table 1). Sayles et al. (1997) saw a 90% transformation within 20 days in a buffered, anoxic system with glass beads added for mixing. An initial lag in transformation might be explained by the time required for the DDT to come into contact with the metal surface for electron exchange (Matheson and Tratnyek, 1994; Weber, 1996). This explanation would be consistent with reductive dechlorination being the means of DDT transformation and electron transfer with the metal surface being the mechanism of transformation. Analyses of samples from the controls verified that both

DDD and DDE existed as impurities (7.5% and 2.4%, respectively, mol/mol basis) in DDT (Sayles et al., 1997). Transformation of DDT by Fe^0 resulted in the formation of approximately equivalent amounts of DDD, suggesting that reductive dechlorination of DDT occurred preferentially at the metal surface (Matheson and Tratnyek, 1994; Weber, 1996). Approximately, 406 μg of DDD accumulated in each reactor after 150 h of treatment indicating that most of the DDD formed did not undergo further dechlorination. This may suggest that dechlorination of DDD by Fe^0 occurs at a much slower rate than that of DDT. This observation is consistent with previous reports suggesting slower rates for each successive dehalogenation by Fe^0 (Matheson and Tratnyek, 1994). Slower dechlorination kinetics for DDD, as compared to DDT, was also reported by Sayles and co-workers (1997). Slower transformation may also be due to the slower rate of transformation for $Fe^{2+} \rightarrow Fe^{3+}$ compared to $Fe^0 \rightarrow Fe^{2+}$ (Matheson and Tratnyek, 1994).

A portion of DDD generated during the treatment of DDT with Fe^0 may have undergone further transformation as significant amounts of DDMU (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene) were detected. DDMU is either a dehalodehydrogenation product of DDD or a reductive dechlorination product of DDE (Aislabie et al., 1997; Sayles et al., 1997; Quensen and Mueller, 1998; Coronacruz et al., 1999; Heberer and Dünnebier, 1999; Foght et al., 2001). Since DDE was present only in insignificant amounts, it supports the conclusion that DDD is undergoing further transformation to generate DDMU. Approximately 85 μg of DDMU accumulated in the reaction vials after 150 h of DDT treatment with Fe^0 . The amount of DDMU produced increased with treatment time (Fig. 1). Conversion of DDT into DDMU has been observed in both biotic (Quensen and Mueller, 1998) and abiotic (Sayles et al., 1997) transformation processes.

Interestingly, the amount of DDE produced was insignificant in all treatments. Even after 30 days of DDT treatment with Fe^0 , the level of DDE in the reaction vials was similar to background levels ($\sim 16 \mu\text{g}$ vs. $19 \mu\text{g}$). These observations are consistent with the findings of Schwarzenbach and co-workers (Schwarzenbach et al., 1993) who showed that DDT transforms into DDE by dehydrodehalogenation and not by reductive dechlorination. It is a significant observation that only traces of DDE were generated in our treatments because DDE is more persistent in the environment than DDT (Boul et al., 1994). DDE is considered a terminal product of microbial transformation of DDT in soils and sediments (Rochkind-Durbinsky et al., 1987).

Small peaks were observed on some GC chromatograms for longer treatment times, suggesting that additional transformation products of DDT were formed. The areas under these peaks were insignificant so no further attempt was made at this time to quantify them. Approximately 61% of the total DDT mass lost during treatment with Fe^0 was recovered as DDD, DDE and DDMU with 39%

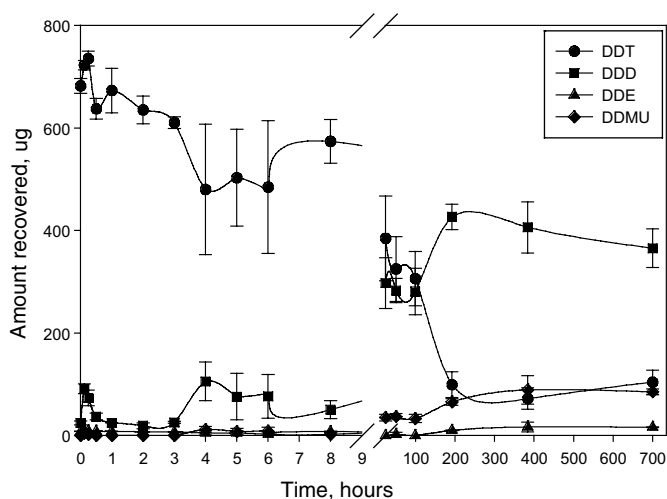


Fig. 1. Kinetics of DDT transformation by Fe^0 and production of metabolites DDD, DDE and DDMU in aqueous solutions.

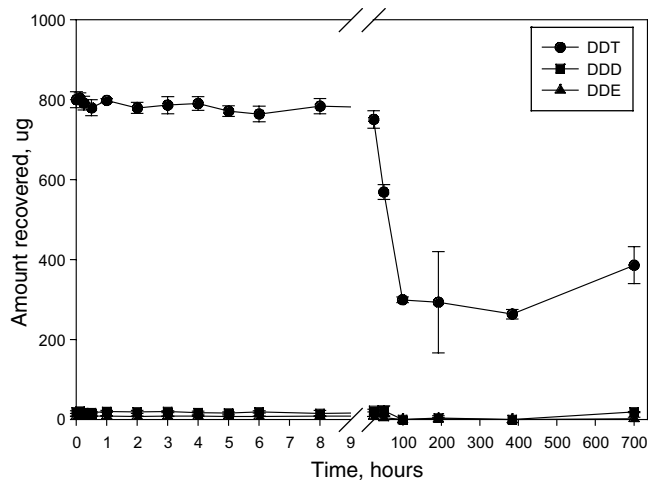


Fig. 2. Kinetics of DDT transformation by FeS and production of metabolites DDD, DDE and DDMU in aqueous solutions.

being unaccounted for Gillham and O'Hannesin (1994) recovered only 27% of their parent compound in the form of its less chlorinated transformation products. Major portions of the unaccounted mass could be attributed to the strong sorption of transformation products to the metal surface or further transformation to non-polar metabolites that were not recovered by our extraction techniques.

The initial rates of DDT removal using FeS were slower compared to Fe⁰ perhaps due to the difference in their redox potential (Figs. 1 and 2). It was observed that 0.75 g and 1.2 g of FeS resulted in comparable levels of DDT transformation (data not shown). This suggests that unlike Fe⁰, DDT transformation by FeS may be independent of the surface area and that Fe⁰ and FeS transform DDT via different pathways. We propose that the pathway of DDT transformation by FeS may be different from DDT transformation mechanism by Fe⁰, though electron transfer is still the suggested mechanism of transformation.

Equal amounts (375 mg each) of Fe⁰ and FeS were used to achieve 1:1 (w/w) mixture to explore the effect of a mixture of Fe⁰ and FeS on the transformation of DDT. The combination of Fe⁰ and FeS removed DDT more effectively (Fig. 3) than these abiotic agents used independently (see Figs. 1 and 2) with 95% of the original DDT mass being removed within 4 days (Table 1). These results clearly demonstrate that the rate of DDT removal from aqueous solutions can be improved by combining abiotic agents due to the complementary nature of the transformation mechanisms involved in DDT removal by Fe⁰ and FeS. It may also be attributed to the ability of FeS to remove the H₂ layer that forms on the Fe⁰ surface, maximizing the ability of the iron surface to transform DDT (Rochkind-Durbinsky et al., 1987).

A significant amount of DDD (360 µg) was accumulated in the reaction vials due to the transformation of DDT by the Fe⁰:FeS mixture after 4 days, but the amount of DDE formed was insignificant and no other transformation products were observed during the treatment. Over 41% of the removed DDT was recovered as DDD, DDE and

DDMU, with 59% being unaccounted for after 8 days of treatment. These results suggest that reductive dechlorination is the primary mechanism involved in DDT transformation by Fe⁰-FeS systems.

3.2. Impact of H₂O₂ addition on DDT transformation kinetics by Fe⁰ and FeS

The effect of H₂O₂ addition on DDT transformation by both Fe⁰ and FeS was evaluated. It has been shown that sequential additions of H₂O₂ enhance transformation of nitroaromatics by Fe⁰ (Mackenzie et al., 1999). Approximately 500 µl of H₂O₂ (50% solution) was added to reaction vials at the beginning or half way through the respective treatment times. Vigorous effervescence was observed immediately after adding H₂O₂ and the vials were vented to prevent any pressure build up before placing them on the shaker. Fig. 4 shows the impact of H₂O₂ addition on DDT removal by both Fe⁰ (Fig. 4A) and FeS (Fig. 4B). When H₂O₂ was added at the start of the reaction time, 97% mass reduction was seen in the Fe⁰ reaction vials after 2 days (Fig. 4A). About 87% of the original mass of the added DDT was transformed within 2 days of treatment when H₂O₂ was added to the Fe⁰ reaction vials half way through the reaction time (Fig. 4A). Only 66% of DDT mass was transformed when H₂O₂ was added ini-

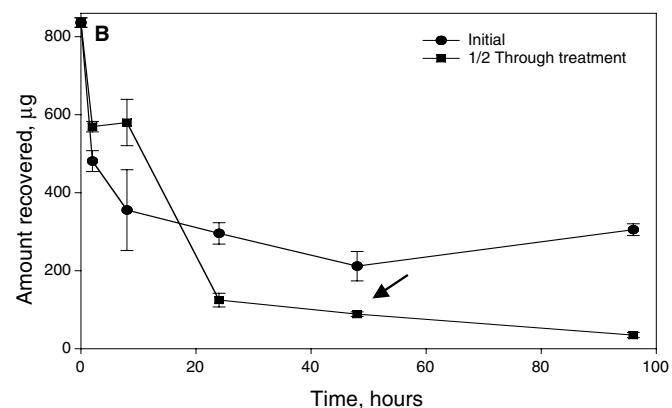
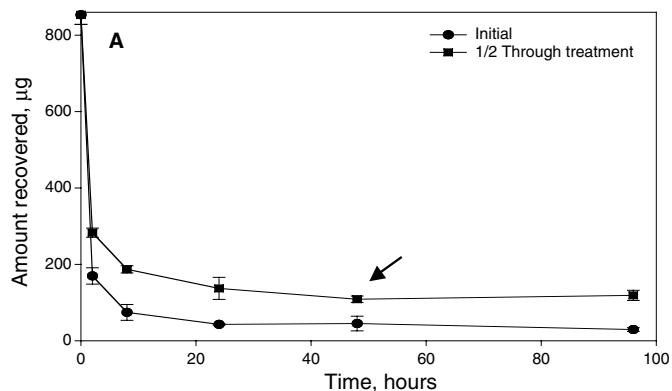


Fig. 4. Impact of hydrogen peroxide (H₂O₂) additions on DDT transformation by Fe⁰ (A) and FeS (B). Arrows indicate H₂O₂ addition half-way through the treatment time.

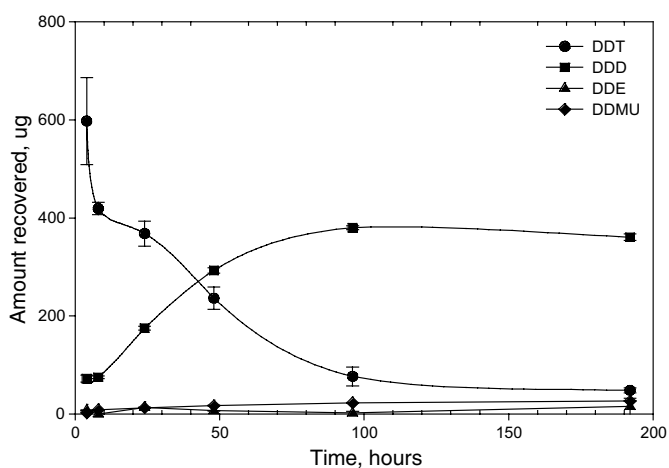


Fig. 3. Kinetics of DDT by 1:1 mixture of Fe⁰ and FeS and production of metabolites DDD, DDE and DDMU in aqueous solutions.

tially to the FeS system (Fig. 4B). FeS was very effective in removing DDT from the aqueous solution when used in combination with H₂O₂ added halfway through the treatment time, with 96% of DDT being removed within 2 days (Fig. 4B). No transformation of DDT was observed when H₂O₂ alone was added to the DDT solution.

In the Fe⁰ system, the timing of the H₂O₂ addition made only a minor difference; 9% transformation for longer treatment times (days) and 15% for shorter treatment times (hours). However, H₂O₂ addition half way through the treatment time was more effective in removing DDT in the FeS system. It was anticipated that the addition of H₂O₂ would oxidize Fe⁰ and therefore reduce its ability to transform DDT. However, faster rates of DDT removal were observed when H₂O₂ was added. This could be due to the removal of H₂ build-up or other precipitates from the Fe⁰ surfaces by the peroxide (Hundal et al., 1997), rendering the iron surfaces more reactive and capable of rapid electron transfer between the metal surface and DDT.

The presence of considerable amounts of DDD and DDMU, and only traces of DDE in the Fe⁰:H₂O₂ system, suggests that reductive dechlorination was the dominant pathway of DDT transformation. Only traces of DDD, DDMU and DDE were observed when H₂O₂ was used in combination with FeS, suggesting again a different pathway for transformation of DDT. The relative amounts of transformation products were lower when H₂O₂ was added half way through the treatment time.

3.3. Impact of Triton X-114 on DDT transformation kinetics by Fe⁰ and FeS

To evaluate whether the aqueous solubility of DDX was limiting its abiotic transformation, experiments were conducted using a non-ionic surfactant, Triton X-114. Previous studies showed significant enhancements in the solubility of DDX in the presence of surfactants, such as Brij 35 and Triton series. These studies showed that only non-ionic surfactants caused enhancements below the critical micelle concentration (CMC) (Kile and Chiou, 1989). Extraction of DDX was performed using toluene as previously described by Sayles et al. (1997). This method was selected because toluene proved better than hexane at extracting DDX from the surfactant solution, although the shaking time after addition of toluene doubled as compared to hexane. Only a 0.13 mM (70.5 mg l⁻¹) concentration of Triton X-114 was used in this study. This concentration was intentionally kept below the CMC level of 0.2 mM to minimize extraneous chemical addition requirements for future field studies.

In the surfactant-Fe⁰ system, 98% of the DDT mass was removed after 16 days (Fig. 5A). Corresponding increases in DDD concentrations were observed reaching approximately 262 µg in 16 days of treatment. Build up of DDMU (250 µg) was also observed within the first 16 days of the treatment, followed by a steady decline (185 µg after 30 days of treatment). The increase in the mass of DDMU

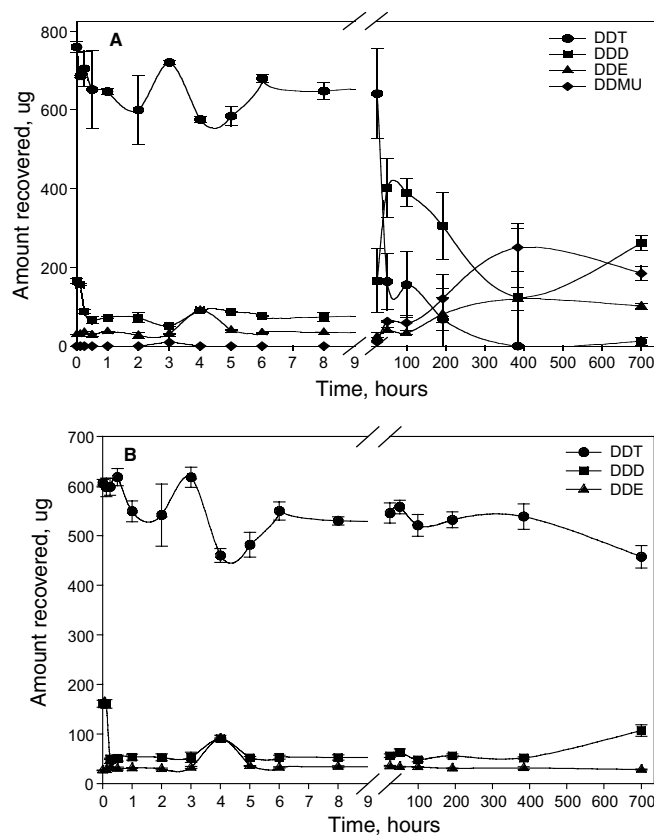


Fig. 5. Kinetics of DDT transformation by Fe⁰ (A) and FeS (B) in 0.13 mM Triton X-114 solution and production of metabolites.

correlated with a decrease in the mass of DDD in solution. The DDE concentration in solution increased to 101 µg within 16 days of treatment. In the surfactant-FeS system, only 44% of the DDT was transformed in the FeS-surfactant system within 16 days of treatment (Fig. 5B). The amount of DDD produced reached 107 µg, while the amount of DDE produced did not exceed background levels. There was no production of DDMU. This is consistent with our previous FeS treatments.

3.4. Impact of Triton X-114 on DDT transformation kinetics by a mixture of Fe⁰ and FeS

To compare the extent and rate of DDT transformation by different techniques in the Triton X-114 solution, a mixture of Fe⁰-FeS (1:1) was used (Table 1). Almost all of the added DDT mass was transformed within 8 h of reaction time (99%). Approximately 319 µg of DDD, 21 µg of DDE and 35 µg of DDMU accumulated in the reaction vials after 8 h of treatment. The build-up of DDD with only minor amounts of DDE is consistent with the primary mechanism of reductive dehalogenation (Schwarzenbach et al., 1993). The relatively limited amounts of DDMU generated by the transformation of DDD is consistent with the hypothesis that secondary dechlorination takes place at a slower rate (Matheson and Tratnyek, 1994; Sayles et al., 1997). The acceleration of DDT transformation in the

Fe⁰–FeS mixture suggests that although Fe⁰ and FeS transform DDT through two distinct mechanisms, they appear to complement each other resulting in accelerated removal of DDT.

3.5. DDD transformation

Experiments were conducted with a DDD stock solution using Fe⁰, FeS, and mixtures of Fe⁰ and FeS to evaluate the transformation kinetics and the involved pathways. No appreciable transformation of DDD was observed in either Fe⁰ or FeS after 16 and 30 days. Only 17% reduction in DDD mass was achieved in 8 days when it was treated with a 1:1 mixture of Fe⁰–FeS. There was no observable production of DDE and only a small amount of DDMU (~9.7 µg) was produced, suggesting that reductive dehalogenation and electron exchange were the dominant mechanisms of DDD transformation by the Fe⁰–FeS mixture. In the Fe⁰–Triton X-114 system, a 50% reduction in DDD was observed after 30 days of treatment. There was an accumulation of approximately 126 µg of DDMU during DDD transformation and 81 µg DDE produced. The addition of H₂O₂ to the Fe⁰ system in the beginning or halfway through the treatment resulted in 40% and 64% removal of DDD, respectively, within 4 days. Approximately 148 µg of DDMU and 17 µg of DDE were produced when H₂O₂ was added in the beginning of the reaction, but only 75 µg of DDMU and negligible amounts of DDE were produced when H₂O₂ was added halfway through the treatment. In the FeS systems, the addition of H₂O₂ resulted in a 43% and 87% reduction within 4 days when added in the beginning or halfway through the treatment. No degradates were produced in either case.

Acknowledgments

Special thanks to Ms. Tina Mitchell for assisting in the laboratory, Ms. Sara Nicholl for assistance in the laboratory and with data interpretation, and Ms. Leilani Arthurs for assistance with proof reading. We would also like to thank Dennis Birdsell and Rian Galloway for their technical assistance with the GC and the Center for Environmental Science and Technology at the University of Notre Dame for the use of their facilities.

References

- Aislabie, J.M., Richards, N.K., Boul, H.L., 1997. Microbial degradation of DDT and its residues—a review. *New Zealand J. Agric. Res.* 40, 269–282.
- Binelli, A., Provini, A., 2003. DDT is still a problem in developed countries: the heavy pollution of Lake Maggiore. *Chemosphere* 52, 717–723.
- Boul, H.L., Garnham, M.L., Hucker, D., Baird, D., Aislabie, J., 1994. Influence of agriculture practices on the levels of DDT and its residues in soil. *Environ. Sci. Technol.* 28 (8), 1397–1402.
- Bratsch, S.G., 1989. Standard electrode potentials and temperature coefficients in water at 298.15 K. *J. Phys. Chem. Ref. Data* 18 (1), 1–21.
- Corona-Cruz, A., Gold-Bouchot, G., Gutierrez-Rojas, M., Monroy-Hermosillo, O., Favela, E., 1999. Anaerobic-aerobic biodegradation of DDT (dichlorodiphenyl trichloroethane) in soils. *Environ. Contam. Toxicol.* 63, 219–225.
- DeLoach, H.K., 1971. Effect of cooking utensil composition and contents on the reductive dechlorination of DDT to DDD. *J. Assoc. Off. Anal. Chem.* 54, 1352–1356.
- Dimond, J.B., Owen, R.B., 1996. Long-term residue of DDT compounds in forest soils of Maine. *Environ. Pollut.* 92, 227–230.
- Foght, J., April, T., Biggar, K., Aislabie, J., 2001. Bioremediation of DDT-contaminated soils: a review. *Biorem. J.* 5, 225–246.
- Foreman, W.T., Gates, P.M., 1997. Matrix-enhanced degradation of *p,p'*-DDT during gas chromatographic analysis: a consideration. *Environ. Sci. Technol.* 31, 905–910.
- Garrison, A.W., Nzungung, V.A., Avants, J.K., Ellington, J.J., Jones, W.J., Rennels, D., Wolfe, N.L., 2000. Phytodegradation of *p,p'*-DDT and the enantiomers of *o,p'*-DDT. *Environ. Sci. Technol.* 34, 1663–1670.
- Gillham, R.W., O'Hannesin, S.F., 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Groundwater* 32, 958–967.
- Glass, B.L., 1972. Relation between the degradation of DDT and the iron redox system in soil. *J. Agric. Food Chem.* 20, 324–327.
- Heberer, T., Dünnebier, U., 1999. DDT metabolite bis(chlorophenyl)acetic acid: the neglected environmental contaminant. *Environ. Sci. Technol.* 33, 2346–2351.
- Hundal, L.S., Singh, J., Bier, E.L., Shea, P.J., Comfort, S.D., Powers, W.L., 1997. Removal of TNT and RDX from water and soil using iron metal. *Environ. Pollut.* 97, 55–64.
- Kelce, W.R., Stone, C.R., Laws, S.C., Gray, L.E., Kempainen, J.A., Wilson, E.M., 1995. Persistent DDT metabolite *p,p'*-DDE is a potent androgen receptor antagonist. *Nature* 375, 581–585.
- Kile, D.E., Chiou, C.T., 1989. Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration. *Environ. Sci. Technol.* 23, 832–838.
- Kupfer, D., 1975. Effects of pesticides and related compounds on steroid metabolism and function. *Crit. Rev. Toxicol.* 4, 83–124.
- Mackenzie, P.D., Horney, D.P., Sivavec, T.M., 1999. Mineral precipitation and porosity losses in granular iron columns. *J. Haz. Mater.* 68, 1–17.
- Matheson, L.J., Tratnyek, P.G., 1994. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* 28, 2045–2053.
- McBlain, W.A., 1987. The levo enantiomer of *o,p'*-DDT inhibits the binding of 17-estradiol to the estrogen receptor. *Life Sci.* 40, 215–221.
- Nowell, L.H., Capel, P.D., Dileanis, P.D., 1999. In Pesticides in Stream Sediment and Aquatic Biota; Distribution, Trends, And Governing Factors. Lewis Publishers, Boca Raton.
- Quensen III, J.F., Mueller, S.A., 1998. Reductive dechlorination of DDE to DDMU in marine sediment microcosms. *Science* 280, 722.
- Rochkind-Durbinsky, M.L., Sayler, G.S., Blackburn, J.W., 1987. In Microbiological Decomposition of Chlorinated Aromatic Compounds. M. Dekker, New York.
- Sayles, G.D., You, G., Wang, M., Kupferle, M.J., 1997. DDT, DDD, and DDE dechlorination by zero-valent iron. *Environ. Sci. Technol.* 31, 3448–3454.
- Schwarzbauer, J., Ricking, M., Franke, S., Francke, W., 2001. Halogenated organic contaminants in sediments of the Havel and Spree Rivers (Germany). Part 5 of organic compounds as contaminants of the Elbe River and its tributaries. *Environ. Sci. Technol.* 35, 4015–4025.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 1993. In: Environmental Organic Chemistry, New York.
- Wade, R., Lotufo, G.R., Steevens, J.A., Houston, J.G., Fredrickson, H.L., Perkins, E.J., Morrow, A.B., Weiss, C.A., Furey, J.S., Felt, D., Duke, M., Talley, J.W., 2002. Assessment of DDT bioavailability in the little sunflower river sediment and agricultural soil, ERDC TR-02-6.
- Weber, E.J., 1996. Iron-mediated reductive transformations: investigation of reaction mechanism. *Environ. Sci. Technol.* 30, 716–719.