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EFFECTIVENESS OF CHEMICAL OXIDATION TO REMOVE ORGANOCHLORINE PESTICIDES FROM SOIL

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ABSTRACT: The effectiveness of chemical oxidants in reducing the concentration of organochlorine pesticides, primarily aldrin and dieldrin, in soil was tested in a bench-scale study. Fenton's reagent, hydrogen peroxide, and potassium permanganate have been shown to destroy chlorinated compounds but their relative effectiveness on organochlorine pesticides was not well documented and was considered uncertain. The soil samples for the study were collected from a former pesticide distribution facility and were composed of clay and clayey silt. Samples of site soil contained up to 240 milligrams per kilogram (mg/kg) aldrin and up to 50 mg/kg dieldrin. Also present were lesser concentrations of other organochlorine pesticides such as chlordane and volatile organic compounds such as tetrachloroethene. The study demonstrated that each of the three oxidants tested can reduce the concentrations of aldrin, dieldrin and chlordane in the site soil. Potassium permanganate destroyed up to 100 percent of aldrin, 35 to 65 percent of dieldrin, and 57 to 71 percent of alpha-chlordane, making this oxidant much more effective than hydrogen peroxide or Fenton's reagent.

INTRODUCTION

Aldrin and dieldrin are closely related organochlorine pesticides that are extremely persistent in the environment. Aldrin has been used as a soil insecticide to control rootworms, beetles, and termites, while dieldrin has been used in agriculture for soil and seed treatment as well as for control of mosquitoes and tse-tse flies. Dieldrin is the oxygenated metabolite of aldrin, and the two chemicals tend to occur together. Both are relatively immobile in soil and relatively insoluble in water. These chemicals have well known adverse health effects, and are persistent, bioaccumulative and toxic pollutants targeted for reduction in the environment by the USEPA. Selected physical and chemical properties of aldrin and dieldrin are summarized in Table 1.

Chemical oxidants such as Fenton's reagent, hydrogen peroxide (H_2O_2), and potassium permanganate ($KMnO_4$) are known to destroy chlorinated solvents and may reasonably be expected to be effective toward aldrin, dieldrin and other organochlorine pesticides. These chemical reagents (or aqueous solutions thereof) can be sprayed onto an ex situ soil pile or injected into the subsurface for in situ treatment of soil. Issues related to the use of each of these oxidants are described below.

Fenton's reagent. Fenton's reagent, an acidified mixture of H_2O_2 and ferrous iron (Fe[II]) is a strong oxidant. It is generally understood that Fenton's reagent generates free hydroxyl radicals (Walling, 1975). The hydroxyl radical is non-selective and may react not only with the target contaminant, but also with soil particles and natural organic matter. Decomposition of Fenton's reagent is exothermic and generates oxygen gas. The amount of heat and oxygen generated depends upon the initial concentrations of H_2O_2 and Fe(II)—in general, higher concentrations H_2O_2 and Fe(II) will generate more gas and more heat more quickly, potentially increasing the temperature of the subsurface dramatically and necessitating the need to manage the oxygen produced.

Because Fenton's reagent is non-selective and because the hydroxyl radical may be regenerated (Fenton's oxidation is catalytic) it is not possible to write a stoichiometric reaction for the decomposition of aldrin or dieldrin by Fenton's reagent.

TABLE 1. Physical and chemical properties of aldrin and dieldrin[a].

Property	Aldrin	Dieldrin
Chemical Formula	$C_{12}H_8Cl_6$	$C_{12}H_8Cl_6O$
Molecular Weight	364.93	380.93
Melting Point	104 – 105.5 °C	175 – 176 °C
Solubility:		
Water at 20 °C	0.010 mg/L	0.110 mg/L
Organic solvents	Very soluble in most organic solvents	Moderately soluble in common organic solvents
Partition coefficients:		
Log K_{ow}	6.5	6.2
Log K_{oc}	7.67	6.67

[a] All information is from Agency for Toxic Substances and Disease Registry (ATSDR), 2000.

Hydrogen Peroxide, H_2O_2. H_2O_2 is a weaker oxidant than Fenton's reagent, but like Fenton's reagent, it is non-selective and decomposes to form oxygen gas. It can potentially react with aldrin and dieldrin either directly, or in Fenton-like manner, with Fe(II) naturally present in the soil serving as the iron source. If aldrin and dieldrin react directly with H_2O_2 to produce carbon dioxide, water and chloride, then the following stoichiometries may apply:

$$\underset{\textit{aldrin}}{C_{12}H_8Cl_6} + 25\,H_2O_2 \rightarrow 12CO_2 + 6Cl^- + 6H^+ + 26H_2O \tag{1}$$

$$\underset{\textit{dieldrin}}{C_{12}H_8Cl_6O} + 24\,H_2O_2 \rightarrow 12CO_2 + 6Cl^- + 6H^+ + 25H_2O \tag{2}$$

However, if oxidation occurs via Fenton-type chemistry, stoichiometric reactions cannot be written for the reasons discussed above for Fenton's reagent.

Potassium Permanganate, $KMnO_4$. Oxidation reactions for the conversion of aldrin and dieldrin to carbon dioxide and water by $KMnO_4$ are given in Equations 3 and 4. Based on these stoichiometries, 7.9 grams (g) $KMnO_4$ is needed to oxidize 1 g aldrin, while 6.6 g $KMnO_4$ is needed to oxidize 1 g dieldrin. However, $KMnO_4$ is non-selective and may be consumed by natural organic matter and other oxidizable species. In general,

$KMnO_4$ demand of the soil is significantly greater, but slower than, the demand of the contaminant.

$$\underset{\textit{aldrin}}{3C_{12}H_8Cl_6} + 50KMnO_4 + 32H^+ \rightarrow 36CO_2 + 50MnO_2 + 18KCl + 32K^+ + 28H_2O \quad (3)$$

$$\underset{\textit{dieldrin}}{C_{12}H_8Cl_6O} + 16KMnO_4 + 10H^+ \rightarrow 12CO_2 + 16MnO_2 + 6KCl + 10K^+ + 9H_2O \quad (4)$$

$KMnO_4$ contains chromium as an impurity. In addition, both $KMnO_4$ and manganese dioxide (a by-product of oxidation by $KMnO_4$) can potentially oxidize soil chromium (Cr[III]) to water soluble hexavalent chromium, Cr(VI). The potential formation and fate of Cr(VI) must be addressed when considering this technology.

Study Objectives. The goal of the bench-scale study was to evaluate the potential of Fenton's reagent, H_2O_2, and $KMnO_4$ to destroy aldrin and dieldrin in the site soil. Specific objectives included the following:

- Assess whether the three oxidants can destroy aldrin and dieldrin;
- Estimate soil demand for $KMnO_4$;
- Characterize the post-treatment water quality for each treatment chemistry;
- Evaluate potential formation and fate of Cr(VI) during $KMnO_4$ treatment.

MATERIALS AND METHODS

Three soil samples (Comp 1, Comp 2 and Grab) were collected from shallow soil. Each soil sample was ground manually to reduce the size of soil aggregates, as this was clay-rich material.

Analytical Methods. Soils were initially characterized by measuring total organic carbon (TOC), metals (EPA 200.8), and pesticides (EPA 8081A). TOC was measured using the Walkley-Black method. Aqueous analytes included dissolved iron, which was measured colorimetrically using a Hach test kit; $KMnO_4$, which was quantified by measuring absorbance at 560 nm; and Cr(VI), which was analyzed colorimetrically using the diphenylcarbazide method. Residual H_2O_2 was measured using peroxide test strips.

Destruction of Aldrin and Dieldrin. Batch tests were conducted to determine whether the three oxidants could destroy aldrin and dieldrin. To 90 g of soil was added 900 mL of treatment solution. The treatment solutions were deionized water (control), acidified H_2O_2, Fenton's reagent, and $KMnO_4$. The initial concentrations of each oxidant are listed in Table 2. Hydrogen peroxide was acidified to pH 3 with sulfuric acid and then added to the soil. When ferrous iron was used, it was added immediately after the hydrogen peroxide. The H_2O_2 and Fenton's reagent solutions were stirred with a magnetic stirrer, while the $KMnO_4$ solutions were placed on a shaker table. After approximately 60 hours, they were centrifuged and the aqueous and soil phases were analyzed for pesticides. The aqueous phase was also analyzed for pH, dissolved iron, residual H_2O_2, and/or residual $KMnO_4$.

TABLE 2. Initial Concentrations of Oxidants in Batch Tests.

Test	H_2O_2, %	Fe(II), %	$KMnO_4$, g/L
Control-Fenton/H_2O_2	0	0	0
H_2O_2 Only	1	0	0
Fenton's Reagent	1	0.0275	0
Control-$KMnO_4$	0	0	0
$KMnO_4$	0	0	5

$KMnO_4$ Soil Demand. For each soil, a series of vials containing 5 g of soil and 30 mL of 10 g/L $KMnO_4$ solution was prepared and placed on a shaker. Periodically the contents of a vial were centrifuged and the aqueous phase analyzed for $KMnO_4$. A series of controls containing no soil were prepared and analyzed in like manner.

Formation and Fate of Cr(VI). For each soil, a series of vials containing 5 g of soil and 30 mL of 1 g/L $KMnO_4$ solution were prepared and placed on a shaker. Periodically after the $KMnO_4$ had disappeared (about one day) a vial was destructively sampled by centrifuging and analyzing the aqueous phase for Cr(VI). A control containing deionized water instead of $KMnO_4$ solution was prepared for each soil and analyzed after three days to confirm that no Cr(VI) was originally present and that the Cr(VI) analyses were not false positives.

RESULTS AND DISCUSSION

Soil screening results (Table 3) indicated that aldrin and dieldrin, as well as heptachlor and chlordane, were present in the samples at concentrations well above cleanup standards for the site. There appeared to be a positive correlation between the aldrin and dieldrin concentrations and the TOC content of the samples, which is consistent with greater sorption of the hydrophobic pesticides.

TABLE 3. Soil Screening Results (concentrations in mg/kg).

Parameter	Comp 1 Result	Comp 2 Result	Grab Result
pH	6.1	6.8	6.9
TOC	10,700	7,840	4,800
Aldrin	4.2	1.4	0.130
Dieldrin	0.470	1.0	0.026
Alpha Chlordane	0.430	0.180	0.0058
Gamma Chlordane	0.710	0.770	0.017
Heptachlor	0.023	< 0.085	< 0.0017
Trichloroethene	< 0.040	0.072	< 0.040
Chromium	7.7	8.7	8.2

Destruction of Aldrin and Dieldrin. The effects of H_2O_2, Fenton's reagent, and $KMnO_4$ on the concentrations of aldrin, dieldrin, and chlordane are illustrated in Table 4. In most cases, there was a net loss of contaminant, as shown by the treatment efficiency presented in Table 5. The concentrations of aldrin, dieldrin and alpha- and gamma-chlordane decreased in treated soil compared to soil exposed only to deionized water (Control). There was often a higher concentration in the treated aqueous sample than in the Control, but the total mass showed a net loss of mass in all but one case. The exception is Comp 2, Fenton's Reagent, which showed increases relative to the control. Presumably, Comp 2 was not well homogenized, so that the initial concentrations in the subsamples used in this series of tests were dissimilar. The treatment efficiencies in Table 5 were calculated by comparing the amount of each COC remaining after treatment to the amount in the associated control sample. Losses can therefore be ascribed to treatment rather than handling and processing.

TABLE 4. Bench test results, mass balance.

		Alpha chlordane			Gamma chlordane			Aldrin			Dieldrin		
Sample	**Test**	**ug/kg**	**ug/L**	**total ug***	**ug/kg**	**ug/L**	**total ug***	**ug/kg**	**ug/L**	**total ug***	**ug/kg**	**ug/L**	**total ug***
Comp 1	Fenton control	84	4	11	140	0	13	840	56	126	96	4.5	13
	H2O2	36	4.2	7.0	61	0	5.5	310	52	75	63	6	11
	Fenton's Reagent	40	4.1	7.2	63	0	5.7	350	50	76	74	7	13
	KMnO4 control	82	2.4	9.5	130	0	12	960	24	108	79	2.9	9.7
	KMnO4 5g/L	26	2	4.1	44	0	3.9	7.8	1.1	1.6	38	2.6	5.5
Comp 2	Fenton control	18	1.1	2.6	110	7.7	17	200	11	28	150	8.7	21
	H2O2	5	2.2	2.4	27	14	15	41	22	23	41	14	16
	Fenton's Reagent	7.9	4.2	4.5	48	25	27	77	45	47	64	25	28
	KMnO4 control	10	2.4	3.1	58	15	19	100	26	32	83	16	22
	KMnO4 5g/L	10	0	0.9	76	0	6.8	0	0	0	88	7	14
Grab	Fenton control	0	0	0	15	0	1.4	120	7.6	18	43	2.3	5.9
	H2O2	0	0	0	0	0	0	20	0.56	2.3	15	1.2	2.4
	Fenton's Reagent	0	0	0	4.5	0	0.4	13	0.44	1.6	11	1.2	2.1
	KMnO4 control	0	0	0	15	0	1.4	120	7.6	18	43	2.3	5.9
	KMnO4 5g/L	0	0	0	0	0	0	0	0.3	0.27	3.4	2	2.1

* Total ug = (ug/kg * 0.09 kg soil)+(ug/L * 0.9 L aq).
0 means not detected in the sample.

The mass of chemical removed by Fenton's reagent and by hydrogen peroxide only was similar in all three samples. This suggests either that naturally occurring iron can serve as the iron source in these systems, or that iron is not important in these systems. The latter may be possible because the soils are relatively high in TOC, which can potentially bind dissolved iron.

TABLE 5. Bench test results, treatment efficiency (percent).

Sample	Test	Alpha chlordane	Gamma chlordane	Aldrin	Dieldrin
Comp 1	H_2O_2	37	56	41	13
	H_2O_2/Fe	35	55	39	0
	$KMnO_4$	57	66	99	43
Comp 2	H_2O_2	7	11	16	24
	H_2O_2/Fe	-72	-59	-70	-32
	$KMnO_4$	71	63	100	35
Grab	H_2O_2	n.a.	100	87	61
	H_2O_2/Fe	n.a.	70	91	65
	$KMnO_4$	n.a.	100	98	65

Percent Removed = 100* (Total μg in Control - Total μg in Treated sample)/(Total μg in Control)
n.a. = sample did not contain detectable alpha chlordane

In the $KMnO_4$ test, aldrin was almost completely removed from all three soils. Aqueous concentrations were also significantly lower than in the control. Overall, 98 to 100 percent of the aldrin was removed. The concentrations of dieldrin and alpha- and gamma- chlordane also decreased in soil and water, although the overall removal was less than for aldrin.

Effect of Oxidants on Water Quality. In addition to the chemicals of interest, the aqueous phase was analyzed for pH, iron and residual H_2O_2, and/or residual $KMnO_4$ (Table 6).

H_2O_2 was still present in the H_2O_2-only test, but not in the Fenton's reagent test, indicating that greater contaminant destruction may have been possible in the H_2O_2-only test if the reaction had run longer. Similarly, based on the amount of dissolved iron in the Fenton systems, it may have been possible to increase the amount of contaminant removed by re-dosing the system with H_2O_2.

Addition of 5 g/L $KMnO_4$ to soil (a 10:1 liquid to soil ratio) increased the pH of the aqueous phase compared to controls. The change was small at this scale, but at field scale may be significant. Residual $KMnO_4$ was present in all three systems. Because a longer reaction time may have resulted in further treatment, it is likely that the treatment efficiencies given in Table 5 are understated.

$KMnO_4$ Soil Demand. The amount of $KMnO_4$ consumed by soils was 46,000 g/kg soil for Comp 1, 39,600 g/kg soil for Comp 2, and 25,800 g/kg soil for Grab. These relative amounts are consistent with the relative amounts of TOC in the soils (see Table 3).

TABLE 6. Post-Treatment Selected Water Quality Parameters.

Sample ID	pH	Fe, mg/L	H_2O_2, mg/L	$KMnO_4$, mg/L
Comp 1				
Control (Fenton/H_2O_2)	5.48	0.04	0	n/a
H_2O_2	4.34	n.a.*	1000	n/a
Fenton's Reagent	3.78	77	0	n/a
Control ($KMnO_4$)	5.94	n/a	n/a	n/a
$KMnO_4$	7.04	n/a	n/a	400
Comp 2				
Control (Fenton/H_2O_2)	6.90	0.05	0	n/a
H_2O_2	5.21	n.a.	1000	n/a
Fenton's Reagent	3.52	130	0	n/a
Control ($KMnO_4$)	6.26	n/a	n/a	n/a
$KMnO_4$	7.16	n/a	n/a	1,040
Grab				
Control (Fenton/H_2O_2)	6.42	0.28	0	n/a
H_2O_2	5.85	n.a.	1000	n/a
Fenton's Reagent	4.27	67	0	n/a
Control ($KMnO_4$)	6.42	n/a	n/a	n/a
$KMnO_4$	6.97	n/a	n/a	2,410

*n.a. = not analyzed.

Formation and Fate of Cr(VI). Cr(VI) was detected in the aqueous phase after soil was exposed to 1 g/L $KMnO_4$ (6:1 liquid to soil ratio). The maximum concentration observed was 45 micrograms per liter (μg/L), seen only in the Grab sample. In all cases, the concentration peaked within 1-2 days of addition of $KMnO_4$ then gradually declined to non-detectable (< 10 μg/L) by 16 days. This apparent natural attenuation of Cr(VI) is due in part to the presence of TOC in the soils.

The Cr(VI) detected in this test is most likely due to chromium impurities in the $KMnO_4$ since the soil contain less than 9 mg/kg Cr and previous testing indicated that the $KMnO_4$ used in this study contained up to 63 mg/kg Cr. The concentration of Cr(VI) that might be observed during field application will depend upon the concentration of $KMnO_4$ used and the length of time the Cr(VI) is exposed to soil. The potential Cr(VI) reducing capacities of the soils are 61,800 mg Cr(VI)/kg soil, 45,300 mg Cr(VI)/kg soil, and 27,700 mg Cr(VI)/kg soil for Comp 1, Comp 2, and Grab samples, respectively.

CONCLUSIONS

The study demonstrated that Fenton's reagent, H_2O_2, and $KMnO_4$ can reduce the concentrations of aldrin, dieldrin, and alpha- and gamma-chlordane in site soils. $KMnO_4$ removed up to 100 percent of aldrin and 35 to 100 percent of dieldrin and alpha- and gamma-chlordane, making it much more effective than the other two oxidants.

Further evaluation is necessary to optimize $KMnO_4$ dose requirements and reaction times using conditions similar to those that would be applied in the field. The use of field-like conditions is important because the dose and rate requirements may be affected by liquid to soil ratio, which was high (10:1) in this study. Complete removal of aldrin, dieldrin, and chlordane can probably be achieved with the proper initial $KMnO_4$ concentration or contact time. Further evaluation is needed to confirm the presence and fate of Cr(VI) and other oxidation products under field-like conditions. The concentration of Cr(VI) in the treatment solution could be higher during field applications, depending upon the method of application, the amount of solution used, and the length of time Cr(VI) is exposed to soil. $KMnO_4$ can theoretically oxidize contaminants to carbon dioxide, water and chloride, but the confirmation of the complete reaction was beyond this scope of work.

REFERENCES

ATSDR. 2000. Toxicological Profile for Aldrin and Dieldrin, September 2000, Atlanta, Georgia.

Walling, C. 1975. Accounts Chem. Res. 8:125-131.