

**TREATABILITY STUDY FOR THE IN SITU CHEMICAL  
OXIDATION TREATMENT OF GROUNDWATER CONTAMINANTS**

BY  
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To the Faculty of Washington State University:

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## **ABSTRACT**

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A bench-scale treatability study was conducted in order to determine the optimal process conditions for the treatment of perchloroethylene (PCE) groundwater contamination using catalyzed hydrogen peroxide propagations (CHP) based in situ chemical oxidation (ISCO). The metric for optimal process conditions was the CHP treatment formulation that achieved 99% contaminant of concern (CoC) destruction while providing the greatest peroxygen longevity in the presence of subsurface solids. Subsurface soils were evaluated for homogeneity in order to determine the number of subsamples required for the treatability study. Solids characterization results indicated that the presence of light and dark soil material affected  $H_2O_2$  decomposition rates differently and therefore required separate treatability studies. Two doses of CHP treatment formulations stabilized by phytate, citrate, or malonate resulted in > 99% destruction of PCE for both the light and dark soil material. Of the treatment conditions that achieved 99% PCE destruction, natural mineral catalyzed  $H_2O_2$  stabilized by phytate had the greatest subsurface longevity in both the light and dark material. Stabilization using 5 mM phytate provided the most cost effective and therefore optimal process conditions for treatment.

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## 1. Introduction

In situ chemical oxidation (ISCO) is an emerging option for contaminated soil and groundwater remediation. ISCO is the process of injecting strong chemical oxidants into the subsurface for the treatment of organic contaminants. The oxidants most commonly applied in the field are permanganate, ozone, hydrogen peroxide and persulfate. Permanganate is very stable in the subsurface following injection, allowing for substantial migration away from the injection well. However, permanganate is only reactive with a narrow range of contaminants. Permanganate has often been the oxidant of choice for treatment of chlorinated ethene contamination and has recently shown potential for the degradation of 2,4,6-trinitrotoluene (TNT), the pesticides aldicarb and dichlorvos, and many substituted phenols (Waldemer and Tratnyek 2006). Ozone is less stable than permanganate in the subsurface but has the capability to treat a wider range of contaminants. Ozone generation is often achieved by passing dry air or oxygen through a corona discharge generator (Nimmer et al. 2000), which increases capital costs for ozone-based ISCO projects.

Peroxygen based ISCO involves the use of hydrogen peroxide or persulfate as an oxidant source. Following injection, each of the peroxygens decomposes into a mixture of radical species. Hydrogen peroxide is very unstable in the subsurface, but is capable of rapidly treating all dissolved, sorbed and nonaqueous phase liquid (NAPL) organic contaminants. Catalyzed hydrogen peroxide propagations (CHP) (i.e. modified Fenton's reagent) reactions involve the use of high concentrations of  $H_2O_2$  (2-12%) with different types of catalysts (iron (III), iron chelates, other metal oxide minerals) to generate a mixture of reactive radicals (Watts and Teel 2005). The use of persulfate as an oxidant is a relatively new ISCO technology. Similar to CHP reactions, various initiators transform persulfate into

radical species capable of degrading organic contaminants (Watts and Teel 2006). Recent studies have documented the ability of persulfate to degrade chlorinated ethenes and petroleum products (Huang et al. 2005), as well as explosives and PCBs (Waisner et al. 2008).

Treatability studies are essential for the successful implementation of full scale ISCO projects. Oxidation treatment goals can be significantly dictated by environmental conditions, and specific treatment goals can dictate remediation design parameters (Crimi and Siegrist 2005). Although variable subsurface conditions make it difficult for bench-scale experiments to predict what will occur in field-scale projects, treatability studies provide useful design information regarding remediation potential. The main objective of a bench-scale treatability study is to establish proof of concept that the target compound can be transformed by oxidative treatments (Huling and Pivetz 2006). Additionally, treatability studies determine the process conditions (such as oxidant/stabilizer concentration) that result in sufficient contact between the oxidant and contaminant of concern (CoC). The results of a treatability study must be validated in an on-site pilot study prior to full scale implementation. A detailed explanation of a peroxygen based ISCO treatability study work plan can be found at [www.estcp.org](http://www.estcp.org).

Unlike peroxygen based ISCO feasibility studies, which are well documented (Ferrarese et al. 2008, Tsai et al. 2008, Waisner et al. 2008, Bergendahl and Theis 2004, Gates and Seigrist 1995), there have been few publications regarding standard procedures involved in a treatability study. Dahmani et al. (2006) presented the results of a persulfate based ISCO treatability study conducted as part of the USEPA Superfund Innovative Technology Evaluation (SITE) program. Currently there is a lack of publications detailing

CHP based ISCO treatability studies. The purpose of this research was to conduct a bench-scale peroxygen based ISCO treatability study for the remediation of a site contaminated by chlorinated solvents. The objectives of this treatability study were to evaluate i) oxidant persistence in the subsurface, ii) CoC destruction and iii) the optimal stabilizer/oxidant combinations for peroxygen longevity.

## **2. Materials and Methods**

### *2.1 Study site and sample collection*

The treatability study site is the location of a dry cleaning facility that served the Marine Corps Recruit Depot at Parris Island, South Carolina. The facility, along with four above ground storage tanks, was demolished in 2001. Chlorinated volatile organics are present in the groundwater at concentrations 2,000 times drinking water standards as a result of years of dry cleaning activity and a 1994 storage tank spill event (Tetra Tech, 2004). Groundwater and subsurface solids were collected from six areas of lithological homogeneity within the contamination plume (Figure 1). Soil cores were collected 2.4 to 4.9 m (8-16 ft) below ground surface (bgs) by a direct push Geoprobe, divided into 0.6 m (2 ft) sections, and sent to the Chemical Oxidations Laboratory for analysis.

### *2.2 Materials*

Hydrogen peroxide (50%), sodium citrate, sodium malonate and sodium phytate were purchased from Sigma Aldrich (St. Louis, MO). Potassium permanganate, sodium bicarbonate and potato starch were purchased from J.T. Baker, Inc. (Phillipsburg, NJ). Sodium thiosulfate (99%), potassium iodide and n-hexanes were purchased from Fisher Scientific (Fair Lawn, NJ.) ORBO™ tubes were purchased from Supelco (Bellefonte, PA).

Deionized water (purified >18 MΩ.cm) from a Barnstead NANOpure II Ultrapure system was used in the preparation of all treatment formulations.

### *2.3 Soil characterization*

Subsurface solids were evaluated for homogeneity based on 1) permanganate demand, 2) hydrogen peroxide decomposition in the presence of solids and 3) visual changes in solids organic matter composition and mineralogy. Solids with similar reactivity were then composited for individual treatability studies.

#### *2.3.1 General reaction systems*

Batch reactions were performed in 40 mL borosilicate volatile organic analysis (VOA) vials fitted with vial caps lined with polytetrafluoroethylene (PTFE) septa. All reactions were conducted at room temperature. Characterization experiments were performed on subsurface solids sampled at 2.4, 3.1, 3.7, 4.3, and 4.9 m (8, 10, 12, 14 and 16 ft) bgs. Solids were collected from the top of each sample sleeve and weighed into 10 g samples. Sample sleeves collected at 4.3-4.9 m (14-16 ft) depths were also sampled at the bottom of the core in order to provide an indication of soil heterogeneity at greater depths.

#### *2.3.2 Permanganate consumption*

The short term permanganate natural oxidant demand (NOD) of each sample was tested as a measure of heterogeneity. Permanganate (3000 mg L<sup>-1</sup>) was added in 10 mL aliquots to reaction systems until an aqueous color change from clear to purple indicated the presence of residual permanganate within the system. Residual permanganate concentrations were quantified via spectrophotometer absorbance at 525 nm using a Genesys 20 Thermospectronic spectrophotometer. Absorbance values were compared to a standard

curve of known permanganate concentrations, and the permanganate consumed ( $\text{mg g}^{-1}$ ) for each sample was calculated.

### *2.3.3 Hydrogen peroxide decomposition*

Samples were evaluated for  $\text{H}_2\text{O}_2$  decomposition and rates of temperature increase following the addition of 5 mL of 11%  $\text{H}_2\text{O}_2$  to the reaction systems. A Hewlett-Packard 0101-0113 soap film flow meter was used to measure the rate at which off gas was produced as a result of  $\text{H}_2\text{O}_2$  decomposition. Changes in temperature were monitored using a standard mercury thermometer. The first order temperature increase rate constants for each sample were calculated by plotting  $\ln(T/T_0)$  as a function of time. The first order rate constant was the slope of the plotted line.

### *2.3.4 Subsurface solids compositing and soil analysis*

Solids with similar peroxygen reactivity were vigorously mixed to form composite subsamples. Soil composites were analyzed for particle size distribution by the pipette method (Gee and Bauder, 1986). Organic carbon was determined by combustion at  $900\text{ }^\circ\text{C}$  with evolved  $\text{CO}_2$  trapped in KOH and measured by back-titration of unreacted KOH (Nelson and Sommers, 1982). Extractable iron and manganese was determined by the sodium citrate-bicarbonate-dithionite (CBD) method (Jackson et al. 1986). Total sulfur was determined using a LECO S sulfur analyzer (Tabatabai 1996).

### *2.4 Initial screening of peroxygen process conditions*

Potential CHP process conditions were screened for excessive oxidant consumption in the presence of soil composites. Batch reactions were conducted at  $20\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$  in 20 mL borosilicate VOA vials. Reaction systems consisted of 10 g of soil and 2 mL of site groundwater. Reactions were initiated with the addition of 2 mL of one of several CHP

formulations. (A total volume of 4 mL of liquid was required to completely saturate soils in order to represent aquifer conditions.) CHP processes evaluated were mineral-catalyzed  $\text{H}_2\text{O}_2$  at the natural soil pH and mineral-catalyzed  $\text{H}_2\text{O}_2$  stabilized by phytate, malonate, or citrate at natural soil pH. Treatment formulations consisted of 8% by volume  $\text{H}_2\text{O}_2$  with stabilizer concentrations ranging from 50 to 300 mM, which were diluted to 4%  $\text{H}_2\text{O}_2$  and 25 to 125 mM stabilizer following addition to the reaction systems. Hydrogen peroxide concentrations were quantified by iodometric titration with 0.1N sodium thiosulfate (Schumb et al. 1955).

### *2.5 CoC destruction and peroxygen longevity*

Reaction systems for CoC destruction were identical to those used in oxidant stabilization experiments, with the addition of ORBO™ standard charcoal tubes to capture off gas. VOA vials (20 mL) with reduced headspace were used in order to limit contaminant volatilization. All reactions were conducted at  $20^\circ\text{C} \pm 2^\circ\text{C}$  with reaction systems incubated in the dark. Peroxygen concentration was measured in parallel reaction systems. PCE was extracted from reaction systems and ORBO™ tubes using hexane. Extracts were analyzed for CoC concentrations by gas chromatography. A Hewlett Packard 5890 series II GC with electron capture detector (ECD) fitted with a  $30\text{ m} \times 0.53\text{ mm}$  EQUITY-5 capillary column having  $1.5\ \mu\text{m}$  film was used with the following program: injector temperature  $220\ ^\circ\text{C}$ ; detector temperature  $270\ ^\circ\text{C}$ ; oven temperature  $100\ ^\circ\text{C}$ ; temperature rise rate  $30\ ^\circ\text{C}/\text{min}$ ; and final temperature  $240\ ^\circ\text{C}$ . pH was measured using a Fisher Accumet AB15 pH meter.

### **3. Results**

#### *3.1 Soil characterization*

Subsurface solids were evaluated for homogeneity in order to determine the number of subsamples required for the treatability study. Soil appearance, permanganate consumption, off gas evolution, first order temperature increase rate constants, and maximum temperature for each sample sleeve are presented in Table 1.

##### *3.1.1 Soil appearance*

Rob Vaughn, a soil scientist, visually inspected cores for the presence of soil organic matter (SOM), which consumes H<sub>2</sub>O<sub>2</sub> (Tyre et al. 1991, Bissey et al. 2006) and CHP catalysts such as iron or manganese oxides (Tyre et al. 1991, Watts et al. 1993). Solids collected 2.44 to 3.05 m (8-10 ft) bgs in all locations as well as 3.05 to 3.66 m (10-12 ft) bgs in locations T3, T4, T5 and T6 consisted of a light sandy material. Solids collected at greater depths consisted of a darker sandy-loam type material, indicating a probable increase in concentrations of SOM and reactive minerals.

##### *3.1.2 Permanganate consumption*

Short term permanganate NOD was calculated to provide a rapid estimation of SOM concentration (Siegrist et al. 2001). Permanganate consumed by the light soil material ranged from 0.7 to 1.7 mg g<sup>-1</sup>. Conversely, the minimum permanganate consumption by the darker soil material was 2.7 mg g<sup>-1</sup>, with consumption values as high as 12 mg g<sup>-1</sup>. Solids sampled 4.88 m (16 ft) bgs at locations T2 and T3 had extremely high permanganate consumption values of 45 and 51 mg g<sup>-1</sup>. These samples were most likely located within a peat layer previously reported at the study site (Vroblesky 2007). The results of the short

term permanganate NOD tests confirmed that SOM concentrations were much higher in the darker soil material than the light soil material.

### *3.1.3 Hydrogen peroxide decomposition*

Off gas evolution rates indicated  $\text{H}_2\text{O}_2$  decomposition occurred at a faster rate in the presence of the darker soil material. Samples containing light soil material collected 3.05 m (10 ft) bgs at locations T4, T5 and T6 were essentially unreactive with  $\text{H}_2\text{O}_2$ , showing no detectable off gas evolution following the addition of  $\text{H}_2\text{O}_2$ . Off gas evolution rates in the remaining light soil material samples ranged from 0.2 to 1.9  $\text{ml min}^{-1}$ . Oxygen evolution rates for the darker material, on the other hand, ranged from 2.8 to 12.5  $\text{ml min}^{-1}$ . Temperature changes also showed  $\text{H}_2\text{O}_2$  decomposition occurred at a faster rate in the presence of the darker soil material. Reaction systems containing the light material remained  $< 30^\circ \text{C}$  while reaction systems containing the darker material experienced rapid increases (k values from 1.0 to  $7.1 \times 10^{-3} \text{ min}^{-1}$ ) to maximum temperatures ranging from 46 to  $66^\circ \text{C}$ .

### *3.1.4 Subsurface solids compositing and soil analysis*

Solids characterization results indicated the light and dark soil material affected  $\text{H}_2\text{O}_2$  decomposition rates differently and therefore required separate treatability studies. Sample sleeves containing light and dark soil material were vigorously mixed with like material and termed light and dark soil composite, respectively. Characteristics of the two soil composites are presented in Table 2.

### *3.2 Initial screening of peroxygen process conditions*

Subsurface  $\text{H}_2\text{O}_2$  stability is the primary limitation of CHP ISCO implementation (Kakarla and Watts 1997). Screening experiments were conducted in order to eliminate CHP process conditions under which the  $\text{H}_2\text{O}_2$  decomposition rates were too great to allow



sufficient contact between the oxidant and CoC for treatment. Decomposition rates resulting in undetectable  $\text{H}_2\text{O}_2$  concentrations within 24 hours of injection were considered too high and the process conditions were eliminated from further consideration.

A reaction concentration of 4%  $\text{H}_2\text{O}_2$  was evaluated for all process conditions, because the addition of higher  $\text{H}_2\text{O}_2$  concentrations to soils resulted in temperature increases above  $40^\circ\text{C}$ . When reaction temperatures are  $> 40^\circ\text{C}$ , decomposition rates accelerate uncontrollably and complete decomposition of  $\text{H}_2\text{O}_2$  occurs within minutes. Hydrogen peroxide decomposition following the addition of CHP treatment formulations without catalysts or stabilizers to the light and dark soil composites is shown in Figures 2a–b. Hydrogen peroxide decomposition was sufficiently catalyzed by naturally occurring minerals in both the light and dark composites at the natural soil pH used in the reactions. Hydrogen peroxide lifetime in the light composite exceeded 24 hours, but rapid decomposition of  $\text{H}_2\text{O}_2$  in the dark composite resulted in undetectable concentrations within the first hour following injection, making mineral catalyzed  $\text{H}_2\text{O}_2$  without stabilization an impractical CHP process condition for the dark soil. One approach to increasing subsurface oxidant longevity is the addition of a stabilizing agent to peroxygen solutions prior to injection. Success at the laboratory scale using phosphate as a  $\text{H}_2\text{O}_2$  stabilizer (Hinchee et al. 1991, Aggarwal et al. 1991, Baciocchi et al. 2003) has not translated to success in the field, most likely due to native microbial enzymatic activity breaking down the  $\text{H}_2\text{O}_2$  (Spain et al. 1989). More recently, the organic acids phytate, malonate and citrate have been shown to stabilize  $\text{H}_2\text{O}_2$  in the subsurface (Watts et al. 2007).

Hydrogen peroxide decomposition following the addition of CHP treatment formulations stabilized by phytate, malonate, or citrate to the dark composite is shown in

Figures 3a– c. The addition of stabilizers extended H<sub>2</sub>O<sub>2</sub> lifetime in the dark composite from less than 1 hour to greater than 24 hours. Detectable levels of H<sub>2</sub>O<sub>2</sub> were present 24 hours following injection for each stabilizer at all concentrations, with higher stabilizer concentrations generally resulting in increased H<sub>2</sub>O<sub>2</sub> retention. A citrate concentration of 125 mM resulted in the highest residual H<sub>2</sub>O<sub>2</sub> concentration (26% of initial injection), followed by 150 mM phytate (24%) and 125 mM malonate (23%). The decrease in H<sub>2</sub>O<sub>2</sub> decomposition rates was most likely the result of the stabilizing agents binding to the soil transition metals, reducing their catalytic activity (Watts et al. 2007). Based on these results, CHP process conditions consisting of mineral-catalyzed H<sub>2</sub>O<sub>2</sub> stabilized by phytate, malonate, or citrate at natural soil pH were further investigated as treatment options.

### *3.3 CoC destruction and peroxygen longevity*

Perchloroethylene (PCE) was the Tentatively Identified Compound (TIC) with the highest groundwater concentration at the study site. Scoping experiments were conducted to evaluate CHP treatment formulations for their ability to treat PCE in the subsurface soil/groundwater matrix. The metric for effective contaminant destruction using peroxygen based ISCO is > 99% destruction. Initial reaction system PCE concentrations were  $12.5 \pm 0.6 \text{ mg L}^{-1}$  (n = 3) for the light composite and  $11.9 \pm 0.6 \text{ mg L}^{-1}$  for the dark composite, with extraction efficiencies of  $68 \pm 2.7\%$  (n = 3) and  $74 \pm 0.6\%$ , respectively. Extraction efficiencies were calculated by spiking the reaction systems with solution containing a known concentration of PCE in place of site groundwater and quantifying the recovery of the contaminant. PCE concentrations were below the lowest standard value ( $0.05 \text{ mg L}^{-1}$ ) in reaction systems containing soil composites with DI water in the place of site groundwater,

indicating that the contamination was present in the aqueous phase rather than sorbed to the soil.

PCE destruction following the addition of CHP treatment formulations stabilized by phytate, malonate, or citrate to the dark and light composites is shown in Table 3. Extraction occurred 48 hours after dosing with treatment formulations. CHP formulations stabilized by phytate had the highest levels of PCE destruction (91.6% to 96.7%) in the dark composite. Stabilization by malonate resulted in 87.0% to 91.7% PCE destruction, and citrate stabilization resulted in 82.5% to 90.6% PCE destruction. PCE destruction was greater in the light composite CHP systems, with the addition of CHP formulations stabilized by malonate resulting in 97.9% to >99% PCE destruction followed by citrate (97.1% to 98.9%) and phytate (96.8% to 97.8%). Concentrations of PCE captured in ORBO tubes in all reactions ranged from 0.3% to 2.6%, representing minimal volatilization loss from the reaction systems and indicating that the majority of PCE loss was the result of CHP treatment.

Treatment involving multiple injections of CHP formulations in order to increase CoC destruction to > 99% was investigated. PCE destruction following two injections of CHP treatment formulations stabilized by phytate, malonate, or citrate to the dark and light composites is shown in Table 4. The addition of a second dose of treatment formulation to the dark composite reaction systems increased PCE destruction for all process conditions, with values ranging from 97.8% to > 99%. PCE destruction in the light composite reaction systems ranged from 95.6% to > 99% following two doses. PCE volatilization from reaction systems was minimal.

The metric for optimal process conditions was the treatment formulation that achieved 99% CoC destruction while providing the highest peroxygen longevity in the

presence of subsurface solids. Hydrogen peroxide concentrations were measured in parallel reaction systems in order to determine peroxygen longevity during treatment. Hydrogen peroxide decomposition following the addition of CHP treatment formulations stabilized by phytate, malonate, or citrate to the dark and light composites is shown in Figures 4a–b. Of the treatment conditions that achieved 99% PCE destruction, natural mineral catalyzed  $H_2O_2$  stabilized by phytate had the greatest subsurface longevity in both the light and dark composite reaction systems. Therefore, this CHP formulation provided the process conditions that resulted in maximum contact between the oxidant and CoC for successful treatment.

CoC destruction and peroxygen longevity following stabilization with lower concentrations of phytate were examined in order to identify the most cost effective treatment option. Phytate (50% solution in water) is available from TCI America for \$75/kg. A reduction in stabilizer concentration would significantly lower project operation and maintenance costs. PCE destruction following two doses of CHP treatment formulations stabilized by 5 to 20 mM phytate ranged from 95.5% to 98.1% (Table 5). Hydrogen peroxide decomposition following the addition of CHP treatment formulations stabilized by 5 to 20 mM phytate to the dark and light composites is shown in Figures 5a–b. Stabilization using lower phytate concentrations was not as effective, but concentrations as low as 5 mM successfully extended  $H_2O_2$  lifetimes in both soil types to 24 hours following the first treatment dose with decomposition rates slowing greatly following the second dose. Therefore, natural mineral catalyzed  $H_2O_2$  stabilized by 5 mM phytate provided the most cost effective process conditions.

#### **4. Summary and Conclusions**

Light and dark soil material collected from the site affected  $\text{H}_2\text{O}_2$  decomposition rates differently and therefore was composited for separate treatability studies. Screening of  $\text{H}_2\text{O}_2$  decomposition rates in the presence of soil composites indicated naturally occurring minerals were sufficient CHP catalysts and the addition of stabilizers would be necessary to extend subsurface  $\text{H}_2\text{O}_2$  lifetime. Two doses of CHP treatment formulations stabilized by phytate, citrate, or malonate resulted in > 99% destruction of PCE for both the light and dark soil composites. Of the treatment conditions that achieved 99% PCE destruction, natural mineral catalyzed  $\text{H}_2\text{O}_2$  stabilized by phytate had the greatest subsurface longevity in both the light and dark material. The recommended process conditions for field application are natural mineral catalyzed 4%  $\text{H}_2\text{O}_2$  stabilized by 5 mM phytate. These results must be validated in an on-site pilot study prior to full scale CHP ISCO implementation.

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**Table 1.** Summary of solids characterization test results.

Sample sleeve location	Sample sleeve Depth (ft)	Soil appearance	Permanganate demand (mg g <sup>-1</sup> )	Off gas evolution (ml min <sup>-1</sup> )	Temperature increase k (min <sup>-1</sup> )	Maximum temperature (°C)
T1	8-10	Light	1.7	0.6	0	23
	10-12	Dark	4.9	2.8	2.5 x 10 <sup>-3</sup>	58
	12-14	Dark	8.5	12.5	2.7 x 10 <sup>-3</sup>	57
	14-16	Dark	2.7	6	4.4 x 10 <sup>-3</sup>	61
	16		6.0	9	1.7 x 10 <sup>-3</sup>	48
T2	8-10	Light	1.4	0.2	0	24
	10-12	Dark	12	12.5	2.1 x 10 <sup>-3</sup>	58
	12-14	Dark	5.8	7.6	2.4 x 10 <sup>-3</sup>	59
	14-16	Dark	5.9	7.3	2.0 x 10 <sup>-3</sup>	55
	16		51	7.1	1.0 x 10 <sup>-3</sup>	46
T3	8-10	Light	1.6	1.9	0	24
	10-12	Light	1.4	0.3	0	24
	12-14	Dark	5.9	3.8	2.2 x 10 <sup>-3</sup>	56
	14-16	Dark	8.3	7.3	3.8 x 10 <sup>-3</sup>	61
	16		45	7.5	2.4 x 10 <sup>-3</sup>	59
T4	8-10	Light	1.2	0.9	0	25
	10-12	Light	1.0	0	0	23
	12-14	Dark	5.9	6.8	3.7 x 10 <sup>-3</sup>	61
	14-16	Dark	5.8	10	3.1 x 10 <sup>-3</sup>	61
	16		8.3	6.8	2.5 x 10 <sup>-3</sup>	58
T5	8-10	Light	1.6	0.3	0	24
	10-12	Light	0.9	0	0	24
	12-14	Dark	8.5	8	3.1 x 10 <sup>-3</sup>	62
	14-16	Dark	5.7	7.6	2.2 x 10 <sup>-3</sup>	60
	16		5.4	6.3	3.5 x 10 <sup>-3</sup>	62
T6	8-10	Light	1.4	1.7	0	25
	10-12	Light	0.7	0	0	26
	12-14	Dark	8.5	8	7.1 x 10 <sup>-3</sup>	66
	14-16	Dark	5.6	4.6	2.9 x 10 <sup>-3</sup>	61
	16		5.2	6.3	3.6 x 10 <sup>-3</sup>	62

**Table 2.** Soil characteristics of light and dark composites.

<b>Soil</b>	<b>Particle Size Distribution</b>			<b>Textural Class</b>	<b>Organic Carbon (%)</b>	<b>Fe (%)</b>	<b>Mn (%)</b>	<b>S (%)</b>
	<b>Sand (%)</b>	<b>Silt (%)</b>	<b>Clay (%)</b>					
Dark Composite	84.70	4.63	10.67	Loamy Sand	0.490	0.160	0.0015	0.523
Light Composite	91.10	2.27	6.63	Sand	0.035	0.014	0.0001	0.017

**Table 3.** PCE destruction following the addition of one CHP treatment formulation (8% H<sub>2</sub>O<sub>2</sub>) stabilized by phytate, citrate, or malonate to the dark or light composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).

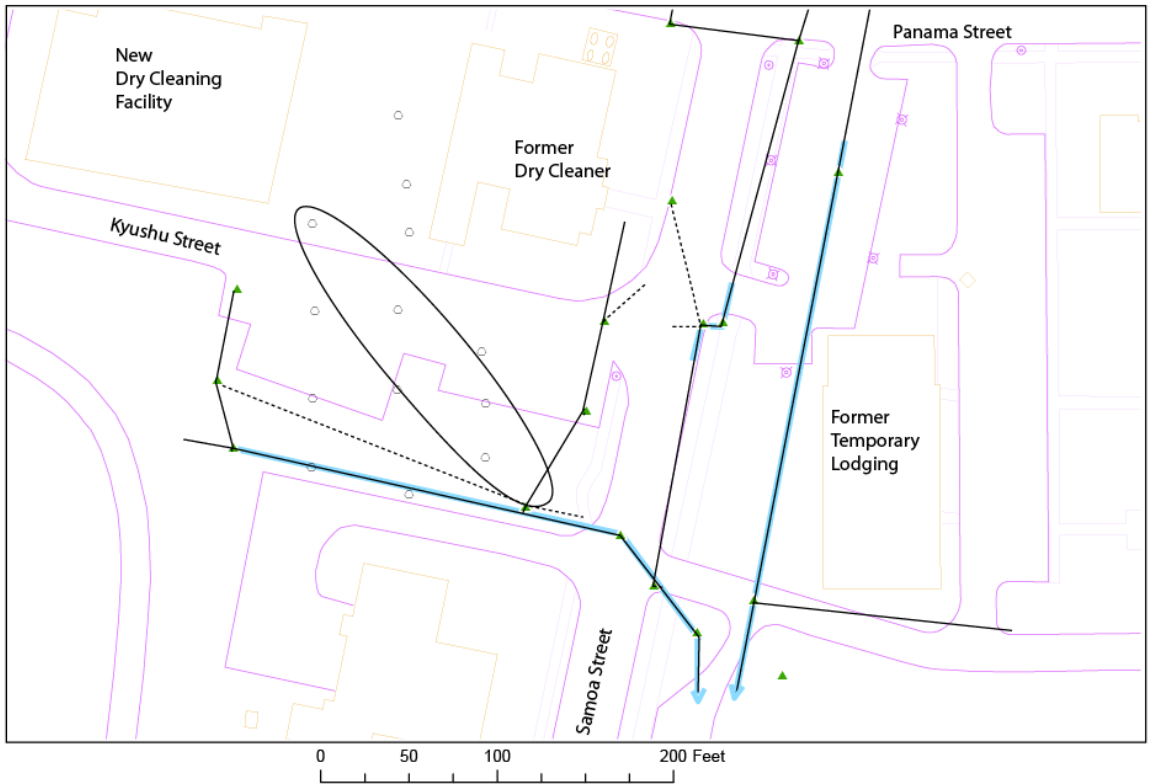
<b>Composite</b>	<b>Stabilizer (mM)</b>	<b>PCE Destruction</b>	<b>Volatilization Loss</b>
Dark	Phytate 25	93.8%	1.4%
	Phytate 50	94.4%	1.0%
	Phytate 75	94.7%	1.9%
	Phytate 100	92.9%	2.3%
	Phytate 125	91.6%	1.2%
	Phytate 150	96.7%	0.3%
	Malonate 50	87.8%	0.6%
	Malonate 75	91.7%	2.4%
	Malonate 100	90.2%	0.4%
	Malonate 125	89.5%	2.5%
	Malonate 150	87.0%	2.2%
	Citrate 25	82.5%	1.3%
	Citrate 50	88.4%	1.8%
	Citrate 75	88.8%	1.7%
	Citrate 100	89.2%	0.6%
	Citrate 125	90.6%	2.3%
	Citrate 150	90.1%	2.6%
	Light	Phytate 25	97.8%
Phytate 50		97.8%	0.6%
Phytate 75		97.1%	0.7%
Phytate 100		97.0%	0.8%
Phytate 125		97.1%	0.7%
Phytate 150		96.8%	0.9%
Malonate 25		98.6%	0.9%
Malonate 50		98.6%	0.9%
Malonate 75		>99%	0.6%
Malonate 100		97.9%	1.2%
Malonate 125		>99%	0.5%
Malonate 150		98.3%	1.0%
Citrate 25		97.8%	0.7%
Citrate 50		97.5%	2.1%
Citrate 75		98.9%	0.6%
Citrate 100		98.1%	1.0%
Citrate 125		97.1%	2.0%
Citrate 150		98.5%	0.8%

**Table 4.** PCE destruction following the addition of two CHP treatment formulations (8% H<sub>2</sub>O<sub>2</sub>) stabilized by phytate, citrate, or malonate to the dark or light composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).

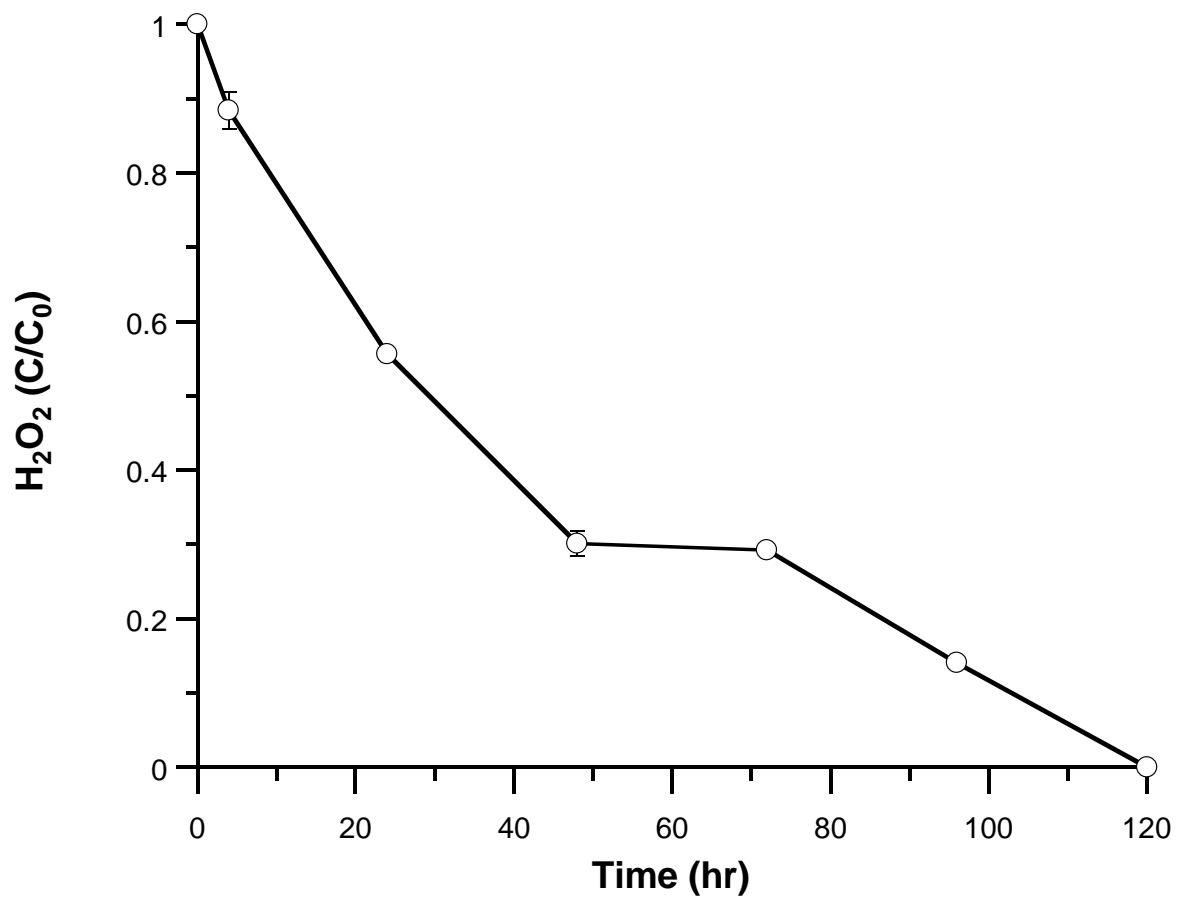
Dose	Composite	Stabilizer (mM)	PCE Destruction	Volatilization Loss	
1 <sup>st</sup>	Dark	Phytate 25	97.7%	0.1%	
		Phytate 50	97.4%	0.4%	
		Phytate 75	97.2%	0.4%	
		Phytate 100	98.4%	1.1%	
		Phytate 125	97.1%	0.2%	
		Phytate 150	96.2%	1.4%	
		Malonate 75	92.8%	0.7%	
		Malonate 100	94.3%	0.6%	
		Malonate 125	94.1%	0.6%	
		Citrate 100	>99%	0.5%	
		Citrate 125	98.4%	0.6%	
		Citrate 150	97.0%	0.7%	
		Light	Phytate 25	98.2%	0.4%
	Phytate 75		95.2%	1.5%	
	Phytate 150		93.4%	1.7%	
	Malonate 75		98.4%	1.3%	
	Malonate 150		96.8%	2.5%	
	Citrate 75		97.0%	2.7%	
	2 <sup>nd</sup>	Dark	Phytate 25	>99%	0.7%
			Phytate 50	>99%	0.8%
			Phytate 75	>99%	0.7%
Phytate 100			>99%	0.8%	
Phytate 125			98.8%	1.0%	
Phytate 150			98.8%	1.1%	
Malonate 75			98.5%	0.5%	
Malonate 100			>99%	0.6%	
Malonate 125			>99%	0.7%	
Citrate 100			97.8%	0.9%	
Citrate 125			98.5%	0.8%	
Citrate 150			98.5%	1.1%	
Light		Phytate 25	>99%	0.8%	
		Phytate 75	>99%	0.8%	
		Phytate 150	97.2%	2.6%	
		Malonate 75	97.8%	2.1%	
		Malonate 150	96.5%	3.4%	
		Citrate 75	97.5%	2.4%	
	Citrate 150	95.6%	4.3%		

**Table 5.** PCE destruction following the addition of two CHP treatment formulations (8% H<sub>2</sub>O<sub>2</sub>) stabilized by lower concentrations of phytate to the light composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).

<b>Composite</b>	<b>Stabilizer (mM)</b>	<b>PCE Destruction</b>	<b>Volatilization Loss</b>
Dark	Phytate 5	97.0%	2.4%
	Phytate 10	95.5%	4.2%
	Phytate 15	95.9%	3.3%
	Phytate 20	96.4%	2.9%
Light	Phytate 5	97.2%	2.5%
	Phytate 10	98.0%	1.6%
	Phytate 15	97.4%	2.4%
	Phytate 20	98.1%	1.7%

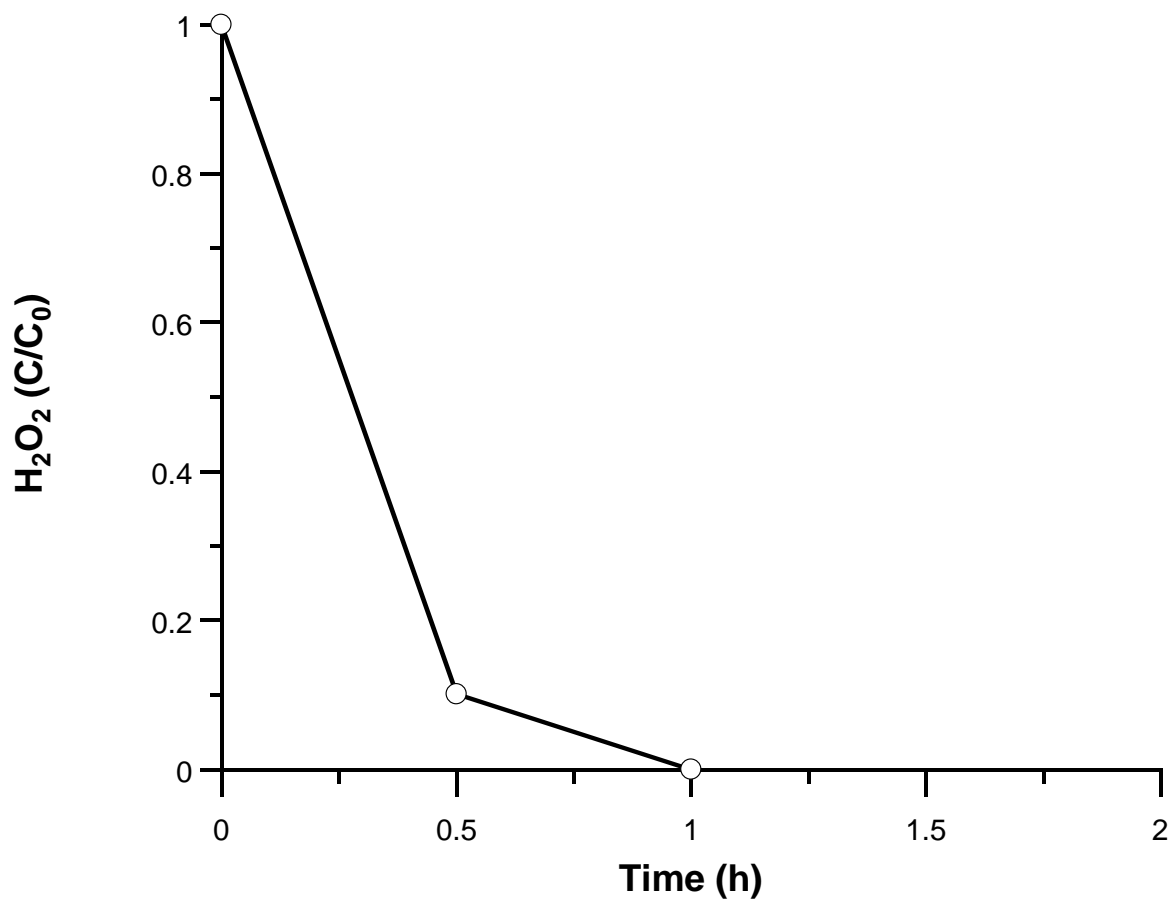


**Figure 1.** Soil sleeve and groundwater sample locations (Don Vroblesky 2007).

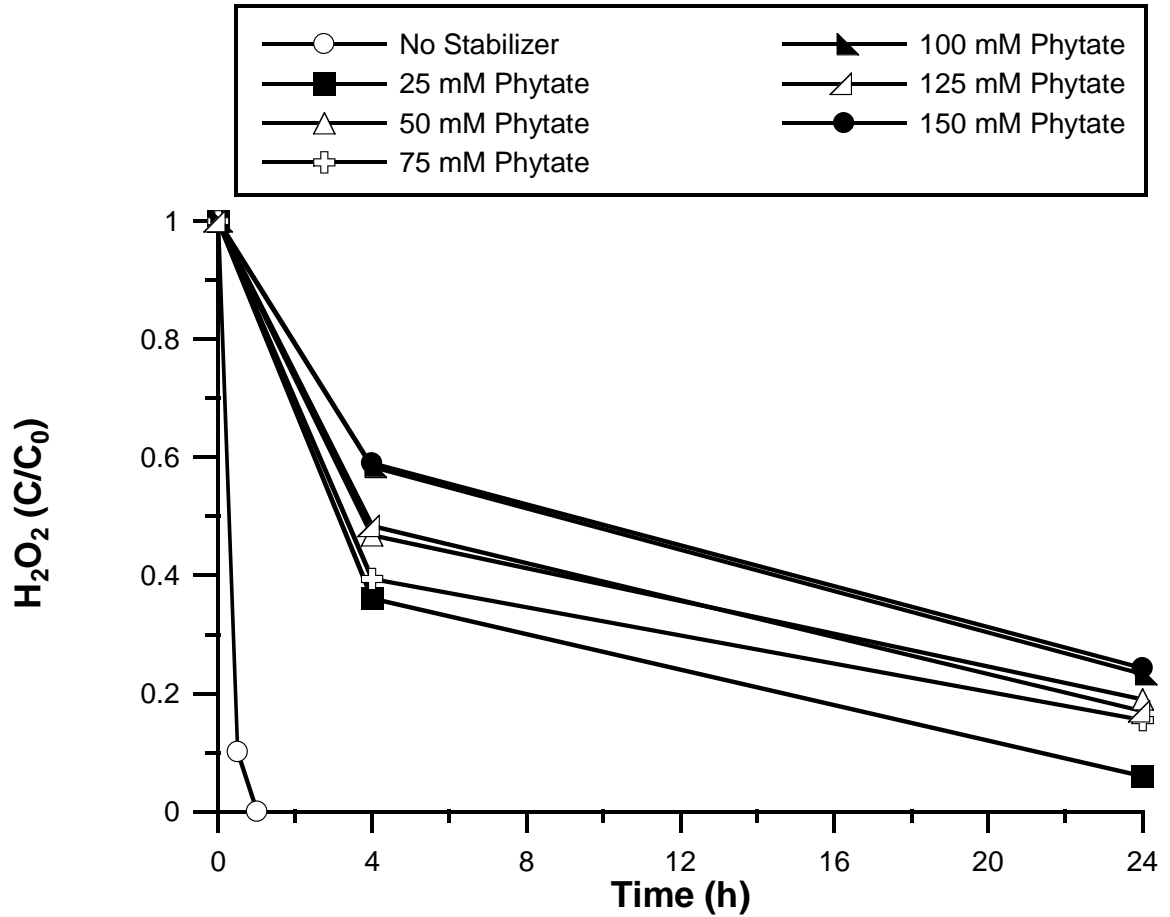


**Figure 2a.** Hydrogen peroxide decomposition following the addition of a CHP treatment formulation (8%  $H_2O_2$ ) without catalysts or stabilizers to the light composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).

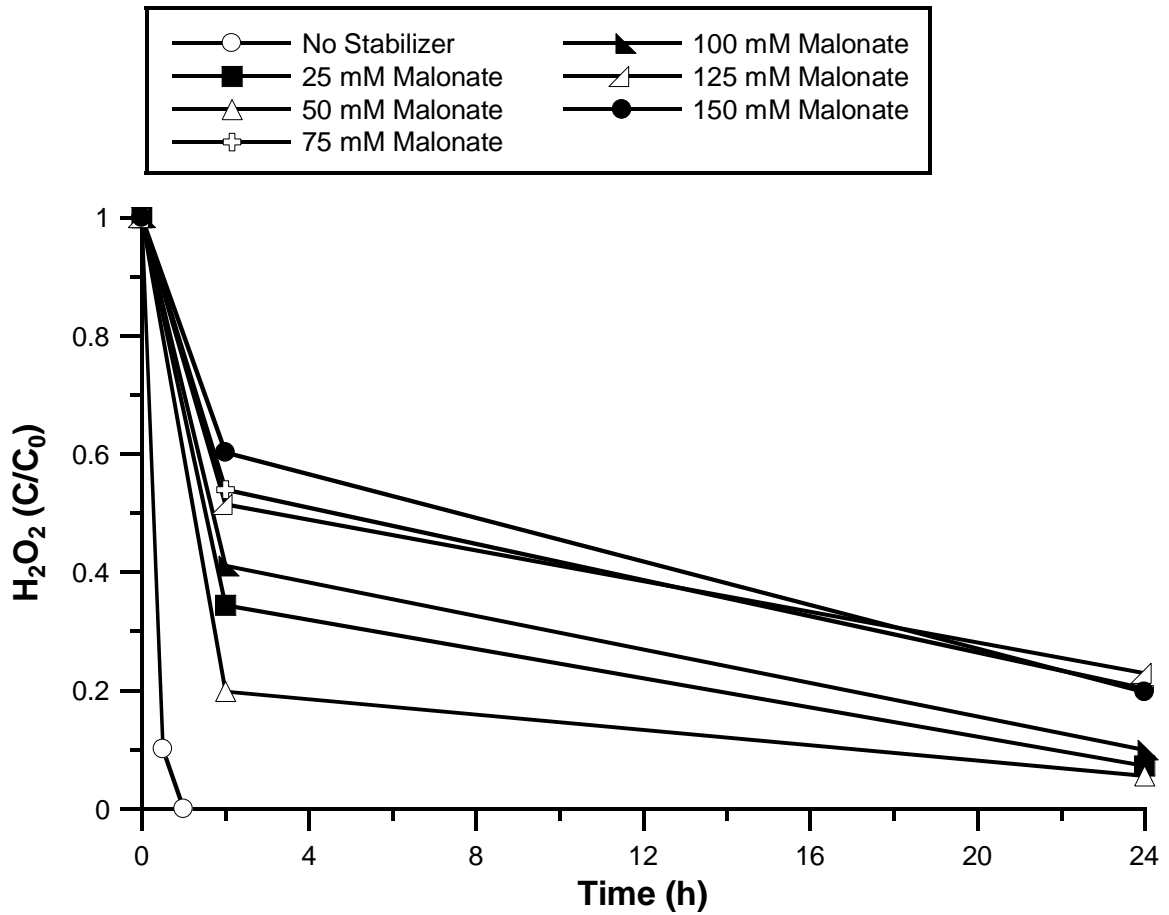




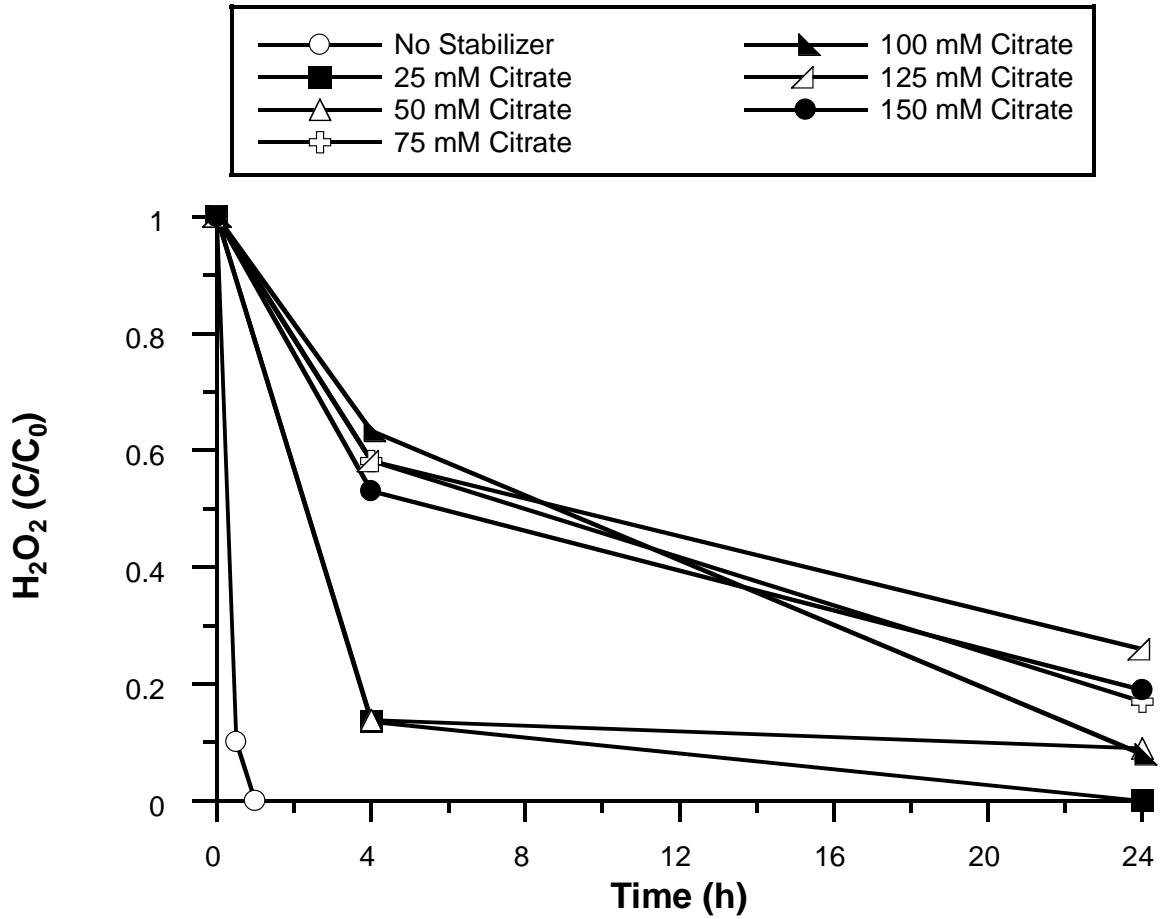
**Figure 2b.** Hydrogen peroxide decomposition following the addition of a CHP treatment formulation (8%  $H_2O_2$ ) without catalysts or stabilizers to the dark composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).



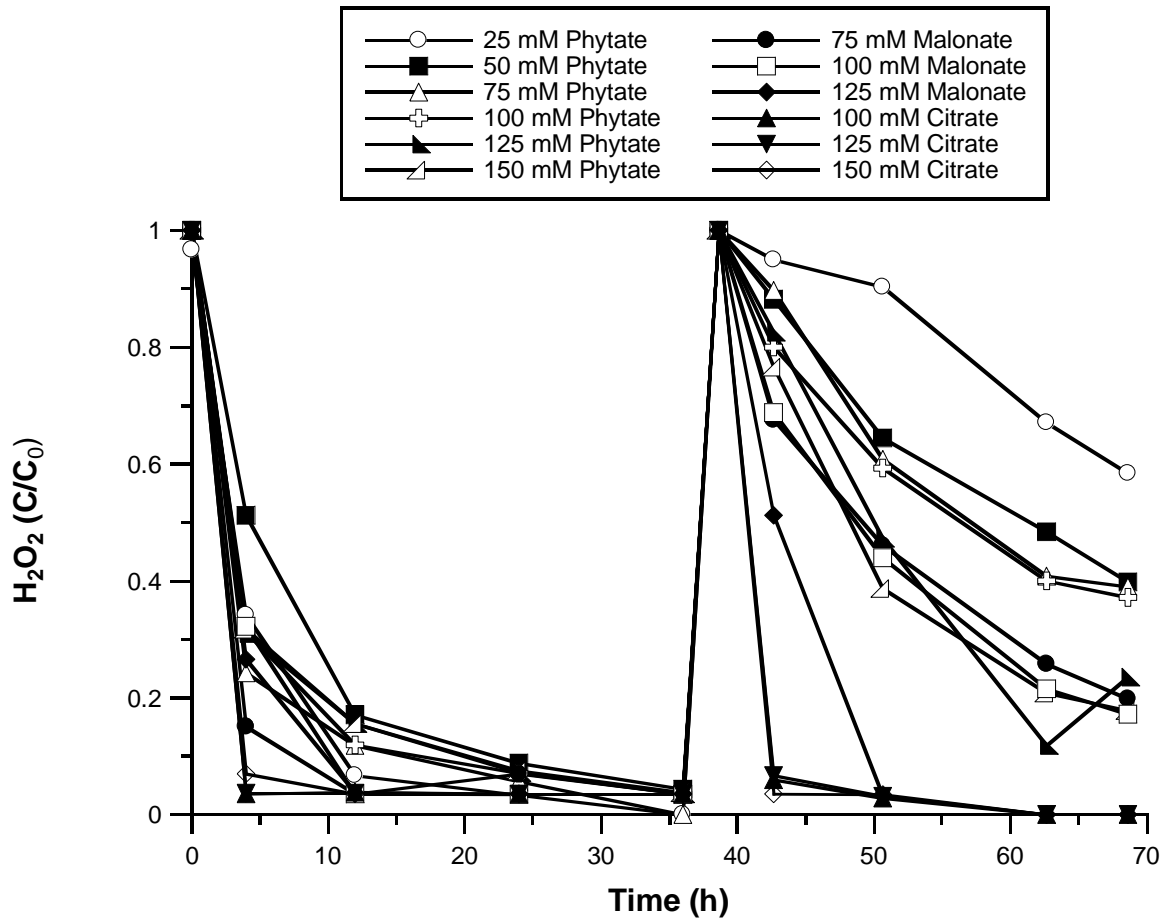
**Figure 3a.** Hydrogen peroxide decomposition following the addition of a CHP treatment formulation (8%  $H_2O_2$ ) stabilized by phytate to the dark composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).



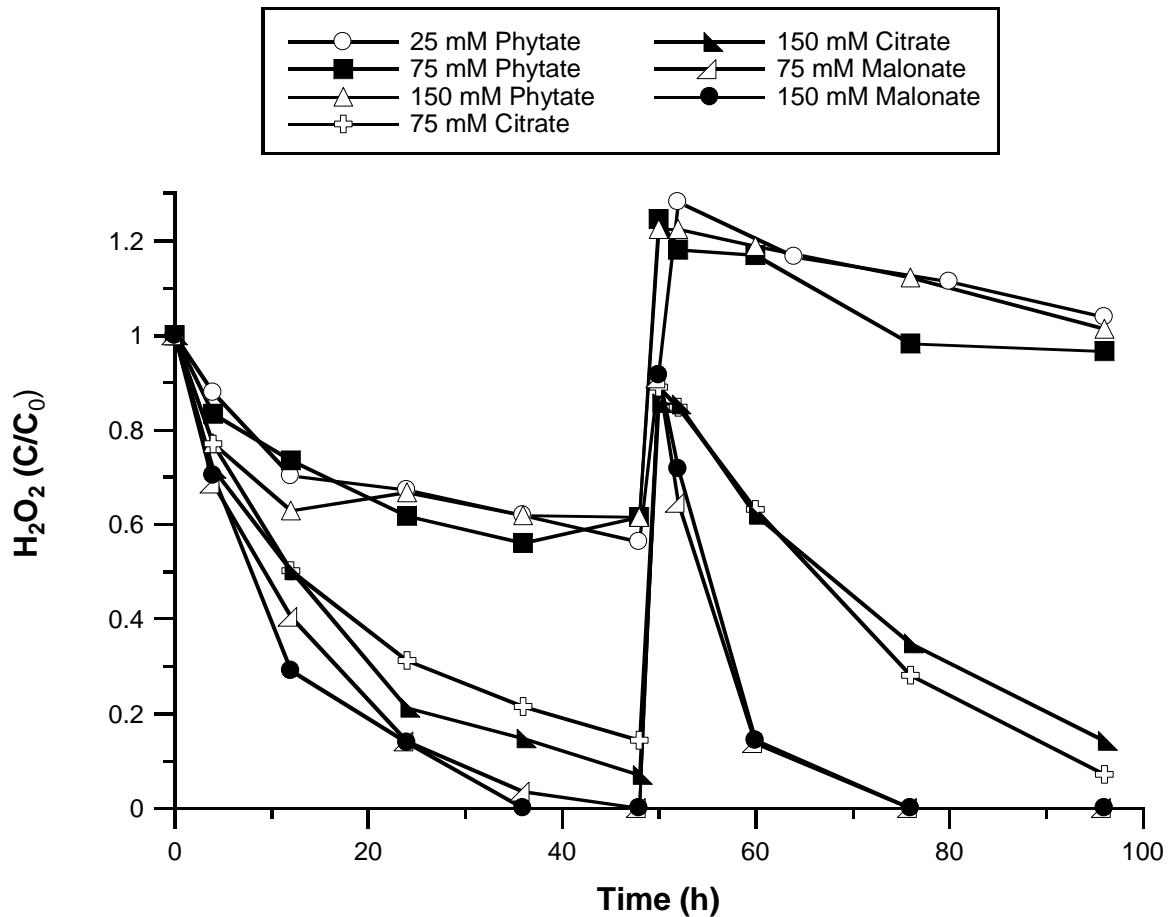
**Figure 3b.** Hydrogen peroxide decomposition following the addition of a CHP treatment formulation (8% H<sub>2</sub>O<sub>2</sub>) stabilized by malonate to the dark composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).



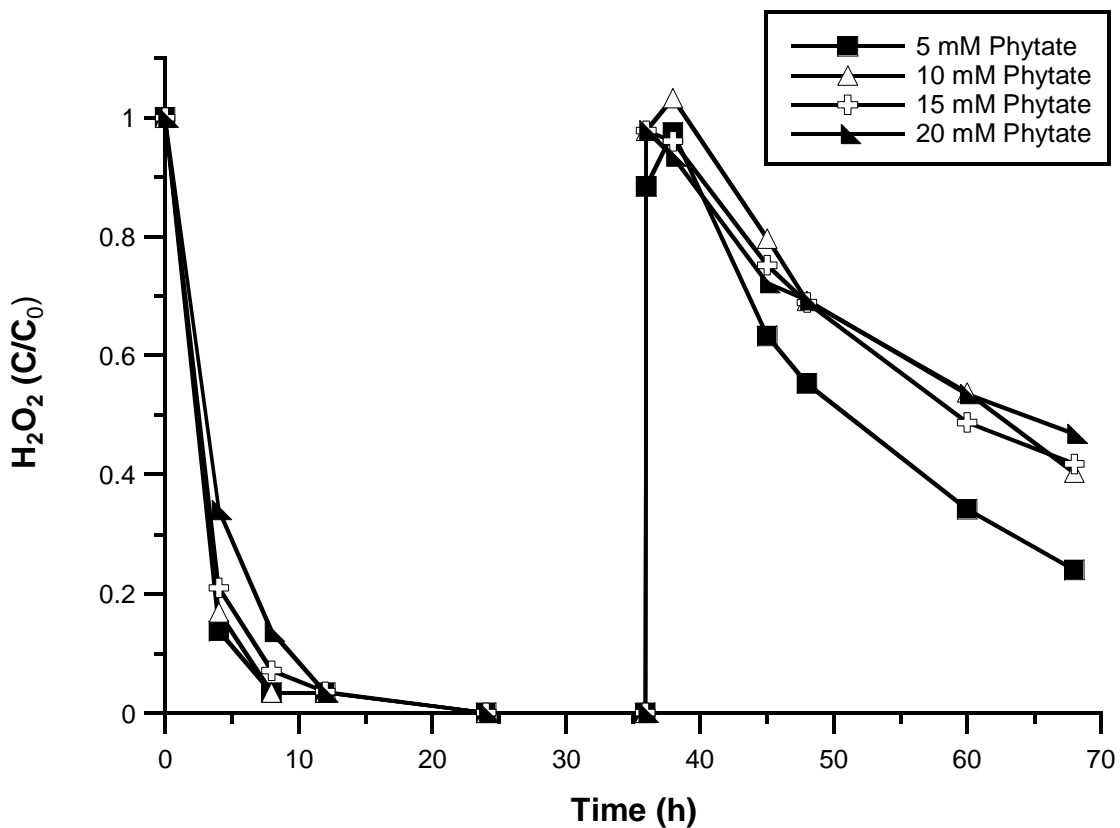
**Figure 3c.** Hydrogen peroxide decomposition following the addition of a CHP treatment formulation (8% H<sub>2</sub>O<sub>2</sub>) stabilized by citrate to the dark composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).



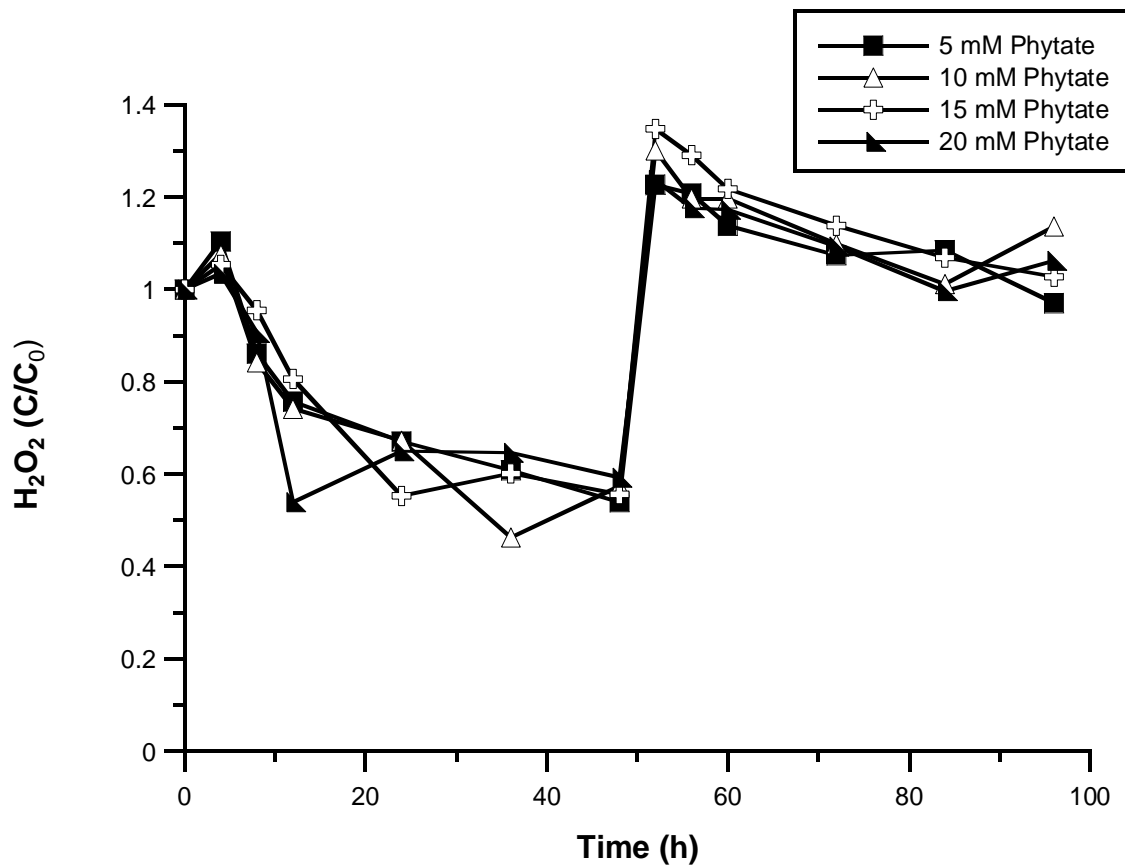
**Figure 4a.** Hydrogen peroxide decomposition following the addition of two CHP treatment formulations (8% H<sub>2</sub>O<sub>2</sub>) stabilized by phytate, citrate, or malonate to the dark composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).



**Figure 4b.** Hydrogen peroxide decomposition following the addition of two CHP treatment formulations (8%  $H_2O_2$ ) stabilized by phytate, citrate, or malonate to the light composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).



**Figure 5a.** Hydrogen peroxide decomposition following the addition of two CHP treatment formulations (8% H<sub>2</sub>O<sub>2</sub>) stabilized by lower concentrations of phytate to the dark composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).



**Figure 5b.** Hydrogen peroxide decomposition following the addition of two CHP treatment formulations (8% H<sub>2</sub>O<sub>2</sub>) stabilized by lower concentrations of phytate to the light composite reaction system (10 g soil/2 ml groundwater + 2 ml formulation).