AFRL-ML-TY-TR-1999-4603

THE EFFECT OF METALLIC IONS ON TRICHLOROETHYLENE DEGRADATION IN SOILS

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Contract No. F41624-98-1-0004

July 1999

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REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 31-JUL-1999	**2. REPORT TYPE** Final Technical Report	**3. DATES COVERED** *(From - To)* 10-APR-1998 -- 10-APR-1999

4. TITLE AND SUBTITLE

The Effect of Metallic Ions on Trichloroethylene Degradation in Soils

5a. CONTRACT NUMBER

F41624-98-1-0004

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Wilkinson, Donald R.; Benjamin, Earl; Imbrogno, Lisa

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

1900B58A

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
Delaware State University
1200 North Dupont Highway
Dover, DE 19901

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory
Materials and Manufacturing Directorate
Airbase Technologies Division
139 Barnes Drive, Suite 2
Tyndall Air Force Base, FL 32403-5323

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/MLQL

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AFRL-ML-TY-TR-1999-4603

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution A: Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Heavy use of environmental contaminants over the past century has led to the accumulation of large quantities of pollutants in the soil system and water supplies. Trichloroethylene, a non-flammable colorless industrial solvent, has been shown to be among the most difficult to remove from the environment. It has been found in no less than 852 of 1430 National Priorities Environmental Contamination Sites identified in a report by the Environmental protection Agency. Some data has suggested that TCE's half-life in soil can be as long as 8,460 hours (approximately 1 year's time) or as long as 39,672 hours (4.5 year's time) if not treated. Health professionals have long noticed the side effect of short-term inhalation of TCE include: dizziness, headaches, slowed reaction time, sleepiness and facial numbness. Along with these health concerns many current reports have suggested a relationship between the use of TCE and cancer formation. Recent advances in technology have lead to the development of new mechanisms to identify the location of trichloroethylene spills and to increase the rate for degradation of trichloroethylene. Several studies have shown that metallic ions can act as catalysts in the degradation of chlorinated solvents by chemical oxidation. One such study was performed by Doong and Wu of National Taiwan University. Their results showed an 84% drop in aqueous carbon tetrachloride content in 33 days. Another study, performed by M. Lisa Imrogno, showed that soil samples that contained high metal concentrations showed an increase in degradation of TCE. These studies led to the questin, "Which individual metals are most effective as a catalyst in the degradation of TCE." A variety of metals were tested including Chromium, Zinc, Manganese and Iron. These results suggest than zinc(II) and chromium (III) better catalyzed TCE's dechlorination. These results are in contradiction to other observed. Iron(III) and manganese(II) did not appear to have a significant effect on TCE's degradation.

15. SUBJECT TERMS

metallic ions, trichloroethylene degradation

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Alison Thomas
U	U	U	UU	144	**19b. TELEPHONE NUMBER** *(Include area code)*

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LIST OF ABBREVIATIONS USED

ASTDR	Agency for Toxic Substances and Disease Registry
CNS	Central Nervous System
EPA	United States Environmental Protection Agency
GC	Gas Chromatograph
L	Liter
mg	milligram
mL	milliliter
µg	microgram
µL	microlite
ppm	parts per million
ppb	parts per billion
TCE	trichloroethylene
VOC	volatile organic chemicals

ABSTRACT

Heavy use of environmental contaminates over the past century has led to the accumulation of large quantities of pollutants in the soil system and water supplies. Trichloroethylene, a non-flammable colorless industrial solvent, has been shown to be among the most difficult to remove from the environment. It has been found in no less than 852 of 1430 National Priorities Environmental Contamination Sites identified in a report by the Environmental Protection Agency. Some data has suggested that TCE's half-life in soil can be as long as 8460 hours (approximately 1 year's time) or as long as 39,672 hours (4.5 year's time) if not treated.

Health professionals have long noticed the side effect of short-term inhalation of TCE include: dizziness, headaches, slowed reaction time, sleepiness and facial numbness. Along with these health concerns many current reports have suggested a relationship between the use of TCE and cancer formation. Recent advances in technology have lead to the development of new mechanisms to identify the location of trichloroethylene spills and to increase the rate for degradation of trichloroethylene. Several studies have shown that metallic ions can act as catalysts in the degradation of chlorinated solvents by chemical oxidation. One such study was performed by Doong and Wu of National Taiwan University. Their results showed an 84% drop in aqueous carbon tetrachloride content in 33days. Another study, performed by Ms. Lisa Imbrogno, showed that soil samples that contained high metal concentrations showed an increase in degradation of TCE. These studies led to the question "which individual metals are most effective as a catalyst in the degradation of TCE". A variety of metals were tested including Chromium, Zinc, Manganese and Iron. These results suggest that zinc(II) and chromium(III) better catalyzed TCE's dechlorination. These results are in contradiction to other observed. Iron(III) and manganese(II) did not appear to have a significant effect on TCE's degradation.

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1.1 HISTORY OF TCE

Heavy use of environmental contaminates over the past century has caused accumulation of large quantities of pollutants into soil and water systems. Of these environmental contaminates TCE has been shown to be among the most difficult to remove from contamination sites.

Trichloroethylene is a non-flammable colorless industrial solvent that has an odor similar to butyl-ether or chloroform. Trichloroethylene's general structure is defined as a halogenated aliphatic hydrocarbon. A halogenated aliphatic hydrocarbon is defined, as a non-aromatic carbon-containing molecule with one or more halogens such as iodine, bromine, chlorine, or fluorine attached to it. [1] Trichloroethylene, along with several other industrial solvents, is located in a small subdivision of this broad classification. This subdivision is entitled Chlorinated Aliphatic Hydrocarbons.

Chlorinated Aliphatic Hydrocarbons are in demand for industrial processes because of certain unique properties that make them ideal solvents for metal processing. These properties include an ability to solubilize organic compounds, along with low volatilization energy. [2] Carbon tetrachloride, methylene chloride, trichloroethylene and chloroform are just a few examples of industrial solvents located in this subdivision.

Trichloroethylene's specific structure is composed of two-carbon atoms bound together with a double bond with three chlorine atoms and one hydrogen in the remaining position. [Figures 1,2] TCE is produced industrially by passing tetrachloroethane over calcium chloride with a catalyst at approximately 300 degrees Celsius. [3]

Imperial Chemical Company Ltd. of Great Britain first introduced trichloroethylene commercially in the late nineteenth century as Westrosol. During this early period TCE was primarily used for degreasing metal and defatting leather skins. [4] Since its initial use as an industrial solvent other applications for TCE have been found. TCE's applications now include industrial processing, dry cleaning, ink printing, along with being used in substances such as adhesives, lacquers and varnishes, spot removers and correct ribbons. Today, TCE can be commercially found as Benzinol, Circosolv, Fleck-Flip, Blacasolv, Cecolene, Perm-a-Chor, Triclene, etc. [5]

1.2 ENVIRONMENTAL EFFECTS OF TCE

Trichloroethylene has been identified as one of the most widespread environmental pollutants. It has been found in no less than 852 of 1430

National Priorities Sites identified in an Environmental Protection Agency (EPA) report. [6] There are several reasons that have contributed to promote accumulation of TCE in the environment, including solubility in water, vapor pressure, a non-polar nature, heavy use and careless disposal. [7]

Once TCE is introduced into the environment, it quickly dissolves into water supplies where it may remain for an extended period of time if not remediated. [8] After its' introduction into a water system, TCE can either move to surface water or it can be transported to underground aquifers. After TCE reaches soil it can easily stick to particles where it may remain for a long period of time. Some data suggested that TCE's, half-life in surface waters can be as long as 8460 hours (approximately 1 year's time). [9] If transported to underground aquifers, TCE half-life has been documented to be as long as 39,672 hours (4.5 year's time). [10]

Heavy use of TCE, as an industrial solvent, and its careless disposal has enhanced environmental concerns. An October 1989 report found that background levels of airborne TCE range from 30 to 460 parts per trillion. [11] Widespread contamination is also seen when looking at water and soil contamination. Various federal and state surveys indicate between 9% and 34% of national water supplies are contaminated with TCE. These sites contain an average 1-2 parts of trichloroethylene per billion parts of water. [12]

These new health concerns have stimulated many federal and state agencies to set maximum contamination levels. The Environmental Protection Agency has set a maximum contamination limit for TCE in water at 0.005mg per liter of water (0.005mg/L) [13]. EPA has also imposed strict regulations for handling and disposal of trichloroethylene. These restrictions are mirrored by theUnited States Department of Occupational Safety and Health Administration by their lowering of the maximum contact level of trichloroethylene to 100ppm per 8 hour period of a forty hour work week. [14]

Along with new restrictions imposed by federal agencies individual companies are now attempting to phase out use of TCE. This is being accomplished by development of less harmful solvents for commercial use.

1.3 HEALTH EFFECTS OF TRICHLOROETHYLENE

Recently, health related concerns have been raised about effects of TCE on humans. Health professionals have long noticed side effects of short term inhalation of TCE includes dizziness, headaches, slowed reaction time, sleepiness and facial numbness. These effects become more severe when concentrations rise above 100ppm where they include impaired heart function, coma and death. [15]

Symptoms of inhalation mirror those of ingestion. When ingesting small amounts of trichloroethylene for long periods of time a person may experience liver and kidney damage, nervous system effects, impaired immune system function, and impaired fetal development in pregnant women. These systems change when exposure is large over a short amount of time. Symptoms for long-term exposure begins at approximately 100 mg of TCE per 1 kilogram of animal size per day [Figure 4]. These symptoms include nausea and fetal abnormalities.

Side effects appear to become severe when concentrations exceed 100 mg of TCE per 1 kilogram of animal size per day. At this concentration symptoms include liver and kidney damage, convulsions, impaired heart function, coma and death. [16] [Figure 4]

Along with environmental concerns, new concerns have been raised about TCE's effect. Many current reports have suggested a relationship between TCE and cancer formation. Although no conclusive correlation could be identified from experimentation data, several studies show a strong link between TCE's uses and cancer formation. One such study was performed by Dr. Brigmon of The National Toxicology Program a subdivision of United States' National Institutes of Health.

> Carcinogenesis studies of epichlorohydrin-free trichloroethylene were conducted by administering the test chemical in corn oil by gavage to groups of 50 male and 50 female F344/N rats and B6C3F1 mice. Dosage levels were 500 and 1,000 mg/kg for rats and 1,000 mg/kg for mice. Trichloroethylene was administered five times per week for 103 weeks, and surviving animals were killed between weeks 103 and 107. Groups of 50 rats and 50 mice of each sex received corn oil by gavage on the same schedule and served as vehicle

> controls. Groups of 50 male and 50 female rats were used as untreated controls.
>
> The results showed that under the conditions of these studies, epichlorohydrin-free trichloroethylene caused renal tubular-cell neoplasms in male F344/N rats, produced toxic nephrosis in both sexes, and shortened the survival time of males.
>
> This experiment in male F344/N rats was considered inadequate to evaluate the presence or absence of a carcinogenic response to trichloroethylene. For female F344/N rats receiving trichloroethylene, containing no epichlorohydrin, there was no evidence of carcinogenicity. Trichloroethylene (without epichlorohydrin) was carcinogenic for B6C3F1 mice, causing increased incidences of hepatocellular carcinomas in males and females and of hepatocellular adenomas in females. [17]

Although this study was enough to suggest a relationship between trichloroethylene exposure and cancer formation in mice and rats, it was not able to draw a similar relationship in humans. Another study, performed by Dr. Henschler, was able to suggest a correlation between trichloroethylene's use and cancer formation in humans.

> A study performed by Dr. Henschler group from Wurzburg University, Germany, has described a high incident of renal cell (kidney) tumor in a group of 169 men who had been exposed to trichloroethylene for at least one year between 1956 and 1975… The average employment was 34 years. A control group was consisted of 190 unexposed workers from the same plant. The standard incident ratio, which measures morbidity compared to that of the Danish Cancer Registry was 7.97.[i.e. about 8 times that expected]. The standardized mortality ratio was 3.28…
>
> …The author [Dr. Henschler] described how TCE exposure in this cardboard factory was "very high". TCE was used to clean machinery, floors and even clothes and hands. The author says that "a causal relationship [with human cancer] is supported by the identification of tumors produced in rats and a valid mechanistic explanation on the molecular level". [18]

1.4 REMEDIATION TECHNIQUES FOR TCE

Recent advances in technology have led to the development of new mechanisms to identify the location of trichloroethylene spills and to increase rates for degradation of trichloroethylene. Some identification methods that have been devised are bioluminescence and a remote detection system using a Fiber-Optic Infrared Reflectance Probe. These methods include activated carbon filtration, reverse osmosis, distillation, ultra violet radiation, bioremediation and chemical oxidation.

1.4.a. ACTIVATED CARBON FILTRATION

Activated carbon filtration has been shown to be an effective mechanism to remove most common organic contaminates such as pesticides, gasoline additives and industrial solvents which include TCE. Activated carbon, normally in the form of carbon granules, is placed into filters between two permeable membranes which prevent the loss of the activated carbon. A pump is then used to cause a pressure gradient which forces water through a carbon filter. Organic contaminates, such as TCE, adhere to an activated carbon filter by a process called adsorption. Contaminated filters are removed along with organic contaminates and properly treated. [19]

Although activated charcoal has been shown to be an effective mechanism to remove organic contaminates on a microscale, it losses efficiency when scaled up for ground water remediation. First problem experienced is an inability of this process to stop movement of contaminates through an aquifer.

Another problem that arises is filtration does not have an ability to remove TCE molecule that have adhered to soil. To remove any pollutants that adhere to soil, liquids have to be repeatedly filtered for an extended period of time. This repeated filtration would take several months at a staggering cost.

1.4.b DISTILLATION

Another mechanism scientists are now using to remove environmental contaminates from contaminated aquifers is distillation. Distillation is a process that relies on evaporation to accomplish water purification. It has been shown to be extremely effective for inorganic contaminates, such as lead and nitrates, along with some non-volatile organic compounds. In distillation, water is heated to form steam then cooled to remove non-volatile pollutants of environmental contaminates. [20]

Although distillation can be an effective mechanism for remediation of non-volatile substances there are many problems when applied to TCE removal. A major problem arises because of trichloroethylene's volatile nature. Because TCE has a evaporation energy lower than that of water it evaporates before water. This rapid evaporation and condensation of TCE in relation to water makes separation of TCE from water difficult using distillation.

1.4.c REVERSE OSMOSIS

Reverse osmosis is also used in remediation of environmental pollutants. The process of reverse osmosis is similar to that of an activated carbon filter. Instead of using activated carbon particles this process uses a porous membrane to separate the clean water from environmental contaminates. In this process water is forced through a porous membrane with high pressure. Membranes allow small water molecules to pass through while retarding movement of a pollutant. This process has many disadvantages when attempting to remediate an aquifer. [21]

Reverse osmosis is also not an ideal method for TCE remediation. This process has problems similar to those found in activated carbon filtration. The first problem that arises is speed. Separation of material though a porous membrane requires an extend amount of time. A second problem occurs when one tries to remove a pollutant from a membrane. Unlike activated carbon filtration pollutants do not adhere to the membrane. This makes removal of the pollutants on a large scale difficult.

1.4.d BIOREMEDIATION

Bioremediation has been used for removal of environmental pollutants from contaminated aquifers is bio-remediation. In bioremediation naturally occurring organisms are used to degrade TCE either to a less harmful substance or to totally consume TCE as a carbon source. These organisms can include various types of plants and bacteria. In this process scientists introduce organisms, such as modified bacteria, into a contaminated aquifer though its water source. These anaerobic bacteria use carbon molecules as a carbon source. Bacteria undergo exponential growth until TCE is depleted, then slowly reduce in number. Scientists have identified three catabolic pathways that carry out dechlorination of TCE. These processes are soluble methane monoxygenase (sMMO), Tolulene 2-monooxygenase, and toluene dioxygenase. [Figure 6] Along with these identification studies scientist have also tested bioremediation for TCE. [22]

> Dr. R. L. Brigmon reported his attempts for bioremediation of a TCE spill in the March 1997 issue of Geosciences. Dr. Brigmon reported that discharges of solvents to a chemical basin at the Department of Energy (DOE) Savannah River Site (SRS) has resulted in a contaminated groundwater plume. Groundwater flow modeling indicates that the leading edge of the trichloroethylene (TCE) plume could emerge at a seep line in the next 10 to 20 years. A treatability study was performed to determine whether the soils and rhizosphere along the seep line can bioremediate the TCE at concentrations of 50 - 100 parts per billion (ppb) in groundwater. Microbial analysis has indicated that indigenous bacteria in soil from the sites are capable of degrading TCE. This information demonstrates that natural or intrinsic bioremediation activities can degrade emergent TCE at a given contamination site. [23]

Although bioremediation has shown promising results, there are many problems associated with this process. One major problem that arises with bioremediation of environmental pollutants is side effects caused by an introduction of non-native organism into a new environment. Introduction of non-natural forms of life into a new environment can cause unknown environmental and health concerns. Another problem occurs when one attempts to remove these organisms from an aquifer after remediation has occurred. Although most bacteria and plants are killed by depletion of their carbon source, some may obtain another carbon source. [24]

1.4.e CHEMICAL OXIDATION

The best method for remediation of TCE may be chemical oxidation. Realizing that metals can act as catalysts for remediation of environmental pollutants, scientists theorized that by increasing concentrations of native metals they could increase rates of degradation. This particular method has been shown to be effective for dechlorinating solvents. An example of this reaction occurs when TCE is put into a solution containing iron particles.[19] Chemical oxidation occurs when a chemical reducer, normally found in the form of a metallic ion, is introduced into a contaminated aquifer. Normally this metal is introduced as a soluble metallic ion. After introduction metal ion spreads throughout the aquifer reducing/dechlorinating TCE. This process removes chlorines from TCE making it less harmful.

There are several advantages in using oxidation to remediate environmental pollutants, such as TCE, from an underground aquifer. An advantage emanates from the ability of this technique to be used on a macroscale effectively. After simply identifying a chemical reducer, a scientist can add a soluble metallic ion into a quantity of water and add it to the aquifer. The second advantage is that chemical reducers have an ability to reach most if not all parts of the aquifer. Another advantage is removal of a reducer.

Because the reducer is a naturally occurring metal no removal technique is necessary. Other advantages for this method are cost, ease and speed.

1.5 REMOVAL OF TCE BY CHEMICAL OXIDATION.

As discussed in the previous section, chemical oxidation by metallic ions has been identified as among the best mechanisms to remove TCE from underground aquifers. Several studies have shown efficient degradation of chlorinated solvents by use of chemical oxidation. These studies have shown excellent results in both microscale and macroscale experimentation.

One such study was performed in Taiwan by Doong and Wu at the National Taiwan University. Doong and Wu performed several decholorination experiments with PCE, CTC and TCA. Their study was entitled "Reductive Dechlorination of Chlorinated Hydrocarbons in Aqueous Solutions Containing Ferrous Sulfide Ions." Their result showed an 84% drop in aqueous carbon tetrachloride content in 33days. [25]

Another project was reported at The 1997 Conference on Hazardous Waste Research by Dr. W. Li and Dr. K.J. Klabunde. Dr. Li determined that zinc and zinc containing compounds could be an effective reductant for dechlorination of organic chlorocarbons that contaminate aquifers. They suggested that zinc could efficiently degrade chlorocarbons such as trichloroethylene (TCE). Their results show that reduction can be performed in aqueous solutions at room temperature. They went on to examine effects of bimetallic combinations of Zn with Ag, Ni, and Pd. The amount of time required to complete dechlorination was found to vary from a few hours to several days. Cryo-Zn (ultrafine granular zinc) particles along with a palladium promoter showed a high efficiency in degrading TCE when compare to others tested. Intermediates were also studied to identify dominant pathways and overall mechanisms. A variety of techniques were employed to analyze gaseous, aqueous, and solid phases. Ethylene, ethane, and monochlorinated hydrocarbons were identified as possible elimination products. Dehydrochlorination was also identified by a production of acetylene.[26]

A similar project was reported in a master's thesis by Ms. Lisa Imbrogno. Ms. Imbrogno tested several level of soil to test their ability to chemically degrade a small amount of TCE. Ms. Imbrogno took soil from three strata 0-5 feet, 10-15 feet and 30-35. These soil samples were separated in two four equal amount. An autoclave was used to sterilize two test samples. These samples were then tested for their ability to degrade. Two unsterilized samples were also tested to determine their ability to degrade TCE. Small amounts of these soils were also tested to determine total organic and metal content. When tested 0-5 feet excavation showed an extremely high iron concentration (77.730 ug/g dry soil) along with an elevated manganese concentration (0.1749 ug/g dry soil) and an elevated lead concentration (0.2915 ug/g dry soil). Lower levels (10-15 feet below the surface) samples appeared to have lower metal content. The metal content of soil samples were determined to be approximately one tenth as much as those found in highest level. Low metal concentrations were again seen in the lowest strata (30-35 feet).

> The shallow range soil, from 0-5 feet depth, was mostly sand with a small amount of fine organic material throughout. The soil collected from 10-15 feet contained almost totally sand with orange silt and clay. No organic matter was observed. The soil from the deepest excavation, 30-35 feet, was like the mid level soil, mostly sand with orange silt and clay. [27]

Using this data Imbrogno then tested each soil in both sterilized for and unsterilized form. Her results showed that sterilized and unsterilized soils had similar degradation.

> There was no difference between the serialized soil activity and the activity of the non-sterilized soils. This would lead to the conclusion that the reaction being observed is not a biological one. The soils used for this study were stored in open containers indoors for a significant amount of time. There is the possibility that bacteria that had been present in the soil when initially collected was not viable at the time that this study took place. The note should be made that TCE biodegradation occurs in anaerobic environments only. The presence of air in the samples cells would have prevented anaerobic bacterial degradation from occurring even if the bacteria were viable. [28]

Imbrogno data suggests differences in their ability to catalyze degradation of TCE. It also showed that soil samples, taken from lower stratas, 10 to 15 feet and 30 to 35 feet, decreased approximately 20% from initial testing over a period of 10 days. Samples taken from 0 to 5 feet showed a much higher degradation rate. Her results also suggest an increase in metal concentration strongly contributed to TCE's decrease.

> The reactivity of the 10 to 15 feet and 30 to 35 feet showed very similar rates of TCE disappearance. In these soils, TCE presence declined dramatically within the first 10 days of experimentation, most often to the levels than 20 percent of the initial chromatographic response.
>
> The 0 to 5 feet soil samples showed little disappearance of TCE over the sampling time. This difference may be due to the higher concentration of soil's total organic carbon (TOC) content. Surface soils commonly contain some degree of organic carbon and, as supported by literature research, as little as 0.1% TOC content can cause significant binding of organic compounds. The soil consistency seems to be the most significant variable in the disappearance of TCE. If the TOC content of he soil is present at even low level, the TCE will be bound and prevented from reaching any neutralizing surface interface that may be present in its environment. If organic carbon is present, TCE is not degraded. [29]

Imbrogno then tested to determine if pH would had an effect on degradation. She varied pH of similar levels. Her results suggested that at low and neutral pH there was no difference for degradation rates of TCE. These results did not hold true for the pH 8.0 samples. These samples showed a low rate of degradation.

> The soils were observed under three different pH conditions 4.0, 5.5, 6.0, and 8.0. The data showed little correlation to any beneficial increase in the degradation when the pH was altered. The most acidic pH, 4.0, showed rapid disappearance of TCE in the mid level soils to almost 7% of initial chromatographic response. The other pH ranges showed decreases to approximately 20% of initial There cannot be any

> conclusion drawn about the effect on rates of reaction due to pH as a result of this data.
>
> There is a possibility that pH 4.0 is above the effective pH range which permits effective rapid reductive dechlorination at the surfaces of the minerals. The pH states of 5.5 to 6.0 and also 8.0 would be also too high and therefore do not promote any effective reactivity with the iron. [30]

Imbrogno compared the degradation of each strata with its metallic content. Her results showed a strong correlation between the metallic content and rate of degradation. This relationship was made clear in the upper strata, 0 to 5 feet, which showed a 93% loss whereas low soil showed a 80% decrease in TCE.

> The data from the 0 to 5 feet excavation was not used in the trend observations due to the lack of degradation resolution from the organic carbon content. All observations about metals and degradation rates were based on the 10 to 15 feet and 30 to 35 feet samples. When the final round of data was collected the area counts were compared with the initial chromatographic response of the sample cell. The percentage difference from the final signal compared to the initial signal response was plotted against the concentration of individual metals in the soil.
>
> The metals concentrations appear to have a linear relationship to the degree of TCE degradation that takes place. The total metal concentration in the medium (10 to 15 feet) level soil is 0.44 ppb. The approximate percentage of TCE loss in this sample was 93%. The low (30 to 35 feet) soil has a concentration of 0.41 ppb. The approximate percent loss of TCE in the low soil was 80%. The medium soil sample has 7% metal concentration in comparison to the low soil. The medium soil also had a 7% higher degree of TCE disappearance. In observation of this linear relationship, a conclusion can be drawn that the increase in the metals in the soil results in a greater percent loss of TCE. [31]

Results derived from Doong, Wu, Li with Klabunde and Imbrogno suggest a relationship between metal content and the increased TCE degradation. This relationship leads one to question which metal ion is most effective for removing of TCE from underground aquifers. Concentration was also identified as a potential factor in remediation of TCE. Therefore, proposed experimentation should determine any correlation between metals with concentration. This experiment would identify metal interactions along with possible mechanisms.

METHOD AND MATERIALS

2.1 INSTRUMENTATION

Specific properties, closely related to trichloroethylene's structure, made identification and quantification very difficult by standard means. These properties include TCE's low volatility energy combined with an electron withdrawing nature. Although these properties prevented detection by standard means, such as Colorimetric Determination or Ultra-Violet detection, techniques using temperature and affinity for stationary phases were suggested for separation and testing of TCE. Since sample mixtures contained several liquids with different volatility points, use of both a Headspace Autosampler coupled with Gas Chromatographic Analysis was necessary.

2.2 HEADSPACE SAMPLING

Headspace sampling is based on a principle that liquids will reach equilibrium between gaseous and liquid in an isolated system at a constant temperature. This sampling technique works best when attempting to separate two liquids; one volatile and the other non-volatile. By isolating two liquids in a given system, while raising temperature, one would expect that a volatile substance would attain equilibrium in the gas phase higher than that of a non-volatile substance. Gas is then removed by using a syringe thereby separating differing phases. Although total separation would not be possible with this technique it would be possible to give relative increases and decreases in concentrations if the conditions of testing remained constant.

Headspace sampling was identified as the method of choice because of a diverse nature of two substances contained in a test mixture. A 1% trichloroethylene kerosene (Jet Fuel) mixture was placed in a water matrix. It became important to separate volatile trichloroethylene samples from slightly volatile kerosene and water matrix. Prior research has shown headspace sampling to be an effective method of separating TCE from a water matrix. A Hewlett Packard 7694 Headspace Autosampler System was used to separate TCE from the water matrix in sample mixtures. This headspace system is capable of performing sampling automatically. Once set, this instrument begins testing with similar experimental condition. Conditions initially selected were chosen from those cited by Imbrogno, although further research was necessary. Headspace conditions set forth in this experiment are found in Table 4.

2.3 GAS CHROMATOGRAPHIC ANALYSIS

Gas Chromatography (GC) is based on a theory that mixtures of substances relatively close in nature could be separated by use of a stationary phase having a stronger affinity with one or more substances in any given mixture. This principle has been applied to several different material phases such as: gas, liquid and supercritical fluids. Although these three phases are currently being used, gas is most used of all three. GC is a preferred method of chemical separation because it can be used for most volatile organic materials and is relatively inexpensive to operate. A gas mixture is passed through a column composed of either solid or a thick wax like material. A GC then separates this mixture by slowing hindering one or more chemicals in most mixtures.

Prior research suggests that Gas Chromatography is the best technique for determining TCE concentrations. Trichloroethylene's low volatility energy along with its heavily chlorinated structure make GC an ideal method. A Hewlett Packard System 6890 Series GC system outfitted with an Electron Capture Detector/ Flame Ionization Detector (ECD/FID) with a HP-5 column (Crosslinked 5% Phenyl Methyl Silicone) was selected to identify and quantify trichloroethylene along with an internal standard. A Hewlett-Packard 6890 series was chosen because of it ability to be remotely programmed and controlled by a HP Ventura Series 4 computer. An accessory endowment to this system is an ability to work in conjunction with a Hewlett Packard Headspace Autosampler. This capability allowed an operator to set testing conditions for a series of samples while attending to other research. An electron capture detector was another highlight of this detector. TCE's heavy chlorinated nature resulted in a detector sensitivite that was approximately 10^4 times as sensitivity to it as to other substance which did not have halogens attached to them. A HP-5 column (Crosslinked 5% Phenyl Methyl Silicone) was selected because it had been shown be effective in separating chlorinated compound in a short period of time. Experimental methods used in this project can be viewed in Table 3 and Figure 11.

2.4 FLAME ATOMIC ABSORPTION

Atomic Absorption (AA) is an analytical method, which can both identify and quantify metallic compounds. AA foundation is derived from quantum theory. This theory states that shifts in electrons can only occur at quantifiable and discrete energy levels. By exposing certain compounds to multichromatic radiation and then using a monochromator to analyze certain wavelengths of radiation one can observe discrete lines where absorption of radiation occurs. Research has also shown that these electron shifts only occur at certain locations in the electro-magnetic spectrum. These shifts are specific for each element and can be used much like fingerprints to identify compounds. This method of analysis has been particularly effective in determination of metallic ions. Along with the identification of certain compounds Beer's Law draws a relationship between the concentration and absorption. This correlation allows for a determination of metal concentration using absorbance. Quantification can be achieved by using a series of standard solutions to determine a relationship between metal content and absorbance. An unknown concentration can then be calculated by using a series of standards.

Atomic Absorption was chosen for determination of metal concentrations because of its relative ease in quantifying several different metals. This was again preferable over other spectroscopic methods because of the wide range of metals tested during experimentation. A Perkin-Elmer model 5100 PC Flame Atomic Absorption was used for testing. In this procedure, metal ions were removed from soil samples by digesting a 10-gram sample by dilute solution of H_2SO_4 at a low heat. This solution was then filtered through medium grade filter paper and remaining solution tested. Using a blank of distilled water the instrument was first zeroed. Next, standardized solutions with concentration of 1, 5 and 10ppm were analyzed. These standard solutions were then used to produce a standard curve. After standardization, test mixtures were tested. This technique proved to be an acceptable method of testing metal concentration.

EXPERIMENTAL

3.0 PRELIMINARY PROJECTS

Although this project's primary purpose is to identify metals that can assist in degradation of trichloroethylene, several preliminary experiments were necessary to set experimental parameters. These preliminary experiments were executed to identify any problems in experimental design. Topics included were: addition of silica gel as a solid support, effectiveness of metal coating silica gel, use of an internal standard, effectiveness of differing metal concentrations on TCE degradation. Execution of these preliminary experiments allowed for a suitable experimental design to be identified.

3.1 DETERMINATION OF A CONCENTRATION TO SIGNAL RATIO

A preliminary project attempted addressed concerns that selected headspace/Gas chromatographic methods could not detect or accurately produce an acceptable signal to concentration ratio. Step one was to determine if chosen methods could detect a given quantity of sample mixture. In order to answer this question a test solution containing TCE was prepared. Although TCE has been found in large bodies of water there was a major dilemma found when preparing a test solution. Because TCE is a strongly non-polar substance, it has a very difficult time mixing with a polar water matrix. Preparation of this mixture was overcome by addition of a less polar kerosene/Jet fuel solution.

This test solution was prepared by placing 1mL of pure trichloroethylene into a 100ml volumetric flask using a 1mL volumetric pipette. 99-mL of kerosene/jet fuel was then added to the volumetric flask. After preparation, a 0.75-mL sample was then added to a 500mL opaque wide-mouth bottle containing 75mL of water. This bottle was then placed on a Burell wrist action shaker for approximately 1hour. Each bottle was removed and a 0.5 mL aliquot of liquid was extracted and placed in a head space vial. This mixture was then tested using Earl Method for both headspace and the GC studies. GC Earl method started at a temperature of 40°C for a period of four minutes. Temperature was elevated to 100°C over a period of three minutes.

3.2 DETERMINATION OF AN INTERNAL STANDARD

Variability in a gas chromatograph signal and headspace sampling made it necessary to determine if fluctuations in testing occurred. To better analyze these variations use of an internal standard was proposed. Based on vaporization energy, electron withdrawing ability and ability to be analyzed on the HP-5 column. P-chlorofluorobenzene, methylene chloride and chloroform were selected as possible internal standards. One microliter aliquots of these pure substances sample were then placed into three headspace vials containing approximately 1mL of water. They were then tested using the method described in Table 3. Although chloroform and methylene chloride were analyzed using the Earl method, p-chlorofluorobenzene was not detected. For analysis of p-chlorofluorobenzene, the Earl method was modified the chromatograph's oven to heat in a stepwise mode. Modified Earl method started with an oven temperature of 40°C for 2 minutes and which was raised to a temperature of 80°C for two minutes and finally to increased to a temperature 110°C for 3 minutes. After modifying this procedure p-chlorofluorobenzene was then retested.

3.3 DETERMINATION OF INITIAL TESTING TIME

Another question raised during testing was at what point should initial testing be completed. Previous studies had brought into question reliability of testing a mixture before an adequate mixing time had occurred. A homogenous distribution of test mixtures was vital to the experimental protocol because without it an accurate determination of TCE could not be obtained. Therefore, a significant amount of time had to be permitted before initial testing could occur. A brief time study was performed to identify a necessary amount of time. This study was performed by placing a 0.75 mL of test mix into two 500mL opaque jars that contained 50g of clean silica gel along with 80 mL of water. These jars

were then closed and placed on the Burell wrist action shaker. 0.5mL sample were then take out at 1, 2, 3,4 and 24 hour. Samples were then tested immediately using the Earl method. Results from the chromatograph were then placed on a Microsoft Excel worksheet. Areas were then graphed to determine if there were any large fluctuations in signals. Along with graphical representation a standard deviation for several signals were also determined using Microsoft Excel.

3.4. EFFECTS OF SILICA GEL ON TCE DEGRADATION.

To better simulate conditions that may be experienced in aquifers it was decided that a solid support should be added to each sample mixture. To allow for addition of this mixture it was necessary to determine if a solid support had any effect on degradation of TCE. Silica gel was identified as a possible solid support for TCE experiments because of its lack of metallic ions that may serve to contaminate any sample tubes. Several cans of clean dehydrated silica gel were obtained from Grace Davison Company of Baltimore, Maryland 21203.

To determine any effects of silica gel on TCE's degradation, several 500-mL wide-mouth sample bottles were cleaned and dried. Sample bottles were then split into two testing groups entitled group A and Control. 0.75-mL aliquot of a 1% solution of TCE in kerosene/ Jet Fuel test solution along with 75mL of water was added to both the Control and the Group A. In addition to water and test mixtures approximately 50 g of silica gel was added to each bottle in-group A. Jars were then sealed and placed on a shaker for testing. Two experimental groups were tested randomly over a period of 15 days. Testing involved removing a 0.5mL aliquot and placing into a headspace vial. Samples were tested by the Earl Headspace/Gas chromatographic method described later in this section. Areas of each chromatographic peak were then identified and placed into a Microsoft Excel worksheet. After being placed into this worksheet, values were used to find the percent decrease of each signal in relation to time. Averages of several trials of both silica gel and non-silica gel containing samples were then determined. Next, a log of each percent decrease was determined and graphed, to determine if one could obtain an increase in percent reduction of trichloroethylene by addition of silica gel. The next graphical representation of effect of silica gel was a kinetic determination. For this kinetic determination, the log of TCE's percent decrease was identified and graphed for both silica gel samples and non-silica gel samples. Slopes of graphical representations were then determined by use of the Excel program. Each slope of these equations was multiplied by 2.303 to determine first order rate constants. These constants were compared to identify if a significant kinetic change had occurred.

3.5 EFFECT OF METAL IONS ON THE DEGRADATION OF TCE

A third parameter studied was the correlation between degradation of trichloroethylene and presence of metal ions. Several different metal ions, from 10 to 8000ppm range, were tested to determine their catalytic effect on reduction of trichloroethylene. A variation between metal ion and TCE concentrations should accurately detect any significant changes in TCE concentration. Metal ions selected were Fe^{3+}, Cr^{3+}, Mn^{2+} and Zn^{2+}. Based on prior research, these metal ions have some effect on degradation of trichloroethylene. Several concentration ranges of each metal ion were selected to determine which would be effective. This experiment suggested that concentrations from approximately 10ppm to 8000ppm would be an effective test range. Following these preliminary studies, metal salts of iron (III) nitrate, chromium (III) nitrate, manganese (II) chloride and zinc (II) nitrate were used. Molecular weights of all salts were then identified and an amount of salt needed to produce proper metal concentration was then calculated. Stock solutions of 8000ppm for each metal ions were prepared and stored in white 500mL polyethylene bottles. These bottles were then shaken to produce a homogenous mixture. Solutions were then diluted to obtain concentrations of 8000ppm, 4000ppm, 2000ppm, 1000ppm…10ppm. 75mL of each of these solutions were placed into 500mL brown wide mouth

sample bottle along with 50-grams of dehydrated silica gel. A pipette was then used to transfer a 0.75 μL sample into each sample bottle. Brown sample bottles were then shaken for approximately 30 minutes on a Burell wrist action shaker. After 30 minutes a 0.5mL sample was taken from each bottle and placed into a clean Hewlett Packard headspace vial. Samples were then tested using the Earl method for the Hewlett Packard headspace and the ErljulyB method for the HP 6890 series GC. ErljulyB, was then used to test each sample. Testing occurred periodically over the next fifteen days. Areas of chromatographic peaks that correlated with trichloroethylene peaks, identified and placed on Microsoft Excel. Percent reduction was then determined, and graphed for each metal at various concentrations. Resulting slopes were then compared to 0ppm control samples to determine if any change for TCE had occurred.

After determining percent TCE degradation a kinetic analysis was necessary. Prior studies by Imbrogno suggested that each reaction was first order.[1] To accomplish this kinetic analysis, log base 10 for the percent reduction for each area was determined and graphed using Microsoft Excel. A slope for each concentration was then calculated along with a correlation coefficient.

Final analysis for each reaction was completed by determining its rate constant. This rate constant helps show any difference in kinetic relationships. To determine this rate constant each slope is multiplied by 2.303. This final step was done to convert base 10 long to a natural log to obtain corrected rate constants. Rate constants were then compared against a 0ppm control to determine if metals had a kinetic effect on degradation of trichloroethylene.

RESULTS AND DISCUSSION

4.1 DETERMINATION OF A CONCENTRATION TO SIGNAL RATIO

Results strongly suggest that procedures used for both headspace and gas chromatographic series are suitable for use. Observations for this study are found in Figure 11. TCE's chromatograph shows a sharp peak at 2.387 minutes when compared to a control. Since no other difference between control and test samples can be observed it was assumed that the extraneous peak was in fact trichloroethylene. This peak, located at 2.387, shows a strong signal for 1µL of sample. Results suggest that Earl headspace and gas chromatographic methods are suitable for testing. [Figure 11]

Results derived from a second portion of this study's preliminary trial also appeared to be positive. In this segment, a chromatographic signal to concentration ratio was determined. [Figure 12] Trichloroethylene signal to concentration was found to have a correlation factor of 0.98 with an equation of ($y = 71834x - 15552$) by use of Microsoft Excel. A similar method was used to identify a correlation factor for chloroform. Chloroform's correlation factor was identified to be 0.9992 with an equation of ($y = 21609 + 5191.6$). Results suggest a linear relationship between concentration and signal for both TCE and chloroform. This determination allows one to identify a direct proportionality between loss in signal to loss in concentration.

4.2 DETERMINATION OF AN INTERNAL STANDARD

This study attempts to identify an internal standard to calibrate differences in gas chromatographic signals. Of three compound tested, two compounds appeared to be a viable internal standard for TCE testing. Methylene chloride and chloroform showed acceptable chromatographic signals. [Figures 14,15,16] P-chlorofluorobenzene was eliminated from further study because a signal could not be identified using experimental testing procedures. P-chlorofluorobenzene was again tested using a modified procedure. [Figure 17] These results were not acceptable for an internal standard.

Results showed that methylene chloride came off at approximately 1.5 minutes with a lower sensitivity than that of either chloroform or TCE. Results of chloroform proved to be better than that of methylene chloride. Retention time of chloroform appeared to be approximately 1.8 minutes with sensitivity close to that of TCE. [Figure 15] TCE's chromatographic peak appeared at 2.8 minutes with a fair amount of sensitivity for 1uL of sample.

Due to great variations in sensitivity, chloroform was selected as the internal standard. Hewlett-Packard's Chemstation was used to compare chromatographs from chloroform and TCE to determine differences in retention time and sensitivity. Next, chloroform and TCE were placed into a single vial. Vials were again tested to determine if any reaction took place during testing. Results suggested that no intermediates could be detected therefore it was assumed that no reaction took place. Chloroform was selected as internal standard. Comparable sensitivity along with similarities in retention time made an ideal choice as an internal standard.

During testing, large fluctuations in test results occurred when using chloroform as an internal standard. These results were then compared to samples without an internal standard. Samples tested without an internal standard had fewer fluctuations in chromatographic response. Chloroform was then eliminated as an internal standard for all remaining samples.

4.3 DETERMINATION OF INITIAL TESTING TIME

This preliminary study attempts to determine time suitable for initial testing. Results from this testing protocol showed small fluctuations in signal value over 24 hours. However, no major decrease for TCE could be identified with this study. Chromatographic signals at 0 hours were calculated to be 64060.0 5Hz*s. This value was then compared to values for 1 hours (60740.2 5Hz*s), 2 hours (56648.9 5Hz*s), 3 hours (64307.5 5Hz*s), and 24 hours (64322.4 5Hz*s). Although tests samples at one hour and two hours decreased by approximately 4000 and 8000 5Hz*s respectively, no significant decrease for signals were identified. Results suggest that immediate testing would not result in a major loss of signal. Therefore immediate testing of sample is a valid testing time.

4.4 EFFECTS OF SILICA GEL ON TCE DEGRADATION.

This study attempts to determine if silica gel's presence affects TCE's removal. Results shown in graph representations suggest that silica gel did not have a significant effect on TCE's degradation. This determination was achieved by analyzing graphical representation of averaged percent decreases, kinetic reductions and rate constants. These results for both silica gel and non-silica gel containing samples were then compared by placing then on a Microsoft Excel graph and using visual comparison. In Figure 22 percent decrease for both silica gel and non-silica gel containing samples showed a similar kinetic trends. Similarities between silica gel and non-silica gel samples can be also shown in kinetic representation shown in Figures 19 and 20.

Similar trends are also found in averaged rate constants for both silica gel and non-silica gel containing samples. An averaged rate constant for non-silica gel containing samples was calculated to be 0.049. This number is compared to an average rate constant for silica gel containing test samples of 0.053. This difference is only 0.004 Hz*s. Therefore, it was concluded that silica gel did not have a significant effect.

4.6 EFFECT OF METAL ION ON THE REDUCTION OF TCE.

4.6.a CONTROL STUDY

As demonstrated previously, silica gel did not appear to have a significant effect on TCE's degradation. Although silica gel was eliminated as a possible catalyst for TCE's degradation, a loss of control samples was observed. To analyze this loss several control samples were tested. These chromatographic signals were summed and an average was obtained. A loss of TCE was then observed for all control solutions.

Although these results showed that silica gel had no effect, several problems were identified while testing. Reductions in amount of TCE in both silica gel and non-silica gel containing samples were identified. Since no mechanism for a trichloroethylene's reduction could be identified it is proposed that loss of sample occurred during testing. Two hypotheses have been developed to explain TCE's loss. Loss during sampling is one proposed explanation for TCE's unusual loss. A second hypotheses that has been suggested is biodegradation of trichloroethylene during sampling.

To compensate for any loss of trichloroethylene during testing, percent decrease, rate constant and kinetic effects were all compared to an averaged 0ppm control. This comparison allows one to determine effects of metal while factoring out losses in trichloroethylene due to sampling error.

4.6.b KINETIC EFFECT

Results of sample metals tested suggested that certain metals did have a kinetic effect on trichloroethylene's removal. Of four metals tested two metals showed an increase in kinetic effect for TCE for removal, while another two metals showed either no observable or a lower rate of removal when compared to an averaged 0ppm control solution. To analyze an effect of each sample metal, several concentrations were tested, using a concentration range from 0ppm to 8000ppm for each sample metal. Various metal concentrations also showed differences in kinetic effect. Results also suggest that higher metal concentration increase kinetic effect of TCE's dechlorination.

Iron(III) appeared to show a very low kinetic rate as compared to a control sample. Results, shown in Figures 23-30 revel that at very low concentration from 10-80ppm iron samples are similar in kinetic change as compared to that of a 0ppm Control solution. This trend somewhat changes when concentration reaches approximately 500ppm. At this concentration kinetics are slightly above that of a control sample. This slight rise in kinetic rate continues to increase for remaining iron sample concentrations. This trend is also seen when observing the rate constants for Iron (III) range of solutions in Table 5.

Another metal that appeared not to have a significant kinetic effect for removing TCE is manganese. Results of manganese are shown in Figures 31-

37. Manganese appeared to be an ineffective catalyst at all concentrations. Although there was a minor kinetic rate increase at a sample concentration of 10ppm versus a 0ppm control solution no other changes were observed. Again, this general trend is observed during a rate constant analysis.

One metal that did appear to cause an increase in kinetic effect at very high concentrations appeared to be zinc. Zinc results are shown in Figures 38-44. Zinc, at lower concentrations, showed almost no change in kinetic degradation of trichloroethylene. This ineffectiveness is apparent for a concentration range from 40 to 4000ppm. Through this concentration range, no significant effect can be observed when comparing the zinc samples vs. a 0ppm control sample. This trend remains constant until the 8000ppm-zinc solution. This 8000ppm-zinc solution showed a significant change in kinetic effect. To confirm these results the rate constant was also analyzed to show similar trends.

Chromium also showed a large kinetic effect when compared to a control sample. Chromium results, as demonstrated in Figures 45-51, shows that at very low concentration, chromium is ineffective in changing the kinetic rate of removal of TCE. This ineffectiveness spans concentrations from 40ppm to 1000ppm samples. Ineffective trend changes for concentrations 2000ppm to 4000ppm. These samples show a significant increase in kinetic effect for TCE's remediation. Again, to confirm these results a rate constant analysis was performed. These results confirmed all previous data.

Results of all sampled metals show that metal ion concentrations does have a kinetic effect on trichloroethylene's rate of degradation. All sample metals show very little effectiveness at low metal concentrations. This suggests that lower concentrations were outside the effective concentration range for the metals. This general trend of ineffectiveness is continued into higher concentrations for both iron (III) and manganese (II), however this trend dramatically changes in higher concentration of chromium (III) and zinc (II). This increase in kinetic effect may be due to the reductive power or changes in catalytic mechanism. Other suggestions include variations in catalytic mechanisms.

4.6.c PERCENT DECREASE

Because kinetic reaction rates can not be effective in determining overall outcome of a reaction, other mechanisms needed to be analyzed to determine what effects the sample metals had on the removal of TCE. To determine its effectiveness, each metal's total percent decrease was also analyzed. This analysis allows one to observe if any overall change is occurring.

Similar to results shown for kinetics, iron did not show a total percent decreases significantly different to that of a control sample. Results suggest that at very low concentrations iron will have no effect compared to a control sample. Iron ineffective range spans from 10ppm to 500ppm concentrations.

Addition of iron (III) at very high concentrations (2000ppm to 8000ppm) actually appears to inhibit remediation of TCE. This is shown at iron concentrations of 1000ppm to 8000ppm. In this experimental range, the 0ppm control appeared to have a higher total percent decrease comparatively.

Manganese samples, shown in Figures 55-62 showed differences in total percent decrease only at highest metal concentrations. Similar to iron, manganese at very low concentration shows little or no difference in total percent decrease vs. 0ppm control solution. This trend spans from a concentration of 40ppm to 4000ppm. However, at a concentration of 8000ppm one can see a significant increase in total percent decrease. This suggests that manganese does not have an effect on total percent decrease at any but the highest concentration.

Zinc samples, shown in Figures 63-69 show some significant degradation for middle to high concentration ranges. For concentrations between 40ppm and 80ppm there appeared to be no significant change in total percent decrease vs. control samples. This trend quickly changes at concentration of 500ppm to show an increase in total percent decrease. This change continues for the remaining sample concentrations.

In chromium samples, shown in Figures 70-76 one can see a larger percent decrease at very low concentration while showing very little difference at higher concentrations. Total percent decrease appears to be most effective from concentrations of 40ppm to 1000ppm. This trend changes at 2000pppm-chromium concentration by showing little or no difference from a control sample. This trend remains constant for the remaining chromium concentrations.

These results suggest that lower concentrations were again outside an effective concentration range for this reaction. At middle concentration range, metals such as chromium, iron and manganese did not appear to have any significant difference vs. a control sample. However, these results also suggest that high experimental concentrations of several metals became active. Results show that high iron concentrations actually inhibited total percent decrease. This again may be due to a weak reductive nature of iron (III) as compared to other metals. Results also suggest that manganese is not an effective catalyst at high metal concentrations. At higher concentrations, only zinc and chromium showed an increase in total percent decrease. Manganese was shown effective at its' highest experimental concentration. Zinc samples showed a major difference in total percent decrease vs. a control sample at most high concentrations. This may be a result of a strong reductive nature of zinc ion as compared to other three sample metals.

CONCLUSIONS

Results obtained suggest that certain metal ions can be effective catalyst for remediation of trichloroethylene. Metals such as zinc(II) and chromium(III) have a capability to remove or decrease trichloroethylene's concentration. Although manganese(II) and iron(III) did not appear to show a significant amount of TCE reduction under certain experimental parameters, other conditions may enhance their effectiveness.

Mechanisms of these reactions are not clearly understood. It is hypothesized that metal ions can catalyze TCE's removal using a free radical mechanism as shown in Figure 10. This oxidative/reductive mechanism is believed to involve a reduction of a metal ion and an oxidation of TCE. This occurs when one electron from a metal is given to chlorine on TCE. This electron movement allows chlorine to become a stable atom thereby dechlorinating TCE. This mechanism under certain condition may be able to remediate other environmental contaminates.

This mechanism has been shown to be an invaluable tool in removing TCE along with other environmental pollutants from underground aquifers. Unique properties of metals and their ions make them ideal for remediation of both surface waters and underground aquifers. Further studies are necessary to allow for an increased effectiveness in remediating environmental contaminates.

Table 1a
PHYSICAL PROPERTIES OF TRICHLOROETHYLENE

Solvent	1,1,2 Trichloroethylene
Category	CHC
CAS Number	C2HCl3
Weight (Daltons)	131.38
Cost	0.45
Boiling Point(C)	86.7
Boiling Point (F)	188.06
Freeze Point (C)	-84.8
Freeze Point (F)	-120.64
Specific Gravity	1.5
Viscosity (cP)	0.532
Vapor Pressure(mmHg)	69
Temp for Vapor pressure (deg C)	25
Henry's Law Constant (atm-m3-mole)	0.0103
Reflective Index	1.475
Dielectric Constant	3.42
Evaporation Rate (BuAC=1)	4.46
Water Solubility (mg-Kg)	1099
Octanol-Water Partition Constant (Log Kow)	2.42
KB No:	130
Hildebrand Solubility Parameter (cal cm-3-2)	9.3
pKa	NA
pH	NA
Azeotrope	NA
Heat of Vaporization (kcal-mole)	8.19
Heat Capacity (cal-K mole)	28.8
Thermal Condutivity (cal- Kmole)	NA
Flash Point (C)	NA
Flash Point (F)	NA
Autoignition Temperature (C)	420
Autoignition Temperature (F)	NA
Explosion Limit % (Upper)	10.5
Explosion Limit % (Lower)	8
Color	Colorless
Corrosive	No
UV Absorption (nm)	197
Odor	Chloroform-Like
Odor Threshold (ppm)	28
Smiles	C(=CCl)(Cl)Cl
Rate Constant Hydroxyl	2.36E-12
Rate Constant Ozone	3.00E-20
Atmospheric Half-Life	6.7days
Ozone Depletion potential (CFC11=1)	NA
Urban Ozone Formation Potential (C2H4=1)	0.09
Global Warming potential (CO2=1)	NA
Probable Biodegradation Time	Weeks
Oxygen Demand, Bio BOD5	NA
Oxygen Demand, Bio BOD20	NA
Oxygen Demand, Chem (COD)	NA
Oxygen Demand, Theoritical (ThOD)	0.37
Bioconcentration - Log BCF	1.23
Soil Absorption (Organic Carbon) - Log KOC	2.02

Table 1b
TOXICOLOGICAL PROPERTIES OF TRICHLOROETHYLENE

OSHA STEL: ppm	200
OSHA STEL: mgm	1080
OSHA Ceiling: ppm	NA
OSHA Ceiling: mgm	NA
NIOSH REL: ppm	25
NIOSH REL: mgm	136
NIOSH STEL: ppm	NA
NIOSH STEL: mgm	NA
NIOSH Ceiling: ppm	NA
NIOSH Ceiling: mgm	NA
NIOSH IDLH: ppm	1000
NIOSH IDLH: mgm	5460
ACGIH TLV: ppm	50
ACGIH TLV: mgm	269
ACGIH STEL: ppm	200
ACGIH STEL: mgm	1070
ACGIH Ceiling. ppm	NA
ACGIH Ceiling: mgm	NA
LD50 Oral (mg/kg)	2402mus
LD50 Skin (mg/kg)	>20000
LC50 Inhilation (ppm)	8450/4H mus
Carcin. NTP	Y
Carcin OSHA	NA
Carcin IARC	N
Carcin. EPA	Y
Unit Risk. Drinking Water (ug/L)	0.6
Unit Risk. Inhalation (ug/L)	0.06
Mutagencity:	Y
Reproductive/Developmenal Toxicity:	Y
Target Organs	Sys. Hrt.Lvr.Kdny. CNS Skin
Route of Entry	Inh. Ing. Con

Table 2
EARL HEADSPACE METHOD

	Matrix
Matrix:	Water
Matrix Boiling Point:	100

	Temperature
Sample Oven	70
Sample Valve:	80
Transfer Line	90

	Time (Minutes)
Gas Chromatographic Cycle:	1.7
Sample EquilibrationTime:	1
Vial Pressurization Time:	0.2
Sample Loop Fill Time :	0.2
Loop Equilibration:	0.05
Sample Injection Time:	0.05
Oven Stabilization Time:	0.5

	Shaking
Agitation	Low

	Parameters
Oven Step:	No
Equilibration Step:	No
Step Size	NA

	Mode
Extractions:	1
Puncture Mode:	Single

Table 3
GAS CHROMATOGRAPHIC METHOD
EARL METHOD

Oven

Initial Temp	40°C
Initial Time	4 00 minutes
Post Temp	40°C
Post Time	0 00 min
Run Time	7.10 min
Maximum Temp	450°C
Equilibration Time	0 min

Ramps:

Number	Rates	Final Temp	Final Time
1	20 00	100°C	0 10

Front Inlet

Mode	Split
Intinal Temp	250°C (On)
Pressure	12 5°C
Split Ratio	10 1
Split Flow	30 3 ml/min
Total Flow	35 3 ml/min
Gas Saver	Off
Gas Type	Helium

Column 1

Column Type	Capillary
Nominal Length	30 0 meters
Nominal Diameter	320 00 um
Nominal Film Thickness	0 0um
Mode	Costant Flow
Initial flow	3 0 mL/min
Nominal Init Pressure	12 5 psi
Average Velocity	44 cm/sec
Inlet	Front inlet
Outlet	Front Detector
Outlet Pressure	Ambient Pressure

Front Detector

Front Detector Type	Electron Capture
Temperature	300°C
Anode Purge Flow	6 0 mL/min (On)
Mode	Constant makeup Flow
Makeup Flow	30 0 mL/min (On)
Makeup Gas Type	Argon Methane 5%
Adjust Offset	63
Electrometer	On

Signals

Signal 1	Electron Capture Det
Data Rate	20 Hz
Type	Front Decetor
Save Data	On
Zero	0 0 (Off)
Range	0
Fast Peaks	Off

Signal 2	Electron Capture Det
Data Rate	20 Hz
Type	Front Decetor
Save Data	On
Zero	0 0 (Off)
Range	0
Fast Peaks	Off

Table 4
MODIFIED GAS CHROMATOGRAPHIC METHOD

Oven

Initial Temp	40°C
Initial Time	2 50 minutes
Post Temp	40°C
Post Time	0 00 min
Run Time	7.88 min
Maximum Temp	450°C
Equilibration Time	0 5 min

Ramps:

Number	Rates	Final Temp	Final Time
1	40°C	80°C	2 00 min
2	80°C	110	2.00 min
3	(Off)	(Off)	(Off)

Front Inlet

Mode	Split
Initial Temp	250C (On)
Pressure	11.2 psi (On)
Split Ratio	10 1
Split Flow	25 7 ml/min
Total Flow	30 6 ml/min
Gas Saver	Off
Gas Type	Helium

Column 1

Column Type	Capillary
Nominal Length	30 0 meters
Nominal Diameter	320 00 um
Nominal Film Thickness	0 0um
Mode	Costant Flow
Initial flow	2 6 mL/min
Nominal Init Pressure	11 2 psi
Average Velocity	40 cm/sec
Inlet	Front Inlet
Outlet	Front Detector
Outlet Pressure	Ambient Pressure

Front Detector

Front Detector Type	Electron Capture
Temperature	300°C
Anode Purge Flow	6 0 mL/min (On)
Mode	Constant makeup Flow
Makeup Flow	30 0 mL/min (On)
Makeup Gas Type	Argon Methane 5%
Adjust Offset	63
Electrometer	On

Signals

Signal 1	Electron Capture Det
Data Rate	20 Hz
Type	Front Decetor
Save Data	On
Zero	0 0 (Off)
Range	0
Fast Peaks	Off

Signal 2	Electron Capture Det
Data Rate	20 Hz
Type	Front Decetor
Save Data	On
Zero	0 0 (Off)
Range	0
Fast Peaks	Off

Table 5
Rate Constants for Reduction of TCE in the Presence of Metals

Concentration	Fe	Mn	Cr	Zn
0ppm	-0.058	-0.044	-0.042	-0.068
10ppm	-0.048	-0.029	-0.038	-0.087
20ppm	-0.050	-0.052	-0.033	-0.047
40ppm	-0.035	-0.080	-0.034	-0.038
80ppm	-0.070	-0.047	-0.037	-0.044
500ppm	-0.051	-0.058	-0.054	-0.034
1000ppm	-0.047	-0.065	-0.103	-0.075
4000ppm	-0.050	-0.044	-0.200	-0.061
8000ppm	-0.047	-0.048	-0.173	-0.231
Control	-0.054	-0.046	-0.045	-0.053

Figure 1.
STRUCTURE OF TRICHLOROETHYLENE

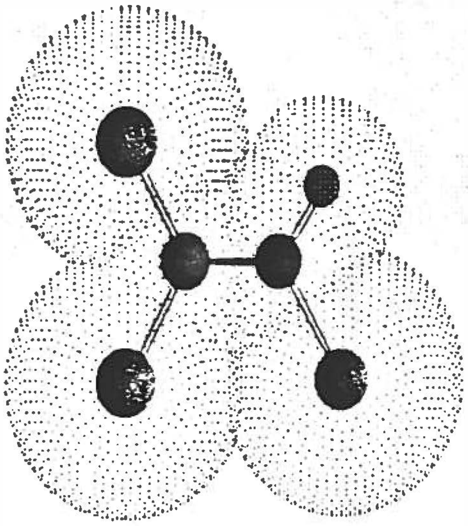


Figure 2.
MOLECULAR ORBITAL FOR TRICHLOROETHYLENE

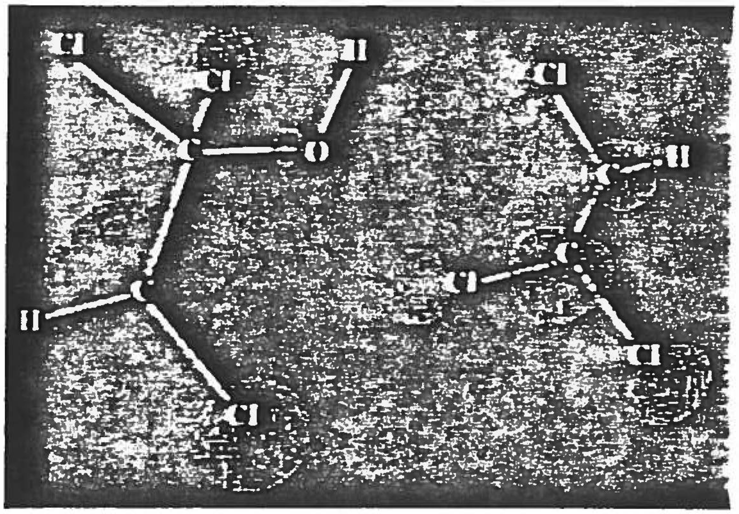
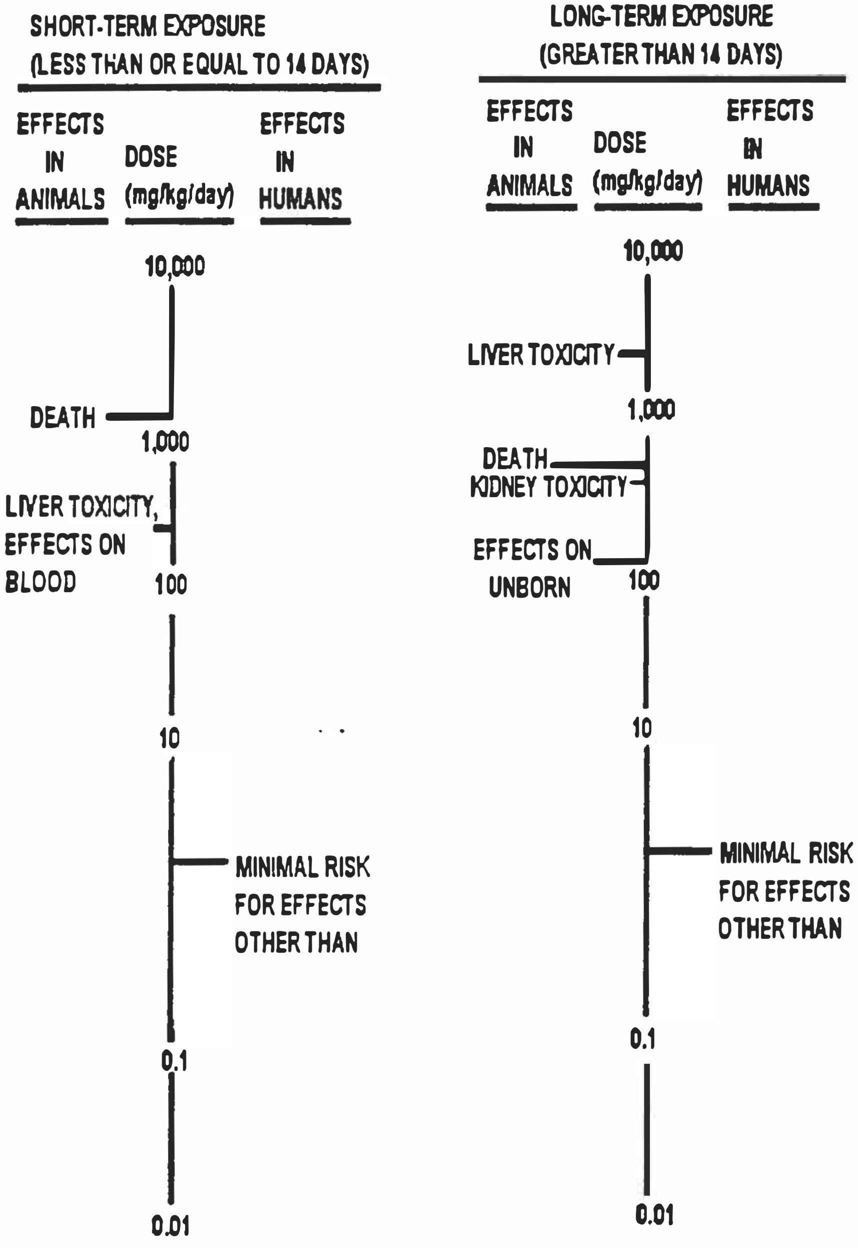
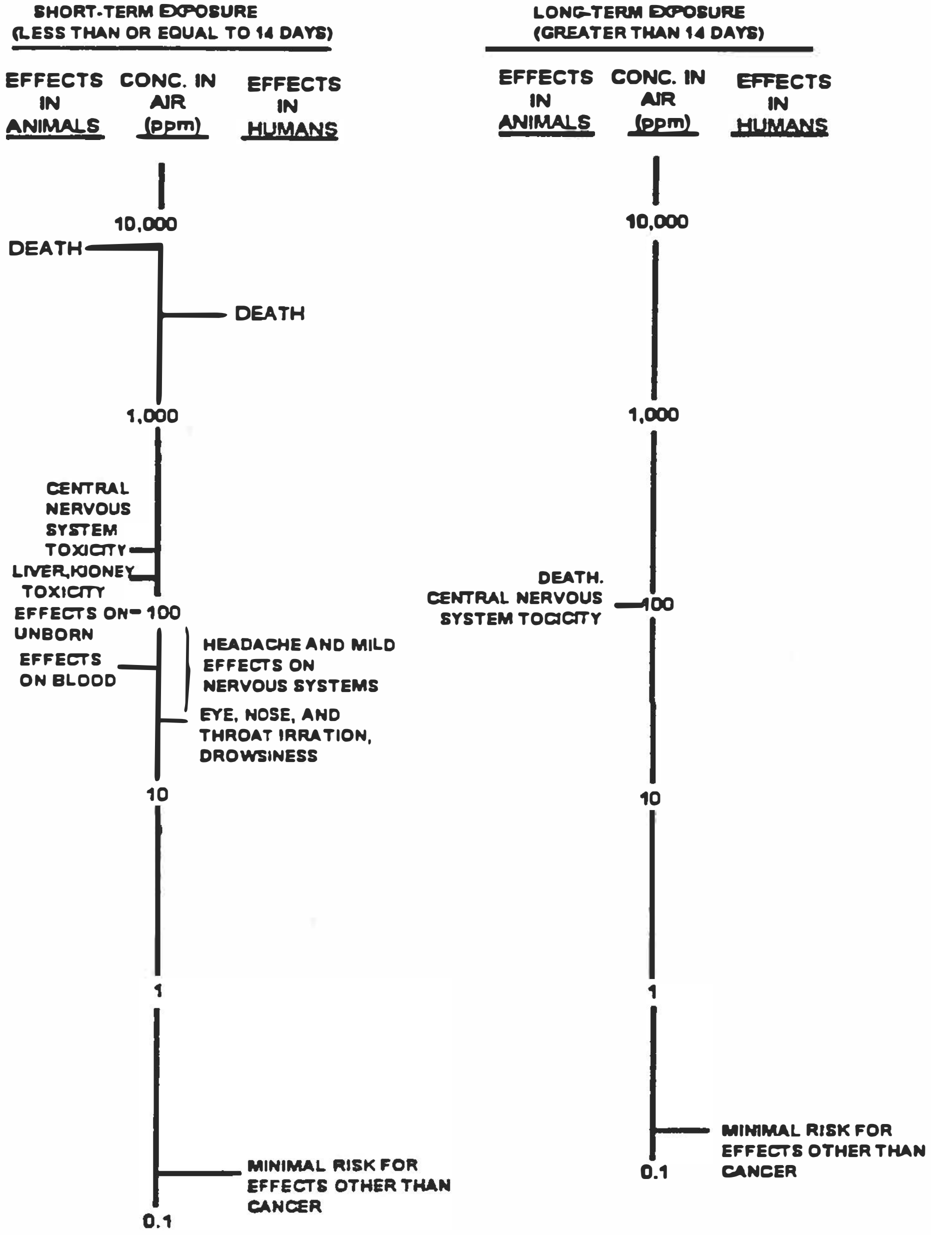


Figure 3.
HEALTH EFFECTS OF TCE INGESTION



HEALTH EFFECTS FROM INGESTING TRICHLOROETHYLENE

Figure 4.
HEALTH EFFECTS OF TCE INHALATION



HEALTH EFFECTS FROM BREATHING TRICHLOROETHYLENE

Figure 5.
MECHANISM FOR BIO-DEGRADATION
Representation of the mechanism by which a biological remediation mechanism is chosen.

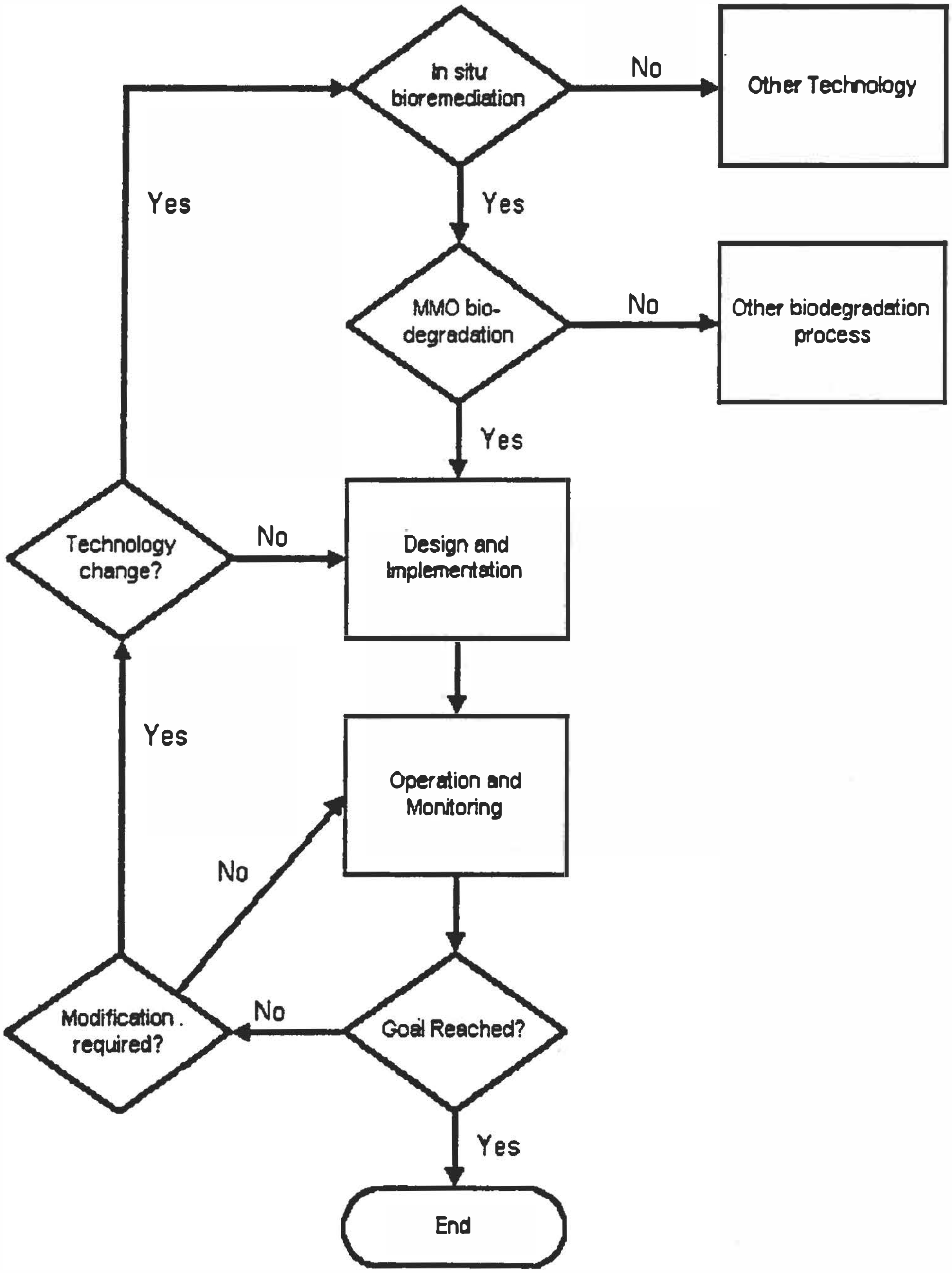


Figure 6
BIOLOGICAL DEGRADATION PATHWAYS
Graphical representation of the sum biological pathways in that can be used to degrade trichloroethylene.

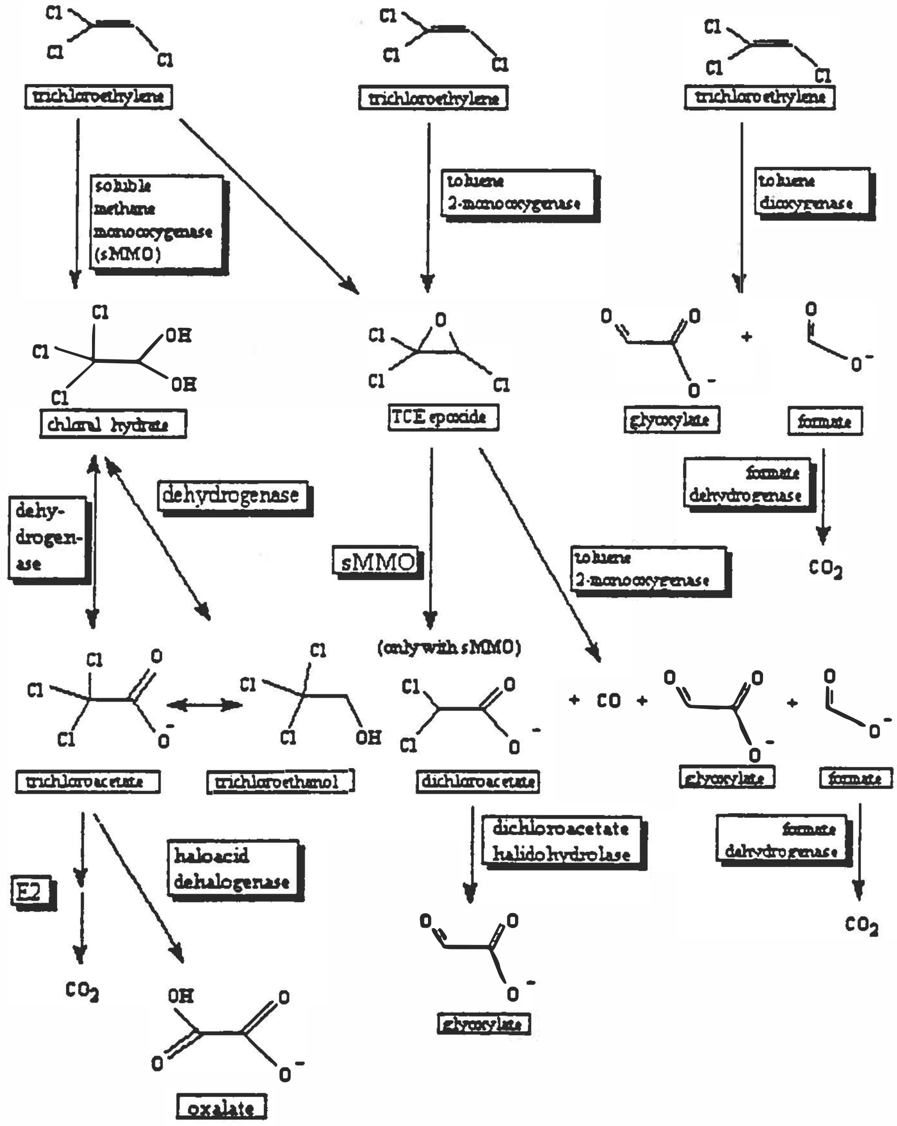


Figure 7
TOLUENE DIOXYGENASE REACTION
Graphical representation of the specific biochemical process that occurs when TCE is place into an environment with the enzyme Toluene dioxygenase.

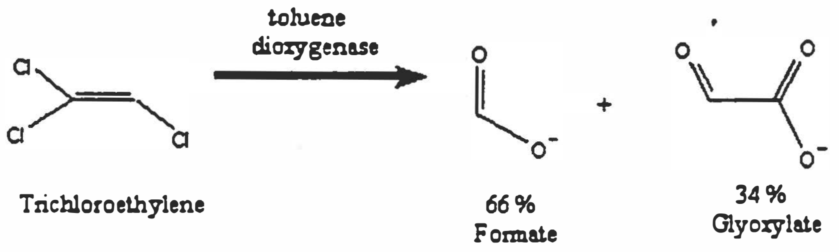


Figure 8
TOLUENE 2-MONOXYGENASE
Represents the specific biochemical process that occurs when TCE is place into an environment with the enzyme toluene 2 monooxygenase.

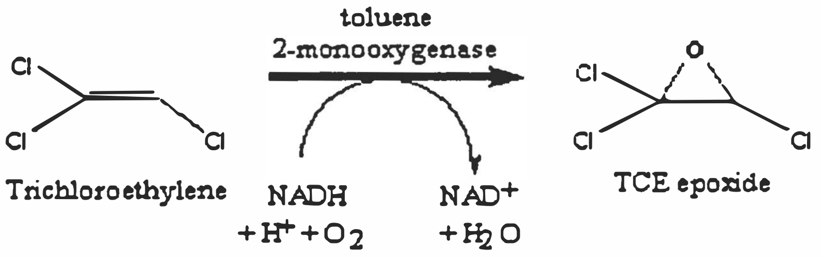


Figure 9
METHANE MONOOXYGENASE
Represents the specific biochemical process that occurs when TCE is place into an environment with the enzyme methane monooxygenase.

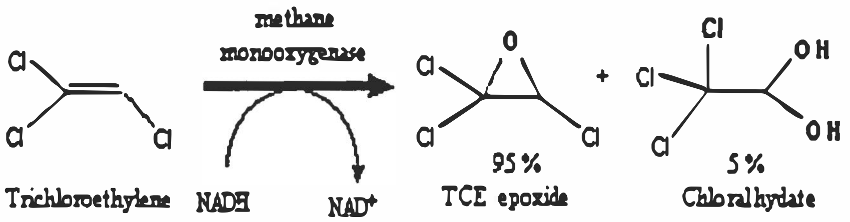
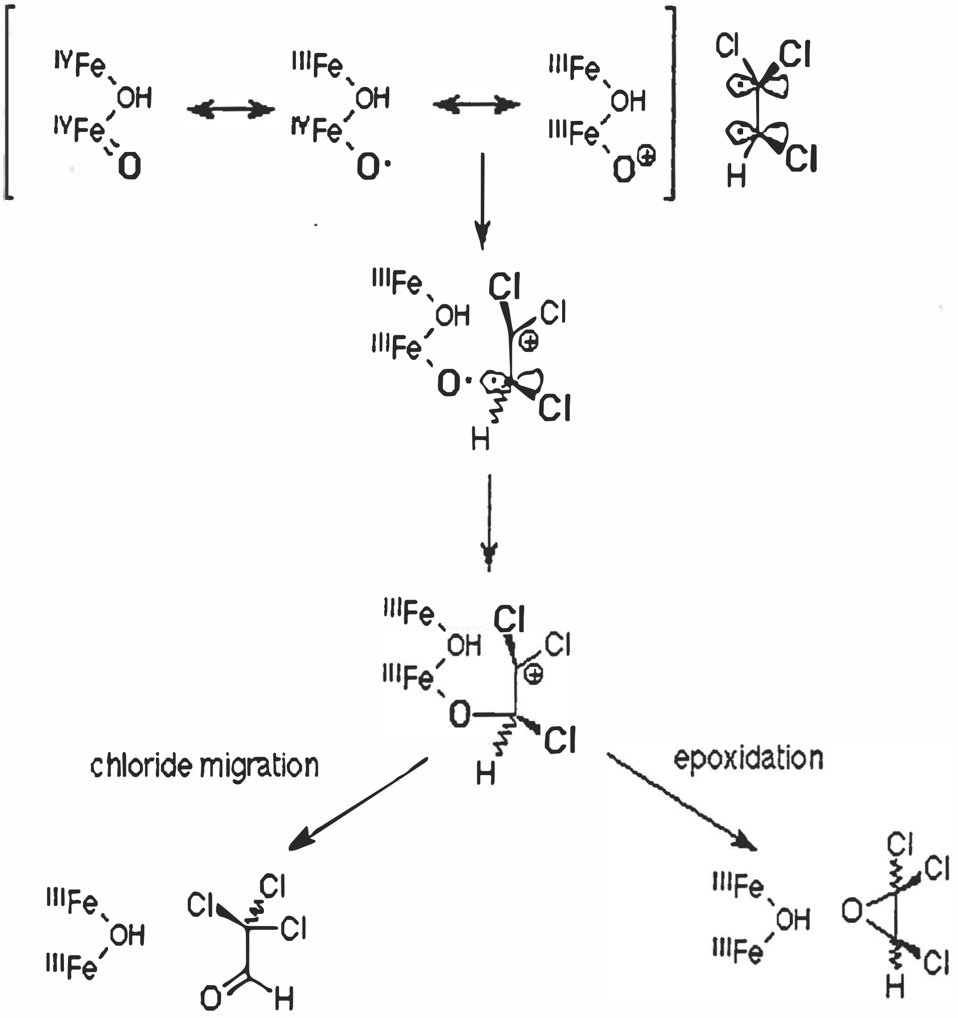


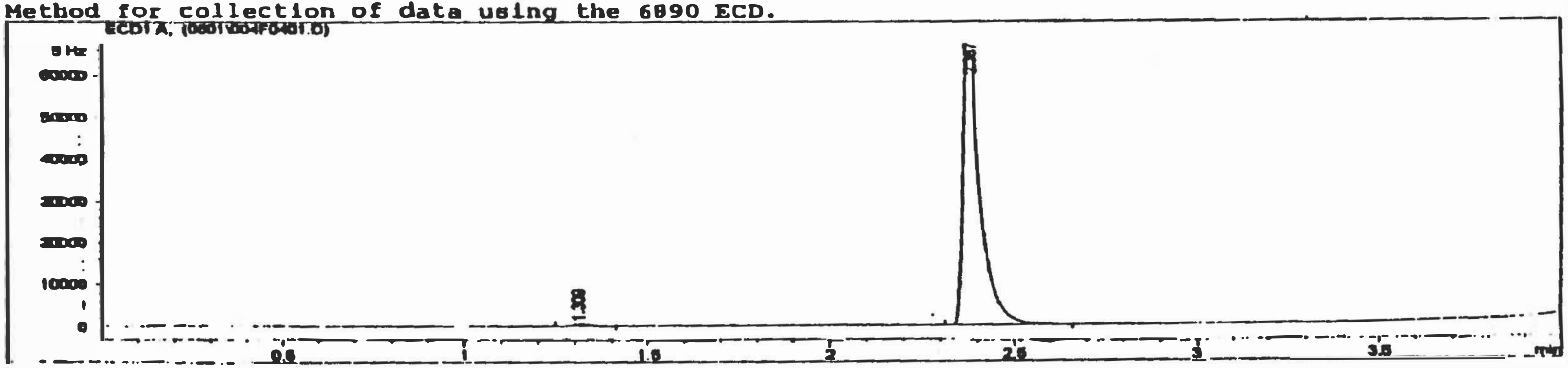
Figure 10
MECHANISM FOR CHEMICAL REDUCTION OF TCE
Represents a possible mechanism for the chemical reduction of Trichloroethylene.



Graphic by: Eva C. Young
Based on data from:
Rosenzweig, A.C., Frederick, C.A., Lippard, S.J., and Nordlund, P. (1993) Crystal structure of a bacterial non-haem iron hydroxylase that catalyses the biological oxidation of methane. Nature 366(6455), 537-543.

Figure 11
CHROMATOGRAPH OF TRICHLOROETHYLENE

```
==================================================================================
Injection Date  : 6/1/98 6:01:29 PM                   Seq. Line :    4
Sample Name     : TCE                                      Vial :    4
Acq. Operator   : Earl                                      Inj :    1
                                                    Inj Volume : Manually
Method          : C:\HPCHEM\2\METHODS\EARL.M
Last changed    : 6/1/98 5:25:21 PM by Earl
Method for collection of data using the 6890 ECD.
```



```
==================================================================================
                            Area Percent Report
==================================================================================

 Peak RetTime Type  Width     Area      Height      Area
   #   [min]        [min]  [5 Hz*s]    [5 Hz]        %
 ----|-------|----|-------|----------|----------|--------|
   1    1.309 BB    0.0533 1686.35156  483.83606  0.77503
   2    2.387 BB S  0.0483 2.15899e5  6.42899e4  99.22497

 Totals :                  2.17586e5  6.47737e4
```

Figure 12
TCE'S SIGNAL TO CONCENTRATION RATIO

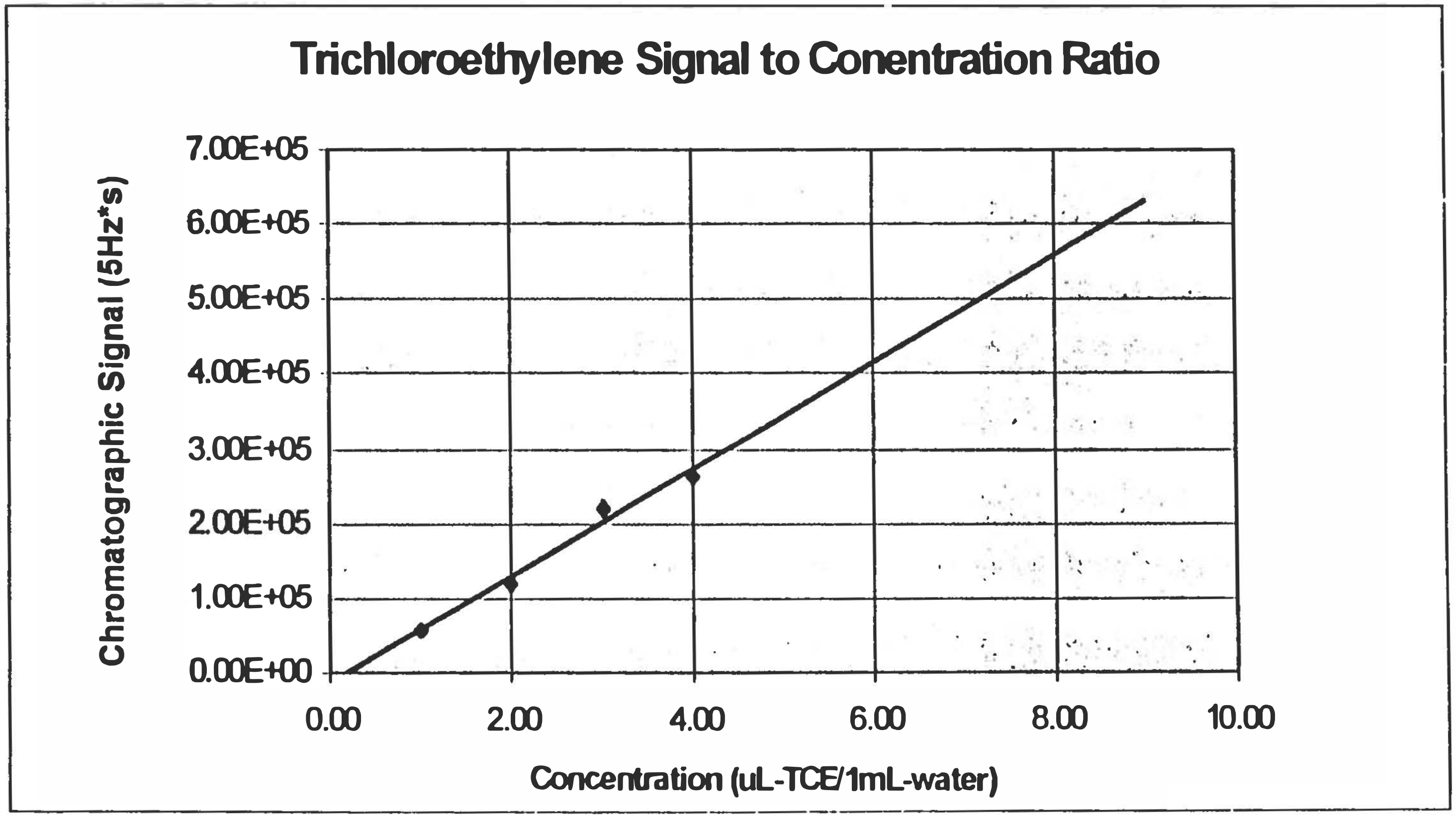
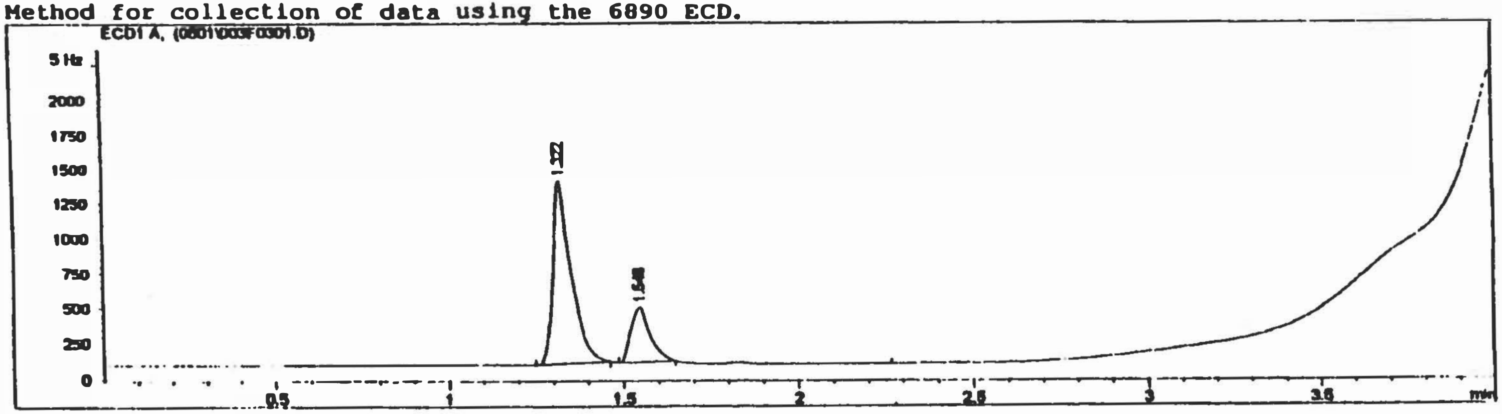


Figure 13
CHROMATOGRAPH OF METHYLENE CHLORIDE

```
=================================================================================
Injection Date  : 6/1/98 5:54:17 PM                Seq. Line :   3
Sample Name     : met cH                                Vial :   3
Acq. Operator   : Earl                                   Inj :   1
                                                  Inj Volume : Manually

Method          : C:\HPCHEM\2\METHODS\EARL.M
Last changed    : 6/1/98 5:25:21 PM by Earl
Method for collection of data using the 6890 ECD.
```



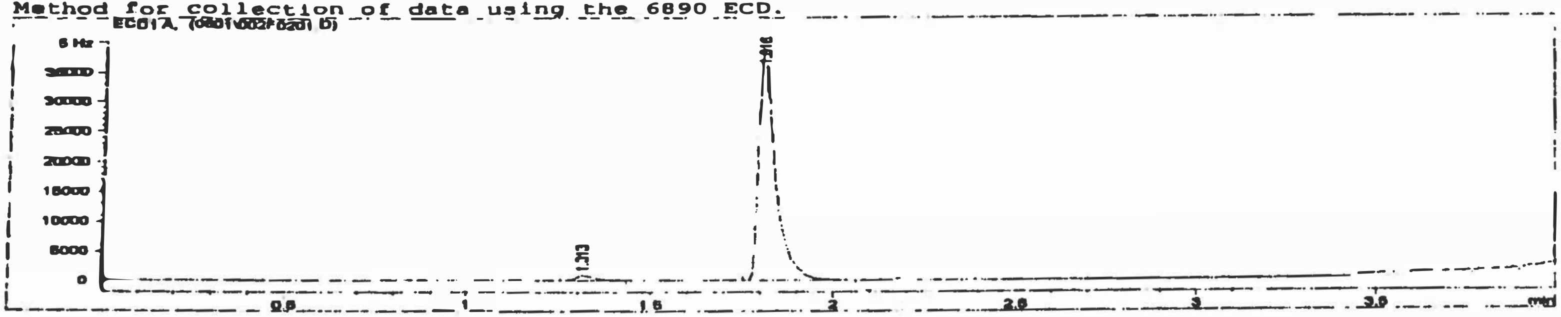
```
=================================================================================
                         Area Percent Report
=================================================================================

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [5 Hz*s]    [5 Hz]       %
----|-------|----|-------|----------|----------|--------|
  1   1.322 BB    0.0486 4645.44434 1310.41663 76.13609
  2   1.548 BB    0.0572 1456.05640  389.78778 23.86391

Totals :                 6101.50073 1700.20441
```

Figure 14
CHROMATOGRAPH OF CHLOROFORM

```
=========================================================================
Injection Date   : 6/1/98 5:47:00 PM                    Seq. Line :    2
Sample Name      : ch                                        Vial :    2
Acq. Operator    : Earl                                       Inj :    1
                                                       Inj Volume : Manually
Method           : C:\HPCHEM\2\METHODS\EARL.M
Laat changed     : 6/1/98 5:25:21 PM by Earl
Method for collection of data using the 6890 ECD.
```



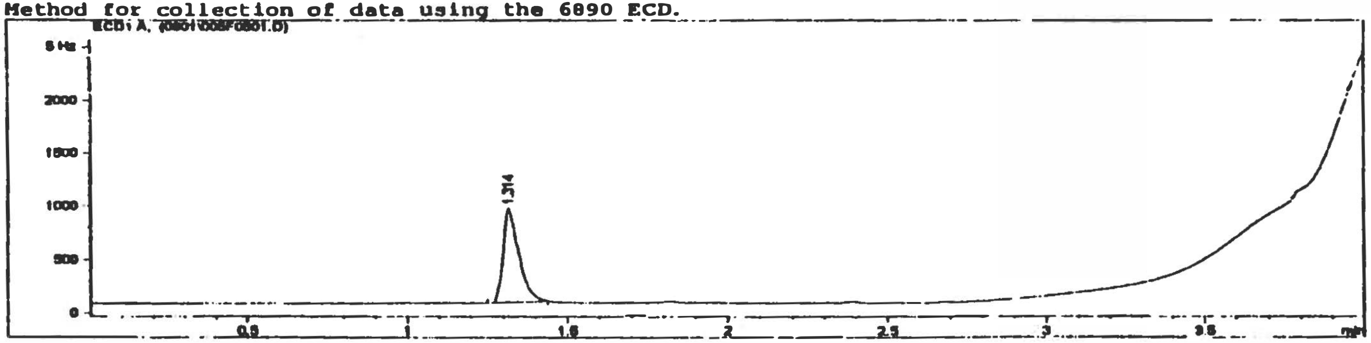
```
=========================================================================
                        Area Percent Report
=========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

   Peak RetTime Type  Width     Area      Height     Area
     #   [min]        [min]   [5 Hz*s]    [5 Hz]      %
   ----|-------|----|-------|----------|----------|--------|
     1   1.313 BB    0.0464 2898.53052  866.65576  2.33137
     2   1.816 BB    0.0467 1.21429e5  3.88510e4  97.66863
```

Figure 15
CHROMATOGRAPH OF PCFB USING EARL METHOD

```
=============================================================================
Injection Date  : 6/1/98 6:08:50 PM                  Seq. Line :    5
Sample Name     : PFCB                                    Vial :    5
Acq. Operator   : Earl                                     Inj :    1
                                                    Inj Volume : Manually
Method          : C:\HPCHEM\2\METHODS\EARL.M
Last changed    : 6/1/98 5:25:21 PM by Earl
Method for collection of data using the 6890 ECD.
```



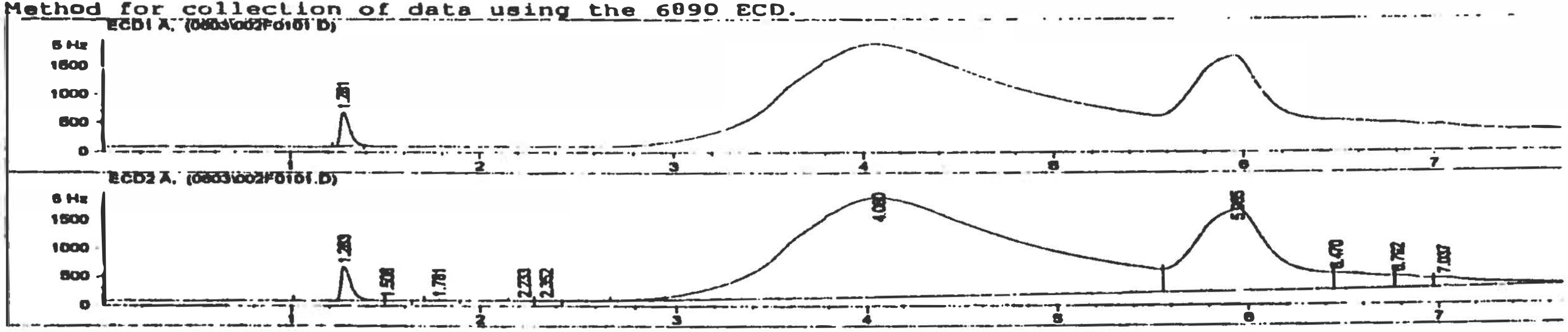
```
=============================================================================
                         Area Percent Report
=============================================================================

Peak RetTime Type  Width     Area      Height     Area
 #    [min]        [min]  [5 Hz*s]    [5 Hz]       %
----|-------|----|-------|----------|----------|--------|
   1   1.314 BB    0.0470 3013.49951  880.84308 1.000e2

Totals :                  3013.49951  880.84308
```

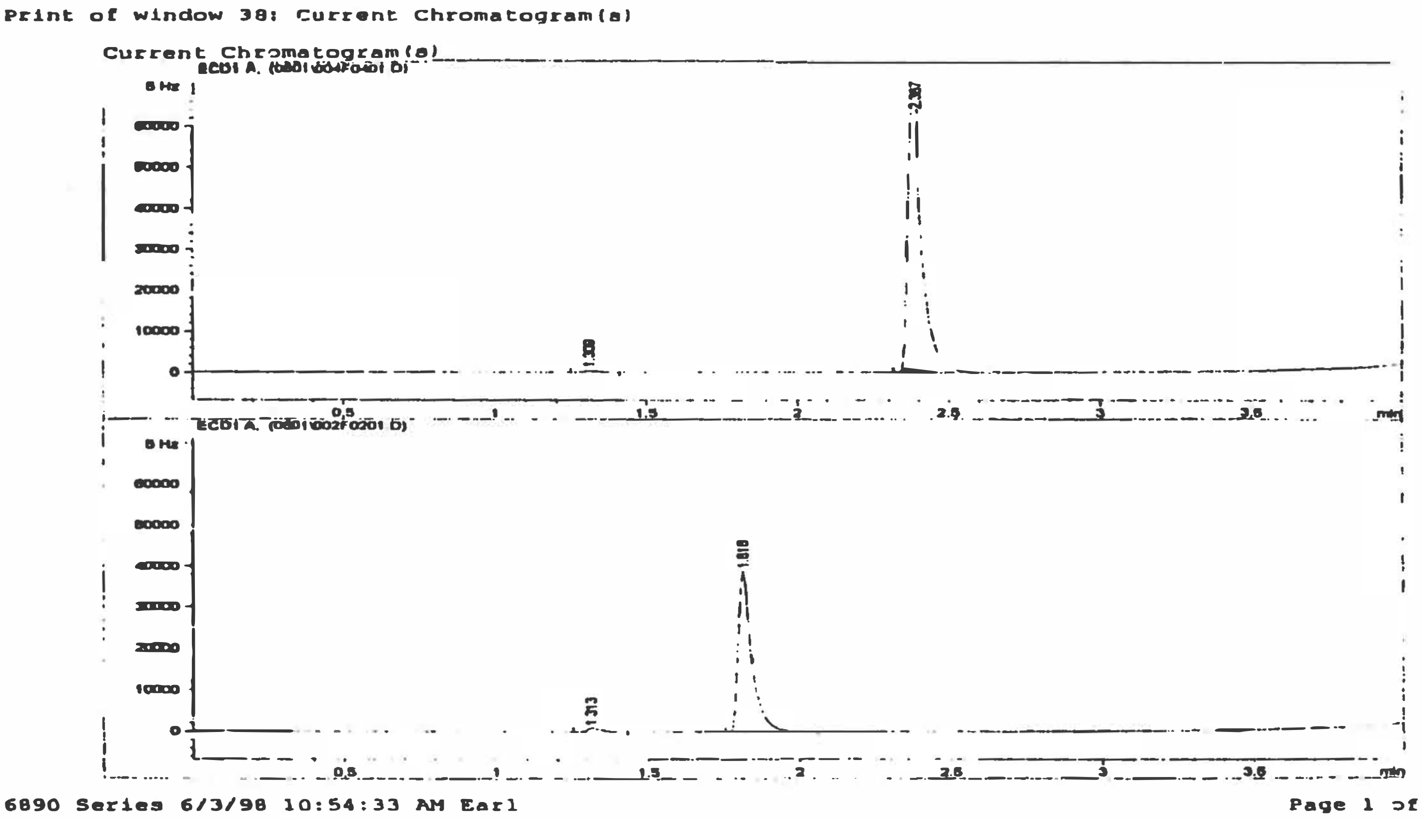
Figure 16
CHROMATOGRAPH OF PARAFLOUROCHLOROBENZENE

```
=================================================================================
Injection Date  : 6/3/98 10:25:30 AM                  Seq. Line :    1
Sample Name     : pFCB/New Method                          Vial :    2
Acq. Operator   : Earl                                      Inj :    1
                                                     Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\EARL.M
Last changed    : 6/3/98 10:20:37 AM by Earl
Analysis Method : C:\HPCHEM\2\METHODS\EARLEND.M
Last changed    : 6/1/98 6:48:54 PM by Earl
Method for collection of data using the 6890 ECD.
```



```
Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]   [5 Hz*s]     [5 Hz]        %
----|-------|----|-------|----------|----------|--------|
  1   1.283 BV   0.0566 2128.00078   589.02124   1.08260
  2   1.508 VB   0.0629   10.25410     2.71695   0.00521
  3   1.781 BV   0.0362   36.48504    15.03085   0.01855
  4   2.233 BV   0.0323    2.17967     1.03160   0.00111
  5   2.352 PB   0.0394    5.73076     2.24585   0.00291
  6   4.080 PV   0.9667 1.42648e5   1732.29871  72.54393
  7   5.965 VV   0.3664 4.13204e4   1433.23718  21.01354
  8   6.470 VV   0.2064 4681.65039   281.08560   2.38086
  9   6.792 VV   0.1362 2303.76978   207.51605   1.17158
 10   7.037 VBA  0.2806 3499.54810   158.56113   1.77970
```

Figure 17
OVERLAY OF TCE WITH CHLOROFORM



Print of window 38: Current Chromatogram(s)

6890 Series 6/3/98 10:54:33 AM Earl

Page 1 of 1

Figure 18

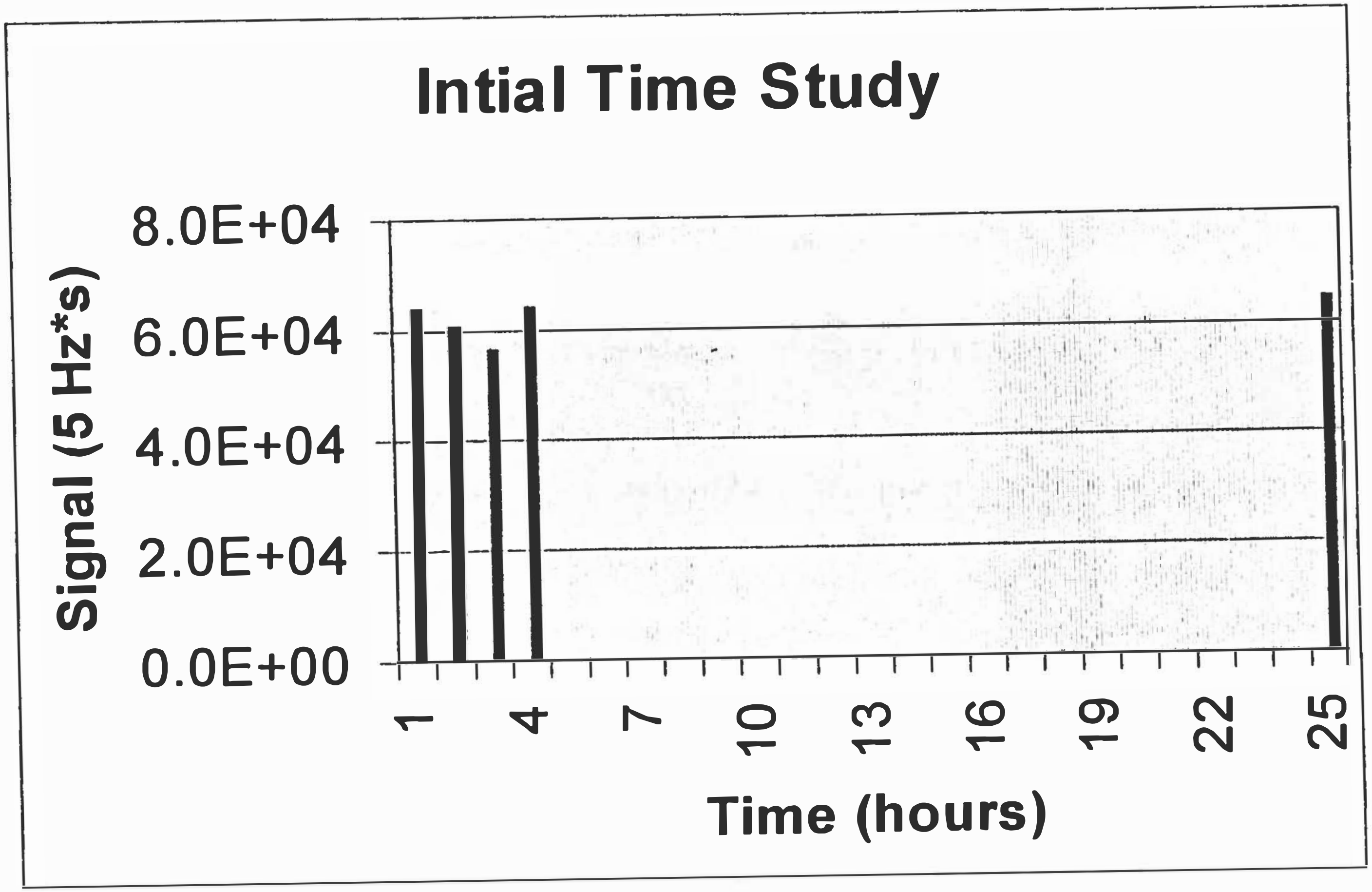

Intial Time Study
Signal (5 Hz*s)
8.0E+04
6.0E+04
4.0E+04
2.0E+04
0.0E+00
1
4
7
10
13
16
19
22
25
Time (hours)

Figure 19

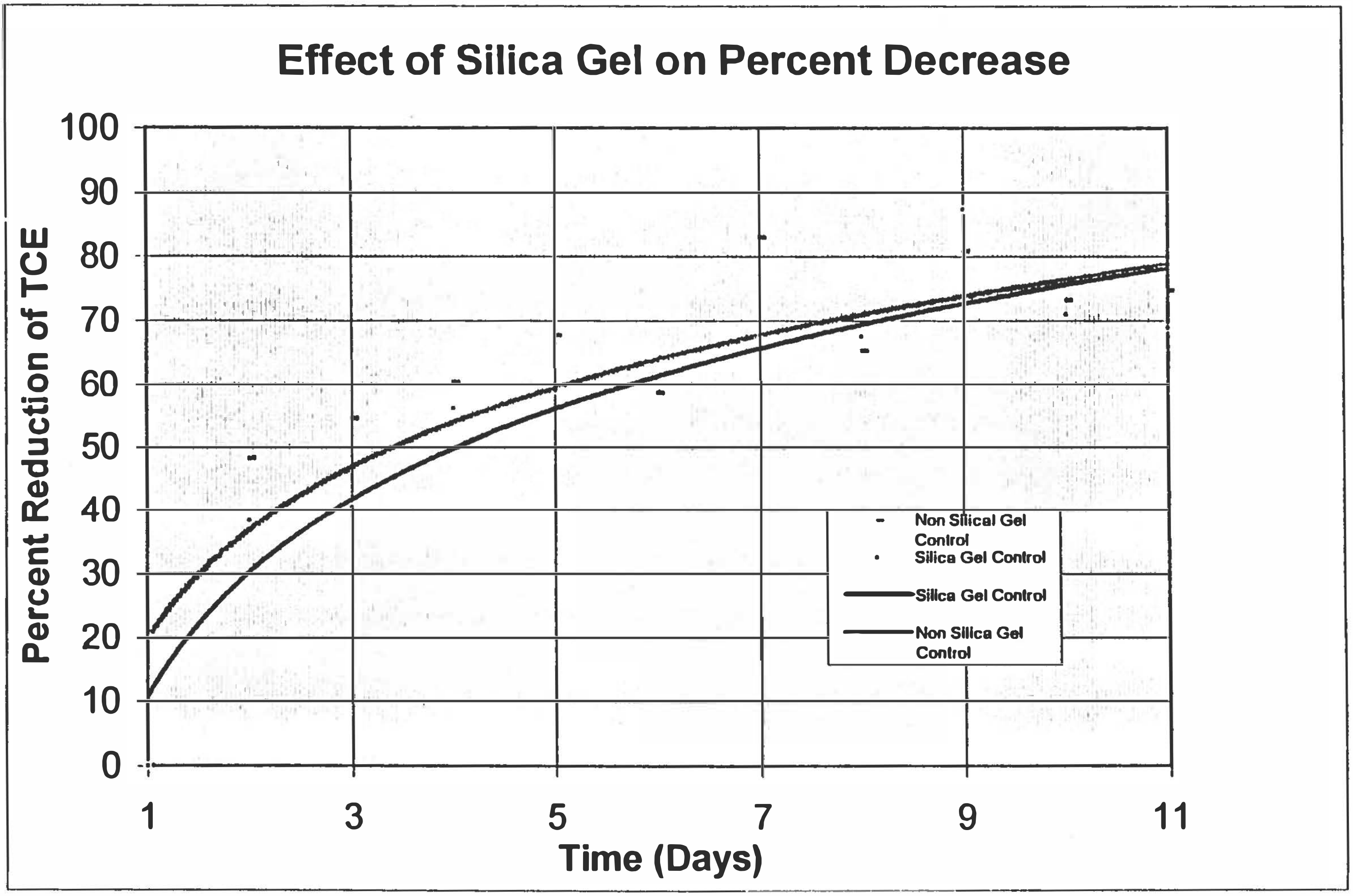

Effect of Silica Gel on Percent Decrease
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
Non Silical Gel Control
Silica Gel Control
Silica Gel Control
Non Silica Gel Control

Figure 20

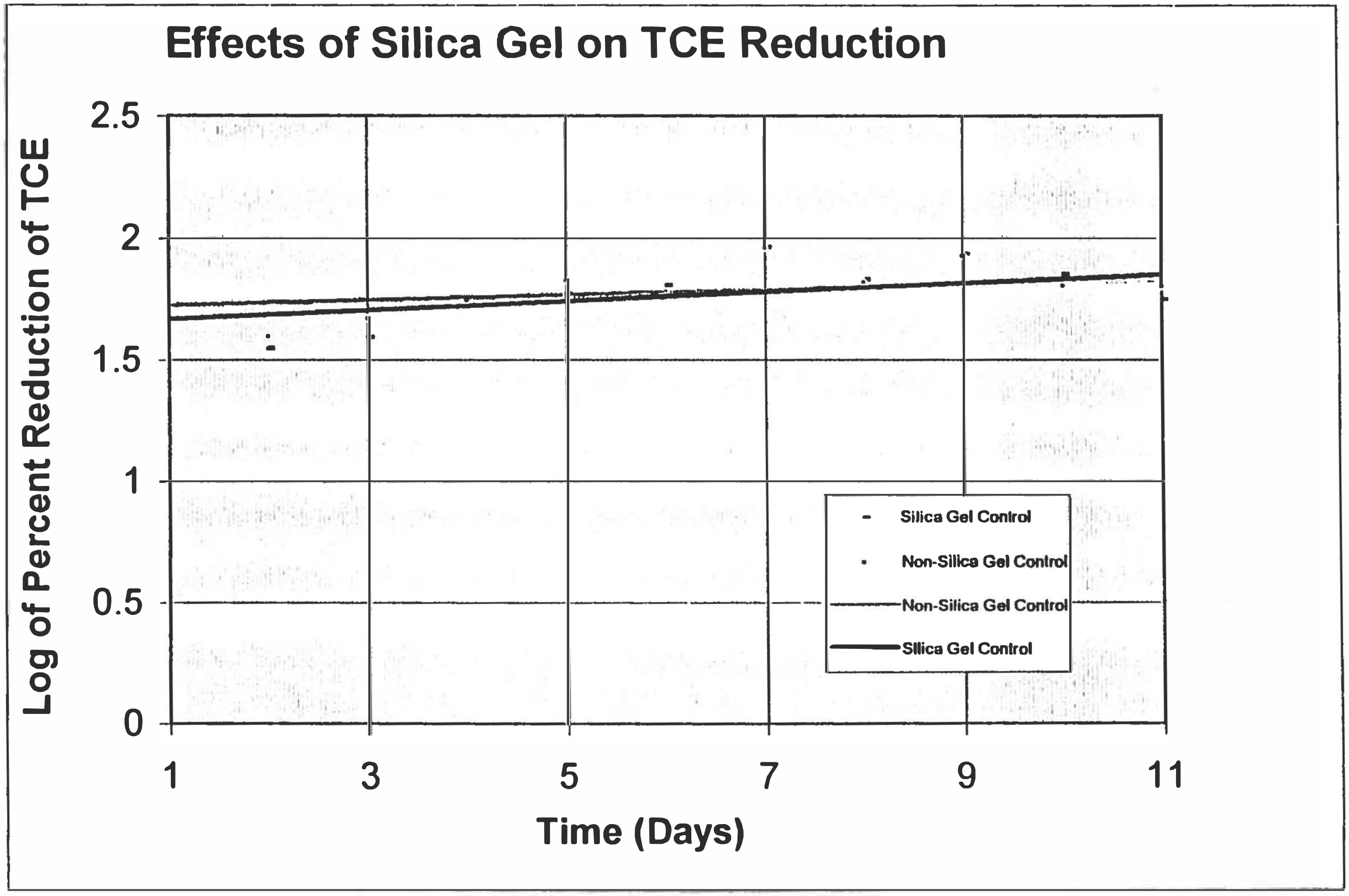

Effects of Silica Gel on TCE Reduction
Log of Percent Reduction of TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
Silica Gel Control
Non-Silica Gel Control
Non-Silica Gel Control
Silica Gel Control

Figure 21

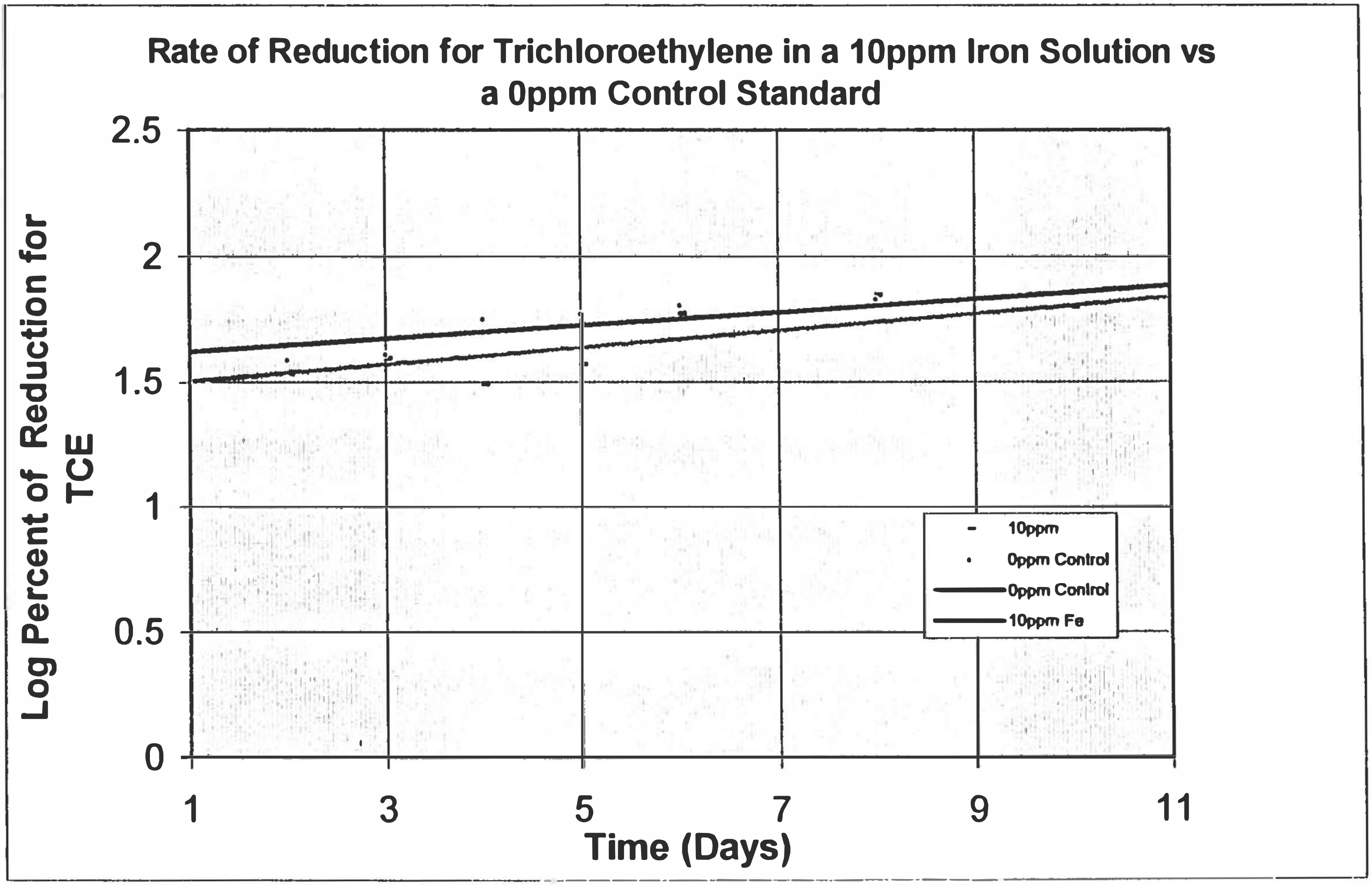

Rate of Reduction for Trichloroethylene in a 10ppm Iron Solution vs a 0ppm Control Standard
Log Percent of Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
10ppm
0ppm Control
0ppm Control
10ppm Fe

Figure 22

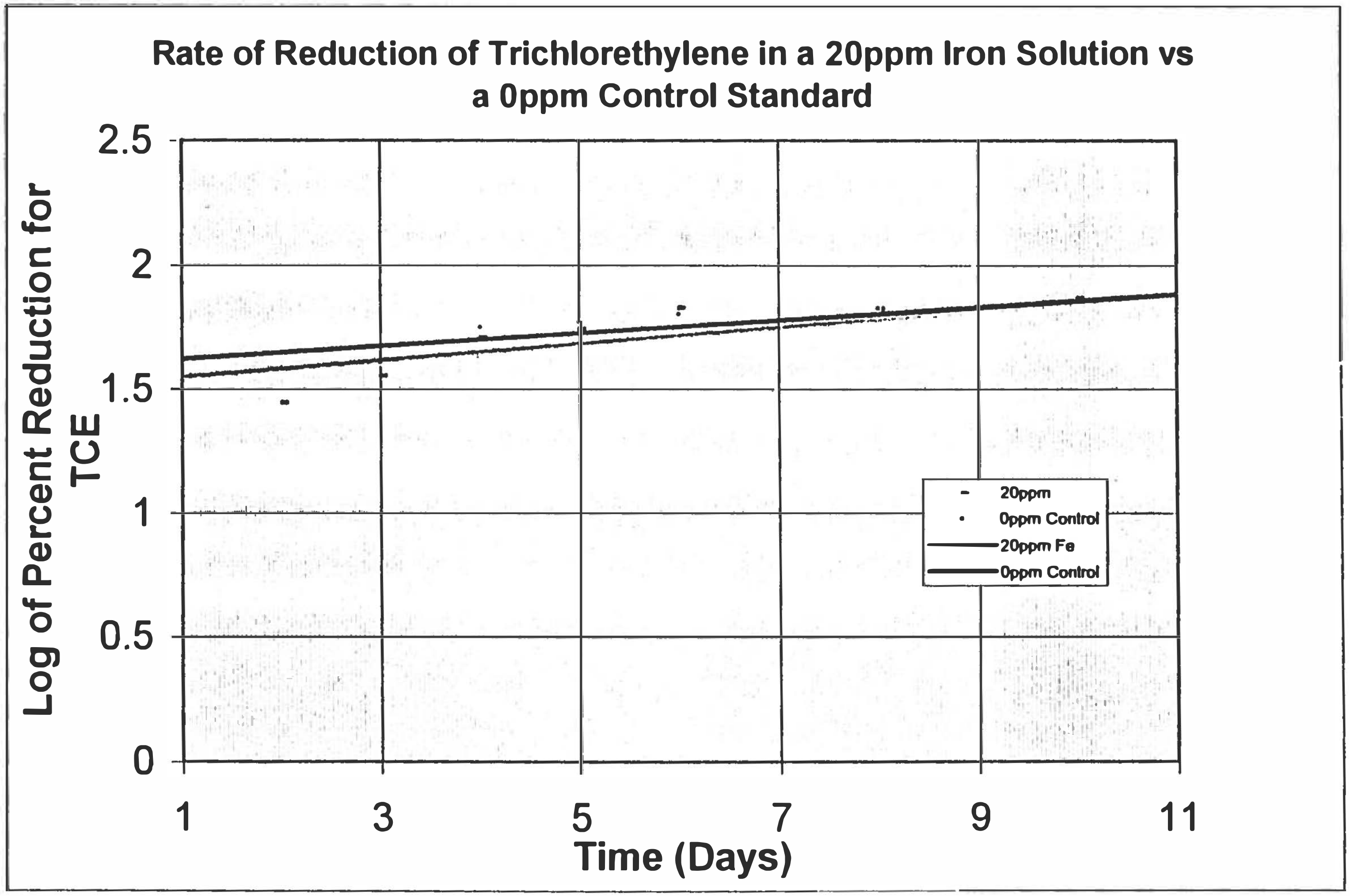

Rate of Reduction of Trichlorethylene in a 20ppm Iron Solution vs a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
20ppm
0ppm Control
20ppm Fe
0ppm Control

Figure 23

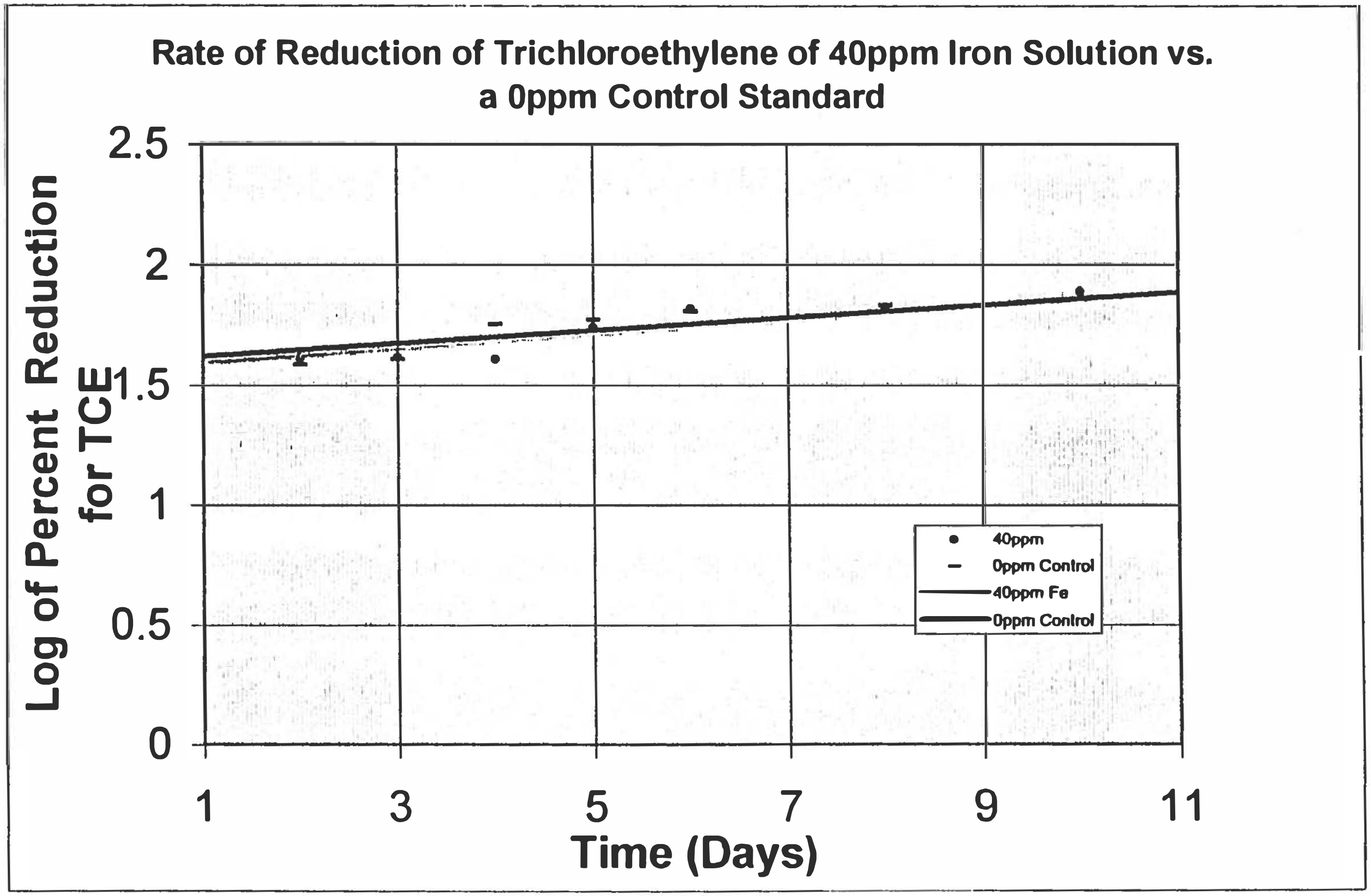

Rate of Reduction of Trichloroethylene of 40ppm Iron Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 40ppm
– 0ppm Control
40ppm Fe
0ppm Control

Figure 24

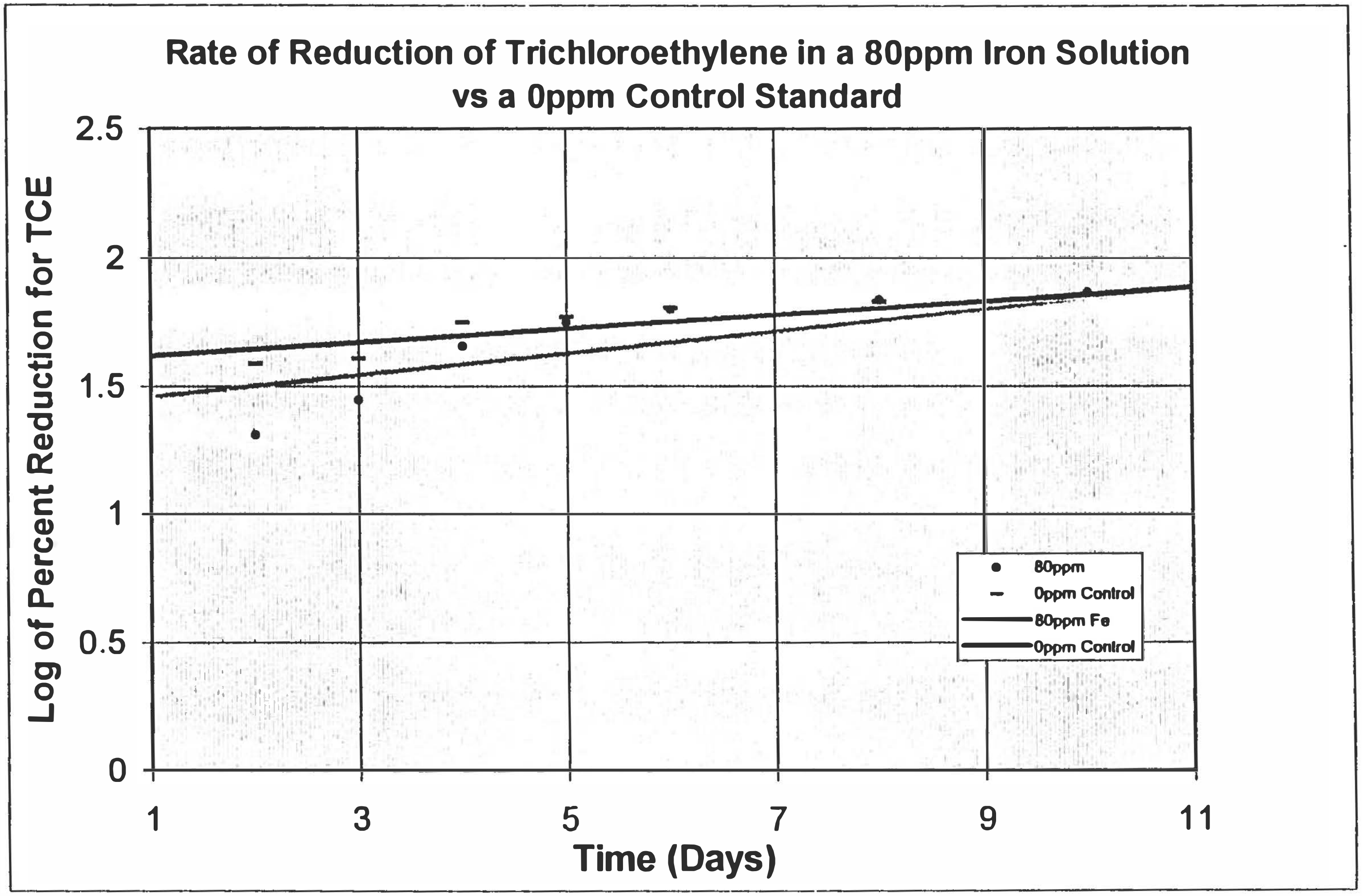
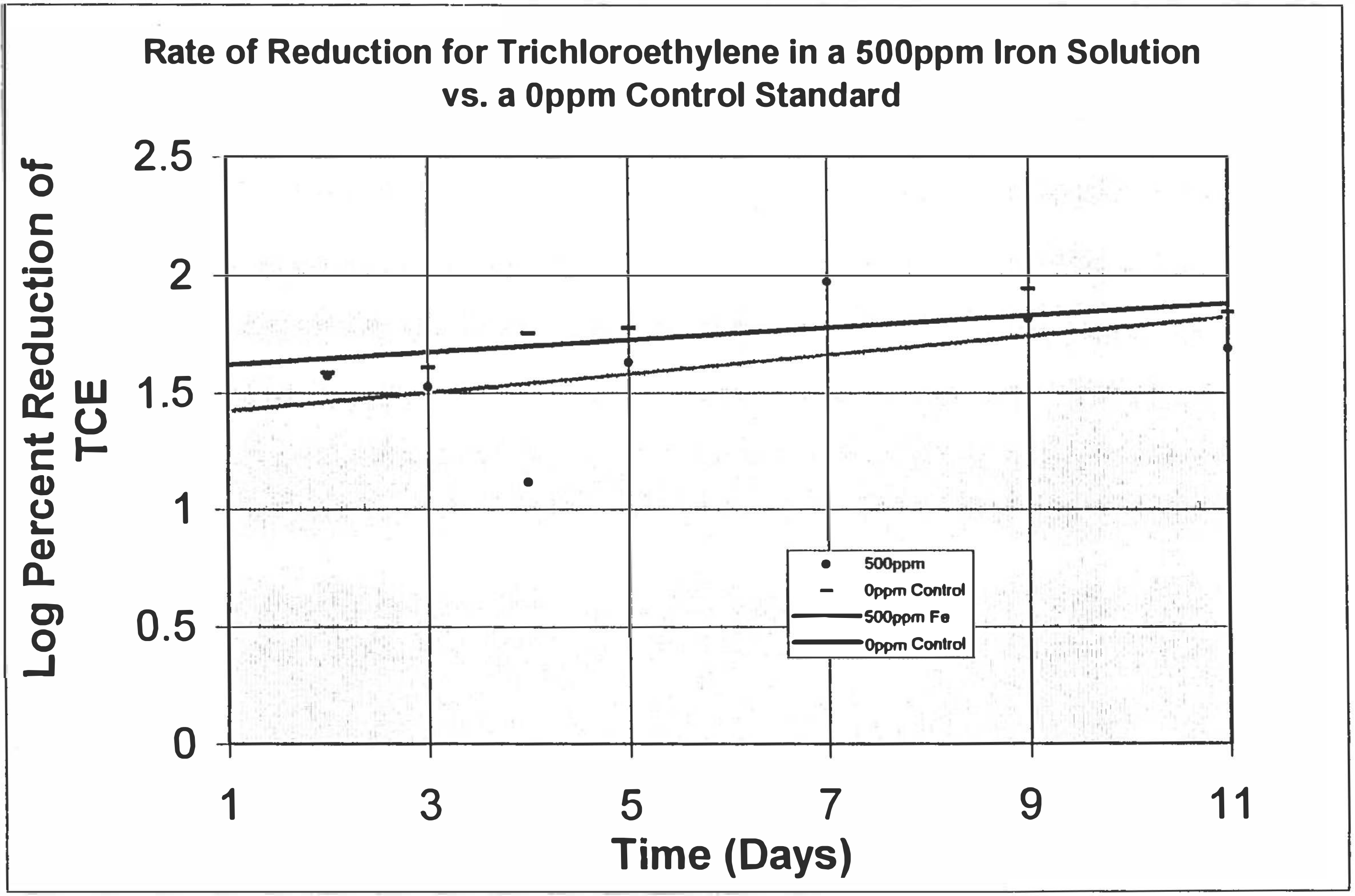

Rate of Reduction of Trichloroethylene in a 80ppm Iron Solution vs a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
80ppm
0ppm Control
80ppm Fe
0ppm Control

Figure 25



Rate of Reduction for Trichloroethylene in a 500ppm Iron Solution vs. a 0ppm Control Standard

Figure 26

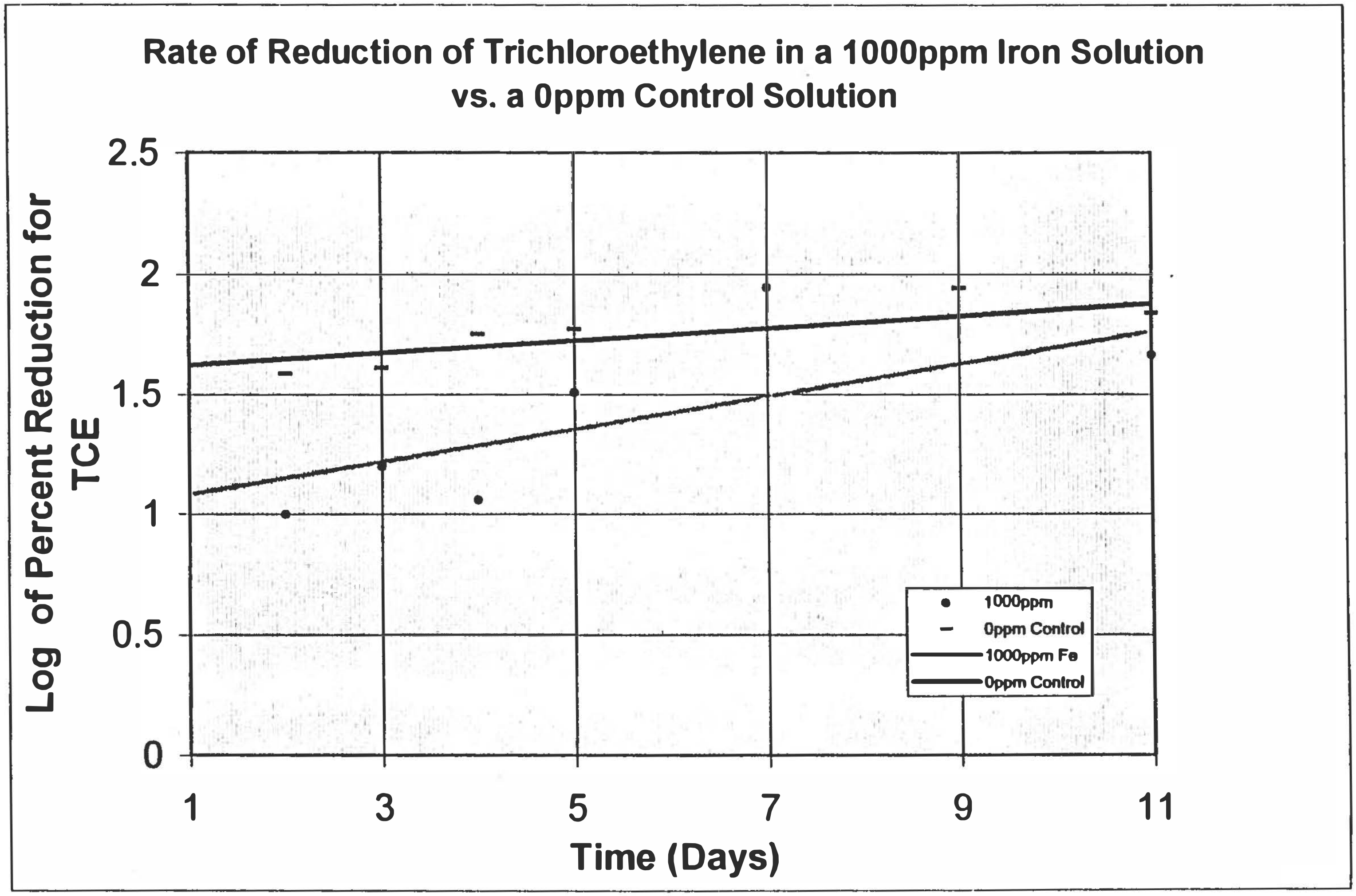

Rate of Reduction of Trichloroethylene in a 1000ppm Iron Solution vs. a 0ppm Control Solution
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 1000ppm
– 0ppm Control
1000ppm Fe
0ppm Control

Figure 27

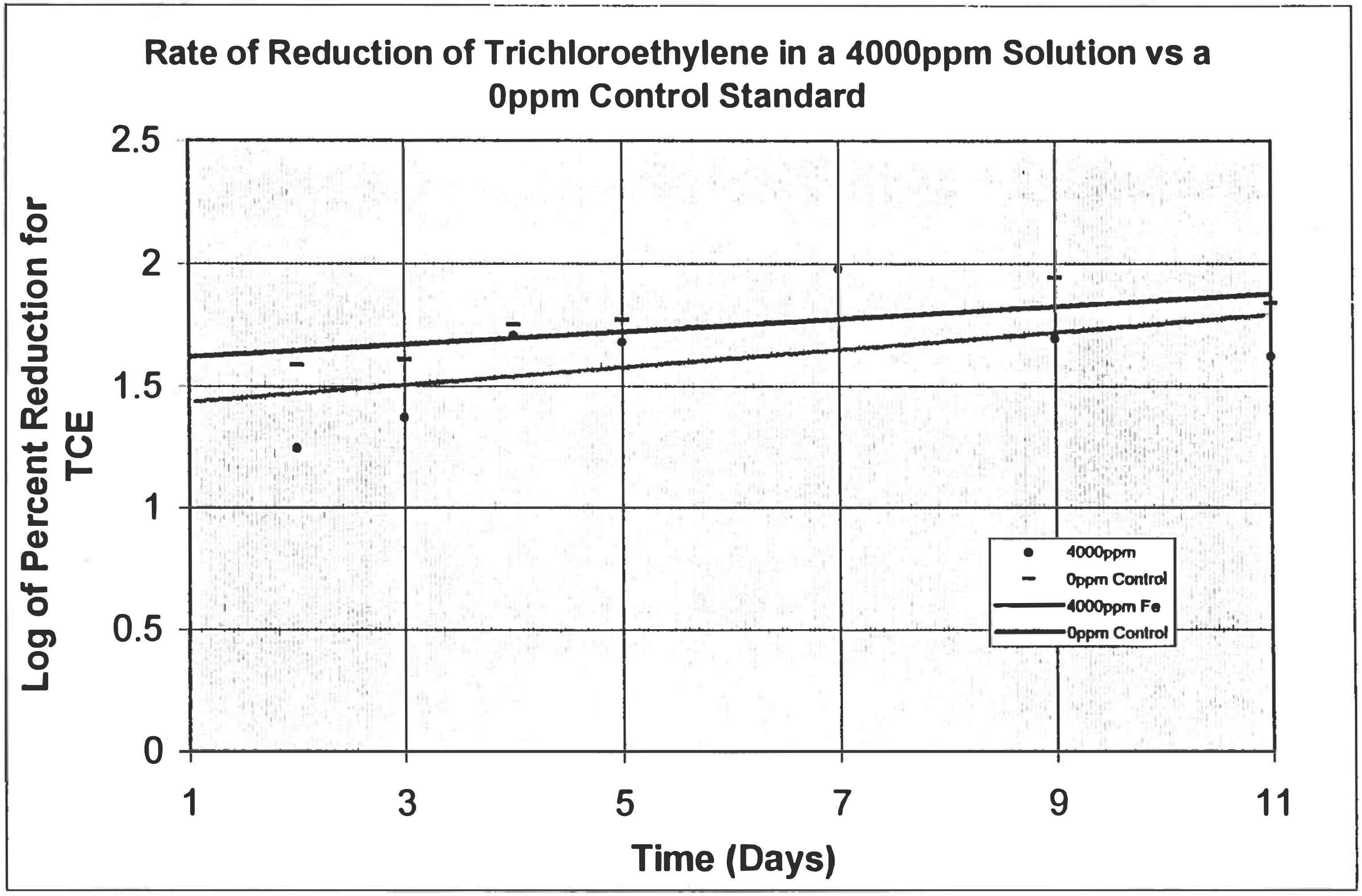

Rate of Reduction of Trichloroethylene in a 4000ppm Solution vs a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
4000ppm
0ppm Control
4000ppm Fe
0ppm Control

Figure 28

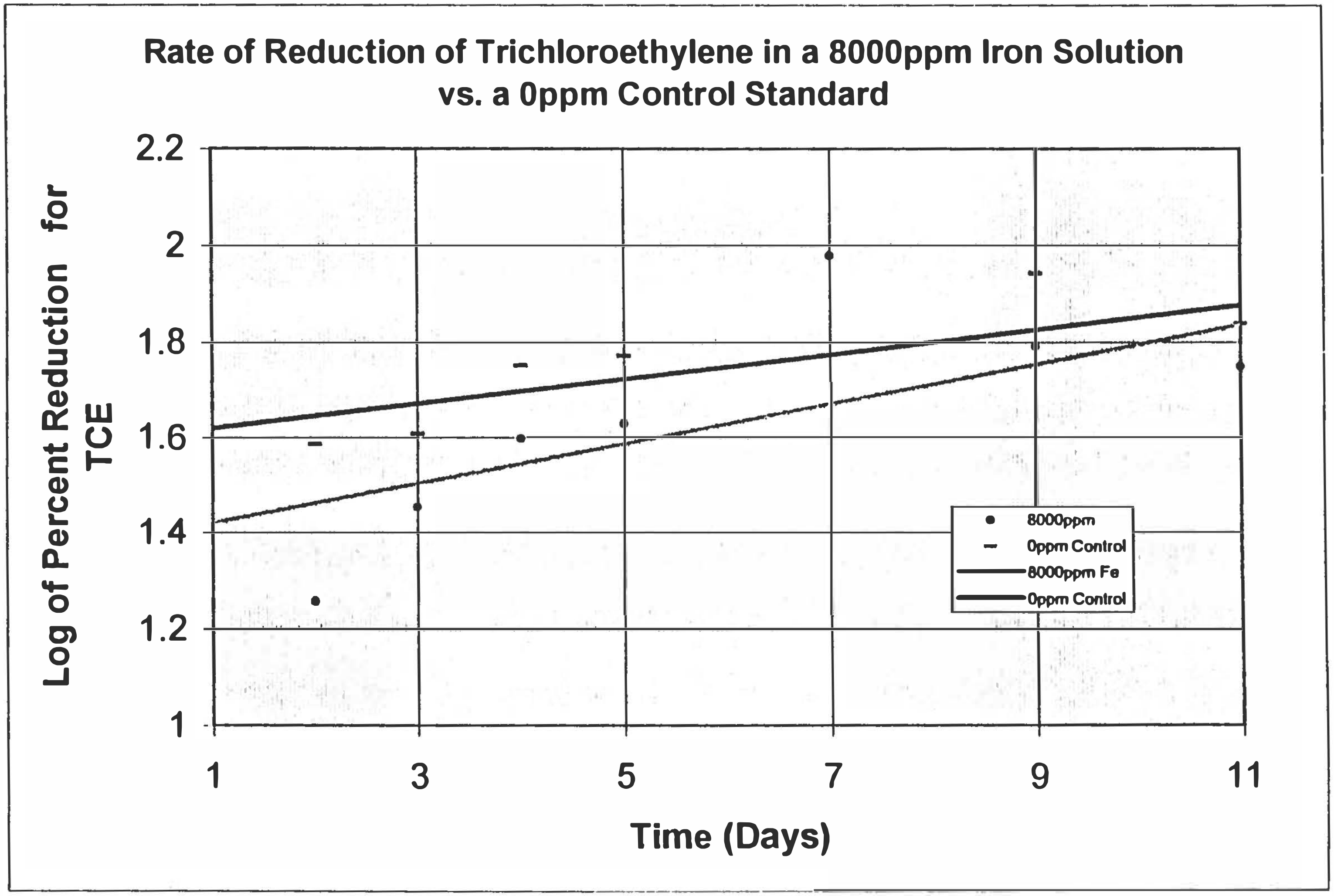

Rate of Reduction of Trichloroethylene in a 8000ppm Iron Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.2
2
1.8
1.6
1.4
1.2
1
1
3
5
7
9
11
Time (Days)
● 8000ppm
– 0ppm Control
8000ppm Fe
0ppm Control

Figure 29

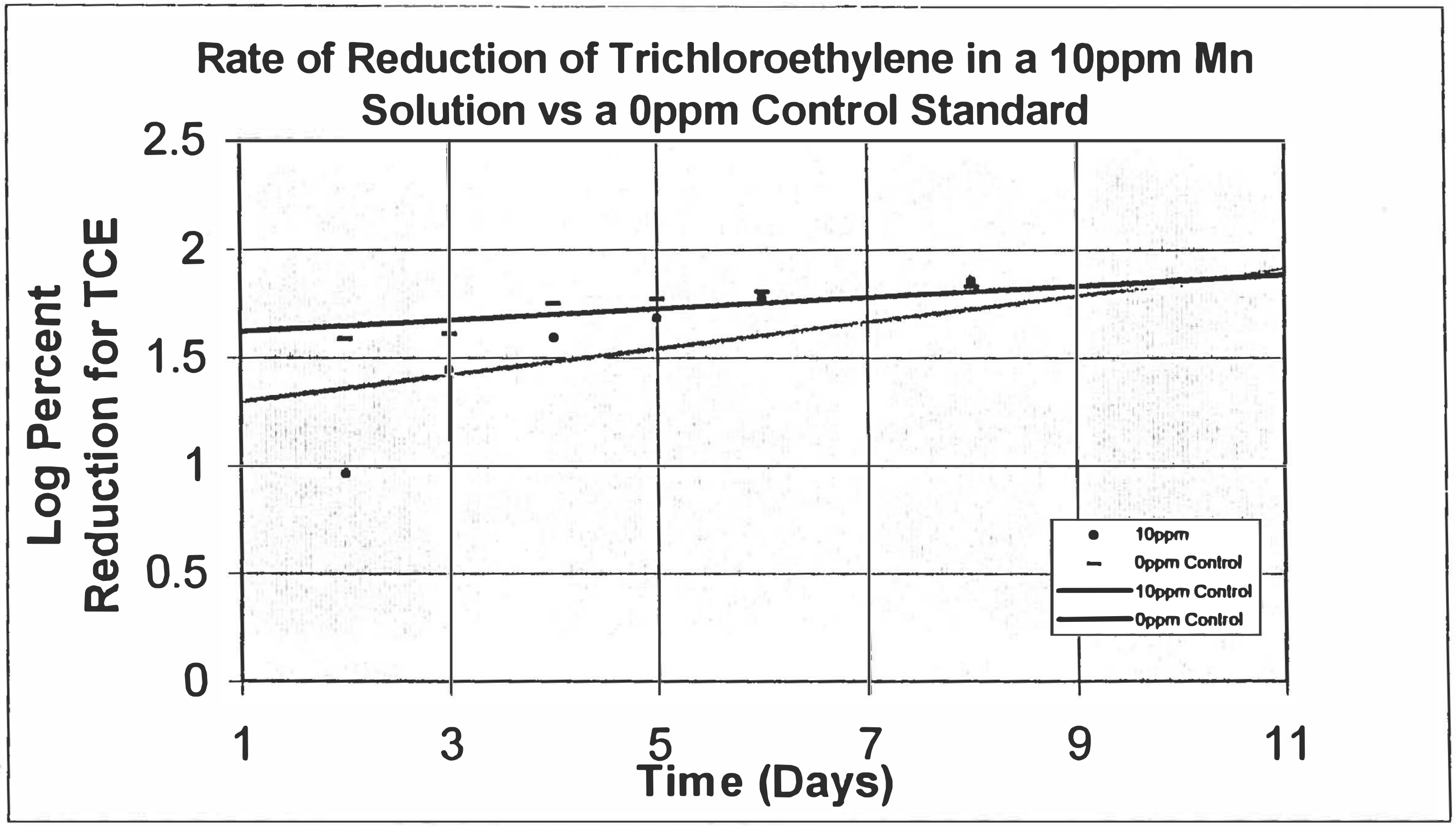

Rate of Reduction of Trichloroethylene in a 10ppm Mn Solution vs a 0ppm Control Standard
Log Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 10ppm
– 0ppm Control
10ppm Control
0ppm Control

Figure 30

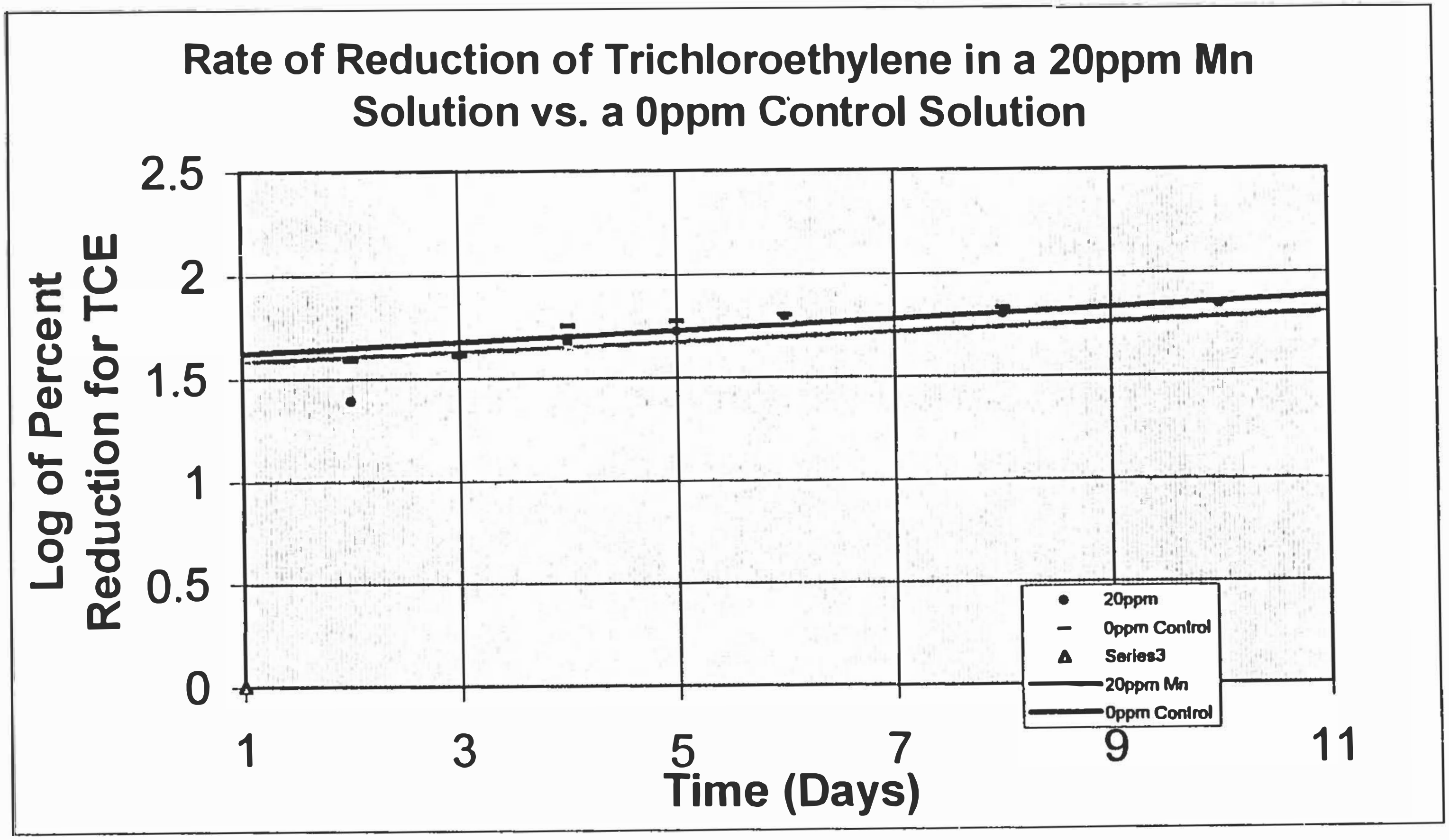

Rate of Reduction of Trichloroethylene in a 20ppm Mn Solution vs. a 0ppm Control Solution
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
20ppm
0ppm Control
Series3
20ppm Mn
0ppm Control

Figure 31

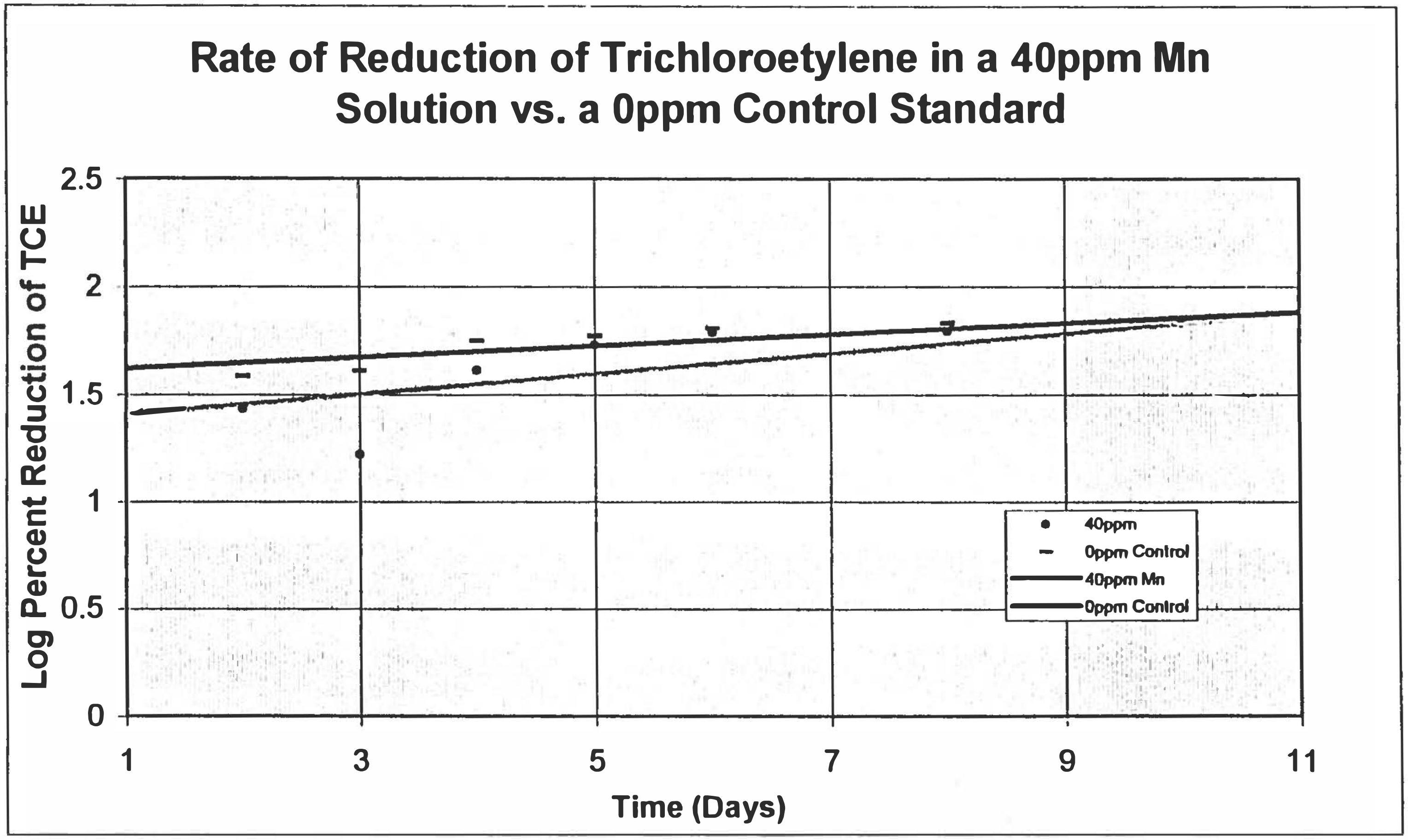

Rate of Reduction of Trichloroetylene in a 40ppm Mn Solution vs. a 0ppm Control Standard
Log Percent Reduction of TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 40ppm
– 0ppm Control
40ppm Mn
0ppm Control

Figure 32

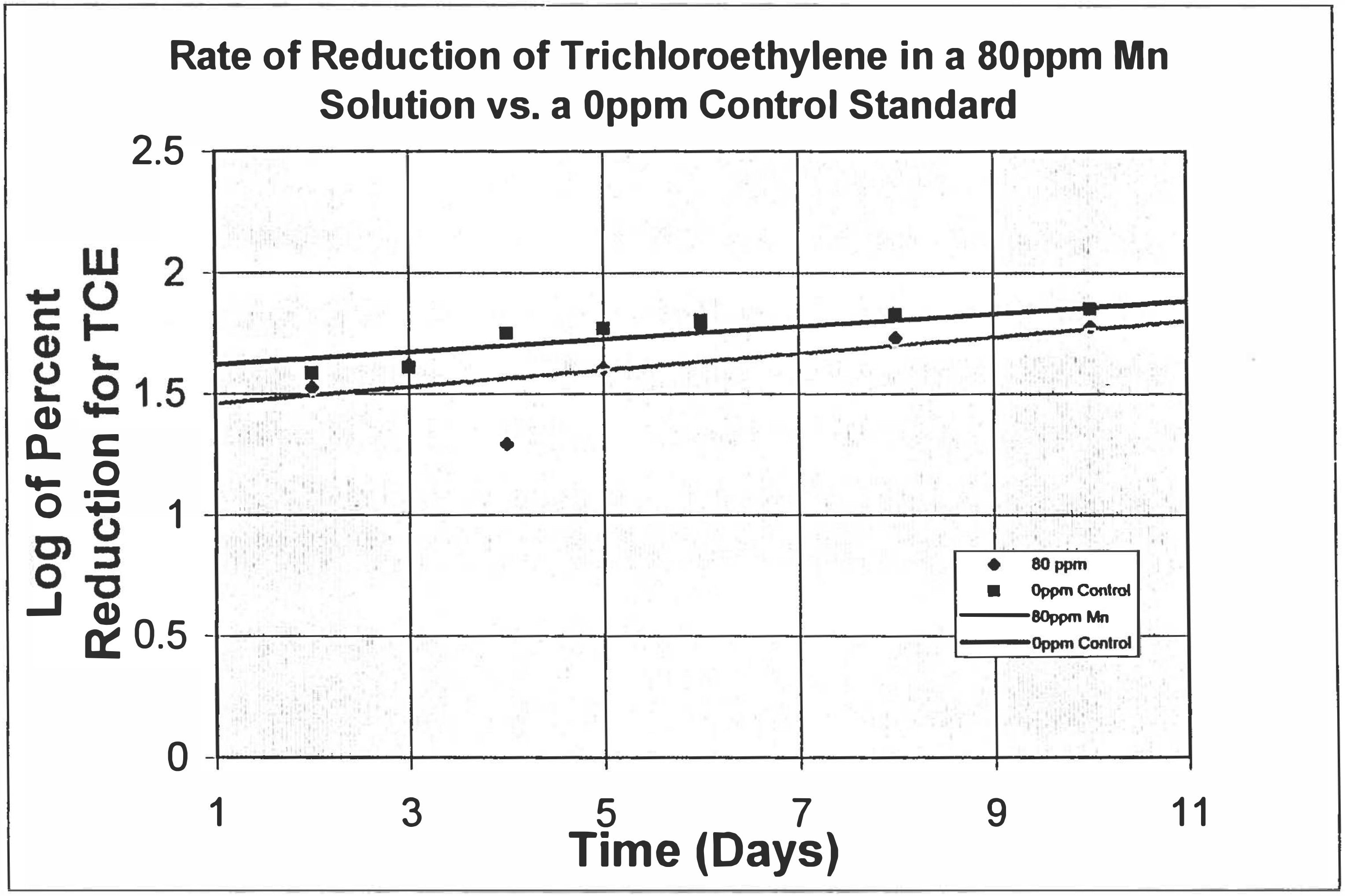

Rate of Reduction of Trichloroethylene in a 80ppm Mn Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
80 ppm
0ppm Control
80ppm Mn
0ppm Control

Figure 33

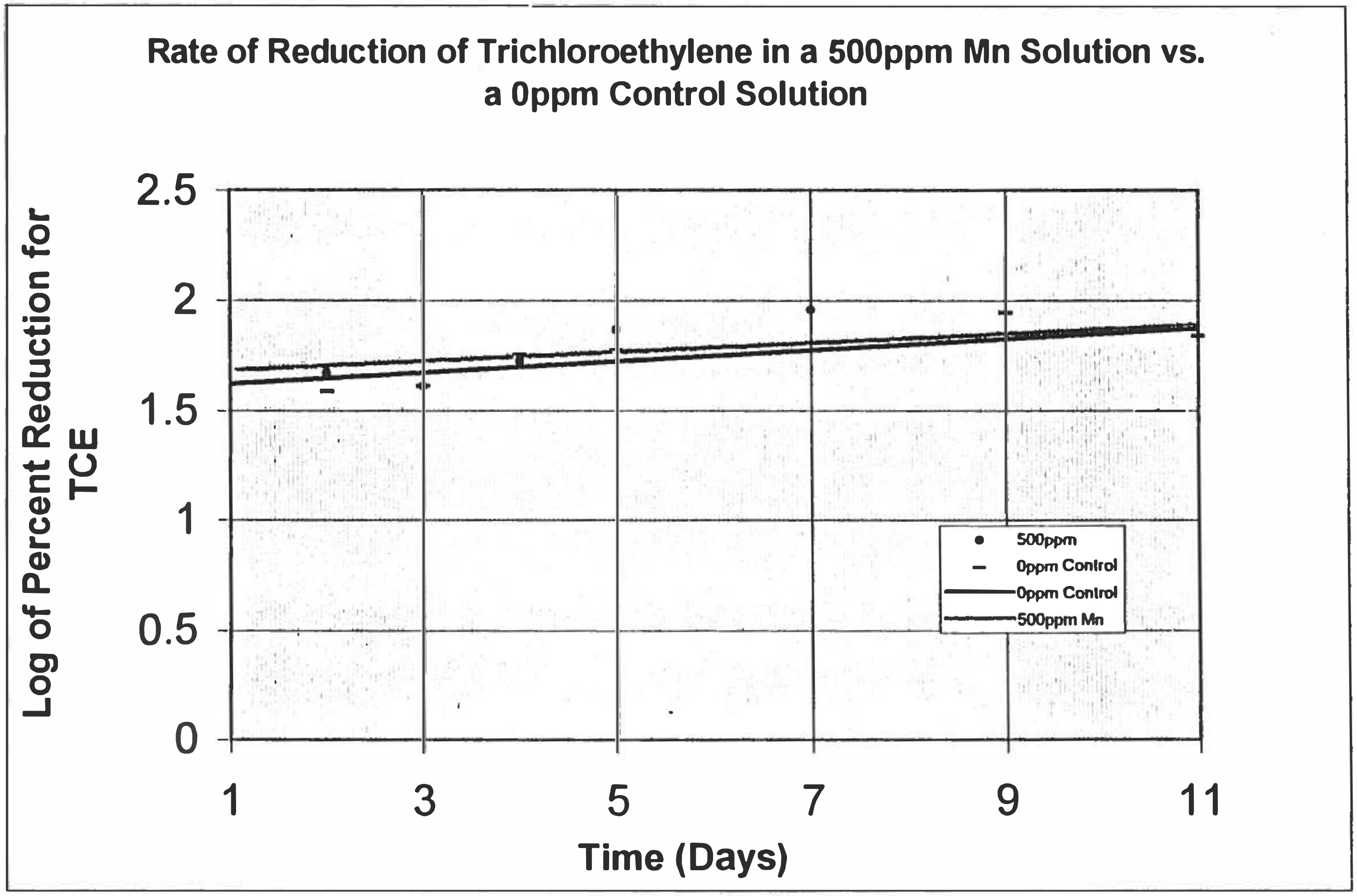

Rate of Reduction of Trichloroethylene in a 500ppm Mn Solution vs. a 0ppm Control Solution

Figure 34

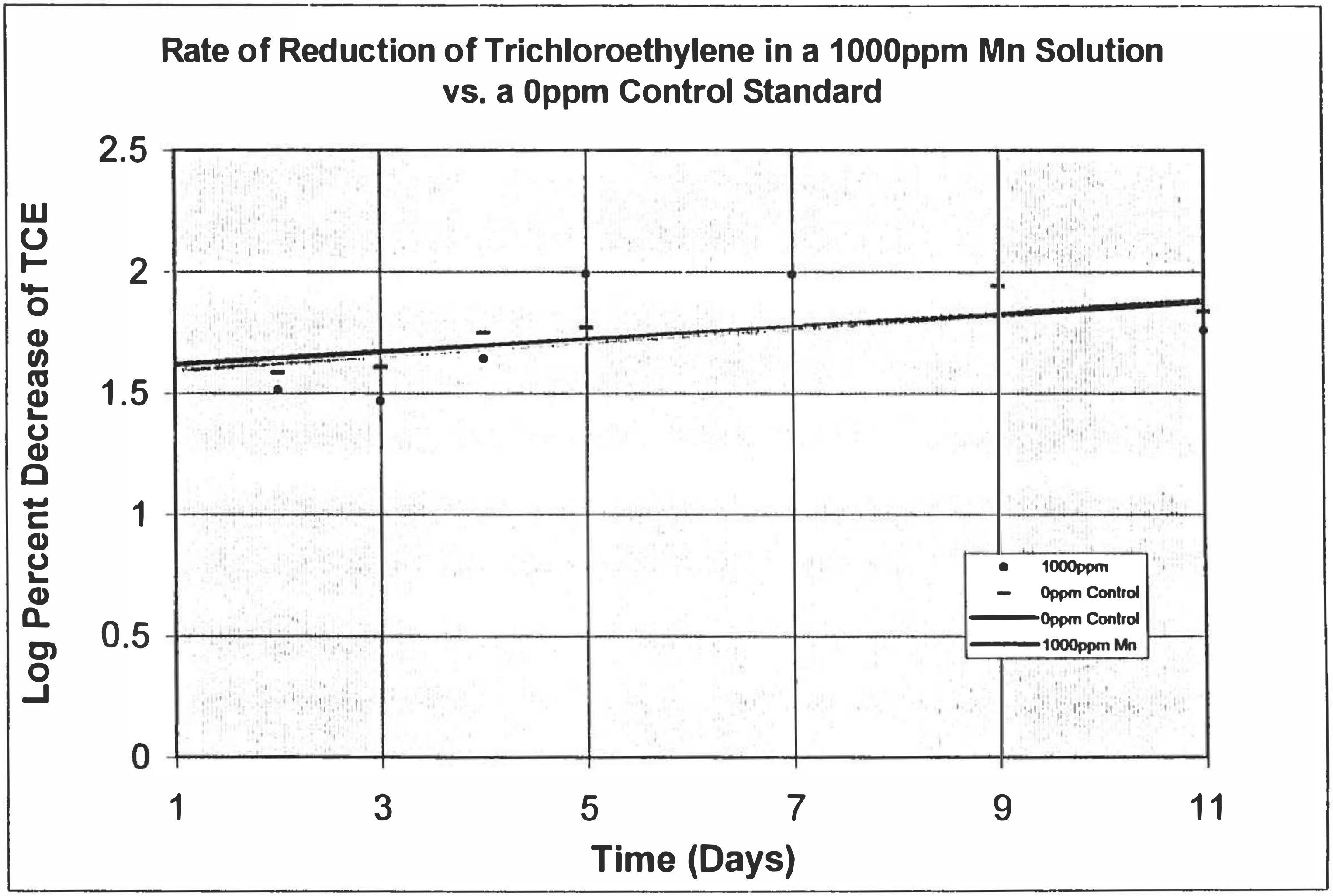

Rate of Reduction of Trichloroethylene in a 1000ppm Mn Solution vs. a 0ppm Control Standard
Log Percent Decrease of TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 1000ppm
– 0ppm Control
0ppm Control
1000ppm Mn

Figure 35

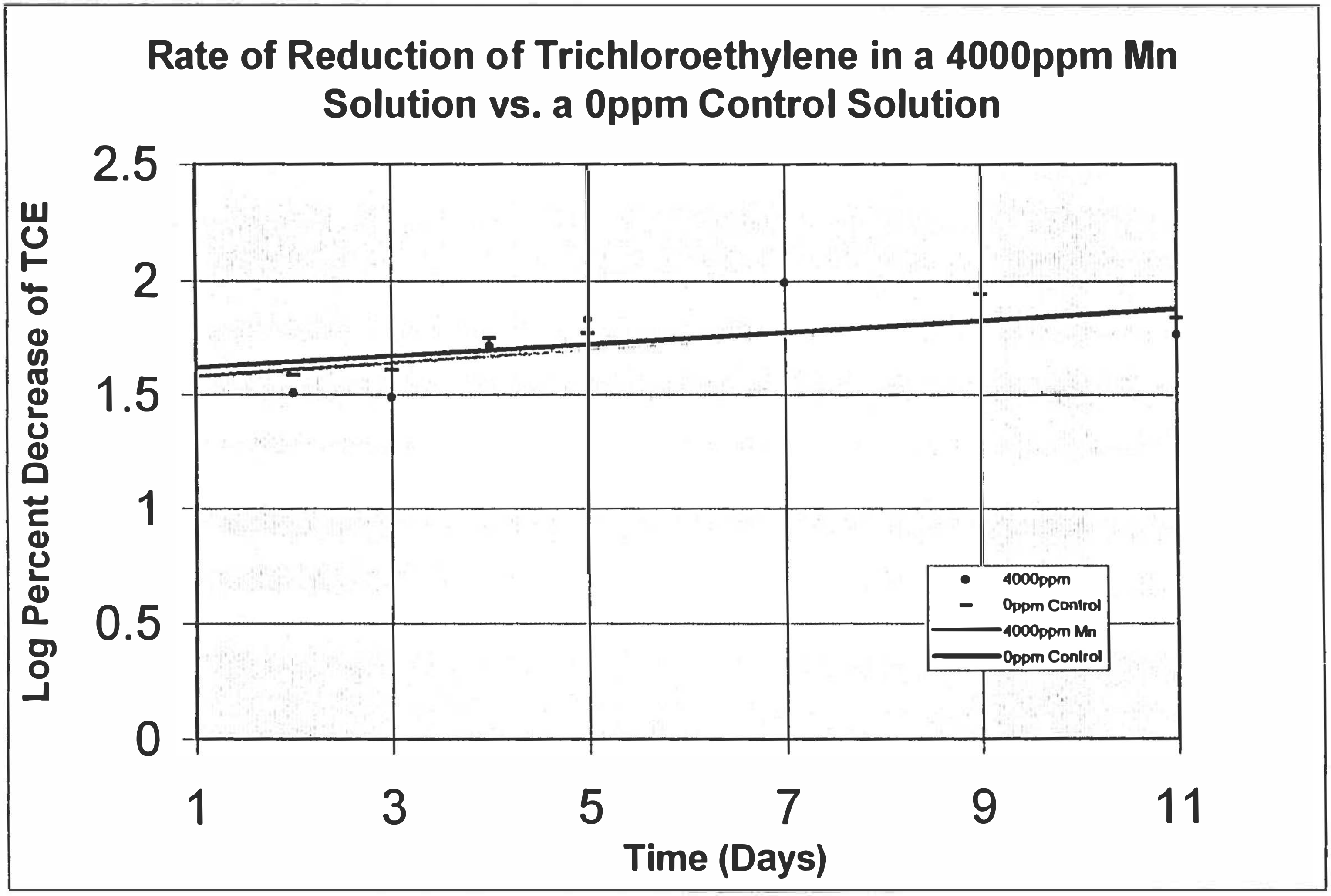
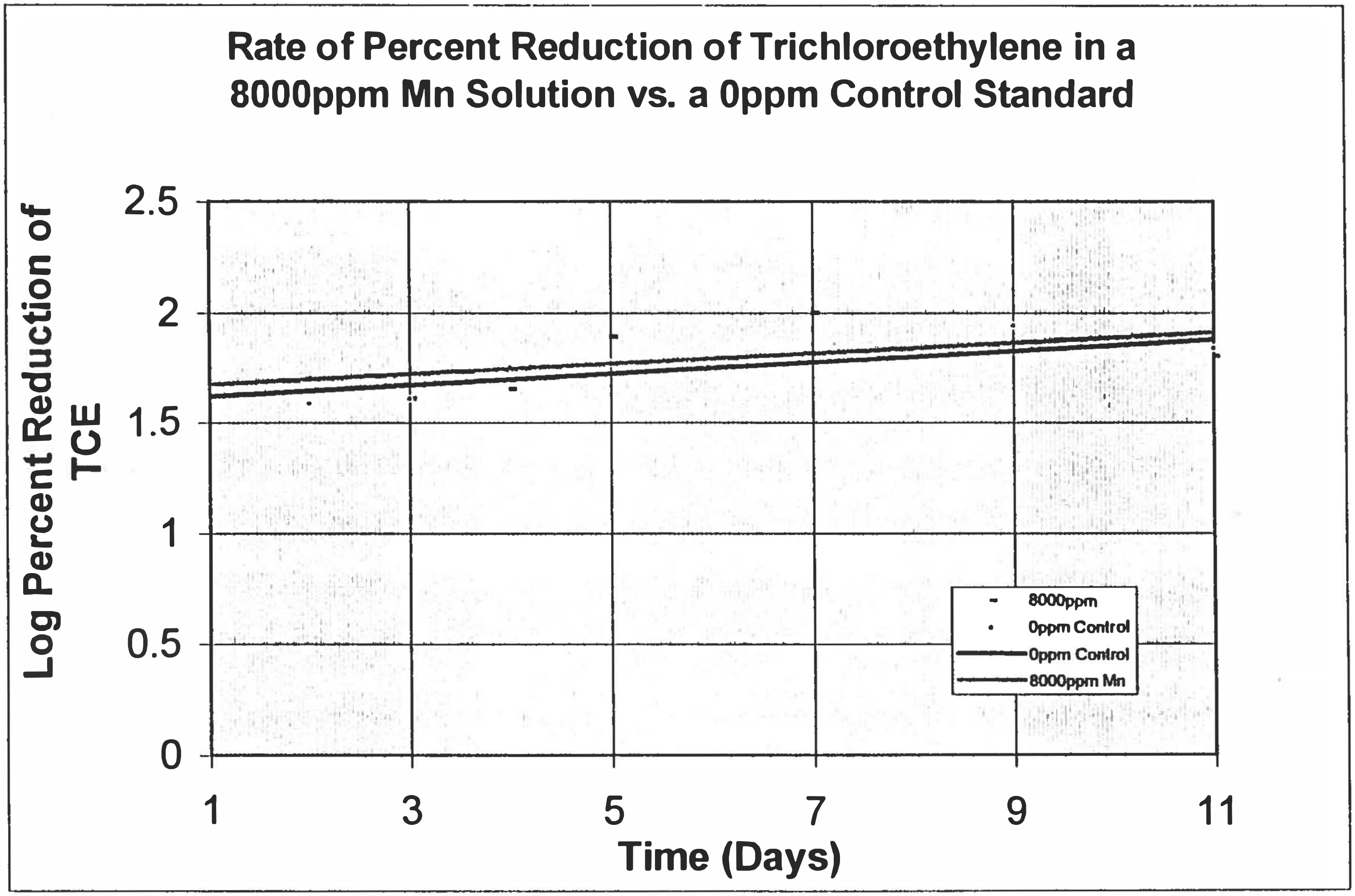

Rate of Reduction of Trichloroethylene in a 4000ppm Mn Solution vs. a 0ppm Control Solution
Log Percent Decrease of TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 4000ppm
- 0ppm Control
4000ppm Mn
0ppm Control

Figure 36



Rate of Percent Reduction of Trichloroethylene in a 8000ppm Mn Solution vs. a 0ppm Control Standard

Figure 37

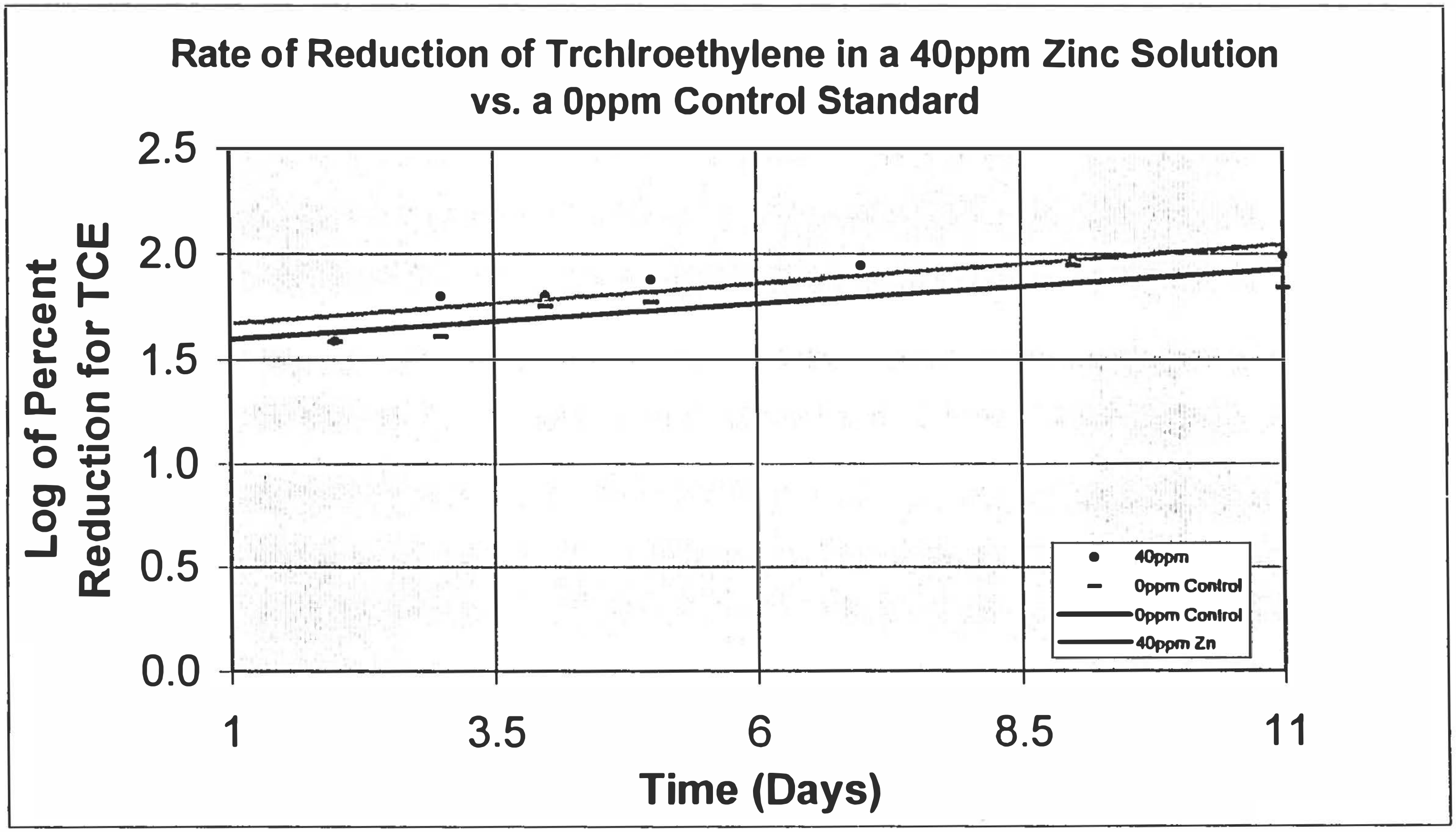
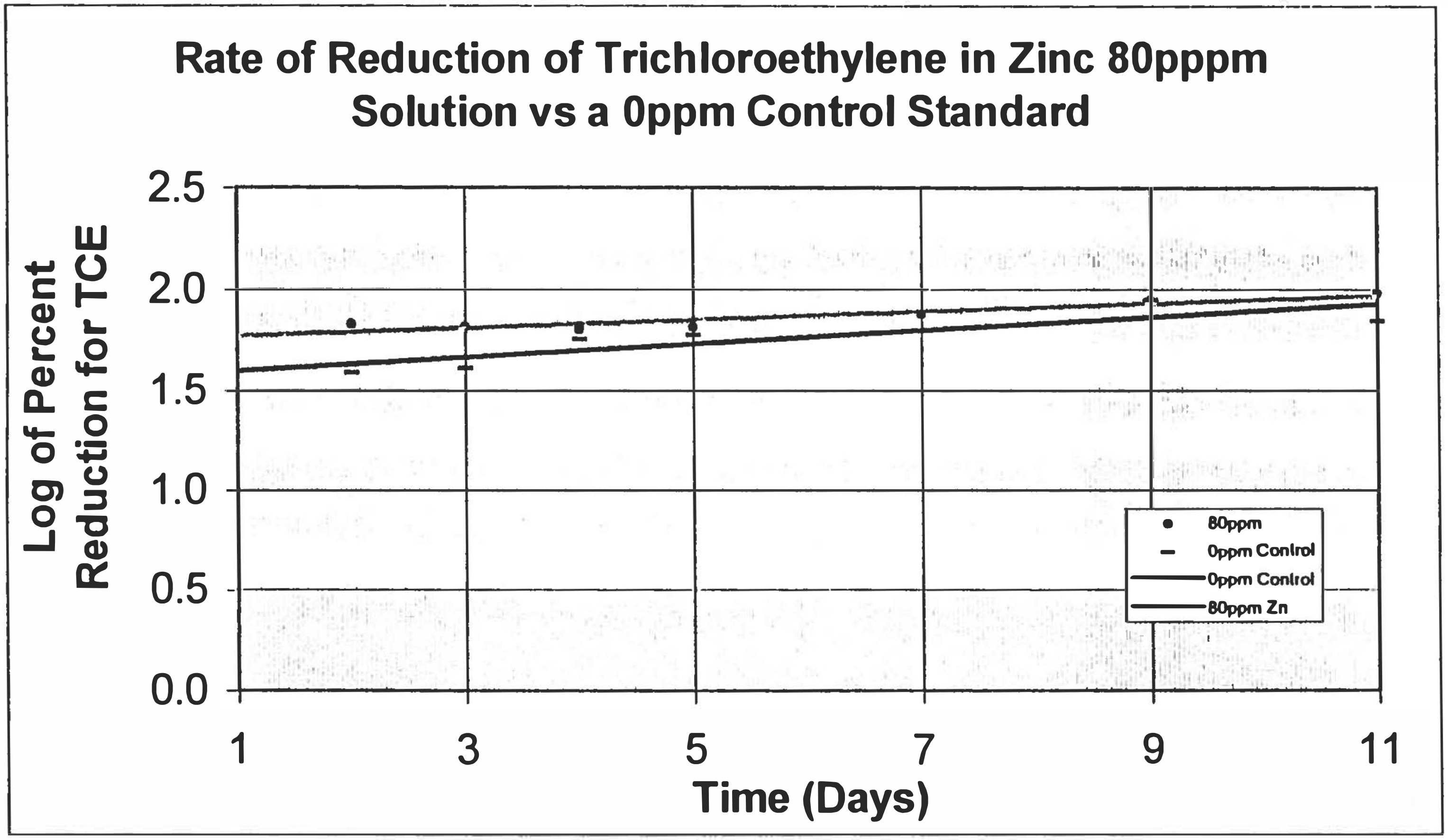

Rate of Reduction of Trchlroethylene in a 40ppm Zinc Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3.5
6
8.5
11
Time (Days)
● 40ppm
– 0ppm Control
0ppm Control
40ppm Zn

Figure 38



Rate of Reduction of Trichloroethylene in Zinc 80pppm Solution vs a 0ppm Control Standard

Figure 39

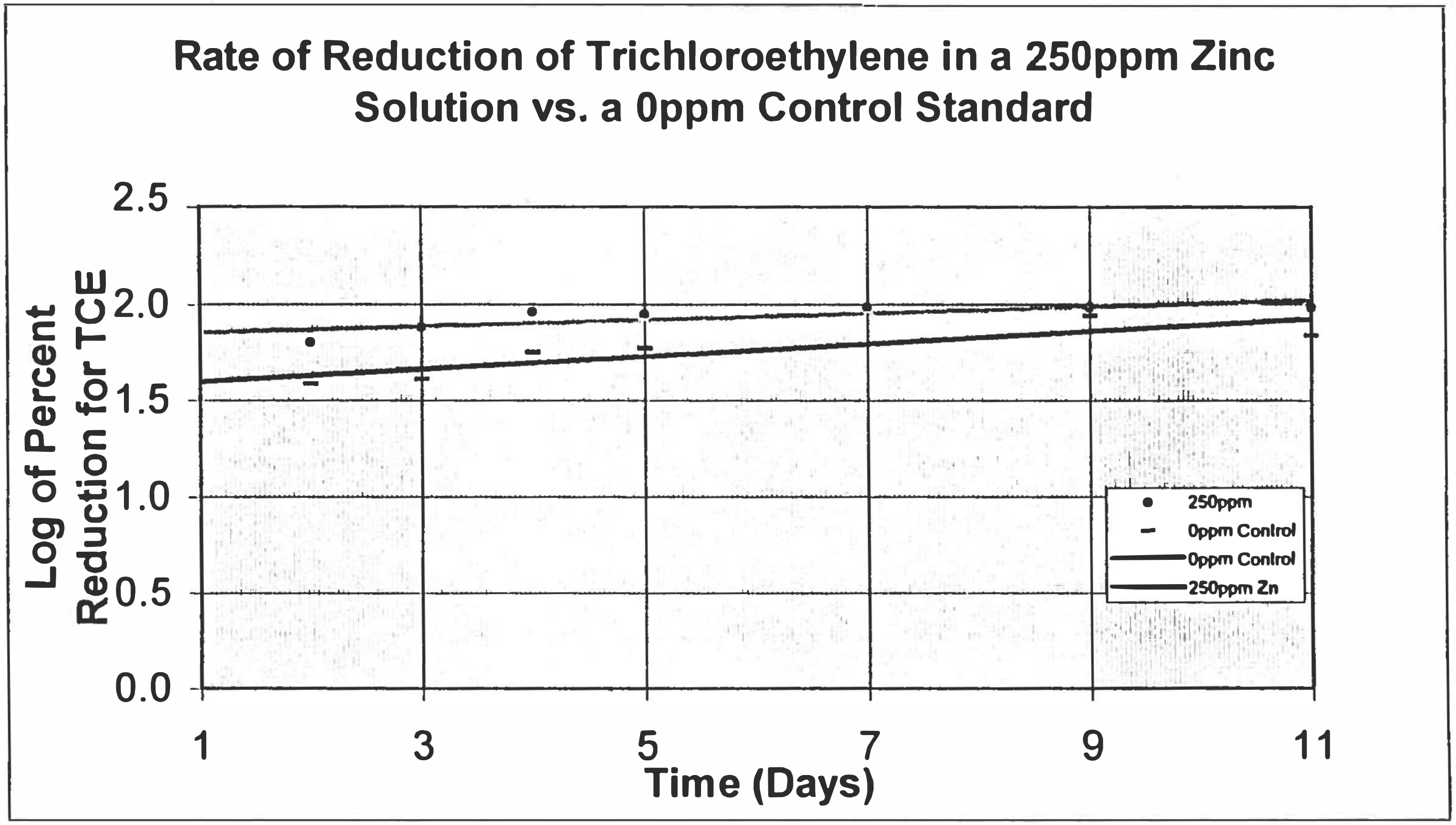

Rate of Reduction of Trichloroethylene in a 250ppm Zinc Solution vs. a 0ppm Control Standard

Figure 40

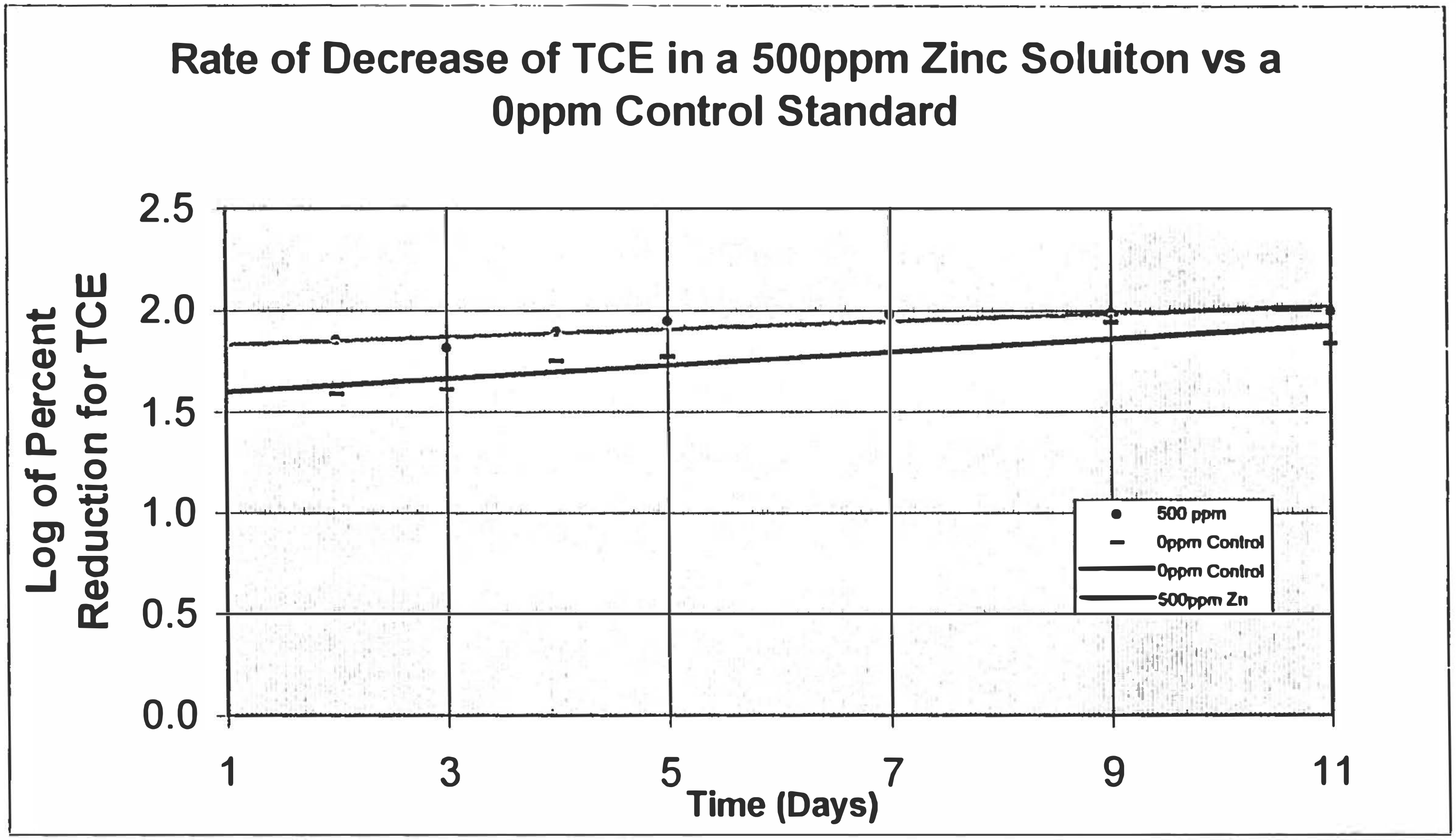

Rate of Decrease of TCE in a 500ppm Zinc Soluiton vs a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3
5
7
9
11
Time (Days)
● 500 ppm
– 0ppm Control
0ppm Control
500ppm Zn

Figure 41

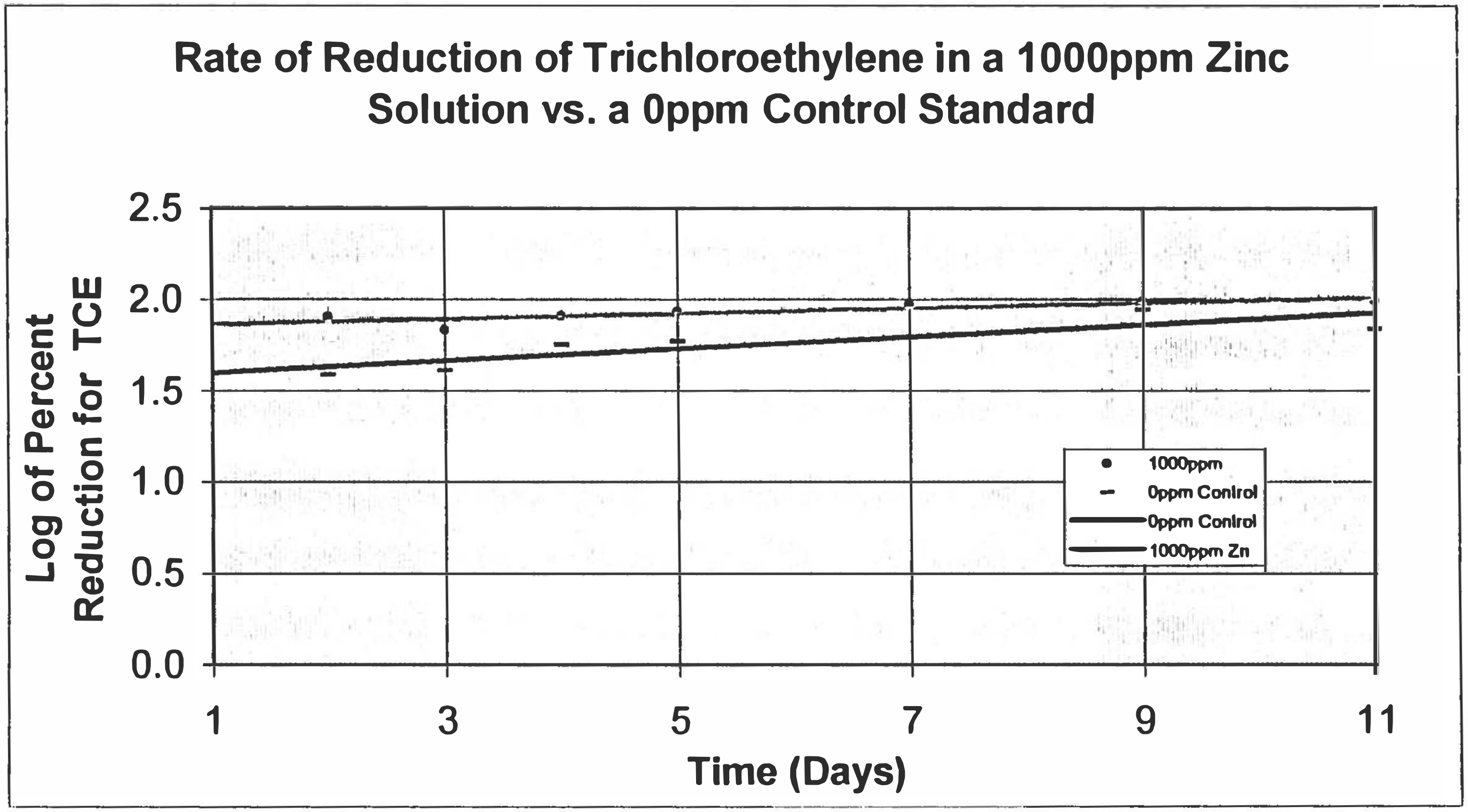

Rate of Reduction of Trichloroethylene in a 1000ppm Zinc Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3
5
7
9
11
Time (Days)
● 1000ppm
- 0ppm Control
0ppm Control
1000ppm Zn

Figure 42

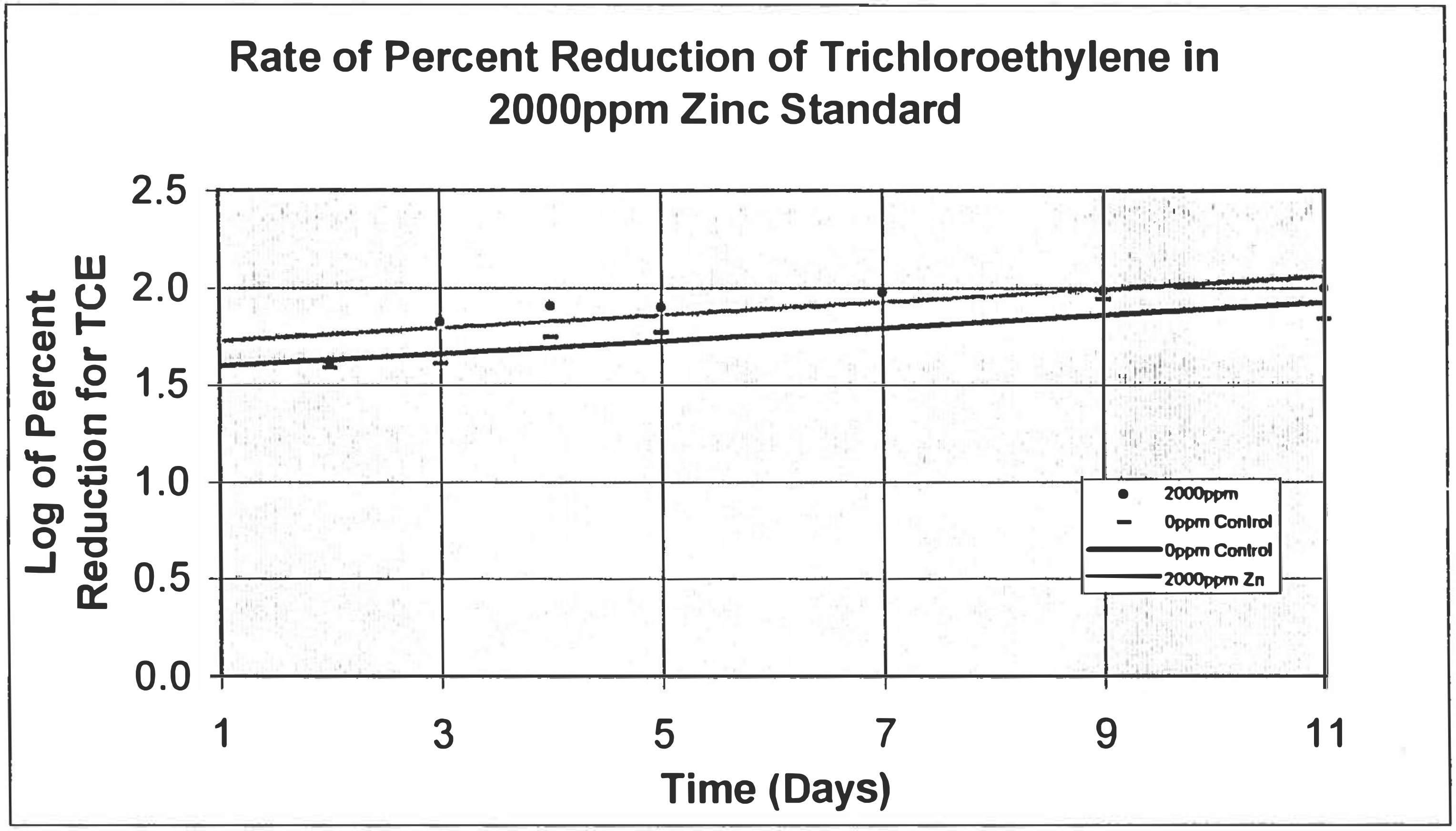

Rate of Percent Reduction of Trichloroethylene in 2000ppm Zinc Standard
Log of Percent Reduction for TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3
5
7
9
11
Time (Days)
2000ppm
0ppm Control
0ppm Control
2000ppm Zn

Figure 43

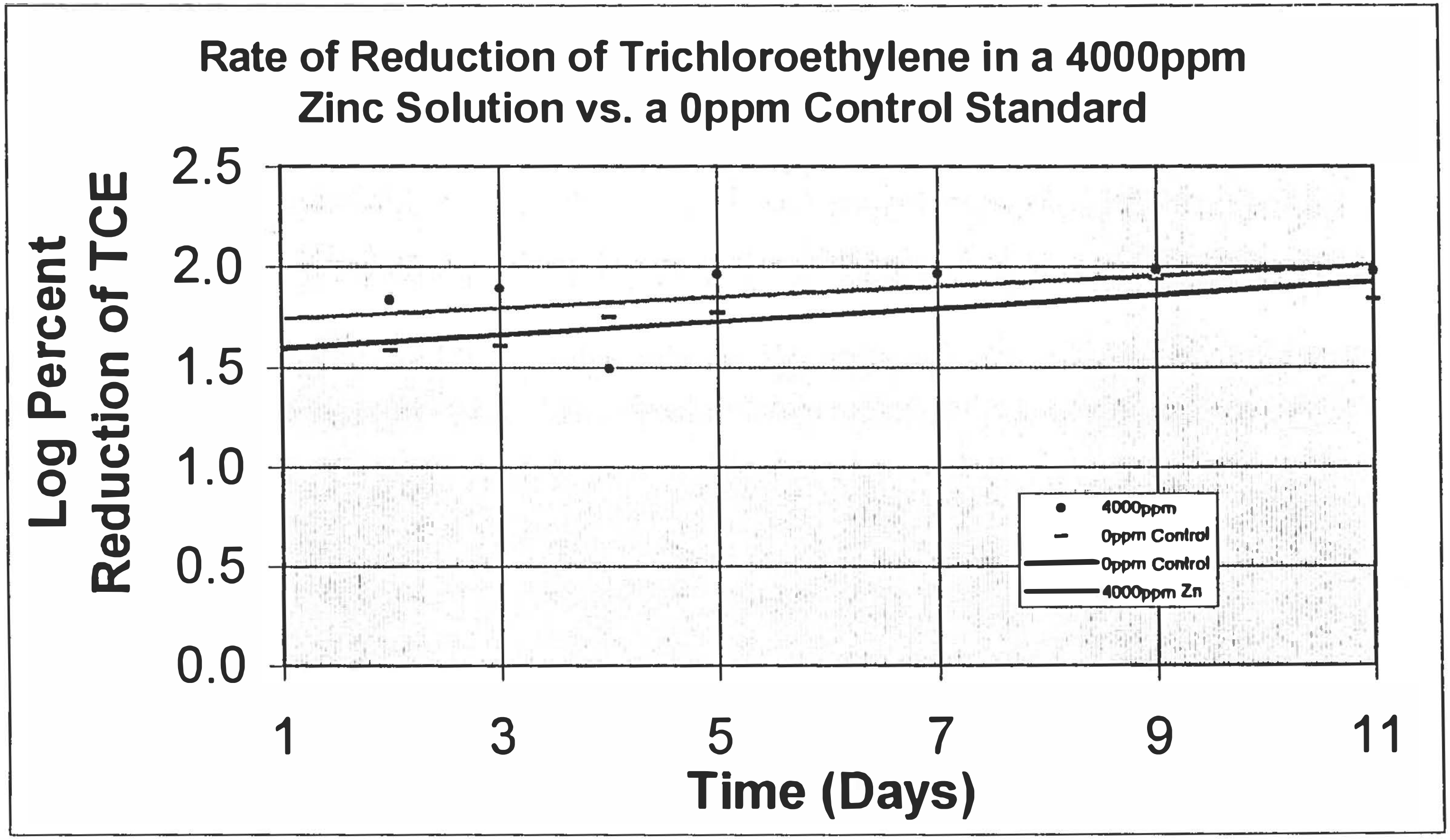

Rate of Reduction of Trichloroethylene in a 4000ppm Zinc Solution vs. a 0ppm Control Standard
Log Percent Reduction of TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3
5
7
9
11
Time (Days)
● 4000ppm
– 0ppm Control
0ppm Control
4000ppm Zn

Figure 44

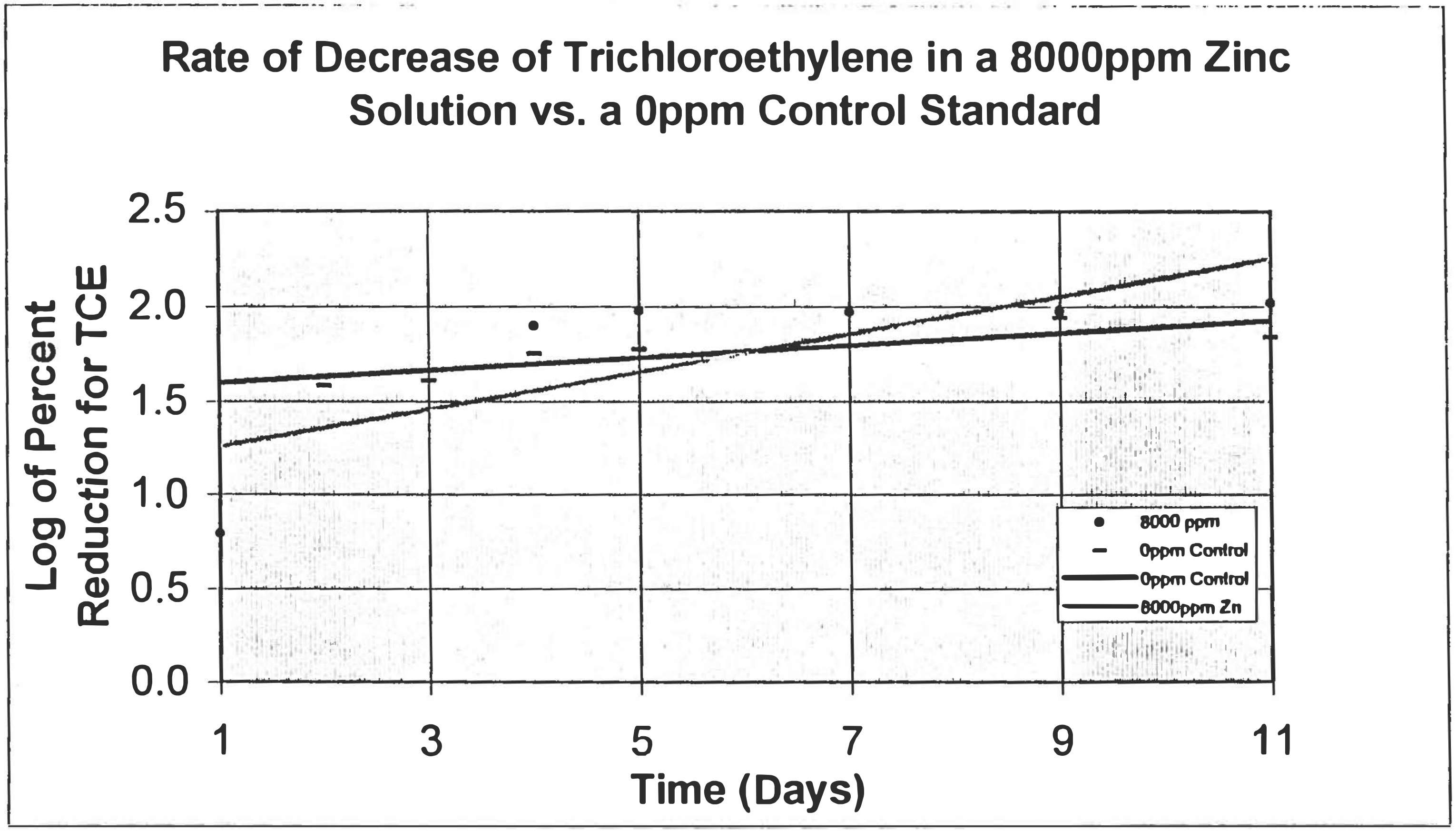

Rate of Decrease of Trichloroethylene in a 8000ppm Zinc Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3
5
7
9
11
Time (Days)
● 8000 ppm
– 0ppm Control
0ppm Control
8000ppm Zn

Figure 45

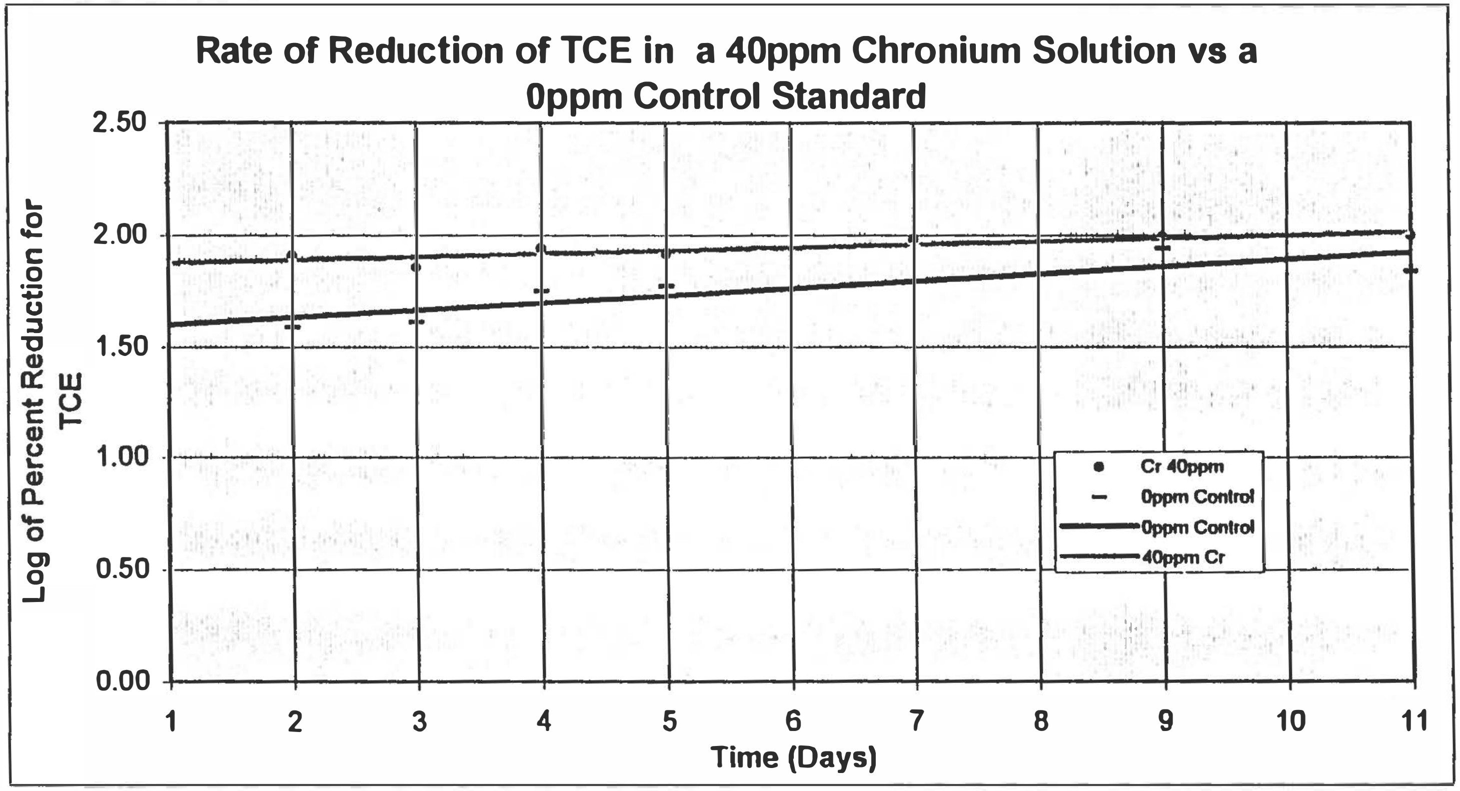

Rate of Reduction of TCE in a 40ppm Chronium Solution vs a 0ppm Control Standard
Log of Percent Reduction for TCE
2.50
2.00
1.50
1.00
0.50
0.00
1
2
3
4
5
6
7
8
9
10
11
Time (Days)
Cr 40ppm
0ppm Control
0ppm Control
40ppm Cr

Figure 46

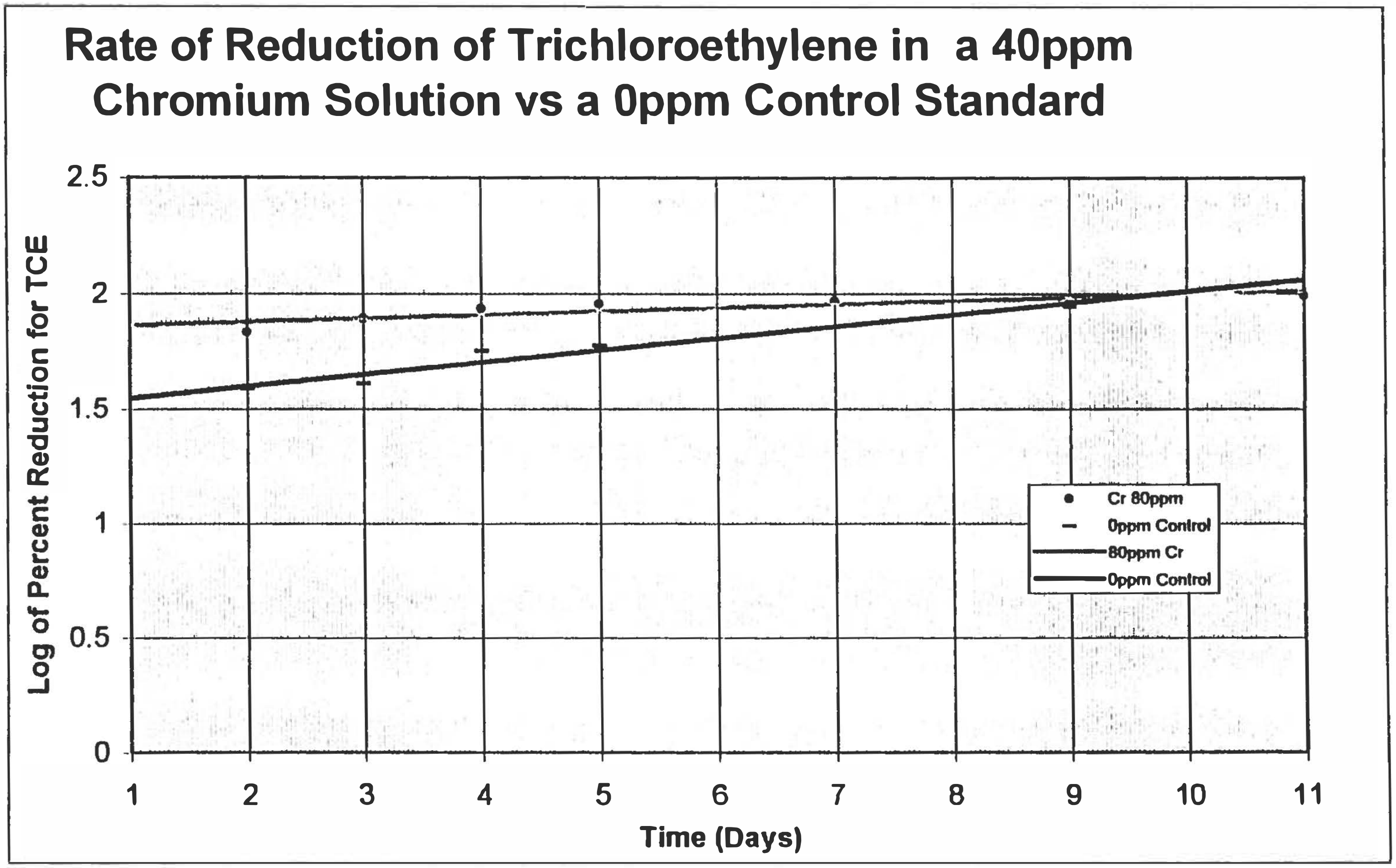

Rate of Reduction of Trichloroethylene in a 40ppm Chromium Solution vs a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
2
3
4
5
6
7
8
9
10
11
Time (Days)
● Cr 80ppm
– 0ppm Control
80ppm Cr
0ppm Control

Figure 47

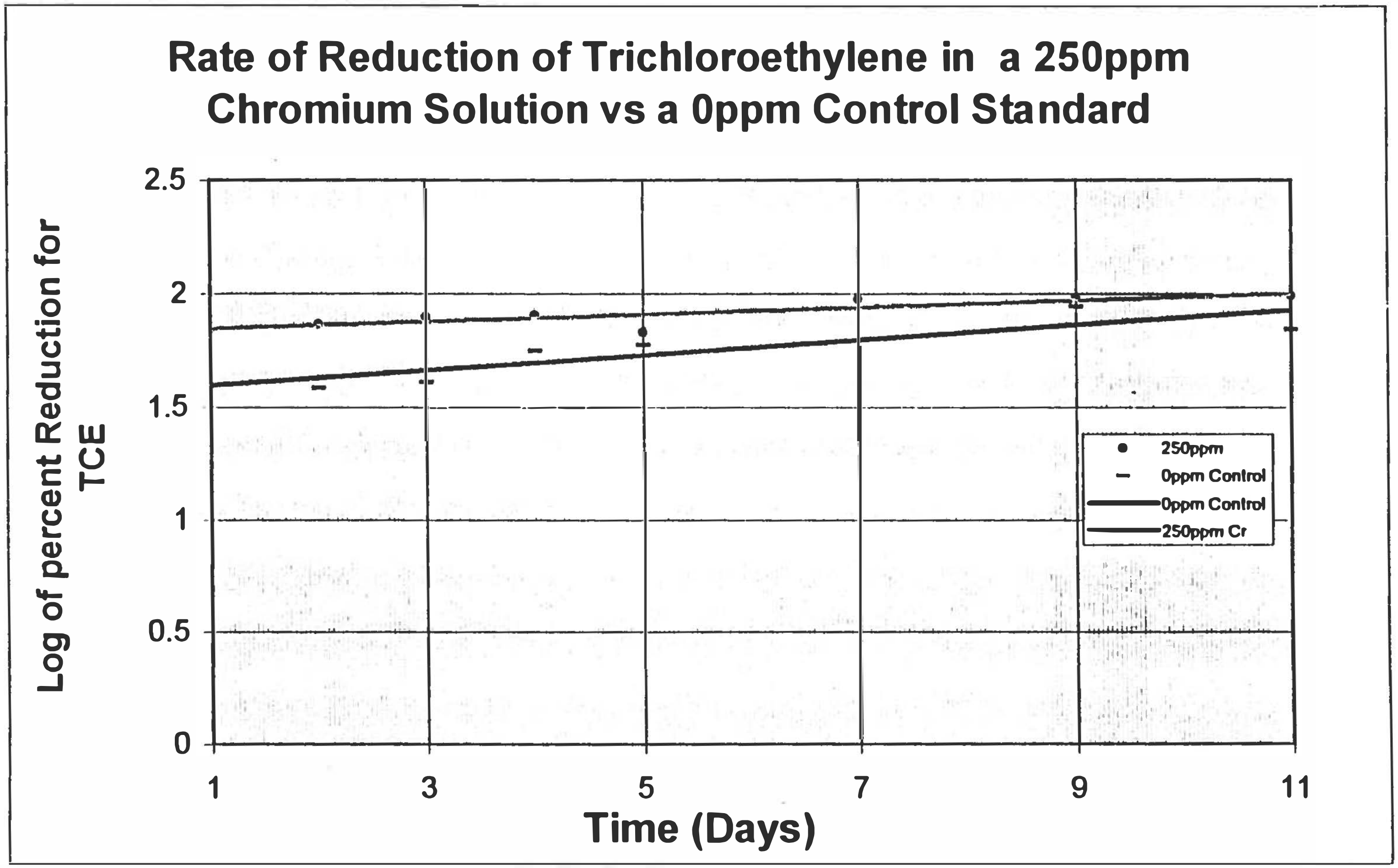

Rate of Reduction of Trichloroethylene in a 250ppm Chromium Solution vs a 0ppm Control Standard
Log of percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 250ppm
– 0ppm Control
0ppm Control
250ppm Cr

Figure 48

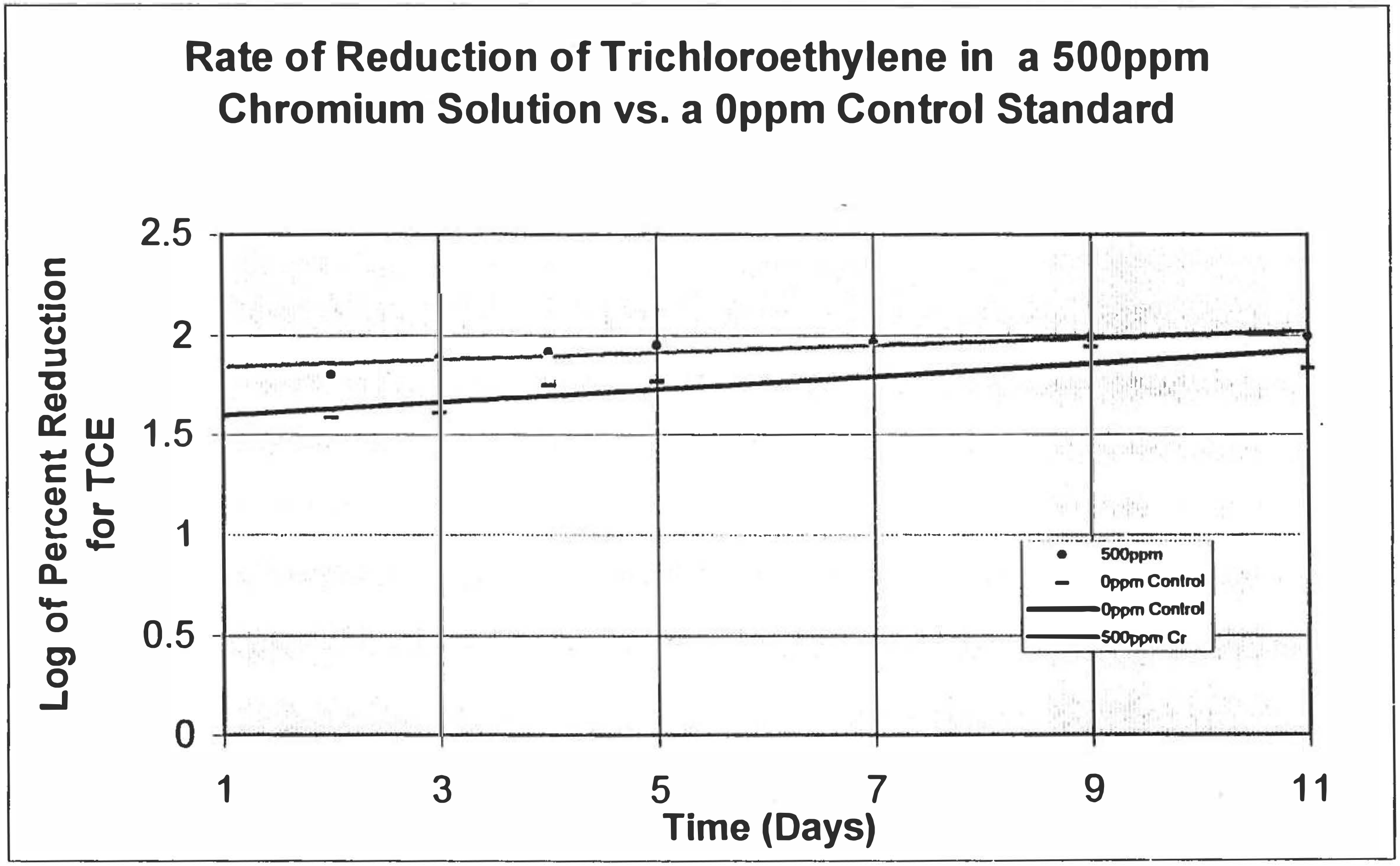

Rate of Reduction of Trichloroethylene in a 500ppm Chromium Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 500ppm
– 0ppm Control
0ppm Control
500ppm Cr

Figure 49

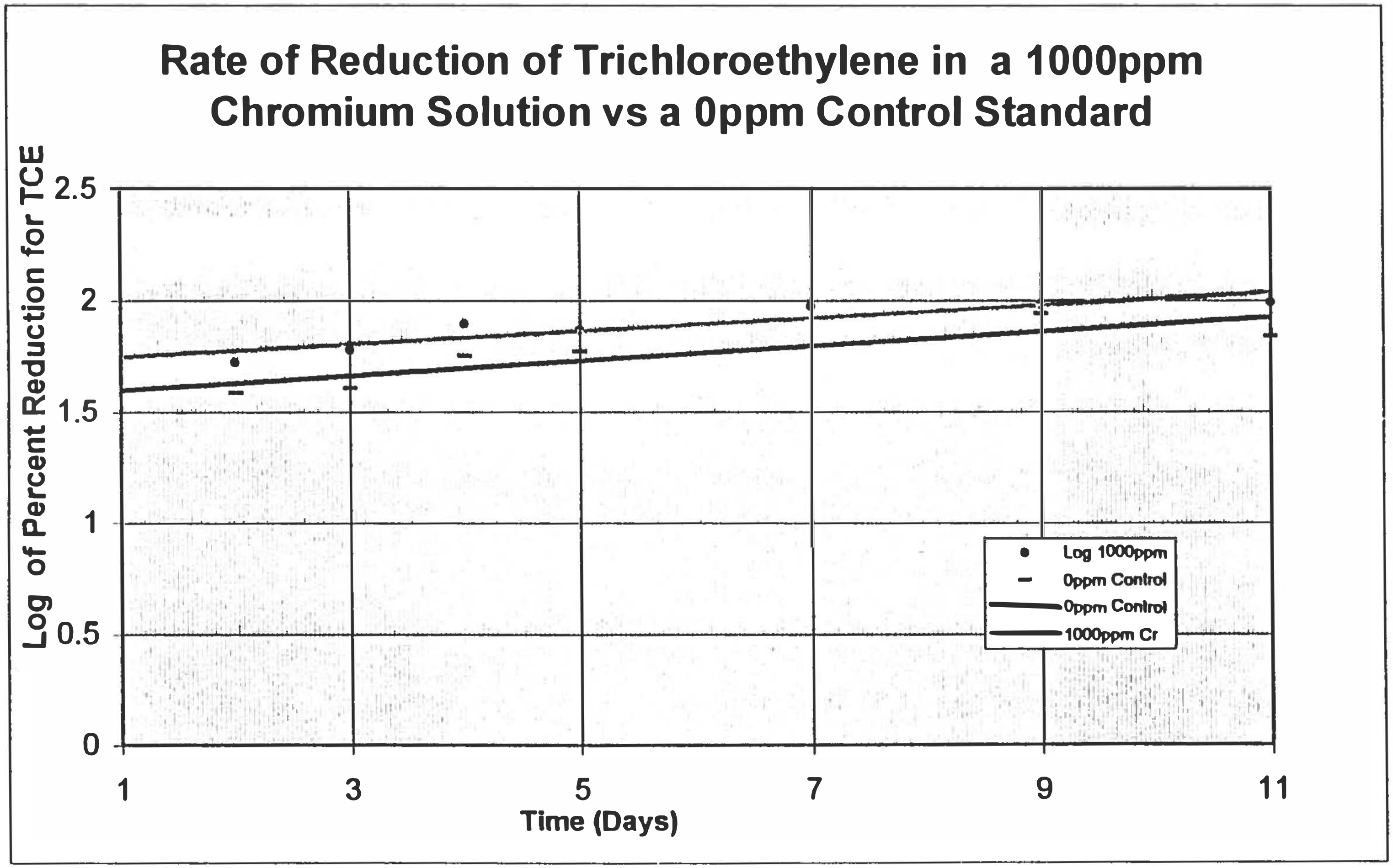

Rate of Reduction of Trichloroethylene in a 1000ppm Chromium Solution vs a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● Log 1000ppm
– 0ppm Control
0ppm Control
1000ppm Cr

Figure 50

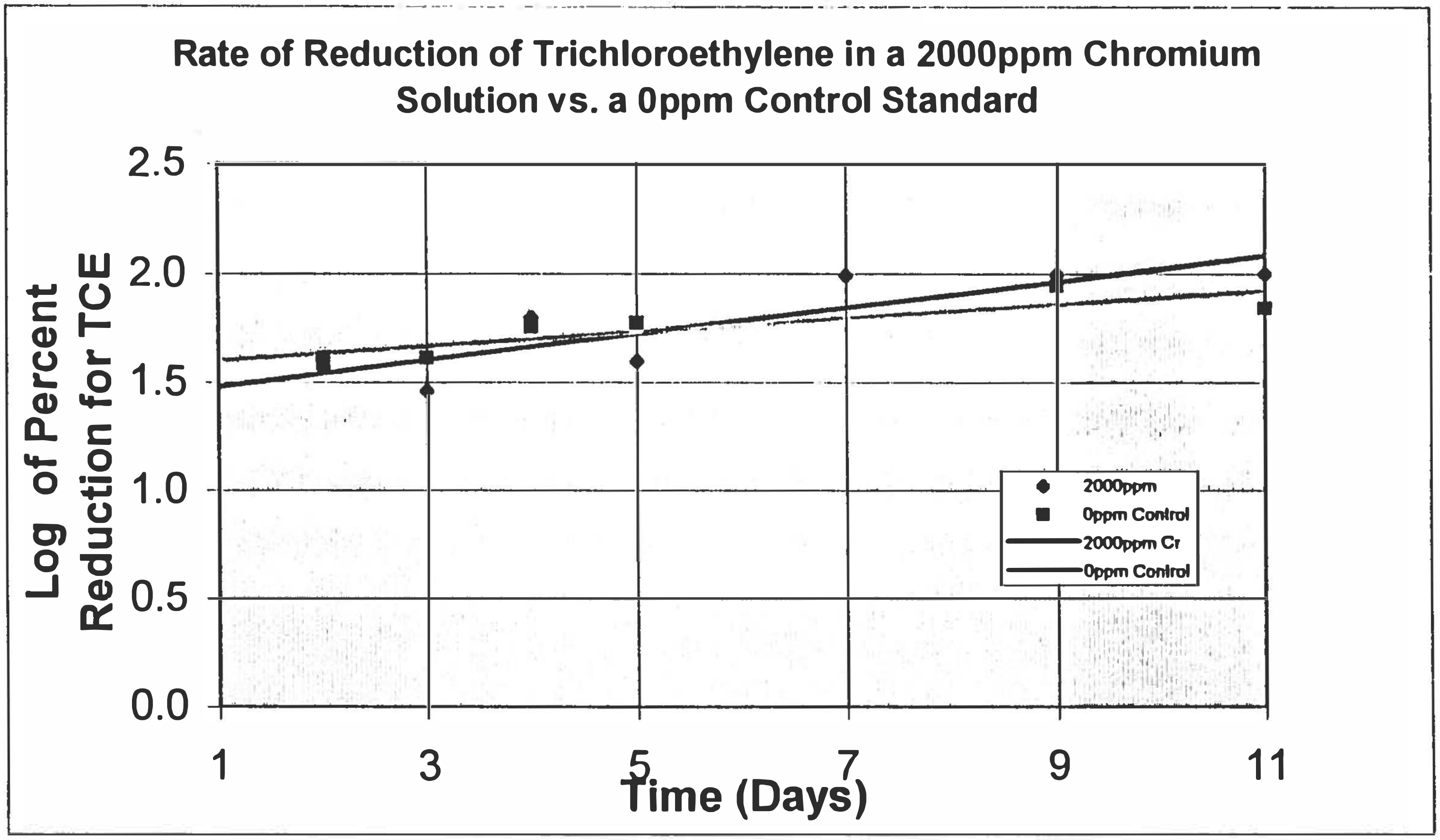

Rate of Reduction of Trichloroethylene in a 2000ppm Chromium Solution vs. a 0ppm Control Standard
Log of Percent Reduction for TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3
5
7
9
11
Time (Days)
2000ppm
0ppm Control
2000ppm Cr
0ppm Control

Figure 51

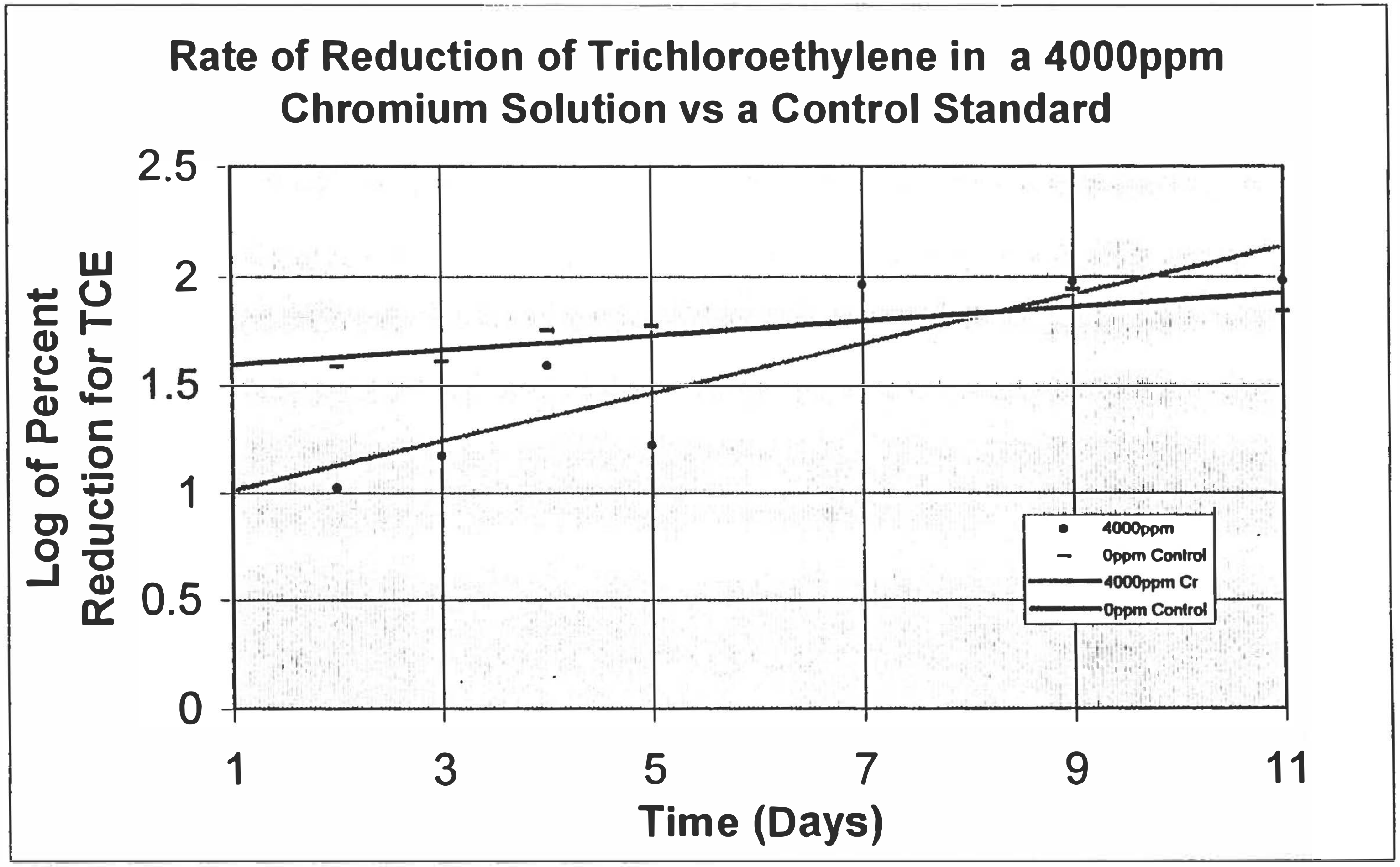

Rate of Reduction of Trichloroethylene in a 4000ppm Chromium Solution vs a Control Standard
Log of Percent Reduction for TCE
2.5
2
1.5
1
0.5
0
1
3
5
7
9
11
Time (Days)
● 4000ppm
– 0ppm Control
4000ppm Cr
0ppm Control

Figure 52

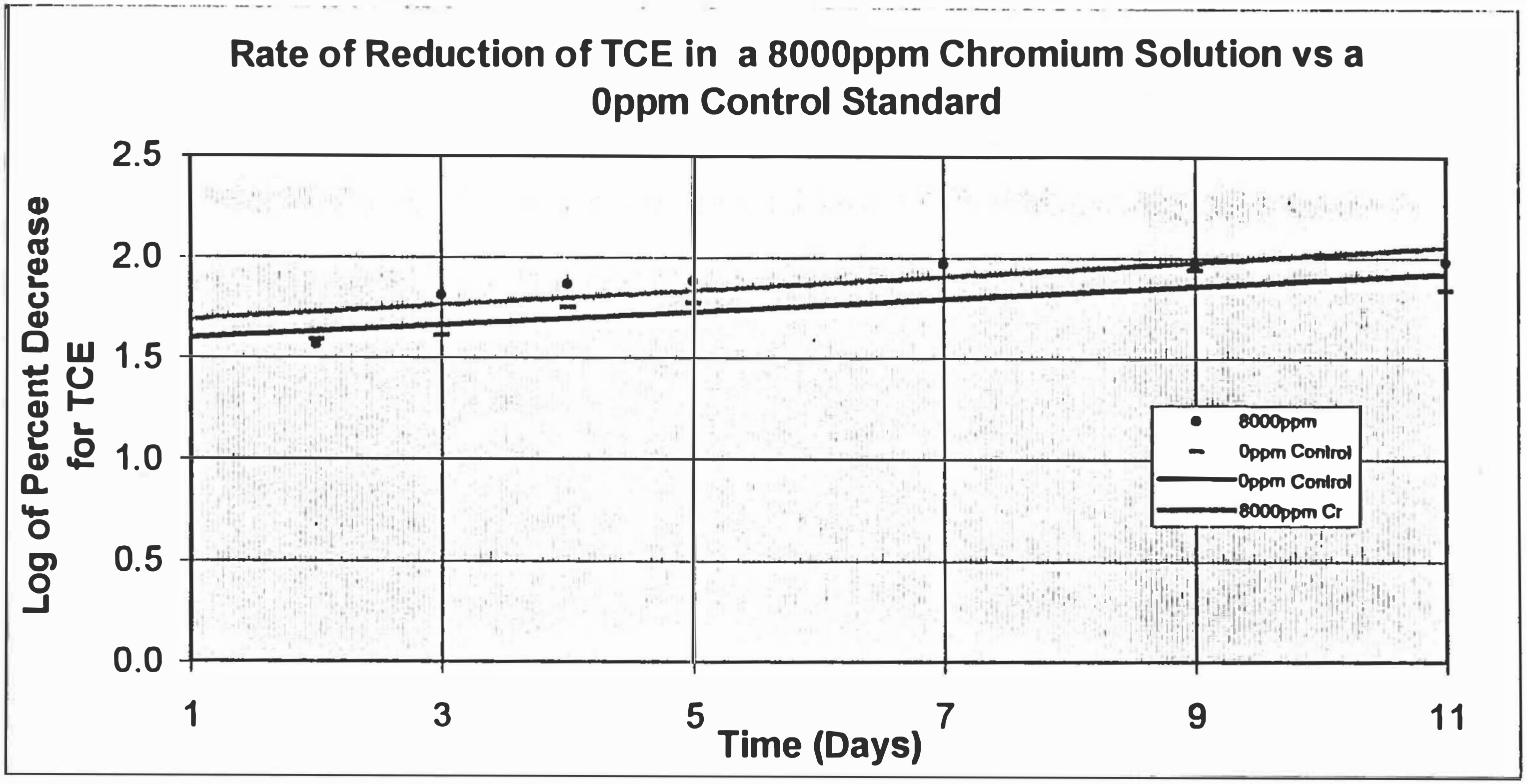

Rate of Reduction of TCE in a 8000ppm Chromium Solution vs a 0ppm Control Standard
Log of Percent Decrease for TCE
2.5
2.0
1.5
1.0
0.5
0.0
1
3
5
7
9
11
Time (Days)
● 8000ppm
– 0ppm Control
0ppm Control
8000ppm Cr

Figure 53

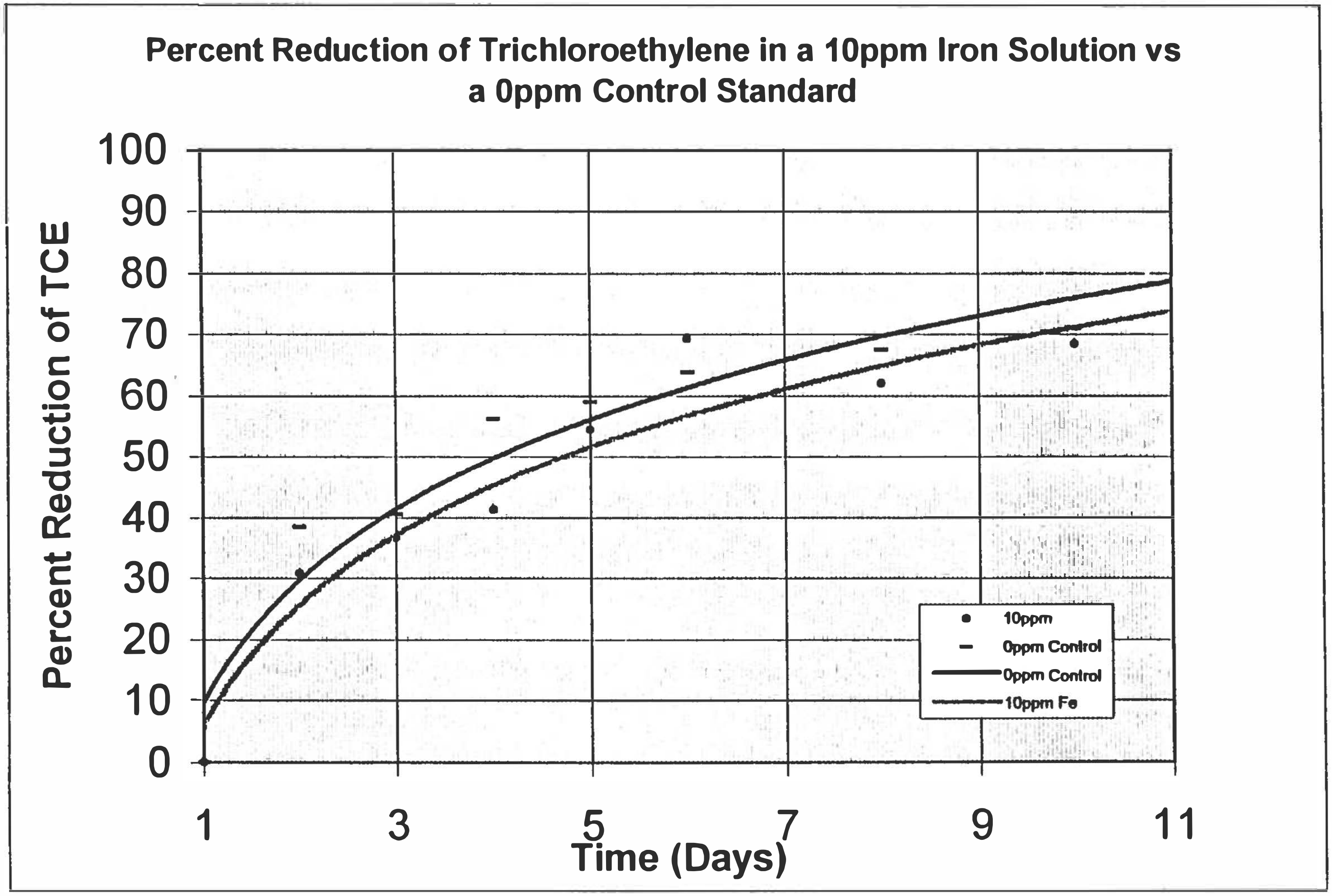

Percent Reduction of Trichloroethylene in a 10ppm Iron Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 10ppm
– 0ppm Control
0ppm Control
10ppm Fe

Figure 54

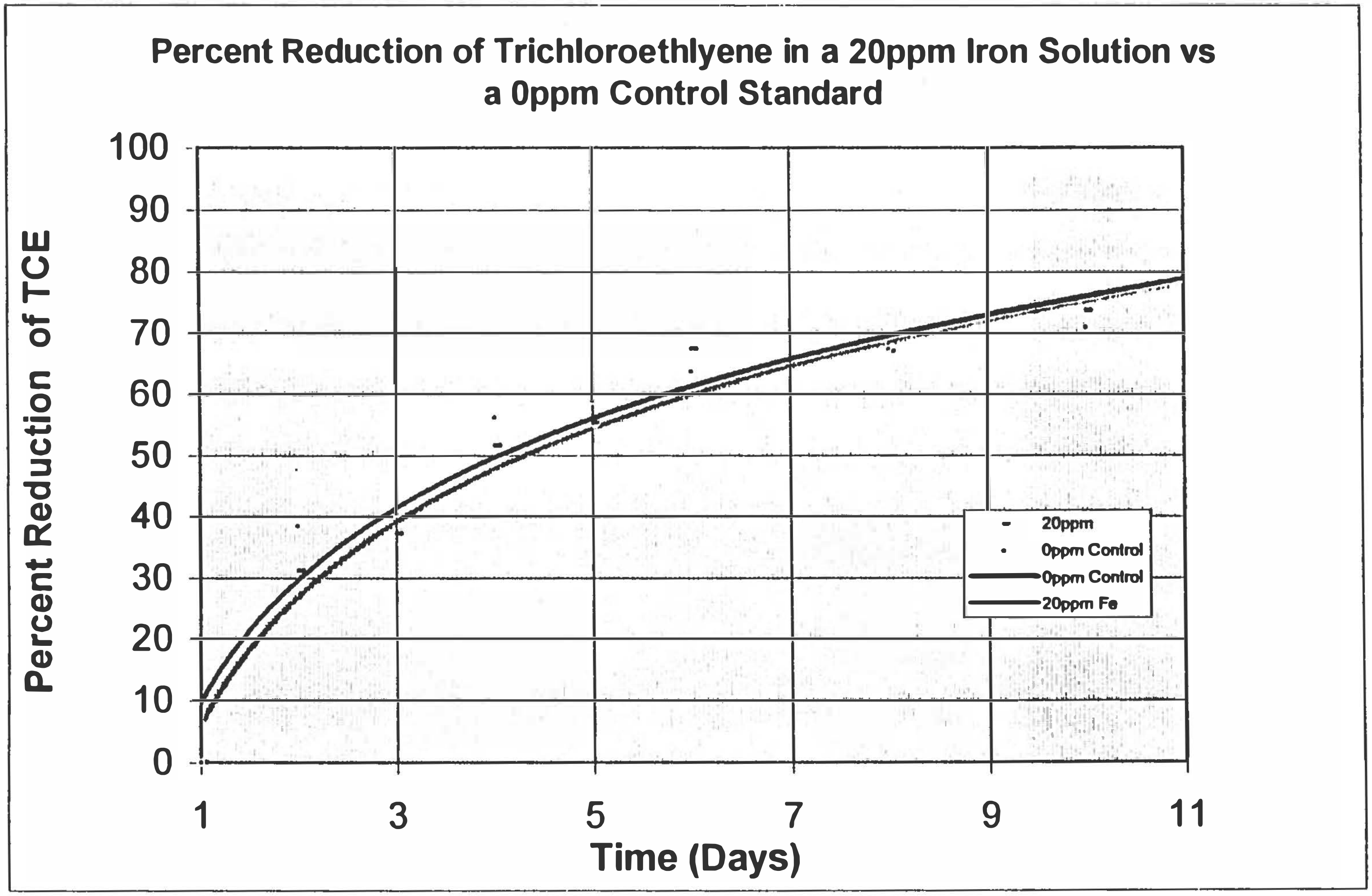

Percent Reduction of Trichloroethlyene in a 20ppm Iron Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
20ppm
0ppm Control
0ppm Control
20ppm Fe

Figure 55

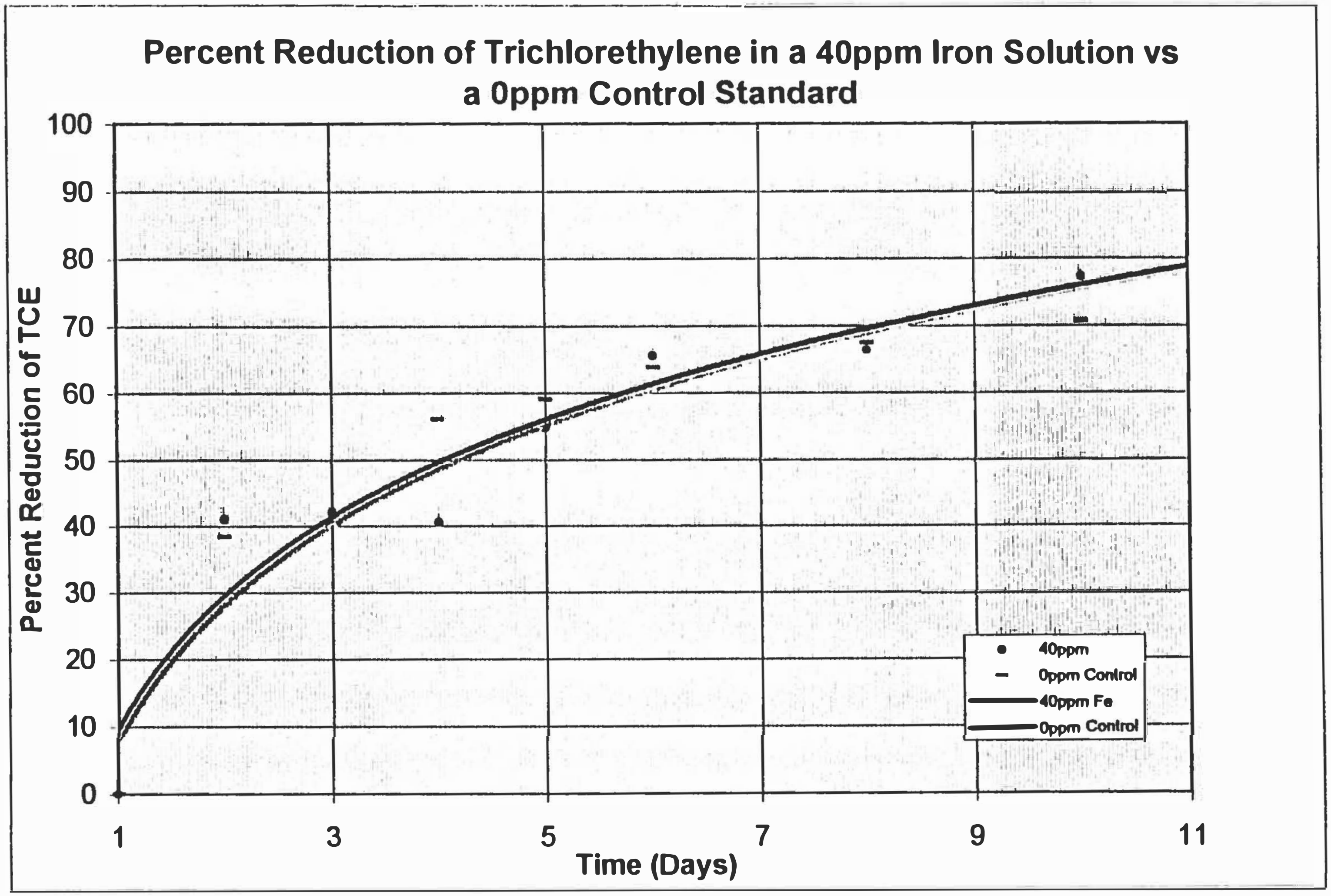

Percent Reduction of Trichlorethylene in a 40ppm Iron Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 40ppm
– 0ppm Control
40ppm Fe
0ppm Control

Figure 56

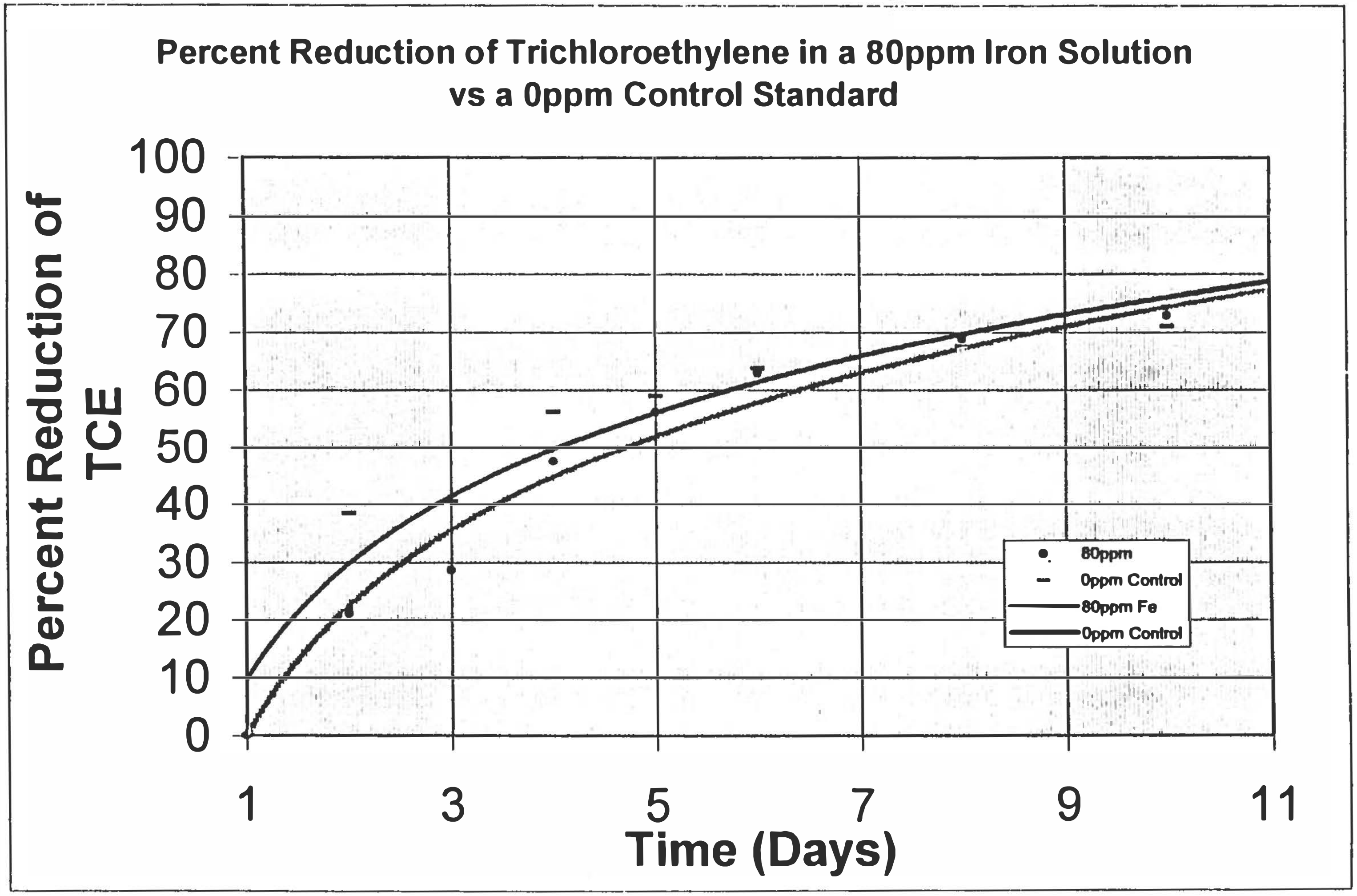

Percent Reduction of Trichloroethylene in a 80ppm Iron Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
80ppm
0ppm Control
80ppm Fe
0ppm Control

Figure 57

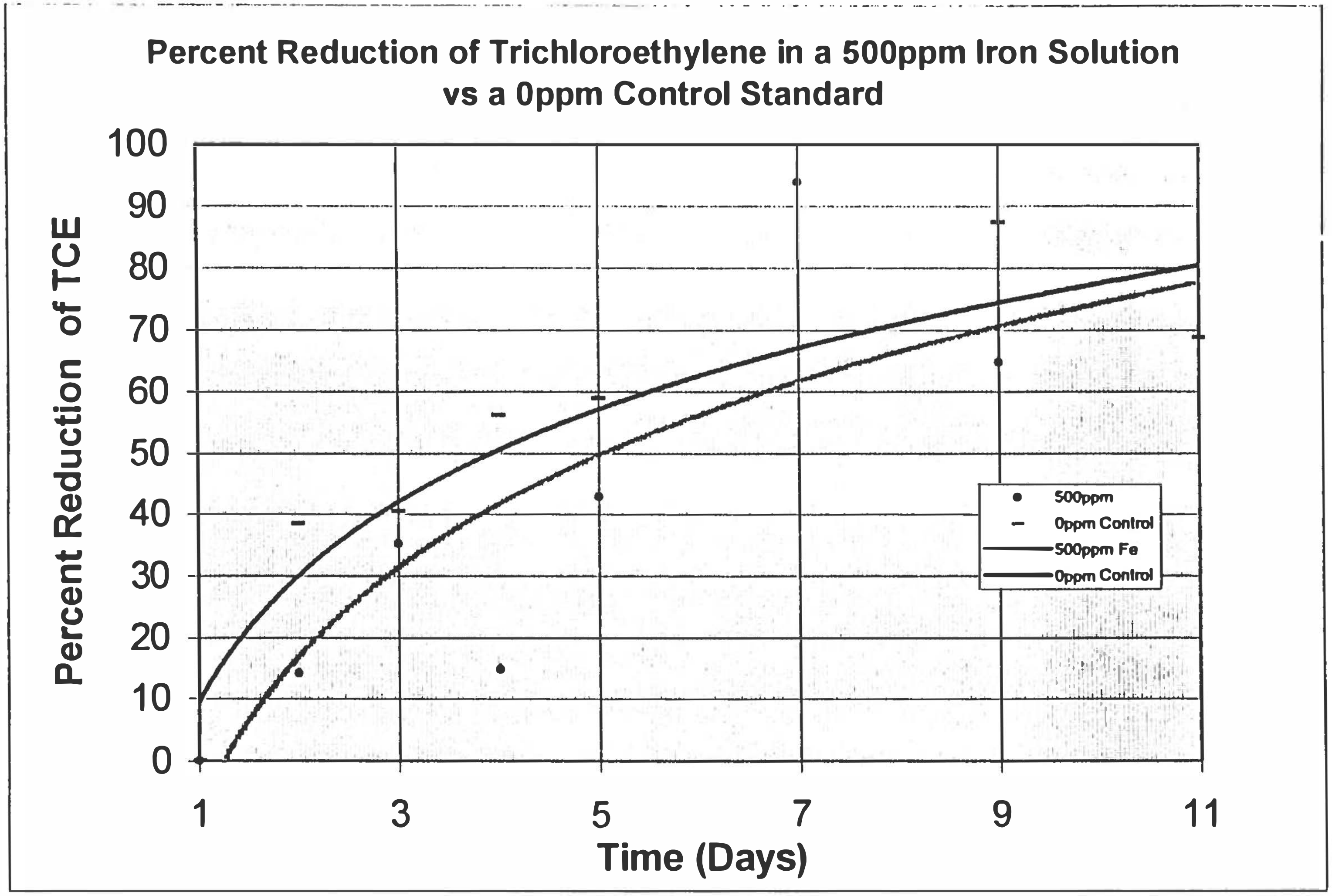

Percent Reduction of Trichloroethylene in a 500ppm Iron Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
500ppm
0ppm Control
500ppm Fe
0ppm Control

Figure 58

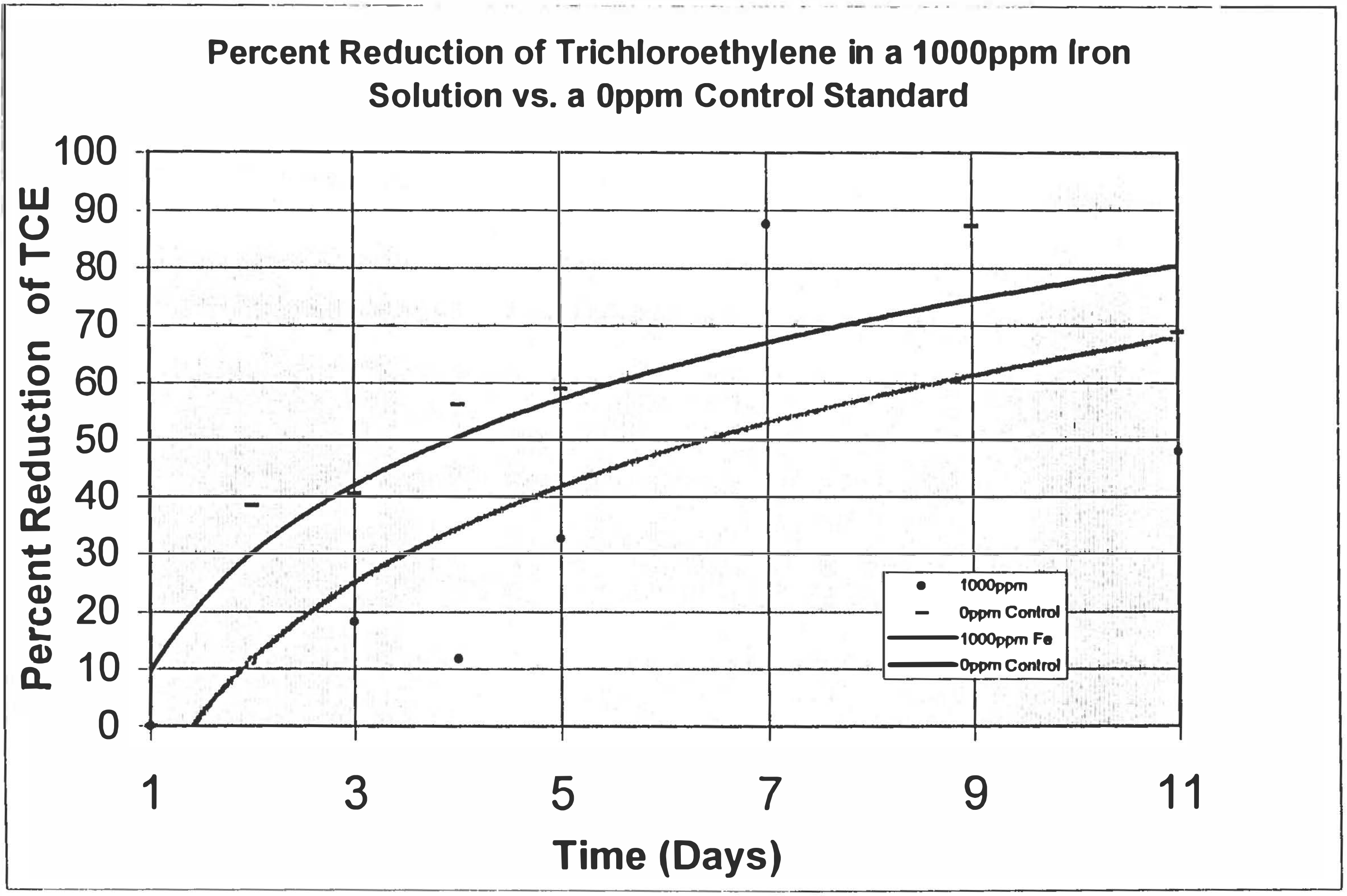

Percent Reduction of Trichloroethylene in a 1000ppm Iron Solution vs. a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 1000ppm
– 0ppm Control
1000ppm Fe
0ppm Control

Figure 59

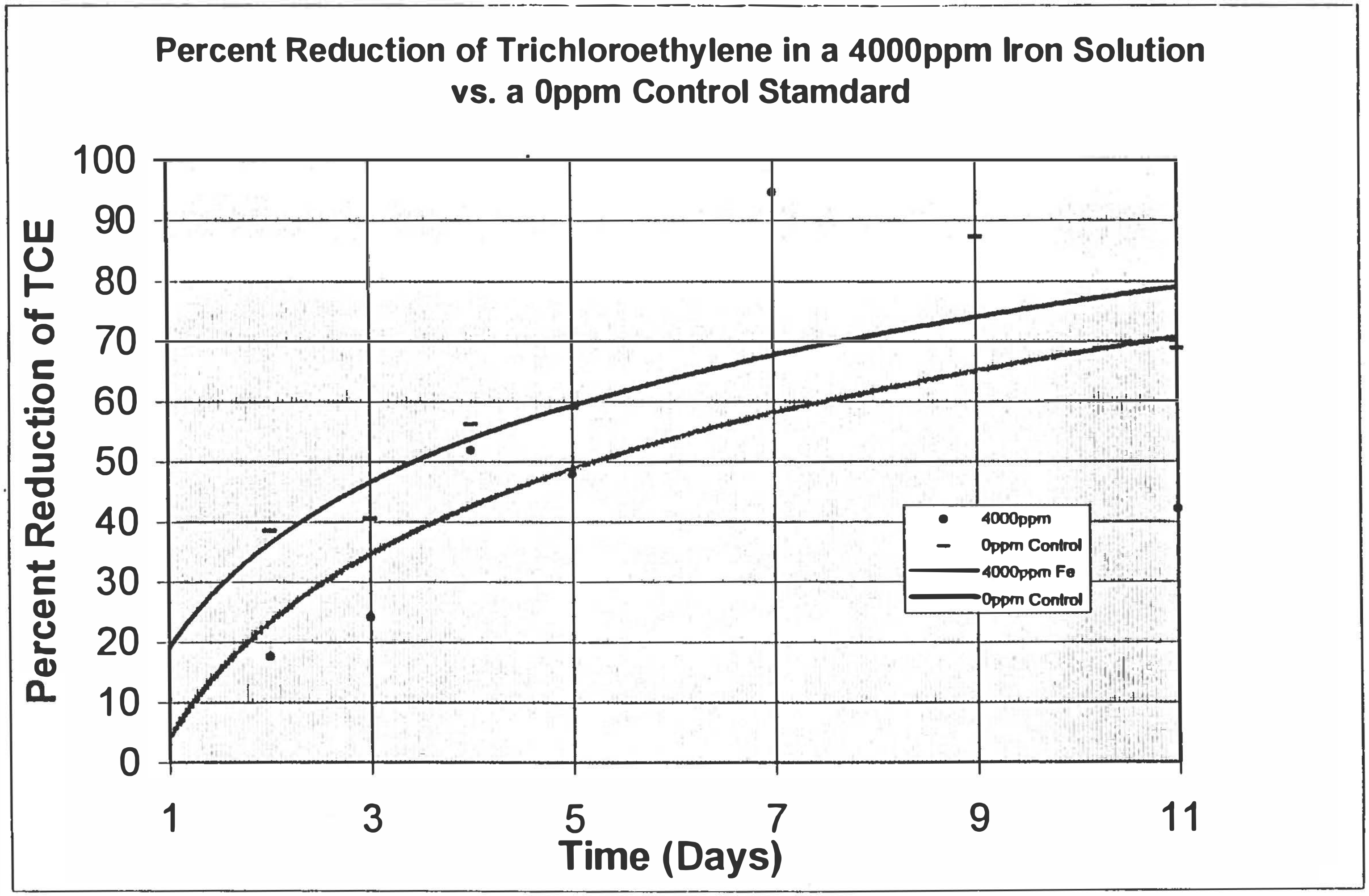

Percent Reduction of Trichloroethylene in a 4000ppm Iron Solution vs. a 0ppm Control Stamdard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 4000ppm
– 0ppm Control
4000ppm Fe
0ppm Control

Figure 60

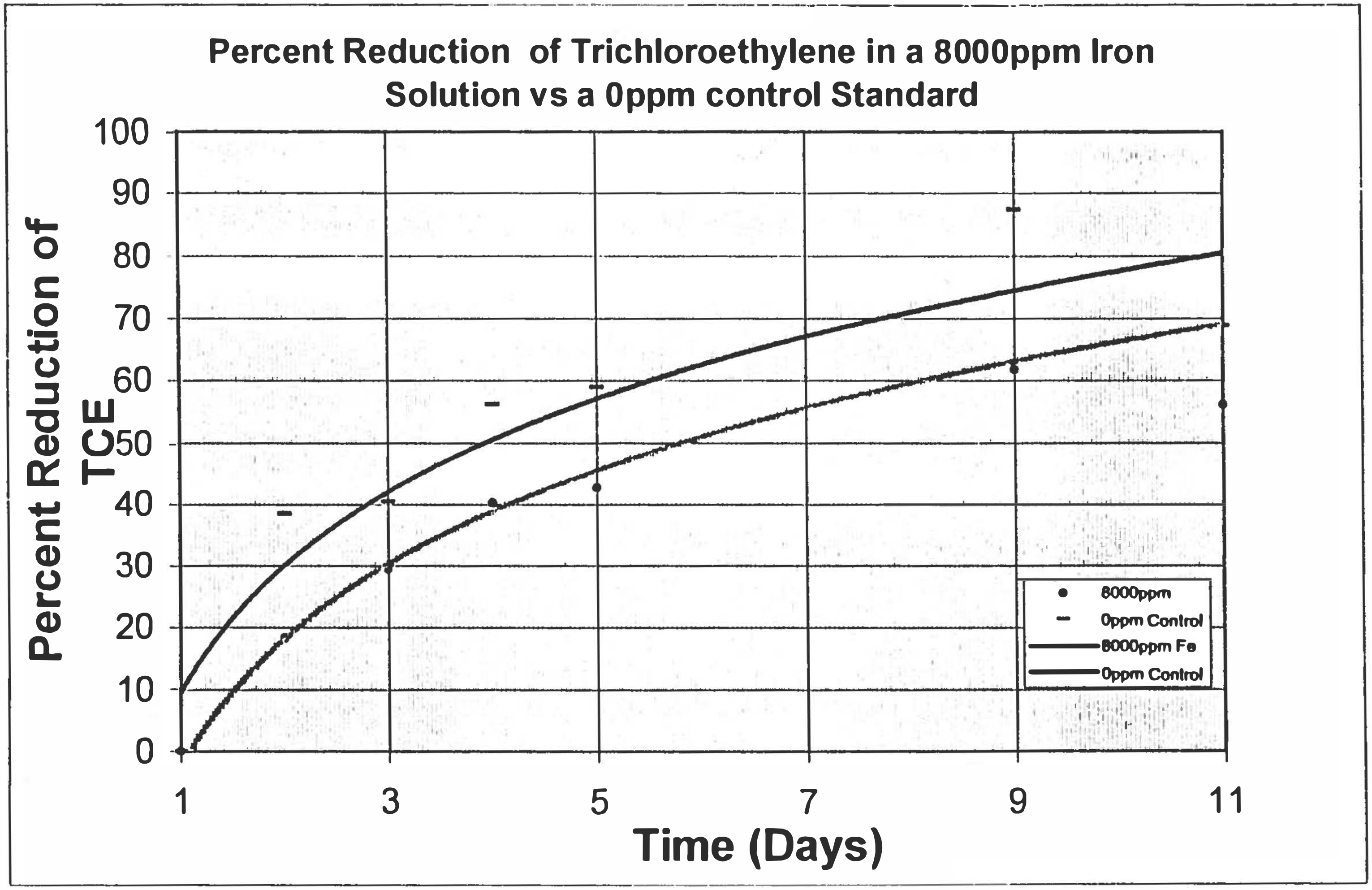
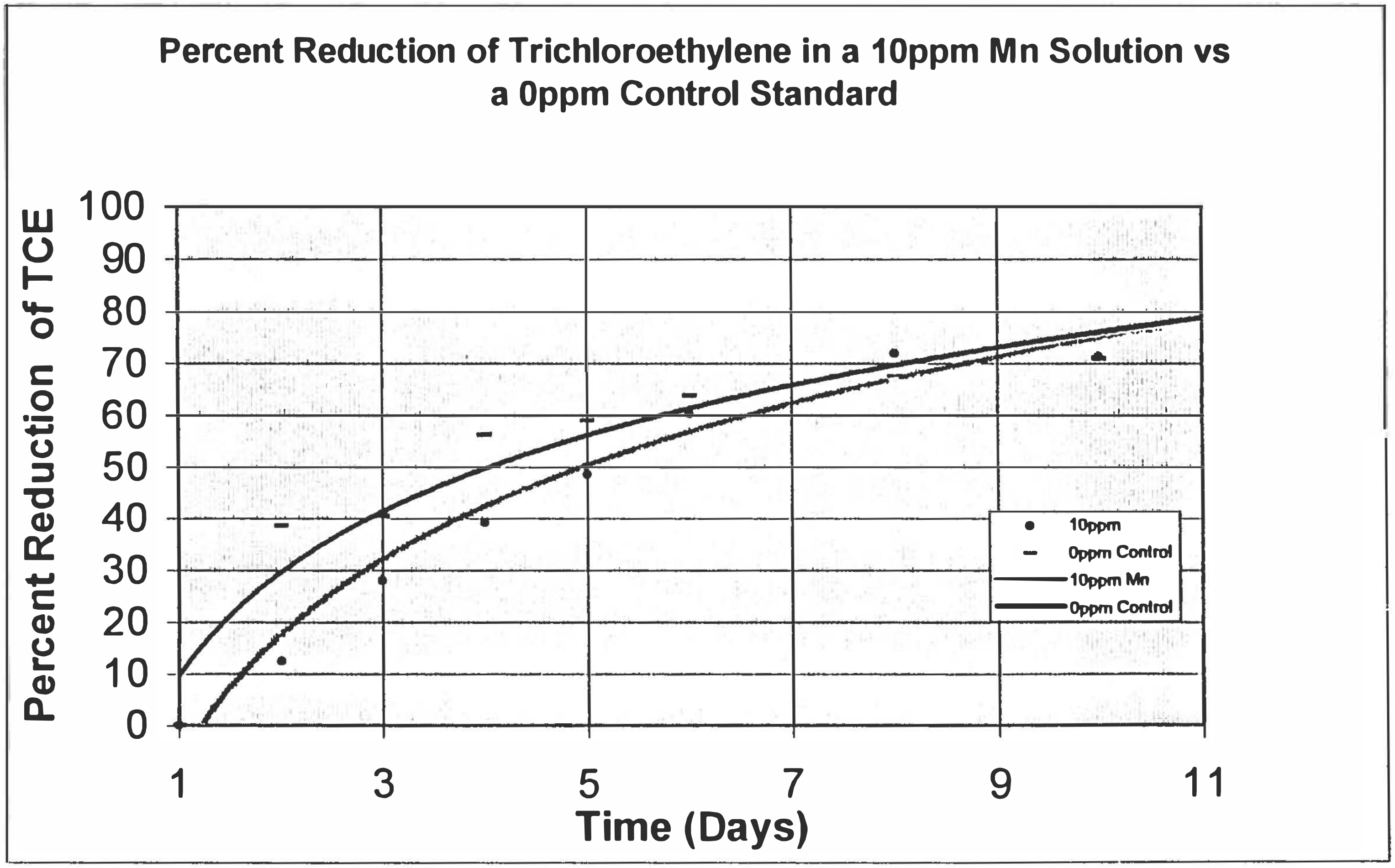
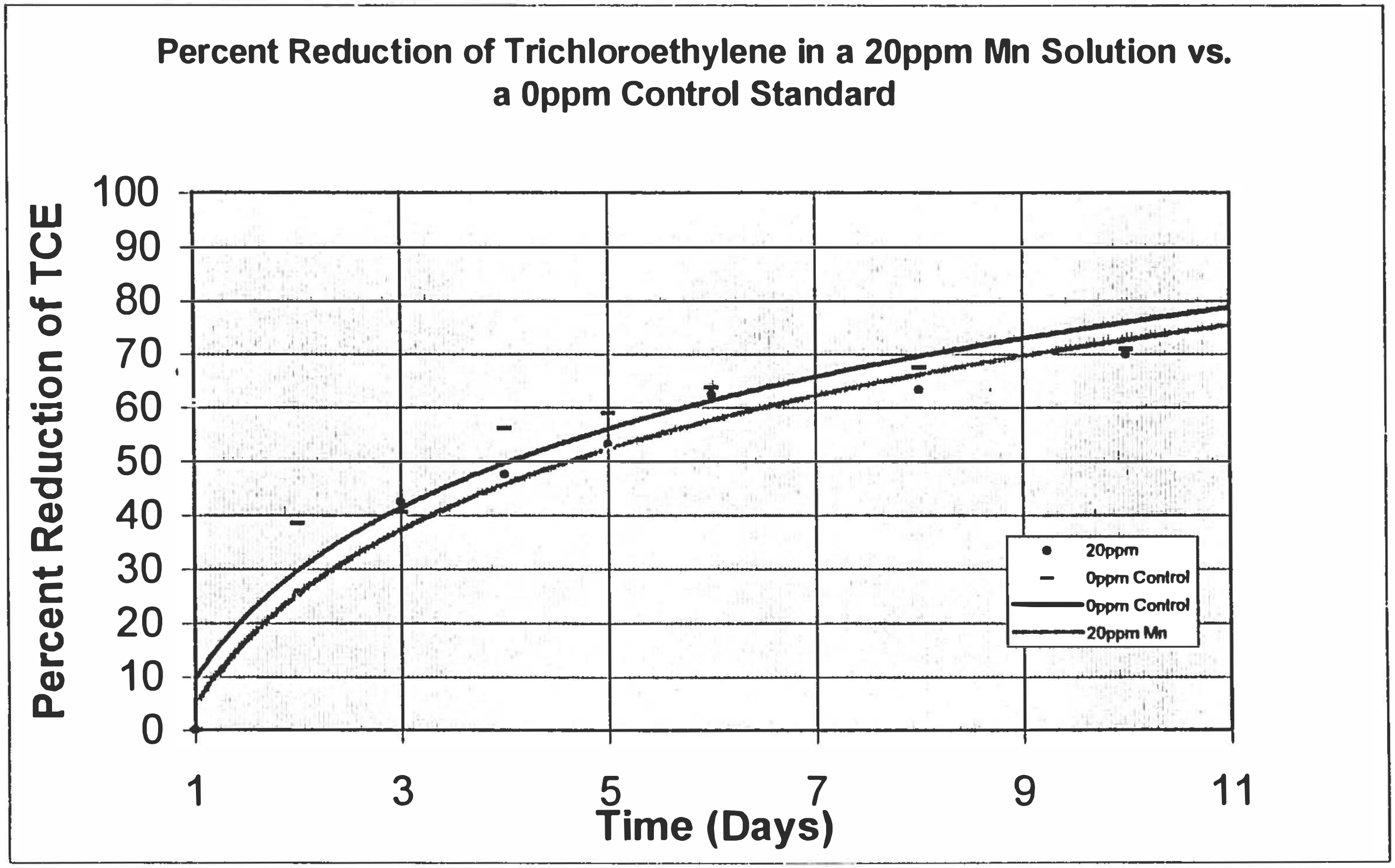

Percent Reduction of Trichloroethylene in a 8000ppm Iron Solution vs a 0ppm control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 8000ppm
– 0ppm Control
8000ppm Fe
0ppm Control

Figure 61



Percent Reduction of Trichloroethylene in a 10ppm Mn Solution vs a 0ppm Control Standard

Figure 62



Percent Reduction of Trichloroethylene in a 20ppm Mn Solution vs. a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 20ppm
– 0ppm Control
0ppm Control
20ppm Mn

Figure 63

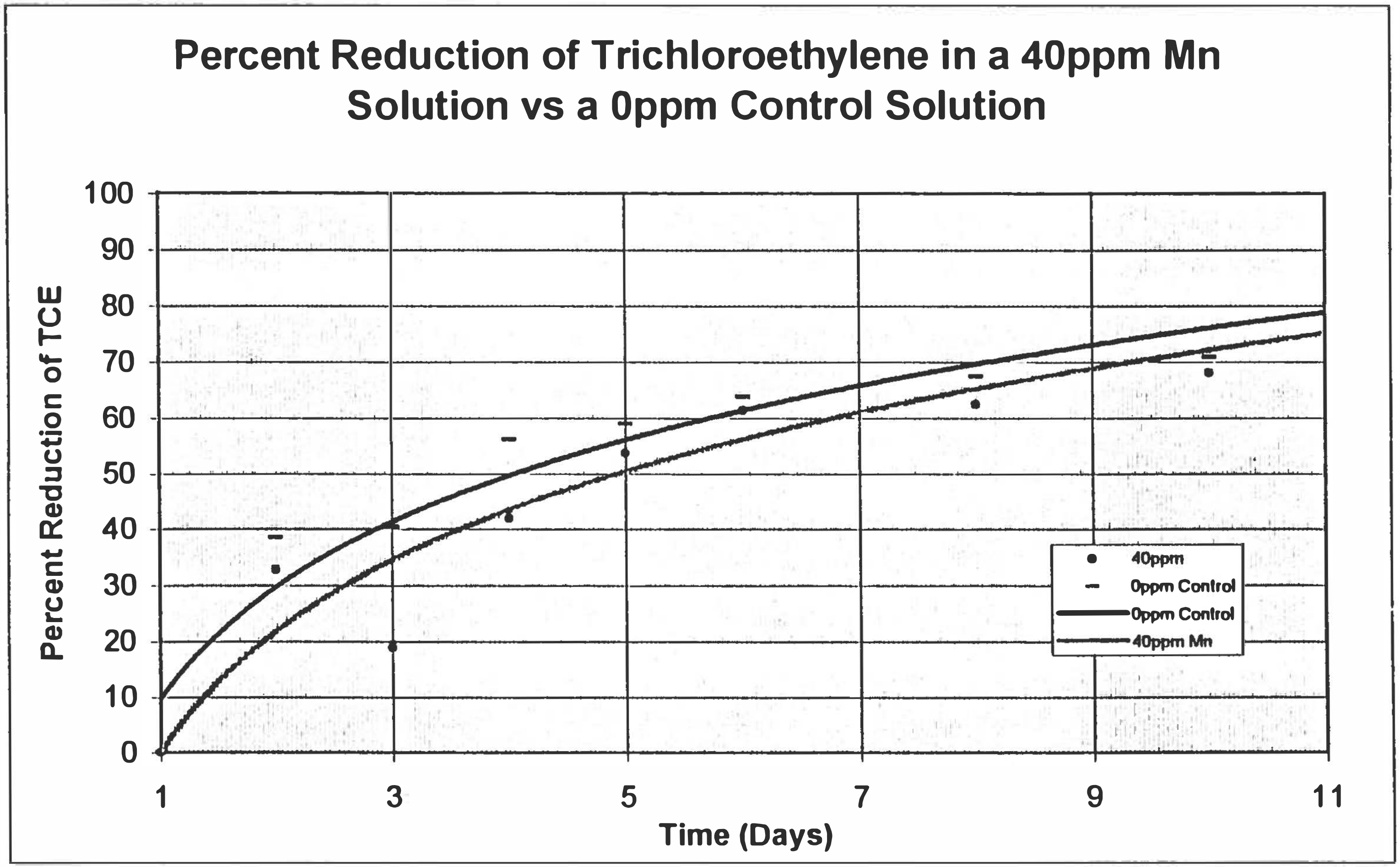

Percent Reduction of Trichloroethylene in a 40ppm Mn Solution vs a 0ppm Control Solution
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 40ppm
– 0ppm Control
0ppm Control
40ppm Mn

Figure 64

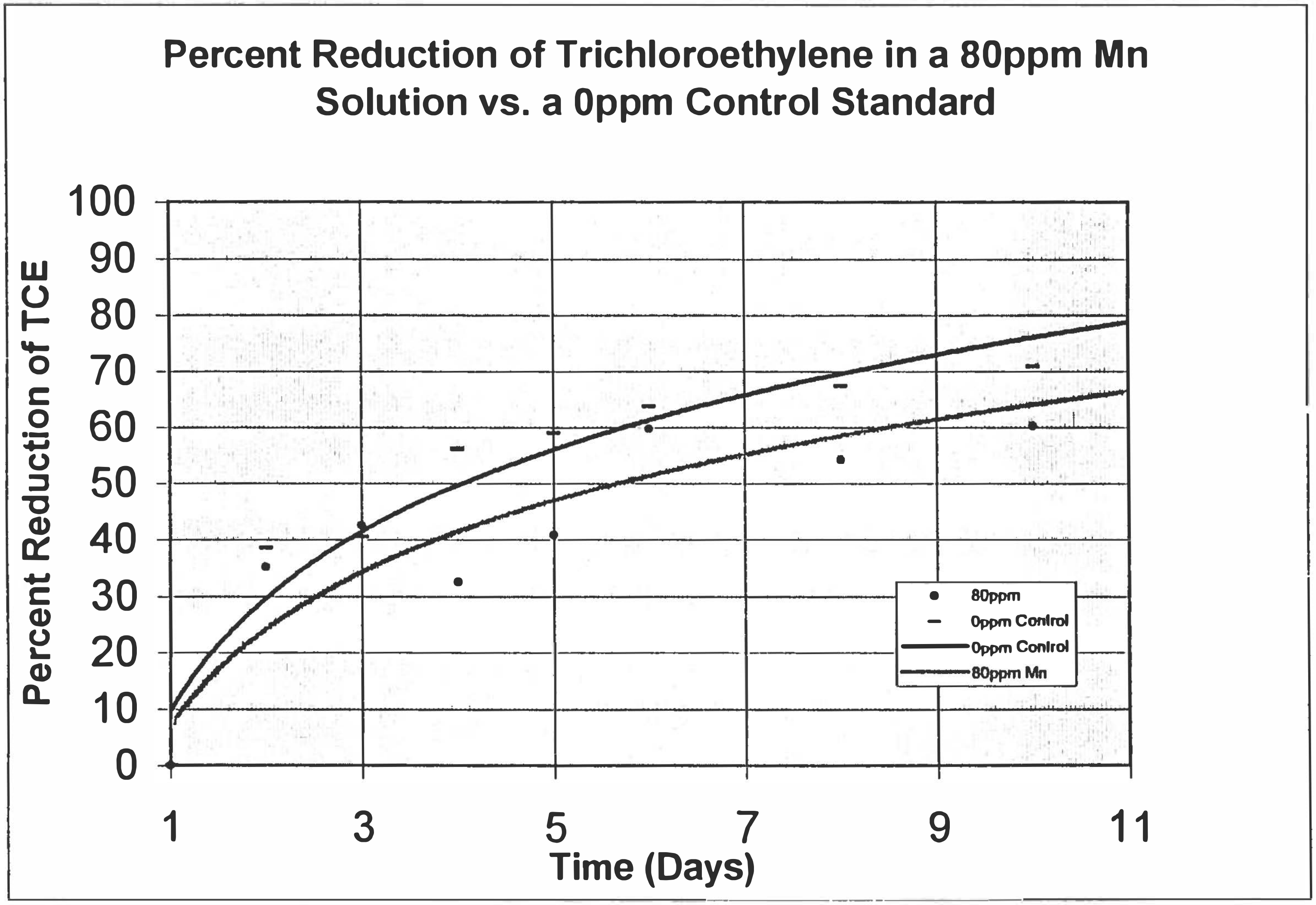
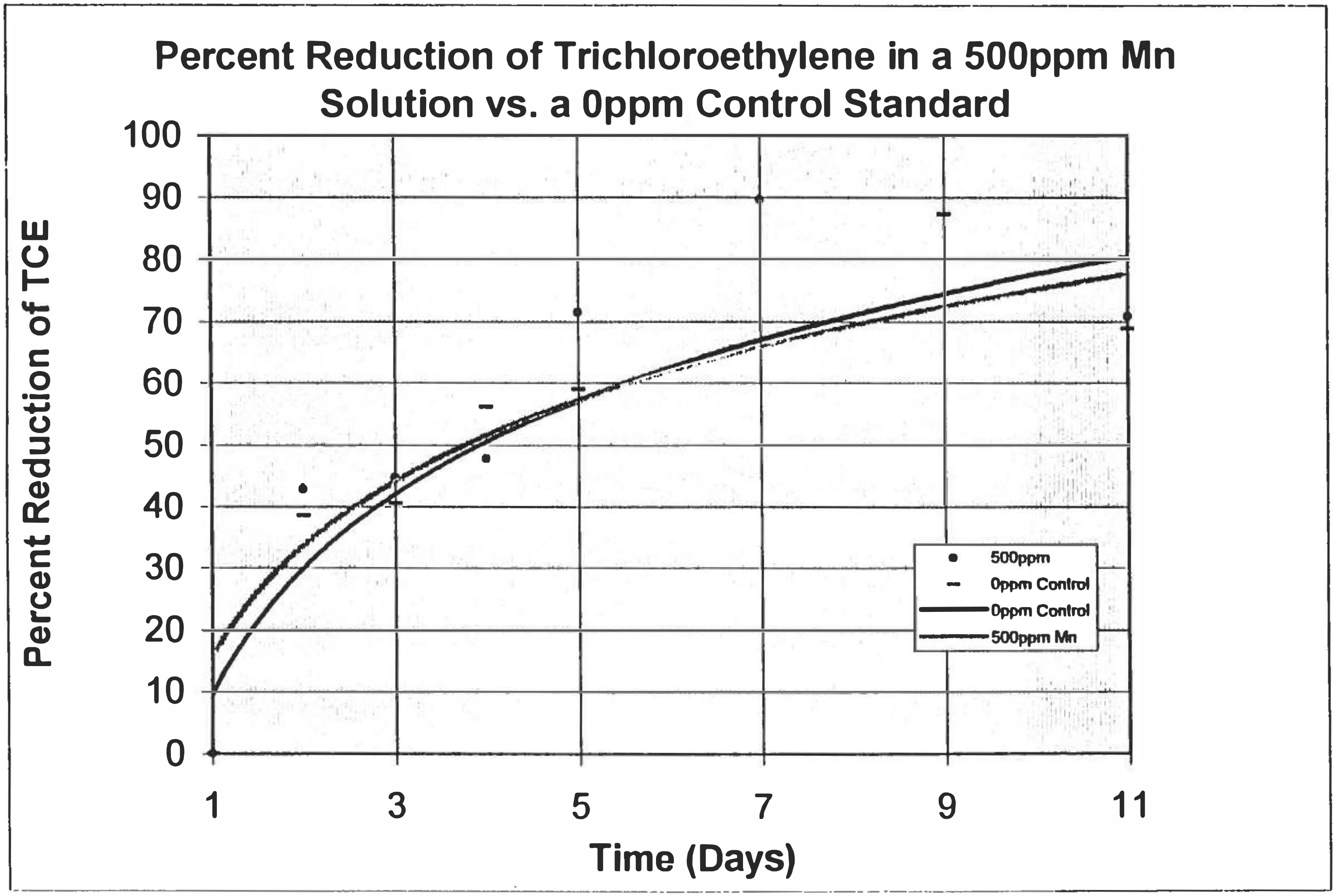

Percent Reduction of Trichloroethylene in a 80ppm Mn Solution vs. a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 80ppm
– 0ppm Control
0ppm Control
80ppm Mn

Figure 65



Percent Reduction of Trichloroethylene in a 500ppm Mn Solution vs. a 0ppm Control Standard

Figure 66

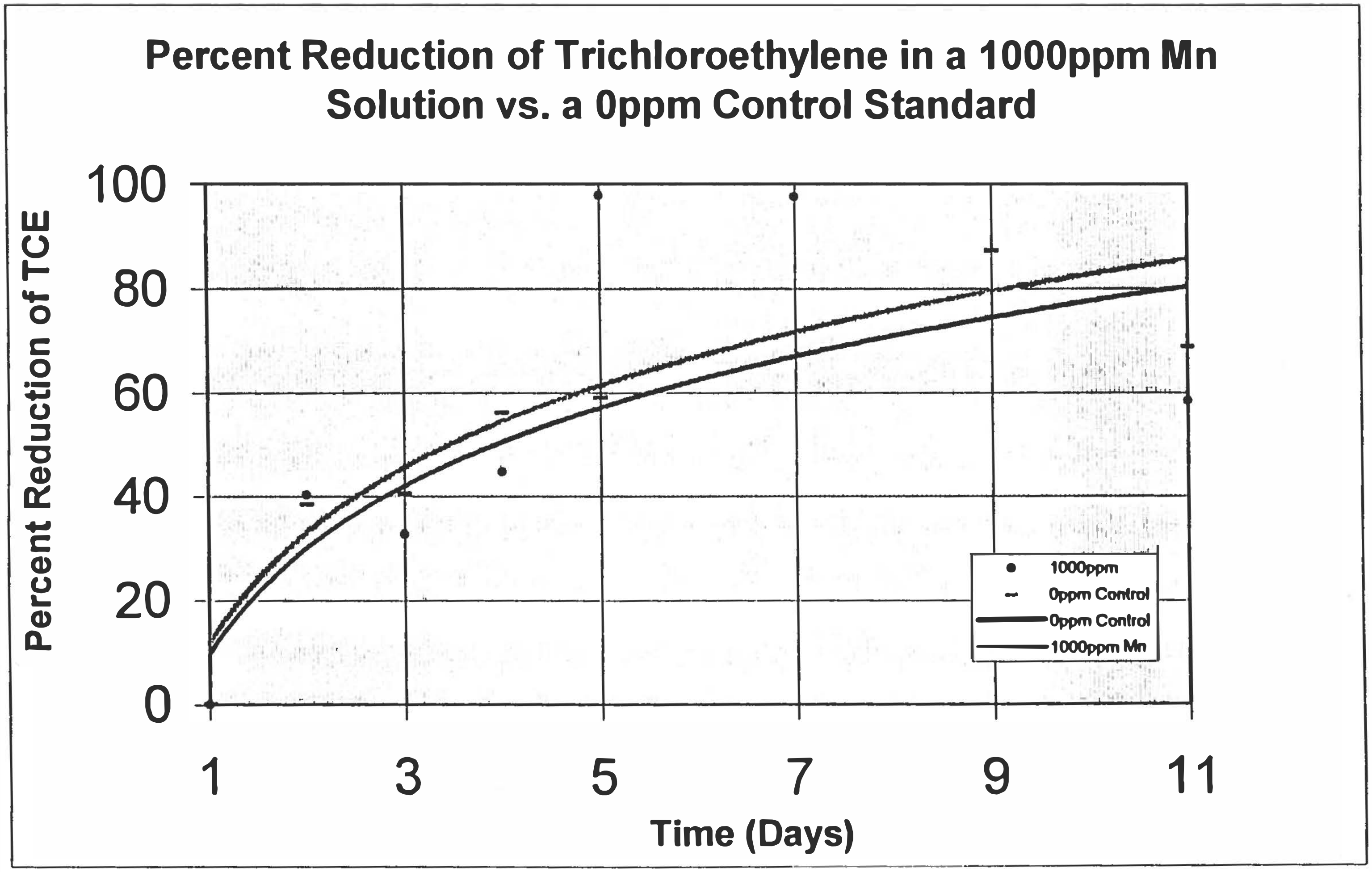

Percent Reduction of Trichloroethylene in a 1000ppm Mn Solution vs. a 0ppm Control Standard
Percent Reduction of TCE
100
80
60
40
20
0
1
3
5
7
9
11
Time (Days)
● 1000ppm
‒ 0ppm Control
0ppm Control
1000ppm Mn

Figure 67

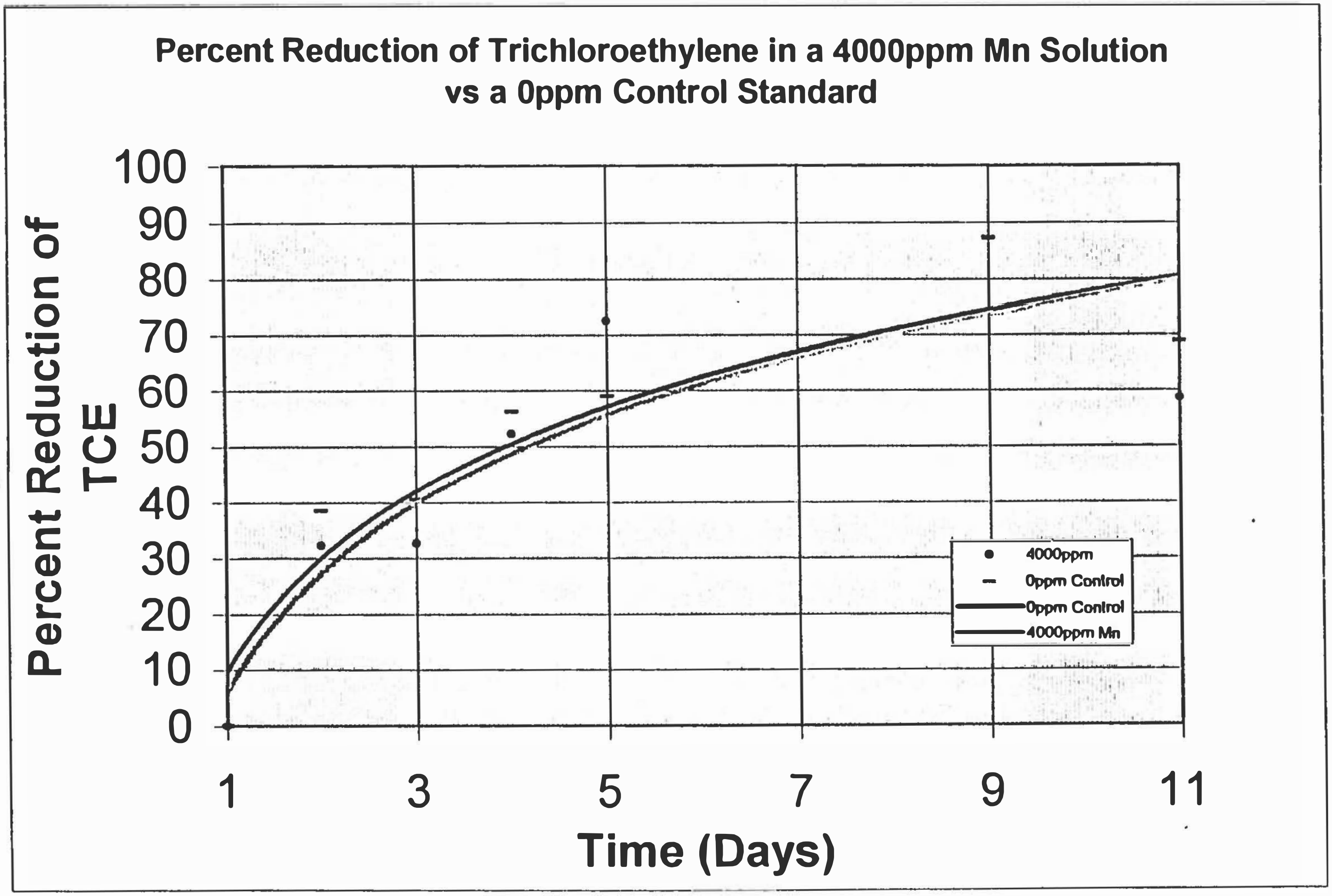

Percent Reduction of Trichloroethylene in a 4000ppm Mn Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
4000ppm
0ppm Control
0ppm Control
4000ppm Mn

Figure 68

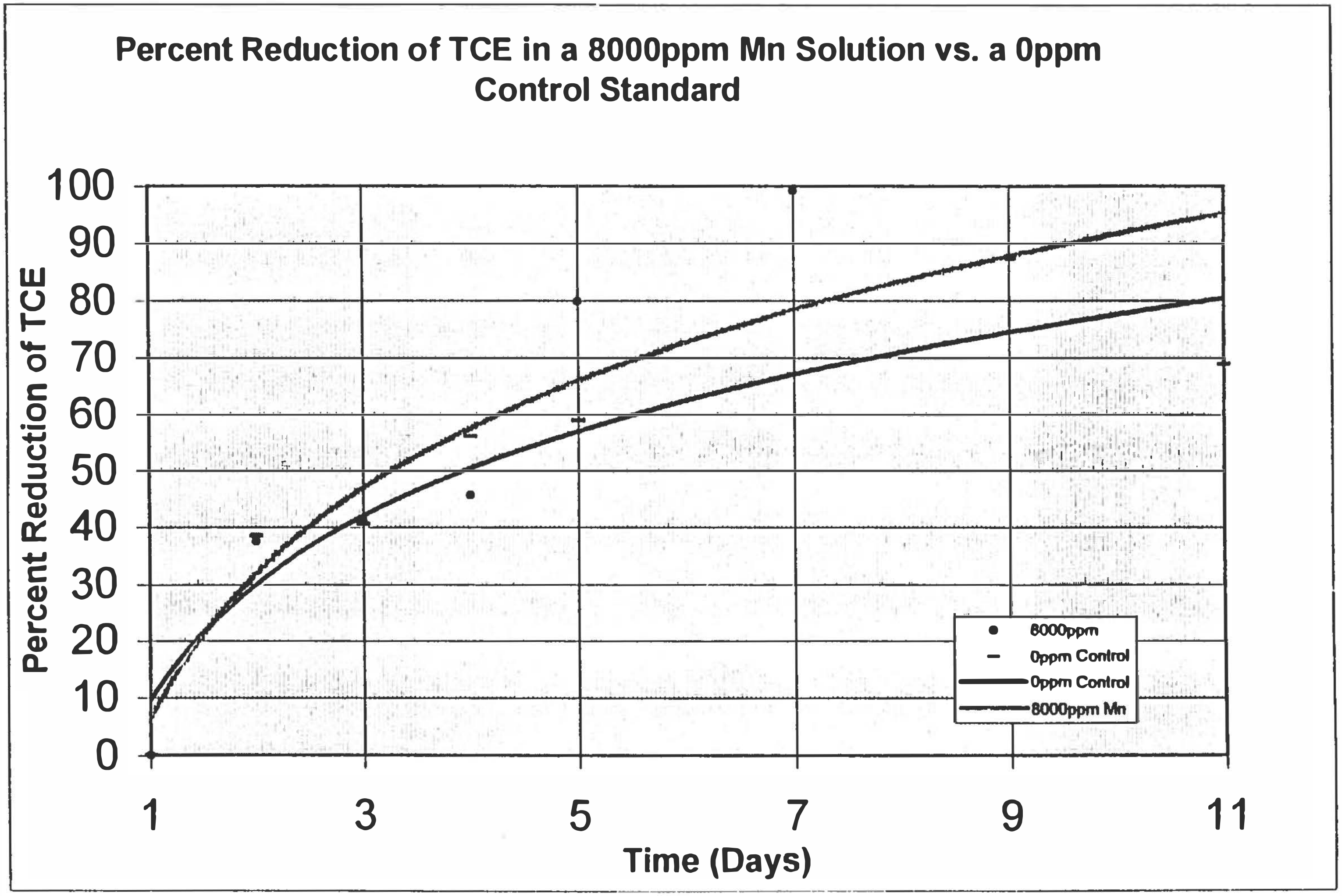

Percent Reduction of TCE in a 8000ppm Mn Solution vs. a 0ppm Control Standard

Figure 69

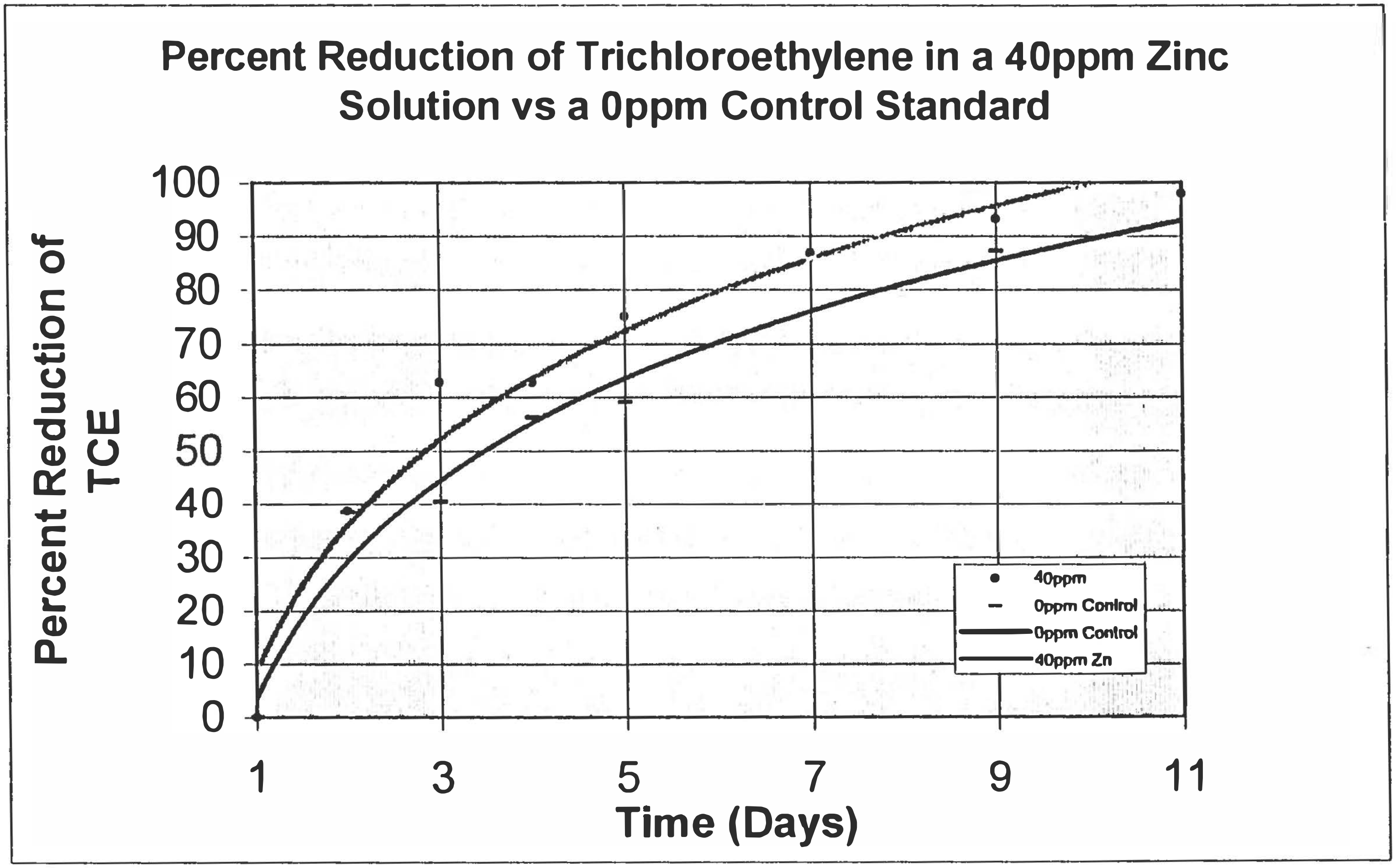

Percent Reduction of Trichloroethylene in a 40ppm Zinc Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 40ppm
– 0ppm Control
0ppm Control
40ppm Zn

Figure 70

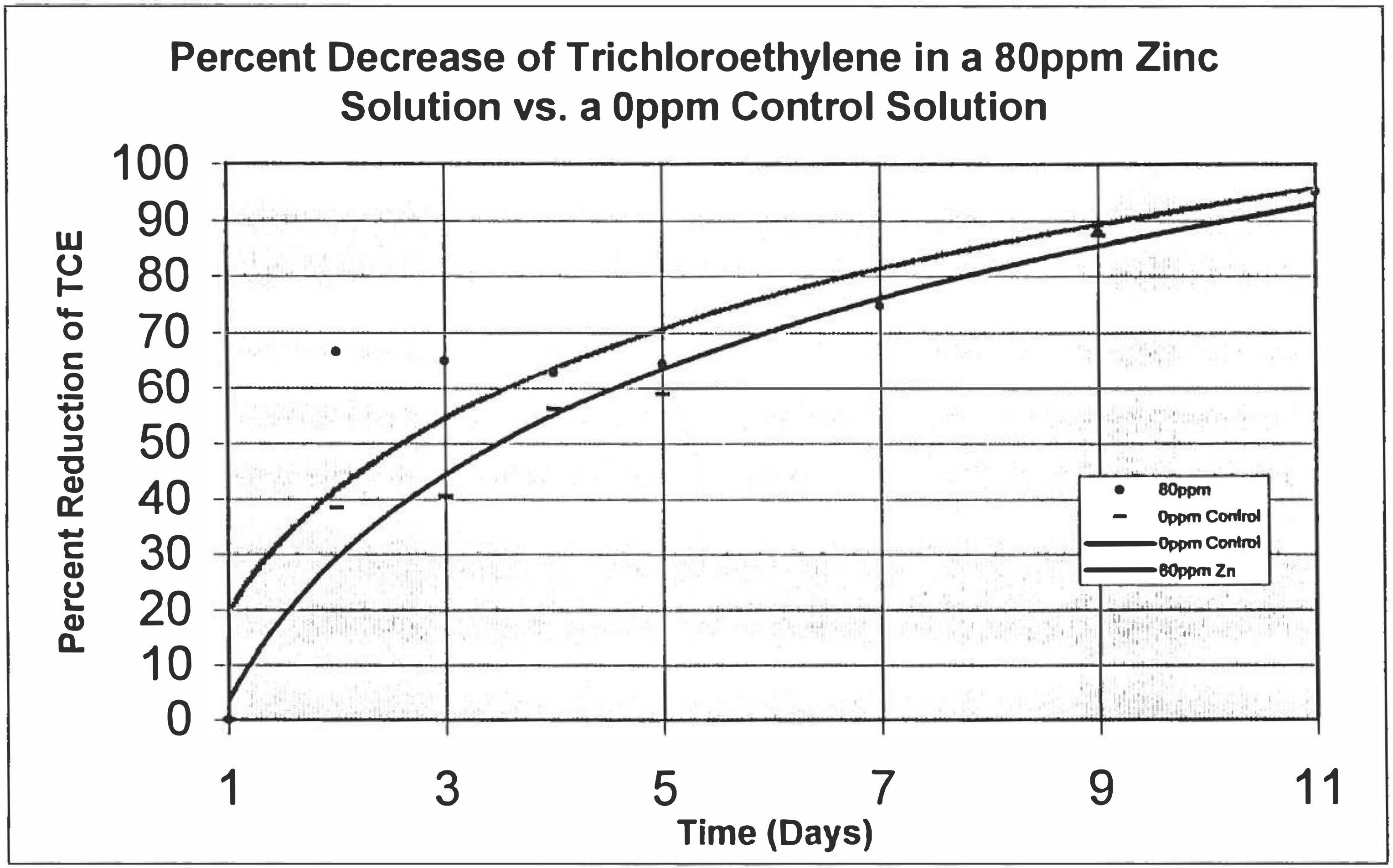

Percent Decrease of Trichloroethylene in a 80ppm Zinc Solution vs. a 0ppm Control Solution
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 80ppm
– 0ppm Control
0ppm Control
80ppm Zn

Figure 71

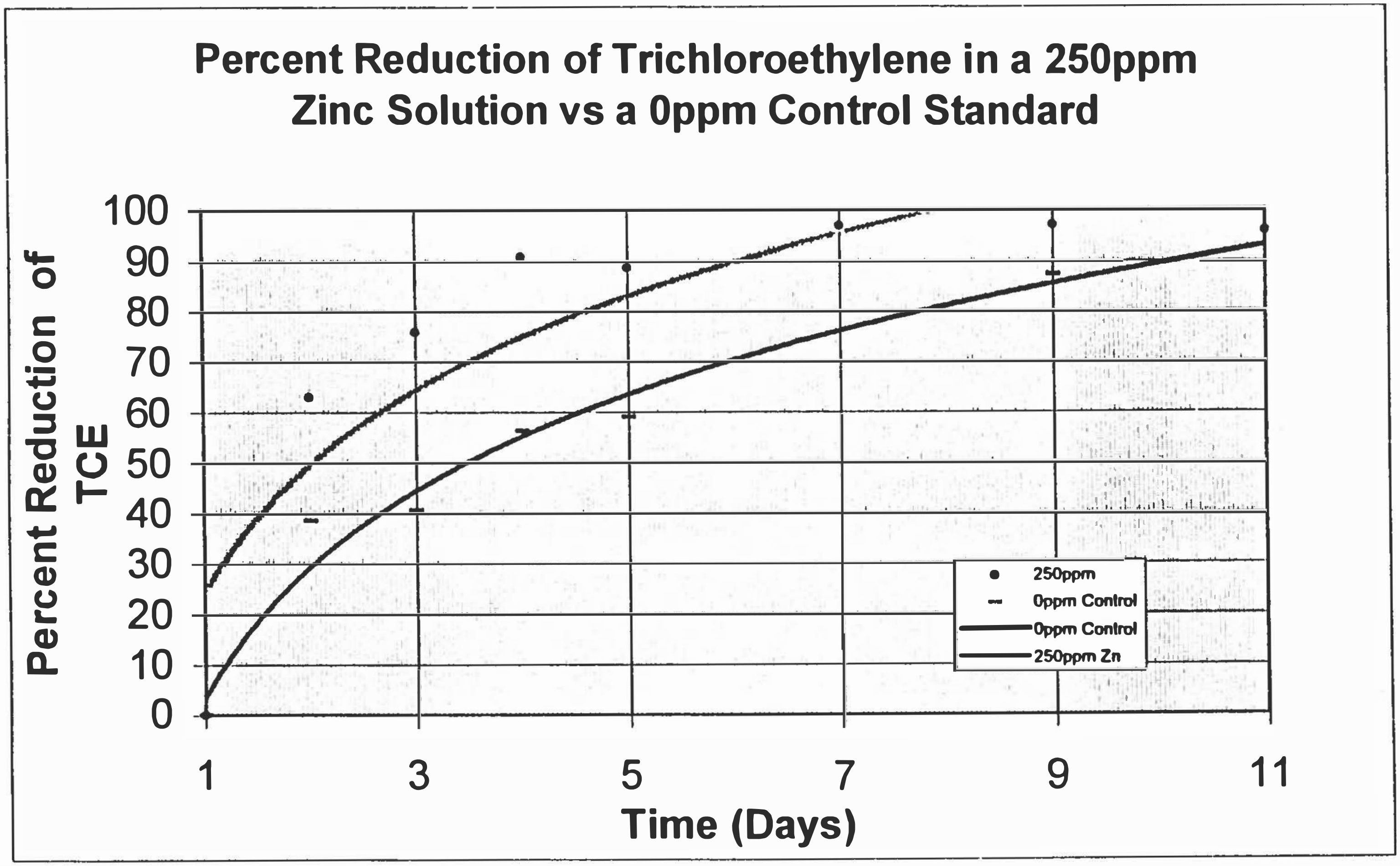

Percent Reduction of Trichloroethylene in a 250ppm Zinc Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 250ppm
- 0ppm Control
0ppm Control
250ppm Zn

Figure 72

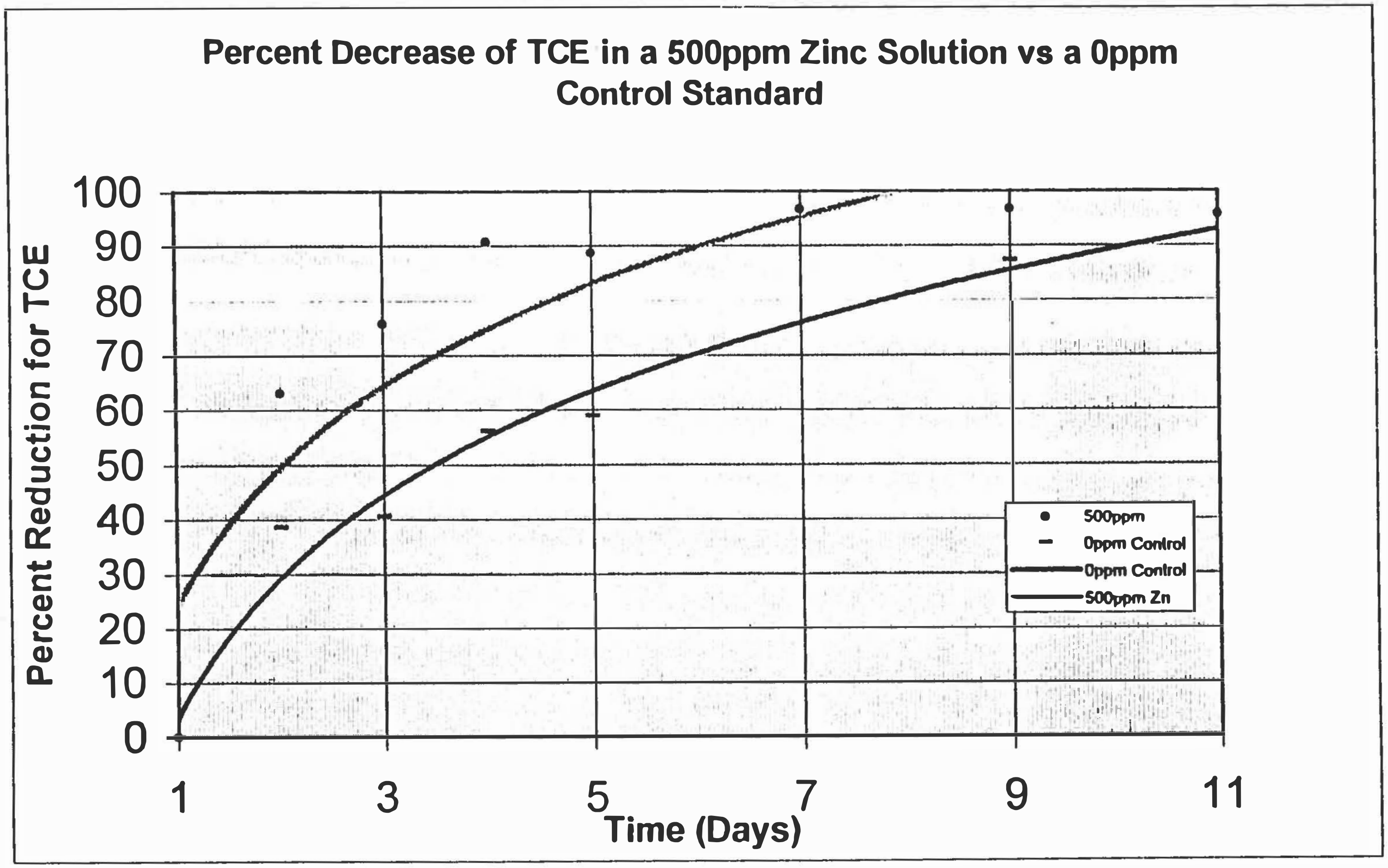

Percent Decrease of TCE in a 500ppm Zinc Solution vs a 0ppm Control Standard
Percent Reduction for TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
500ppm
0ppm Control
0ppm Control
500ppm Zn

Figure 73

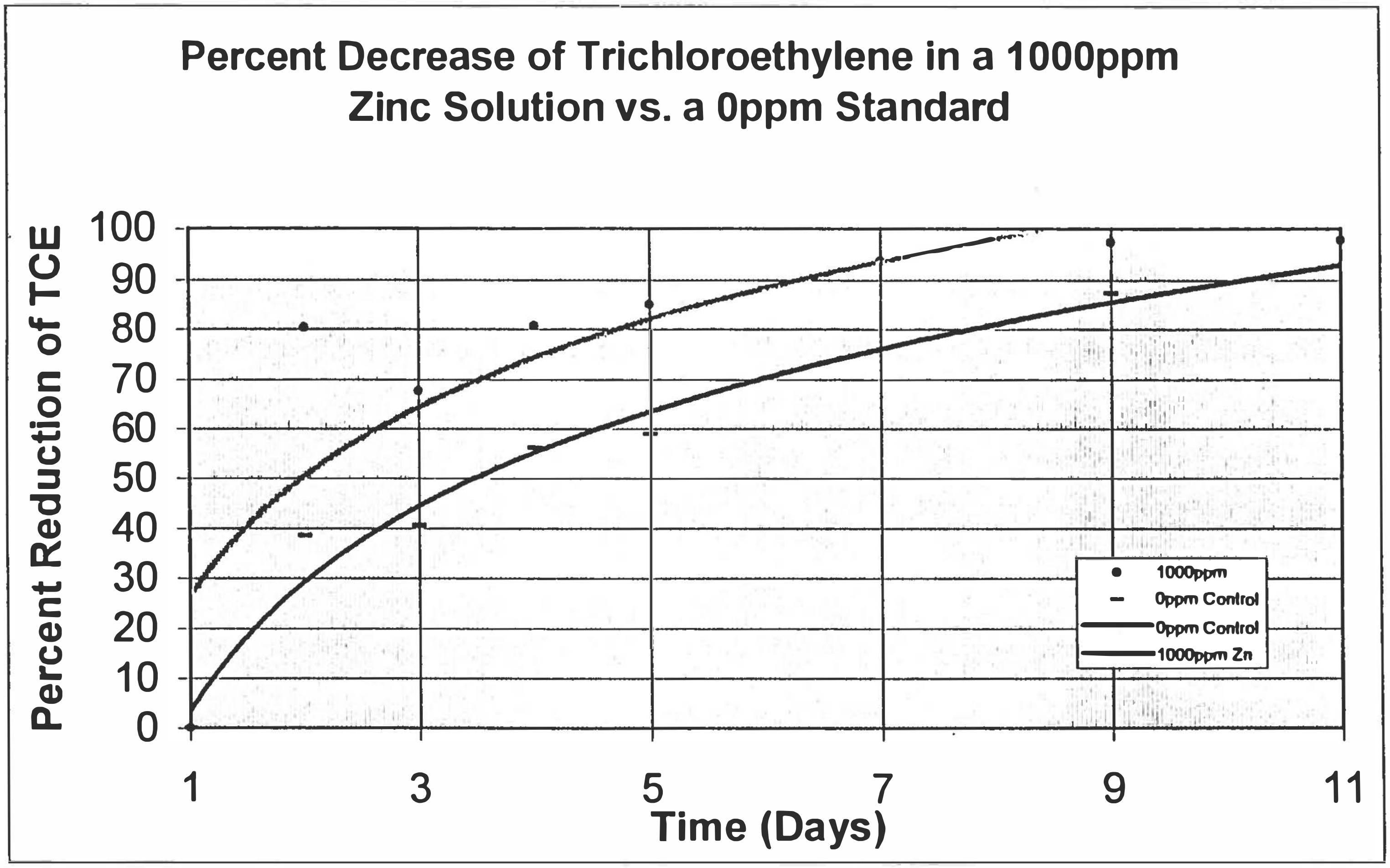

Percent Decrease of Trichloroethylene in a 1000ppm Zinc Solution vs. a 0ppm Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 1000ppm
– 0ppm Control
0ppm Control
1000ppm Zn

Figure 74

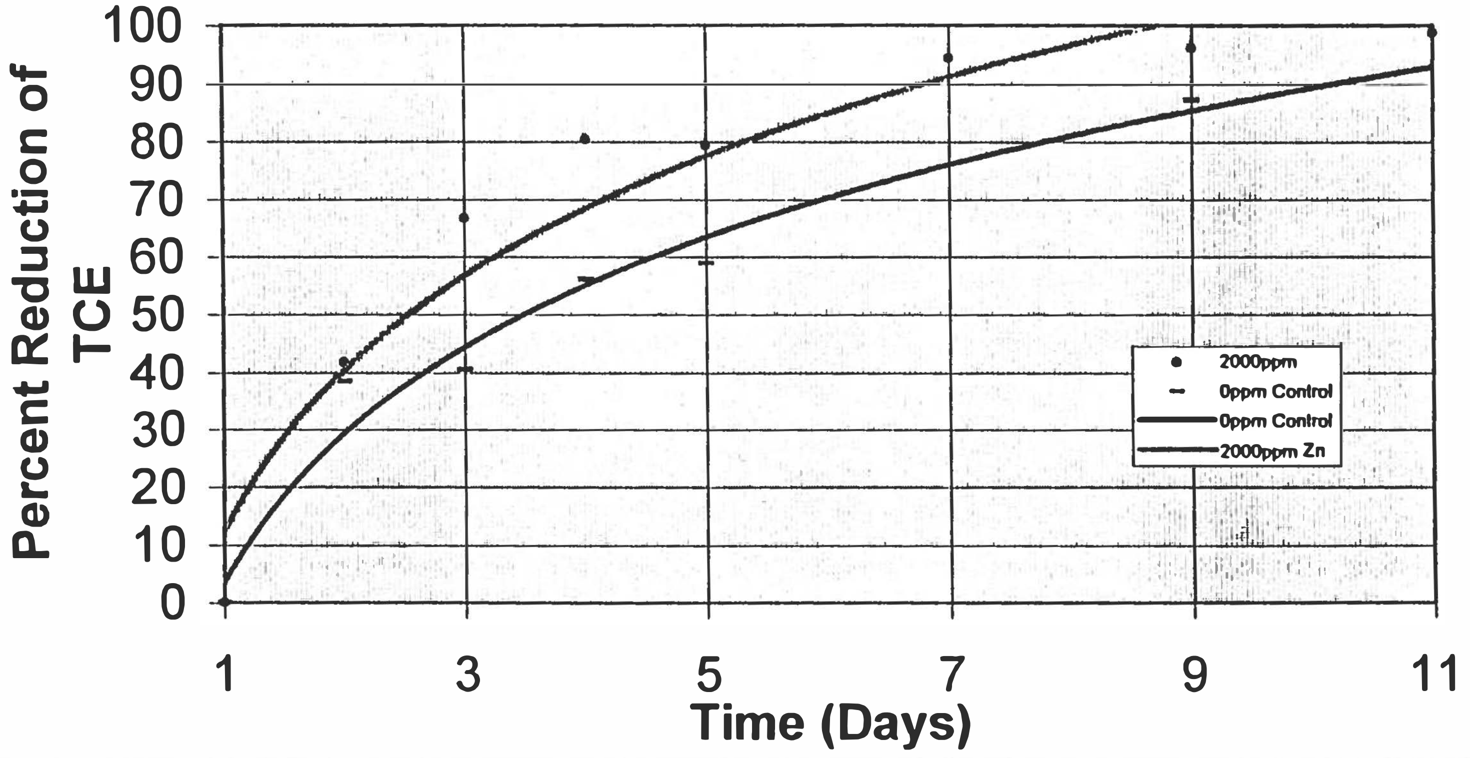

Percent Reduction of Trichloroethylene in a 2000ppm Zinc Solution vs. a 0ppm Control Standard

Figure 75

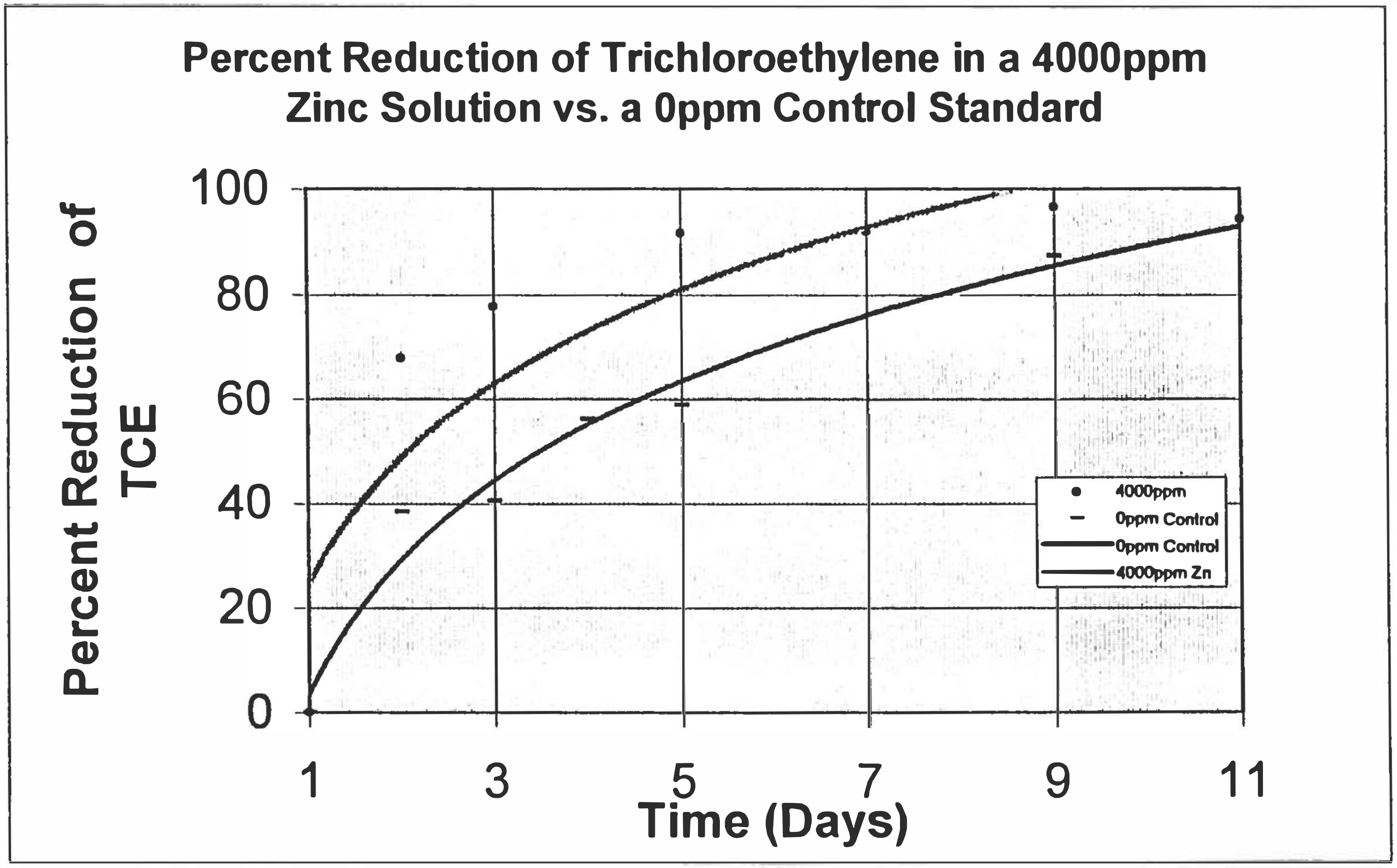

Percent Reduction of Trichloroethylene in a 4000ppm Zinc Solution vs. a 0ppm Control Standard
Percent Reduction of TCE
100
80
60
40
20
0
1
3
5
7
9
11
Time (Days)
● 4000ppm
– 0ppm Control
0ppm Control
4000ppm Zn

Figure 76

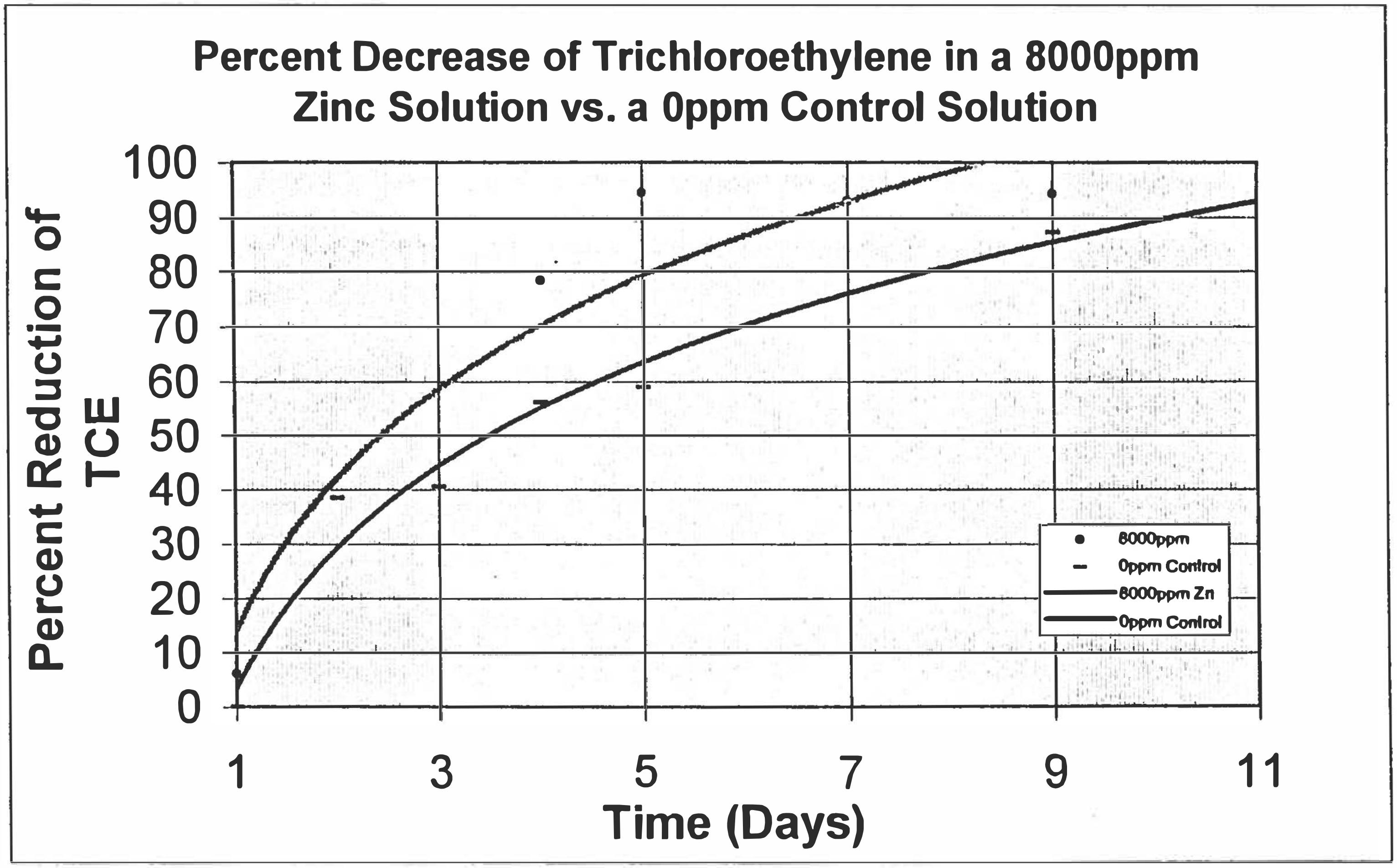

Percent Decrease of Trichloroethylene in a 8000ppm Zinc Solution vs. a 0ppm Control Solution
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 8000ppm
– 0ppm Control
8000ppm Zn
0ppm Control

Figure 77

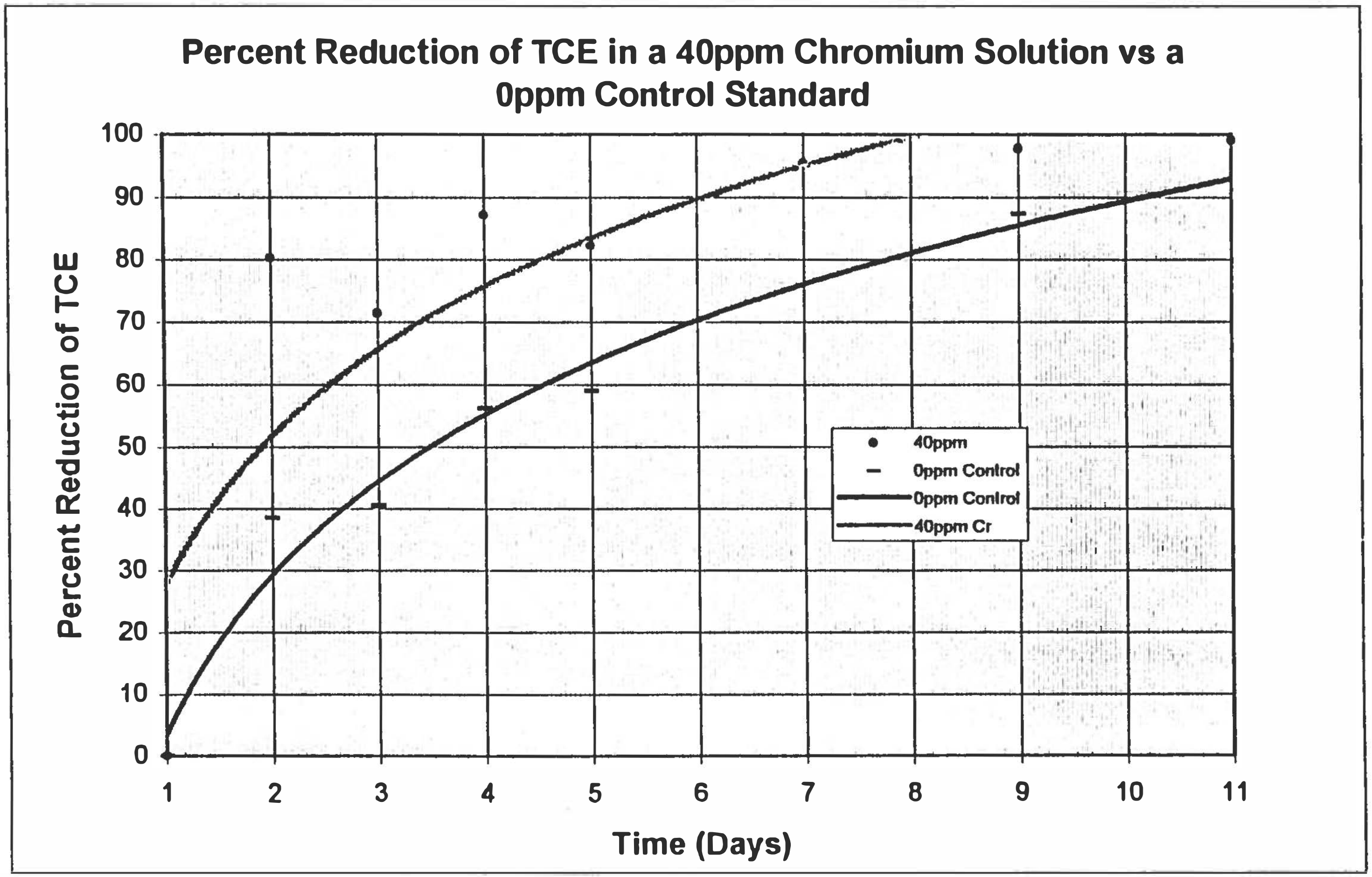

Percent Reduction of TCE in a 40ppm Chromium Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
Time (Days)
40ppm
0ppm Control
0ppm Control
40ppm Cr

Figure 78

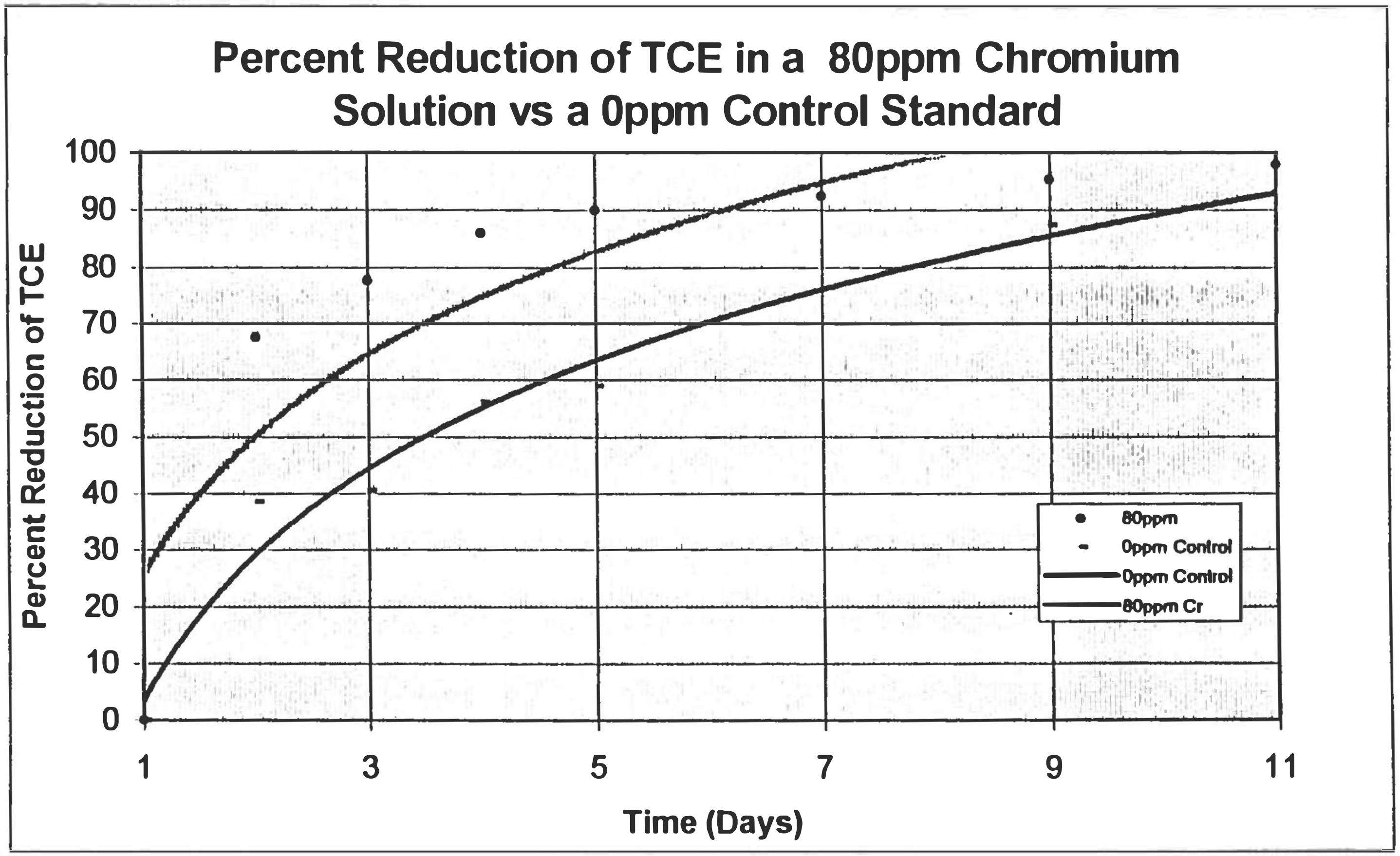

Percent Reduction of TCE in a 80ppm Chromium Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
90
80
70
60
50
40
30
20
10
0
1
3
5
7
9
11
Time (Days)
● 80ppm
- 0ppm Control
0ppm Control
80ppm Cr

Figure 79

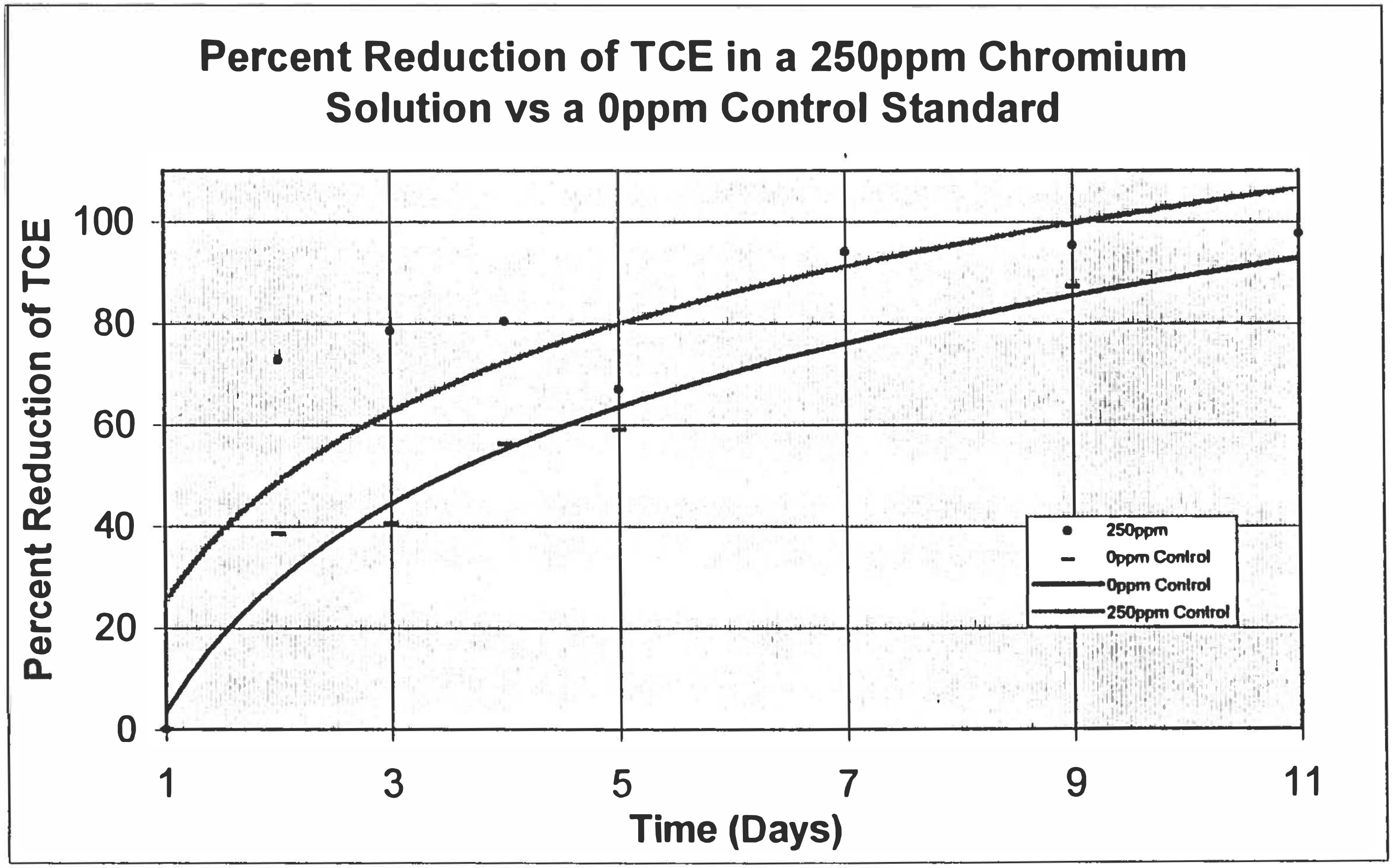

Percent Reduction of TCE in a 250ppm Chromium Solution vs a 0ppm Control Standard
Percent Reduction of TCE
0
20
40
60
80
100
1
3
5
7
9
11
Time (Days)
● 250ppm
– 0ppm Control
0ppm Control
250ppm Control

Figure 80

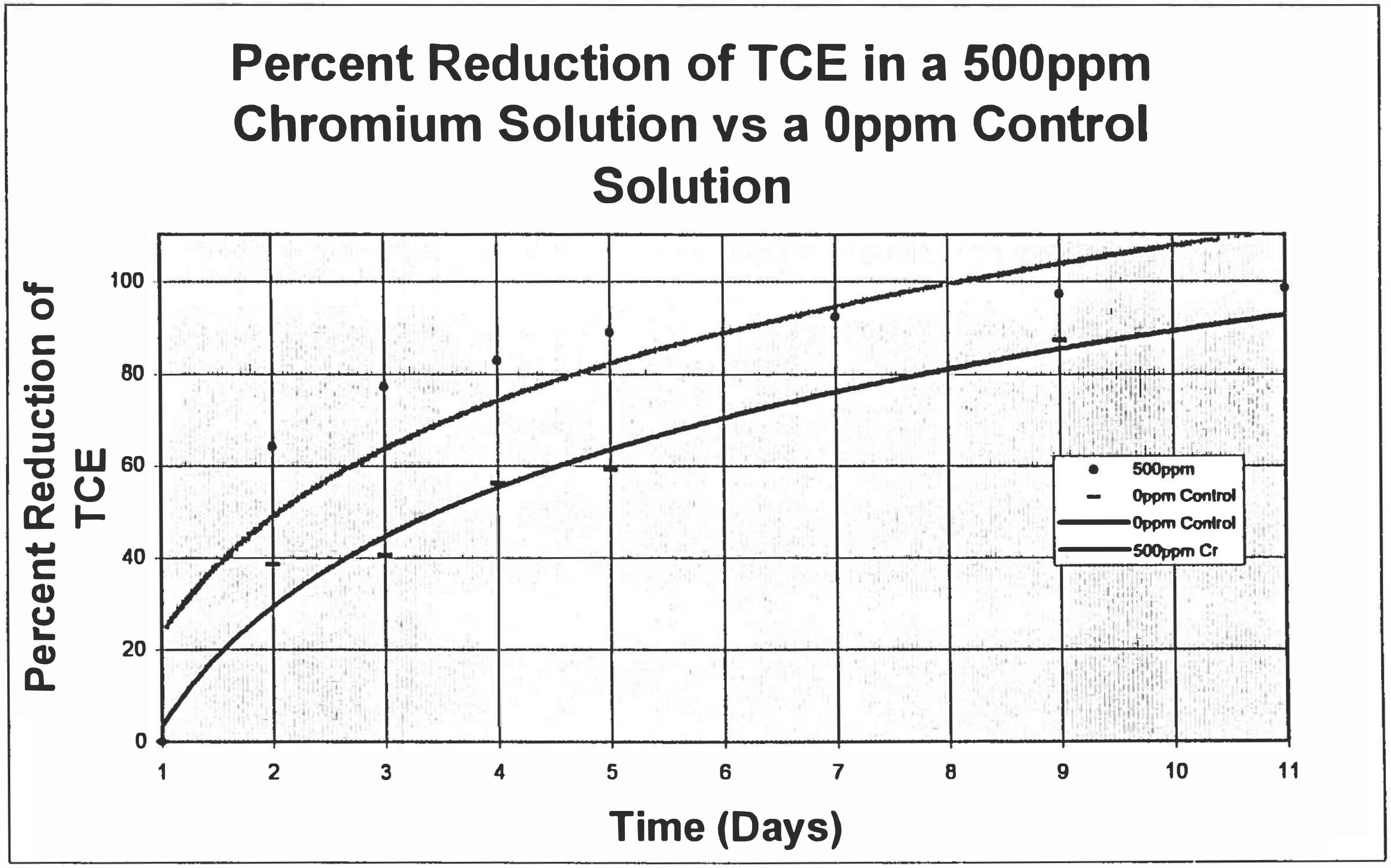

Percent Reduction of TCE in a 500ppm Chromium Solution vs a 0ppm Control Solution
Percent Reduction of TCE
0
20
40
60
80
100
1
2
3
4
5
6
7
8
9
10
11
Time (Days)
● 500ppm
▬ 0ppm Control
0ppm Control
500ppm Cr

Figure 81

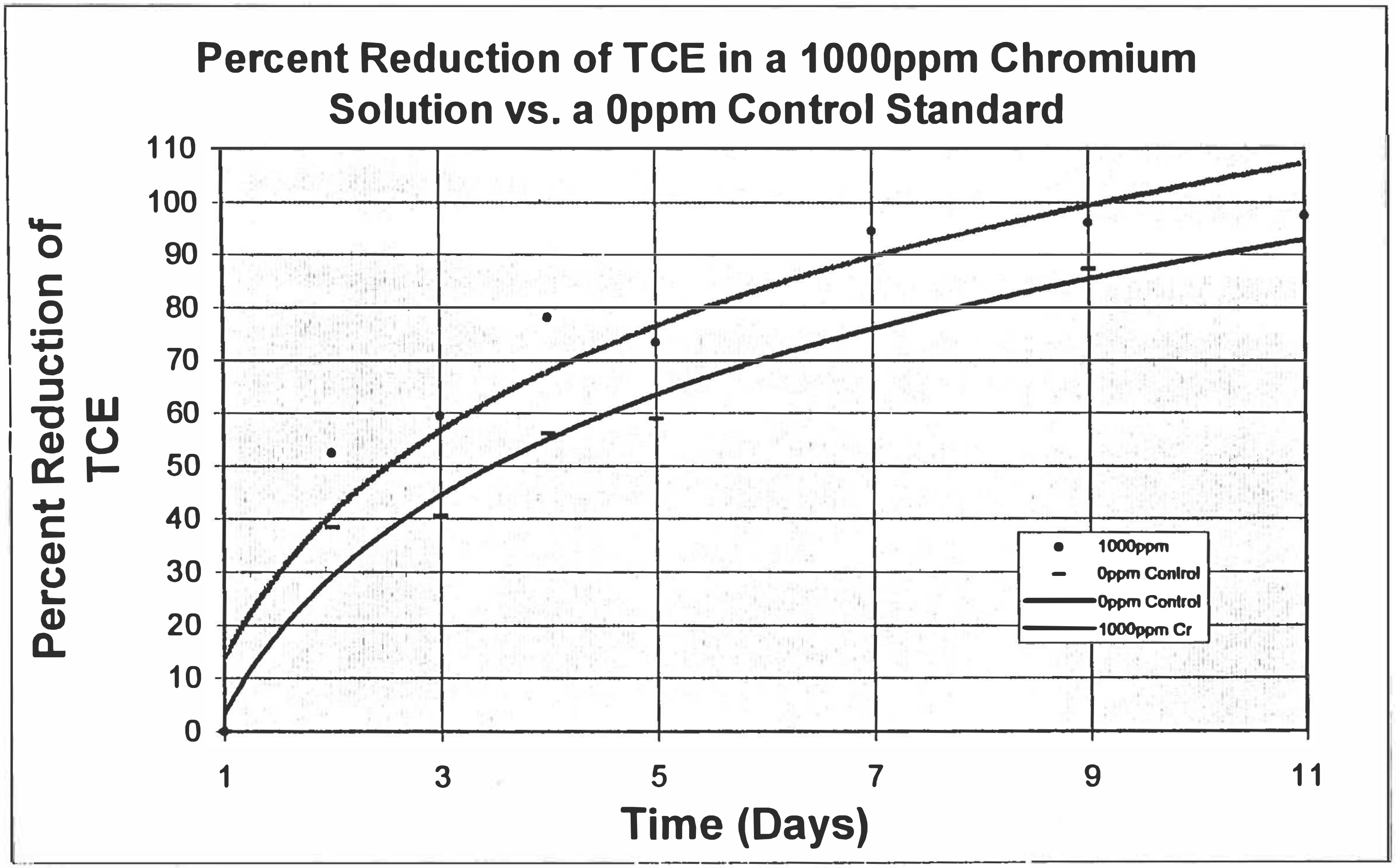

Percent Reduction of TCE in a 1000ppm Chromium Solution vs. a 0ppm Control Standard
Percent Reduction of TCE
0
10
20
30
40
50
60
70
80
90
100
110
Time (Days)
1
3
5
7
9
11
● 1000ppm
– 0ppm Control
0ppm Control
1000ppm Cr

Figure 82

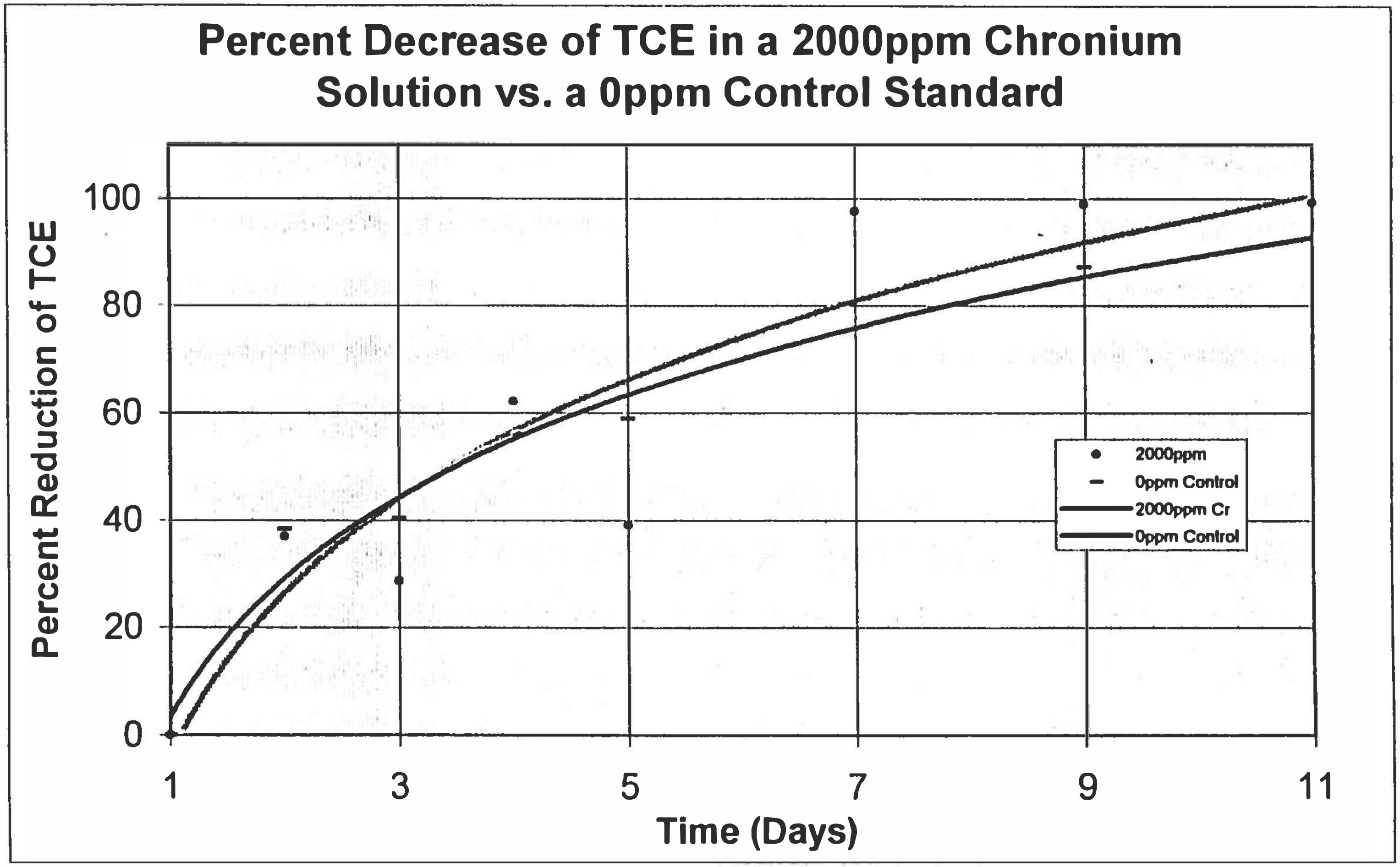

Percent Decrease of TCE in a 2000ppm Chronium Solution vs. a 0ppm Control Standard
Percent Reduction of TCE
0
20
40
60
80
100
1
3
5
7
9
11
Time (Days)
● 2000ppm
– 0ppm Control
2000ppm Cr
0ppm Control

Figure 83

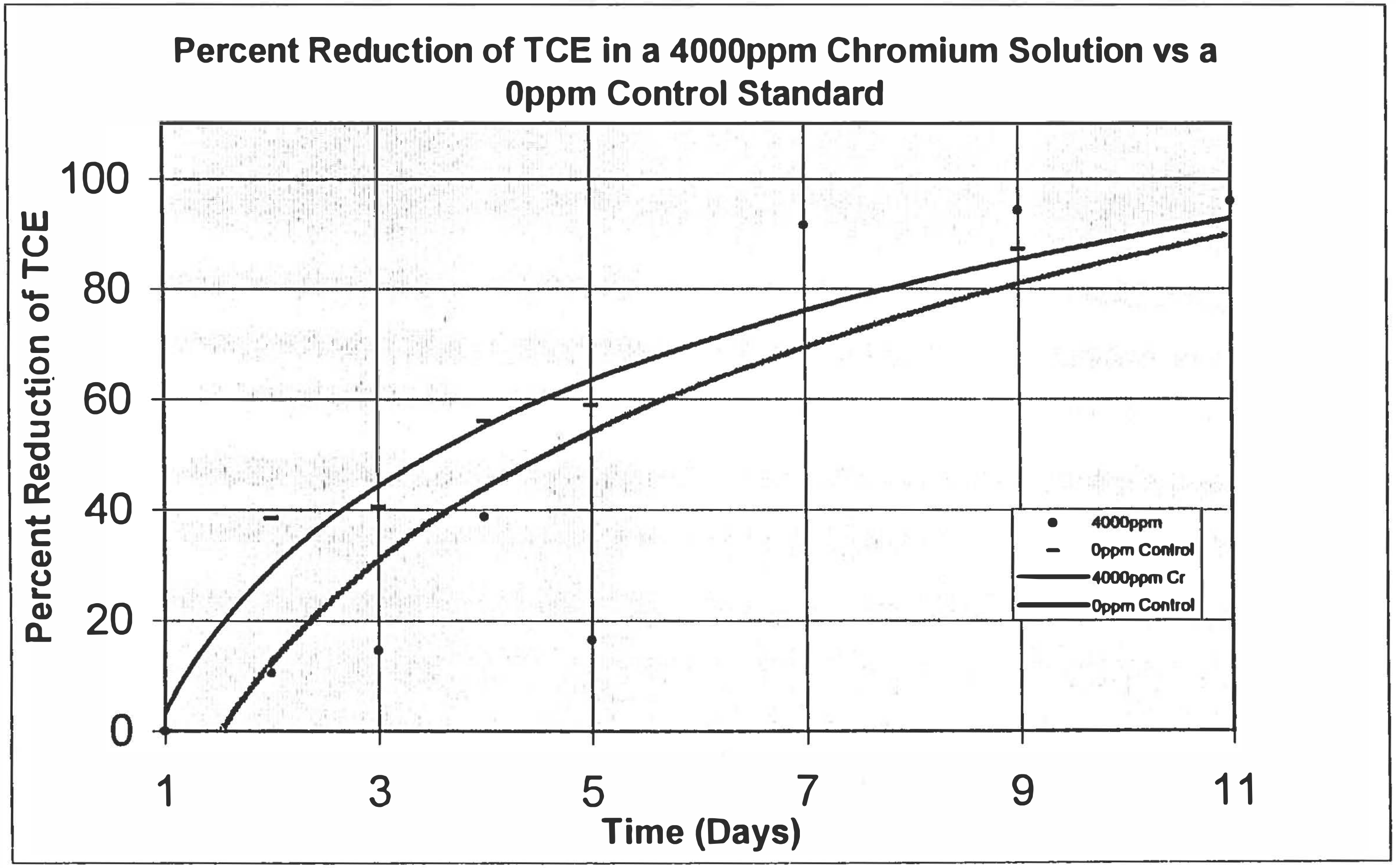
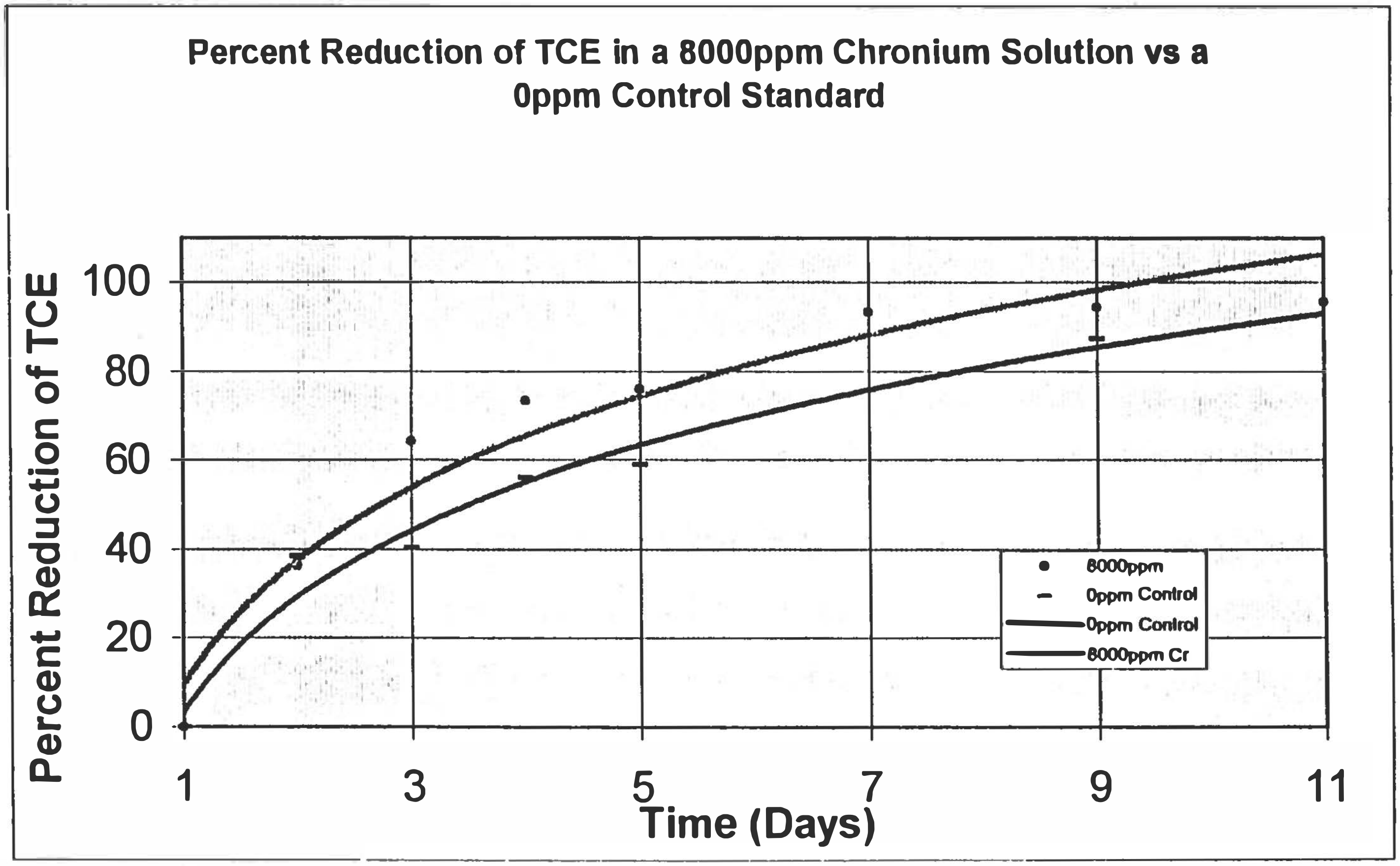

Percent Reduction of TCE in a 4000ppm Chromium Solution vs a 0ppm Control Standard
Percent Reduction of TCE
100
80
60
40
20
0
1
3
5
7
9
11
Time (Days)
● 4000ppm
– 0ppm Control
4000ppm Cr
0ppm Control

Figure 84


Percent Reduction of TCE in a 8000ppm Chronium Solution vs a 0ppm Control Standard
Percent Reduction of TCE
0
20
40
60
80
100
1
3
5
7
9
11
Time (Days)
● 8000ppm
– 0ppm Control
0ppm Control
8000ppm Cr

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