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PHOTOCATALYTIC DESTRUCTION OF CHLORINATED SOLVENTS WITH SOLAR ENERGY*

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ABSTRACT

Sandia National Laboratories and the Solar Energy Research Institute are developing a photocatalytic process to destroy organic contaminants in water. Tests with common water pollutants are being conducted at Sandia's Solar Thermal Test Facility using a near commercial-scale single-axis tracking parabolic trough system with glass pipe mounted at its focus. Experiments at this scale provide verification of laboratory studies and allow examination of design and operation issues at a real-life scale. The catalyst, titanium dioxide (TiO_2), is a harmless material found in paint, cosmetics and toothpaste. Experiments were conducted to determine the effect of key process parameters on destruction rates of two chlorinated organic compounds which are common water pollutants: trichloroethylene and trichloroethane. In this paper, we summarize the engineering-scale results of these experiments and analyses.

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BACKGROUND

Solar thermal hardware and systems have been under development at Sandia National Laboratories for the last 15 years to produce both electricity and thermal energy. The goal of that development work is to advance the engineering and scientific understanding of solar thermal technology. These developments have led to more reliable systems which are more efficient, have lower costs and have longer lifetimes. Sandia continues to develop central receiver, trough and dish systems.

Over the same period, photocatalytic processes have also been investigated extensively by international researchers [1-13]. Ollis [1] and Matthews [2] have shown that sunlight activated titanium dioxide catalyst can completely oxidize organic chemicals. In this process ultraviolet light is absorbed by the titanium dioxide and forms holes and electrons which interact with dissolve oxygen in the water to generate hydroxyl radicals and superoxide ions [4,5]. These species non-selectively oxidize the contaminants. Examples of organic compounds that can be destroyed by this process are chlorinated solvents, polychlorinated biphenyls (PCBs), dioxins, pesticides, and dyes. This process can completely mineralize these organics yielding only carbon dioxide, water, and dilute mineral acids (e.g., HCl) as the final oxidation products [1-10].

Because of stricter requirements on hazardous waste disposal, increased concern for the environment, and the need for innovative technologies to handle hazardous waste problems, we melded our expertise in solar concentrating hardware with an extensive literature base in photocatalysis and initiated a development program. This is a joint program between Sandia and the Solar Energy Research Institute (SERI) sponsored by the U.S Department of Energy as a part of the U.S. Solar Detoxification of Hazardous Waste Initiative. SERI has responsibility for managing the program and performing much of the fundamental research. Sandia has responsibility for conducting experiments on and developing components for engineering-scale systems. The objective of this effort is to develop a solar-drive, photocatalytic process to destroy contaminants in water.

Previous experiments with our trough system have demonstrated destruction of salicylic acid and trichloroethylene using concentrated sunlight reflected from a 465 m^2 trough system, shown in Figure 1 [14-16]. In this process, water containing low concentrations (ppm range) of contaminants and the suspended semiconductor photocatalyst, titanium dioxide (TiO_2), flows through a glass pipe reactor mounted at the focus of the trough. An advantage of this process over conventional treatment methods such as air stripping or carbon adsorption is that the contaminants are completely destroyed rather than transferred from one phase or medium to another.

This paper reports on a continuation of our work, focusing on establishing the effects of process variables such as the variation of reaction rates with time of day and the rates for a two-component system. These results were used to determine daily and seasonal variations in processing rates expected in an actual system. The goal of this work is to field test and demonstrate the technology at an industrial or remediation site by late 1991.

SYSTEMS AND METHODS

Engineering Scale Parabolic Trough

Photocatalytic experiments were conducted with a system consisting of a series of six parabolic troughs. These troughs were originally installed in the 1980's to perform qualification testing and demonstrate the potential of using solar energy to produce industrial heat or steam for electricity generation. We modified the system by removing the original black receiver pipes and convective covers and installing 38 mm (1.5 in) diameter borosilicate glass pipes in their place to serve as a photoreactor. The troughs have 3M FEK-244 aluminized acrylic film that has a reflectivity of approximately 70% in the near ultraviolet (300-400 nm). These troughs concentrate sunlight about fifty times. The system can be operated in either recirculating (batch) or single pass (plug flow) modes at flow rates up to 100 liters per minute (26 gallons per minute) with two 3800 liter (1000 gallon) tanks used for reservoirs of test solution and one 3800 liter (1000 gallon) tank for holding clean water. Figure 2 is a schematic of this system. The residence time for one pass is about 2.5 minutes at the maximum flow rate. The total reactor length is 218 m (720 ft) and the total aperture area of the trough is 465 m^2. Samples can be withdrawn at each 36.4-m (120 ft) section and from the tanks.

Materials

The TiO_2 photocatalyst (Degussa P-25, primarily anatase) had an average particle size of 30 nm. Surface analysis determined the surface area to be 54 m^2/gram with the majority of the area being provided by meso-pores (large pores 20 - 500 angstroms). In all the experiments reported in this paper, a catalyst loading of 0.1% was used. In previous experiments, this value was determined to be the optimal loading, yielding the highest reaction rate for destruction of salicylic acid [15]. Other researchers have seen the same result with other compounds [7,11]. We used Fisher reagent-grade trichloroethylene (TCE) and trichloroethane (TCA). Deionized water was used in all experiments reported.

Analysis

Analyses of trichloroethylene and trichloroethane concentrations were performed with a Hewlett-Packard Model-5890 gas chromatograph equipped with an automated headspace sampler (HP-19395A), tandem PID/ELCD detectors (IO Corporation), and a HP 530 series capillary column coated with an HP-1 crosslinked methyl silicone gum (30 m x 0.53 mm x 2.65 μm films). The detection limit for TCE and TCA is approximately 5 parts per billion (ppb).

EXPERIMENTAL RESULTS

Summary of Previous Results

Previous tests have quantified the effects of added hydrogen peroxide and initial contaminant concentration and are briefly summarized here. Hydrogen peroxide used in conjunction with titanium dioxide tended to increase the reaction rate for salicylic acid [15]. For trichloroethylene, hydrogen peroxide with titanium dioxide changed the kinetic behavior of the process and reduced the amount of time required to attain a given level of destruction [16]. Tanaka, et al. have also seen beneficial effects of added hydrogen peroxide on destruction of trichloroethylene [12].

In another series of experiments, the initial concentration of TCE was varied from approximately 120 to 5000 ppb to assess its effect on the reaction rate. A catalyst loading of 0.1 wt% was used. Results from these tests are shown in Figure 3. No intermediates were detected.

The curves showed a change in the order of the reaction from zero-order to first order. This transition has also been seen by other researchers [13] and can be described by Langmuir-Hinshelwood type kinetics of the form:

$$\ln(C/C_o) + K(C/C_o - 1) = -kKt$$

which is an implicit function of concentration, C, and represents a sum of zero- and first-order terms. All the data in Figure 3 can be described by this equation using the same two parameters: k, K [16]. Another interesting result of this data is that for every test in the series, the trichloroethylene was destroyed below 5 parts per billion before exiting the trough system.

Destruction Rates at Different Times of the Day

A number of experiments were conducted at different times during the day to assess the effect of intensity on the destruction rate of trichloroethylene. For these experiments we

operated the trough at four times during the day under similar conditions of catalyst loading (0.1 wt%) and initial concentration (approximately 6000 ppb). As shown in Figure 4, the destruction rate increases towards solar noon. This effect can be attributed to two factors: 1) the variation in ultraviolet radiation with air-mass and thus solar position and 2) the change in effective aperture area and optical efficiency with incident angle. By using spectral-directional optical properties of the reflective material and the Pyrex glass along with measurement of the direct normal insolation, we were able to calculate the ultraviolet intensity on the glass pipe reactor and correlate it to the destruction efficiency. Although data from the literature indicate reaction rates varied with the intensity to the 0.5 power [21], we found our data could be described more closely with a linear rather than a square root relation between the residence time required to achieve 95% destruction and the intensity. A statistical fit to the data yielded a power function between residence time and intensity with an exponent of -0.84.

Processing Rates for Destruction of TCE with Time of Day and Season

As ultraviolet radiation enters the atmosphere it is absorbed and scattered by air molecules, water vapor and liquid droplets and aerosols. Measurements have been made of the global horizontal and direct normal components of terrestrial ultraviolet radiation and correlations developed to characterize the UV resource variation with atmospheric conditions [17-19]. By using these models to describe variation of the terrestrial UV radiation with air mass, we were able to calculate processing rates at different times of the day and seasons taking into account measured kinetics, the incident angle, and optical properties of the reflective material of the trough and glass piping. Processing rates for a 1000 m^2 trough system having a 2.1 m aperture and 38 mm I.D. glass reactor are shown in Figure 5 as a function of time of day. These curves were calculated for clear-sky conditions (no clouds). The processing rate is less during the early morning and late afternoon than at solar noon because the sun is lower and the available ultraviolet is reduced due to Rayleigh scattering and absorption.

Integrating the curves in Figure 5 between sunrise and sunset yields a daily processing rate. Using Typical Meteorological Year (TMY) data for Albuquerque, New Mexico [20], the processing rate for clear-sky conditions was scaled to estimate daily processing rates under real-life solar conditions. These results are plotted in Figure 6.

By averaging the daily values over the year, a yearly average-daily processing rate can be estimated. This calculation was done for seven location across the United States: Albuquerque, NM, Denver, CO. Oakland, CA, Wilmington, DE, Miami, FL, El Paso, TX, and Juneau, AL and are shown in Figure 7. As can be seen, the highest processing rates occur in the southwest where there is high solar insolation. Although lower rates occur at

lower insolation areas such as on the east coast and in the northern part of the country, it is important to note that the process can be carried out in all regions of the country.

Destruction of Trichloroethane (TCA) and Trichloroethylene (TCE)

Both TCA and TCE are chlorinated solvents used in industry and tend to appear as contaminants in ground water. The major difference between these compounds is that TCA is alphatic, having only single C-C bonds and therefore is more difficult to break down whereas TCE, which contains a more reactive double bond, is easier to destroy.

In addition to the inherent differences in the structures of TCA and TCE and the effect of these differences on reaction rates, there was concern that the presence of one compound may interfere with the destruction of another compound. To quantify these differences in reaction rates, three experiments were conducted with trichloroethane (TCA) and trichloroethylene (TCE): TCA alone, TCE alone, and a mixture of the two. A catalyst loading of 0.1 wt% was used. Figure 8 demonstrates the results. The squares represent TCA and the triangles TCE. The hollow symbols represent the cases when the solution contain only one compound, the solid symbols represent the case when solution contained a mixture of the two compounds.

The TCA was oxidized much slower than the TCE due to its alphatic molecular structure. In addition, the rate of destruction of TCE was the same whether TCA was present or not. The same holds true for the destruction of TCA whether TCE was present or not. There is essentially no interference in destruction of one compound by the other compound at the concentrations tested.

CONCLUSION

We have examined the effect of intensity on the destruction of TCE by measuring the destruction rate at different times in the day. We used these measurements and combined them with models of the variation of ultraviolet with air mass along with TMY data for a number of sites to estimate processing rates for solar detoxification systems. Processing rates may be high enough in regions of high solar insolation (e.g. in the southwestern Unites States) to be practical for treating large volumes of contaminated water. We also did a series of experiments to measure the reaction rate of TCA alone and in the presence of TCE. The rate of destruction of TCA was slower than the rate for TCE implying that the design and size of a system could be governed by the component with the slowest reaction rate. We found that the presence of one compound did not interfere with destruction of the other component.

SERI and Sandia are currently planning a field demonstration of the solar detoxification process at a remediation or industrial site. The demonstration could occur by late 1991. We plan to address a number of additional issues before this process is field tested. At Sandia we will evaluate destruction rates for other common groundwater pollutants and various combinations of them. The catalyst activity lifetime will be determined under various ion concentrations. A control system will be developed to adjust the flow rate and assure the required effluent concentration is achieved. Methods are being developed to immobilize the catalyst (eliminating the suspension and removal of the catalyst particles) and to mount the catalyst support in the glass reactor pipe. Catalyst supports are being screened at SERI and the most promising support will be tested in Sandia's full-scale trough system.

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Figure 1. Photograph of the 465 m^2 trough system located at Sandia National Laboratories in Albuquerque, NM used to perform photocatalytic experiments. The trough measures 218 m long by 2.1 m wide and uses a 38 mm I.D. borosilicate glass pipe.

Figure 2. Schematic of the large trough system. The system can operate at rates up to 100 liters per minute (25 gallons per minute). Incident sunlight is concentrated about 50 times.

Figure 3. Destruction of TCE at various initial concentrations with 0.1% TiO_2. Each symbol represents a point between trough sections.

Figure 4. Measured destruction of trichloroethylene at four times during the day. A catalyst loading of 0.1 wt% was used. The initial concentration was approximately 6000 ppb.

Figure 5. Calculated processing rate for 95% TCE destruction at various times of the day. Processing rates are lower in the morning and evening than at solar noon because the optical efficiency and ultraviolet intensity are lower.

Figure 6. Daily processing rates for TCE destruction under cloudless conditions and implementing TMY for Albuquerque, NM.

Figure 7. Yearly-averaged daily processing rate for TCE destruction at seven U.S. locations. The highest rates occur in the southwest where there is the greatest insolation.

Figure 8. Destruction of trichloroethane and trichloroethylene. The squares represent TCA and the triangles TCE. The hollow symbols represent destruction when each compound is oxidized alone and the solid symbols are a mixture of the two.

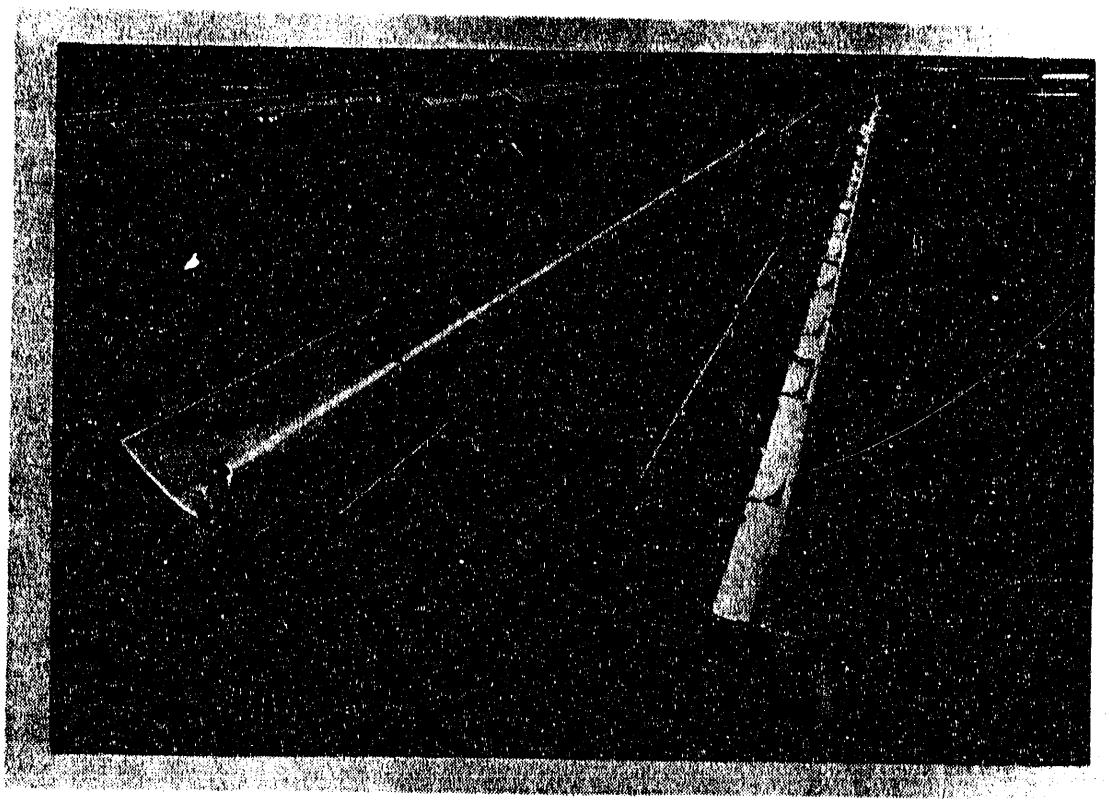

Fig 1.

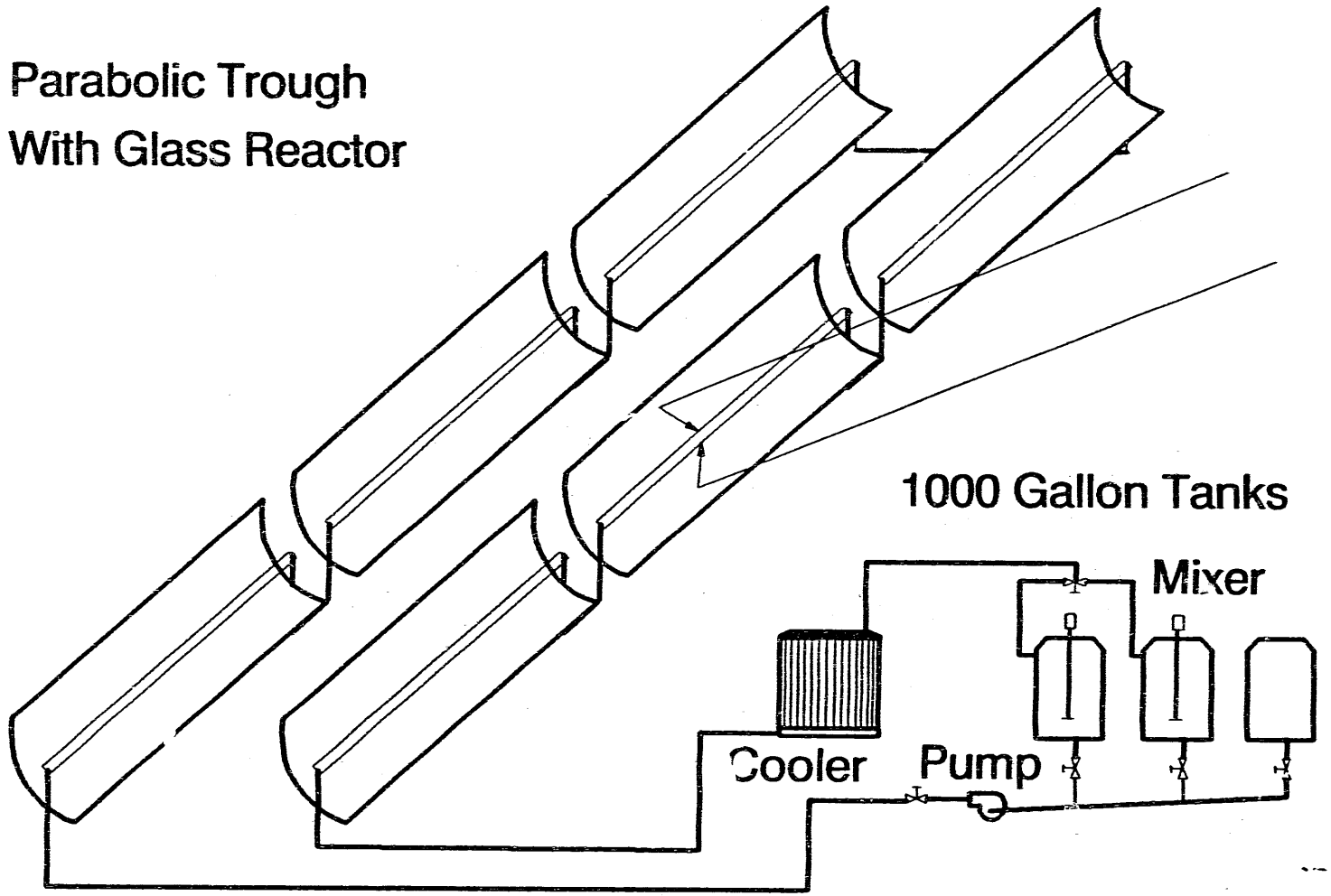

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Fig 2

TCE Destruction at Various Initial Concentrations

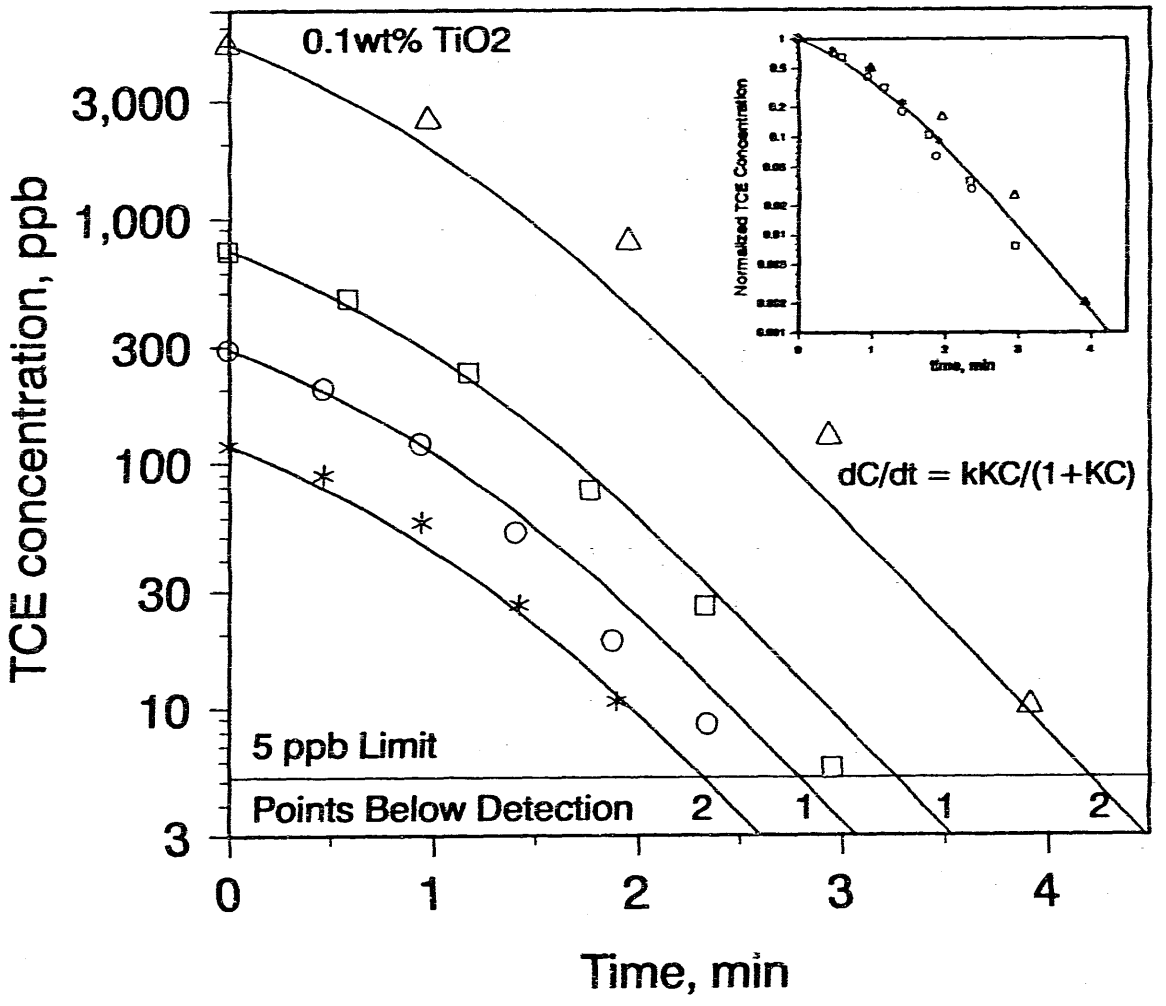

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Fig 3

Destruction of TCE At Various Times of The Day

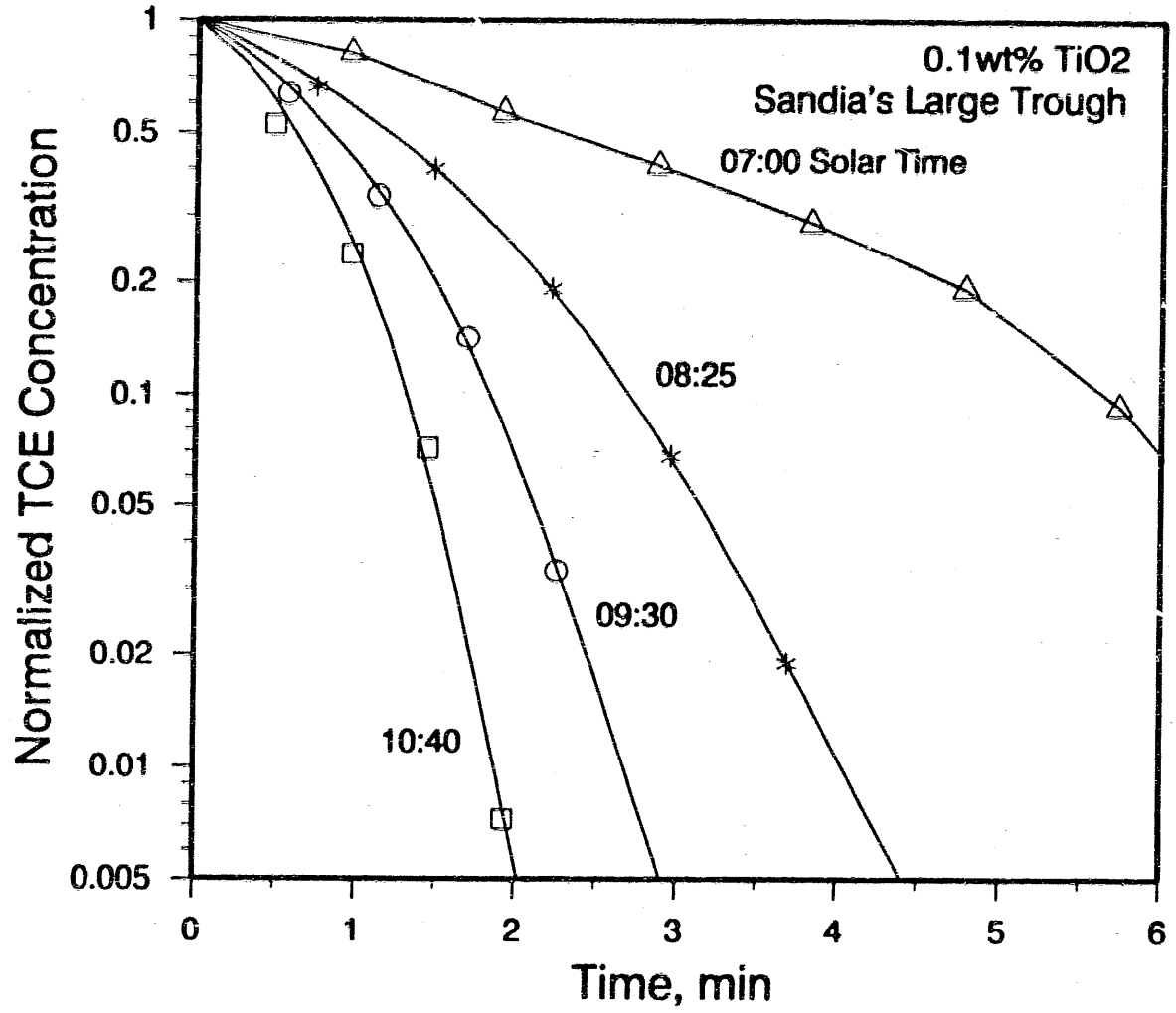

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Fig 4

Variation of Processing Rate With Season And Time of Day

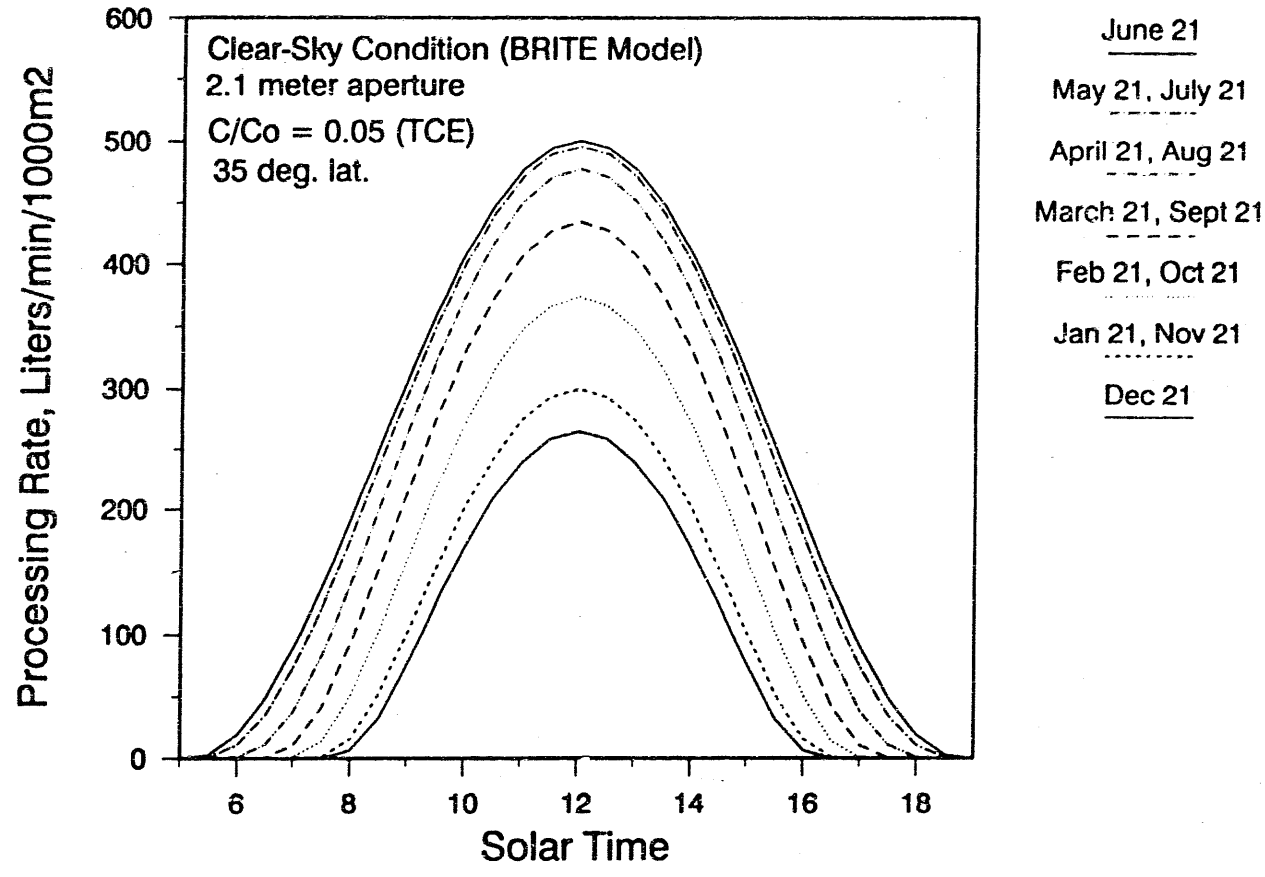

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Fig 5

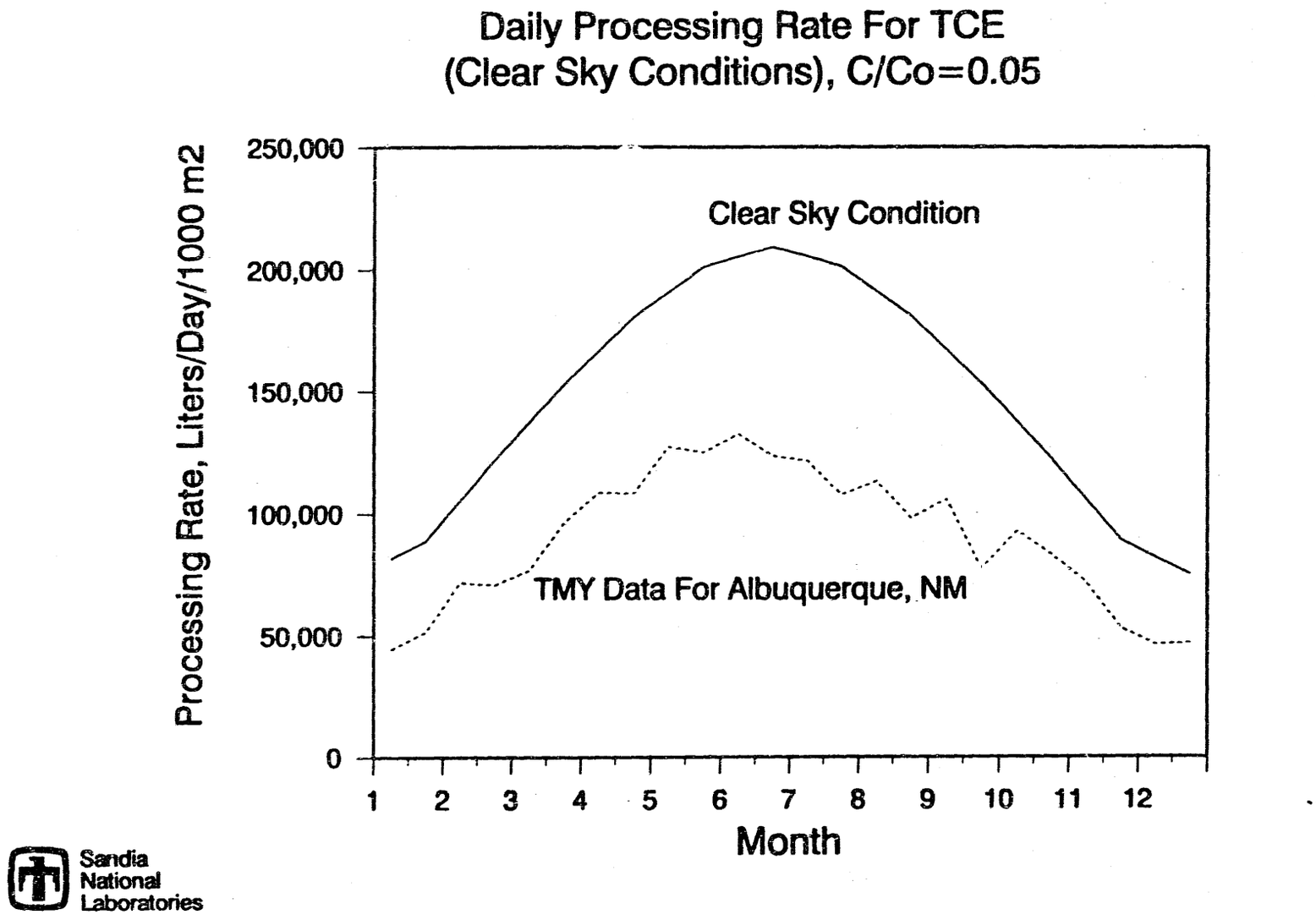

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Fig 6

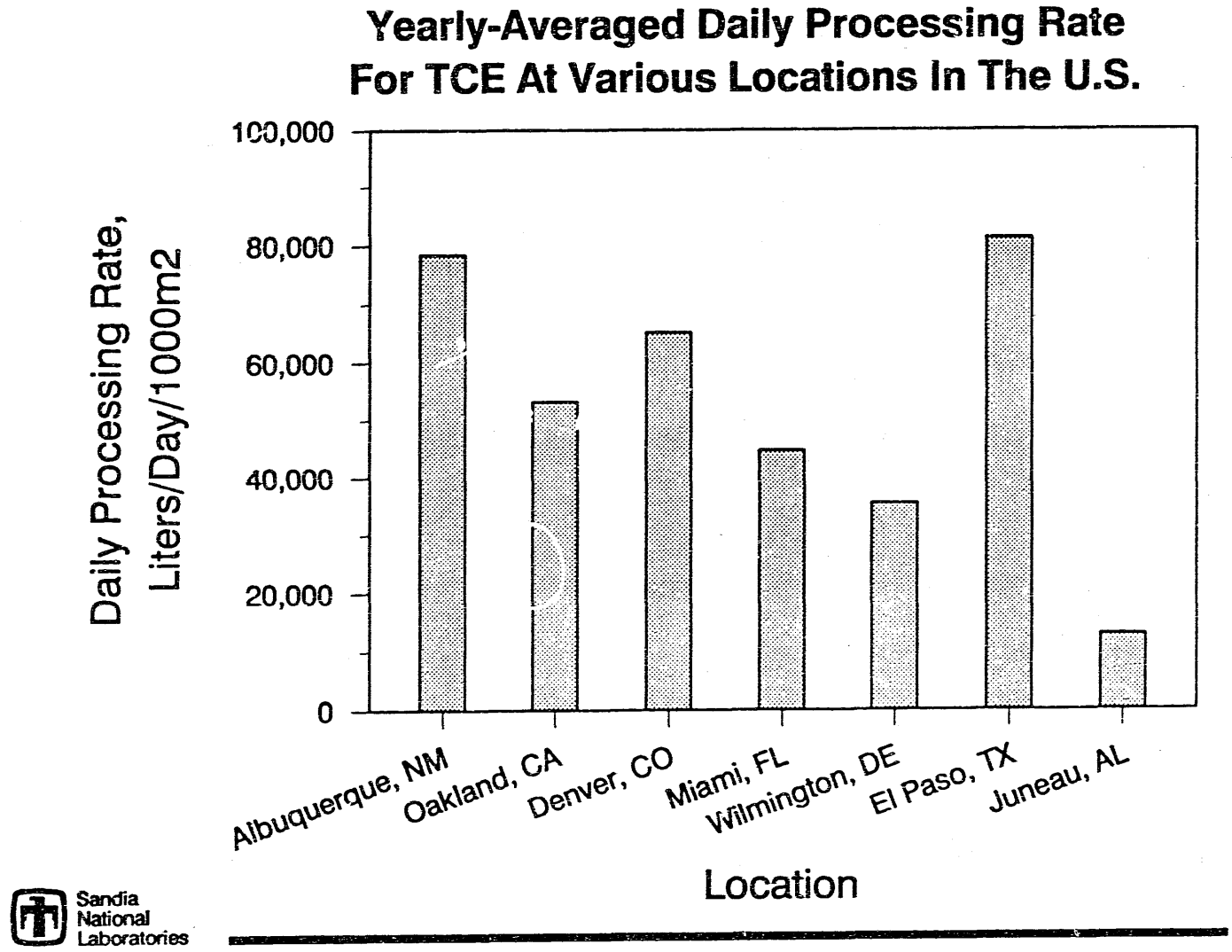
Yearly-Averaged Daily Processing Rate
For TCE At Various Locations In The U.S.
Daily Processing Rate,
Liters/Day/1000m2
100,000
80,000
60,000
40,000
20,000
0
Albuquerque, NM
Oakland, CA
Denver, CO
Miami, FL
Wilmington, DE
El Paso, TX
Juneau, AL
Location
Sandia
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Fig 7

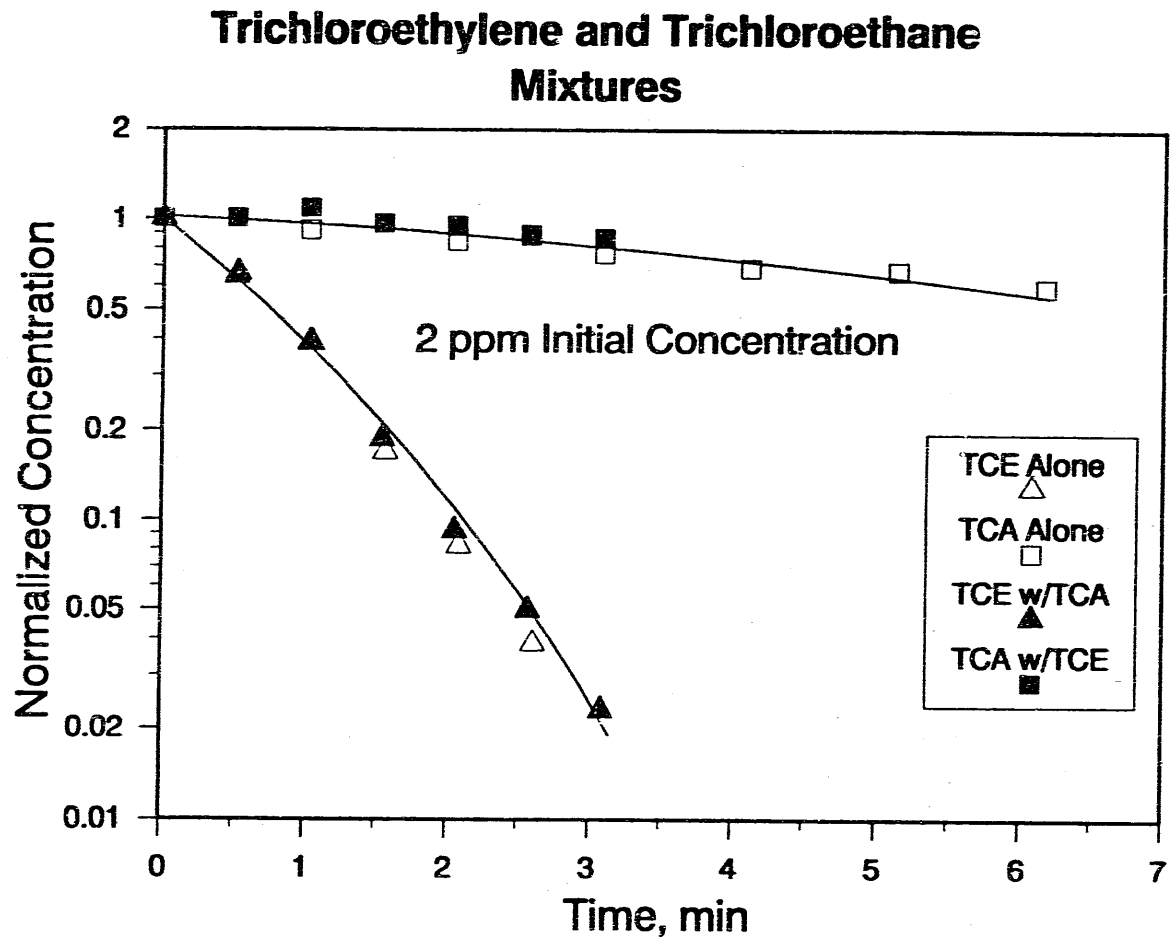

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Fig 8

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