Gas Phase Photocatalytic Degradation on TiO₂ Pellets of Volatile Chlorinated Organic Compounds from a Soil Vapor Extraction Well

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ABSTRACT: The degradation of trichloroethylene (TCE, $Cl_2C=CHCl$) and tetrachloroethylene (PCE, $Cl_2C=CCl_2$) in a gas stream from a soil vapor extraction (SVE) well was demonstrated with an annular photocatalytic reactor packed with porous TiO_2 pellets in a field trial at the Savannah River Site in Aiken, SC. The TiO_2 pellets were prepared using a sol-gel method. The experiments were performed at 55 to 60°C using space times of 10^8 to 10^{10} $g \cdot s \cdot mol^{-1}$ for TCE and PCE. Chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) were detected as minor products from side reactions. On a molar basis, the amounts CCl_4 and $CHCl_3$ produced were about 2 and 0.2% of the reactants, respectively.

KEY WORDS: gas phase photocatalysis, titanium dioxide, perchloroethylene, soil vapor extraction, soil remediation.

I. INTRODUCTION

Many soils and groundwater supplies have become contaminated with volatile organic compounds (VOCs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) resulting from leaking underground storage tanks and improper disposal practices (Naft, 1992). Recognition of this problem has resulted in urgent calls for research to develop effective, inexpensive techniques for groundwater remediation. The treatment methods now in use for VOC-contaminated groundwater include

soil vapor extraction (SVE) and groundwater air stripping. SVE is used to remove VOCs from the vadose (unsaturated) zone. Depending on the types of structures and materials encountered within this zone, a considerable fraction of the VOCs can be retained that will leach slowly to groundwater, frustrating cleanup efforts directed at the groundwater. Interbedded layers of clay and sand within the vadose zone at the Savannah River Site are known to contain high levels of contaminants. When treatment of the effluents from SVE systems is required under air-quality regulations, granulated activated carbon (GAC) columns are most frequently used. However, remediation by these methods is incomplete because pollutants are not destroyed, but shifted to another phase. Contaminants sorb to activated carbon until the adsorptive capacity of the carbon is reached. At that point, the carbon can be either regenerated for further use or disposed of as waste. After several regeneration cycles, the carbon loses its activity and must be discarded; the costs of transport and processing for regeneration or disposal can be significant. VOCs vented to the atmosphere contribute to smog and if persistent, lead to widespread environmental contamination.

Heterogeneous photocatalysis using semiconductor particles is capable of mineralizing most organic contaminants and is recognized as having great potential in the treatment of polluted water (Borgarello et al., 1986; Ollis et al., 1991). Most studies have been performed with powder suspensions of TiO_2 in aqueous solutions (Pruden and Ollis, 1983; Ahmed and Ollis, 1984; Matthews, 1986, 1988; Tanaka et al., 1989; Hisanaga et al., 1990; Turchi and Ollis, 1990; Sabate et al., 1991; Sabin and Vogler, 1992). Dibble and Raupp (1990, 1992) reported the photocatalytic oxidation of TCE using TiO_2 powder in a gas-phase system but did not demonstrate that complete mineralization was achieved. Recently, Milne and Nimlos (1992) warned that the incomplete photocatalytic oxidation by TiO_2 of TCE, PCE, and perhaps other chlorinated hydrocarbons in the gas phase can yield considerable quantities of phosgene. We previously reported that TCE can be completely mineralized to CO_2 and HCl in the gas phase by using TiO_2 pellets prepared using sol-gel techniques (Yamazaki-Nishida et al., 1993, 1994). In those laboratory experiments, a steady-state condition was maintained for several days, while stoichiometric amounts of CO_2 were detected in the effluent by on-line gas chromatography. In June 1992, a photocatalytic reactor was field tested for 5 d at the Savannah River Site in Aiken, SC. The reactor was used to treat the PCE- and TCE-contaminated effluent from an SVE unit. To the best of our knowledge, this is the first paper to describe the use of a TiO_2-based photocatalytic reactor to degrade gas-phase contaminants in the field.

II. EXPERIMENTAL SECTION

The TiO_2 pellets were prepared using a sol-gel technique and fired at 300°C (Yamazaki-Nishida et al., 1994). The diameter of the pellets was about 1 mm.

Porosities of 50 to 56% and specific surface areas of 160 to 194 $m^2 \cdot g^{-1}$ were measured by BET analysis. Analysis by powder X-ray diffraction indicated that the TiO_2 pellets were pure anatase. Annular photoreactor cells were made by a glass blower using Corning 7740 borosilicate glass tubing, as illustrated schematically in Figure 1. The diameters of the inner and outer glass tubes were 2.8 and 3.8 cm, respectively, and the thicknesses, 1.5 and 2 mm, respectively. The reactor cross-section was 2.9 cm^2 and its height, 13.4 cm. Four nipples (outer diameter, 6 mm; length, 2 cm) attached at each end of the photoreactor served as inlets and outlets for the gas stream. The TiO_2 pellets (30 g) were packed in the annulus surrounding a 4-W fluorescent black lightbulb (GE F4T5-BLB) positioned in the middle of each photoreactor. The flow rate of photons reaching the catalyst in each reactor (wavelength <400 nm) was found to be 1.24×10^{-6} einstein/s using uranyl oxalate as an actinometer (Rabek, 1982).

The demonstration photoreactor used in the field test incorporated four annular photoreactor cells arranged in parallel: the gas entering the reactor passed into a manifold that distributed the stream to the four cells, and a second manifold collected the effluent. Pressure differences measured across each annular photoreactor cell were found to be equal, verifying that the gas distribution was balanced. The inlet and outlet manifolds were made of no. 316 stainless steel tubes ($\frac{1}{2}$ and $\frac{3}{4}$ in. o.d.), sealed at both ends and each arrayed with silver soldered nipples to accommodate short pieces of Norprene plastic tubing ($\frac{3}{16}$ in.) that connected the manifolds to the photoreactor cells. A pressure gauge, thermometer, flow meter, and two valves incorporated into the reactor system (Figure 2) were joined by $\frac{1}{4}$ in. o.d. 316 stainless steel tubing. These components, a switch and ballasts for the lamps, and a cooling fan were installed in a suitcase (13 × 21 × 7.5 in.) for portability (Figure 2).

A relative humidity meter (Fisher Scientific) was used to measure the humidity of the gas stream. The humidity of the inlet stream was controlled by passing the gas through coiled copper tubing ($\frac{1}{4}$ in. o.d.) immersed in an ice bath; a glass container at the bottom of the coil collected the condensate. A second copper coil leading from the collector and out of the ice bath served to rewarm the gas. Thermostat-controlled (Glas Col PL 312) heating wire (Cal-Cord) wrapped around this coil, the stainless steel inlet tubing and the inlet manifold served to raise the temperature of the gas before it entered the photoreactor. Significant amounts of heat were also generated by the lamps. Liquid crystal temperature indicators (RLC-10, OMEGA) were attached to the outsides of the cells, and by monitoring these, the thermostats were adjusted so that the reactor temperature was at least 55 to 60°C. Heat loss was minimized by covering the cells and inlet lines with insulation.

The inlet gas stream was drawn from an SVE well located in the M area of the Savannah River Site, Aiken, SC (Figure 3). In normal operation, gas is extracted from the well with a trailer-mounted SVE unit (maximum capacity of 500 ft^3/min at 280 torr vacuum) and passed through two granular activated-carbon (GAC)
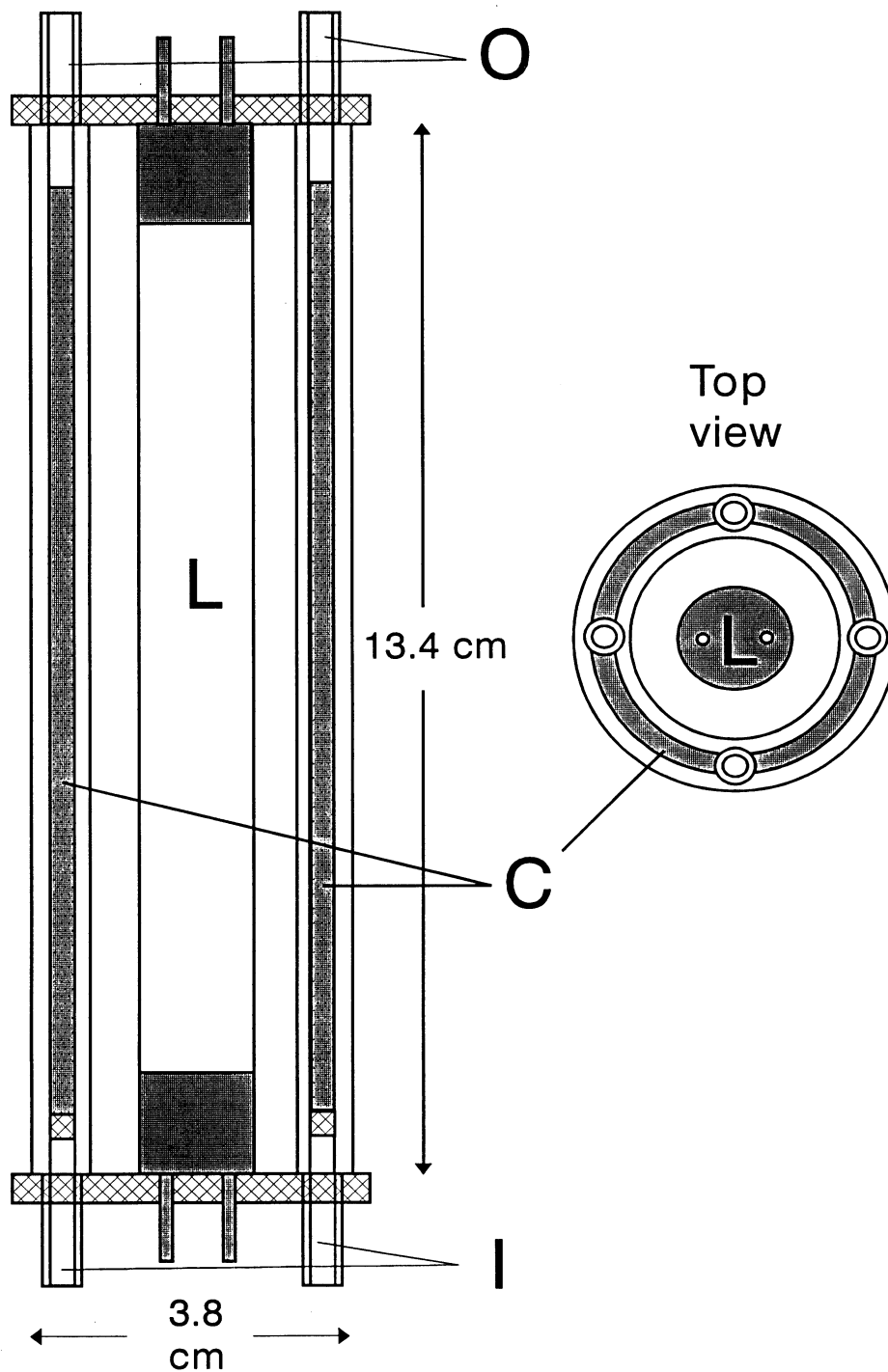
FIGURE 1. Schematic diagram of an annular photoreactor cell. (C) catalyst; (L) lamp; (I) gas inlet tubes; (O) gas outlet tubes.
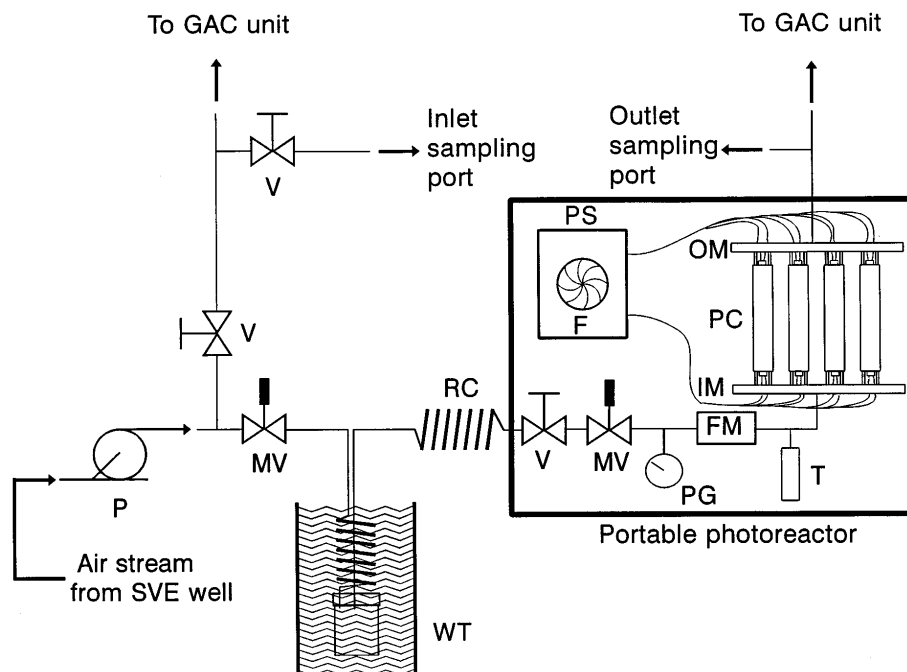
FIGURE 2. A schematic diagram of the photoreactor system. (P) pump; (V) 2-way valve; (MV) monitoring valve; (WT) water trap; (RC) rewarming coil; (PG) pressure gauge; (FM) flowmeter; (T) thermometer; (SVE) soil vapor extraction; (IM) inlet manifold; (PC) photocatalytic flowcells; (OM) outlet manifold; (GAC) granular activated carbon.

columns before being discharged to the atmosphere. As a result of the high VOC concentrations and a limited supply of GAC, the SVE unit had to be taken off line prior to the start of experiments. Teflon tubing ($\frac{1}{4}$ in. i.d.) was used to connect the wellhead to a small, oil-free pump (Gast model 1089). Because the photoreactor was designed to handle a smaller flow rate than that of the small pump, a system of valves was used to divide the inlet gas stream. A portion of the inlet gas stream flowed through the photoreactor system in a single pass. The unused fraction and the photoreactor effluent were routed to the GAC columns (Figure 2).

A photoionization detector (H-Nu model PI-101) was used at the site to make rough estimates of the amount of organic contaminants at the inlet and outlet. Inlet and outlet gas samples were taken using either Tedlar (Analytical Testing Corp., Model ZH 126, capacity 1 l) or Teflon (Alltech Associates, Inc., catalog no. 41184, capacity 1.2 l) sampling bags with stainless steel valves and a septum port. The samples were stored at ambient temperature in the dark and transported to the laboratory for analysis. Sample holding times ranged from several hours to no
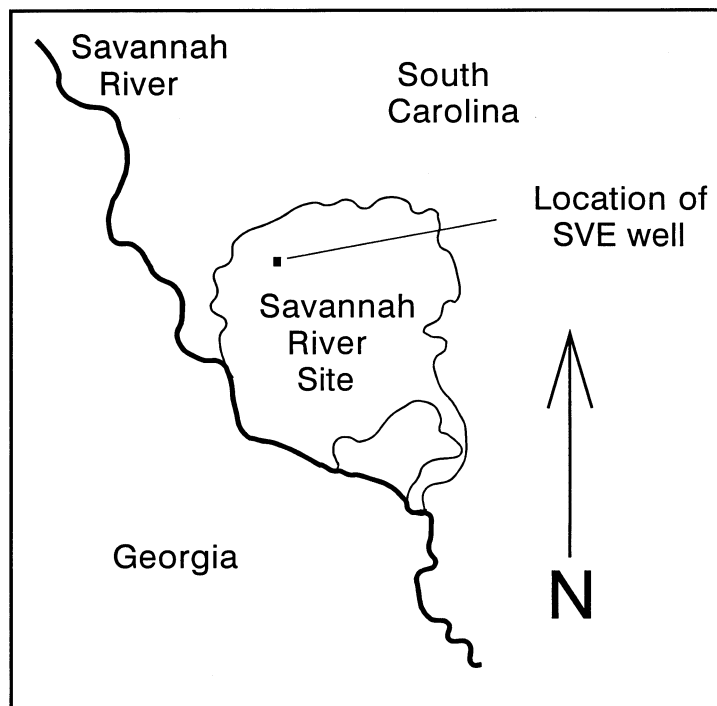
FIGURE 3. Location of the Savannah River Site.

more than 3 d. Samples were injected directly into a gas chromatograph/mass spectrometer (GC/MS, Hewlett-Packard, model 5890/5971) equipped with a 30 m × 0.53 mm × 3 μm VOCOL column or preconcentrated on a Tenax/silica gel/charcoal trap with an OI Analytical 4460A purge and trap concentrator. Quantitation of trapped samples was performed by internal standardization with chlorobenzene-d5 and 1,4-difluorobenzene. It has previously been demonstrated that the alcohol diluent (methanol was used in this investigation) in the internal standard reacts with phosgene in the samples to form methylchloroformate (Windberry *et al.*, 1988). At one point (27 h after igniting the lamps), a portable GC/MS (Viking/Spectra Trak 600) was brought to the site and linked to the reactor via a length of $\frac{1}{4}$ in. i.d. Tygon tubing for on-line sampling and analysis of reactor inlet and outlet gases. The gases were injected directly into the MS, bypassing the GC.

III. RESULTS AND DISCUSSION

Experiments were performed at three different reactant flow rates: 40, 100, and 200 ml · min^{-1}, as shown in Figures 4 through 6.

A. Reactant Gas

The reactant gas stream was found to contain 1,1,1-trichloroethane (1,1,1-TCA, CCl_3-CH_3, 64 to 160 ppmv), TCE (222 to 1100 ppmv), and PCE (1900 to 7000 ppmv). 1,1-Dichloroethylene (1,1-DCE, CCl_2-CH_2, 30 to 55 ppmv) was also detected, but the amount was less than the minimum reporting value. As shown in Figure 4, the concentrations of 1,1,1-TCA, TCE, and PCE fluctuated over a wide range. However, the [1,1,1-TCA]:[TCE] and [PCE]:[TCE] ratios were constant: 0.18 ± 0.02 and 5.16 ± 0.76, respectively. These fluctuations did not seem to have any relationship to the ambient temperature, but may have been due to diurnal changes in barometric pressure. On-line MS analysis revealed clusters of peaks around m/e = 94 to 96, 129 to 134, and 164 to 170 that were interpreted to indicate the presence of TCE and PCE.

O_2 and H_2O interact with TiO_2 (Forss and Schubnell, 1993) and have been shown to be essential for the complete photocatalytic mineralization of p-chlorophenol (Barbeni *et al.*, 1984) and TCE (Yamazaki-Nishida *et al.*, 1993), but our recent experiments have suggested that excess H_2O is undesirable, possibly masking reaction sites on the catalyst surface. The water trap was designed to lower the inlet mole fraction from 0.22 (measured at the well head) to 0.007 atm (the saturation vapor pressure of H_2O in air at 0°C). It is possible, especially at times of heaviest loading when [PCE] exceeded saturation at 0°C (5000 ppmv), that some PCE was condensed in the trap. Because inlet samples were taken from a point upstream from the trap, inlet concentrations may at times overestimate the actual amount reaching the photocatalytic cells. A pilot or full-scale reactor incorporating a water trap could be designed to periodically purge the condensate, to avoid any need to treat liquid waste.

According to the BET analysis, the TiO_2 pellets are highly porous materials with large internal surface areas. Considerable time is required to establish adsorption equilibrium between the bulk gas stream and the catalyst surface. In a bench-scale experiment using a similar annular photoreactor, it took about 4 h for TCE (450 ppmv) to reach a steady state, passing through the TiO_2 bed at 300 ml/min without irradiation. For this reason, during the field experiment, the reactant gas stream was passed through the system at 1100 ml/min before irradiation. After about 3 h, the level of organic contaminants at the outlet was almost equal to that at the inlet, as indicated by the photoionization detector. At this point, the flow rate was adjusted to 100 ml/min, and the lamps were ignited.

B. Photodegradation

Figure 5 shows the concentrations of 1,1,1-TCA, TCE, and PCE at the outlet using the same ordinate scale as Figure 4. The reactor space-time (approximately equal to the residence time and defined as the amount of catalyst, W, divided by the molar flow rate, F, of each reactant measured at the reactor inlet [Hill, 1977]) for
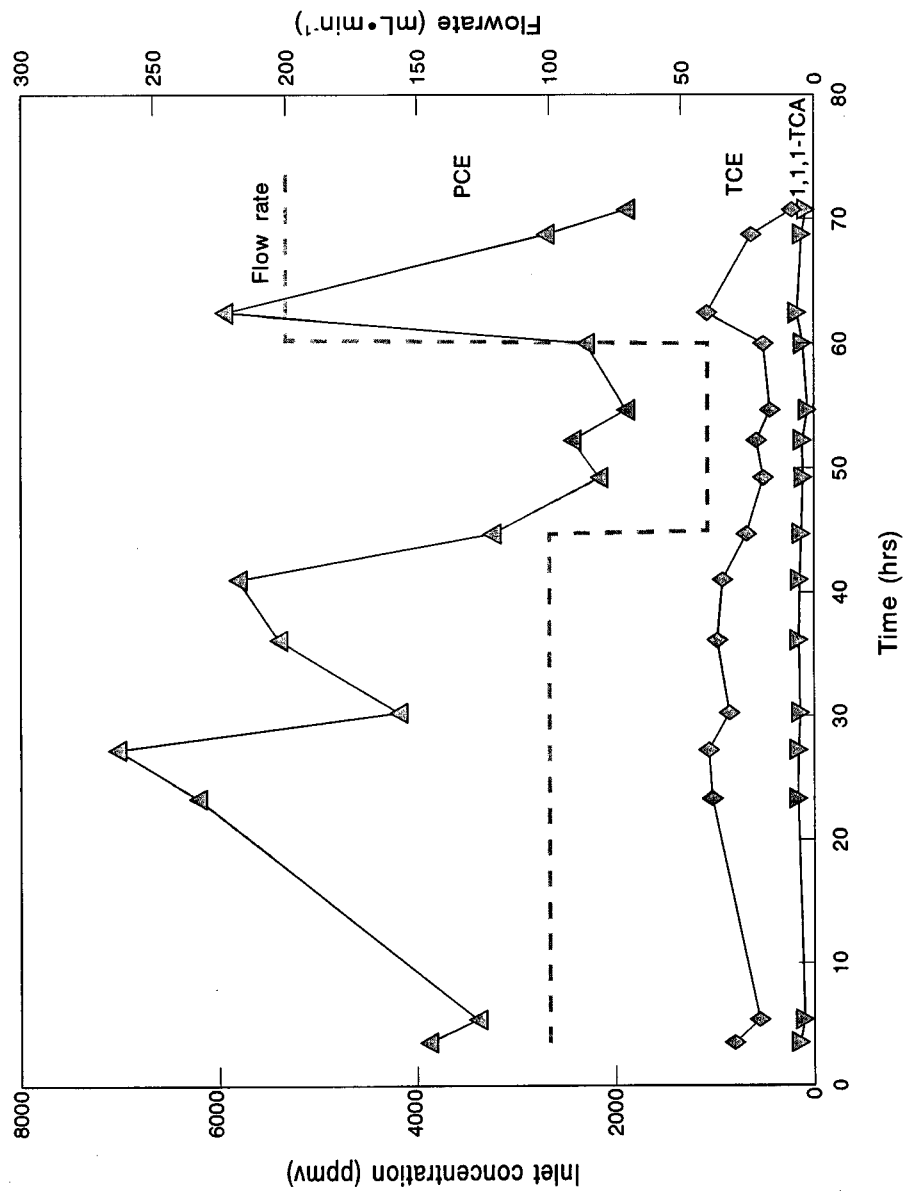
FIGURE 4. Concentrations of 1,1,1-TCA (▼), TCE (♦), and PCE (▲) in the influent gas stream. Three different flowrates were used during the field test. (See text for definitions of acronyms.)
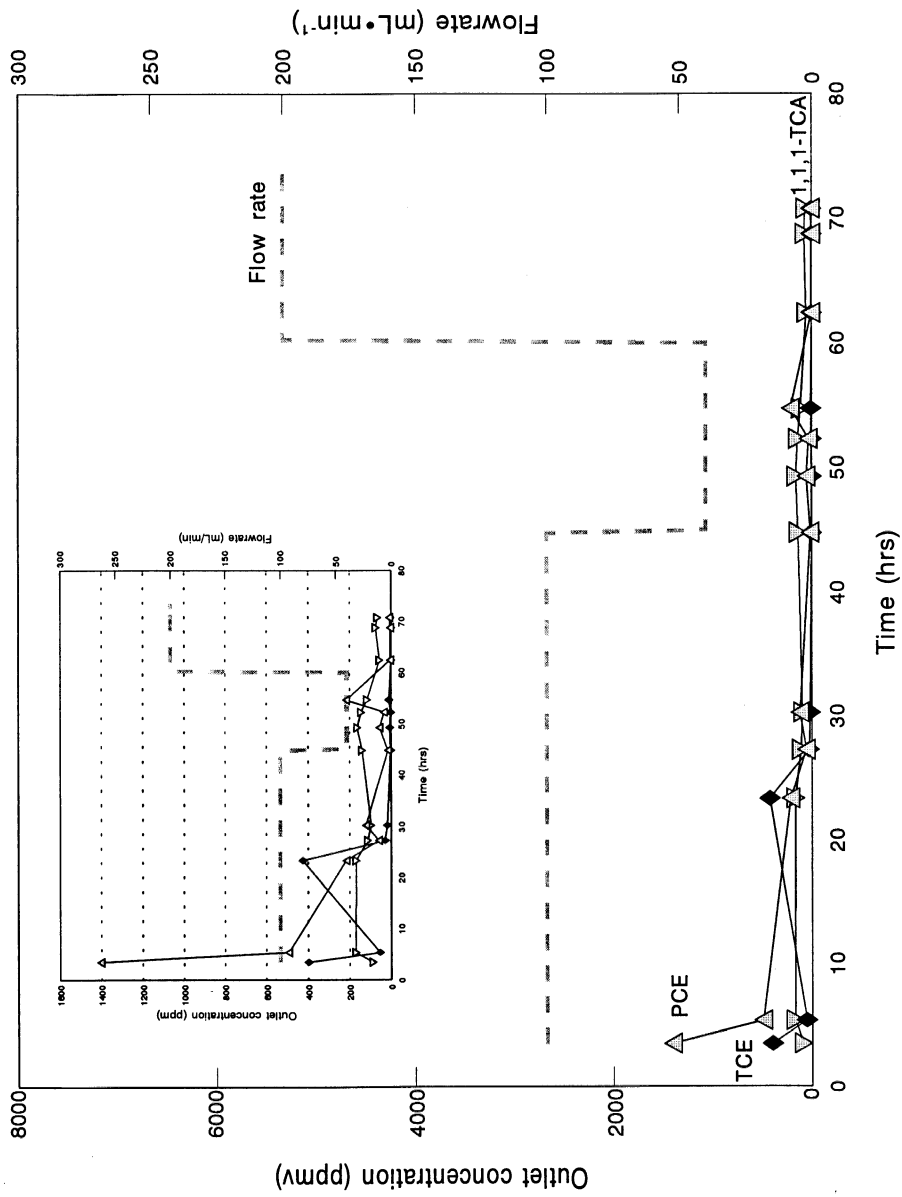
FIGURE 5. Concentrations of 1,1,1-TCA (▼), TCE (◆), and PCE (▲) in the effluent gas stream. The earliest sample (3.5 h) was taken before the reactor lamps were turned on. Inset shows the same data on an expanded ordinate scale. (See text for definitions of acronyms.)

PCE and TCE were calculated to be in the ranges of 1.4×10^8 to 2.1×10^9 and 7.5×10^8 to 9.1×10^9 g · s · mol, respectively. The conversions of PCE and TCE were always about 100%. 1,1-DCE was not detected in the effluent gas, so most of this component appears to have been degraded as well. Data necessary to determine a mass balance were not collected during this experiment, so conversion or degradation only implies the disappearance of parent contaminants; however, all components detected in the outlet gas stream using the methodology described are reported. 1,1,1-TCA was found in the outlet gas stream at levels comparable to those in the inlet stream, and so does not appear to be degraded in this process. Table 1 summarizes the space times and conversion efficiencies for PCE and TCE degradation and the apparent overall and normalized quantum yields for PCE, TCE, and 1,1-DCE degradation. The *apparent* overall quantum yield is defined as the sum of the degradation rates for each reactant (moles per second) divided by the flow rate of the photons of wavelengths <400 nm entering the reactor (einstein per second). The *actual* quantum yields (moles of photons used to drive a reaction forward per mole of photons absorbed by the catalyst) may be quite different, but we have chosen to examine this parameter as defined in order to characterize the efficiency achieved with the conditions used. The high conversion rates of PCE, TCE, and 1,1-DCE show that there was enough space time for the degradation of these compounds and suggest that it should be possible to treat higher concentrations or to run the reaction at higher flow rates. The apparent overall quantum yields in this field demonstration were 1.3 to 21.2% (Table 1). In earlier experiments using a photoreactor with a tubular rather than annular configuration, the complete mineralization of TCE alone (demonstrated by detection of quantitative amounts of CO_2) was reported. The apparent quantum yield in those experiments was about 17% (Yamazaki-Nishida *et al.*, 1994). If all of the steps in the reaction are photocatalytically mediated, this value is approximately the same as the theoretical maximum because 6 mol of electrons are transferred in the complete oxidation of each mole of TCE. Four and eight moles of electrons must be transferred to mineralize PCE and 1,1-DCE, so the maximum apparent quantum yields should be 25 and 12.5%, respectively. For the simultaneous degradation of TCE, PCE, and 1,1-DCE, the calculated yields for each component were not compared with the theoretical maxima. However, assuming that mineralization occurred and that there were no other reaction mechanisms, we have estimated a normalized quantum yield, defined as the sum of the rates of electron transfer needed to achieve the observed degradation rates for each compound expressed as a percentage of the flow rate of photons with wavelengths <400 nm. These values ranged from 5.6 to 91.9% (Table 1). Free-radical chain reactions, direct reaction of intermediates with oxygen, and accumulation of intermediates on the catalyst surface are other mechanisms that may account for the observed high efficiency of the system. Elucidation of these processes will require further investigation and is of interest as it may enable prediction of conditions under which the degradation rates could be greatly accelerated.

TABLE 1
Volumetric Flow Rate, Space-Time, and Conversion Efficiency (X) for TCE and PCE, Apparent Overall and Normalized Apparent Quantum Yield (QY) for TCE, PCE, and 1,1-DCE during Irradiation in the Field Demonstration Reactor at Savannah River Site

Time (h)	Flow rate (ml · min^{-1})	TCE		PCE		Overall appar. QY (%)	Normalized appar. QY[a] (%)
		Space-time (10^8 g · s · mol^{-1})	X (%)	Space-time (10^8 g · s · mol^{-1})	X (%)		
3.5	100	20.1	50.3	4.2	63.9	4.3	18.5
5.4	100	29.0	90.3	4.8	85.4	5.1	21.9
23.3	100	25.6	32.4	5.0	93.3	4.8	20.0
27.3	100	15.3	97.3	2.3	99.2	12.0	51.0
30.3	100	18.9	97.8	3.9	97.1	7.4	31.9
44.8	100	23.7	99.8	5.0	99.5	5.9	25.5
49.3	40	78.8	98.9	18.7	97.4	1.6	6.9
52.3	40	69.6	99.6	16.6	98.6	1.8	7.8
54.7	40	91.0	97.6	21.3	88.6	1.3	5.6
62.4	200	7.5	100.0	1.4	99.9	21.2	91.9
68.8	200	12.8	99.9	3.0	99.9	10.1	44.9
70.8	200	36.4	98.6	4.3	99.6	6.3	26.5

[a] Rate of electron teansfer needed for mineralization of all converted component as a percentage of photon flow rate.

C. **Reaction Products**

During operation of the reactor with the lamps on, chloroform and carbon tetrachloride were detected in the effluent, but not in the influent gas streams (Figure 6). The amount of CCl_4 was one order of magnitude higher than that of $CHCl_3$, and the concentrations of both contaminants were low relative to the levels of TCE and PCE in the influent. The highest level of CCl_4 (277 ppmv) was observed shortly after the lamps were turned on. During this time, the effluent gas was more humid than the influent. This may have been due to water desorbing from the catalyst: the catalyst was not heated to the normal operating temperature (55 to 60°C) until the lamps were turned on. The large area of the catalyst surface and its hydrophilic nature suggest that significant amounts of water could have been sorbed during the sizing and packing of the TiO_2 pellets and during the operation to reach a steady state before irradiation. After 20 h of operation at 55 to 60°C, influent and effluent humidity levels were equal (0.007 atm) and the CCl_4 levels were 40 to 100 ppmv. These results suggest that humidity may be an important factor in the mineralization of PCE and TCE, for which optimal conditions should be determined. Alternatively, thermal desorption of PCE from the catalyst surface may have made the gas-phase PCE concentrations in the reactor far higher than those measured at the inlet in the period immediately following lamp ignition. In general, as shown in Figure 6, the concentration of CCl_4 does not appear to be correlated with the reactor flow rate, suggesting that it is not an intermediate in the main degradation path of TCE or PCE to CO_2 and HCl, but is produced in a side reaction favored by conditions not currently understood. Some of the variation in the reported CCl_4 levels may derive from sorption to the sample bags. Excess water on the catalyst may favor this reaction or, alternatively, water may occupy sites on the TiO_2 surface, preventing CCl_4 from being degraded further. Production of carbon tetrachloride and chloroform is consistent with a free-radical reaction mechanism. Nimlos *et al*. (1993), in a study of TCE degradation with a TiO_2/UV system, identified molecular chlorine in their reactor and attributed the high degradation rates observed in their study to free-radical reactions involving chlorine atoms and to free-radical chain reactions as well. However, they did not observe carbon tetrachloride or chloroform and did not identify these compounds as probable products of PCE degradation. They also noted that donation of electrons from TiO_2 to reactants or intermediates (i.e., reductive reactions) may also play a role. Differences in the physical and crystalline structures of catalysts may account for variations in the products and intermediates observed in the degradation of chlorinated ethylenes.

The allowable site boundary concentrations, issued by the South Carolina Dept. of Health and Environmental Control and the threshold limit values (TLV) set by the American Conference of Governmental Industrial Hygienists are lower (i.e., stricter) for CCl_4 and $CHCl_3$ than for TCE and PCE (South Carolina Department of Health and Environmental Control Air Pollution, 1991; American Confer-
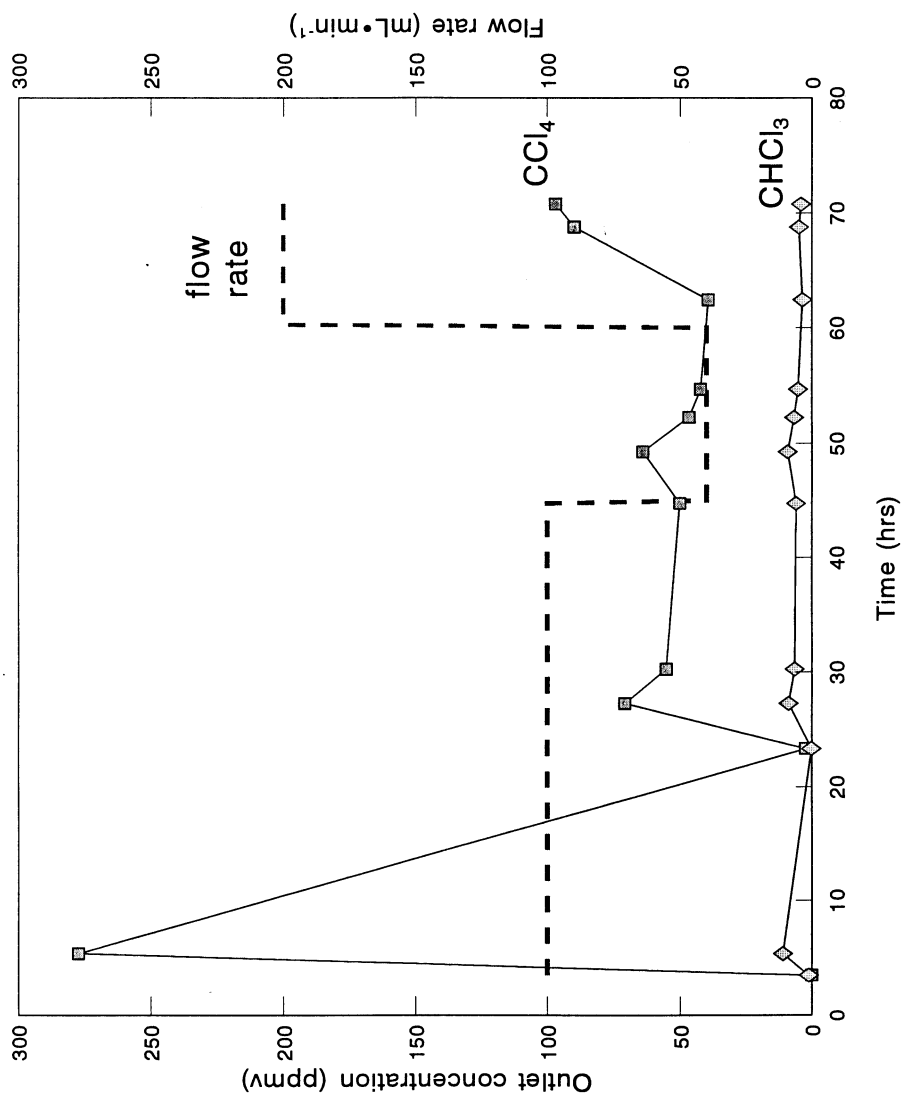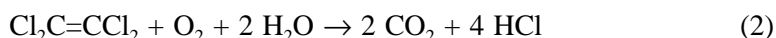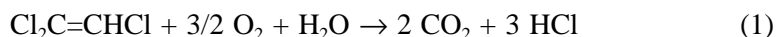
FIGURE 6. Concentrations of CHCl$_3$ (♦) and CCl$_4$ (■) in the effluent gas stream. The earliest sample (3.5 h) was taken before the reactor lamps were turned on.

ence of Governmental Industrial Hygienists, 1992). It has been reported in the case of TiO_2 powders using a slurry photoreactor that the degradation rates for 1,1,1-TCA and CCl_4 are slower than those of TCE and PCE (Tanaka *et al.*, 1989; Ollis, 1985). These saturated organic compounds seem to have less interaction with the catalyst. It may be possible to degrade these compounds by increasing the space time or optimizing the reaction temperature and water vapor content. The fact that CCl_4 is a highly oxidized compound suggests that finding operating conditions unfavorable to its formation may be a better strategy.

In the gas phase, oxidation of PCE with ·OH radicals and homogeneous photolysis of TCE with high-intensity UV lamps have been reported to produce a toxic gas, phosgene (Kirchner *et al.*, 1990; Blyston *et al.*, 1992; Nimlos *et al.*, 1993). In these experiments, phosgene was not detected as a reaction product. This may be due to the hydrolysis of phosgene by water trapped in the pores of the TiO_2 pellets. It is also possible that phosgene was produced at concentrations too low to detect, or was degraded in the sampling bags or during analysis to products escaping detection. The sampling and analysis method used in this study has been used successfully under similar circumstances by the same personnel to detect phosgene produced by photolytic and other photocatalytic reactors. In addition, on-line MS analysis did not reveal the base peak for phosgene (m/e = 63). However, sample spiking was not performed, so the failure to detect any particular compound is not certain evidence of its absence. Sampling and analysis protocols are under development to verify the results presented in this paper during a field trial in the fall of 1993.

Corrosion was observed on the stainless steel fittings of the gas-sampling bags and the reactor outlet manifold, indicating production of HCl. Mineralization of TCE and PCE are expressed as the following equations:

$$Cl_2C=CHCl + 3/2\ O_2 + H_2O \rightarrow 2\ CO_2 + 3\ HCl \qquad (1)$$

$$Cl_2C=CCl_2 + O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 4\ HCl \qquad (2)$$

The large quantities of HCl produced in these reactions would require that a full-scale reactor have a scrubbing system to remove the acid before venting the effluent to the environment.

IV. **CONCLUSIONS**

These field experiments have demonstrated that TCE and PCE can be degraded and possibly mineralized by photocatalysis at 55 to 60°C in annular reactors packed with TiO_2 pellets without detectable production of phosgene. Modification of sampling and analysis protocols was made for verification of these results during a field trial in the fall of 1993; a report on that work will be forthcoming.

The overall apparent quantum yield was calculated to be 1.3 to 21.2% for the degradation of TCE, PCE, and 1,1-DCE. The normalized quantum yields were 5.6 to 91.9%, suggesting that the full capacity of the reactor was not being utilized at most times. Further work needs to be performed in order to optimize the reaction for the mineralization of 1,1,1-TCA and CCl_4.

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