PHOTOTREATMENT OF PERCHLOROETHENE IN SOIL VAPOR AT THE HARRISON LANDFILL, TUCSON, AZ

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ABSTRACT

Perchloroethene (PCE) was scrubbed from contaminated landfill soil vapor by contact with a mixture of 2-propanol and acetone and then destroyed by a reductive dehalogenation process during exposure to sunlight in a photoreactor. The treatment system (scrubber and photoreactor) was deployed at the 120-acre Harrison Landfill, which was closed and capped in 1997. Soil vapor containing 100-200 $\mu g\ L^{-1}$ PCE (and other chlorinated organics) was readily obtained by diverting a flow of soil vapor from the city's full-scale carbon adsorption treatment system to our experimental phototreatment system.

Two types of field experiments have been conducted to date. In the first quasi-batch mode, the solvent was pre-loaded with PCE throughout the night and then exposed to sunlight while being recirculated in the photoreactor during the day. In the second continuous mode, both the scrubber and photoreactor were operated simultaneously for extended periods. The effectiveness of the photoreactor was determined by comparing liquid-phase concentrations of PCE and other targets in the reactor influent and effluent. PCE concentrations were lowered by 90 percent in a matter of hours. Results also indicate that the reaction was inhibited by oxygen in the soil vapor (currently 15 percent due to the injection of air by city contractors). However, we were able to eliminate (photoreduce) interfering oxygen and the target PCE by increasing the number of photoreactor tubes.

***Key words:** perchloroethene, photolysis, reductive dehalogenation, soil vapor*

SITE DESCRIPTION

The Harrison Landfill, owned by the city of Tucson, is located in southeastern Tucson, Ariz. (Figure 1). The 120-acre facility includes a barrow area and a methane-monitoring and gas-extraction system. Immediately east of the facility lies an inactive landfill (county-owned) and a mobile home park. A privately owned green waste collection lot (H & R Materials) is located due north of the landfill. A housing tract is located within one-half mile to the northwest, and undeveloped properties border the site to the west and south. The Harrison Landfill (HL) was originally a sand and gravel pit that was excavated to a depth of 50 ft below the surface (bls). The landfill was constructed over native soil with no intervening liner. Land filling of residential and commercial refuse began in 1972 and continued until 1997. At closure, a surface cap 3.5-5.0 ft in thickness was constructed. The cap consists of a lower layer of compacted topsoil, a middle layer of compacted high-silt soil, and an upper layer of non-compacted topsoil. In some areas, refuse is buried as much as 100 ft bls. Local depth to groundwater is 230 to 290 ft bls.

As part of the landfill closure activities, surface grading for runoff control and vegetative seeding were carried out. To control off-site gas migration, a soil vapor extraction (SVE) system was installed in 1995, and later expanded in 1997, from an initial capacity of 250

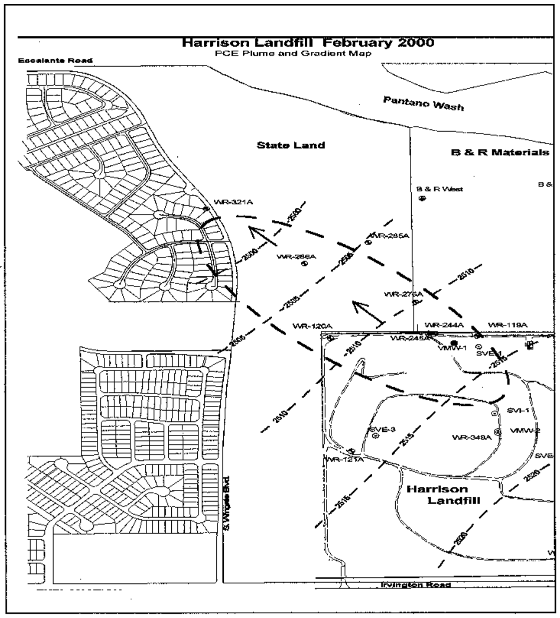

Figure 1. Harrison Landfill (bottom right corner). The oval-shaped area stretching northeast (down gradient) from the landfill represents the PCE plume ($5 \mu g\ L^{-1}$ concentration contour) in the groundwater below. Map courtesy of HydroGeoChem, Inc.

standard cubic feet per minute (scfm) to 1,600 scfm with a maximum vacuum pressure of 10 inches of mercury.

In 1996, a local groundwater investigation was completed in accordance with EPA regulations (40 CFR 258 Subpart E – Groundwater Monitoring and Corrective Action). Priority pollutants detected in groundwaters extracted from site wells included a variety of volatile and semi-volatile halo-organics (collectively labeled VOCs herein) including perchloroethene (PCE), trichloroethene (TCE), vinyl chloride (VC), dichloromethane (DCM), dichlorodifluoromethane (Freon 12), and trichlorofluoromethane (Freon 11) among others (Table 1). VOCs were not detected in the up-gradient well. Of the VOCs detected in the down-gradient wells, only PCE, TCE, 1,2-dichloropropane, and VC exceeded their respective human health-based guidance levels (Arizona), and only PCE, TCE, and DCM exceeded maximum contamination levels (EPA).

The original investigation was followed by a field study to assess the subsurface distribution of VOCs. Analytical results from multiple-depth soil gas and groundwater samplers indicated that PCE concentrations at the air-water interface were 2.5 times higher than concentrations measured in deeper water. Furthermore, soil vapor PCE concentrations increased with depth in the vadose zone. Findings suggested that the deep vadose zone continued to be a source of contamination for local groundwater and that the existing perimeter gas control system did not efficiently remove deep soil gas.

To minimize the source of groundwater contamination, the SVE system was expanded for relatively deep soil vapor extraction. The system was designed to remove VOCs from unsaturated sediments near the water table. It consisted of three SVE wells and a single gas injection well located in the center. The air injected at the water table forced the contaminated soil gas toward the SVE wells. Extracted air was then treated via adsorption on activated carbon and released to the atmosphere. The system operated at an injection rate of 250 scfm and an extraction rate of 900 scfm. Treatment was provided in four, 2000-lb carbon vessels. The average PCE concentration during the study was $145 \mu g\ L^{-1}$, and the average rate of PCE removal was five kg day^{-1} (HydroGeoChem).

PRELIMINARY INVESTIGATIONS

Our two-pronged approach to the problem of landfill remediation was to optimize the mass transfer of PCE from gas to liquid phase, and to then photo-reduce the PCE by exposure to sunlight. We investigated these problems separately in the laboratory, then combined our efforts for landfill application as described below.

Table 1. Data summary of volatile organic compounds (VOCs), well SVE-BC, Harrison Landfill (all concentrations in µg/L). Samples taken from the soil vapor extraction system before carbon adsorption units. Note the significant reductions across the board since 7/21//99. Soil vapor PCE concentrations were 20-40µgL^{-1} during phototreatment system trials (Jan-Feb 2000). ND; not detected (detection level).

SAMPLE DATE	7/21/99	12/28/99	2/2/00
Benzene	12	1.1	1.8
Chloroethane (Ethyl Chloride)	1.2	ND(0.088)	0.71
Chloroform	ND (2.0)	0.27	ND (1.0)
1,4-Dichlorobenzene (p)	9.9	0.92	1.7
1,1-Dichloroethane (1,1-DCA)	53	6.9	13
1,1-Dichlorethene (1,1-DCE)	6.8	0.54	0.94
cis-1,2-Dichloroethene (cis-1,2-DCE)	6.2	1.7	2.3
Dichloromethane (Methylene Chloride)	**230**	**23**	**48**
Ethylbenzene	15	1.1	1.5
Freon 11 (Trichlorofluoromethane)	**110**	**9.8**	**17**
Freon 12 (Dichlorodifluoromethane)	**2,000**	**39**	**120**
Freon 113 (1,1,2-Trichlorotrifluoroethane)	8.4	1.3	2.5
Freon 114(1,2-Dichlorotetrafluoroethane)	73	8	12
Tetrachloroethene (PCE)	**190**	**19**	**29**
Toluene	120	6.6	8.3
Trichloroethene (TCE)	**84**	**7.3**	**11**
1,2,4-Trimethylbenzene (Pseudocumene)	7.9	0.79	0.93
1,3,5-Trimethylbenzene (Mesitylene)	18	0.47	0.62
m,p-Xylenes	32	3.5	5
o-Xylene	13	1	1.5
Vinyl chloride (VC)	**13**	**0.76**	**1**
Total VOCs	3,003	133	279
Total NON-FREON VOCs	812	75	127

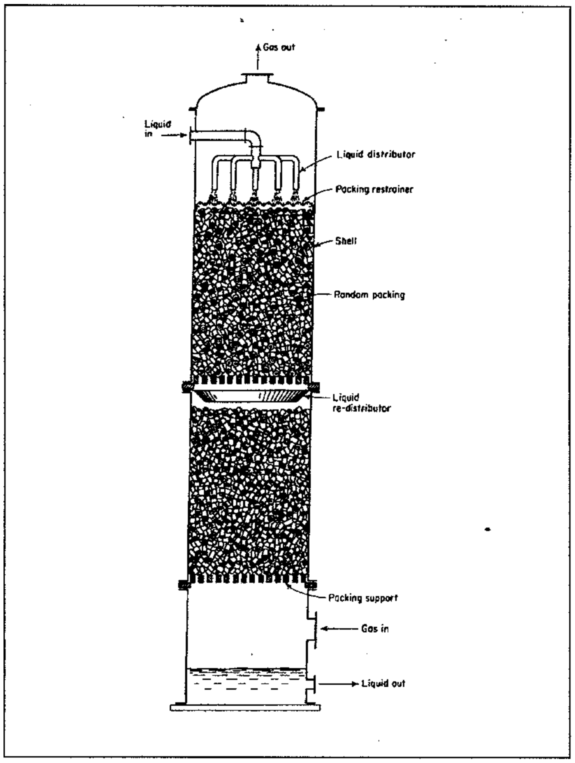

Figure 2. Typical configuration of countercurrent gas-stripping or gas-scrubbing towers. (Adapted from Treybal)

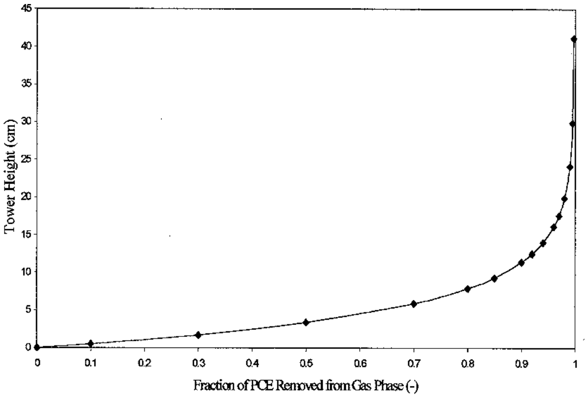

Figure 3. Tower height requirements as a function of transfer efficiency objectives. Calculations apply to the gas-to-liquid transfer (gas scrubbing) of PCE. The liquid phase consists of a 9:1 solvent mixture of 2-propanol and acetone. Flow is countercurrent with liquid introduced from the top of the tower. Column media consist of ½-inch ceramic saddles. Solid diamonds represent the results of individual calculations.

Scrubber column design

A countercurrent flow-packed column was chosen to transfer PCE from landfill gas to an organic solvent. This type of scrubber column is characterized by a continuous gas phase and a discontinuous liquid phase. Figure 2 illustrates the general configuration for this type of mass transfer equipment. In the column, the liquid trickles down over the tower, packing media as the gas is blown upward through the column. In this case, where transfer of a constituent from the gas to the liquid is desired, the operation is termed aeration or gas scrubbing (Lee and Tsui, 1993).

The countercurrent flow design has a distinct advantage over other commonly used configurations, such as bubble chambers and co-current towers. Countercurrent flow provides contact between the cleanest liquid with the cleanest gas at the column's head and the most contaminated liquid with the most contaminated gas at the column's base. Ignoring kinetic limitations, this minimizes the final concentration in the gas phase, since a concentration gradient is maintained from the gas to the liquid throughout the scrubber column length. Consequently, this type of mass transfer equipment is generally utilized when very low contaminant levels are required in the effluent gas. For the specific case of PCE transfer from landfill gas to an organic solvent mixture, the process effluent gas must have the lowest practical PCE concentration, and so a countercurrent configuration was chosen for the gas scrubbing operation.

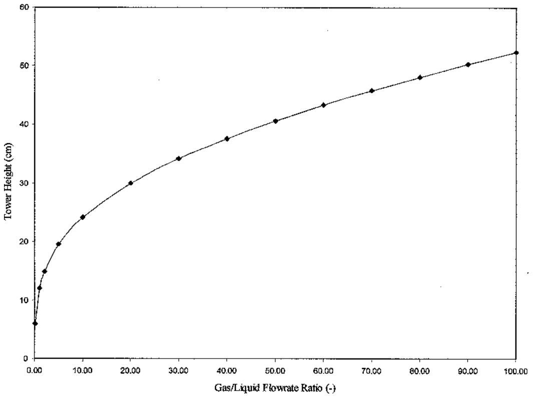

Figure 4. Tower height requirements for 2-log (99%) PCE scrubbing efficiency as a function of the ratio of gas and liquid flow rates. The liquid phase consists of a 9:1 solvent mixture of 2-propanol and acetone. Flow is countercurrent with liquid introduced from the top of the tower. Column media consist of ½-inch ceramic saddles. Solid diamonds represent the results of individual calculations.

Scrubber column model calculations

The removal efficiency and design specifications of the packed column were modeled using the two-resistance (a.k.a. two-film) theory of interphase mass transfer (Treybal, 1987). This approach is widely used in such applications, although water, rather than an organic solvent, typically constitutes the liquid phase. The theory posits that a stagnant film of fluid exists on each side of the gas-liquid interface. The total resistance to mass transfer of a constituent between the phases is the sum of the resistance to transfer through the stagnant gas film, plus the resistance to transfer through the stagnant liquid film. Because of the assumption of quiescence in the fluid comprising each film layer, mass transfer can only occur due to diffusion. Therefore, the rate of mass transfer can be described by Fick's law, in which the flux through the film is the product of the constituent's diffusivity and concentration gradient across the film. It is further assumed that no resistance occurs at the interface itself, so equilibrium between the phase concentrations is instantly and continuously established at the interface. Specific details of the model calculations will be published later.

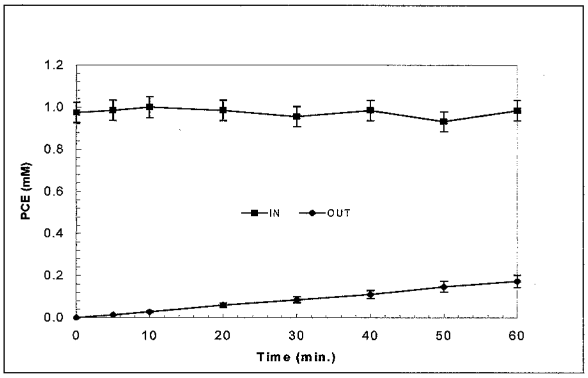

Figure 5. Influent and effluent PCE concentrations in a 60cm × 5cm scrubber column. The liquid phase consists of a 9:1 solvent mixture of 2-propanol and acetone. Flow is countercurrent with liquid introduced from the top of the tower. Column media consist of ½-inch ceramic saddles. During the period of operation, the solvent was recycled from a 500-mL reservoir, accounting for the gradual accumulation of liquid-phase PCE (and deterioration of transfer efficiency). Solid squares (influent) and diamonds (effluent) represent the results of individual calculations.

The model may be run for a specified removal efficiency to determine the required tower height, or it may be run using a given tower height to calculate the scrubbing efficiency. For the field design, the efficiency required was specified for given gas and liquid flow rates, and the required tower height was calculated. Figure 3 is a summary of model

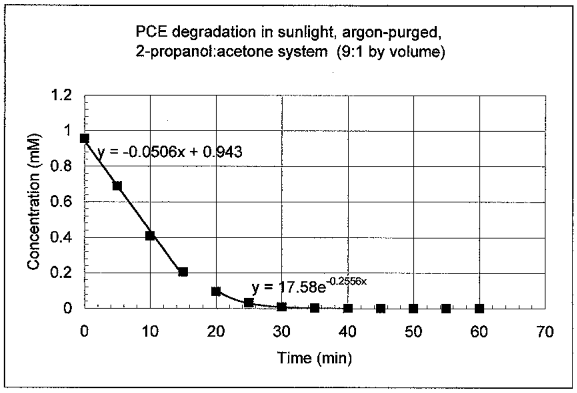

Figure 6. Kinetics of PCE transformation in sunlight in a solvent mixture of 2-propanol and acetone. The solvent was purged with argon to remove molecular oxygen before the addition of PCE and exposure to sunlight. Solid lines are lines of best fit to zero-order and first-order (in PCE) portions of the graph. Reactors consisted of 26-ml borosilicate glass containers. Temperature was about 25°C.

calculations for the tower height required to achieve a given fraction removal of the PCE from the influent landfill gas. The plot calculations assume a liquid flow rate of 0.1 L min^{-1} and a gas flow rate of 1.0 L min^{-1}. In these calculations, the influent liquid concentration of PCE is assumed to be zero. This is not a conservative assumption (due to solvent recycling in field applications). However, it was considered reasonable for the particular field application intended in view of the lab results, which showed the photo-catalytic reactor to be very efficient in degrading PCE.

Tower height requirements for 99% transfer of gas-phase PCE were calculated as a function of the ratio of the gas-to-liquid volumetric flow rates (Figure 4). The ratio corresponds to the unit-less ratio of the gas flow rate to the liquid flow rate.

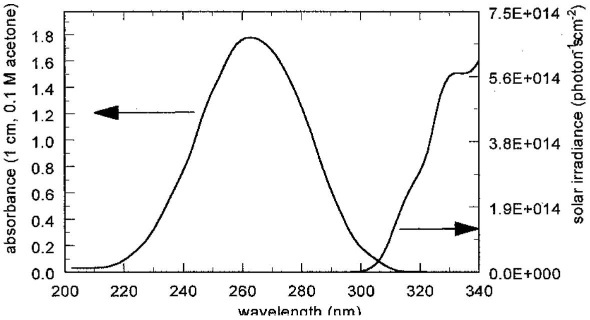

Figure 7. Electronic spectrum of ˜1.0 M acetone in water (absorbance units) and the solar actinic irradiance (photons $cm^{-2}s^{-1}$) at the earth's surface (calculated from Seinfeld).

The model calculations are based on ideal transfer rates for PCE from an otherwise clean air stream to a pure solvent mixture of 2-propanol and acetone (9:1 by volume). Consistent with expected field conditions, a gas-to-liquid flow ratio of 10 and a removal efficiency of 99% are used as model inputs, and a tower height of about 30cm is calculated to be required. Incorporating an oversize factor of two to account for the likelihood of non-idealities in the field and the error engendered by model assumptions, a scrubbing column of 60cm packed length was selected for the field trials.

Scrubber column laboratory trials

Experimental results indicated that column performance was reasonably well predicted by the theoretical model when the 2-propanol/ acetone solvent mixture was free of PCE (Figure 5). At least 90% of the gas-phase PCE was transferred to the clean solvent mixture. The gradual deterioration of PCE transfer efficiency was probably due to accumulation of PCE in the solvent since there was no PCE treatment step in this experiment. Nevertheless,

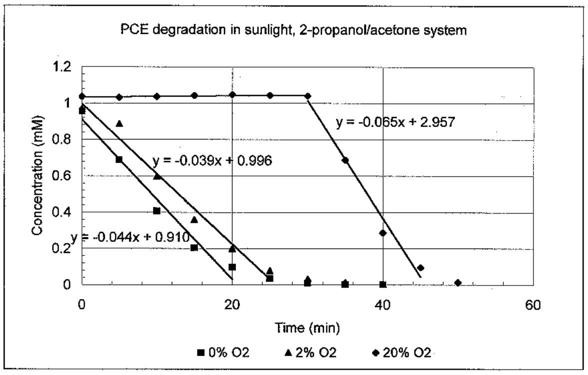

Figure 8. Lag-time effect of dissolved molecular oxygen (O_2) on the kinetics of PCE degradation in 2-propanol/acetone (9:1 by volume). Photoreactors (26 mL borosilicate glass vials) were filled with solvent containing 1 mM PCE and then purged with argon to obtain the 0% and 2% O_2 levels. Note that 20% O_2 (near-ambient air level) delays PCE destruction by 30 - 40 minutes in the photoreactor vials.

transfer efficiency was always greater than 80% over the one-hour course of the tests, and we determined that the scrubber design was sufficient for our landfill application.

Photo-reductive reaction mechanism

It is well known that acetone and other ketones absorb light in the near-ultraviolet (UV) range to initiate the reaction process (Calvert and Pitts, 1966). In the presence of molecular oxygen (O_2), acetone can be used to sensitize the photo-oxidation of alcohols (Coxon, 1987). This reaction could also be viewed as photo-reduction of O_2. In principle, this photochemical system should be capable of reducing many target species besides O_2, depending upon the redox potential of the target. Here we apply some of the fundamental knowledge gained on ketone photochemistry over the past four decades to the problem of remediating contaminated landfills.

In its excited state, acetone extracts a hydrogen atom from a molecule of isopropanol, producing an organic radical that is capable of reducing a variety of halogenated targets, including carbon tetrachloride (CT) and PCE. As described in more detail in our recent publication (Betterton et al., 2000), both chlorinated alkanes and alkenes have proven to be appropriate target contaminants for the liquid-phase reactions. A variety of aliphatic and aromatic ketones and alcohols are suitable for the liquid phase. We selected a solvent mixture containing 2-propanol and acetone (9:1 by volume) for our investigations.

Laboratory-based kinetic studies have shown that dehalogenation reactions in the photo-promoted system are very fast. In the millimolar range, PCE concentrations were lowered by an order of magnitude in a just few minutes (Figure 6).

Initial reaction rates were zero order in target concentrations, shifting to first-order kinetics as reactants approached micromolar levels. Results imply a change in the step that limits the overall rate of reaction from the light-initiated step (probably) to the radical-target reaction step at relatively low concentrations of the target. A complete reaction mechanism is not yet available, however, primarily because of uncertainty related to radical-radical extinction reactions.

Several observations of potential practical importance have been observed during our preliminary laboratory and rooftop studies. First, the destruction of CT and PCE can be driven by sunlight, even in borosilicate glass

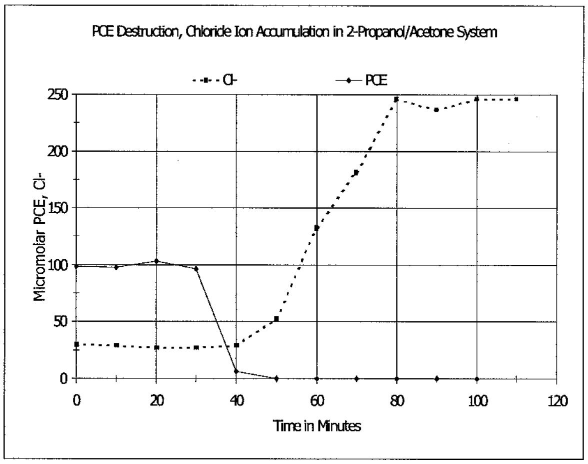

Figure 9. PCE destruction and chloride ion (Cl^-) accumulation in the 2-propanol/acetone solvent mixture during a typical rooftop experiment. Photoreactor was a 26 mL borosilicate glass vial. Initial concentrations for PCE and Cl^- in the solvent were 100 μM and 25 μM, respectively. Roughly two chloride ions were generated for each PCE molecule destroyed (photo-reduced) in the solvent mixture.

reactors. Only a small fraction of the solar spectrum that penetrates borosilicate glass is absorbed by acetone (Figure 7). Nevertheless, dehalogenation reactions are fast under ideal sunlit conditions. The second observation of obvious practical importance is that the presence of O_2 impedes the destruction of halogenated targets, presumably due to the consumption of light-derived radicals by O_2. When O_2 is present in the gases to be treated, reactor design will have to include sufficient detention time for the sequential destruction of O_2 and the target. O_2 effects are illustrated in Figure 8.

Photolysis experiments

Preliminary experiments designed to establish the feasibility of PCE and CT dehalogenation by photo-promoted reduction were carried out at the bench scale (Betterton et al., 2000). Two reactor types were utilized. The first was a 26 mL borosilicate glass vial filled with the solvent containing ≈ 1mM of the target compound and irradiated with sunlight. Samples were withdrawn periodically for analysis, and kinetic relationships were derived from these results.

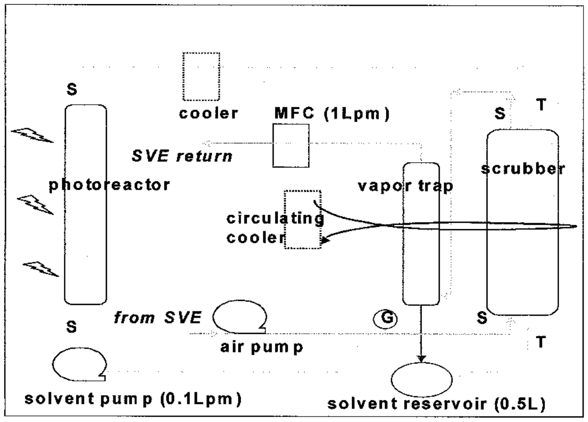

Figure 10. General schematic for the gas scrubber and photoreactor at the Harrison Landfill soil vapor treatment facility. The experimental 1 L min^{-1} treatment system is situated within the fenced confines of an existing carbon-adsorption treatment facility. The gas scrubber was designed for transfer of PCE from the extracted soil vapor to the 2-propanol/acetone solvent mixture. The photoreactor relies on the reduction of PCE by photo-generated 2-propanol radicals.

The second reactor type was a 20 mL glass tube that also contained the solvent and target. In this case, however, UV light (295 nm - 325 nm), originating from a Xenon arc lamp, was transmitted to the reactor via an optical fiber with cladding removed from the tip only. By calibrating the light source using ferrioxalate actinometry, it was possible to determine the total flux of UV light into the reactor and make calculations of quantum yield (Rabek, 1982).

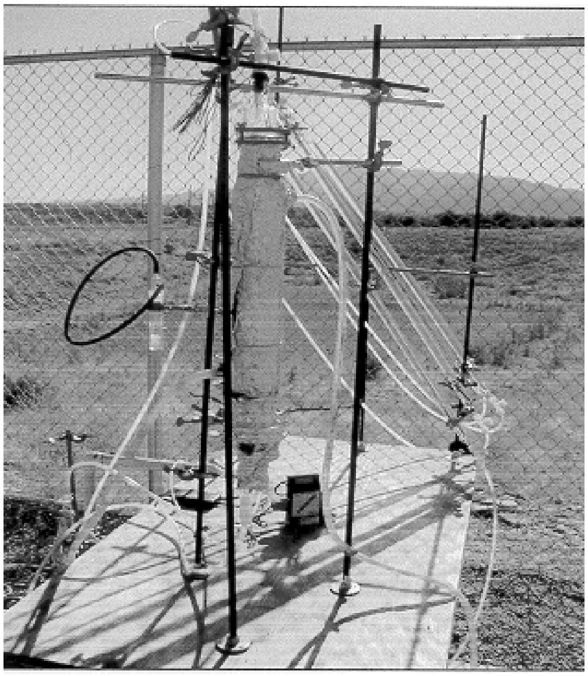

Figure 11. The Harrison Landfill phototreatment system. The scrubber column (foreground) is cooled to near 0^{o}C with circulating antifreeze and is wrapped in aluminum foil for shading. Soil vapor enters the base of the scrubber while solvent enters from the top and trickles downward through the ceramic packing media. The four photoreactor tubes (rear) are tilted to provide normal incident radiation at solar noon.

For the purpose of this report, we concentrate on results from the sunlight-driven reactor as a source of preliminary data for assessment of process kinetics and feasibility.

Representative data are provided in Figure 6. These show that the kinetics of PCE degradation in the 0.1 to 1.0 mM concentration range were approximately zero-order. The conditional zero-order rate constant was $\approx 5.3 \times 10^{-5}$ M min^{-1}. Millimolar concentrations were lowered by an order of magnitude in less than 20 minutes. The observed reaction rate was probably light-limited. In the micromolar concentration range, reaction kinetics were first-order in PCE with a rate constant for PCE disappearance of $\approx$ 0.26 min^{-1}. These results suggest that the concentration of PCE in the solvent will affect destruction rates, which will be zero-order, first-order, or mixed-order, depending on PCE concentration. In none of these experiments was TCE or any other partially dehalogenated intermediate observed. Since we could not measure ethane or ethene using the analytical procedures employed here, the mechanism (pathway) and products of PCE transformation remain to be established.

Photoreactor rooftop trials

In other preliminary experiments, PCE was treated in a tube that was eventually used in the field. This work was designed to confirm that PCE was treatable using sunlight and the 120 cm × 2.5 cm Pyrex tube before installing it in the field. The photoreactor was operated as a batch reactor in this case. Reactor performance was established by measuring PCE concentration as a function of time. Results suggest that reaction kinetics remained zero-order in PCE concentration down to $\approx 100\ \mu$M PCE with a reaction rate constant of $\approx 1.7 \times 10^{-5}$ M min^{-1}. The reduced reaction rate in the column reactor (compared to the 26 mL glass vials) probably resulted from lower light flux per volume of fluid in the larger system.

In addition to PCE disappearance, liquid-phase concentrations of chloride ion were measured by ion chromatography (Dionex DX-100; AS-14 analytical column) as a step toward reaction-product analysis (Figure 9). About

50% of the chlorine, originally present in the PCE target, was accounted for as chloride ion. The brief lag that preceded the appearance chloride ion (5-10 min) suggests that the process may produce short-lived intermediates. We are in the process of identifying these reaction intermediates.

HARRISON LANDFILL PHOTO-TREATMENT SYSTEM

Armed with the experience gained in the laboratory, a two-stage treatment system was designed and constructed at the Harrison Landfill. A block diagram and photograph of the system are shown in Figures 10 and 11. Soil vapor (30°C, 10-15% O2 by volume) was diverted by vacuum pump (Gast model DAA-V114-GB) from the city's carbon adsorption system at 40 L min^{-1}. A mass flow controller (Aalborg model GFC17) regulated the gas flow to 1.0 L min^{-1} through the scrubber, a 60 cm x 5 cm jacketed Pyrex column (Ace) with ½" ceramic Intalox® saddles (Jaeger) as packing material. The outer jacket of the scrubber was cooled to near 0^{o}C with antifreeze and a recirculating cooler (Fisher model). Influent and effluent gas samples were collected from ports at the bottom and top of the scrubber column, respectively.

Acetone evaporated from the gas scrubber was recovered using a jacketed, 30 cm x 3 cm distillation column (Ace) that was also cooled to nearly 0°C. Recovered solvent was returned by gravity feed to the 500 mL Pyrex solvent reservoir, and effluent gas was returned to the SVE system.

PCE-loaded solvent was pumped (Masterflex pump model L/S 7524-40) with a Teflon pump head from the 500 mL Pyrex reservoir (Ace) at 100 mL min-^{1} into the bottom of the first photoreactor tube (1.2m x 2.5 cm Pyrex; 590 mL). Up to four photoreactor tubes were connected in series to increase the residence time and to allow the solvent to photolytically remove dissolved O_2. Inlet and outlet sample ports in each tube allowed withdrawal of liquid-phase samples without introducing ambient air. Following treatment in the photoreactor, the solvent was cooled to nearly 0^{o}C by passage through the recirculating cooler and returned to the scrubber. The total solvent volume in the closed system (four photoreactor tubes) was 3.2 liters, and the photoreactor volume was 2.4 liters, or 75% of the total volume.

Gas samples were withdrawn from the scrubber column with a 60 mL gas- tight syringe (Hamilton) and transferred to evacuated 100 mL aluminum canisters (Tracer; 3 x 60 mL injections into each canister) for transport to the laboratory and subsequent analysis by gas chromatography (Hewlit-Packard 5890 ECD). Solvent was collected using 3 mL syringes (Hamilton) and transferred to sealed, 2 mL brown-glass vials (Supelco).

In a standard experiment, the solvent was equilibrated (chilled) for several hours before soil vapor was admitted to the system. Thereafter, influent and effluent gas samples were withdrawn at hourly intervals to measure scrubbing efficiency for PCE and other target contaminants.

The effectiveness of the photoreactor was determined by comparing liquid-phase concen-

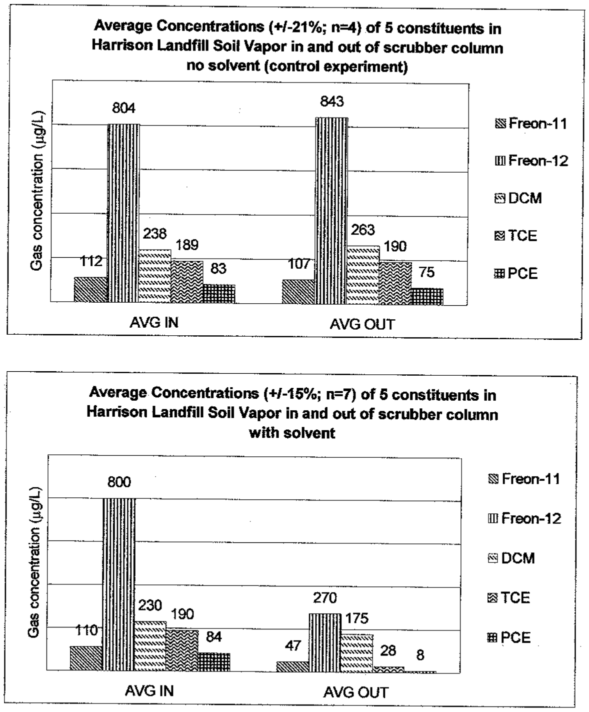

Figure 12. Relative concentrations of PCE and other halogen-containing gases scrubbed from soil vapor at the Harrison Landfill. The top figure shows the gas-phase results of a control experiment when the scrubber was run dry (no solvent). The bottom figure shows the results with 2-propanol/acetone solvent mixture (9:1 by volume) in the scrubber. PCE was identified via gas chromatography using authentic standards. All other gases were tentatively identified by comparison to independent city of Tucson analysis, relative amounts present, retention times, and other indirect evidence.

trations of PCE and other targets in the reactor influent and effluent. The accumulation of chlorinated-reaction intermediates due to the light-dependent transformation of PCE was followed by comparing ion chromatograms corresponding to liquid-phase samples withdrawn at different points in the field experiment. Loss of acetone from the two-solvent system was monitored spectrophotometrically (Shimadzu UV-2101-PC).

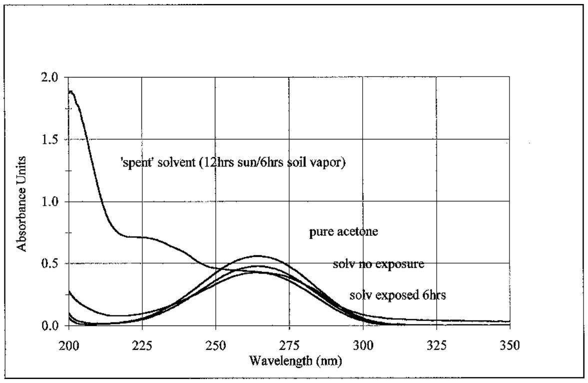

Figure 13. Absorbance spectra for the 2-propanol/acetone solvent mixture (9:1 by volume) were determined using a Shimadzu Model UV-2101PC spectrophotometer consisting of the dual-path photometer unit and host computer workstation. The analytical wavelength range was from 350 nm to 200 nm; measurements were taken at one-nm increments using a one-nm slit width and slow scan speed. Spectrocell Model R-3100-T cuvettes (fuv quartz, spectral range 170-2200 nm, 10 cm path length) were used exclusively. We used the spectra to determine losses in acetone during experimental runs at the landfill. Early experiments had significant losses in acetone, which we corrected by the addition of a solvent trap. The plot illustrates changes in the absorbance spectra during our latest experiments. Slight losses in acetone occurred over the course of 12 hours exposure to sunlight. Significant changes in the low-end spectra occurred as landfill gas dissolved into the solvent.

EXPERIMENTAL RESULTS AND CONCLUSIONS

In its initial configuration, the photoreactor consisted of a single glass tube that provided a detention period of approximately 30 minutes. Comparison of PCE concentrations entering and exiting the tube indicated that little or no PCE was destroyed in a single pass through the column, most likely because dissolved O_2 impeded the PCE reac-

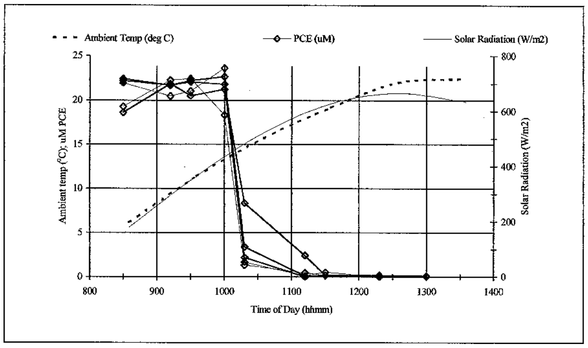

Figure 14. Results of photochemical treatment of Harrison Landfill soil vapor conducted January 6, 2000. The photoreactor ran in plug-flow batch mode after being saturated with soil vapor (PCE) by running the scrubber overnight. Two effects are noteworthy. First, oxygen (O_2) delays PCE dehalogenation for approximately 120 minutes under these conditions. Second, once the O_2 is photochemically reduced, PCE is rapidly destroyed over a further 120 minutes. Conditions at the site were partly sunny and 20 - 25°C. The soil vapor contained 13% O_2.

tion or because acetone was rapidly lost from the system due to its volatility. Consequently, the system was modified to recover fugitive acetone from the exit gas stream, and an O_2 sensor (Instrumentation Laboratory model Ohio 600) was installed in line to measure O_2 in the soil vapor. O_2 readings from 10-15% were routinely observed, suggesting that poor photoreactor performance was due to inadequate detention time for sequential reduction of O_2 followed by PCE. Laboratory experiments have shown that O_2 is always reduced first, because it reacts so rapidly with the photo-generated 2-propanol reductant. As a remedy, column capacity was increased fourfold by adding three additional (identical) tube sections in series.

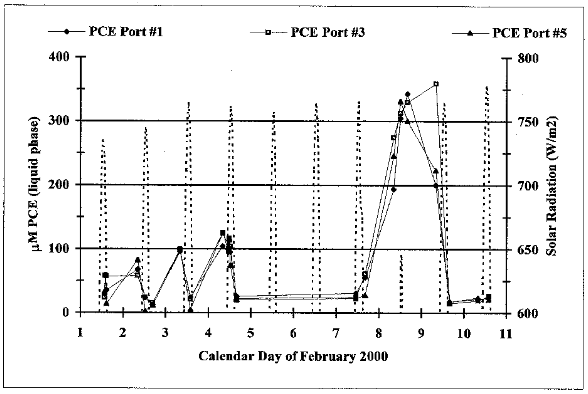

Figure 15. Continuous phototreatment of soil vapor at Harrison Landfill, February 1-10, 2000. The gas scrubber and photoreactor were operated simultaneously. Solar radiation peaks (dotted) indicate solar noon. Note that PCE levels of ≈ 50-100 µM were observed in the morning and virtually reduced to zero by mid-afternoon each day (2/8 the exception). No samples were collected over the weekend (2/5 - 2/6). Also note that cloudy conditions persisted on 2/8 (decreased solar radiation), and PCE levels increased to >300µM by the morning of 2/9, but were again reduced to near zero by mid-afternoon when sunny conditions returned.

The efficiency of the solvent vapor trap was checked by comparing the absorbance spectrum in the 200-400 nm range derived from the fresh solvent mixture with that of "spent" solvent following extended use. Field data described here were derived from the modified four-tube photoreactor with the solvent vapor trap.

At the landfill, the scrubber consistently extracted > 90% of the PCE in the soil vapor (Figure 12). There was no evidence of PCE loss due to leaks, for example, in a solvent-free (control) experiment. A number of other halogenated compounds, including TCE, and possibly Freon 11 and Freon 12, were also detected in the solvent. Tentative identification of freons was based on comparisons with the city of Tucson routine soil vapor analysis, but has not yet been verified using authentic standards.

Although scrubber operation is considered adequate from the standpoint of technology demonstration, performance was considerably less efficient than predicted by the model. Efficiency greater than 90% was observed, while 99% efficiency was predicted (see above). There are several possible explanations for the apparent discrepancy. For example, calculations were premised on assumptions that solvents introduced at the top of the column were free of PCE, and there were no other gas- or liquid-phase constituents that might impede PCE transfer. Under the circumstances of these tests, agreement between model predictions and empirical results is considered adequate.

Photoreactor performance was somewhat erratic because of the variable nature of O_2 levels in the solvent. O_2 levels in the extracted soil vapor varied from 2-15%, depending on the recent history of the city's full-scale treatment operations. At various times, the city injected air into the landfill to speed the vacuum recovery and thereby increased the O_2 concentration in the soil vapor. Periods of poor performance apparently did not result from loss of acetone or from accumulation of interfering compounds that absorbed light energy at the same wavelength as acetone. Spectra derived from solvents after extended use (up to six hours) indicated that acetone levels were essentially unchanged (Figure 13) and that, despite the accumulation of energy-absorbing substances at wavelengths < 250 nm, there was little interference with acetone absorbance at longer wavelengths.

Results suggest that photoreactor detention periods of more than one hour are necessary to ensure adequate PCE transformation in the presence of high levels of O_2. HL data (Figures 14 and 15) show that it is indeed possible to photochemically destroy PCE quite rapidly, once all the dissolved O_2 has been photochemically reduced, probably to organic peroxide intermediates (Rubin). The kinetics of O_2 reduction in the photoreactor have not been investigated, but O_2 elimination took about two hours under the cloudy conditions prevailing during the experiment conducted on Jan 6, 2000. After that, it took a further two hours to reduce PCE levels from about 200 μM to less than 10 μM. Obviously, dissolved O_2 in extracted landfill gases (transferred to the solvent mixture in the scrubbing column) can delay the onset of PCE transformation for periods of the detention time in the photoreactor. However, in a strictly anaerobic landfill, this problem will be greatly diminished.

Instead of increasing reactor detention periods, it should be possible to increase reaction rates by focusing more sunlight on the photoreactor. There has been no attention to light gathering and focusing up to this point in the study, but we intend attaching parabolic reflectors to the photoreactor tubes to increase the light intensity. We estimate a potential ten-fold gain of photon flux in the photoreactor, and this should increase photolysis rates by the same factor, if the system is indeed light-limited.

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