

Evaluation of Solvent Flotation Coupled with Photodegradation for Decontamination of Soil

Kapila, S.^A, Lo, Yun-Hsieh^A, Orazio, Carl^A, Puri, R.K.^A, Yanders, A.F.^A, Elsewi, A.A.^B, Overcash, M.^C, McPeters, A.^C

^AEnvironmental Trace Substances Research Center, University of Missouri, Columbia, Missouri 65203

^BEnvironmental Division, Southern California Edison Company, Rosemead, California

^CDept. of Chemical Engineering, North Carolina State University, Raleigh, NC

INTRODUCTION

Many sites in the United States and other countries are known to be contaminated with polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), as a result of either accidents or industrial activities. The only generally accepted technology for destruction of these compounds in solid matrices such as soil is high temperature incineration. However, this process is prohibitively expensive and alternate methods of degradation need to be researched and implemented. This is particularly timely in view of the recent suggestion that the currently accepted level of concern for 2,3,7,8 TCDD in soil of 1 ppb should be revised to 10 ppb¹. The practical implication of this ten-fold increase in the permissible level is that the extremely high destruction efficiencies of 99.9999% which can normally be reached only by high temperature incineration may not be necessary in treating many sites.

Photodegradation, i.e., destruction achieved through exposure to UV light, has been shown to be highly efficient in selected solutions and in the vapor phase. It has been reported to be the most significant natural mechanism for removal of dioxins in the environment². A number of studies dealing with photodegradation of dioxins and furans have been published³⁻⁸. Degradation efficiencies ranging from 0-100% have been reported. As expected, the rate of degradation was found to be dependent on the physical state of the matrix, the nature of the solvent, the nature of the irradiation source and the duration of exposure. The highest degradation efficiencies were observed in non-absorbing solvents. The process has not been regarded as a promising technique for decontamination of soil due to the sharp attenuation of light beyond a fraction of a millimeter in soil. Thus, desorption of contaminants and their transport to the surface is necessary for a practical photodegradation-based decontamination technology. The overall objective of the studies described in this paper was to evaluate the effectiveness of solvent-mediated mobilization and photodegradation of dioxins and furans as a means of soil decontamination. The specific objectives of the studies were: (i) to determine partition behavior of dioxins and co-

contaminants in soil, and the solvent systems most amenable for photodegradation, (ii) to determine the correlation between soil properties and the degree of solvent saturation required for effective desorption and transport (iii) to determine the removal efficiency of selected solvents through flotation experiments.

A. Partition Experiments

The purpose of these experiments was to determine the equilibration period and the distribution coefficient for PCDD-PCDFs in soil and binary solvent systems. The initial experiments were carried out in shake flasks. Aliquots of contaminated, air-dried soils with known concentrations of dioxin were placed in amber glass bottles, and the solvent was added at 30-100% saturation levels. The soil/solvent mixtures were allowed to equilibrate for periods ranging from 4 hrs to 168 hrs. After each equilibration period, the solvent was forced from the soil by adding organic-free water to the bottom of the container with a syringe. The solvent layer was siphoned and analyzed for dioxins. The distribution coefficient (k) was calculated as the ratio of TCDD conc. in solvent vs TCDD conc. in soil.

B. Field Trials

The objective of the field trials at the Visalia, California, and Times Beach, Missouri, sites was to demonstrate the applicability of solvent-mediated mobilization and subsequent photodegradation of polychlorinated dibenzo-p-dioxins and related compounds in soil. These two sites were selected because of the differences in the mode and nature of contamination at the two sites. Differences in soil characteristics and meteorological conditions at the two sites also permit a better evaluation of the treatment process.

The experimental protocol to meet this objective encompassed the following tasks.

1. Construction and installation of the experimental plots.
2. Removal of contaminated soil and other materials from the storage bins at Visalia or the contaminated soil pile at Times Beach.
3. Homogenization and placement of materials in experimental plots.
4. Initial sampling and analysis of materials from the plots.
5. Application of appropriate solvent mixture to the test plots at 80% saturation levels.
6. Periodic addition of water to a set of test plots and one control plot.
7. Second, third and fourth sampling and analysis of materials at one month, three month and six month time intervals.
8. Tabulation and statistical analysis of the data.
9. Evaluation of results and submission of report.

The field experiments are being conducted in stainless steel treatment bins. The bins were fabricated at the Science Instrument Shop of the University of Missouri-Columbia. The sides and bottom of the bins were constructed with 1/16" stainless steel plates. A 1/16" perforated stainless steel sheet was placed in the containers 1 cm above the bottom. Two 3/8" swagelok fittings were welded to the containers. Half of the bins are equipped with a water sensing device. The purpose of the device is to maintain a constant level of water above the soil surface. Eight treatment bins are being used at the Visalia site. Each bin holds approximately 0.29 m³ of contaminated soil.

The contaminated soils were screened and homogenized in a rotary tumbler. The homogenized materials were placed in the containers to a depth of 6", i.e., within 1" of the top edge. The materials were packed to achieve $\geq 70\%$ natural density. Five core samples

were taken, and the holes created were filled with excess homogenized material. The solvent mixture was applied to the plots at 80% of the void space level. No solvents were added to the control plots. The experiments were planned to monitor the mobilization and photodegradation efficiencies under field conditions. Half of the solvent-only bins were covered with opaque plastic or other suitable material to prevent exposure to sunlight while permitting free exchange of air. After an equilibration period of 36 hrs, half of the plots were flooded and the water level controlled to maintain a water layer approximately 2.0 cm deep above the soil surface. Four core samples were taken from each plot after 30, 60, 120 and 180 day intervals. The cores were sectioned in sections ranging from 0.5 to 4 cm in depth.

RESULTS AND DISCUSSION

The preliminary laboratory experiments were conducted to determine the optimal solvent composition for both the desorption and the mobilization of dioxins. The requirements of the solvent mixture were set by the diffusivity model of Overcash and co-workers⁹. According to this model, the mobility of dioxins is largely determined by concentration gradients; thus, solvents with a high boiling point and a very low extinction coefficient in the U. V. range were predicted to be the most suitable. Aliphatic hydrocarbons from C₉H₂₀ to C₁₄H₃₀ were selected as the solvents of choice. However, these nonpolar solvents exhibit poor wettability towards polar soil surfaces; consequently, a high boiling alcohol was added to the aliphatic solvent. Experiments were also conducted with binary solvent mixtures which contained xylene in addition to alkanes and alcohols. The rationale for introduction of xylene to the mixture is based on the high solubility of dioxins and related compounds in aromatic solvents. However, aromatic solvents, because of their high extraction coefficient and the relatively low absolute amount of dioxins in the soil, were found to be of little use for the present application. One of the most important criteria for selection of a solvent was the equilibration period needed to reach steady-state concentration in the solvent-soil system. It is obvious that the equilibration period will increase with the viscosity of the fluid; thus the longer chain (high boiling point) solvents will require longer equilibration periods. The results indicate that the most appropriate solvent system for field application would be a mixture of C₉-C₁₀ alkane mixed with butanol. This is supported by desorption experiments with contaminated soil from Times Beach. The results conform to the established relationship between viscosity and mass transfer and clearly demonstrate that equilibration is reached rapidly in lower chain homologs with lower viscosities. Subsequent experiments were carried out to measure the partitioning of tetra through octachloro dibenzo-p-dioxin in soil/dodecane butanol systems. It was determined that at 80 - 100% saturation, greater than 95% of the chlorinated dioxins had partitioned into the solvent phase.

Initial concentrations of dioxins and co-contaminants in soils for field experiments were established through five core samples taken from each bin prior to treatment. The levels of dioxins were found to vary appreciably between the bins. The concentration of octachloro dioxins varies from 200 - 800 ppb. As mentioned earlier, 60 liters of soltrol (a mixture of C₁₁-C₁₂ hydrocarbons obtained from Phillips Petroleum) was mixed with reagent grade butanol. The alkane to alcohol ratio was kept at 5:1. Thirty-six hours after the application of the solvent mixture, the solvents plus dissolved contaminants were brought to the surface by addition of water from the bottom of the bins. Solvents containing high concentrations of soil-borne contaminants were mobilized to the surface. Core samples were

taken after one month, two month and four month time periods. The core samples were sectioned and analyzed as discussed in the experimental section. The data revealed that little or no change in dioxin concentration occurred in the control bin (without solvent and water). Significant mobilization of dioxins occurred in bins which were treated only with solvents. However, movement occurred in both the shaded and open areas and the differences were not highly significant, indicating that a concentration-dependent diffusion model may represent only a part of the process. Mobilization may also be related to capillary movement. No significant declines in total OCDD/OCDF amounts were observed in the solvent treated bins, indicating that even though mobilization occurs toward the surface, the photodegradation is quite limited. The situation was, however, quite different in the case of bins which were flooded with water. In these cases, a drop of up to 80% in the total dioxin amount was observed after a one-month period. The effects of solvent application on degradation of other contaminants such as pentachlorophenols are also being investigated. Detailed results from these studies will be presented at the Conference.

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