

## SOLVENT OPTIMIZATION FOR THE PHOTODEGRADATION BY SUNLIGHT OF 2,3,7,8-TCDD ON CONTAMINATED SOILS

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Known solvents for TCDD were screened for TCDD solubilization from spiked soil, diffusion rates in the soil-solvent mix and other factors affecting photodegradation. The best solvent found was a mixture of tetradecane with 2-propanol. Photodegradation was increased with this mixture.

### INTRODUCTION

Decontamination of soils containing 2,3,7,8-TCDD poses a formidable technical challenge, since this compound is apparently not subject to biological attack. The susceptibility of 2,3,7,8-TCDD to dechlorination by ultraviolet light offers the potential for *in situ* treatment by sunlight if the other physical requirements can be met throughout the contaminated soil depth. Basically, these other requirements must be provided by a solvent or solvents which can be applied to the soil surface. Earlier investigators [1,2] used mixtures of ethyl oleate and xylene to treat contaminated soils. Both reported substantial decreases in TCDD concentration near the surface after UV exposure. The studies reported in this paper started with ethyl oleate as the primary solvent, but other organic compounds were added as the technical requirements of the solvent system were better defined.

Since photodegradation can occur only at the soil surface, physical processes to transport TCDD to the surface are obviously necessary. One major objective of this study was to provide systematic information about transport phenomena and the other physical processes involved that can interact to accelerate or limit the desired photodegradation. The second objective was to demonstrate a practical solvent treatment process that would allow photodegradation of TCDD on contaminated soils at depths of 0-5 cm.

### EQUIPMENT AND METHODS

All experiments utilized pure 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and/or the <sup>14</sup>C-labelled analog; both obtained commercially. Ultraviolet exposures in the laboratory were made under an Oriol lamp with a 200 watt Mercury (Xenon) lamp and filters to remove unwanted wavelengths. In the important 290-320 nm wavelength range, the lamp beam intensity was about 10X greater than sunlight. Sunlight exposures were made during the months of June and July in Raleigh, NC. Spiked soil was obtained by adding a Norfolk sandy loam to

TCDD dissolved in ethanol and letting the wet mass air-dry with mixing. Analyses for TCDD were made by a commercial laboratory following EPA Protocol 8280.

#### PRELIMINARY TESTS OF EQUIPMENT AND CONCEPT

To establish the effectiveness of the Oriel lamp beam, solutions of TCDD in ethyl oleate and in hexadecane were exposed for varied lengths of time. Photodegradation was rapid in hexadecane and slower in ethyl oleate. In ethyl oleate, 75% of the TCDD was lost in 10 hours. Next, laboratory tests were made to determine if TCDD diffusion to an exposure surface would occur in ethyl oleate solution. In this test, a filter pad blocked the Oriel beam from the TCDD solution below the pad. Nevertheless, 72% of the TCDD below the filter was destroyed in 96 hours exposure, confirming that TCDD had diffused upward through the solvent-wet filter. Finally, spiked soils were treated with 13.8% ethyl oleate and exposed to the Oriel lamp beam and to sunlight. Results were limited in both cases. Significant photolysis occurred only in the top 6 mm of the soil. About 8% of the TCDD in a 25 mm deep sample was destroyed. Obviously, factors were limiting the photolysis as demonstrated with TCDD in ethyl oleate solution. To identify the limiting factors, a list of the characteristics of an optimal solvent was prepared.

#### CHARACTERISTICS OF OPTIMUM SOLVENT

1. Quickly dissolves all TCDD.
2. Provides diffusion path at fast rate.
3. Does not absorb ultraviolet rays.
4. Acts as hydrogen donor.
5. Remains on soil—low volatility.
6. Effective in presence of soil moisture.
7. Low human or environmental drawbacks.
8. Available at reasonable cost.

Major laboratory studies were necessary to screen a selected number of solvents and solvent mixtures for the first two characteristics. Screening of solvents for the other characteristics required only literature searches or simple laboratory tests.

#### STUDIES OF TCDD SOLUBILIZATION AND DIFFUSION RATES IN SOIL-SOLVENT MIXTURES

Screening tests were made using <sup>14</sup>C-labelled TCDD to measure the rate of partitioning of TCDD from spiked soil into a large excess of solvent under static conditions. Solutioning occurred rapidly only with the low molecular weight alcohols and with dimethyl sulfoxide. Ethyl oleate and tetradecane dissolved TCDD at slower rates, but were the most

promising of the less volatile compounds. More viscous materials such as olive oil and PEG-300 were very slow. Mixtures of alcohols with ethyl oleate or tetradecane gave promising results. Three systems were selected for more quantitative study: ethyl oleate plus ethanol, tetradecane plus 2-propanol and dimethyl sulfoxide alone.

Laboratory tests were developed to measure the diffusion rates or movement of  $^{14}\text{C}$ -labelled TCDD in the soil-solvent mixtures of interest. Two equal soil-solvent mixtures were prepared for each diffusion test, with TCDD in only one. The two mixtures were loaded into a glass cylinder with a marked interface between them. After 96 hours, the total soil column was cut into samples. Activity tests then determined the final TCDD distribution in the soil on both sides of the interface. This distribution was used to calculate effective diffusion rates. The results showed that adding alcohols to ethyl oleate or tetradecane improved the solubilization rate and greatly increased the movement of TCDD. Highest transport rates were obtained with the tetradecane/2-propanol mixture. Based on these results, laboratory exposure tests were made with spiked soils treated with the 2/1 tetradecane/2-propanol solvent mix, the 2/1 ethyl oleate/ethanol mix and with dimethyl sulfoxide.

#### LABORATORY EXPOSURES WITH SELECTED SOLVENTS

Spiked soil containing about 45 ng/g of TCDD was treated with (1) 12.4% of a 2/1 mixture of tetradecane with 2-propanol, (2) 13.3% of a 2/1 mixture of ethyl oleate with ethanol and (3) 8.8% of dimethyl sulfoxide. Each soil-solvent combination was mixed thoroughly, then loaded into the exposure cylinders. Tamped soil depths were about 25 mm. The samples were exposed under the Oriel beam for 96 hours. Solvent evaporation during exposure was determined by weight loss. Results are summarized in Table 1. For comparison, the preliminary test with only ethyl oleate (13.8%) is also shown.

Sample	Solvent mix	% Solvent evaporated	% TCDD destroyed
822	Dimethyl sulfoxide	43	16
848	Ethyl oleate/ethanol	18	19
821	Tetradecane/2-propanol	24	28
605	Ethyl oleate only (from early test)	low	8

Table 1: Photodegradation of TCDD on spiked soils

The results show a substantial increase in the percent of TCDD destroyed in comparison to the early test with ethyl oleate alone. Best results were obtained with the tetradecane/2-propanol solvent mix. Results with dimethyl sulfoxide were poorer, but solvent concentration was lower in this test.

#### SUMMARY AND CONCLUSIONS

1. Many technical factors must be considered in selecting the best solvent treatment for photodegradation of 2,3,7,8-TCDD on contaminated soils.

2. Critical factors include: dissolution rate of TCDD from spiked soil into solution, diffusion rates in the soil-solvent mixture, low UV absorption by the solvent, solvent volatility, solvent miscibility with soil moisture, and presence of a hydrogen donor.
3. Ethyl oleate, and other high molecular weight organic compounds, have limitations in one or more factors.
4. Low molecular weight alcohols provide rapid solutioning of TCDD in mixtures with less volatile solvents.
5. Screening tests led to a 2/1 mixture of tetradecane with a miscible alcohol as the most promising solvent.
6. Laboratory UV exposures have confirmed higher percentages of TCDD photodegradation, when using a mixture of tetradecane and 2-propanol.
7. Further improvements are necessary to demonstrate a practical process.

#### REFERENCES

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