TRANSPORT OF 2,3,7,8-TETRACHLORODIBENZO-*P*-DIOXIN IN SOIL CONTAINING ORGANIC SOLVENTS

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Studies were conducted to measure the transport of TCDD in soil with organic solvents. Modeling then determined effective diffusion coefficients of TCDD through the soil/solvent medium. Using this information, more complex experiments involving the effects of sunlight on the TCDD concentration profile were mathematically described. This model could be useful in many field situations in which organics are present, either as co-contaminants or as part of the cleanup process.

INTRODUCTION

The extreme persistence of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) as a soil contaminant is well-known. However, movement may occur when other organic chemicals provide a transportation medium in the form of a bulk liquid phase (*eg.* waste oil, tank leakage of trichloroethylene, solvent spills). Barring the physical movement of the soil particles, this migration is predominantly by diffusion and convection involving the interaction of the organic fluid with the soil. After a site or area has had the direct source removed (*eg.* a leaking tank), migration of trace substances is primarily by diffusional processes, particularly when the contaminant has low water solubility.

For TCDD in soils, transport with liquid organic solvent phases present is especially relevant to the eventual disposition of the chemical because there is very little TCDD movement without such co-contaminants. A model of diffusional and convectional transport would have relevance in the mathematical description of the application of TCDD-contaminated oil to land, the residual migration in solvent plumes when the leaking tank source was removed, or in other circumstances when solvents in soils may cause leaching or removal of TCDD. For example, one possible cleanup technique for TCDD-contaminated soil involves the application of organic solvents to the contaminated soil, and the subsequent solubilization, movement and photodegradation of the TCDD (Exner, 1984, Liberti, *et al.*, 1978).

The movement of TCDD in soils in the presence of organic solvents is poorly understood because TCDD diffusivity and the role of a liquid organic phase are not well quantified. This report describes experiments and modeling undertaken to fill some of the gaps in the current knowledge of the physical constants related to this transport. The objectives of the studies were to find effective diffusivities of TCDD in an organic phase in soil and to develop a model for TCDD transport in soil containing organic solvents.

DIFFUSION STUDIES

Experimental

The diffusion studies were simplified experiments to isolate the diffusional aspect of TCDD movement in a liquid organic phase in soil. The experimental procedure has been described in detail elsewhere (Overcash, *et al.*, 1990). In short, two soil/solvent cells of about 1.5 cm depth were prepared, one containing ^{14}C-labelled TCDD and one without. The cells were then placed in contact in a diffusion apparatus, covered with a plastic cover, and left undisturbed for 96 hours. After the diffusion time had elapsed, the soil was cut into 3–5 mm layers which were analysed by scintillation counting for the labelled TCDD. Thus concentration profiles as a function of depth and distance from the interface were developed. Five solvents were studied, tetradecane, ethyl oleate, n-butanol, isopropanol, and dimethyl sulfoxide, in twenty diffusion studies. Three different levels of solvent (full, ~ 70%, and ~ 30% saturation) were used.

To test the assumption that diffusion was the main TCDD transport pathway, one of the studies in ethyl oleate was conducted with the spiked soil half on the top of the diffusion column, the reverse of the usual procedure. Ethyl oleate has a low vapor pressure and therefore the loss by evaporation was negligible. The results of this study did not differ appreciably from those obtained through the usual method; thus convection was neglected in the model for the experiments.

Results

The experimental setup can be described with the following two mass balances:

$$\frac{\partial C_b}{\partial t} = D_{eff}\frac{\partial^2 C_b}{\partial x^2} + k_d a\Gamma - k_a C_b \qquad (1)$$

and

$$a\frac{d\Gamma}{dt} = k_a C_b - k_d a\Gamma \qquad (2)$$

where C_b is the bulk concentration of TCDD in solution, Γ is the concentration of adsorbed TCDD, k_a and k_d are the rate constants for TCDD adsorption from solvent to soil and desorption to solvent from soil, respectively, a is the ratio of surface area of the soil particles to solution volume, and D_{eff} is the effective diffusivity of the TCDD through the soil.

The modeling of these studies utilized the description of the TCDD adsorption/desorption kinetics developed in earlier experiments (McPeters, *et al.*, 1990a). Thus, rate and equilibrium constants for these processes were already known. The equations were solved numerically using an IMSL packaged equation solver, and the D_{eff} was adjusted until the best fit to the data was found.

The results of the studies at full saturation are given in Table 1. The fit of the model to the data was very good, with correlation coefficients above 0.96 for the majority of cases at all levels of saturation. The resulting effective diffusivities were compared with free solution diffusivities (D_{WC}) estimated using the Wilke-Chang equation (Wilke

Test #	Solvent	Temp (deg C)	$D_{WC} \times 10^{-6}$ (cm²/sec)	% TCDD past interface	$D_{eff} \times 10^{-6}$ (cm²/sec)	R^2
698	ethyl oleate	16	1.64	13.2	0.593	0.99
700		16	1.64	6.7	0.283	0.96
727		28	2.21	21.8	1.92	0.98
743		27	2.15	18.5	1.07	0.98
744		27	2.15	20.3	1.39	0.98
745		27	2.15	12.0	0.664	0.98
725	tetradecane	28	4.92	30.1	3.83	0.96
726		28	4.92	25.0	3.54	0.73
910		24	4.68	25.5	2.65	0.96
767	dimethyl sulfoxide	29	3.28	33.7	2.66	0.97
768		29	3.28	33.5	2.49	0.99

Table 1: Results of diffusion studies at full saturation

and Chang, 1955). In most cases, the comparison was favorable. However, in the case of isopropanol the diffusivity calculated from the model appeared to be too high, and it was concluded that evaporation of the alcohol had affected the TCDD transport in this sample.

SUNLIGHT EXPOSURE STUDIES

Experimental

This series of tests was conducted over a 3 month period during the summer. The objectives of the studies were to determine the effects of sunlight exposure on TCDD-contaminated soil that had been treated with an organic solvent mixture. A complete description of the experimental procedure is given elsewhere (McPeters, *et al.*, 1990b), but a brief description follows. Soil columns of 6 cm depth containing ^{14}C-labelled TCDD in Norfolk sandy loam containing 4% water by weight were treated with a tetradecane/n-butanol mixture. This solvent mixture had been determined to be the most appropriate in several earlier studies. Most of the columns, each having varying characteristics to test several different features of the studies, were then exposed to sunlight for a total of 30 sunny days. The columns were periodically weighed to determine solvent losses.

After the exposure period, the columns were divided into several segments. Each soil sample was then analysed for total ^{14}C and for TCDD. The difference between the two was assumed to be the degradation products from TCDD photolysis.

Results

To model the sunlight exposure tests, an equation describing convective movement of the solvent and transport of the TCDD was added to the model for the diffusion studies. The boundary conditions also were different, since the total TCDD amount was no longer constant. The equations were then solved by numerical methods, using the effective diffusivities and adsorption/desorption kinetics previously determined.

The soil columns showed TCDD losses of between 20 and 55%, depending on the conditions of the sample. The difference between the amount of ^{14}C and TCDD was assumed to be due to TCDD photolysis. However, some of the TCDD was lost by unknown processes, as determined by the ^{14}C mass balance. The soil columns were contained in glass syringes, and solvent leakage could have occurred around the bottom of the plunger. Separate studies and calculations showed that TCDD volatilization could not have been a major pathway for loss, but the more volatile degradation products could have evaporated.

CONCLUSIONS

The diffusion and sunlight exposure studies show evidence of the transport and photodegradation of TCDD in soil containing certain organic solvents. Models of these studies quantify the physical constants necessary to describe this behavior, and provide a framework for the modeling of actual field contamination situations in which an organic phase is present in the soil.

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