Reprint

149430

Chemosphere, Vol.18, Nos.1-6, pp 1305-1312, 1989
Printed in Great Britain

0045-6535/89 $3.00 + .00
Pergamon Press plc

COMPARISON OF THE RATE OF TCDD TRANSPORT AT TIMES BEACH AND AT EGLIN AFB

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An analysis of the available data on the rate of transport of 2,3,7,8-TCDD is presented. The analysis demonstrates that the rate of transport of 2,3,7,8-TCDD is very slow via vaporization. The analysis finds that over 99 percent of the 2,3,7,8-TCDD applied to the roads at Times Beach is still in the soil.

BACKGROUND

During the early 1970's, Northeastern Pharmaceutical Company and Chemical Company (NEPACCO) produced hexachlorophene at their Verona, Missouri site. Waste products from their process included the compound 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The TCDD was primarily contained in a distillation residue. This residue was mixed with waste-oil and was used to oil roads and horse arenas for dust control. The most widely publicized site where the waste was used for dust control was Times Beach, Missouri. In the past three years, a large body of research has been done on the transport of TCDD in soils. The object of this paper is to use this body of research to better understand what happened at Times Beach.

LITERATURE REVIEW

The longest running TCDD soil transport experiment was established by Dr. Alvin Young (USAF) in April of 1972 at Eglin Air Force Base (AFB). In this experiment, Dr. Young applied Agent Orange contaminated with TCDD to the bottoms of some trenches approximately 10 cm deep. In February of 1984, Dr. Young and a sampling team from Monsanto (1) returned to these trenches and took a series of soil cores. The results of this work found that all of the originally applied TCDD was still contained in the soil. However, the TCDD had moved both upwards and downwards in the 12 years since the experiment had began. The peak TCDD concentration was found to be at a depth of 9 cm. Vapor phase transport of TCDD through the soil air voids was found to adequately describe the movement of TCDD in the Eglin Soil.

Previously, we (2) have reported on the soil columns taken from the sides of roads sprayed with TCDD contaminated waste oil. These soil columns exhibited a peak TCDD concentration at a depth of approximately 5 to 10 cm. However, it was known that the road surfaces were sprayed with the waste oil and there was no way to identify the initial soil column TCDD profile. The soil at Eglin AFB is mostly sand while the soil at Times Beach is classified as a silty clay loam. Stronger binding of the TCDD to the Times Beach soil than the Eglin soil would be expected based on the differences in soil composition. A stronger binding of TCDD to the Times Beach soil would imply a slower rate of soil

transport than at Eglin AFB. However, the field data for Times Beach implied a faster movement of TCDD than at the Eglin AFB experimental trench site.

The apparent contradiction in the rates of transport of TCDD at Eglin AFB and at Times Beach led us to establish a set of four experimental field plots at the Times Beach Research Station in August of 1984 (3). These experimental field plots were designed to measure the rate of TCDD transport in the Times Beach Soil. The experimental plots were exposed to 14 months of the Missouri climate. Soil cores were taken periodically from each of the plots and analyzed for TCDD. The results of this study confirmed our expectation that the rate of TCDD transport in Times Beach soil was very slow. A loss of TCDD was detected only at the very surface of the soil fully exposed to the environment. An experiment specifically designed to detect movement of TCDD by vaporization in a soil column confirmed existence of the phenomena but at a very slow rate.

In an independent experiment Kapila, et al. (4), conducted laboratory studies on the rate of soil transport of TCDD. Using constant temperature soil columns, Kapila and associates measured an apparent increase in TCDD transport as a function of increasing temperature. Taken as a whole, the above body of experimental work defines the bounds on the rate of TCDD transport via vaporization in a soil column. The next section of this paper describes how the above set of data was used to quantitatively establish these bounds.

THEORETICAL

Material Balance Equation

Previously, we (1,5) have presented an unsaturated zone TCDD transport model based on a solid and a vapor phase being in contact with each other. Transport through the vapor phase is assumed to be hindered by the long complex path of the soil air voids. The material balance model is essentially the same as that used by Jury (6) and is given as:

$$\frac{\partial C_a}{\partial t} = \frac{(\varepsilon^2/\tau)}{\varepsilon + P_t/(K P^o M_w \rho_{molar})} \frac{\partial}{\partial Z} D_{ab} \frac{\partial C_a}{\partial Z} \qquad (1)$$

The material balance, given as Equation 1, is solved using boundary conditions 1 and 2:

B.C. 1 - Air-Soil Interface Concentration

at $Z = 0$; $C_a = 0$ for all t (2)

B.C. 2 - Constant Concentration Some Depth in Ground

at $Z = L$; $C_d = 0$ for all t (3)

The diffusivity, D_{ab}, the molar density, ρ_{molar}, and the vapor pressure, P^o, are all functions of temperature. Daily high soil surface temperatures of 40 C have been measured during the day with corresponding lows of 20 C during the night (7). The vapor pressure of TCDD is 8.61×10^{-8} pascals at 20 C and is 2.21×10^{-6} at 40 C. Thus, the daily 20 C temperature change will change the vapor pressure of TCDD by a factor of 25. In addition, the molar density, ρ_{molar}, will decrease 6 percent and the diffusivity, D_{ab}, will increase 10 percent over the same 20 C temperature range. Since the soil temperature will also vary from season to season, an energy balance model is required to correctly estimate the impact of temperature variations on the mass transport process.

Energy Balance Equation

The energy balance equation is the same as previously presented by Tung, Freeman, and Schroy (7). A brief description is presented below. The one-dimensional transient energy balance equation may be written as:

$$\rho_{soil} C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial Z^2} \qquad (4)$$

To solve this equation for the temperature waves that pass through a soil column, requires two boundary conditions:

B.C. 3 - Surface Energy Flux

$$\text{at} \quad Z = 0; \quad k \frac{\partial T}{\partial Z} = q_r + q_c + q_b \text{ for all } t > 0 \qquad (5)$$

B.C. 4 - Constant Temperature at Some Depth in Ground

at $Z = L$; $T = T_g$ for all $t > 0$

The term, q_r, represents the radiative solar input into the soil column. The term, q_c, is convective heat transfer between the soil and the air. The term, q_b, represents the black body radiative loss of energy from the soil surface. These soil surface energy fluxes are complex functions of soil temperature, weather conditions, and site location. Schroy and Weiss (8) have previously presented methods for the computation of q_r, q_c, and q_b. For details of the soil temperature model and the numerical solution, see Tung, Freeman, and Schroy (7).

ANALYSIS OF EXPERIMENTAL DATA

If the above theoretical model is correct for unsaturated zone behavior,all of the observed experimental data can be understood using the model to simulate each experiment. We shall start the analysis with the Eglin AFB experiment of Dr.Young. Figures 1 and 2 shows the model fit to the Eglin AFB field data. The Eglin AFB data (1) were fit using a value for K of Equation 3 of between $3.5 \times 10^{+4}$ and $8.5 \times 10^{+5}$. The model fit is very good and correctly reproduces the experimental data. These values of the equilibrium constant imply that the vapor space concentration of TCDD is below saturation.

Using a specially designed soil core slicing apparatus, Kapila (4) was able to reproducibly segment a soil core into increments as small as 1 mm. By injecting a solution containing 100 ng of TCDD at a known point within the soil core, Kapila could observe any movement of TCDD from the initial known point. By injecting a core and then holding it at a constant temperature for a known time, Kapila hoped to observe the influence of temperature on the rate of TCDD transport within a soil column. Kapila conducted such an experiment on Times Beach soil. The theoretical model described above can be used to study Kapila's experiment.

Kapila conducted two experiments at 20 C. The first experiment incubated the soil column for 2 hours before is was segmented into 2 mm increments. The second experiment incubated the soil column for 30 days. Assuming that all of the 100 ng of TCDD were injected into a single soil increment (1 mm wide) at the center of the column, the equilibrium constant of Equation 3 was varied to fit the data obtained after 2 hours of incubation. Using the resulting value for the equilibrium constant of Equation 3, the 30 day, 20 C, incubation experiment was then simulated. The results indicate that the movement of TCDD, after 30 days, would be much greater than observed. In fact, TCDD should have been found in those sections where Kapila found none above the detection limit. Thus, we may conclude that the TCDD profile observed at 2 hours is simply an artifact of the method used to inject the TCDD solution into the soil column (i.e. the solution was not injected into a single soil increment 1 mm wide).

The 2 hour, 20 C TCDD profile was used to characterize the initial TCDD concentration profile within the soil column. The theoretical model was used to simulate the other experimental runs of Kapila. Figure 3 presents the results of the study at 40 C with an incubation time of 30 days. As can be seen, the theoretical model follows the trend of the measured data but does not reproduce it. Also plotted on Figure 3, is the assumed initial concentration profile taken from the 20 C, 2 hour experiment. As can be seen, only a small fraction of the initial TCDD is predicted to move during the course of the 30 day experiment at 40 C. These simulations indicate that the results presented by Kapila are due to an artifact in the method used to load the TCDD solution into the soil column. However, Kapila's data do provide information on the limiting rate of TCDD transport in a soil column. The value of the equilibrium constant K of Equation 3 used to simulate Kapila's data is $6 \times 10^{+4}$.

We have previously presented a series of estimates of the initial TCDD concentration in the top 1 cm of soil (2,3,5). These estimates have all been in the 10 to 30 ppm range. Table 1 presents the concentrations of TCDD measured in two cores taken from Times Beach and previously reported (2). The total TCDD present in core 2 would be equivalent to an initial concentration of 6.318 ppm TCDD in the top 1 cm of soil. Using the value for K of $6 \times 10^{+4}$ from the above analysis of Kapila's experiments

allows for the prediction of the rate of TCDD movement by vaporization in the soil after initial application. The theoretical model outlined above was used to simulate the transport for 10 years of 6.318 ppm of TCDD from the top 1 cm of soil. The model predicts that only 0.05 percent of the TCDD vaporized into the atmosphere. In addition, the model predicts that the TCDD would move only 2.0 cm into the ground and that no TCDD should be detectable below 5 cm in a soil column. Figure 4 presents the concentration profile data of Table 1. Clearly TCDD has moved below the 5 cm depth. Therefore, we must conclude that another transport mechanism is responsible for this movement besides that of simple vaporization. The differences between the Eglin experiment and the waste-oil laydown at Times Beach suggests that repeated oilings of the road with various organics liquids may have lead to a bulk chromatographic movement of TCDD into the soil at Times Beach. After the organic carrier had vaporized, the continued slow redistribution of TCDD by vaporization could occur. The predicted vaporization flux of TCDD from the soil surface into the air is 6×10^{-8} kg/d-m^2. Theoretical studies by Eduljee (9) predict that the vaporization flux is dependent on the soil moisture content. Eduljee predicts that the vaporization flux of TCDD should fall in the range of 3.6×10^{-7} to 8.6×10^{-8} kg/d-m^2. The model predicted vaporization flux of 6×10^{-8} kg/d-m^2 (using an equilibrium constant of $6 \times 10^{+4}$) is consistent with the theoretical predictions of Eduljee.

The last experiment to review is the Times Beach Research Plots that we established in 1984 (3). No statistically meaningful changes were detected in the top 1 cm of any of the plots over the 16 month course of the experiment. However, surface scrapings from plots A and C did show statistically significant reductions in the TCDD level present. Using the value of $6 \times 10^{+4}$ obtained above for the equilibrium constant of Equation 3, a simulation of the behavior of plot C - control was completed. The results of this simulation predict that only 0.01 percent of the TCDD present in the top 1 cm of soil should have been lost due to vaporization over the time period of the experiment. In addition, the model predicts that 0.1 percent of the TCDD present in the top 1 mm should have vaporized during the experiment. The observed reduction in TCDD concentration in the top 3 mm of soil was approximately 50 percent. Thus, we conclude that another mechanism such as surface photodegradition of the TCDD occurred during the experiment.

The clean soil over dirty soil experiment of plot C - nursery demonstrated a very slow rate of TCDD transport in soil. The apparent rate of TCDD transport was found to be 1.4×10^{-11}kg/d m^2. This transport flux is below that predicted by Eduljee for vaporization into the air. The low flux of TCDD in this experiment was probably due to the reduction in transport area and the high organic carbon content of the nursery soil used to cover the Times Beach soil.

CONCLUSIONS

We have shown a viable explanation for the available data on the vaporization and movement of TCDD in soil columns. Based on this analysis, the following conclusions can be reached:

1. Vaporization of TCDD from a soil column is a very slow process. Both theoretical and measured values for the vaporization flux of TCDD from a soil column are of the order of 6×10^{-8} kg/d m^2.
2. The dispersion of the TCDD applied to the soil at Eglin AFB can be entirely explained by the vaporization of TCDD from the initial point of application.
3. The concentration profiles found in the roadsides of Times Beach, Missouri can not be explained by the vaporization model presented above. Instead, we suggest that the profiles can be explained if the roads were repeatedly oiled with organic liquids. These organic liquids would serve as a chromatographic carrier and would in effect "wash" the TCDD into the ground.
4. Most of the TCDD initially applied to the roads of Times Beach is still contained in the soil beneath the road surface.
5. The soil column experiments of Kapila allows for the computation of a limiting value of $6 \times 10^{+4}$ for the equilibrium constant K of Equation 3 for Times Beach soil. This is consistent with the value obtained from the field experiment of Young at Eglin AFB.

NOMENCLATURE

a	-	Air-soil interfacial area per unit soil volume
C_a	-	Concentration of TCDD in air
C_d	-	Concentration of TCDD in soil
C_p	-	Heat capacity of soil
D_{ab}	-	Diffusivity of TCDD in air
h	-	Hindrance factor
K	-	Empirical equilibrium partitioning coefficient between soil and air
k	-	Thermal conductivity of soil
L	-	Soil depth where temperature and concentration does not change during a year
M_w	-	Molecular weight of TCDD
P^o	-	Vapor pressure of TCDD
P_1	-	Partial pressure of TCDD in gas space
P_t	-	Total barometric pressure
q_b	-	Black body radiation loss to the sky
q_c	-	Convective energy exchange between soil and atmosphere
q_r	-	Radiative energy received by soil from the sun
R	-	Volumetric rate of volatilization of TCDD into air voids
T_g	-	Soil temperature at a depth L
t	-	Time
Z	-	Depth into the ground

Greek Symbols

ε	-	Soil void fraction
ρ_{molar}	-	Molar density of air in soil void space
ρ_{soil}	-	Density of soil
τ	-	Tortuosity factor, $\tau = 2$ for an average soil
ϕ	-	Average diameter of soil particle

Table 1
Concentration of TCDD Found in Two Cores Taken From a Times Beach, Missouri Roadside

Soil Depth cm	to	cm	Core 2 Conc. ppb	Core 3 Conc. ppb
0.00	-	2.54	52.	41.
2.54	-	5.08	141., 97.4	105.
5.08	-	7.62	196.	92., 112
7.62	-	10.16	154., 274	14.
10.16	-	12.70	119., 101	0.8
12.70	-	15.24	60.	3.
15.24	-	17.78	13.	2.
17.78	-	20.32	5.2	0.9
20.32	-	22.86	2.7	7.7

Notes: 1. Data from Tables 3 and 4 of reference 2.

FIGURE 1. SIMULATION OF EGLIN AFB TCDD PROFILE CORE 4N NONAMENDED BIODEGRADATION PLOT

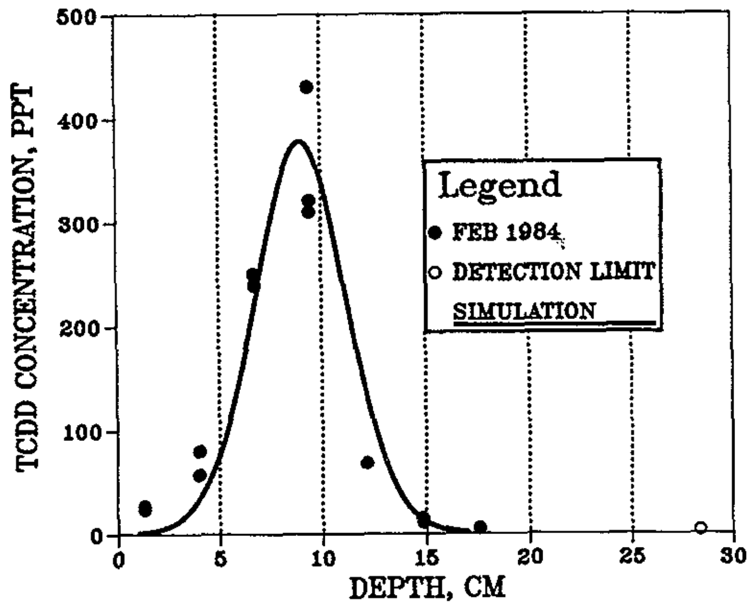


FIGURE 2. SIMULATION OF EGLIN AFB TCDD PROFILE CORE 5N NONAMENDED BIODEGRADATION PLOT

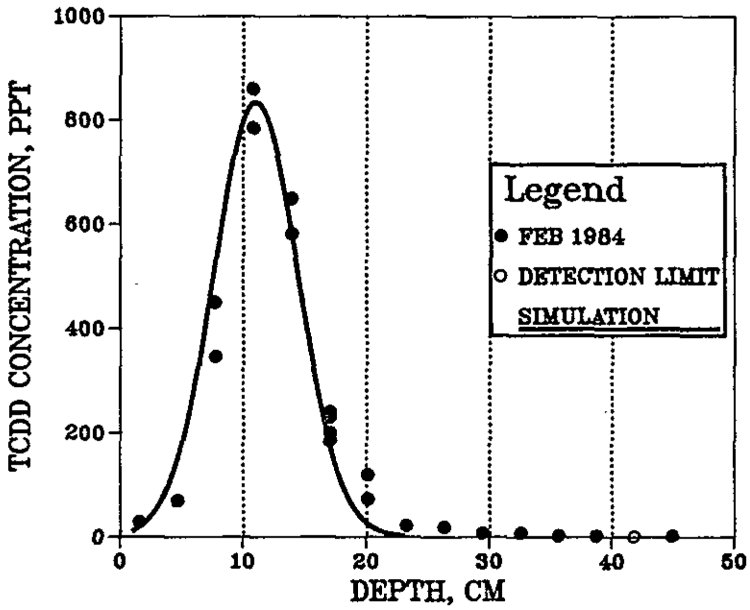
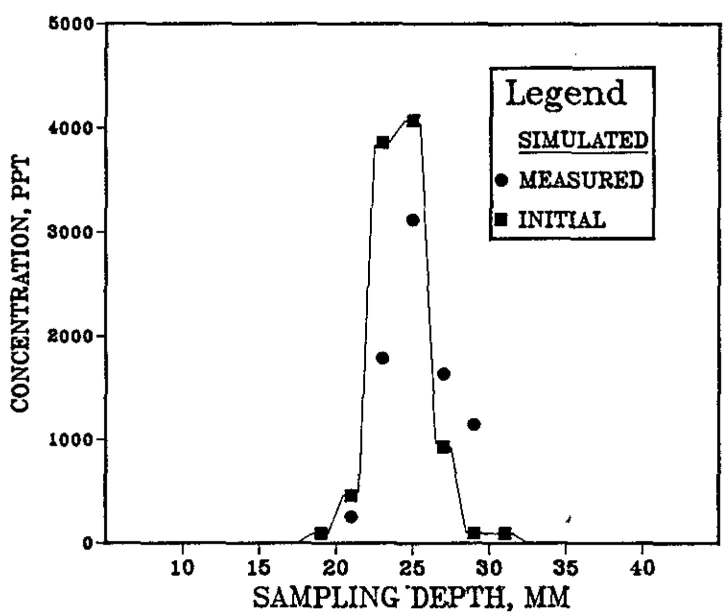


FIGURE 3. SIMULATION OF KAPILA 40 C, 30 DAY TCDD EXPERIMENT



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