PREPUBLICATION DRAFT

MODELING THE TRANSPORT OF 2,3,7,8-TCDD AND OTHER LOW VOLATILITY CHEMICALS IN SOILS

by

Raymond A. Freeman and Jerry M. Schroy
Monsanto Co.
800 N. Lindbergh Blvd.
St. Louis, Missouri 63167

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ABSTRACT

A model has been developed to describe the transport of low volatility organic chemicals in a column of soil. The mathematical model calculates the rate of movement through the soil by solving the dynamic material and energy balances around the soil column. The model is used to make predictions on the transport of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) at the Eglin Air Force Base Agent Orange biodegradation test plots. The model predicts a vertical movement of TCDD, buried in 1972, through the soil column. Soil column profile data confirm the vertical movement of TCDD.

BACKGROUND

The compound 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has a very low vapor pressure (2.0×10^{-7} pascals at 25.0 C) (1) and a very low water solubility (3.17×10^{-7} g/liter at 25.0 C) (2). Although the vapor pressure and water solubility of DDT and TCDD are not identical, they are similar. For comparison DDT has a vapor pressure of 2.5×10^{-5} pascals (20 C) and a water solubility of 1.2×10^{-6} g/liter at 20 C (3). Thus, the environmental mobility of TCDD should be similar to DDT.

Several investigators have shown that DDT is mobile in the the environment via vaporization. Guenzi and Beard (4) found that the presence of a least a monomolecular layer of water is needed for DDT vaporization to occur. Farmer et al. (5) found that DDT will volatilize from soil, and Hee et al. (6) found that DDT will volatilize from glass when applied as a film. Beall and Nash (7) demonstrated that DDT will volatilize from soils and can be absorbed from the air by soybean plants.

Freeman and Schroy (8) have reviewed the pesticide literature and found that other chemicals such as lindane, Dieldrin, Heptaclor, and Trifluralin are also volatile. From the literature review, the following generalizations

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were made on the environmental mobility of chemicals such as DDT and TCDD:

1. A chemical with a low water solubility and a low vapor pressure can volatilize with rates that are important to the chemical's ultimate environmental fate.
2. Chemicals with low water solubilities will not migrate in soils due to bulk water flow (rain, irrigation, floods, etc.).
3. Soil temperature variations will have a strong impact on the movement of a chemical in the soil.
4. Low volatility chemicals may bind strongly with dry soil. However, when a monomolecular layer of water is present the chemical can become more mobile.

Thus, TCDD should be mobile via vaporization in the environment. Nash and Beall (9) have demonstrated that TCDD is volatile both in laboratory microcosm and field plot experiments. Shown in Figure 1 are the air concentrations of TCDD measured by Nash in the microcosm experiment.

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Liberti et al. (10) gathered data on Seveso soil, using deep-tray tests, which showed TCDD losses from the subsurface layers after exposure to the sun. Liberti's explanation for the loss was due to free radical movement into the soil column. A more reasonable explanation is due to the transport of TCDD to the soil surface where it could be photochemically destroyed or vaporized.

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THEORY

PREVIOUS MODELS

Many models have been developed to describe the movement of pesticides in the environment. Jury (11) developed an analytical model to describe the movement of pesticides via vaporization. Jury's model makes several simplifications, such as constant soil temperature, and was constructed to allow for "environmental screening" of a new pesticide before development. Mayer (12) has studied the boundary conditions to use with the transport equations that describe the movement of chemicals in a soil column.

Other investigators such as Oddson (13), Leistra (14), Davidson (15), and Lindstrom (16) have studied the movement of chemicals via convective transport in water. These models generally ignore the possibility of vapor phase transport and require constant soil properties and temperatures. These conditions rarely are obtained under actual field conditions.

MATERIAL BALANCE EQUATIONS

Freeman and Schroy (8) constructed a model based on a solid and a vapor phase being in contact with each other. The model uses the following material balance equations:

$$\frac{\partial C_d}{\partial t} = \frac{2\,\rho_{molar} D_{ab}}{\Phi}\left[\frac{C_a}{M_w\,\rho_{molar}} - \frac{K C_d P^o}{P_t}\right]\frac{M_w a}{\rho_{soil}} = R \quad (1)$$

$$\frac{\partial C_a}{\partial t} = h\frac{\partial}{\partial Z}\left(D_{ab}\frac{\partial C_a}{\partial Z}\right) - \frac{R}{\epsilon} \quad (2)$$

These two nonlinear partial differential equations must be solved simultaneously and this requires a large amount of computer time. Numerical and theoretical studies of the material balance equations have allowed some simplifications.

The vapor phase equation changes five orders of magnitude faster than the soil phase equation. Thus, the vapor phase is always in equilibrium with the soil phase. Therefore, the material balance equations may be re-written as:

$$\frac{\partial C_d}{\partial t} = \frac{\epsilon h}{\epsilon + P_t/(K P^o M_w \rho_{molar})}\,\frac{\partial}{\partial Z}\left(D_{ab}\frac{\partial C_d}{\partial Z}\right) \quad (3)$$

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ENERGY BALANCE EQUATION

The energy balance equation is the same as previously presented by Freeman and Schroy (8). 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. 1 - Surface Energy Flux

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

B.C. 2 - Constant Temperature at Some Depth in Ground

$$\text{at } Z = L; \quad T = T_g \quad \text{for all } t \geq 0 \qquad (6)$$

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 (17) has previously presented methods for the computation of q_r, q_c, and q_b.

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Models, using the energy balance equation and either the simplified or the complex material balance equations, gave predicted profiles which were found to fit the soil core profiles taken from Times Beach, Missouri equally well. A model, using the simplified material balance equations and energy balance equation, was used to predict the soil TCDD profiles measured at Eglin Air Force Base in Florida.

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EGLIN AIR FORCE BASE

In April of 1972, Dr. Alvin Young (USAF) established several biodegradation plots at Eglin AFB (18). The area selected for the biodegradation plots was clean and had not been sprayed with Agent Orange or other herbicides. Trenches approximately 10 centimeters (4 to 5 inches) deep were dug into the soil, and Agent Orange containing 40 ppb of TCDD was applied to the trench bottom. The application loading was 0.95 liter of Agent Orange on an area of 0.930 square meters (10 square feet) or 0.1 ml Agent Orange/cm^2 (19). After the Agent Orange was applied, the trenches were back filled with soil.

Samples were subsequently taken from the plots and analyzed for TCDD by the Air Force. These samples showed an apparent decrease in the total TCDD content of the soil over time, and this is discussed below. In February of 1984, Dr. Young and a team from Monsanto took a set of core samples from the biodegradation plots.

The cores taken by the Monsanto team were segmented into approximately 2 centimeter increments and analyzed for TCDD. The results of these analyses are given in Table 1. The data for cores 4N and 5N are plotted in Figures 2 and 3. As is readily apparent from both Figures 2 and 3, the TCDD has moved upward through the soil layer from the initial approximate depth of 10 centimeters.

Using the transport model previously presented in this paper, a simulation of the TCDD movement was done. The initial mass of TCDD was estimated by integrating the soil TCDD concentration profile in each core. The total initial TCDD mass was assumed to have been contained in an one centimenter increment of the soil buried at a depth of approximately 10 centimeters. The calculated initial TCDD concentration profiles are shown in Figures 4 and 5. The initial peak TCDD concentration of core 4N was computed to be 2100 ppt (by wt.) and 7160 ppt (by wt.) for core 5N.

The simulation was solved for a time span of 12 years. The final peak concentration of TCDD was adjusted, by varying the equilibrium partition coefficient,K, until the measured value was obtained. The equilibrium partition coefficient,K, is an empirical parameter that describes the concentration relationship between the soil and the adjacent air spaces. The spread of the calculated concentration profile is compared to the measured data in Figures 2 and 3. The model fits the data well.

The good agreement between the model and the data suggests that all of the TCDD originally applied by Dr. Young in 1972 is still contained in the biodegradation plots. However, the TCDD is moving very slowly away from the position where it was initially placed. The symmetry of both the measured and calculated concentration profiles suggests that the rate of downward movement is equal to the rate of upward movement. The good agreement with the data also implies that although vapor transport may not be the only mechanism, the model provides a good structural form to represent all transport mechanisms.

The results of the Air Force and Monsanto analyses of Eglin AFB soil are compared in Table 2. The analyses by the Air Force shows an apparent decrease of dioxin concentration with time. Young and Arnold (20) have re-analyzed archived Air Force soil samples and found that most of the originally applied TCDD could be recovered using an exhaustive extraction procedure. Therefore, the question of the fate of the TCDD remained an open question until the completion of this study.

In addition to the extraction problems found by Young and Arnold, variations in initial TCDD loading are apparent. The Monsanto cores from the same plot show a factor of 3 variation in the average TCDD concentration. When compared to the initial calculated TCDD concentration and area loading, one of the Monsanto cores lies below and one lies above the average. The day 5 and day 414 Air Force data are 3 to 4 times greater than the calculated initial TCDD levels. The day 513 and day 707 data are below calculated initial average TCDD concentration and loading.

Some of the variation in the data appears to be due to the difficulty of spreading 0.950 liters of Agent Orange over 0.93 square meters of surface uniformly. The change in concentration with time noted in the Air Force Data appears due to the variation in loading and to analytical problems, rather than any reduction in the level of TCDD with time.

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CONCLUSIONS

Based on the above analysis, the following conclusions about the fate and mobility of TCDD can be reached:

1. All of the TCDD buried in the biodegradation plots is still contained in the soil.
2. The apparent biodegradation of TCDD, previously reported by Young (18), can be explained by the variations in the initial loading of the biodegradation plots and by analytical problems.
3. The movement of TCDD in a soil column can be modeled by a temperature-driven diffusion process.
4. The rate of TCDD movement is very slow. The TCDD in the Eglin AFB biodegradation plots has moved only about 10 centimeters in 12 years.

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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	- Hinderance factor, $h = \epsilon / \tau$
K	- Empirical equilibrium partitioning coefficient between soil and air
k	- Thermal conductivity of soil
L	- Soil depth where temperature does not change during a year
Mw	- Molecular weight of TCDD
P^o	- Vapor pressure of TCDD
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

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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

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Table 1

Measurements of TCDD Concentration Profiles

In Eglin AFB Biodegradation Plots

Core Increment, centimeters	TCDD Concentration, ppt (wt.) Core 4N	Core 5N
0.00-2.54	24, 27	29
2.54-5.08	57, 80	70
5.08-7.62	239, 250	346, 450
7.62-10.16	321, 310, 430	785, 860
10.16-12.70	68	582, 650
12.70-15.24	15, 11	185, 200, 230, 240
15.24-17.78	5	73, 120
17.78-20.32	**	22
20.32-22.86	**	19
22.86-25.40	**	8
25.40-27.94	ND (3)	8
27.94-30.48	ND (3)	3, 3
30.48-33.02		3
33.02-35.56		ND (1)
35.56-38.10		2
>38.10		ND (1)

Notes: 1. ND - None detected at a detection limit given in parenthesis as ppt by wt.

2. Analyses given for compacted sample cores, where:
Core 4N - compaction was 1.91 cm in 31.8 cm
Core 5N - compaction was 11.43 cm in 63.5 cm

** Analytical protocol failed (ie., poor recovery).

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Table 2

Total TCDD Mass Loading In Eglin AFB Biodegradation Plots

Test Description	Calculated TCDD Loading, grams/sq. meter	TCDD Concentration, ppt(wt.) (1)	
Liquid loading	5.22×10^{-5}	86	(2)
Air Force Data			
Day 5	22.88×10^{-5}	375	(3)
Day 414	15.25×10^{-5}	250	(3)
Day 513	4.58×10^{-5}	75	(3)
Day 707	2.81×10^{-5}	46	(3)
Monsanto Data (4)			
Core 4N	3.36×10^{-5}	55	(5)
Core 5N	11.46×10^{-5}	188	(5)

Notes:
1. Average TCDD concentration in a 38.1 cm core.
2. Calculated average loading over entire trench.
3. Measured
4. Monsanto samples taken 12 years after initial burial.
5. Calculated based on data in Table 1.

FIGURE 1. MEASURED TCDD AIR CONCENTRATIONS IN MICROCOSM EXPERIMENTS

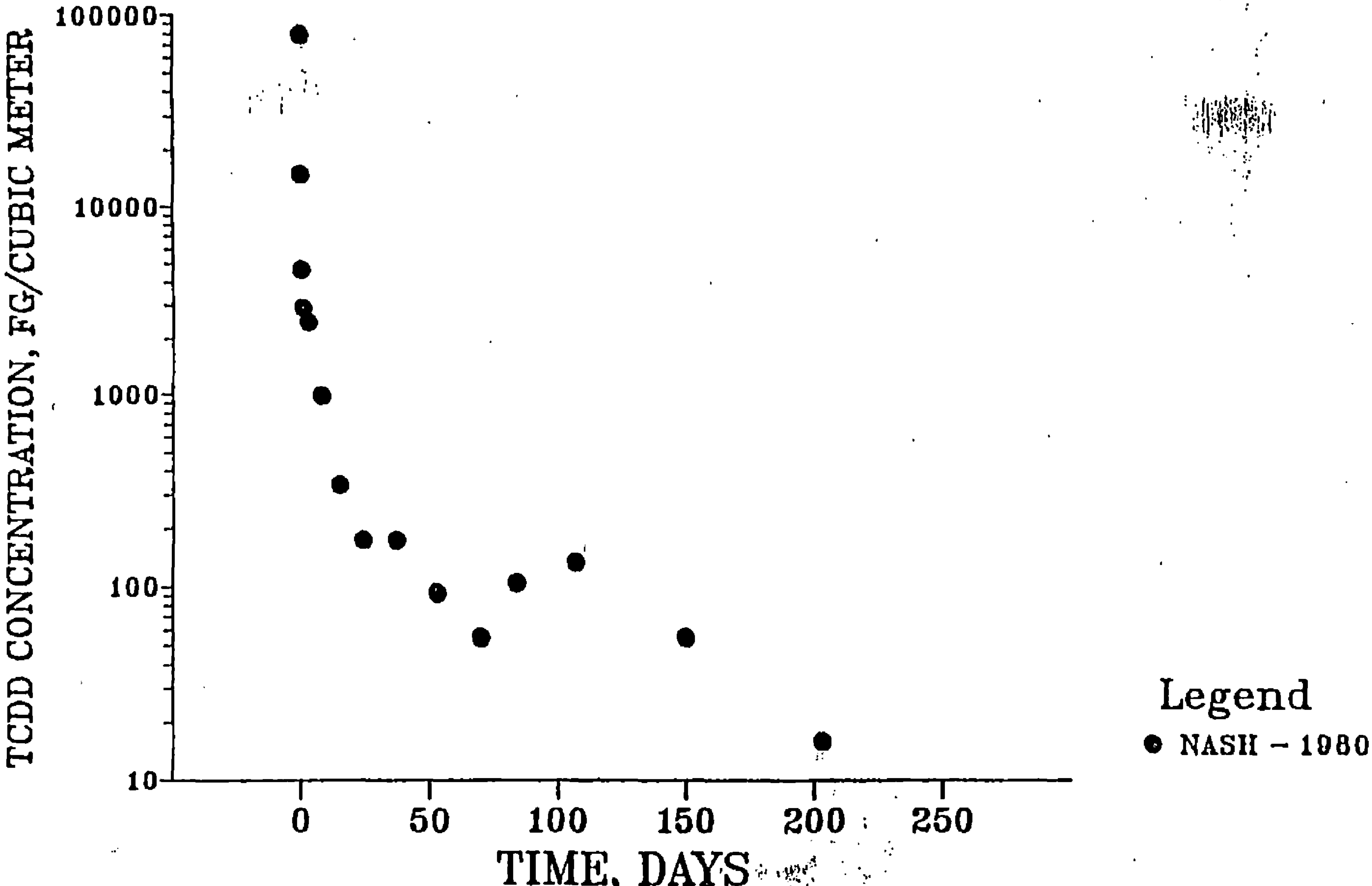


FIGURE 2. SIMULATION OF EGLIN AFB TCDD PROFILE
CORE 4N

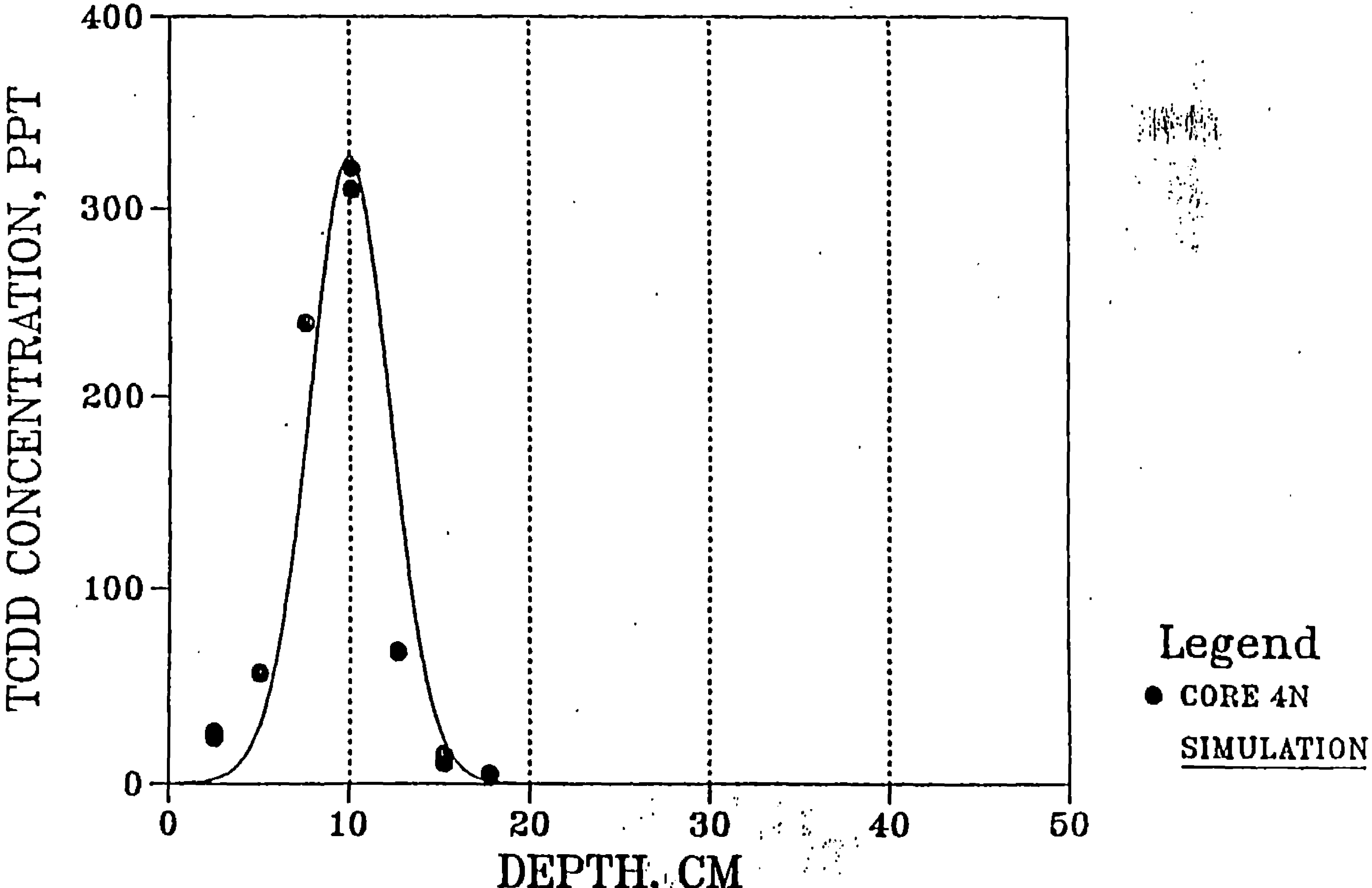


FIGURE 3. SIMULATION OF EGLIN AFB TCDD PROFILE CORE 5N NONAMENDED BIODEGRADATION PLOT

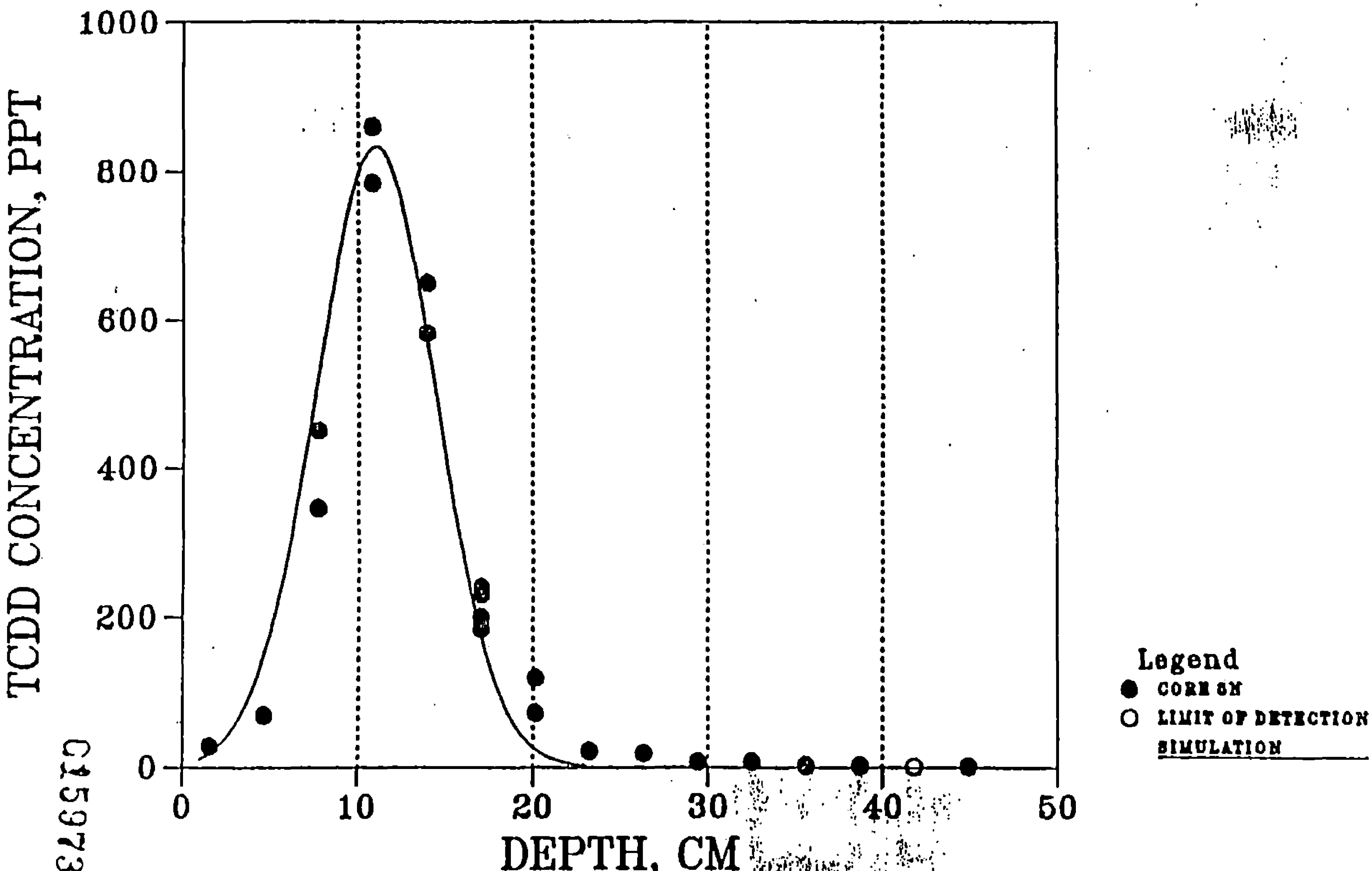


FIGURE 4. INITIAL EGLIN AFB TCDD PROFILE CORE 4N NONAMENDED BIODEGRADATION PLOT

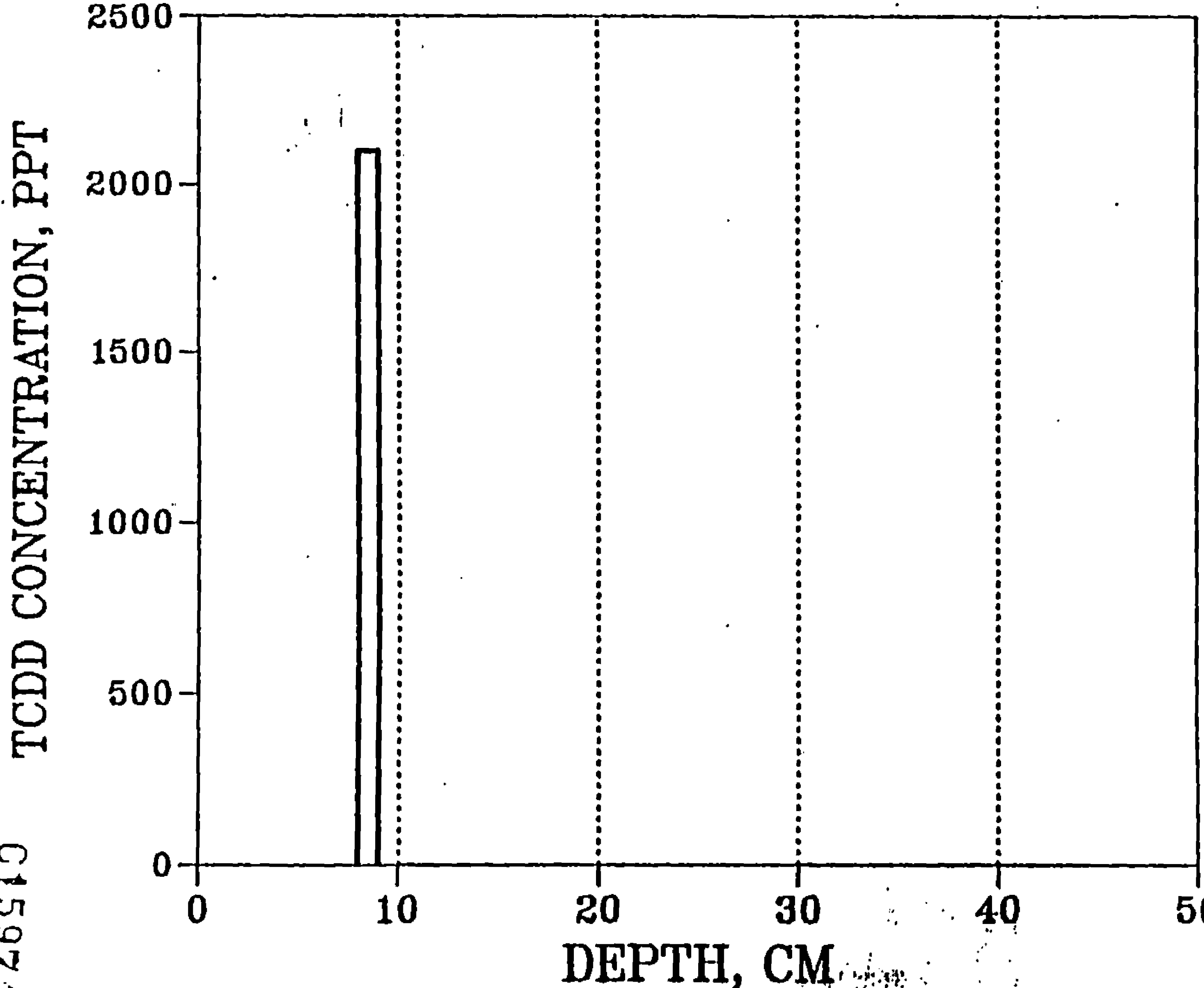
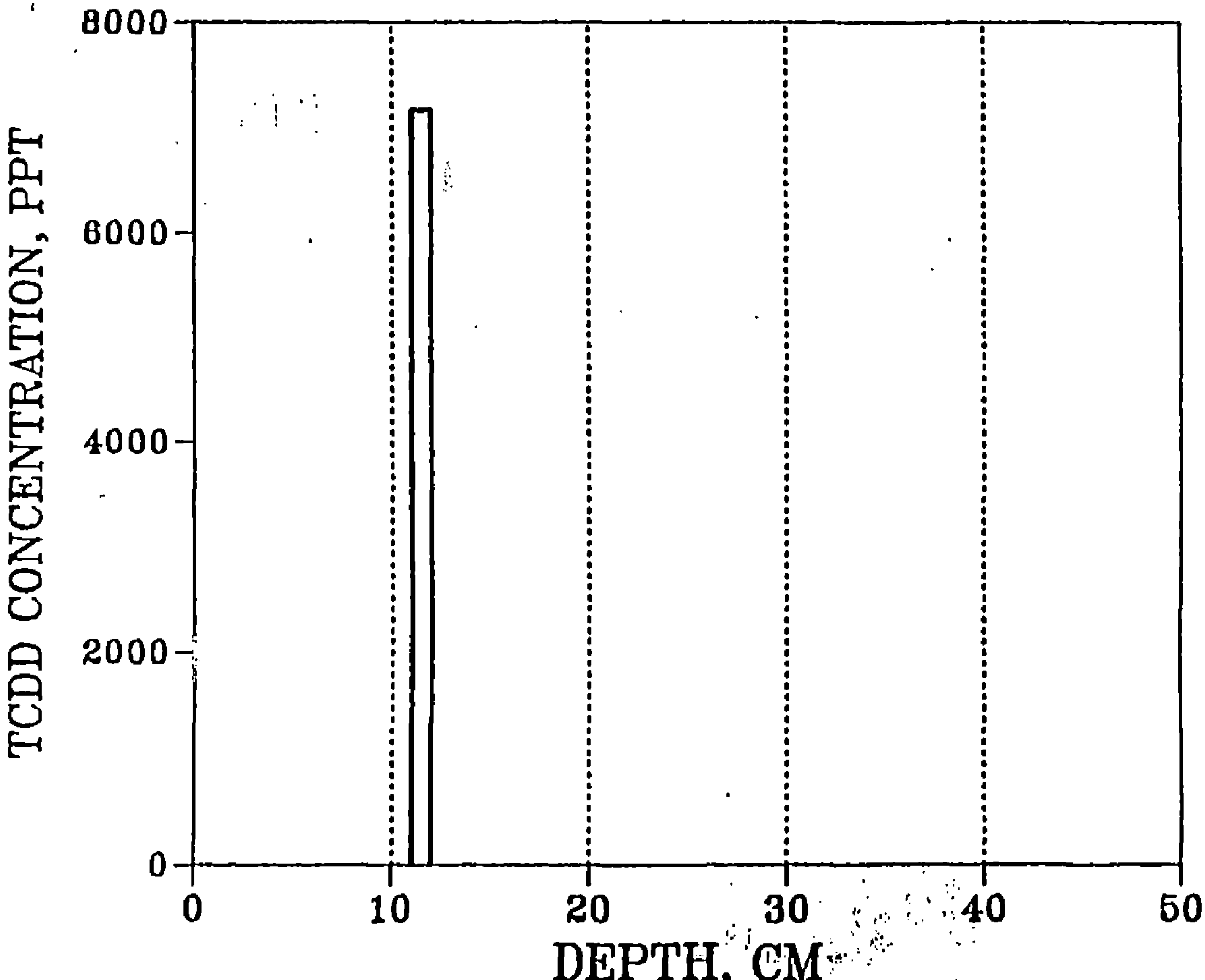


FIGURE 5. INTIAL EGLIN AFB TCDD PROFILE
CORE 5N NONAMENDED BIODEGRADATION PLOT



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