Sorption processes of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin on soil in the presence of organic liquids

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Abstract

Soil contaminated with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) often contains organic solvents as co-contaminants or as part of the clean-up process. The rate constants for adsorption and desorption of TCDD to Norfolk loamy sand in four organic liquids have been determined from a kinetic analysis of new experimental data. Intraparticle diffusion and external mass transfer limitations played a minor role in the mechanisms of adsorption and desorption.

Screening studies have also been carried out in order to determine the efficacy of 15 single organic solvents and seven solvent mixtures in TCDD removal from Norfolk loamy sand. Low-molecular weight and low-viscosity solvents removed the most TCDD during the duration of the experiment. The addition of low-molecular weight alcohols to more viscous solvents greatly increased the capacity for TCDD removal.

1. Introduction

The problem of soil contamination with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) has caused much concern in recent years as several accidents and other events have created pollution of this type in different areas of the country and the world [1–3]. Although the carcinogenic and mutagenic properties of this chemical at low concentrations have yet to be demonstrated as significant risks for humans [4], public perception of danger is quite high. There is considerable pressure to clean-up areas in which such contamination has occurred.

The question of TCDD fate and transport arose soon after the contamination problem first came to public attention in the early 1970s. Several models to determine the environmental fate of the chemical have been proposed [5, 6], but basic physical property research is a necessary first step. Accordingly, many studies to determine transport-related properties of TCDD have been underway for several years [7–11].

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Due to the extremely low water solubility of the chemical (found to be as low as 12.5 ppt [12], little movement occurs due to groundwater leaching. However, TCDD is seldom the sole substance incorporated into contaminated soil. Organic solvents are sometimes introduced into the soil in the initial contamination event, as in the case of a leaking tank or landfill. Organic liquids can also be purposely added to soil at a later time. For instance, one possible decontamination method involves the application of solvents to TCDD-tainted soil and the subsequent solubilization and photodegradation of the chemical [13, 14].

TCDD partitions strongly into many organic liquids, and the octanol–water partition coefficient is very high. Log K_{ow} has been reported to be 6.64 and 6.80 by Marple et al. [9] and Shiu et al. [10], respectively. Thus, the transport of TCDD often involves other organics that are also present in the soil. Several recent studies have shown the effects of organic cosolvents on the adsorption behavior of TCDD or similar chemicals [15–19]. However, a wide range of organic liquids has not been studied. Since equilibrium and rate constants for adsorption and desorption are crucial to an analysis of TCDD transport, knowledge of the kinetics of TCDD adsorption to soil in the presence of organic solvents can be of much use in the understanding of TCDD movement in contaminated soil.

The objectives of the present studies were to determine the efficacy of various organic liquids in the removal of TCDD from soil and to quantify the kinetic parameters necessary to describe the adsorption/desorption behavior. Finding a suitable solvent or solvents for use in in situ soil decontamination was also a desired result. Several mixtures of relatively non-volatile organics with alcohols were also studied to determine if the addition of alcohols increased TCDD dissolution. The information gained in these experiments could be used in further studies of TCDD movement in soil when these organic liquids are present.

2. Experimental procedures

2.1. Adsorption/desorption studies

These studies were conducted to find rate and equilibrium constants for TCDD adsorption/desorption on soil with organic liquids. Four solvents were chosen for the study: tetradecane, 1-butanol, ethyl oleate, and dimethyl sulfoxide. These are known solvents for TCDD that have shown promise in studies to remove the chemical from soil in field contamination situations [20]. For each solvent, five samples in 15 ml glass vials were prepared. One was designed to study the desorption process and contained TCDD-spiked soil and pure solvent. Three were to study the adsorption process and contained clean soil and solvent spiked with various levels of TCDD. The adsorption isotherms were expected to be linear in the low concentration ranges involved in this study [18, 21], but this was verified by the use of three different solvent TCDD concentrations.

Table 1
Composition of Norfolk loamy sand

Particle size	Composition (%)	Diameter [30] (d_p) (μ)	External surface area (a) ($cm^2 g^{-1}$)
Sand	84.8	50.0–840.0	41.0[a]
Silt	10.7	2.0–50.0	9.1×10^4 [a]
Clay (primarily kaolinite)	4.5	≤ 2.0	1.5×10^5 [30]

[a] External area calculated as surface area of spheres with the given diameter.

The last sample was a control to ensure that no TCDD would adsorb to the glass vials. This control was done with the highest concentration spiked solvent in a vial with no soil.

The composition of the loamy sand used in the studies is shown in Table 1. TCDD, like other non-ionic organic compounds, adsorbs primarily to the organic carbon fraction of the soil, the soil mineral fraction being relatively unimportant [22, 23]. The humic material is thought to be associated with the soil particles or exist freely as very small ($\leq 2\,\mu m$) particles. Organic matter has extremely high surface area ($\sim 1 \times 10^6 cm^2 g^{-1}$), most of which is due to the high internal porosity of the material. The percentage of organic carbon in the Norfolk loamy sand under consideration was 0.29% (analyzed by NCSU Agronomic Services Division, Raleigh, NC), which is quite low compared to many soils.

The procedure for spiking clean soil with ^{14}C-labeled TCDD was as follows. Air-dry soil (approximately 0.3% moisture) that had been sieved through a 20 mesh screen was spiked with ^{14}C-labeled TCDD to a concentration of 50–60 ng g^{-1}. The spiking procedure involved adding ethanol containing radiolabeled TCDD to air-dry soil and allowing the ethanol to evaporate with thorough soil mixing and crushing. Ethanol wets and penetrates the soil particles well, and this method of spiking the soil was chosen as the one that would give the most effective TCDD adsorption to the particles. The labeled TCDD, obtained from Cambridge Isotope Laboratories (Woburn, MA), had an activity of 122 μCi μmol^{-1} with about 50% of the TCDD molecules containing one ^{14}C atom in a random ring location. For these experiments, one part labeled TCDD was diluted with 40 parts unlabeled TCDD to yield a suitable activity for scintillation counting, about 3 μCi μmol^{-1}. The ethanol used for spiking the soil samples had a TCDD concentration of about 250 ng g^{-1}.

Typically, for 100 g soil 24 g (~ 30 ml) of spiked ethanol were used, enough to completely wet the soil sample. The soil was poured into the ethanol/TCDD solution. The resulting mix, after thorough stirring, was transferred into a tray and the alcohol allowed to evaporate with frequent soil mixing. This process took about 24 h with the soil spread in a layer about 5 mm deep. After the shallow layer of damp soil began to dry on the top surface, it was stirred continuously with a spatula. As the soil mass

approached dryness, it was crushed several times with a flat spatula to break up the damp crumbs that formed. When drying was complete, the sample was transferred to a glass container and tumbled for 10–30 min to ensure complete blending. Typical time between spiking and conducting the experiment was 6 months. The sample of spiked soil used in the desorption studies had a TCDD concentration of 56.4 ng g^{-1} as determined by extraction and GC/MS analysis following EPA protocol 8280 [24].

When the soil is spiked from ethanol as described above, it is postulated that a certain percentage of the TCDD actually adsorbs chemically or physically to the soil particles. However, some of the chemical is also probably contained as a film on the soil without being adsorbed. This situation is comparable to the state of TCDD contamination in the field, as a spill of contaminated solvent would evaporate and leave the TCDD in much the same manner.

For the adsorption studies, the solvents to be tested were spiked with ^{14}C-labeled TCDD at three concentrations of about 50, 100, and 150 ng g^{-1}. The samples were prepared by dilution of stock solutions of TCDD in isooctane. Very small amounts of the concentrated stock solutions were introduced into 120 ml sample bottles. The bottles were then left open under the hood to allow the isooctane to volatilize. Although TCDD has extremely low vapor pressure and therefore would not be expected to evaporate, experience has shown that TCDD is hard to resolubilize when the solution containing it is allowed to dry completely. Thus, when the isooctane had evaporated almost to dryness, enough of the organic solvent to be tested was added to the sample bottle to bring the solution to the correct TCDD concentration. The amount added was about 40 ml, so isooctane made up less than 1% of the solution.

After the spiked soil and solutions were prepared, the samples were set up for the adsorption and desorption tests. Each sample consisted of about 3 g soil and 12 ml solvent contained in a 15 ml clear glass screw-cap centrifuge tube. After the addition of pure solvent to the spiked soil and clean soil to the spiked solvent samples, all the tubes were placed horizontally on a shaker table and gently swirled for the first 24 h. After that time the tubes were swirled once a day during the remaining time of the experiment. The temperature was controlled for the duration of the experiment at 25 °C ± 1 °C.

Periodically, at intervals up to a final contact time of 66 days, the samples were removed from the controlled-temperature box and centrifuged at 2000 rpm for 5 min to ensure that all soil particles were at the bottom of the tube. A 200 μl sample of the solution was then carefully removed from the top portion of each tube. The aliquots that had been removed were tested by scintillation counting for TCDD, as the ^{14}C label enabled the detection of the TCDD in the solution. The sample of the solution was added to about 18 ml Scintiverse II (Fisher Scientific, Fair Lawn, NJ) liquid in a glass scintillation vial. Scintillation counting was then done using a Packard TriCarb Scintillation Spectrometer, Model 2405. Blanks containing the appropriate solvent in Scintiverse II were run with each sample to determine the background radiation, which varied from 25–35 disintegrations (D) min^{-1}. Corrections were made for counting efficiency, and final determinations of sample activities varied from 50 to 1000 D min^{-1}.

2.2. Solvent screening studies

Several less rigorous desorption tests were also done to compare the effectiveness of organic solvents in removing TCDD from Norfolk loamy sand, and to aid in the development of an in situ method for soil decontamination. This set of desorption studies were conducted to screen solvents for efficacy of TCDD removal from soil, with qualitative results the main focus. Fifteen studies were done with single solvents and seven with solvent mixtures.

Solvents to be included in the studies were chosen on the basis of several factors. Most importantly, the solvents had to have very low UV radiation absorbance in the 297–312 nm range where TCDD absorbs for photolytic reaction. Other requirements were that the solvents be relatively non-toxic and have no serious ecological drawbacks, be available at a reasonable cost, and be biodegradable. After review of known solvents for TCDD in light of these considerations, 15 solvents were selected. Six alcohols were included to cover a range of boiling points, molecular weights, and soil-wetting properties. Polyethylene glycol 300 was added as an example of a nonvolatile, water-miscible solvent. Tetradecane was chosen to represent a non-volatile aliphatic hydrocarbon. Ethyl oleate and oleic acid were chosen due to previous research in the area of TCDD dissolution from soil [14]. Based on studies with olive oil [25], four natural oils were included.

For each test, 1.5 g of spiked soil was weighed into a 30 ml amber glass bottle and 15 ml solvent added. The bottles, which had screw caps with Teflon liners, were then closed and allowed to stand with no stirring. Periodically, samples of the liquid were removed with a glass medicine dropper, and the bottles were gently swirled at the outset of the study and then after each sampling. The swirling process involved six circular motions with the bottle held in an upright position and took about 5 s. This amount of swirling was enough to create a well-mixed system without breaking up the soil structure. The time allowed for settling and the solvent depth above the soil were sufficient to ensure that no particles were removed with the solvent during the sampling procedure. One milliliter aliquots were taken after 2, 6, and 30 h. The bottles were undisturbed for 13 days, then shaken vigorously, and allowed to settle for two more days, after which time the final aliquot was taken. The aliquots that had been removed were then tested by scintillation counting for the ^{14}C-labeled TCDD.

Because non-volatile solvents may be preferable for in situ treatment of TCDD-contaminated soil, increasing the amount of TCDD that these solvents remove from the soil is desirable. Thus, desorption studies were also conducted using mixtures of non-volatile solvents with low-molecular weight alcohols.

Solvent mixtures were prepared by adding 10 ml of ethyl oleate or cottonseed oil to 5 ml of different alcohols with a range of boiling points. Mixtures of ethyl oleate with methanol, ethanol, 1-propanol and 1-butanol were miscible, forming clear solutions. The ethyl oleate/ethylene glycol mixture, however, separated into two phases. One solvent mixture was prepared with cottonseed oil as the non-volatile solvent and 1-butanol as the alcohol. This mixture was miscible, but a cottonseed oil/ethanol mixture tried initially was not. The six ethyl oleate/alcohol mixes and one cottonseed oil/1-butanol mix were added to ^{14}C-labeled TCDD-spiked soil samples as previously

described. As a control, 15 ml of ethyl oleate was added to a seventh soil sample. For this series of tests, the bottles were left open to allow volatile solvents to evaporate. This simulated a field situation where after solvent addition to the soil, the more volatile solvent would soon vaporize. The TCDD would not be expected to evaporate due to the extremely low vapor pressure of the chemical [7], 3.46×10^{-9} mmHg at 30 °C.

Another difference in the mixture studies was that the soil/solvent samples were not swirled, reducing mixing. This procedure was also intended to mimic soil application. Aliquots of solvent were removed after 4 and 36 h. The bottles were weighed initially and before and after each aliquot removal to quantify solvent evaporation. The aliquots were tested by scintillation counting using the same procedures described above.

3. Results and analysis

3.1. Adsorption/desorption studies

The data from the adsorption/desorption studies were in the form of TCDD concentrations in the liquid over time. From these results, it was desired to find rate and equilibrium constants for TCDD adsorption to soil and desorption from soil. The results of the spiked solution controls showed that negligible TCDD adsorbed to the glass tubes during the course of the experiments.

From the form of the data, with TCDD concentration in the liquid samples changing gradually over a period of several days or weeks, it was clear that the adsorption and desorption processes did not reach equilibrium quickly. Therefore, the model utilized rate constants to describe the adsorption and desorption rates.

At the outset of data analysis, one question to be answered was whether or not intraparticle diffusional limitations played a significant role in the TCDD desorption. For TCDD adsorbed in the internal pores of the soil particles, transport to the bulk solution would occur somewhat more slowly than for that adsorbed mostly on the surface of the soil particles. The magnitude of this effect can be estimated by

$$t_d \simeq \frac{d_p^2}{D}, \tag{1}$$

where t_d is the time for diffusion from inside of the particle to the surface (s), d_p is the particle diameter (cm), and D is the diffusivity of TCDD in the solvent ($cm^2 s^{-1}$). Taking average values of the diffusivity ($5 \times 10^{-6} cm^2 s^{-1}$) and particle diameter (5×10^{-5} cm), it can be seen that an estimate for the diffusion time is of the order of 5×10^{-4} s. Over the time scale of this experiment, this diffusion time would obviously have very little effect.

As predicted, the addition of intraparticle transport to the model does not significantly affect the results. That is, the lag times associated with internal particle diffusion were small enough as not to be observed. The mineral nature of the larger

Table 2
Weight percent of the original TCDD that had been solubilized after given time in short-term desorption studies

Solvent	15 min	1 h	2 h	24 h
Tetradecane	14	24	29	39
Ethyl oleate	35	37	39	49
1-butanol	44	53	58	77

sand and silt particles discourages TCDD adsorption, which occurs almost exclusively on the very small particles that make up the organic carbon fraction of the soil [26]. Although there probably is in actuality TCDD adsorption on the inner surfaces of these very small particles, the time for diffusion to the outer surface is very short due to the very short diffusion distances. Thus, this effect can be ignored. There are also very few aggregates in the soil after the initial soil treatment of sieving and crushing. If larger quantities of aggregates were present, internal diffusion limitations would likely have a greater effect on the transport.

It is postulated that the process of spiking the soil from TCDD solution in ethanol caused only a portion of the TCDD to adsorb chemically or physically to the soil particles. As the solvent evaporated, some of the TCDD was deposited in the soil as a film on the soil particles. This portion of the TCDD would solubilize relatively quickly, while the adsorbed portion would take much longer. In order to find an appropriate initial condition for the kinetic analysis of the desorption studies, several shorter-term desorption tests were completed. These were carried out using the same procedure as the longer-term studies, but sampled after short contact times. Results (Table 2) showed that although the time for removal varied among solvents due to differences in soil-wetting character, approximately 40% of the TCDD could be considered to easily be accessible. This estimate was found using the average of the amount of TCDD in solution at 1 h and was then assumed to be independent of the isotherms for adsorption and desorption. The slowest solvent to remove the TCDD, tetradecane, dissolved 39% within 24 h. This time scale can still be considered to be "immediate" for the purposes of the kinetic analysis, since the experimental period extended over 66 days.

In the modeling process, the isotherms for adsorption and desorption are assumed to yield identical rate and equilibrium constants; i.e. hysteresis is expected to have little effect on this process. Evidence for other organics on soil have shown that while hysteresis in adsorption is sometimes an experimental artifact, it can also be real and significant for some compounds [27]. The results of these studies indicate that for these solvents hysteresis was not a large factor since calculations using both adsorption and desorption tests yielded similar values of the kinetic parameters.

The equations used to simulate the adsorption/desorption experiments are shown below. The TCDD concentration adsorbed to the soil particles is denoted by Γ (ng cm^{-2}) and C (ng cm^{-3}) is the concentration measured by these experiments in

the bulk solution phase. It is assumed that the gentle mixing of the tubes enables good contact between the soil particles and the solution, so that mass transfer limitations are not an issue.

If equilibrium is attained between the particle and the surface liquid one can write

$$a\Gamma = KC, \tag{2}$$

where a is the ratio of surface area of the particles to mass of particles $(cm^2 g^{-1})$ and K is the equilibrium partition coefficient between adsorbed and solution-phase TCDD $(cm^3 g^{-1})$. When the desorption process is kinetically controlled, the time rate of change of the TCDD concentration in the particle can be written as

$$a\frac{d\Gamma}{dt} = k_a \theta C - k_d a\Gamma, \tag{3}$$

where k_a is the rate constant for adsorption $(cm^3 g^{-1} s^{-1})$, k_d is the counterpart for desorption (s^{-1}), θ is the fraction of surface area left open for adsorption, and t is time (s). This equation reduces to the equilibrium equation when the derivative of Γ with time goes to zero and θ is assumed to be approximately equal to 1 (low-surface coverage), showing that K can be defined as

$$K = \frac{k_a}{k_d}. \tag{4}$$

The initial condition for Eq. (3) depends on the type of sample being modeled. If the original TCDD spike is contained in the solution, the initial condition is

$$C = C_0 \quad \text{at } t = 0,$$

where C_0 $(ng\,cm^{-3})$ is the initial concentration of TCDD in the solvent. When the original spike is contained on the soil, an alternate initial condition must be used. Since, as described above, some of the TCDD is not actually adsorbed to the soil, it is assumed that that portion dissolves in the solvent immediately. Thus, there is a non-zero initial concentration of TCDD in the solvent that is related to the amount originally adsorbed to the particles by a mass balance. The initial condition then becomes

$$\Gamma = \Gamma_0 \quad \text{and} \quad C = C_0 \qquad \text{at } t = 0,$$

where Γ_0 $(ng\,cm^{-2})$ is the initial concentration of TCDD on the particles. C_0 and Γ_0 are related by a mass balance in this case.

In order to determine the effect of θ, the fraction of the surface area left open for adsorption, an order of magnitude estimate was made. From the description of the TCDD molecule given by Boer et al. [28], the maximum area occupied by one adsorbed TCDD molecule was estimated to be $5 \times 10^{-15}\,cm^2$, so about $9 \times 10^{-3}\,cm^2\,ng\,TCDD^{-1}$. Since the total surface area of the soil is dominated by the internal surface of the organic matter, the surface area is about $1 \times 10^6\,cm^2\,g^{-1}$ organic matter, or about $1.3 \times 10^4\,cm^2\,g^{-1}$. The original concentration of TCDD on the soil was about $60\,ng\,TCDD\,g^{-1}$, so the maximum fractional TCDD surface

coverage is estimated to be only 4×10^{-5}. The fraction of open surface area, θ, was therefore assumed to be ~ 1 in the calculations that follow.

The second equation for the rate of adsorption/desorption of TCDD from the particle is equivalent to the rate of decrease or increase of the bulk TCDD concentration, shown by

$$-\frac{dC}{dt} = \left(\frac{M_p}{V_f}\right) a \frac{d\Gamma}{dt}, \tag{5}$$

where M_p (g) is the mass of the particles and V_f (cm^3) is the volume of the fluid.

Using the fact that K, the equilibrium constant, is equal to k_a/k_d, these equations can be solved analytically to find

$$\frac{C}{C_0} = 1 - \frac{(M_p/V_f)K}{1 + (M_p/V_f)K} \times \left\{ 1 - \exp\left[-k_d\left(1 + \frac{M_p}{V_f}K\right)t \right] \right\} \tag{6}$$

for the case of the initial TCDD spike in the solvent, and

$$\frac{C}{(M_p/V_f)T_0} = \frac{1}{1 + (M_p/V_f)K} \left\{ 1 - \left[P\left(1 + \frac{M_p}{V_f}K\right) - \frac{M_p}{V_f}K \right] \right.$$

$$\left. \times \exp\left[-k_d\left(1 + \frac{M_p}{V_f}K\right)t \right] \right\} \tag{7}$$

for the case of the initial TCDD spike on the soil. In Eq. (7), T_0 (ng g^{-1}) is the total original concentration of TCDD per gram of soil, and P is the fraction of the TCDD that is actually chemically or physically adsorbed to the particles. The remainder exists as an easily dissolved film on the soil. All variables in Eqs. (6) and (7) can be determined, and k_d is adjusted for the best fit to the data.

Several assumptions were made in the formulation of the above equations. First, as has already been mentioned, it is assumed that TCDD concentration in the bulk solution phase is relatively uniform as a result of the swirling of the tubes and the short diffusion distances. That is, the thickness of the mass transfer film surrounding the soil particles in which there is a concentration gradient is small.

Another assumption is that concentration in the bulk solution after 66 days is the final equilibrium concentration. This enables the calculation of the equilibrium constant using the final TCDD concentration in solution of Eq. (6) or (7). This method of finding K is justified based on the partitioning of TCDD into octanol, which comes to equilibrium in about a week [9]. Other studies [18] have also shown that equilibrium in samples of this type is reached within this time frame, and that equilibrium is reached much more quickly with soils with low amounts of organic matter such as the Norfolk loamy sand used in the present study. Therefore, the assumption that the solutions in this case reached equilibrium during the course of the experiment appears to be valid.

As described above, the best estimate of the fraction of TCDD that was not chemically or physically adsorbed to the soil was found to be 40%. That is, 40% is

Table 3
Equilibrium coefficients and rate constants for TCDD adsorption/desorption in various solvents

Solvent	K $(cm^3 g^{-1})$	K_{oc} $(cm^3 g^{-1})$	$k_d \times 10^3$ (h^{-1})	$k_a \times 10^3$ $(cm^3 g^{-1} h^{-1})$	R^2
Dimethyl sulfoxide	0.096	33.0	16.0	1.5	0.99
1-Butanol	0.19	66.0	24.0	4.6	0.99
Tetradecane	0.26	90.0	2.4	0.62	0.99
Ethyl oleate	0.56	190.0	1.9	1.1	0.99

immediately available for transport as if it were not adsorbed. Therefore, in the modeling of the present desorption studies, a value of P of 0.6 was used.

Isotherm data were evaluated to determine whether the assumption of linearity was valid. As expected, the calculated values of K showed no regular variation with original TCDD concentration; i.e. the parameter n in the Freundlich equation

$$a\Gamma = KC^{1/n} \tag{8}$$

was approximately equal to 1 for all organic liquids tested in this study. This is what was predicted a priori since the concentrations (up to 150 ppb) were far below the solubility limits for TCDD in these solvents.

The equilibrium and rate constants calculated using Eqs. (7) and (6) are shown in Table 3. The values for K are average values for those found from each of the 4 samples. The values for k_d are those calculated from Eq. (7), and confirmed using Eq. (6). The desorption experiments were determined to yield more reliable results in the calculation of k_d, since the concentration differences from sample to sample were higher. Because of this larger difference, the accuracy of the calculated k_d values is greater than would be found if the adsorption studies had been used for this calculation.

Graphical representations of samples of the desorption and adsorption data are shown in Figs. 1 and 2. The model fits the data well in most cases, as shown in Fig. 3. This figure compares model predictions of the TCDD concentration that would be in solution to the data taken in the adsorption and desorption studies. The average deviation of the model predictions from the data is 5.6%. This comparison, together with the fact that all correlation coefficient (R^2) values for the k_d calculation were at least 0.99, show that the model describes the data with reasonable accuracy.

From Table 3, it can be seen that K is roughly increasing with increasing solvent viscosity and soil-wetting character as determined by visual inspection. This may reflect the ease of solvent contact with the soil particles and the TCDD adsorbed on those particles. The rate of adsorption/desorption as expressed in the rate constants k_a and k_d also increase with increasing K, showing that the more the equilibrium tends toward higher TCDD concentrations in the solvent, the more quickly that equilibrium is reached. This is concurrent with the observations of Walters and Guiseppi-Elie [18], who observed this same phenomenon. In these researchers' experiments,
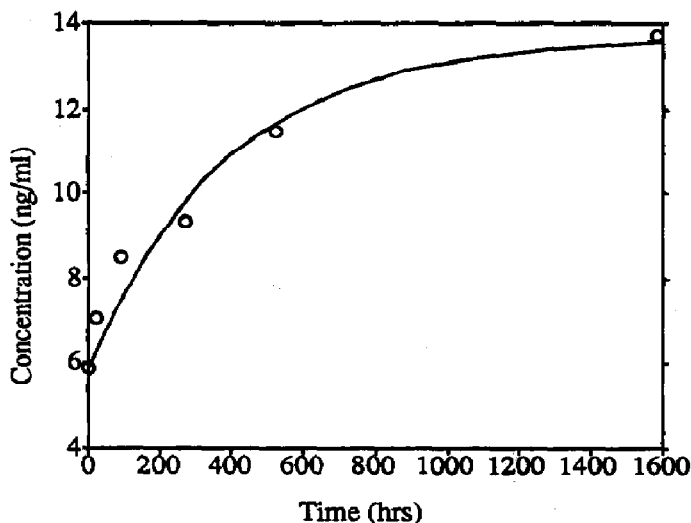
Fig. 1. Concentration (ng/ml) of TCDD in tetradecane versus time in desorption study.
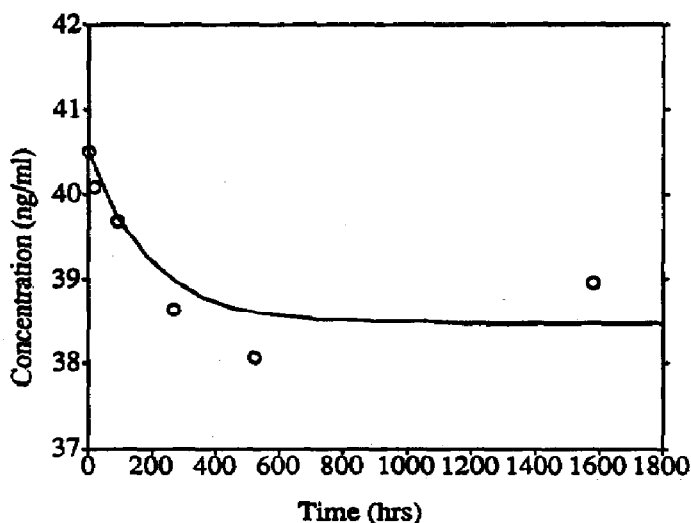

Fig. 2. Concentration (ng/ml) of TCDD in 1-butanol versus time in adsorption study.

samples with different soil types approached equilibrium at differing rates. Those with higher organic carbon content, and therefore higher TCDD adsorption potential, came to equilibrium much more slowly than those with low organic carbon content. The present studies also show that the rate of adsorption increases with increasing K faster than the rate of desorption.

The organic carbon partition coefficients (K_{oc}) shown in Table 3 were found using
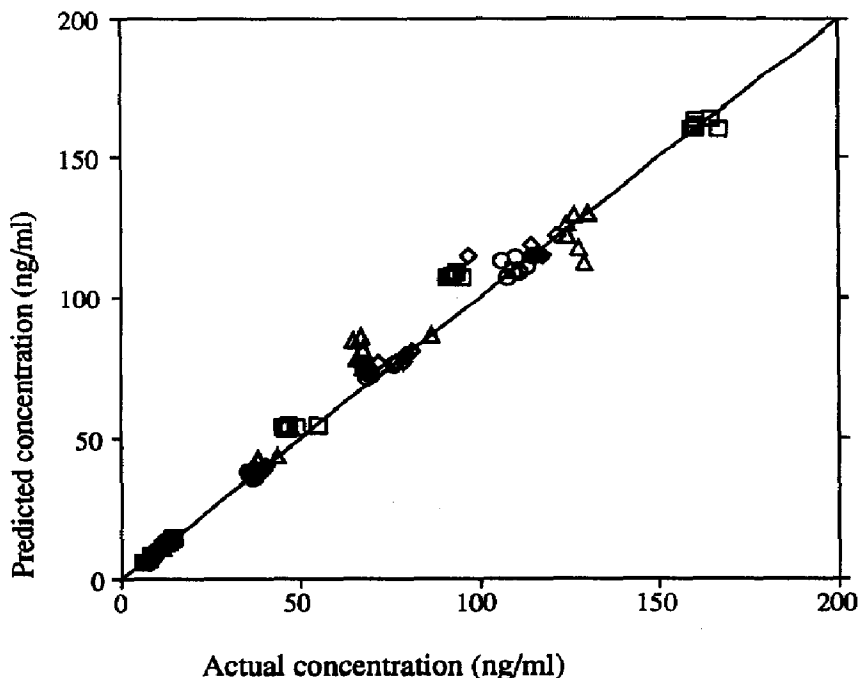
$$K_{oc} = K/f_{oc},$$

(9)

Fig. 3. Comparison of predicted to actual concentration (ng/ml) of original TCDD in solution. (O) Tetradecane; (□) dimethylsulfoxide; (◇) 1-butanol; (△) ethyl oleate.

where f_{oc} is the fraction of organic carbon in the soil, equal in this case to 2.9×10^{-3}. The values of K_{oc} range from 33 for dimethyl sulfoxide to 190 for ethyl oleate. These can be compared to values of K_{oc} found in the experiments of Walters and Guiseppe-Elie [18] for the equilibration of TCDD-spiked soil samples with methanol. The values of $K_{m,oc}$ (mol g^{-1}) found for two different soils of low and high organic carbon content were 2.2 and 3.5, respectively. These are equivalent to K_{oc} values of 90 and 140, somewhat higher than might be estimated using the present results for 1-butanol. However, in comparing K_{oc} values, caution must be exercised since different values obtained from a number of soils usually result in a spread of 10% to 140% [29].

Most of the TCDD in these soil/solvent systems is in the solvent phase at equilibrium, as shown by the relatively low K_{oc} values. In comparison, reported values for $\log K_{oc}$ for TCDD in a soil/water system are very large, ranging up to 7.51 [26].

3.2. Solvent screening studies

The main purpose of the desorption studies was to determine solvents that readily remove a large percentage of TCDD from soil. Of the 14 solvents, ethanol was the best for removing TCDD from the soil used in the studies, bringing 83% of the compound into solution during the course of the experiment. Methanol, 1-propanol, 1-butanol, and dimethyl sulfoxide also removed at least 75% of the TCDD. The high molecular weight oils fared the worst at TCDD removal, solubilizing less than 40% in 16 days.

Table 4
Weight percent of the original TCDD that had been solubilized after given time in single-solvent desorption studies

Solvent	2 h	6 h	20 h	16 days
Methanol	80	80	77	75
Ethanol (denatured)	65	79	82	83
1-propanol	87	71	76	80
Isopropanol	65	64	65	70
1-butanol	46	64	70	78
Ethylene glycol	32	57	63	70
Dimethyl sulfoxide	—[a]	68	79	—[a]
Tetradecane	27	26	31	55
Ethyl oleate	22	47	46	59
PEG-300	1	7	21	49
Oleic acid	10	25	42	61
Cottonseed oil	6	9	13	27
Corn oil	3	5	14	15
Olive oil	4	7	13	37
Soybean oil	3	7	14	26

[a] No data taken at these times.

From Table 4, it can be seen that there is a rough correlation between solvent molecular weight and TCDD removal, and the lower-molecular weight solvents solubilizing a larger final percentage of TCDD from the soil. The results also illustrate the efficacy of the more polar solvents, as well as those with lower viscosity. However, caution must be exercised in drawing conclusions from the data, since only one test was done for each solvent and the low amount of mixing could have affected the results.

Table 5 shows results of tests with solvent mixtures, including the percent of total TCDD in solution after 4 h and 36 h, and the percent of alcohol evaporated after the same time intervals. The control sample with ethyl oleate shows only 39% of the TCDD in solution after 36 h. This is lower than the 46% found in solution after 30 h in the first series of tests, probably due to the elimination of swirling in this solvent mixture series.

The amount of TCDD in solution after 36 h was greatly increased by the addition of methanol, ethanol or 1-propanol to ethyl oleate in the solvent mix. Addition of 1-butanol had slightly less effect. Results from these four tests after 4 h show a relatively large difference between the four alcohols, probably due to differences in the rate of TCDD desorption. The effect after 4 h decreases rapidly with molecular weigtht. The smaller alcohol molecules with less organic character appear to be the most effective in partitioning TCDD from the spiked soil. Results from the ethyl oleate/ethylene glycol solvent mix are difficult to interpret since the soil remained in the heavier ethylene glycol phase, while the aliquots were taken in the upper ethyl oleate phase. The results with the cottonseed oil/1-butanol mixture show that addition of a miscible

Table 5
Weight percent of the original TCDD that had been solubilized after given time and percentage of alcohol evaporated in mixed-solvent desorption studies

Solvent	Percentage TCDD in solution		Percentage alcohol evaporated	
	4 h	36 h	4 h	36 h
100% ethyl oleate	22	39	—	—
67% ethyl oleate, 33% methanol	74	84	75	94
67% ethyl oleate, 33% ethanol	65	81	39	92
67% ethyl oleate, 33% 1-propanol	48	77	15	82
67% ethyl oleate, 33% 1-butanol	33	65	5	50
67% ethyl oleate, 33% ethylene glycol[a]	8	9	0.1[b]	0.4[b]
100% cottonseed oil	6–9	13	—	—
67% cottonseed oil, 33% 1-butanol	23	71	10	65

[a] Mixture not miscible. Two phases on soil.
[b] Ethylene glycol in bottom phase – not volatile.

alcohol can greatly increase the amount of TCDD brought into solution. As expected, the rate of alcohol evaporation from the open bottles was rapid with methanol, but decreased steadily as the molecular weight and boiling point temperature increased.

The exact mechanism for the greater TCDD desorption with the addition of alcohols could not be determined from these macroscopic studies. However, a mechanism similar to the cosolvent theory proposed by Rao et al. [15] could be operating. This theory states that there is a log-linear relationship between the equilibrium partition coefficient and the volume fraction solvent in a water/solvent mixture. A similar mechanism could be at work, with the alcohols with lower partition coefficients facilitating the desorption of TCDD when mixed with organics with higher partition coefficients.

The kinetic model was not used to examine the data from the solvent screening studies. It was determined that the lack of mixing of the samples and the evaporation of the volatile component of the solvent mixtures presented such complexities that the model would not yield useful results.

4. Conclusions

These studies of the adsorption/desorption kinetics of TCDD in the presence of organic liquids have implications for the modeling of transport processes of TCDD in soil contamination situations when solvents are also present. It is apparent that these processes do not take place rapidly within a few hours. In the cases under consideration equilibrium was reached within 4–8 weeks. It can be concluded that desorption

and adsorption rates are not mass transfer limited, at least with the soil and solvents studied here.

The addition of intraparticle TCDD transport to the model did not significantly affect the results. Thus, the assumption of minimal intraparticle diffusional limitations was made in the analysis. These diffusional resistances may have more effect when soil aggragates are present, or in different soil textures.

Calculation of K and k_d values leads to the conclusion that there is a trend in the data of decreasing values of k_d with increasing values of K. This has also been observed by other researchers. Physically, this means that as the equilibrium shifts away from the solvent, the equilibration process takes longer.

The soil organic carbon partition coefficient (K_{oc}) was found to range from 33 to 190 for the solvents studied. These values are comparable to data found in the literature for similar solvents. The equilibrium for TCDD in these soil/solvent systems is heavily weighted toward the solvent as shown by the relatively low K_{oc} values.

Two sets of screening studies designed to quantify the desorption of TCDD from soil under conditions similar to those in the field contamination situation were carried out. The first utilized single organic solvents and the second solvent mixtures. These studies were not amenable to modeling, but several qualitative conclusions can be drawn.

The most efficacious solvent of those tested for TCCD dissolution was methanol, with other low-molecular weight alcohols and dimethyl sulfoxide also faring well. As expected, polar organic liquids with low-molecular weight and low-viscosity were seen to affect the largest amount of TCDD removal from soil.

The mixed-solvent desorption studies showed that the addition of low-molecular weight alcohols to non-volatile organics can increase the amount of TCDD dissolution considerably. The smaller the molecules of the alcohol added, the more quickly the TCDD was partitioned into solution.

5. Nomenclature

a	ratio of particle surface area to particle mass ($cm^2 g^{-1}$)
C	TCDD concentration in solution phase ($ng\,cm^{-3}$)
C_0	initial TCDD concentration in solution phase ($ng\,cm^{-3}$)
d_p	particle diameter (cm)
f_{oc}	fraction organic carbon
K	equilibrium constant ($cm^3 g^{-1}$)
k_a	rate constant for adsorption ($cm^3 g^{-1} s^{-1}$)
k_d	rate constant for desorption (s^{-1})
K_{oc}	organic carbon partition coefficient ($cm^3 g^{-1}$)
M_p	total particle mass (g)
P	fraction of TCDD actually adsorbed to soil particles
R^2	correlation coefficient
t	time from solvent contact with soil (s)
T_0	total original TCDD concentration for spiked soil ($ng\,g^{-1}$)

t_d	time of desorption (s)
V_f	total fluid volume (cm^3)
Γ	TCDD concentration adsorbed to particle surfaces ($ng\,cm^{-2}$)
Γ_0	initial TCDD concentration adsorbed to particle surfaces ($ng\,cm^{-2}$)
θ	fraction of surface area left open for adsorption

References

[1] C.S. Helling, A.R. Isensee, E.A. Woolson, P.D.J. Ensor, G.E. Jones, J.R. Plimmer and P.C. Kearney, Chlorodioxins in pesticides, soil and plants, J. Environ. Quart., 2 (1973) 171.

[2] J. Josephson, Chlorinated dioxins and furans in the environment, Environ. Sci. Technol., 17 (1983) 124A.

[3] O. Hutzinger, M.J. Blumich, M.v.d. Berg and K. Olie, Sources and fate of PCDDs and PCDFs: An overview, Chemosphere, 14 (1985) 581.

[4] A. Fellman, Dioxin in the environment: Its effect on human health, American Council on Science and Health, 1995 Broadway, 16th Fl., New York, NY, 10023, 1984.

[5] R.A. Freeman and J.M. Schroy, Environmental mobility of dioxins, in: R.C. Bahner and D.J. Hansen (Eds.), Aquatic Toxicology and Hazard Assessment: Eighth Symp. American Society for Testing and Materials, Philadelphia, PA, 1985, p. 422.

[6] T. Mill, Prediction of the environmental fate of tetrachlorodibenzodioxins, in: M.A. Mamrin and P.W. Rodgers (eds.), Dioxins in the Environment, Chap. 12, McGraw-Hill, New York, NY, 1985, pp. 173–194.

[7] J.M. Schroy, F.D. Hileman and S.C. Cheng, Physical/chemical properties of 2,3,7,8-TCDD, Chemosphere, 14 (1985) 877.

[8] D.R. Jackson, M.H. Roulier, H.M. Grotta, S.W. Rust and J.S. Warner, Solubility of 2,3,7,8-TCDD in contaminated soils, in: C. Rappe, G. Choudhary and L.H. Keith (Eds.), Chlorinated Dioxins and Dibenzofurans in Perspective, Lewis Publishers, Chelsea, MI, 1986, p. 153.

[9] L. Marple, B. Berridge and L.Throop, Measurement of the water-octanol partition coefficient of 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin, Environ. Sci. Technol., 20 (1986) 397.

[10] W.Y. Shiu, W. Doucette, F.A.P.C. Gobas, A. Andren and D. Mackay, Physical-chemical properties of chlorinated dibenzo-*p*-dioxins, Environ. Sci. Technol., 22 (1988) 651.

[11] R.K. Puri, T.E. Clevenger, S. Kapila, A.F. Yanders and R.K. Malhotra, Studies of parameters affecting translocation of tetrachlorodibenzo-*p*-dioxin in soil, Chemosphere, 18 (1989) 1291.

[12] L. Marple, R. Brunck and L. Throop, Water solubility of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, Environ. Sci. Technol., 20 (1986) 180.

[13] A. Liberti, D. Brocco, I. Allegrini, A. Cecinato and M. Possanzini, Solar and UV photodecomposition of 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin in the environment, Sci. Total Environ., 10 (1978) 97.

[14] J.H. Exner, In place detoxification of dioxin-contaminated soil, Hazard. Waste, 1 (1984) 217.

[15] P.S.C. Rao, A.G. Hornsby, D.P. Kilcrease and P. Nkedi-Kizza, Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation, J. Environ. Quart., 14 (1985) 376.

[16] P. Nkedi-Kizza, P.S.C. Rao and A.G. Hornsby, Influence of organic cosolvents on sorption of hydrophobic organic chemicals by soils, Environ. Sci. Technol., 19 (1985) 975.

[17] Z. Yousefi and R.W. Walters, Use of soil columns to measure sorption of dioxins to soils, in: J.C. Evans (Ed.), Toxic and Hazardous Wastes: Proc. 19th Mid-Atlantic Industrial Waste Conf., Technomic Pub. Co., 1987, p. 181.

[18] R.W. Walters and A. Guiseppi-Elie, Sorption of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin to soils from water/methanol mixtures, Environ. Sci. Technol., 22 (1988) 819.

[19] D.R. Jackson and D.L. Bisson, Mobility of polychlorinated aromatic compounds in soils contaminated with wood-preserving oil, J. Air Waste Mgmt Assoc., 40 (1990) 1129.

[20] A.L. McPeters and M.R. Overcash, Screening of solvents to partition TCDD from spiked soils and facilitate diffusion to the surface for photolysis, SCE RD&D Series 88-RD-62, Southern California Edison, Rosemead, CA, 1988.

[21] S.W. Karickhoff, Organic pollutant sorption in aquatic systems, J. Hyd. Eng., 110 (1984) 707.

[22] C.T. Chiou, L.J. Peters and V.H. Freed, A physical concept of soil-water equilibria, Science, 206 (1979) 831.

[23] C.T. Chiou, L.J. Peters and V.H. Freed, Soil-water equilibria for nonionic organic compounds, Science, 213 (1981) 683.

[24] E.J. Dougherty, Transport Processes of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in Soil Containing Organic Liquids, Ph.D. Thesis, North Carolina State University, 1991.

[25] H. Wipf, E. Homberger, N. Neuner and F. Schenker, Field Trials on Photo-Degradation of TCDD on Vegetation After Spraying with Vegetable Oil, in: F. Cattabeni, A. Cavallaro, G. Galli (Eds.), Dioxin: Toxicological and Chemical Aspects, N.Y. Spectrum Publications, Inc., Jamaica, NY, 1978, p. 201.

[26] D.R. Jackson, M.H. Roulier, H.M. Grotta, S.W. Rust, J.S. Warner, M.F. Arthur and F.L. DeRoos, Leaching potential of 2,3,7,8-TCDD in contaminated soils, in: Land Disposal of Hazardous Waste, Proc. 11th Ann. Res. Symp. at Cincinnati, OH, April 29–May 1, 1985, Hazardous Waste Engineering Research Laboratory, EPA/600/9-85/013, Cincinnati, OH, 45268, p. 153.

[27] P.S.C. Rao and J.M. Davidson, Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models, in: M.R. Overcash and J.M. Davidson (Eds.), Environmental Impact of Nonpoint Source Pollution, Ann Arbor Science Publishers, Ann Arbor, MI, 1980.

[28] F.P. Boer, F.P. van Remoortere and W.W. Muelder, The preparation and structure of 2,3,7,8-tetrachloro-*p*-dioxin and 2,7-dichloro-*p*-dioxin, Science, 94 (1972) 1006.

[29] W.J. Lyman, Adsorption coefficient for soils and sediments, in W.J. Lyman, W.F. Reehl and D.H. Rosenblatt (Eds.), Handbook of Chemical Property Estimation Methods, McGraw-Hill, New York, 1982, p. 2–4.

[30] D. Hillel, Fundamentals of Soil Physics, Academic Press, New York, NY, 1980.