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SORPTION, MOBILITY AND FATE OF 1,2,7,8-TETRACHLORODIBENZO-*p*-DIOXIN IN SOILS AND SAND

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Introduction

Combustion and incineration processes are believed to be the major sources of dioxins to the environment. Incineration of medical and municipal wastes in the early 1990s in the USA were estimated to generate 0.7–5 kg dioxin Toxic Equivalents (TEQ)/yr and 1-3 kg TEQ/yr of PCDD/PCDF emissions, respectively.[1] Incinerator performance has been improved resulting in an annual decrease of dioxins/furans emissions from 13.5 kg TEQ/yr to 2.8 kg TEQ/yr from 1987 to 1995.[2] Recently backyard burning of household waste has been shown to produce more PCDD/PCDFs per mass burned than a typical modern municipal waste incinerator [3] and has been estimated to account for 22% of the dioxin emissions in North America from 1996-1997.[4] These combustion processes result in direct deposition of dioxins on soil. While degradation studies of PCDD/PCDFs have been conducted on contaminated soils, little is known about the sorption, transport, and fate of dioxins in various soil types.[5] Transport may occur because 1,2,7,8-tetrachlorodibenzo-*p*-dioxin (1278-TCDD) was found to be a major congener of the dioxins in ball clay.[6] Ball clay had been used as an anti-caking agent in soybean meal of animal feed but its use has subsequently been discontinued. The main goal of this study was to identify the fate and transport of 1278-TCDD in various soils and sand through the use of laboratory batch and soil column experiments.

Materials and Methods

Sorption, fate and transport experiments of 1278-TCDD were conducted using a Sandy clay loam [(USDA textural designation) coarse silty, mixed, superactive, frigid, aeric calciaquoll, as determined by AGVISE Laboratories (AGVISE), Northwood, ND, USA} obtained from Galesburg, ND, USA. Other soils used were obtained from AGVISE as follows: 1) loam; 2) sandy loam [(sandy loam-A)]; 3) silty clay loam; and 4) silt loam. Standard, washed laboratory sand was obtained from J. T. Baker Chem. Co., Phillipsburg, NJ, USA and kaolin and bentonite clays were obtained from Sigma Chemical Co., St. Louis, MO, USA. Sorption studies were conducted using a batch equilibration technique where the ratio of soils, sand, and kaolin to 0.0l M $CaCl_2$ was 1.6g to 8ml, except for the bentonite, which was a 0.16g to 8ml. [^{14}C] 1278-TCDD (1.0, 0.1 or 0.01µCi) was added to individual vials so that the solution concentrations were 0.590, 0.059, and 0.006 µg/ml (ppm), respectively. Each of the concentrations was run in triplicate. The slurries were agitated by rotation of the vial top to bottom (360°/5sec). At 48, 96, and 168h the vials were centrifuged at 1,700 rpm, triplicate 100µl samples were removed, and ^{14}C was analyzed by liquid scintillation counting (LSC).

Column miscible-displacement experiments were conducted using the five soils or sand, which had been dried at 85° C for 24h and each evenly packed into separate glass columns (8.4cm dia. x

15.0cm long) with a stainless steel bottom end cap. Sandwiched between the soil-filled glass column and the end cap were a 40 mesh stainless steel screen and six layers of cheesecloth. Over a 24h period each soil column was slowly wetted from the bottom with 0.01M $CaCl_2$. This maintained soil structure, reduced the amount of entrapped air, and allowed the pore volume (PV; i.e. wetted pore space) to be determined. After saturation 0.01M $CaCl_2$ flow was established from the top so that steady-state pore water velocities (approximately 3.4 to 3.7 mm min^{-1}) were achieved, which resulted in void volume times that ranged from 40 to 45 min. Once steady-state flow velocity was achieved, the concentration of the applied solution was increased to 0.05M $CaCl_2$ and the conductivity of the eluate was monitored to determine the Cl^- break-through curve (BTC). After the Cl^- BTC was completed on each column, the column was re-equilibrated with 0.01M $CaCl_2$ and a pulse of 40ml [^{14}C] 1278-TCDD (approximately 1.00µCi, 5.0 µg) was applied to the surface of each of the five soils or sand columns. After the 40ml of 1278-TCDD had infiltrated the surface of the column, it was eluted with at least 4.4 L of 0.01M $CaCl_2$ (in excess of 10 PV). The column eluate was collected in 20ml fractions and analyzed for ^{14}C. The soils were extruded from the columns and cut into 1cm sections. The sections were dried and assayed for ^{14}C by combustion analysis on a Packard Model 307 Oxidizer, Meridan, CT. The top section from each column was extracted sequentially with toluene, ethyl acetate, and methanol in an Accelerated Solvent Extractor (Model 200; ASE; Dionex, Sunnyvale, CA, USA). Thin-layer chromatography (TLC) analysis on these extracts was conducted using silica gel plates (250µm; Whatman Lab. Div., Clinton, NJ, USA) developed with hexane:methylene chloride (1:1; authentic 1278-TCDD Rf=0.72).

Model Description

A Freundlich sorption isotherm was used to describe the equilibrium batch experiments:

$$s = K_d C^n \qquad [1]$$

where s is the concentration of 1278-TCDD sorbed to the soil (mg g^{-1}), K_d is the adsorption coefficient (L/g), C is the dissolved concentration (mg L^{-1}), and n is an empirical constant controlling the shape of isotherm function (n=1 is linear). A nonlinear, least-squares approximation method was used to obtain the best-fit of Eq. [1] to the observed data, and the coefficient of determination (r^2) was calculated to measure the goodness of best-fit.[7] The parameters K_d and n were optimized to achieve the best-fit description of the observed data. For the column model we used HYDRUS-1D Version 2.0 an advective-dispersive model with fully kinetic-linear sorption, where α is the rate of sorption and r^2 the coefficient of determinant.[8]

Results and Discussion

The batch (Table 1 for the various soils, including sand, kaolin, and bentonite clays) experiments indicated that 1278-TCDD readily partitioned out of the dissolved phase and sorbed to the soil. The lower two initial concentrations for all the soils except sand and bentonite resulted in equilibrium concentrations in the solution phase of zero after 72h. The K_d and n values were all calculated from the highest initial concentrations. The K_ds for the 1278-TCDD for the soils ranged from 1.514 to 0.363 L/g with the clays exhibiting higher K_ds (4.153 L/g and 0.885 L/g for bentonite and kaolin, respectively). The sorption isotherms were all non-linear. The Freundlich n values were all less than one, which resulted in an isotherm that approached a finite asymptote. This implies that sorption had reached a limit and may reflect more complex interactions between the solid soil component and the solute, or perhaps competitive sorption.

Sorption affinity was identified for the various soil components (sand, silt, clay, organic matter, and specific surface area). The amount of 1278-TCDD sorbed to the soil was directly related to the soil's surface area. The sorption of 1278-TCDD to the sand and the kaolin may reflect the high hydrophobicity of the 1278-TCDD which would cause 1278-TCDD to leave the polar water phase for a less polar substrate such as the sand or kaolin. Because 1278-TCDD was significantly more extractable from the sand than the soils using the organic solvents, 1278-TCDD sorption to sand is believed to be weak compared to the soil. However, little speculation regarding sorption of 1278-TCDD to sand surface area or organic content of could be made, because of the low recovery of ^{14}C.

Table 1. K_d values from column and batch studies on soils, sand and clays of 1278-TCDD.

Soil Type	**Column Studies**			**Batch Studies**	
	K_d values (L/ g)	**α (1/h)**	**r^2**	**K_d values (L/ g)**	**n**
clay loam	0.26	0.00015	0.987	0.387	0.66
sandy clay loam	0.56	0.0071	0.932	1.514	0.80
loam	nd			0.354	0.68
silty clay loam	0.61	0.00015	0.987	0.824	0.77
silt loam	0.13	0.00068	0.947	0.363	0.70
sand	nd			1.013	0.84
kaolin-clay	na			0.839	0.76
bentonite-clay	na			0.415	0.77

nd = not determined (limited elution of 1278-TCDD), na = not applicable (column not run)

Table 2. Breakthrough data of 1278-TCDD from soil columns.

Soil Type	**Organic Content (%)**	**pH**	**Pore Vol. (PV) (ml)**	**Percent Eluted**	**Elution Peak (Rel. PV)**	**Percent Sorbed**	**Percent of Sorbed**	
							top cm	**top 3cm**
clay loam	7.5	7.9	592	22.0	0.25	41.7	9.9	16.5
sandy clay loam	3.3	7.6	565	41.2	1.77	83.3	27.2	39.1
loam	9.2	7.8	492	0.6	0.18	117	67.5	110
silty clay loam	5.3	8.2	513	15.1	0.30	61.2	3.2	11.9
silt loam	7.5	7.9	592	18.1	0.25	63.5	9.1	24.1
sand	0	-	352	0.4	1.23	54.0	6.7	26.4

When the sand results were excluded, it was found that the percent 1278-TCDD sorbed to the various soils generally correlated with the percent organic content (Table 2). Significant transport of 1278-TCDD through clay loam, sandy clay loam, silty clay loam and silt loam soils because 22.0, 41.2, 15.1, and 18.1%, respectively, of applied ^{14}C eluted through the soil columns (Table 2). Little ^{14}C was transported and eluted from the sand (0.4%, Table 2) or loam (0.6%) soil columns. Additionally, except for the sand and sandy clay loam, the elution peak of the ^{14}C was rapid (i.e. 0.18-0.30 relative PV), which indicated that there might have been colloid transport of 1278-TCDD. The chloride BTCs for all the columns indicated that there was no physical bypass flow of solute through macropore systems within the soil column. The chloride BTCs were all modeled using standard convective-dispersive processes with retardation coefficients of 1, which indicated no sorption or preferential flow. The sand (washed and sieved) column would have had no colloidal material present, and little or no 1278-TCDD was present in its effluent. Although, the sorption to the sand was not as strong as the other soils (as indicated by the batch experiments and later by the solvent extraction analysis) very little 1278-TCDD eluted from the column. The other soils would have contained more soil colloids, which can present a strong sorption surface and are small enough (<1μm) to be transported through the soil pores. Additionally, the effluent samples from the soil columns were observed to be cloudy, which is suggestive of colloids. When 1278-TCDD was applied to the column it was possible that it rapidly sorbed to colloids at the top of the column and the 1278-TCDD/colloid complex was transported through the entire column. This colloid facilitated transport could result in the transport of dioxin through soil to sufficient depths to contaminate groundwater.

When extruded, it was found that 1278-TCDD was significantly redistributed through the soil column profile of the clay loam, sandy clay loam, silty clay loam, silt loam and sand soils (data not shown). After combustion analysis, it was found that 41.7%-117% of the applied 1278-TCDD was retained by the various soils. Only in the loam column was the majority of ^{14}C sorbed in the first cm (67.9%) or the top three cm 110%. For the other soil columns, ^{14}C was distributed through the length of the columns (Table 2.). Most of the ^{14}C (36.2-95.7%) from soil columns could be extracted using toluene, while 2.1-32.1% was nonextractable by all three solvents. Virtually all the ^{14}C sorbed to the sand column was extractable by toluene, ethyl acetate, and methanol (36.2, 35.4 and 28%, respectively). ^{14}C Toluene, ethyl acetate, and methanol extracts were analyzed by TLC. 1278-TCDD was virtually the only compound observed (1278-TCDD, R*f*= 0.72, 80.6- 97.8% ^{14}C extracted from the soil). Minor metabolites (0.1- 10.1%) were found in ^{14}C extracts of the soil.

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