Sorption, mobility, and fate of 1,4,7,8-tetrachlorodibenzo-p-dioxin in soils.

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Introduction

Most dioxins are released into the environment through low temperature combustion processes,[1] which include waste incineration and metal refining. Incineration of medical and municipal wastes in the early 1990s was estimated to generate 0.7g –5 kg dioxin Toxic Equivalents (TEQ)/yr and 2-3 kg TEQ/yr of polychlorinated dibenzo-*p*-dioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs) emissions, respectively.[2] Governmental regulatory controls on waste incinerators have resulted in an annual decrease of dioxins/furans emissions from 13.5 kg TEQ/yr to 2.8 kg TEQ/yr from 1987 to 1995.[3] Recently backyard burning of household waste has been shown to produce more PCDDs/PCDFs per mass burned than a typical modern municipal waste incinerator[4] and has been estimated to account for 22% of the dioxin emissions in North America from 1996-1997.[5] These combustion processes result in direct deposition of dioxins on soil. While degradation studies of PCDDs/PCDFs have been conducted on contaminated soils, little is known about the sorption, transport, and fate of dioxins in various soil types.[6] 1,4,7,8-Tetrachlorodibenzo-*p*-dioxin (1478-TCDD) was also found to be a significant congener of the dioxins in ball clay.[7] 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 1478-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 1478-TCDD were conducted using a Glyndon; sandy clay loam (coarse silty, mixed, superactive, frigid, aeric calciaquoll) [USDA series name; USDA textural designation (taxonomic description)], determined by NDSU Soil Testing Laboratory, Fargo, ND, USA and obtained from Galesburg, ND, USA. Other soils used were obtained from AGVISE Laboratories, Northwood, ND, USA as follows: 1) Renshaw; loam (sandy-skeletal, mixed, frigid entic hapludolls); 2) Gardena; clay loam (course-silty, superactive, frigid aeric calciaquolls); 3) Bearden; silty clay loam (fine-silty, mixed superactive, frigid aeric calciaquolls); and 4) LaDelle; silt loam (fine-silty, mixed superactive, frigid cumulic hapludolls). Soils were passed through a 2mm sieve. 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 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] 1478-TCDD (1.0, 0.1 or 0.01µCi) was added to individual vials so that the solution concentrations were 5.79, 0.80, 0.58, and 0.058µg/ml (ppm), respectively. Each of the concentrations were run in triplicate. The slurries were agitated by rotation of the vial top to bottom (360°/5sec). At 0.5, 1, 5, 24, 48, and 168h the vials were centrifuged at 1,700xg, 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, which had been dried at 85° C for 24h and each evenly packed in 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 wetted from the bottom with 0.01M $CaCl_2$ to reduce the amount of entrapped air and allow 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 - 3.7 ml min^{-1}) were achieved, which resulted in times of displacement of one volume of void that ranged from 40 - 45 min. Once steady-state flow velocity was achieved, 0.05M $CaCl_2$ was applied and the conductivity of the eluate was monitored to determine the Cl^- break through curve (BTC). The column was then re-equilibrated with 0.01M $CaCl_2$ and a pulse of 40ml [^{14}C] 1478-TCDD 0.01M $CaCl_2$ (approximately 1.00µCi, 5.0 µg) was applied to the surface of each of the five soils columns. After the 1478-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 effluent 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 1478-TCDD Rf=0.72).

Model Description

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

$\boldsymbol{s = K_dC^n}$ [1] where s is the concentration of 1478-TCDD sorbed to the soil (mg g^{-1}), K_d is the distribution coefficient [(mg/ g)/(mg/L], 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 fit.[8] The parameters K_d and n were optimized to achieve the best-fit description of model to the observed data. The first order kinetic rate constant for 1478-TCDD, ω, was determined by the equations: $\boldsymbol{C(t)=C_0e^{-\omega t}}$ [2] and $\boldsymbol{t_{1/2}= \ln 2 / \omega}$ [3] where C_0 is the initial concentration, $C(t)$ is the solution concentration at time t, $t_{1/2}$ is the time required for half of the original mass of TCDD in the aqueous phase to be adsorbed onto the solid phase. For the column model we used an advective-dispersive model with fully kinetic-linear sorption, where ω is the rate of sorption and r^2 the coefficient of determinant. A nonequilibrium transport convective-dispersive equation from HYDRUS-2D software was used to describe the 1478-TCDD miscible displacement experiments.

Results and Discussion

The batch (Table 1 for the various soils and kaolin and bentonite) experiments indicated that 1478-TCDD readily partitioned out of the dissolved phase and sorbed to the soil. The K_d and n values were all calculated from the highest initial concentrations. The K_ds for the 1478-TCDD for the soils ranged from 0.16 to 0.29 [(mg/g)/(mg/L] (Freundlich adsorption) and 0.40 to 0.68 [(mg/g)/(mg/L] (linear adsorption) as shown in Table 1. The sorption isotherms were all linear with the Freundlich n values equal to one. Most of 1478-TCDD was absorbed to the soil in the first two days. The first order rate constant ω, from eqs. 2 and 3, ranged from 0.04 min^{-1} to 0.1 min,$^{-1}$ and $t_{1/2}$ ranged from 7 min to 17 min. This indicated that 1478-TCDD decreased to half in the aqueous phase between 7 min and 17 min because of soil sorption. A K_d of 3.59 L g^{-1} with an n of 1.5 was obtained for the silt loam from the column study using inverse fitting by HYDRUS-2D.

Sorption affinity was identified for the various soil components (silt, clay, organic matter, and specific surface area). The amount of 1478-TCDD sorbed to the soil was directly related to the soil's surface area. A significant negative correlation existed between organic matter and sorption of 1478-TCDD (data not shown, see Ref 10), with weak initial correlations at 48h (r =-0.18), but increased by 96h (r =-0.68). These batch experiments, along with those of from 1278-[11] and 1378-TCDD[12] studies, indicate that: 1) organic matter was an important factor in the sorption of TCDDs to soil, 2) the aqueous concentration of TCDDs quickly decreases in the first 48h in soil with low organic matter, 3) a longer contact time is required to approach sorption equilibrium in high organic matter soils, and 4) after 96h TCDDs are more tightly bound to high organic matter soils. 1478-TCDD sorption to kaolin may reflect the high hydrophobicity of the 1478-TCDD, which would cause 1478-TCDD to leave the polar water phase for a less polar substrate such as kaolin.

Table 1. K_d values from batch studies on soils and clays of 1478-TCDD.

Soil Type	Freundlich adsorption K_d [(mg/g)/(mg/L]	n	r^2	Linear adsorption K_d [(mg/g)/(mg/L]	n	r^2
silty clay loam	0.268	0.872	1.0	0.505	1	0.99
sandy clay loam	0.293	0.84	1.0	0.680	1	0.99
silt loam	0.302	0.913	1.0	0.464	1	0.99
clay loam	0.164	0.809	1.0	0.405	1	1.0
loam	0.267	0.892	1.0	0.453	1	1.0

K_d 's for kaolin and bentonite were not determined due to total sorption of 1478-TCDD.

Table 2. Break through data of 1478-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
silty clay loam	7.5	7.9	454	0.04	ne	95.2	67.2	83.7
sandy clay loam	3.3	7.6	489	0.16	0.76	77.0	53.7	74.2
silt loam	9.2	7.8	590	0.99	0.35	84.7	36.5	59.9
clay loam	5.3	8.2	542	0.64	0.26	87.3	54.4	80.6
loam	7.5	7.9	587	0.61	0.25	91.1	33.2	72.3

ne =not eluted

Only limited transport (0.04 to 0.99%) of the applied ^{14}C 1478-TCDD eluted through the soil columns (Table 2), which indicated stronger sorption compared to the other TCDDs studied.[11,12] Additionally, except for sandy clay loam, the elution peak of the ^{14}C was rapid (i.e. 0.25-0.35 relative PV), which indicated that there might have been colloid transport of 1478-TCDD. The chloride BTC for all the columns indicated that there was no physical bypass flow of solute through the soil column. When the chloride BTC's were modeled, using standard convective-dispersive processes, the retardation coefficients were 1. 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 1478-TCDD was applied to the column it is possible that it rapidly sorbed to colloids at the top of the column and the 1478-TCDD/colloid complex was transported through the entire column as has been observed with the 1278-TCDD[11] and 1378-TCDD.[12] 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 1478-TCDD was not significantly redistributed through the soil column profile of the soils. After combustion analysis, it was found that 77.0-95.2% of the applied 1478-TCDD was retained by the various soils with the majority of ^{14}C sorbed in the first cm (36.5-67.2%) or the top three cm (59.9-83.7%). Most of the ^{14}C (57.6-99.0%) from soil columns could be extracted using toluene, while 2.1-32.1% was nonextractable by all three solvents. ^{14}C Toluene, ethyl acetate, and methanol extracts were analyzed by TLC. 1478-TCDD was the only compound observed (1478-TCDD, R*f*= 0.72, 80.6-97.8% ^{14}C extracted from the soil). No metabolites were found in ^{14}C extracts of the soil. These results indicate that, although 1478-TCDD is strongly sorbed, it persists with little or no transformation, which also indicates soil degradation of 1478-TCDD does not readily occur. Similar findings for the 1278- and 1378-TCDD have been reported.[11,12]

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