SORPTION, MOBILITY AND FATE OF 1,3,7,8-TETRACHLORODIBENZO-*p*-DIOXIN IN SOILS AND SAND

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Introduction

Major sources of dioxins are combustion and incineration processes. In the early 1990s medical and municipal wastes were estimated to generate 0.7g –5 kg dioxin Toxic Equivalents (TEQ)/yr and 2-3 kg TEQ/yr of PCDD/PCDF emissions, respectively.[1] Improvements in incinerator performance and removal of highly polluting incinerators decreased annual emissions of dioxins/furans from 13.5 kg TEQ/yr to 2.8 kg TEQ/yr from 1987 to 1995.[2] Backyard burning of household waste has recently 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/Fs have been conducted on contaminated soils, little is known about the sorption, transport, and fate of dioxins in various soil types.[5] The main goal of this study was to identify the fate and transport of 1,3,7,8-tetrachlorodibenzo-*p*-dioxin (1,3,7,8-TCDD) in various soils and sand through the use of laboratory batch and disturbed soil column experiments.

Materials and Methods

Sorption, fate and transport experiments of 1,3,7,8-TCDD were conducted using a sandy loam (sandy loam-G) {coarse silty, mixed, superactive, frigid, aeric calciaquoll, [3.3 % organic matter, cation exchange capacity (CEC) = 51.1 meg/100g, and pH = 7.6 as determined by AGVISE Laboratories, Northwood, ND]} obtained from Galesburg, ND, USA. Other soil types used were obtained from and characterized by AGVISE Laboratories as follows: 1) loam [AGVISE soil ID = EL7-L-PF (0-24"), 7.5 % organic matter, CEC = 26.0, and pH = 7.9]; 2) sandy loam [(sandy loam-A), AGVISE soil ID = LB-SL, 9.2 % organic matter, CEC = 25.5, and pH = 7.8]; 3) clay loam [AGVISE soil ID = M-CL, 5.3 % organic matter, CEC = 25.6, and pH = 8.2] and 4) silt loam [AGVISE soil ID = HCB-SL-PF, 7.5 % organic matter, CEC = 29.6, and pH = 7.9]. 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, respectively, except for the bentonite, which was a 0.16g to 8ml. [^{14}C] 1,3,7,8-TCDD (1.0, 0.1 or 0.01µCi) was added to individual vials so that the solution concentrations were 0.630, 0.063, 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^o/5sec). At 48, 96, and 168h the bottles were centrifuged at 1,700 rpm, triplicate 100ìl samples were removed, and radioactivity was analyzed by liquid scintillation counting (LSC).

Column miscible-displacement experiments were conducted using the sandy loam-G [bulk density (ρ_b) = 1.82g/ml], loam (ρ_b =1.16g/ml), sandy loam-A (ρ_b =1.92g/ml), clay loam (ρ_b =1.4g/ml), silt loam (ρ_b =1.09g/ml), or sand (ρ_b = 4.80g/ml), which had been dried at 85 ^{o}C for 24h and evenly packed in glass columns (8.4 cm dia. x 15.0 cm long) with a stainless steel bottom end cap. In a single column sandwiched between the soil 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 determined the pore volume (PV; i.e. wetted pore space). After saturation 0.01M $CaCl_2$ flow was established through the column (top to bottom) so that steady-state pore water velocities (approximately 3.4 to 3.7 mm min^{-1}) were achieved. Once steady-state flow velocity was achieved on each column, the concentration of the applied solution was increased to 0.05M $CaCl_2$ and the electrical conductivity of the eluates was monitored to determine the Cl^- break-through curve (BTC). After the Cl^- BTC was completed on each column, each column was re-equilibrated with 0.01M $CaCl_2$ and a pulse of 40ml [^{14}C] 1,3,7,8-TCDD (approximately 1.00µCi, 5.0 µg) was applied to the surface of the sandy loam-G, loam, sandy loam-A, clay loam, silt loam, and sand columns. After the 40ml of 1,3,7,8-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 20 ml fractions of column effluent were analyzed for ^{14}C. The soils were extruded from the columns and cut into 1cm sections. During the extrusion process some soil columns were found to be compressed approximately 1 cm. 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 fractions was conducted using silica gel plates (250µm; Whatman Lab. Div., Clinton, NJ, USA) developed with hexane:methylene chloride (1:1).

Model Description

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

$$s = K_d C^n \tag{1}$$

where s is the concentration of 1,3,7,8-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 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 best-fit.[6] The parameters K_d and n were optimized to achieve the best-fit description of the observed data.

Results and Discussion

The batch (Table 1 for the various soils, including sand, kaolin, and bentonite clays) experiments indicated that 1,3,7,8-TCDD readily partitioned out of the dissolved phase into the sorbed phase. The K_ds for the 1,3,7,8-TCDD for the various soils ranged from 0.17-0.87 L/g with the clays exhibiting higher K_ds (5.69 L/g and 8.12 L/g for bentonite and kaolin, respectively). The n values for the 1,3,7,8-TCDD ranged from 0.63-0.93, respectively, which indicates that the sorption process was first-order because the isotherm was approximately linear (i.e., $n \approx 1$). The higher K_d values from this study may have resulted from using mollic soil epipedon, which have high organic matter (3.3-9.2 % organic carbon content, Table 2). Lai et al.[7] noted in their study that sorption depends on the total amount of organic matter.

There was only limited detection of radioactivity in the column effluent for most of the soil types including the sand (0-1.4 %, Table 2). However, significant amounts ^{14}C were eluted from the loam (26.8 %) and silt loam (24.9 %) soil columns. Additionally, except for the sand, the elution peak of the

Table 1. K_d values (L/ g) from batch studies on soils, sand and clays of 1,3,7,8-TCDD.

Soil Type	K_d values (L/ g) 1,3,7,8-TCDD	*n*
Loam	0.87	0.93
Sandy Loam-G	0.44	0.78
Sandy Loam-A	0.33	0.75
Clay Loam	0.17	0.63
Silt Loam	0.41	0.82
Sand	0.46	0.87
Kaolin	8.12	0.83
Bentonite	5.69	0.91

Table 2. Breakthrough data of 1,3,7,8-TCDD from soil columns. (NA, not applicable)

Soil Type	Organic Content (%	Pore Volume (PV) (ml)	Percent Eluted	Elution Peak (Rel. PV)	Percent Sorbed	Percent of top cm	Sorbed top 3cm
Loam	7.5	583	26.8	0.25	50.0	31.8	84.4
Sandy loam-G	3.3	464	0	NA	60.6	95.4	99.7
Sandy loam-A	9.2	488	1.4	0.20	69.2	73.4	95.5
Clay loam	5.3	608	1.1	0.221	101	11.0	28.0
Silt loam	7.5	600	24.9	0.32	39.6	37.6	84.4
Sand	0	280	0.6	1.16	75.6	28.1	78.8

1,3,7,8-TCDD was very rapid (i.e. 0.2-0.32 relative PV), which indicated that 1,3,7,8-TCDD might have followed preferred pathways (see below) in its movement through the various soil columns. Also, when the columns were extruded, it was found that 1,3,7,8-TCDD was significantly redistributed through the soil column profile of the various soil types (data not shown). After the combustion analysis for ^{14}C, it was found that 39.6 %-101 % of the applied 1,3,7,8-TCDD was retained by the various soils. Most of the^{14}C sorbed to the top three cm (78.8-99.7 %), except for the clay loam where ^{14}C from 1,3,7,8-TCDD was distributed throughout the column. The ^{14}C from 1,3,7,8-TCDD in the first centimeter of the soils ranged from 11.0-95.4 % of the ^{14}C. Toluene extracts contained most of the ^{14}C (54.9-87.1 %), while 2.2-11.9 % of the ^{14}C from 1,3,7,8-TCDD was nonextractable. The ^{14}C from toluene extracts of all the soils was analyzed by TLC. 1,3,7,8-TCDD was virtually the only compound observed (1,3,7,8-TCDD, R*f*= 0.69). Very minor quantities of metabolites may have been present in the toluene extract of sand.

Numerous studies have clearly shown that water and chemicals can move through soil along preferred pathways[8-11] (e.g. macropores, cracks, root channels, worm holes, funnel flow, and instability of wetting front). These preferential flow pathways can result in rapid movement of chemicals to the water table. When screening models ignore preferential flow pathways, they do not accurately predict observed spatial patterns of groundwater contamination.[12] Preferential flow is especially important for those chemicals that are toxic at the parts per billion or trillion concentration,[2] such as the dioxins. Consequently, we hypothesize that 1,3,7,8-TCDD can be leached to significant depths and eventually to groundwater in structured soils, perhaps by preferential flow. Significant leaching of highly sorbed chemicals (e.g. phosphorous) can occur and bypass the soil matrix entering the groundwater. Gachter et al.[13] reported that soil macropores and artificial drainage systems are the most important pathways for the vertical and lateral transport of soluble reactive phosphorus from the soil into surface waters. To our knowledge, to date no study has addressed transport of dioxins in soil especially by preferential flow.

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Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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