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Effectiveness of Activated Carbon and Biochar in Reducing the Availability of Polychlorinated Dibenzo-*p*-dioxins/Dibenzofurans in Soils

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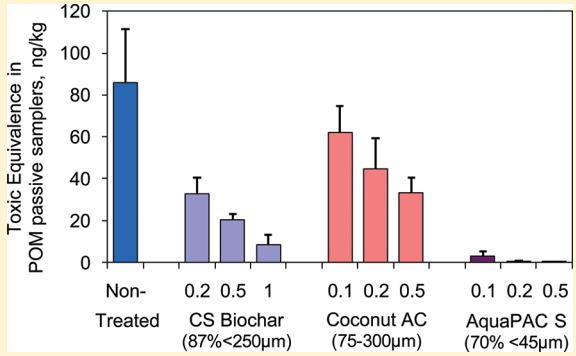
Supporting Information

ABSTRACT: Five activated carbons (ACs) and two biochars were tested as amendments to reduce the availability of aged polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs) in two soils. All sorbents (ACs and biochars) tested substantially reduced the availability of PCDD/Fs measured by polyoxymethylene (POM) passive uptake and earthworm (*E. fetida*) biouptake. Seven sorbents amended at a level of 0.2 × soil total organic carbon (0.2X) reduced the passive uptake (physicochemical availability) of total PCDD/Fs in POM by 40% to 92% (or toxic equivalent by 48% to 99%). Sorbents with finer particle sizes or more macropores showed higher reduction efficiencies. The powdered regenerated AC and powdered coconut AC demonstrated to be the most effective and the two biochars also performed reasonably well especially in the powdered form. The passive uptake of PCDD/F in POM increased approximately 4 to 5 fold as the contact time between POM and soil slurry increased from 24 to 120 d while the efficacy of ACs in reducing the physicochemical availability remained unchanged. The reduction efficiencies measured by POM passive uptake for the regenerated AC were comparable to those measured by earthworm biouptake (bioavailability) at both dose levels of 0.2X and 0.5X. The biota-soil accumulation factor (BSAF) values for unamended soil ranged from 0.1 for tetra-CDD/F to 0.02 for octa-CDD/F. At both dose levels, the regenerated AC reduced the BSAFs to below 0.03 with the exception of two hexa-CDD/Fs. The reduction efficiencies measured by earthworm for coconut AC and corn stover biochar were generally less than those measured by POM probably due to larger particle sizes of these sorbents that could not be ingested by the worms.



INTRODUCTION

The soil in the vicinity of a large scale chemical manufacturing facility in Midland, MI is impacted by polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) primarily due to historic emissions from industrial waste incinerators. Because some PCDD/F congeners are persistent, bioaccumulative, and toxic, the fate and transport, bioavailability, and ecological and human health risk of PCDD/Fs in soils and sediments have been the focus of recent research.[1−3] Elevated levels of hydrophobic organic contaminants (HOCs) such as PCDD/Fs in soil and sediment can be indicative of potential exposure but assessing the extent of exposure can prove difficult as only a fraction of the HOCs are available to receptors.[4] Several studies have shown that the bioavailability of the PCDD/Fs in soils is much lower than the assumption of 100% bioavailability.[5−7] Cornelissen et al. showed that the available fraction of PCDD/Fs in soils from a former wood impregnation site in Sweden was considerably less than predicted.[8] The limited bioavailability of HOCs has been attributed to strong sorption of the HOCs to native black carbon in soils and sediments.[9]

Recently *in situ* sorbent amendment, such as activated carbon (AC) and biochar, has been identified as a new direction for the management of contaminated sediment sites.[10] The addition of AC has been shown to decrease bioaccumulation of HOCs such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in sediments[11,12] and soils.[13−15] The reduction of biouptake by AC is generally through decreasing the bioavailable fraction of the contaminants.[16] Recent studies have documented the effectiveness of

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various biochars in the sorption of both HOCs and heavy metals.[17] Adding AC or biochar into contaminated soil/sediment is appealing because it not only reduces the availability of contaminants but also provides opportunity for carbon sequestration.[10]

Fagervold et al. reported the use of passive sampler, polyoxymethylene (POM), and earthworm, *Eisenia fetida*, to assess the efficacy of AC amendment in reducing the availability of PCDD/Fs in floodplain soils.[7] Passive sampler such as POM has been used by other reserachers[8] to measure the freely dissolved aqueous concentration of contaminants (physicochemical availability). Earthworms are commonly used to measure bioavailability (bioaccumulation) of contaminants in soil because earthworms are near the base of the food chain and form a key exposure pathway for terrestrial animals. Matscheko et al. reported biota to soil accumulation factor (BSAF) values for PCDD/Fs in terrestrial earthworms of 0.09 to 1.1.[18] Fagervold et al. reported lower BSAF values of 0.02 to 0.17 for PCDD/Fs in floodplain soil and the addition of AC into soil reduced the BSAF values to below 0.02.[7]

The objectives of this study were to 1) evaluate the effectiveness of various types of ACs and biochars in reducing the availability (both physicochemical availability and bioavailability) of PCDD/Fs in soils; 2) optimize dose levels of AC and biochar; 3) determine critical properties of AC/biochar such as particle size and pore size that impact efficacy; and 4) evaluate the feasibility of using the AC and biochar amendment for a field pilot study. The efficacy of these amendments in reducing the availability of PCDD/Fs in soils was assessed using both passive samplers (POM) and terrestrial organisms (earthworms).

EXPERIMENTAL SECTION

Soil Samples. Composite soils contaminated with PCDD/Fs were collected from two locations (Soils A and B) in the vicinity of a large scale chemical manufacturing facility. Each composite soil was taken from three sampling points within each location at depth of 0−15 cm after the removal of the overlying vegetation. Soils were passed through a 2 mm sieve to remove large objects such as gravel, leaves, and grass roots, homogenized, and stored at ambient temperature in sealed containers until further use.

Total Organic Carbon Content (TOC). Three aliquots (1−2 g) of each soil were dried (105 °C) overnight, pulverized, and combined. The samples were acidified using HCl (6N) to remove inorganic carbon and dried (105 °C) overnight before TOC measurement. The TOC of soils were measured using a Shimadzu model TOC-V analyzer equipped with a SSM-5000a combustion unit.

Activated Carbon and Biochar Amendment. The characteristics and origin of the five ACs and two biochars (sorbents) used in the study are summarized in Table S1. The two biochars were a corn stover-based biochar (CS Biochar, 87% mass <250 μm, specific surface area or SSA of 67.2 m^2/g) and a pine wood chip-based biochar (P Biochar, 83% mass <250 μm, SSA of 102 m^2/g). The five ACs included a coconut-based AC (Coconut AC, 75−300 μm, SSA of 1320 m^2/g), two bituminous coal-based ACs (TOG LF and TOG NDS, both 45−180 μm, SSA of 1220 and 1170 m^2/g), a lignite coal-based AC (DARCO, 45−180 μm, SSA of 968 m^2/g), and a coal/coconut-based regenerated (reactivated) AC after the virgin AC had been used in food and beverage industry (AquaPAC S, 70% mass <45 μm, SSA of 1150 m^2/g). The major difference between AC and biochar is that biochar is not activated after pyrolysis during their manufacturing processes. These sorbents contained negligible amount of PCDD/Fs (toxic equivalent <1 ng/kg). To evaluate the effect of particle size on the effectiveness of the sorbents, Coconut AC, CS Biochar, and P Biochar were ground to a similar particle size distribution as AquaPAC S (70% mass <45 μm). The SSA of the ground Coconut AC, CS Biochar, and P Biochar were 1290, 70.4, and 180 m^2/g, respectively. Sorbents were gradually introduced into soil in a glass jar, while the soil was manually mixed and the jars were then placed on a roller mill rotating at 4 rpm for 24 h. The moisture contents of Soils A and B before amendment were 8% and 14% (wet wt based), respectively. The efficacy of sorbent amendment was assessed using both POM passive uptake test and earthworm bioaccumulation test.

Polyoxymethylene (POM) Passive Uptake. Polyoxymethylene (76 μm thick) was obtained from CS Hyde Company (Lake Villa, IL). The procedures for POM exposure to soil slurry were described elsewhere.[7] Briefly, twenty grams (dry wt.) of soil and appropriate amount of precleaned POM strips (0.2 g for Soil A and 0.1 g for Soil B) were added into a 250-mL glass bottle. Deionized water (~ 220 mL) containing 25 mg/L of sodium azide and 0.01 M calcium chloride[19] was added to each bottle. The bottles were sealed and rotated for 24 or 120 d on a roller mill at 4 rpm. After exposure, the POM strips were cleaned and analyzed for PCDD/Fs. This approach does provide a measure of the relative reduction of freely dissolved PCDD/Fs in the aqueous phase although the exposure time may not be long enough for equilibrium to be established for all congeners.

Twenty-five treatment groups (three replicates per treatment) were included for POM exposure. Eighteen of them were amended with sorbents at their original particle sizes (intact, exposure time 24 d): nontreated Soils A and B, Soil A with seven sorbents at a dose level to achieve a ratio of sorbent to soil total organic carbon (sorbent: soil TOC) of 0.2:1 (0.2X), Soil A with AquaPAC S and Coconut AC (at 0.1X and 0.5X), and CS Biochar (at 0.5X and 1X), Soil B with TOG LF, DARCO, and AquaPAC S at 0.2X. Four of the 25 treatments were amended with sorbents at their original particle sizes (intact, exposure time 120 d): nontreated Soil A and Soil A amended with TOG LF, DARCO, and AquaPAC S at 0.2X. Three of the 25 treatments were amended with ground Coconut AC, CS Biochar, and P Biochar at 0.2X (exposure time 24 d).

Bioaccumulation in Earthworms. Nine treatment groups (four replicates per treatment) were included: Soil A amended with three sorbents (AquaPAC S, Coconut AC, and CS Biochar at their original particle sizes) at two dose levels (0.2X and 0.5X) plus three control groups (nontreated Soil A, an artificial soil as the lab control, and culture substrate sphagnum peat moss as a background control). The artificial soil (AS) was prepared by combining 10% (dry wt) sphagnum peat, 20% kaolin clay, and 70% quartz sand.[20] Dry constituents of the AS were mixed thoroughly and was moistened with deionized water 48 h prior to test initiation, adjusted to a pH of 7 (±0.5). The water holding capacities for AS and Soil A were 55% and 66%. The pH of Soil A was 7.6, and the pH change after sorbent amendment was negligible.

Bioaccumulation of PCDD/Fs in earthworms, *Eisenia fetida*, was conducted following the method outlined by Fagervold and co-workers[7] with the following modification. Soil (300 g dry wt) was added to each test vessel (600-mL glass beaker) 24 h

Table 1. Effectiveness of Different Sorbents in Reducing PCDD/F Levels in POM Samplers Exposed to Soil Slurries

soil treatment[a]		total PCDD/Fs		TM17[b]		TEQ[c]	
sorbent name (particle size, specific surface area)	exposure time, d	avg ± Stdev, ng/kg	reduction, %	avg ± Stdev, ng/kg	reduction, %	avg ± Stdev, ng/kg	reduction, %
Soil A							
nontreated	24	4530 ± 1130	-	1230 ± 280	-	85.8 ± 25.9	-
CS Biochar (87% < 250 μm, 67.2 m^2/g)	24	2160 ± 141	52.3	770 ± 19	37.5	32.6 ± 7.8	62.0
P Biochar (83% < 250 μm, 102 m^2/g)	24	2720 ± 320	40.0	891 ± 92	27.7	35.3 ± 2.2	58.9
Coconut AC (75−300 μm, 1320 m^2/g)	24	2610 ± 864	42.4	918 ± 244	25.5	44.4 ± 15.1	48.2
TOG NDS (45−180 μm, 1170 m^2/g)	24	1510 ± 211	66.6	660 ± 95	46.4	18.0 ± 4.7	79.0
TOG LF (45−180 μm, 1220 m^2/g)	24	1520 ± 410	66.4	736 ± 240	40.3	17.8 ± 13.5	79.3
DARCO (45−180 μm, 968 m^2/g)	24	821 ± 170	81.9	453 ± 110	63.2	2.13 ± 0.96	97.5
AquaPAC S (70% <45 μm, 1150 m^2/g)	24	423 ± 68	90.7	248 ± 51	79.9	0.70 ± 0.17	99.2
nontreated	120	19500 ± 2820	-	6090 ± 987	-	473 ± 83	-
TOG LF (45−180 μm, 1220 m^2/g)	120	6080 ± 1210	68.9	3040 ± 771	50.1	85.0 ± 8.3	82.0
DARCO (45−180 μm, 968 m^2/g)	120	2050 ± 229	89.5	1120 ± 112	81.6	18.6 ± 9.2	96.1
AquaPAC S (70% <45 μm, 1150 m^2/g)	120	1560 ± 80	92.0	870 ± 59	85.7	9.08 ± 3.10	98.1
Soil B							
nontreated	24	2610 ± 360	-	973 ± 163	-	36.2 ± 7.2	-
TOG LF (45−180 μm, 1220 m^2/g)	24	1080 ± 122	58.7	473 ± 63	51.4	5.57 ± 3.06	84.6
DARCO (45−180 μm, 968 m^2/g)	24	584 ± 213	77.6	342 ± 123	64.8	0.81 ± 0.30	97.8
AquaPAC S (70% <45 μm, 1150 m^2/g)	24	557 ± 150	78.6	356 ± 99	63.4	0.81 ± 0.09	97.8

[a]Sorbents were dosed at 0.2 × total organic carbon of each soil. [b]TM17: total concentration of the 17 2,3,7,8-substituted dioxins and furans. [c]TEQ: Toxic equivalent of the 17 2,3,7,8-substituted dioxins and furans, which was determined according to the toxic equivalent factors recommended by WHO in 2005 (Van den Berg et al., 2006). The concentration of congeners below the limit of detection was treated as zero when the TEQ was calculated.

prior to the addition of earthworms. Soil moisture was maintained at 40−60% of the water holding capacity. Six adult worms with similar weight (250−600 mg each) were added into each vessel. Test vessels were held in an environmental chamber maintained at 20 ± 2 °C with a 16/8 h light/dark cycle photoperiod (400−800 lx). Dried, ground cow manure (2.1 g/vessel) was added as a food source initially and weekly afterward. At the end of the 28 d exposure, the earthworms were removed from soil and depurated on wet tissue paper for 24 h. Worms were then rinsed, dried by blotting, weighed, freeze-dried, and analyzed for PCDD/Fs and lipid contents. The lipid content of worms were determined according to procedures described elsewhere,[7] and a Jenway 6405 UV/vis spectrophotometer (Bibby Scientific Limited, Stone, Staffordshire, UK) at wavelength of 490 nm was used. The biota-soil accumulation factors (BSAFs) of individual PCDD/F congeners were calculated as described by Fagervold et al.[7] The concentrations of PCDD/Fs and lipids in worms were based upon replicate samples (n = 4) for each treatment, while the concentrations of PCDD/Fs in soil were based upon replicate samples (n = 4) for the whole batch of soil used for the earthworm bioaccumulation study. The TOC of the nontreated soil was used for all BSAF calculation.

PCDD/Fs Analysis. The 17 2,3,7,8-substituted tetra- to octa- PCDD/F congeners and total tetra- to octa- homologues in soil, POM, and earthworm samples were determined following procedures described previously.[7] Sample extraction and purification were based on U.S. Environmental Protection Agency method 1613B.[21] The PCDD/Fs were quantified using high resolution gas chromatography/high resolution mass spectroscopy. The 17 2,3,7,8-substituted tetra- to octa-PCDD/Fs are considered to be toxic, and their relative potencies with respect to 2,3,7,8-TCDD are estimated using the toxic equivalent factor (TEF). The toxic equivalent (TEQ) of individual congener is the concentration of the congener multiplied by its TEF recommended by the World Health Organization.[22] In this paper, tetra-, penta-, hexa-, hepta-, and octa-chlorinated dibenzo-*p*-dioxins/dibenzofurans are denoted as TCDD/F, PeCDD/F, HxCDD/F, HpCDD/F, and OCDD/F. The concentrations of congeners below the limit of detection were treated as zero when TEQ was calculated.

RESULTS AND DISCUSSION

Soil Characteristics and PCDD/Fs in Soils. The two composite soils evaluated in this study varied by both soil textures and PCDD/F profiles. Soil A was a loamy sand (sand 91%, silt 8%, and clay 1%) with an TOC of 3.71%, while Soil B was a loam (sand 67%, silt 25%, and clay 8%) with an TOC of 1.91%. The total concentrations of tetra- to octa-PCDD/Fs (Total PCDD/Fs) in the Soils A and B used for POM passive sampler exposure study were 55.4 ± 3.7 and 25.0 ± 1.0 μg/kg, the total of the 17 2,3,7,8-substituted tetra- to octa-PCDD/F congeners (TM17) were 44.9 ± 3.1 and 21.2 ± 0.8 μg/kg, and the total TEQs were 394 ± 19 and 132 ± 4 ng/kg, respectively. The concentration of each homologue group of PCDD/Fs in these two soils is presented in Supporting Information (SI) Figure S1. In terms of total homologue patterns, both Soils A and B were primarily impacted by OCDD. The PCDD/Fs in these soils are believed to be associated primarily with historical emissions from industrial waste incinerators according to their congener and total homologue patterns.[23,24] However, these two soils exhibited somewhat different TEQ congener profiles. The TEQ for Soil A comprised primarily 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD representing 61% of the total TEQ. In contrast, the contribution of TEQ for Soil B was somewhat evenly distributed across the 17 congeners.

Effect of AC/Biochar on POM Passive Uptake. The passive uptake of PCDD/F in POM from the two soils with various sorbents at dose level of 0.2X (0.2 × TOC of soil) is summarized in Table 1. The total homologue, TM17, and TEQ

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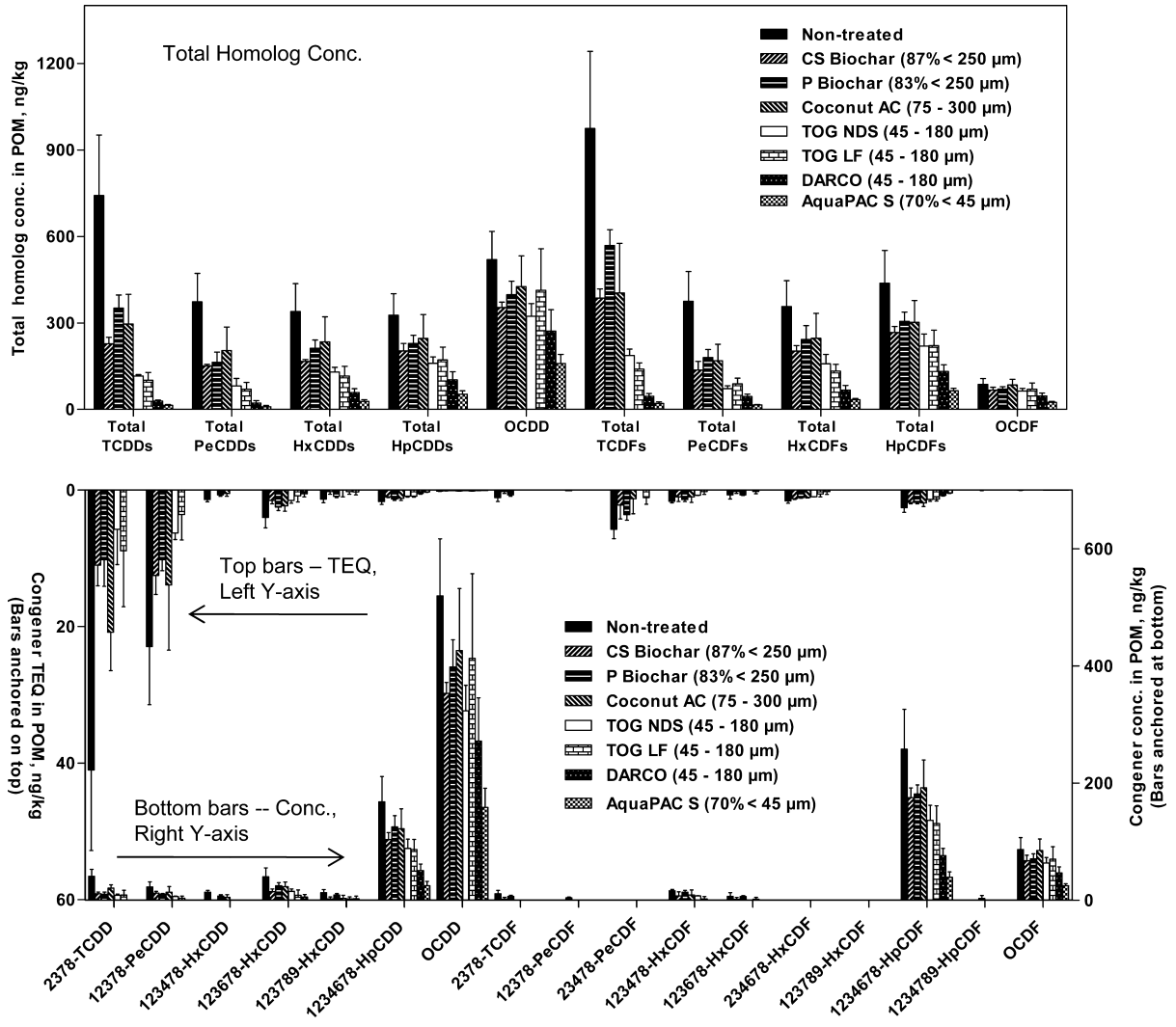

Figure 1. PCDD/F profiles in POM samplers exposed for 24 d to Soil A amended with activated carbon and biochar (dose level: 0.2 × soil total organic carbon).

congener profile of PCDD/Fs in POM passive sampler exposed for 24 d to Soil A treated with seven sorbents are shown in Figure 1. The Total PCDD/Fs, TM 17, and TEQ for the POMs exposed to untreated Soil A for 24 d were 4530, 1230, and 85.8 ng/kg, respectively. The PCDD/F homologue pattern in POMs exposed to unamended Soil A was noticeably different from that in the soil. The lower chlorinated congeners (tetra- to hexa-CDD/Fs) were enriched, while the highly chlorinated counterparts (OCDD/F) were less abundant in the POMs compared to the soil. This difference in profiles is due to the relatively higher aqueous solubility and smaller molecular size of the lower chlorinated congeners resulting in faster mass transfer of these compounds from soil to the POMs.

The addition of either AC or biochar to soil at 0.2X reduced the passive uptake of PCDD/Fs in POMs (Table 1). The Total PCDD/Fs in the POMs exposed to Soil A for 24 d ranged from 2720 to 423 ng/kg, with reduction efficiencies varying from approximately 40% to 91%. The TM17s and TEQs were decreased correspondingly, with reduction efficiencies ranging from 25.5% to 79.9% (918 to 248 ng/kg) and 48.2% to 99.2% (44.4 to 0.7 ng/kg), respectively. Among the seven sorbents, the AquaPAC S reactivated carbon was the most effective (99.2% TEQ reduction) and the Coconut AC was the least effective (48.2% TEQ reduction). The two biochars performed slightly better than the Coconut AC (62.0% and 58.9% TEQ reduction for CS Biochar and P Biochar). In general, the lower chlorinated congeners demonstrated higher reduction efficiencies for PCDD/F passive uptake by POM. The difference can be attributed to higher aqueous solubility and faster mass transfer (among soil, sorbent, and POM) for lower chlorinated congeners. Similar congener effect has also been observed for studies with PCBs in sediments[11,12,16] and PCDD/Fs in soils.[7] The higher chlorinated congeners such as HpCDD/Fs and OCDD/F have much lower TEF values and contributed only a small fraction to the total TEQ for both soils. Therefore, the reduction efficiency of the AC or biochar in terms of TEQ was much higher than those in terms of Total PCDD/Fs or TM17. The addition of AC into Soil B resulted in similar trends in reducing the passive uptake of PCDD/F into POMs (Table 1). The total homologue, TM17, and TEQ congener profile of PCDD/Fs in POMs exposed to Soil B treated with TOG LF, DARCO, and AquaPAC S are shown in Figure S2. These observations are consistent with previous findings by Fagervold et al.[7] where they reported the addition of AC to soils collected from the floodplain of the Tittabawassee River resulted in similar reduction in the passive uptake of the PCDD/Fs.

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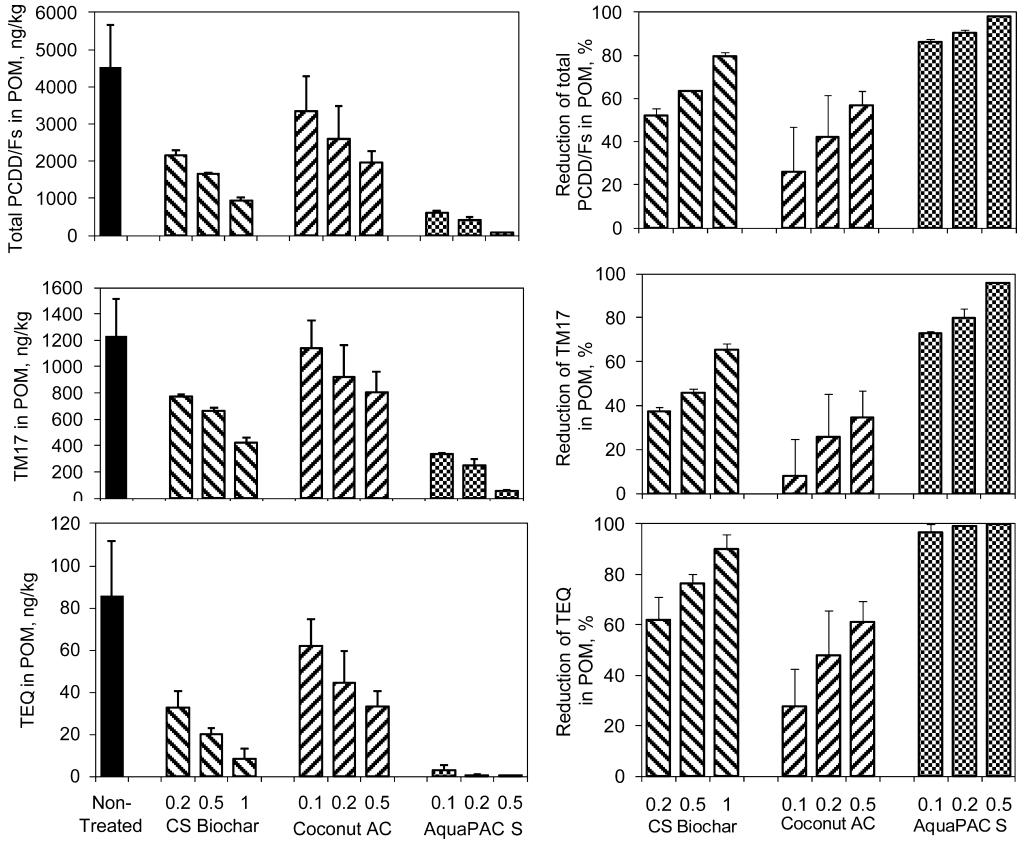

Figure 2. Activated carbon and biochar dose responses in reducing PCDD/Fs in POM samplers exposed to Soil A for 24 d (numbers on the *X*-axis showing dose levels of 0.1−1 × soil total organic carbon; particle sizes of CS Biochar, Coconut AC, and AquaPAC S are 87% < 250 μm, 75−300 μm, and 70% < 45 μm, respectively).

Effect of Soil/POM Contact Time on PCDD/F Passive Uptake. Increasing the soil/POM contact time from 24 to 120 d with unamended soil or soil treated with AC (TOG LF, DARCO, AquaPAC S) resulted in a 2.5 to 5.5 fold increase in the uptake of PCDD/Fs in the POMs (Table 1 and Figure S3). This increase of uptake by POM with time might result from the slow kinetics of both PCDD/F release from soil and POM uptake from aqueous phase. While the total mass of PCDD/Fs in the POMs increased with extended contact time, the congener profiles remained similar (Figures 1 and S4), and the reduction efficiencies of AC treatments remained unchanged. Hawthorne and co-workers determined the equilibration time required for POM samplers with the same thickness (76 μm) to measure polychlorinated biphenyl (PCB) aqueous concentrations in sediment slurries.[25] They found that the lower-molecular weight congeners approach equilibrium with POM samplers in 14 d or less, while the octachloro-congeners require 42 d. Considering that PCDD/Fs and PCBs are similar in molecular size and other properties, the contact time of 120 d in this study may represent near true equilibrium condition.

AC/Biochar Dose Response on PCDD/F Passive Uptake. Three sorbents (AquaPAC S, Coconut AC, and CS Biochar) were amended to Soil A at a range between 0.1X and 1X (i.e., 0.1−1 × TOC of soil). The uptake of PCDD/Fs into the POMs after soil/POM contact time of 24 d is summarized in Figures 2 (overall reduction) and S5 (total homologues profile). The AquaPAC S was highly effective in reducing the PCDD/F passive uptake even at a low dose of 0.1X with corresponding reduction efficiencies for Total PCDD/Fs, TM17, and TEQ of 86%, 73%, and 97%, respectively. Higher sorbent doses typically exhibited greater reduction in the passive uptake of PCDD/Fs in POM samplers from soil. However, the reduction was not directly proportional to the sorbent dose. In contrast, Tomaszewski and co-workers reported that doubling the AC dose nearly doubled the reduction effectiveness of DDT uptake in semipermeable membrane devices from field contaminated sediment.[26] Other theoretical analysis suggests that the concentration ratio between treated and untreated ($C_{treated}/C_{untreated}$) is inversely proportional to sorbent dose.[27,28] However, this relationship was not observed in the present study either. In the present study the lack of a proportional reduction in uptake with increased AC dose could be attributed to a combination of factors including the relatively high reduction efficiency at the lowest dose level tested, strong binding of the residual compounds, and lower overall concentration of contaminants in the soil.

Effect of Particle/Pore Size of Sorbents on POM Passive Uptake. All AC and biochar amendments in this study were effective in reducing the uptake of PCDD/F in POM, with reduction efficiencies trending from highest to lowest: AquaPAC S > DARCO > TOG LF = TOG NDS > CS Biochar = P Biochar > Coconut AC. Two major parameters, particle size and pore size, are critical for an AC (or biochar) to be an effective sorbent. The source material of AC is one of the major factors affecting the pore size of the AC. In general, AC produced from coconut shells exhibit a predominance of micropores, coal based AC have a wider range of transitional pores (mesopores and micropores), and peat or wood derived AC have extensive macropores. Besides source material,

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activation process increases the number of micropores in AC. Micropores contribute to the majority of the specific surface area (SSA) or adsorption sites, whereas macropores and mesopores facilitate the mass transfer of chemicals into AC adsorption sites.[29]

When comparing the effectiveness of various sorbents, both sorption capacity (i.e., SSA, or the abundance of micropores) and the mass transfer kinetics impact the uptake of PCDD/Fs by the POMs. The kinetics element was particularly critical especially for the experiments conducted in a relatively short time scale in this study, i.e., sorbents were introduced into the soil one day prior to the POM/soil slurry contact for 24 d. The intraparticle mass transfer of contaminants in the AC or biochar could be impacted by both particle sizes and pore sizes. Among the AC evaluated in the study, the Coconut AC had the highest SSA (1320 m^2/g) and more micropores. However, this AC also had the largest particle size hence the mass transfer kinetics was slower than for the other sorbents. It appears that the slower mass transfer is the dominant factor impacting the efficacy of the Coconut AC. Therefore, Coconut AC appeared to be the least effective under the experimental condition of the study. In contrast, AquaPAC S had both high SSA (1150 m^2/g) and small particle sizes. The mass transfer in AquaPAC S was much faster than that in Coconut AC. Therefore, AquaPAC S exhibited the highest reduction efficiency. To ascertain whether the particle size of the sorbents plays a major role in determining the effectiveness of the sorbent, Coconut AC, CS Biochar, and P Biochar were ground to a similar particle size distribution as AquaPAC S, i.e., 70% of the mass <45 μm. The grinding process did not increase the SSA of the sorbents, especially for Coconut AC and CS Biochar (Table S1). The uptake of PCDD/Fs in POMs was determined in soil treated with these three ground sorbents. Ground Coconut AC, CS Biochar, and P Biochar all exhibited substantially greater reduction efficiency than the corresponding intact (as received) sorbents (Figure 3). Reducing the particle size of the Coconut AC greatly increased its reduction efficiency (44.4% to 99.5% in terms of TEQ), and the ground Coconut AC appeared to be as effective as AquaPAC S. These results demonstrate that the smaller the particle size of the sorbents, the greater reduction efficiency. Similar particle size effects of sorbents have been observed by other researchers using sediments impacted by PCBs, PAHs, or DDT.[26,30] It is anticipated that at longer contact times slow mass transfer through the large size AC particles would catch up to result in similar effectiveness as the small sized ACs.[27]

Some kinetic effects were also observed with TOG LF, TOG NDS, and DARCO although attributable to differences in pore sizes instead of particle sizes. These ACs had the same nominal particle sizes (45−180 μm) but different pore size distributions. The TOG LF and TOG NDS were made from bituminous coal and contained a wide range of micropores and mesopores. The DARCO originated from lignite coal and contained more macropores compared to the two bituminous coal-based ACs. The TOG LF and TOG NDS exhibited almost identical efficacies, and the only differences between the two were that the latter was acid-washed and contained a small amount of fines. The DARCO exhibited substantially higher reduction efficiency than the two TOG ACs did although DARCO had slightly lower SSA (970 m^2/g compared to 1200 m^2/g) suggesting that the macropores in DARCO facilitated the transport of PCDD/F molecules to the interior surface.

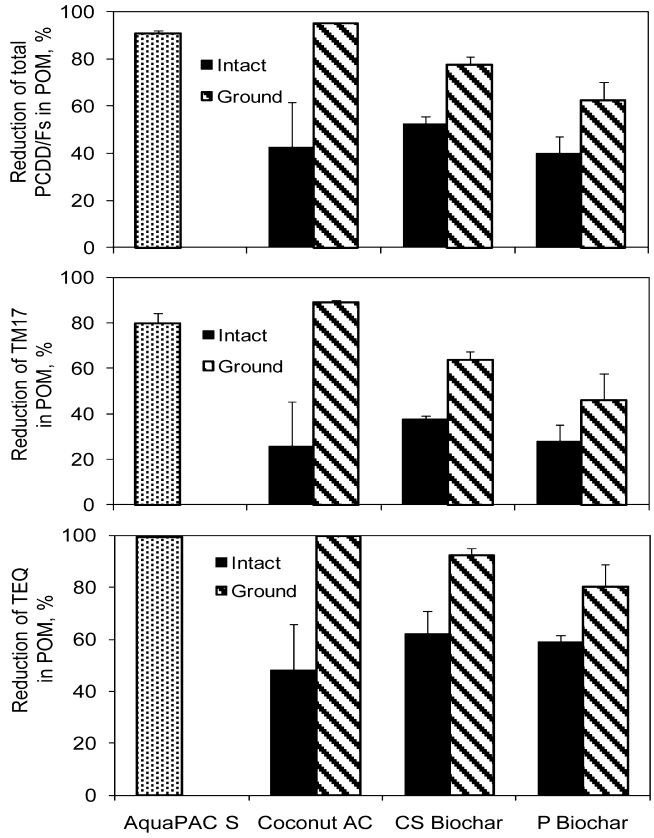

Figure 3. The effect of particle size of activated carbon and biochar in reducing PCDD/Fs in POM samplers exposed to Soil A for 24 d (dose level: 0.2 × soil total organic carbon; particle sizes of intact AquaPAC S, Coconut AC, CS Biochar, and P Biochar were 70% < 45 μm, 75−300 μm, 87% < 250 μm, and 83% < 250 μm, respectively; ground sorbents had particle sizes of 70% < 45 μm).

The two biochars exhibited SSA that was approximately 10-fold lower than those of the ACs. However, these two biochars demonstrated the highest reduction efficiency per unit SSA. These biochars are basically nonactivated carbons derived from corn stover or pine wood. The biochars contained abundant macropores which made the adsorption sites readily available for PCDD/Fs. These results agree with the notion that smaller particle size and more macropores provide a more favorable environment for mass transfer of PCDD/Fs into micropores of AC/biochar.

Effect of AC/Biochar Amendment on Bioaccumulation. The AC and biochar amendment substantially reduced the biouptake of PCDD/Fs by the earthworm, *E. fetida*. The reduction of bioaccumulation was summarized in Table S2 (overall reduction) and Figure S6 (total homologues profile). The Total PCDD/Fs, TM17, and TEQ in the earthworms exposed to untreated Soil A were 3100, 1740, and 38.9 ng/kg, respectively. The AquaPAC S was the most effective in reducing the bioavailability of PCDD/Fs in earthworms with reduction efficiencies of 90% and 88% for Total PCCD/Fs, 89% and 83% for TM17, and 91% and 96% for TEQ at the 0.2X and 0.5X dose levels, respectively. The Coconut AC at 0.5X exhibited a 59% reduction in Total PCCD/Fs with a resulting 48% reduction in TM17 and 80% reduction in TEQ. The reduction efficiencies of CS Biochar at 0.2X were 52% for Total PCCD/Fs, 58% for TM17, and 28% for TEQ. Surprisingly, the amendment of Coconut AC at 0.2X and CS

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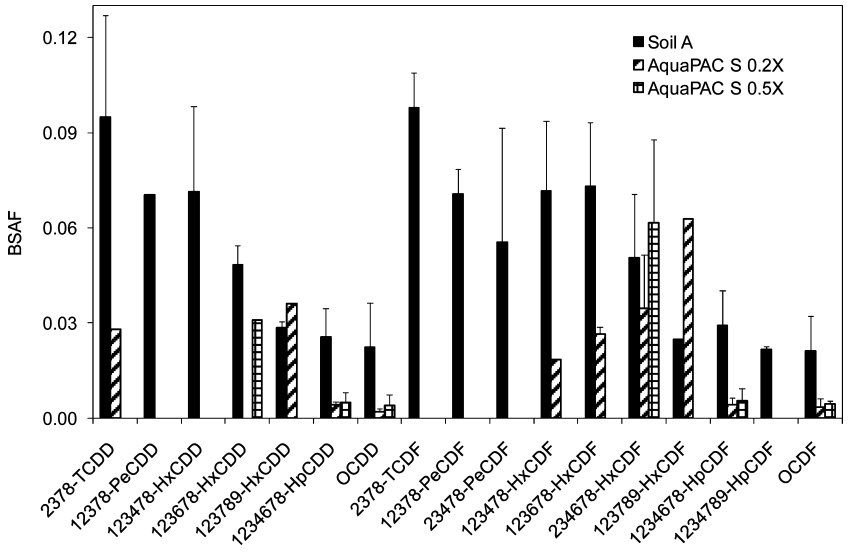

Figure 4. PCDD/F biota-soil accumulation factors (BSAF) in soil A amended with AquaPAC S (particle sizes of AquaPAC S: 70% < 45 μm).

Biochar at 0.5X were not effective in reducing the biouptake of the PCDD/Fs by the earthworms. Rather, these two treatments resulted in even slightly higher tissue concentrations than untreated (Table S2 and Figure S6) for unknown reasons.

The BSAF values of the 17 tetra- to octa-2,3,7,8-chlorinated congeners are shown in Figure 4 for Soil A treated with AquaPAC S at two dose levels. The BSAF values for nontreated Soil A ranged from 0.1 for TCDD/F to 0.02 for OCDD/F, decreasing as the congener size increases. The AquaPAC S reduced the BSAFs to below 0.03 with the exception of two HxCDFs due to their very low concentrations that were close to the analytical detection limits and had higher uncertainties. The concentrations of lower chlorinated congeners such as tetra- and penta-CDD/Fs in earthworm tissue were reduced to below the analytical detection limit; therefore, the BSAFs for these congeners were reduced to near zero. This observation was consistent with the findings of Fagervold et al.[7] using soils from the Tittabawassee River floodplain although the PCDD/Fs originated from different sources. The reduction efficiencies of Coconut AC and CS Biochar were not so substantial, and the dose responses were not consistent. This may result from the larger particle size distribution for these two sorbents which is discussed further below.

Comparison of AC/Biochar Effectiveness Measured by POM and Earthworm. The comparison between the reduction efficiency for PCDD/F passive uptake in POMs and that for biouptake in earthworms are shown in Figure 5. The reduction efficiencies measured by POM passive uptake for AquaPAC S were comparable to those measured by earthworm biouptake at two dose levels (0.2X and 0.5X). However, the reduction efficiencies measured by earthworm biouptake for Coconut AC and CS Biochar were generally less than those measured by POM passive uptake. Passive sampling techniques have been used to successfully predict the bioaccumulation potential of HOCs in soils and sediments.[31−33] Theoretically, uptake in the POMs is an indicator for freely dissolved aqueous concentrations. Although passive uptake from the porewater may not be the only uptake mechanism by earthworms (ingestion being another), the freely dissolved porewater concentration remains a valid indicator for bioaccumulation.[33,34] As a result, the reduction efficiencies in the present study measured by earthworm uptake and by POM passive uptake are expected to be similar (such as for the case of AquaPAC S). This expectation is based on the premise that earthworms ingest both soil and sorbents indiscriminately, and biouptake through ingestion is a major process in determining bioaccumulation of PCDD/Fs. However, earthworms might intentionally avoid ingestion of larger particle size AC or biochar. Therefore, the lower reduction efficiencies measured by earthworm biouptake observed for Coconut AC and CS Biochar may be the result of the larger particle size distribution for these two sorbents used in the study.

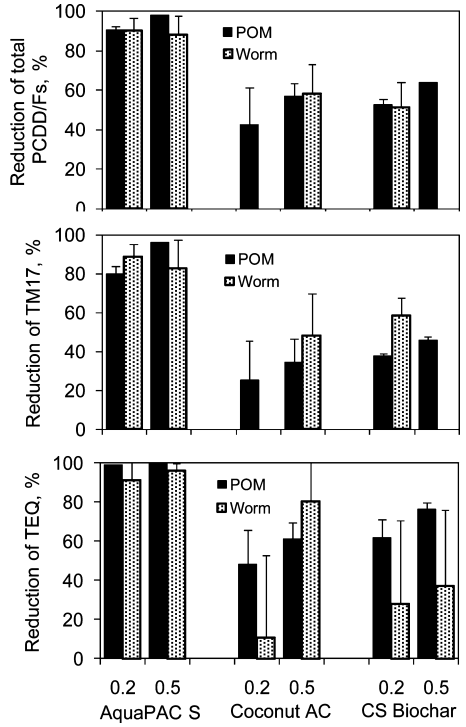

Figure 5. Activated carbon and biochar dose responses in reducing PCDD/Fs in POM samplers and worm tissues exposed to Soil A (numbers on the *X*-axis showing dose levels of 0.2−0.5 × soil total organic carbon; particle sizes of AquaPAC S, Coconut AC, and CS Biochar were 70% < 45 μm, 75−300 μm, and 87% < 250 μm, respectively).

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■ ASSOCIATED CONTENT

Supporting Information

Two tables and six figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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