

ATTACHMENT I

GEOCHEMISTRY PROTOCOL AND RESULTS

***GEO MORPH[®] SITE CHARACTERIZATION
UPPER TITABAWASSEE RIVER***

REPORT

Title:

METHOD DEVELOPMENT FOR DETERMINATION OF THE DISTRIBUTION OF
POLYCHLORINATED DIBENZO-*p*-DIOXIN/DIBENZOFURANS ON SOIL FRACTIONS FROM THE
TITTABAWASSEE RIVER FLOODPLAIN

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ABSTRACT

The objective of this study was to develop a method to size-fractionate Tittabawassee River floodplain soils and to determine the distribution of polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs) in different fractions.. Both fractionation approaches showed enrichment of organic carbon in the fine fractions (5-53 μm and <5 μm). The enrichment of organic carbon in fine fractions (5-53 μm and <5 μm) correlated with an increase in the PCDD/Fs concentrations as quantified by the estimated toxic equivalent (E-TEQ) in these fractions. Either fractionation approach did not indicate the enrichment of black carbon in any fraction.

Particle size distribution analysis using laser diffraction demonstrated that the soil fractions obtained by dry-sieving contain some level of particles outside the size range specified by the sieves. In addition the dry-aerosol cyclone separation did not satisfactorily separate and isolate particles with size of <5 μm . Thus, the fractionation of Tittabawassee River floodplain soil by dry-sieving coupled with dry-aerosol cyclone separation was only partially successful in segregating floodplain soils according to particle sizes. Compared with dry-sieving approach, the wet-sieving approach was successful in this aspect.

Therefore, the fractionation by wet-sieving coupled with sedimentation will be used for future fractionation study for the Tittabawassee River floodplain soils.

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TITLE

METHOD DEVELOPMENT FOR DETERMINATION OF THE DISTRIBUTION OF POLYCHLORINATED DIBENZO-*p*-DIOXIN/DIBENZOFURANS ON SOIL FRACTIONS FROM THE TITTABAWASSEE RIVER FLOODPLAIN

INTRODUCTION

Understanding the fate, transport and bioaccessibility of hydrophobic organochlorines in soils and sediments is an important component of the risk management decision process. Hydrophobic organochlorine compounds such as polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs) are strongly associated with soil or sediment matrices and the environmental fate of these materials is impacted primarily through solids-mediated transport. Therefore, the distribution of these hydrophobic organochlorines in various grain size fractions in soils and sediments may provide insight into both the transport and the bioaccessibility of PCDD/Fs.

The objective of this study is to develop a method which could be used to fractionate Tittabawassee River floodplain soil and sediment samples based on particle size. After fractionation the distribution of PCDD/Fs in the individual fractions (and bulk soil) was determined. The following hypotheses were evaluated in this study: 1) PCDD/Fs are unevenly distributed in the Tittabawassee floodplain soil matrices; 2) Soil properties/ characteristics help explain the distribution of PCDD/Fs levels in Tittabawassee floodplain soil, e.g., higher levels of PCDD/Fs are associated with soil fractions exhibiting higher total organic carbon or black carbon contents.

Two soil samples from the Tittabawassee floodplain were collected from areas previously identified to contain elevated levels of PCDD/Fs. Soil samples were fractionated into different size fractions, e.g., sand, silt and clay. The distribution of PCDD/Fs in each fraction was determined. Floodplain soils and their sub-domains were characterized for total organic carbon/total organic matter, black carbon content, and elemental analysis (carbon/hydrogen/nitrogen elemental ratio, C/H/N). The correlation between the distribution of PCDD/Fs and the organic carbon (e.g. total organic carbon and black carbon) of each fraction was determined.

Two approaches were assessed to realize the fractionation: 1) dry-sieving combined with dry-aerosol cyclone, and 2) wet-sieving combined with sedimentation.

EXPERIMENTAL

Soil Samples

Soil samples were collected from two locations along the Tittabawassee River floodplain, one from West Michigan Park (WMP, refer to map in Figure 1 for sampling location Dow-SHL-02770) and the other from Imerman Park (IP, refer to map in Figure 2 for sampling location Dow-THT-02769). These samples were collected from areas that have previously been identified to contain elevated levels of PCDD/Fs. The sampling locations were agreed upon between Michigan Department of Environmental Quality (MDEQ) and The Dow Chemical Company (TDCC). From each sampling location, soil samples from 0-2 inch below ground surface were taken after the overlying grass had been removed. Soil samples were sealed and transported back to the laboratory and stored at 4°C. Soil samples were sieved through 2 mm sieve after collection to remove large objects such as gravels, leaves and grass roots, sealed and stored at 4°C.

Soil Fractionation

Soil samples were fractionated into different size fractions, i.e., sand, silt and clay. Two separate fractionation approaches were compared: 1) dry-sieving combined with aerosol cyclone based on American Society for Testing and Materials (ASTM) method D421-85 (ASTM, 2003a), and 2) wet-sieving combined with sedimentation based on ASTM method D 422-63 (ASTM, 2003b).

The mass distribution of different fractions and the distribution of PCDD/Fs in each fraction were determined. The correlation between the distribution of PCDD/Fs and the characteristics of each fraction, e.g., total organic carbon content (f_{oc}) and black carbon content (f_{bc}), were determined. The particle size distribution (PSD) of bulk WMP soil and its sub fractions were determined by laser diffraction particle size analyzer to evaluate the efficacy of the two fractionation approaches (i.e. wet vs. dry).

Both the wet and dry fractionation approaches resulted in several different size classes of particles. Scheme A separates the soils into two fractions: $<250 \mu\text{m}$ and $250\text{--}2000 \mu\text{m}$. The objective of this scheme was to obtain further characterization of the fraction of $<250 \mu\text{m}$. Scheme B is based on the U.S. Department of Agriculture (USDA) definition of sand, silt and clay fractions in soil (Marshall and Holmes, 1979). According to USDA, sand, silt and clay particles are differentiated according to their particle sizes in the following way: sand ($50\text{--}2000 \mu\text{m}$), silt ($2\text{--}50 \mu\text{m}$) and clay ($< 2 \mu\text{m}$).

The soils were fractionated into sand ($53\text{--}2000 \mu\text{m}$), silt ($5\text{--}53 \mu\text{m}$) and clay ($< 5 \mu\text{m}$). A standard American Society for Testing and Materials (ASTM) stainless steel sieve with an opening of $53 \mu\text{m}$ was used to separate sand ($> 53 \mu\text{m}$) from silt and clay particles. This specific sieve was used because it represents the only ASTM standard test sieve which is available that generates particles sizes nearest to $50 \mu\text{m}$. The choice of $5 \mu\text{m}$ instead of $2 \mu\text{m}$ as the cut-off size for the differentiation between clay and silt was based on the cut-off size of aerosol cyclone for dry-sieving approach and on the logistic considerations for sedimentation for wet-sieving approach.

Dry sieving Combined with Aerosol Cyclone

The flowchart for the fractionation utilizing dry sieving combined with aerosol cyclone is shown in Figure 3. Soil samples were air-dried and soil aggregates were manually crushed using a mortar and pestle. For fractionation scheme A, an ASTM standard sieve with opening of $250 \mu\text{m}$ was used to separate the soils into two fractions: $<250 \mu\text{m}$ and $250\text{--}2000 \mu\text{m}$. For scheme B, an ASTM standard sieve with opening of $53 \mu\text{m}$ was used to separate the soils into two fractions: $<53 \mu\text{m}$ and $53\text{--}2000 \mu\text{m}$. A micro-feeder (MF-2, Siboto) and a $5 \mu\text{m}$ cut-off stainless steel cyclone were utilized to separate particles with diameters below $53 \mu\text{m}$ into silt ($5\text{--}53 \mu\text{m}$) and clay ($< 5 \mu\text{m}$) fractions. The micro-feeder transfers dry soil sample at an aerosol flow rate of 30 liters per minute and a pressure of 2 psi into the stainless steel cyclone. This separates particles with aerodynamic diameters as low as $5 \mu\text{m}$. Particles with diameters less than $5 \mu\text{m}$ were collected in a Teflon bag from the upper exit of the cyclone. Particles with diameter of 5 to $53 \mu\text{m}$ were collected in a reservoir below the cyclone.

Wet Sieving Combined with Sedimentation

Fractionation of soil samples utilizing sedimentation and wet-sieving is based on the Society of Agronomy standard method (Day, 1965) and ASTM method D 422-63 (ASTM, 2003b). Particles with different diameters will settle in water at different settling velocities. According to Stokes' Law, the settling equation for a spherical particle in water is

$$u = \frac{1}{18} \frac{\rho_p - \rho_l}{\mu} g d^2$$

where u is the settling velocity of the particle, ρ_p and ρ_l are the density of the particle (2.65 g/cm³ for soil) and water (1 g/cm³), respectively, μ is the dynamic viscosity of water, g is the acceleration of gravity, and d is the particle diameter. For a water column with a given height, the time required for a particle with known diameter to settle can be determined from the settling velocity. The flocculation and compression during sedimentation are two factors that hinders the complete separation of soil according to particle diameters. The initial height of a particle in the water column is another factor that hinders the complete separation of particles with different diameters because the traveling time of a particle to the bottom of the water column depends on both its initial height and settling velocity. Therefore, re-suspension and sedimentation will need to be repeated until the yield of fine particles is negligible.

The flowchart for the fractionation utilizing wet sieving combined with sedimentation is shown in Figure 4. For each fractionation scheme, approximately 300 g soil samples placed in a 1-L glass jar and approximately 500 ml MilliQ (Deionized water purified through a Milli-Q water treatment system, Millipore Corporation, Bedford, MA, USA) water was added. The glass jar was sealed and shaken for 24 h on a shaker machine before the soil slurry was subjected to the fractionation procedure.

For fractionation scheme A, the soil slurry in the 1-L glass jar was stirred using a spatula for 30 sec before it was settled for 1 min. This would allow sand and silt particles greater than approximately 40 μ m to settle (10 cm water column). The suspension was siphoned and passed through an ASTM standard sieve with opening of 250 μ m in order to remove remaining organic matter particles in the suspension

with diameters greater than 250 μm . The sieved suspension was collected in a 2-L glass beaker. This material retained on the sieve was placed back into the original 1-liter glass jar containing the remaining soil slurry to be fractionated. Approximately 500 ml MilliQ water was added into the 1-L glass jar and stirred for 30 sec. The above re-suspension and sedimentation steps were repeated for 6 cycles. For the last two cycles, the soil slurry was sonicated for 10 min following the addition of MilliQ water. The yield in the last cycle was negligible. The siphoned suspension was centrifuged at 2000 g for 30 min to recover the fraction $<40 \mu\text{m}$. The fraction $> 40 \mu\text{m}$ left in the glass jar was air-dried, crushed using spatula, and sieved through 250 μm sieve to obtain $>250 \mu\text{m}$ and 40-250 μm fraction. The 40-250 μm fraction was combined with $<40 \mu\text{m}$ fraction to obtain $<250 \mu\text{m}$ fraction.

For scheme B, the soil slurry in the 1-L glass jar was stirred using a spatula for 30 sec before it was settled for 5 min. This would allow sand and silt particles greater than approximately 20 μm to settle (10 cm water column). The suspension containing particles $< 20 \mu\text{m}$ was siphoned and passed through an ASTM standard sieve with opening of 53 μm in order to remove remaining organic matter particles in the suspension with diameters greater than 53 μm . The sieved suspension was collected in a 2-L glass beaker. The material on the sieve was placed back into the original 1-L glass jar containing soil slurry to be fractionated. Approximately 500 ml MilliQ water was added into the 1-L glass jar and stirred for 30 sec. The above re-suspension and sedimentation steps were repeated for 8 cycles. For the last two cycles, the soil slurry was sonicated for 10 min following the addition of MilliQ water. The yield in the last cycle was negligible. The fraction $> 20 \mu\text{m}$ left in the glass jar was air-dried, crushed using spatula, and sieved through 53 μm sieve to obtain $>53 \mu\text{m}$ and 20-53 μm fraction. The siphoned suspension containing the fraction $<20 \mu\text{m}$ was collected in 2-L beakers. The suspension was stirred for 30 sec, and settled for 75 min. This would allow particles greater than 5 μm to settle through a 10 cm water column, the suspension was then siphoned from 2000 ml level to 700 ml level mark (10 cm water column). The siphoned suspension was centrifuged at 2000 g for 30 min to recover $<5 \mu\text{m}$ fraction. The re-suspension-sedimentation-siphon-centrifugation cycle was repeated until the yield is negligible (8 cycles). The 5-20 μm fraction was centrifuged at 2000 g for 30 min to remove excess water and was combined with the 20-53 μm fraction to obtain 5-53 μm fraction.

Analytical Methods

Elemental Analysis (C/H/N) and Total Organic Carbon Content (f_{oc})

A Perkin Elmer 2400 CHN Analyzer was used to determine the weight percentage of carbon, hydrogen and nitrogen (CHN). CHN analysis was conducted by Quantitative Technologies, Inc (QTI, Whitehouse, NJ, USA). All soil samples were acidified with 6N HCl to remove the inorganic carbon in the samples before samples were sent to QTI for CHN analysis. As a result the elemental carbon content from this C/H/N analysis represents the total organic carbon content (f_{oc}) of the sample. The total organic matter content is obtained from the total organic carbon content by multiplying by a factor of 1.724 (Nelson and Sommers, 1982).

Black Carbon Content (f_{bc})

The black carbon content (f_{bc}) in each of the soils and soil fractions was determined using combustion techniques (Gustafsson *et al.*, 1997). Briefly, aliquots of acidified (6N HCL) dry samples were weighed and combusted under air for 24 h at 375°C, so that the labile organic matter was oxidized but the black carbon fraction in the sample was retained. The organic carbon content of the sample after combustion at 375°C (f_{oc}^{375}) was determined following the above procedure. The black carbon content (f_{bc}) was calculated from the total organic carbon content (f_{oc}) in the sample, the organic carbon content of the sample after combustion (f_{oc}^{375}), and the weight loss due to combustion at 375°C. Note that the black carbon content is operationally defined (*i.e.*, intact in air combustion at 375°C for 24 h). Black carbon, which includes soot, coal and coal derived particles, coke etc, has been reported to be ubiquitous in soil or sediment (Gustafsson *et al.*, 1997; Ghosh *et al.*, 2001; Cornelissen and Gustafsson, 2005). Different terms are used to denote this black carbon such as hard carbon, condensed phase organic carbon, carbonaceous geosorbents.

Particle Size Distribution Analysis

The particle size distribution (PSD) analysis for the West Michigan Park (WMP) soil and its fractions was analyzed by a Beckman Coulter LS13 320 laser diffraction particle size analyzer. This analysis was conducted by Particle Technology Labs (PTL, Downers Grove, IL, USA).

PCDD/Fs in Solid Samples

All PCDD/Fs analysis was conducted by the Trace Laboratory in the Environmental Analytical Chemistry Laboratory at The Dow Chemical Company (Dow, Midland, MI, USA). The toxic equivalency factors (TEFs) values for dioxins and furans used to calculate toxic equivalent (TEQ) were according to values published by World Health Organization (WHO) (i.e., WHO-TEQs).

The PCDD/Fs pre-screening analysis for the two bulk soils followed a modified U.S. Environmental Protection Agency (U.S. EPA 1613b) procedure. The results were quantified using WHO-TEQs. The fast analysis method (1613 RT/TRP) was used to determine the estimated toxic equivalents (E-TEQs) for all soil samples in this study. The fast analysis method (1613 RT/TRP) determines the concentration of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4(6),7,8-HxCDF (the two hexachlorodibenzofurans co-elute in the fast method), E-TEQs were obtained based on historical PCDD/Fs congener patterns in Tittabawassee River floodplain soil/sediments according to the following way: $E\text{-TEQ} = 1.1 \times \Sigma (\text{TEQ of the above congeners})$. The fast analysis method significantly reduced the turnaround time without adverse impact on the data quality.

RESULTS AND DISCUSSION

Dry-sieving combined with dry-aerosol cyclone

Soil mass distribution and PCDD/Fs distribution in different size fractions

The soil mass distribution and PCDD/Fs measured by estimated toxic equivalent (E-TEQ) in fractionated West Michigan Park (WMP) soil are presented in Table 1. For fractionation scheme A, WMP<250 μm fraction contained 86% of the soil mass and 95% of the E-TEQ. For fractionation scheme B, WMP53-2000 μm fraction contained 88% of the soil mass and 76% of the E-TEQ. WMP5-53 μm and WMP<5 μm two fractions together contained ~12% of the soil mass and ~30% of the E-TEQ. The mass balances for soil mass were both 100% for the two fractionation schemes. The mass balances for E-TEQ were 106% for both fractionation schemes.

The soil mass distribution and PCDD/Fs measured by estimated toxic equivalent (E-TEQ) in fractionated Imerman Park (IP) soil are presented in Table 2.

For fractionation scheme A, IP<250 μm fraction contained 93% of the soil mass and approximately 49% of the E-TEQ. For fractionation scheme B, IP53-2000 μm fraction contained ~83% of the soil mass and approximately 42% of the E-TEQ. IP5-53 μm and IP<5 μm two fractions together contained approximately 17% of the soil mass and approximately 16% of the E-TEQ. The mass balances for soil mass were both 100% for the two fractionation schemes. The mass balances for E-TEQ were only approximately 56% and 57% for fractionation schemes A and B, respectively. The results from the two fractionation schemes suggested that the majority of the soil mass and PCDD/Fs were associated with the 53-250 μm .

The low mass balance on PCDD/Fs E-TEQ for IP soil and its fractions was due to the heterogeneity of the soil although the soil was thoroughly homogenized before fractionation. The E-TEQ for WMP soil was 3150 ng/kg (Analyzed in Aug. 2006). This was in good agreement with preliminary analysis of WHO-TEQ of 3007 ng/kg. The E-TEQ for IP soil was 4400 ng/kg (Analyzed in Aug. 2006). This was, however, much higher than the preliminary analysis of WHO-TEQ of 1559 ng/kg. Thus, three more replicates of IP soil were analyzed in Oct. 2006 for E-TEQ. The E-TEQs were 3850, 1580, 1840 ng/kg. Thus the average of the four measurements, 2918 ng/kg, was used in this report. The relative large variation was due to the soil heterogeneity.

Particle Size Distribution of Bulk and Dry-sieved Soil

Particle size distribution results for West Michigan Park (WMP) soil and its dry sieved fractions are shown in Figure 5. Figure 5A shows the soil volume (mass) abundance at each size interval for WMP bulk soil and WMP 250-2000 μm , <250 μm fractions. Dry-sieving of the soil did not completely segregate particles based on size. For example, the results from the particle size distribution analysis for the WMP 250- 2000 μm soil fraction showed that approximately 40% of the mass is less than 250 μm while for the WMP<250 μm fraction approximately 10% of its mass is greater than 250 μm . Figure 5B shows the soil volume (mass) abundance at each size interval for WMP bulk soil and WMP 53-2000 μm , WMP5-53 μm and WMP<5 μm fractions. For fraction WMP53-2000 μm , approximately 32% of its mass is less than 53 μm . For fraction WMP 5-53 μm , approximately 11% of its mass is less than 5 μm and 11% greater than 53 μm . For fraction WMP <5 μm , approximately 83% of its mass is greater than 5 μm .

It is important to note that dry-sieving was utilized to generate soil fractions WMP 250-2000 μm and WMP <250 μm (scheme A) and WMP 53-2000 μm and WMP <53 μm (scheme B). Before dry-sieving, soil samples were manually crushed using mortar and pestle to break soil aggregates. The particle distribution results suggested that this crushing process was not an efficient approach for size-fractionating soil. First of all, it could not completely break soil aggregates, secondly, it likely generated more fine particles. The effectiveness of dry-aerosol cyclone to separate soil fraction WMP <53 μm into WMP5-53 μm and WMP<5 μm fractions is also questionable. The particle size distribution of these two fractions (WMP5-53 μm and WMP<5 μm) suggested that the two fractions showed almost identical particle size distribution.

Dry-sieving coupled with dry-aerosol cyclone treatment was partially successful in segregating soil particles based upon size. However, the wet-sieving/sedimentation methods (below) proved to yield soil sub-fractions with higher percentage of the desired particle size range.

Total Organic Carbon (f_{oc}) and Black Carbon (f_{bc}) Contents of Bulk and Dry Sieved Soil

The total organic carbon content (f_{oc}) and black carbon content (f_{bc}) for the bulk soil and soil fractions are shown in Table 3. The total organic matter content can be obtained from the total organic carbon content by multiplying by a factor of 1.724 (Nelson and Sommers, 1982). However, organic carbon content was used in the discussion below because organic matter content is not an accurately measurable entity (Nelson and Sommers, 1982).

The organic carbon contents for bulk WMP and IP soil were 2.50% and 2.37%, respectively. For both soils, the organic carbon contents for 5-53 μm fraction and <5 μm fraction were significantly higher (approximately two-fold) than the corresponding bulk soil. The organic carbon contents for other fractions were generally very close to those of the corresponding bulk soils. The black carbon contents for soil fractions were generally close to those for bulk soils. There was no strong evidence suggesting the enrichment of black carbon in certain fractions. The correlation between PCDD/Fs concentration as measured by E-TEQs and organic

carbon contents in bulk soil and dry sieved soil fractions are shown in Figure 6. There was a strong linear correlation between the E-TEQs and organic carbon contents in bulk WMP soil and fractions generated from WMP soil, with correlation coefficient r^2 of 0.98. This correlation was not so strong for the bulk IP soil and fractions generated from IP soil, which gives r^2 of 0.31.

These results confirmed that the majority of PCDD/Fs in Tittabawassee river floodplain soils were associated with soil organic fractions, which is consistent with literature reports about the association behavior of highly hydrophobic organic contaminants in soil or sediment in the environment. Elevated E-TEQ in fine fractions (5-53 μm and <5 μm) correlated well with high organic carbon contents in these fractions.

Wet-sieving combined with sedimentation

Soil mass distribution and PCDD/Fs distribution in different size fractions

The soil mass distribution and PCDD/Fs measured by estimated toxic equivalent (E-TEQ) in fractionated West Michigan Park (WMP) soil by wet-sieving combined with sedimentation are presented in Table 4. For fractionation scheme A, WMP<250 μm fraction contained ~86% of the soil mass and ~121% of the E-TEQ. For fractionation scheme B, WMP53-2000 μm fraction contained ~72% of the soil mass and ~26% of the E-TEQ. WMP5-53 μm and WMP<5 μm two fractions together contained ~25% of the soil mass and ~75% of the E-TEQ representing an ~ three-fold enrichment of the E-TEQ in this fraction. The mass balances for soil mass were ~ 98% and ~97% for the fractionation scheme A and B, respectively. The mass balances for E-TEQ were 149% and 101% for fractionation scheme A and B, respectively.

The soil mass distribution and PCDD/Fs measured by estimated toxic equivalent (E-TEQ) in fractionated Imerman Park (IP) soil by wet-sieving combined with sedimentation are presented in Table 5. For fractionation scheme A, IP<250 μm fraction contained 94% of the soil mass and approximately 66% of the E-TEQ. For fractionation scheme B, IP53-2000 μm fraction contained ~64% of the soil mass and approximately 60% of the E-TEQ. IP5-53 μm and IP<5 μm two fractions together contained approximately 33% of the soil mass and approximately 39% of the E-TEQ

representing only a slight enrichment of the E-TEQ in this fraction. The mass balances for soil mass were 101% and 98% for fractionation scheme A and B, respectively. The mass balances for E-TEQ were approximately 68% and 99% for fractionation scheme A and B, respectively. The distribution of the PCDD/Fs appeared different in the two soil samples (IP and WMP) using the wet sieve/sedimentation fractionation scheme. For the IP soil the majority of the soil mass and PCDD/Fs were associated with the 53-250 μm . In contrast, for the WMP soil the majority of the soil mass was in the >53 μm fraction while most (~75%) of the PCDD/Fs were associate with the < 53 μm soil particles.

Particle Size Distribution

Particle size distribution results for West Michigan Park (WMP) soil and its fractions by wet-sieving combined with sedimentation are shown in Figure 7. Figure 7A shows the soil volume (mass) abundance at each size interval for WMP bulk soil and WMP 250-2000 μm , <250 μm fractions. Figure 7B shows the soil volume (mass) abundance at each size interval for WMP bulk soil and WMP 53-2000 μm , WMP5-53 μm and WMP <5 μm fractions. Compared with dry-sieving approach, the wet-sieving approach was more successful in segregating particles based on size.

Total organic carbon (f_{oc}) and black carbon (f_{bc}) contents

The total organic carbon content (f_{oc}) and black carbon content (f_{bc}) for the bulk soil and soil fractions are shown in Table 6. The organic carbon contents for bulk WMP and IP soil were 2.50% and 2.37%, respectively. For both soils, the organic carbon contents for 5-53 μm fraction and <5 μm fraction were significantly higher than the corresponding bulk soil. The organic carbon contents for 53-2000 μm fractions and <250 μm fractions were generally lower than those of the corresponding bulk soils. The correlation between PCDD/Fs concentration as measured by E-TEQs and organic carbon contents in bulk soil and soil fractions are shown in Figure 8. There was a strong linear correlation between the E-TEQs and organic carbon contents in bulk WMP soil and fractions generated from WMP soil, with correlation coefficient r^2 of 0.83. This correlation was not so strong for the IP soil, which may have been due to the heterogeneity of IP soil. Similar to dry-sieving approach, there was no strong evidence suggesting the enrichment of black carbon in specific soil fractions.

These results confirmed that the majority of PCDD/Fs in Tittabawassee river floodplain soils were associated with soil organic fractions, which is consistent with literature reports about the association behavior of highly hydrophobic organic contaminants in soil or sediment in the environment. Elevated E-TEQ in fine fractions (5-53 μm and $<5 \mu\text{m}$) correlated well with high organic carbon contents in these fractions.

CONCLUSIONS

The objective of this study was to develop a method to size-fractionate Tittabawassee River floodplain soils and to determine the distribution of polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs) in different fractions. Both fractionation approaches showed enrichment of organic carbon in the fine fractions (5-53 μm and $<5 \mu\text{m}$). The enrichment of organic carbon in fine fractions (5-53 μm and $<5 \mu\text{m}$) correlated with an increase in the PCDD/Fs concentrations as quantified by the estimated toxic equivalent (E-TEQ) in these fractions. Either fractionation approach did not indicate the enrichment of black carbon in any fraction.

Particle size distribution analysis using laser diffraction demonstrated that the soil fractions obtained by dry-sieving, as compared to the wet sieving/sedimentation, contain greater percentage of particles outside the size range specified by the sieves. In addition the dry-aerosol cyclone separation did not satisfactorily separate and isolate particles with size of $<5 \mu\text{m}$. Thus, the fractionation of Tittabawassee River floodplain soil by dry-sieving coupled with dry-aerosol cyclone separation was only partially successful in segregating floodplain soils according to particle sizes. Compared with dry-sieving approach, the wet-sieving approach was more successful in this aspect.

Therefore, the fractionation by wet-sieving coupled with sedimentation will be used for future fractionation study for the Tittabawassee River floodplain soils.

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Table 1 Soil mass and PCDD/Fs distribution in West Michigan Park soil by dry-sieving combined with aerosol cyclone

Fractionation Scheme	Fraction	Soil Mass (% of Total)	PCDD/Fs	
			E-TEQ ^a , ng/kg	% of Total ^b
A	250 – 2000 μm	14.4%	2440	11.1%
	< 250 μm	85.7%	3500	95.3%
	<i>Total mass balance</i>	100%	-	106%
B	53 – 2000 μm	87.5%	2720	75.6%
	5 – 53 μm	8.6%	7330	20.1%
	< 5 μm	3.5%	8840	9.8%
	<i>Total mass balance</i>	99.7%	-	106%

^a: Estimated toxic equivalent (E-TEQ) was obtained based on historical PCDD/Fs congener patterns in Tittabawassee River floodplain soil/sediments according to the following empirical formula: E-TEQ = 1.1 × Σ (TEQ of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and the co-elutes of 1,2,3,4(6),7,8-HxCDF).

^b: E-TEQ for bulk West Michigan Park soil was 3150 ng/kg.

Table 2 Soil mass and PCDD/Fs distribution in Imerman Park soil by dry-sieving combined with aerosol cyclone

Fractionation Scheme	Fraction	Soil Mass (% of Total)	PCDD/Fs	
			E-TEQ ^a , ng/kg	% of Total ^b
A	250 – 2000 μm	6.9%	3010	7.1%
	< 250 μm	93.2%	1530	48.9%
	<i>Total mass balance</i>	100%	-	56.0%
B	53 – 2000 μm	82.8%	1460	41.5%
	5 – 53 μm	11.5%	2600	10.3%
	< 5 μm	5.4%	2870	5.3%
	<i>Total mass balance</i>	99.7%	-	57.0%

^a: Estimated toxic equivalent (E-TEQ) was obtained based on historical PCDD/Fs congener patterns in Tittabawassee River floodplain soil/sediments according to the following empirical formula: E-TEQ = 1.1 × Σ (TEQ of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and the co-elutes of 1,2,3,4(6),7,8-HxCDF).

^b: Based on average E-TEQ for bulk Imerman Park soil of four measurements: 4400 (analyzed in Aug., 2006, the next three measurements were analyzed in Oct. 2006), 3850, 1580 and 1840 ng/kg, respectively.

Table 3 PCDD/Fs concentration and organic carbon and black carbon content in bulk and fractionated West Michigan Park and Imerman Park soils by dry-sieving combined with aerosol cyclone

Soil ID	E-TEQ ng/kg	OC Normalized E-TEQ ng/kg	Organic Carbon (OC) %	Black Carbon (BC) %	BC/OC %
WMP	3150	125820	2.50	0.39	15.5
WMP250-2000µm	2440	142985	1.71	0.31	17.9
WMP<250 µm	3500	136315	2.57	0.38	14.7
WMP53-2000 µm	2720	123654	2.20	0.36	16.6
WMP5-53 µm	7330	141235	5.19	0.74	14.3
WMP<5 µm	8840	157827	5.60	0.78	13.9
IP	2918	122904	2.37	0.31	13.1
IP250-2000 µm	3010	107290	2.81	0.50	18.0
IP<250 µm	1530	67341	2.27	0.32	14.2
IP53-2000 µm	1460	68177	2.14	0.25	11.6
IP5-53 µm	2600	67987	3.82	0.49	12.9
IP<5 µm	2870	68641	4.18	0.42	9.9

WMP: West Michigan Park soil; IP: Imerman Park soil; E-TEQ: Estimated toxic equivalent; OC: Organic carbon; BC: Black carbon

Table 4 Soil mass and PCDD/Fs distribution in West Michigan Park soil by wet-sieving combined with sedimentation

Fractionation Scheme	Fraction	Soil Mass (% of Total)	PCDD/Fs	
			E-TEQ ^a , ng/kg	% of Total ^b
A	250 – 2000 µm	11.7%	7530	27.9%
	< 250 µm	86.1%	4420	121%
	<i>Total mass balance</i>	97.8%	-	149%
B	53 – 2000 µm	72.1%	1150	26.3%
	5 – 53 µm	18.6%	7650	45.1%
	< 5 µm	6.4%	14600	29.7%
	<i>Total mass balance</i>	97.1%	-	101%

^a: Estimated toxic equivalent (E-TEQ) was obtained based on historical PCDD/Fs congener patterns in Tittabawassee River floodplain soil/sediments according to the following empirical formula: E-TEQ = 1.1 × Σ (TEQ of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and the co-elutes of 1,2,3,4(6),7,8-HxCDF).

^b: E-TEQ for bulk West Michigan Park soil was 3150 ng/kg.

Table 5 Soil mass and PCDD/Fs distribution in Imerman Park soil by wet-sieving combined with sedimentation

Fractionation Scheme	Fraction	Soil Mass (% of Total)	PCDD/Fs	
			E-TEQ ^a , ng/kg	% of Total ^b
A	250 – 2000 µm	6.4%	1070	2.3%
	< 250 µm	94.3%	2030	65.6%
	<i>Total mass balance</i>	101%	-	67.9%
B	53 – 2000 µm	64.3%	2720	60.0%
	5 – 53 µm	26.4%	2660	24.0%
	< 5 µm	7.0%	6010	14.5%
	<i>Total mass balance</i>	97.7%	-	98.5%

^a: Estimated toxic equivalent (E-TEQ) was obtained based on historical PCDD/Fs congener patterns in Tittabawassee River floodplain soil/sediments according to the following empirical formula: E-TEQ = 1.1 × Σ (TEQ of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and the co-elutes of 1,2,3,4(6),7,8-HxCDF).

^b: Based on average E-TEQ for bulk Imerman Park soil of four measurements: 4400 (analyzed in Aug., 2006, the next three measurements were analyzed in Oct. 2006), 3850, 1580 and 1840 ng/kg, respectively.

Table 6 PCDD/Fs concentration and organic carbon and black carbon content in bulk and fractionated West Michigan Park and Imerman Park soils by wet-sieving combined with sedimentation

Soil ID	E-TEQ ng/kg	OC Normalized E-TEQ ng/kg	Organic Carbon (OC) %	Black Carbon (BC) %	BC/OC %
WMP	3150	125820	2.50	0.39	15.5
WMP250-2000µm	7530	367317	2.05	0.13	6.5
WMP<250 µm	4420	274534	1.61	0.14	8.6
WMP53-2000 µm	1150	161972	0.71	0.09	12.6
WMP5-53 µm	7650	213687	3.58	0.16	4.5
WMP<5 µm	14600	275472	5.30	0.17	3.2
IP	2918	122904	2.37	0.31	13.1
IP250-2000 µm	1070	34740	3.08	0.16	5.1
IP<250 µm	2030	130968	1.55	<0.08	<5
IP53-2000 µm	2720	256604	1.06	<0.09	<8
IP5-53 µm	2660	93662	2.84	0.12	4.3
IP<5 µm	6010	124948	4.81	0.17	3.6

WMP: West Michigan Park soil; IP: Imerman Park soil; E-TEQ: Estimated toxic equivalent; OC: Organic carbon; BC: Black carbon

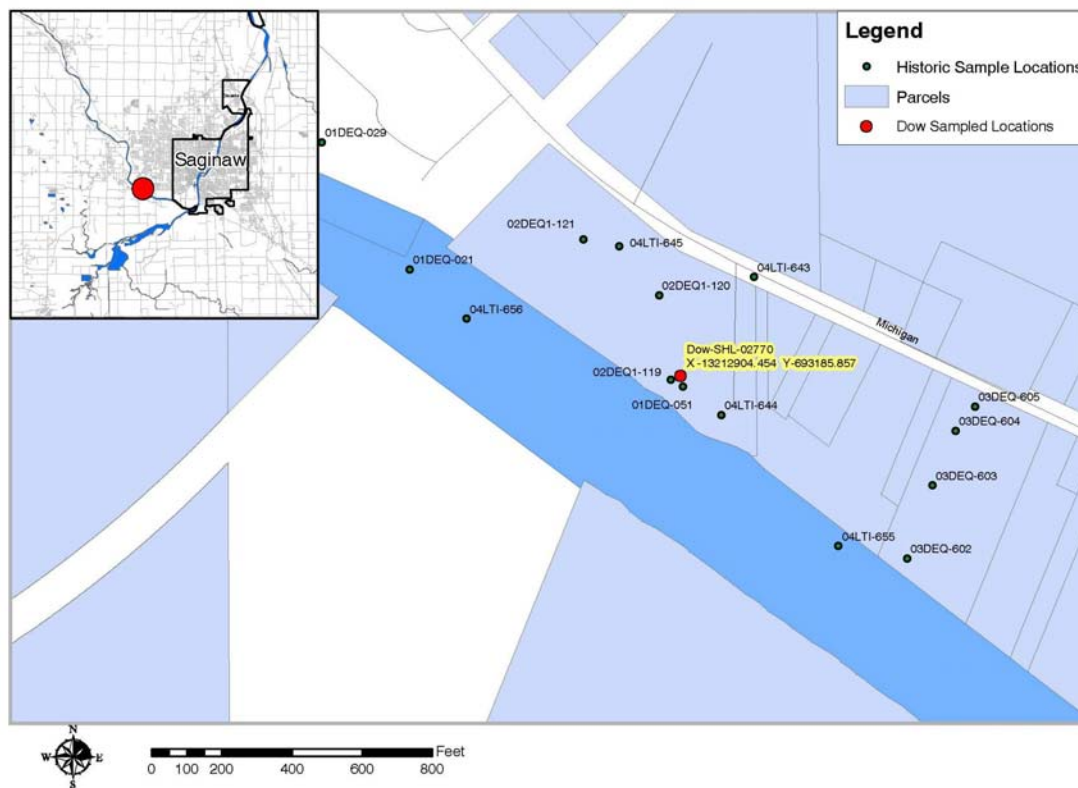


Figure 1. Sampling location from West Michigan Park

West Michigan Park (WMP) soil used for this study was sampled from location labeled as Dow-SHL-02770.

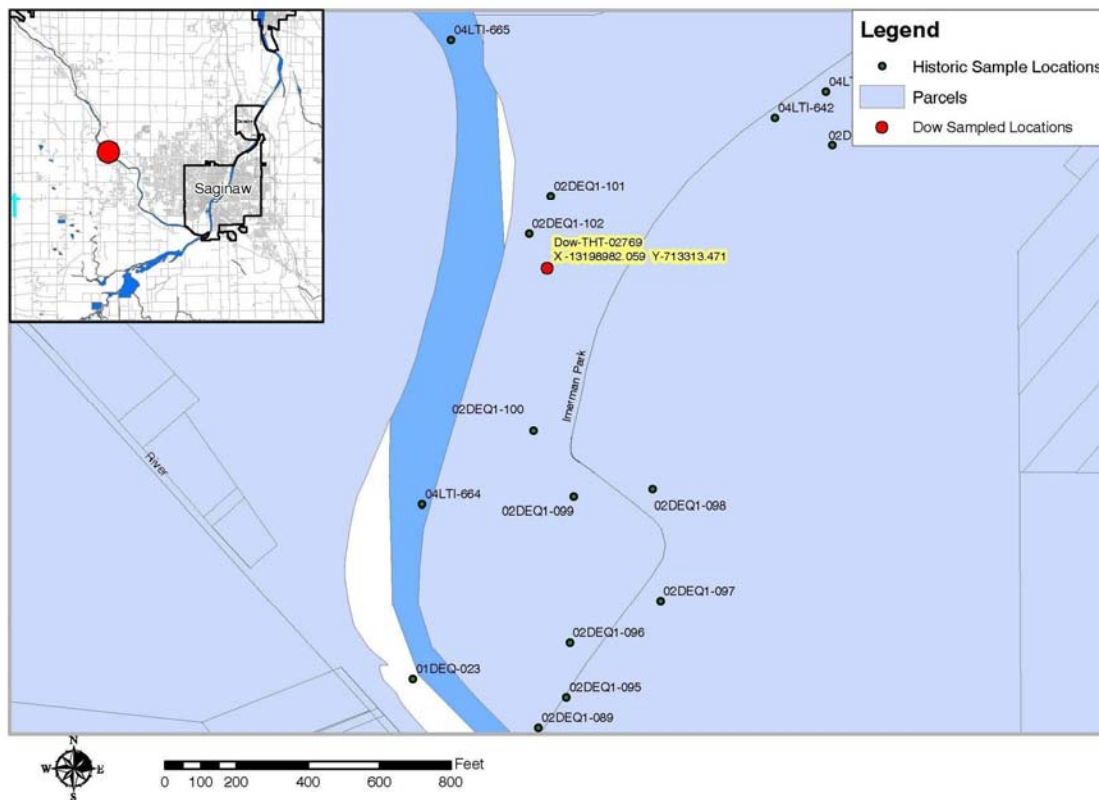


Figure 2. Sampling location from Imerman Park

Imerman Park (IP) soil used for this study was sampled from location labeled as Dow-THT-02769.

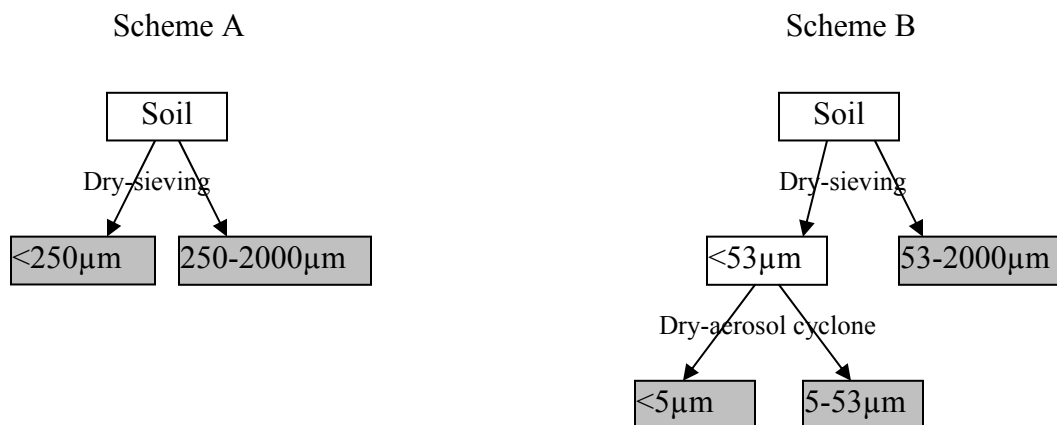


Figure 3. Fractionation scheme for dry-sieving coupled with aerosol cyclone

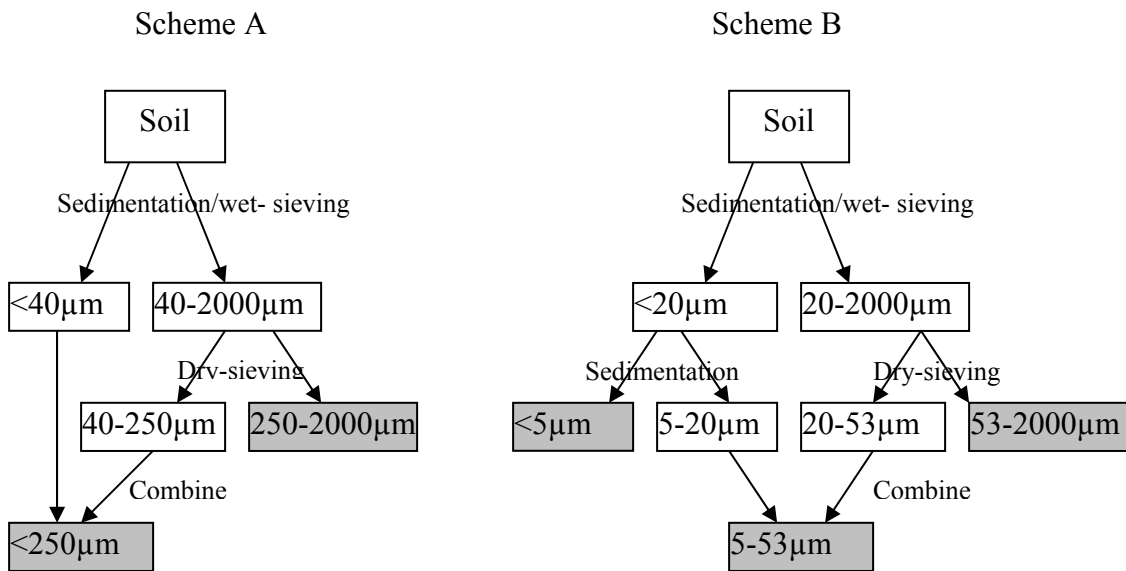


Figure 4. Fractionation scheme for wet-sieving combined with sedimentation

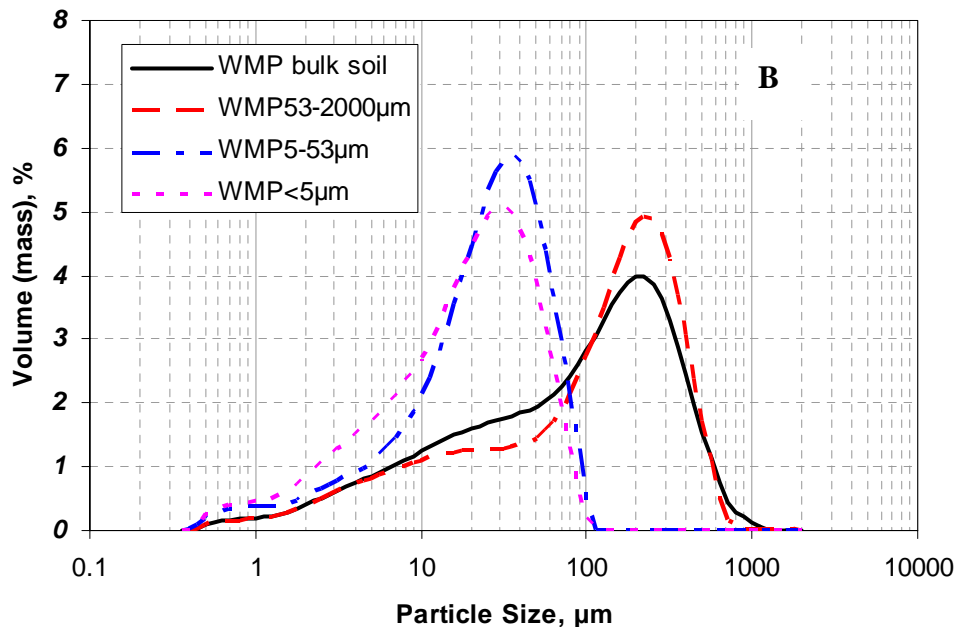
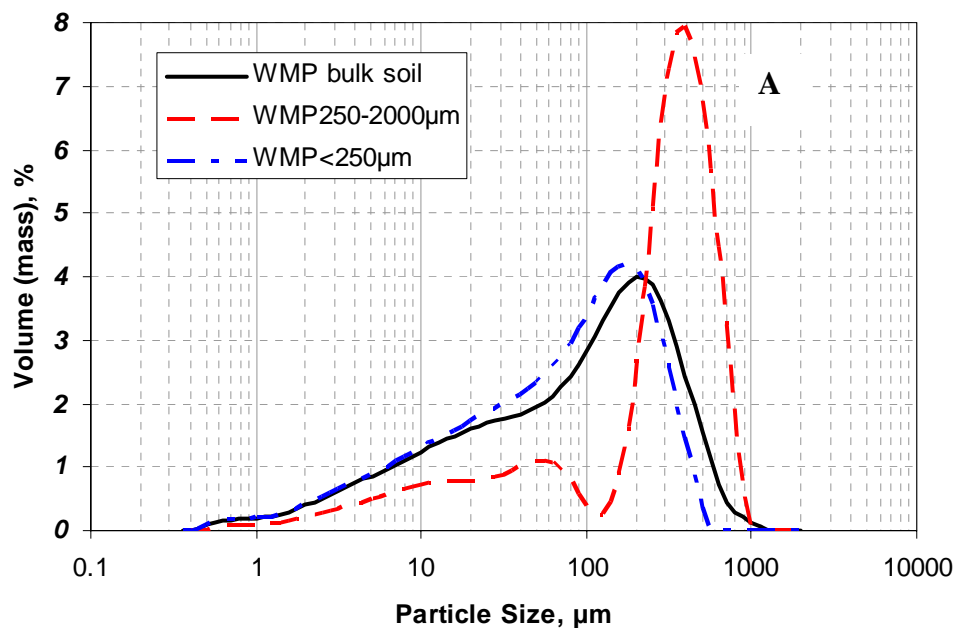


Figure 5. Particle size distribution of bulk and fractionated West Michigan Park soil by dry-sieving combined with aerosol cyclone

Figure A: West Michigan Park bulk soil and fraction 250-2000 μm and <250 μm; Figure B: West Michigan Park bulk soil and fraction 53-2000 μm, 5-53 μm and <5 μm.

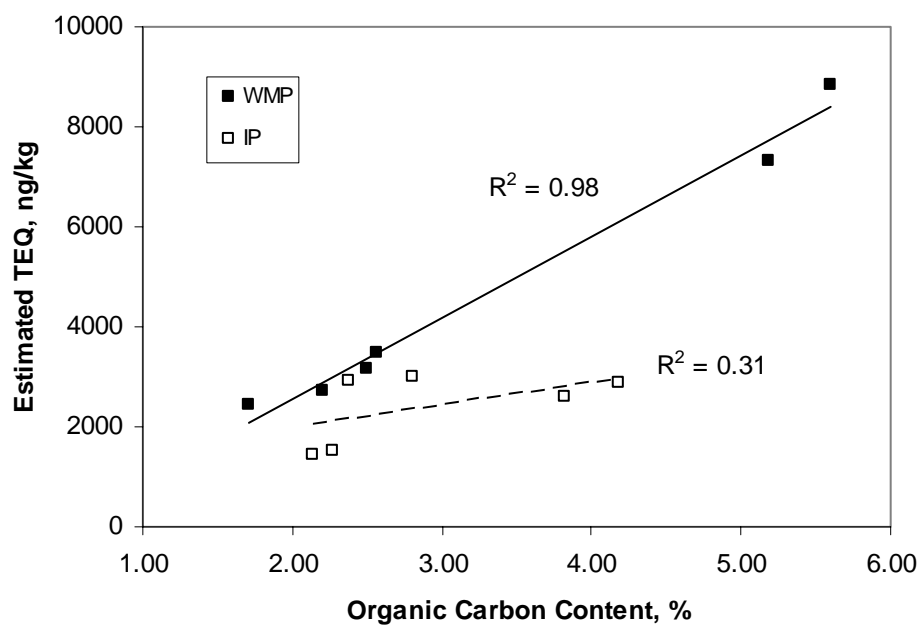


Figure 6. Correlation between estimated toxic equivalent (E-TEQ) and organic carbon content for dry-sieving

Solid squares are for West Michigan Park (WMP) soil and its fractions, Open squares are for Imerman Park (IP) soil and its fractions. Solid and dotted lines are linear regression lines between estimated TEQ concentration and organic carbon content in bulk and fractionated WMP and IP soil.

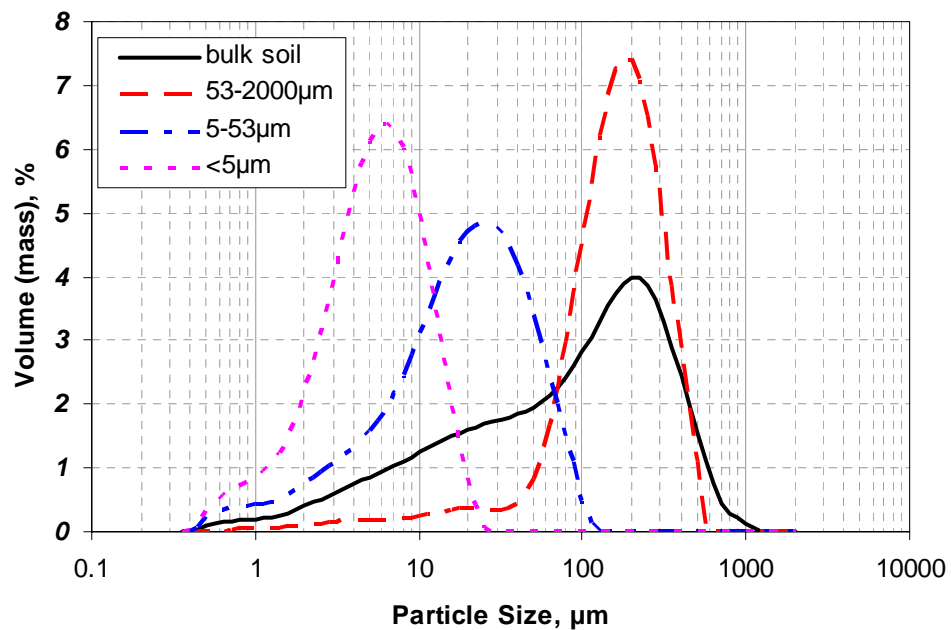
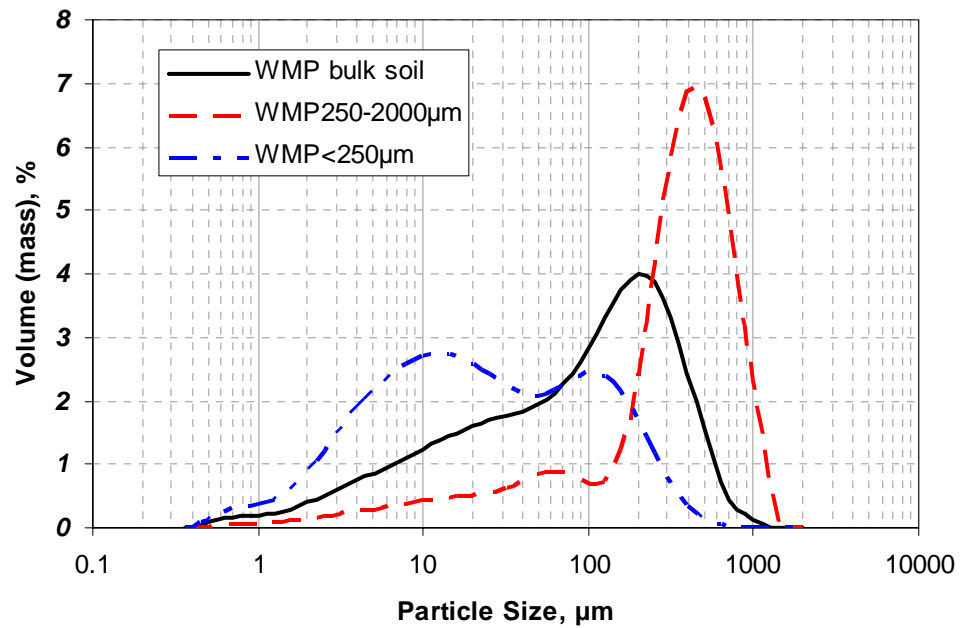


Figure 7. Particle size distribution of bulk and fractionated West Michigan Park soil by wet sieving combined with sedimentation

Figure A: West Michigan Park bulk soil and fraction 250-2000 μm and <250 μm ; Figure B: West Michigan Park bulk soil and fraction 53-2000 μm , 5-53 μm and <5 μm .

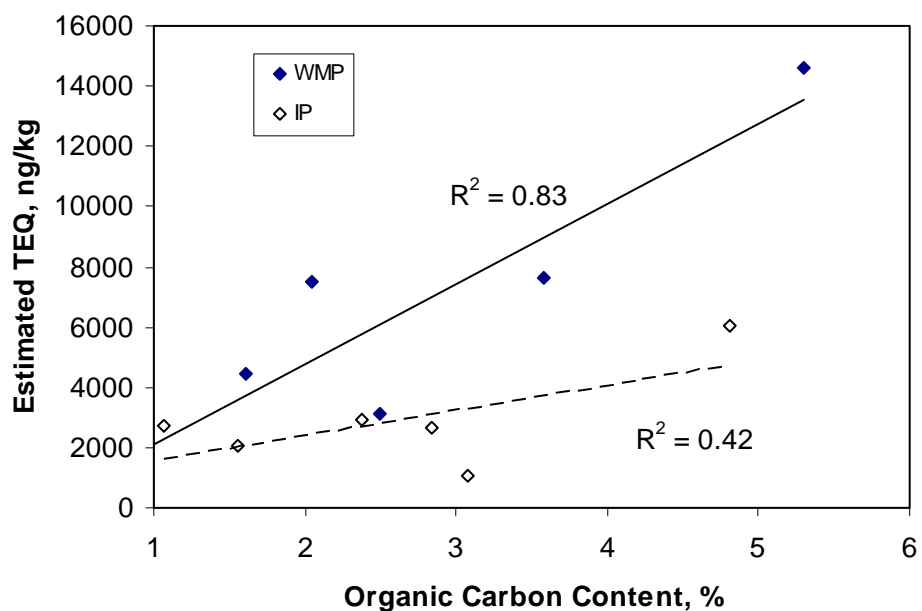


Figure 8. Correlation between estimated toxic equivalent (E-TEQ) and organic carbon content for wet-sieving

Solid diamonds are for West Michigan Park (WMP) soil and its fractions, Open diamonds are for Imerman Park (IP) soil and its fractions. Solid and dotted lines are linear regression lines between estimated TEQ concentration and organic carbon content in bulk and fractionated WMP and IP soil.

Geochemistry Data Supplement

January 31, 2007

Fractionation of Tittabawassee River Floodplain Soils

Eleven bulk soil samples were collected from Tittabawassee River floodplain at various depth along a transect in Reach L. The soils were transported back to the laboratory (Midland, MI) and sieved through a 2 mm brass sieve. The soils were then fractionated by size according two schemes (*i.e.*, A and B) by wet-sieving and sedimentation. For Scheme A, the soils were separated into two size fractions, 250-2000 μm and $<250 \mu\text{m}$; and for Scheme B, the soils were fractionated into three size fractions, 53-2000 μm , 5-53 μm and $<5 \mu\text{m}$. Detailed fractionation procedures are described in the report submitted to Michigan Department of Environmental Quality entitled "Method development for determination of the distribution of polychlorinated dibenzo-*p*-dioxin/dibenzofurans on soil fractions from the Tittabawassee river floodplain," included in this Attachment.

The distribution of soil mass in each fraction and the distribution of polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs) as measured by the estimated toxicity equivalent (E-TEQ) in each fraction were determined (Table 1 and Table 2). The PCDD/Fs congener patterns are presented in Appendix A, attached. Floodplain soils and their sub-domains were characterized for total organic carbon content and black carbon content (Table 3). Selected soils and their sub-domains were characterized for their specific surface area (Table 4).

Table 1 Soil mass and PCDD/Fs E-TEQ distribution for fractionation Scheme A

Soil Location	Depth (ft bgs)	Bulk E- TEQ (g)	250-2000µm			<250µm			Soil Mass Balance (%)	E-TEQ Balance (%)
			Soil mass %	E-TEQ (ng/kg)	E-TEQ %	Soil mass %	E-TEQ (ng/kg)	E-TEQ %		
			(%)	(ng/kg)	(%)	(%)	(ng/kg)	(%)		
RL-246+00-SW20	3-4	530	7.8	49	0.7	88.4	390	65.0	96.2	65.8
RL-246+00-SW20	4-5	2200	8.5	11000	42.4	87.8	1500	59.8	96.2	102.2
RL-246+00-SW20	5-6	3400	24.5	46000	331.9	72.2	8700	184.7	96.7	516.6
RL-246+00-SW20	6-7.5	10000	9.4	15000	14.1	84.5	10300	87.0	93.9	101.1
RL-246+00-SW20	7.5-8.5	22000	5.3	43000	10.4	93.5	4500	19.1	98.9	29.5
RL-246+00-SW85	0-0.6	930	15.0	94	1.5	82.6	1550	137.7	97.6	139.2
RL-246+00-SW85	0.6-1.5	830	20.0	870	20.9	77.0	1100	102.0	96.9	122.9
RL-246+00-SW85	1.5-2.5	24	25.6	<10	NA	70.8	32	94.4	96.4	94.4
RL-246+00-SW265	0-0.8	970	1.7	400	0.7	96.5	760	75.6	98.2	76.3
RL-246+00-SW265	0.8-1.1	1900	9.7 ^a	2600	13.3	75.6	1100	43.7	85.2	57.0
RL-246+00-SW265	1.1-3.1	68	0.0	0	0.0	93.2	78	106.9	93.2	106.9

^a: This fraction is essentially all <250 µm due to incomplete removal of aggregates when soaking soil prior to fractionation

NA: Not applicable

Table 2. Soil mass and PCDD/Fs E-TEQ distribution for fractionation Scheme B

Soil Location	Depth (ft bgs)	Bulk E-TEQ (ng/kg)	53-2000 μ m			5-53 μ m			<5 μ m			Soil Mass Balance (%)	E-TEQ Balance (%)
			Soil mass %	E-TEQ (ng/kg)	E-TEQ %	Soil mass %	E-TEQ (ng/kg)	E-TEQ %	Soil mass %	E-TEQ (ng/kg)	E-TEQ %		
			(%)	(ng/kg)	(%)	(%)	(ng/kg)	(%)	(%)	(ng/kg)	(%)		
RL-246+00-SW20	3-4	530	74.0	210	29.3	15.5	1200	35.0	8.7	1700	27.8	98.1	92.1
RL-246+00-SW20	4-5	2200	63.2	570	16.4	21.1	2200	21.1	10.8	3200	15.8	95.2	53.3
RL-246+00-SW20	5-6	3400	80.5	150000	3551.1	11.3	14000	46.4	5.1	21000	31.5	96.8	3629.0
RL-246+00-SW20	6-7.5	10000	68.4	4200	28.7	16.1	16000	25.7	10.2	22000	22.5	94.7	77.0
RL-246+00-SW20	7.5-8.5	22000	72.7	1500	5.0	14.0	12000	7.6	9.1	16000	6.6	95.8	19.2
RL-246+00-SW85	0-0.6	930	84.2	670	60.7	9.4	4100	41.4	4.0	7200	31.0	97.6	133.1
RL-246+00-SW85	0.6-1.5	830	86.3	640	66.5	6.6	3100	24.7	4.5	5000	27.2	97.4	118.5
RL-246+00-SW85	1.5-2.5	24	89.4	<10	NA	6.4	230	61.1	3.8	305	48.6	99.6	109.7
RL-246+00-SW265	0-0.8	970	31.5	1500	48.7	44.4	660	30.2	19.6	870	17.6	95.5	96.5
RL-246+00-SW265	0.8-1.1	1900	28.0	1400	20.7	41.2	1100	23.9	23.1	1400	17.0	92.4	61.6
RL-246+00-SW265	1.1-3.1	68	22.3	49	16.1	39.1	68	39.1	31.9	77	36.1	93.3	91.3

NA: Not applicable

Table 3. Total organic carbon and black carbon content of soils and soil fractions

Sample ID/Depth (ft)	Fraction	Total organic carbon (%)	Black carbon (%)	E-TEQ (ng/kg)	Organic carbon normalized E-TEQ (ng/kg-OC)
RL-246+00-SW20 3-4	Bulk soil	0.86	0.13	530	61628
	250-2000µm	0.36	0.13	49	13611
	<250µm	0.61	<0.10	390	63934
	53-2000µm	0.22	<0.10	210	95455
	5-53µm	1.62	0.60	1200	74074
	<5µm	2.86	0.50	1700	59441
RL-246+00-SW20 4-5	Bulk soil	0.69	0.14	2200	318841
	250-2000µm	0.35	<0.10	11000	3142857
	<250µm	0.64	0.11	1500	234375
	53-2000µm	0.14	<0.10	570	407143
	5-53µm	2.08	0.40	2200	105769
	<5µm	2.56	0.47	3200	125000
RL-246+00-SW20 5-6	Bulk soil	0.38	0.13	3400	894737
	250-2000µm	<0.10	<0.10	46000	NA
	<250µm	0.51	<0.10	8700	1705882
	53-2000µm	0.13	<0.10	150000	115384615
	5-53µm	1.99	0.44	14000	703518
	<5µm	<0.10	0.43	21000	NA
RL-246+00-SW20 6-7.5	Bulk soil	1.11	<0.10	10000	900901
	250-2000µm	0.41	<0.10	15000	3658537
	<250µm	0.63	0.17	10300	1634921
	53-2000µm	0.22	<0.10	4200	1909091
	5-53µm	1.98	0.96	16000	808081
	<5µm	2.18	0.39	22000	1009174
RL-246+00-SW20 7.5-8.5	Bulk soil	0.36	<0.10	22000	6111111
	250-2000µm	0.26	<0.10	43000	16538462
	<250µm	0.32	<0.10	4500	1406250
	53-2000µm	<0.10	<0.10	1500	NA
	5-53µm	0.26	0.32	12000	4615385
	<5µm	1.91	0.47	16000	837696

NA: Not applicable.

Table 3. Total organic carbon and black carbon content of soils and soil fractions
(Continued)

Sample ID/Depth (ft)	Fraction	Total organic carbon (%)	Black carbon (%)	E-TEQ (ng/kg)	Organic carbon normalized E-TEQ (ng/kg-OC)
RL-246+00-SW85 0-0.6	Bulk soil	2.42	0.38	930	38430
	250-2000µm	1.37	0.13	94	6861
	<250µm	2.13	0.38	1550	72770
	53-2000µm	0.85	0.19	670	78824
	5-53µm	8.54	2.32	4100	48009
	<5µm	12.37	1.60	7200	58205
RL-246+00-SW85 0.6-1.5	Bulk soil	0.78	0.13	830	106410
	250-2000µm	<0.10	<0.10	870	NA
	<250µm	0.87	0.12	1100	126437
	53-2000µm	0.19	<0.10	640	336842
	5-53µm	5.99	0.62	3100	51753
	<5µm	8.53	0.57	5000	58617
RL-246+00-SW85 1.5-2.5	Bulk soil	0.33	<0.10	24	7273
	250-2000µm	0.36	<0.10	<10*	NA
	<250µm	<0.10	<0.10	32	NA
	53-2000µm	0.37	<0.10	<10	NA
	5-53µm	2.23	0.16	230	10314
	<5µm	5.00	0.50	305	6100
RL-246+00-SW265 0-0.8	Bulk soil	5.57	1.98	970	17415
	250-2000µm	23.96	6.24	400	1669
	<250µm	5.46	1.59	760	13919
	53-2000µm	7.10	2.52	1500	21127
	5-53µm	4.56	1.25	660	14474
	<5µm	5.73	0.81	870	15183
RL-246+00-SW265 0.8-1.1	Bulk soil	3.42	1.20	1900	55556
	250-2000µm	5.76	2.16	2600	45139
	<250µm	2.96	0.93	1100	37162
	53-2000µm	2.52	1.03	1400	55556
	5-53µm	3.05	0.59	1100	36066
	<5µm	4.46	0.76	1400	31390
RL-246+00-SW265 1.1-3.1	Bulk soil	1.46	0.24	68	4658
	<250µm	1.47	0.23	78	5306
	53-2000µm	0.50	0.10	49	9800
	5-53µm	1.04	0.34	68	6538
	<5µm	2.35	0.33	77	3277

NA: Not applicable.

Table 4. Specific surface area

Sample ID/Depth (ft)	Fraction	Specific surface area (m ² /g)
RL-246+00-SW20	Bulk soil	3.42
5-6	250-2000μm	0.47
	<250μm	3.54
	53-2000μm	0.70
	5-53μm	5.78
	<5μm	27.60
RL-246+00-SW85	Bulk soil	0.96
0-0.6	250-2000μm	0.41
	<250μm	0.94
	53-2000μm	0.45
	5-53μm	2.03
	<5μm	9.66
RL-246+00-SW265	Bulk soil	5.92
0-0.8	250-2000μm	2.55
	<250μm	6.00
	53-2000μm	3.39
	5-53μm	4.10
	<5μm	16.84

Appendix A

Appendix A: PCDD/Fs congener pattern (Continued)

Sample ID/Depth (ft bgs)	Fraction	Moisture Content %	2,3,7,8- TCDD (ng/kg)	2,3,7,8- TCDF (ng/kg)	1,2,3,7,8- PeCDF (ng/kg)	2,3,4,7,8- PeCDF (ng/kg)	1,2,3,4,7,8- + 1,2,3,6,7,8- HxCDF (ng/kg)	Aggregate Indicator Congener Concentration (ng/kg)	Estimated Total TEQ (ng/kg)
RL-246+00-SW20	Bulk soil	4.2	<9	37000	17000	13000	13000	80000	10000
6-7.5	250- 2000µm	0	<18	69000	20000	16000	11000	120000	15000
	<250µm	26.9	12	44000	17000	14000	13000	87000	11000
	<250µm (duplicate)	26.9	9	36000	15000	12000	11000	74000	9600
	53-2000µm	0	<7	16000	6200	5000	4400	32000	4200
	5-53µm	33.7	<12	57000	25000	20000	20000	120000	16000
RL-246+00-SW20	<5µm	51.4	24	84000	34000	26000	25000	170000	22000
	Bulk soil	1.9	16	71000	50000	27000	35000	180000	22000
	250- 2000µm	0	41	190000	55000	48000	35000	330000	43000
	<250µm	14.5	6	19000	6900	5400	4200	35000	4500
	53-2000µm	0	<4	5500	2500	1800	1900	12000	1500
7.5-8.5	5-53µm	29.4	<8	43000	20000	16000	15000	94000	12000
	<5µm	49.9	16	56000	26000	20000	20000	120000	16000

Appendix A: PCDD/Fs congener pattern (Continued)

Sample ID/Depth (ft bgs)	Fraction	Moisture Content %	2,3,7,8-TCDD (ng/kg)	2,3,7,8-TCDF (ng/kg)	1,2,3,7,8-PeCDF (ng/kg)	2,3,4,7,8-PeCDF (ng/kg)	1,2,3,4,7,8- + 1,2,3,6,7,8-HxCDF (ng/kg)	Aggregate Indicator Congener Concentration (ng/kg)	Estimated Total TEQ (ng/kg)
RL-246+00-SW85 0-0.6	Bulk soil	14.3	15	3300	1400	1200	1200	7000	930
	250-2000µm	0	<4	340	130	110	130	710	94
	<250µm	35.8	22	4600	1700	1500	1500	9400	1300
	<250µm (duplicate)	35.8	19	7100	2500	2200	2000	14000	1800
	53-2000µm	0	7	2100	1200	850	1000	5100	670
	5-53µm	55.3	68	14000	6100	5200	5200	31000	4100
	<5µm	64.7	110	25000	10000	8800	9400	54000	7200
RL-246+00-SW85 0.6-1.5	Bulk soil	8	<7	2300	1900	980	1700	6900	830
	250-2000µm	0	<4	5200	520	770	300	6800	870
	<250µm	21.7	5	4500	1700	1400	1200	8700	1100
	53-2000µm	0	<4	2900	710	740	410	4800	640
	5-53µm	48	17	11000	4600	3900	3900	23000	3100
	<5µm	64.2	40	17000	7700	6200	6400	38000	5000
RL-246+00-SW85 1.5-2.5	Bulk soil	5.2	<4	75	35	25	35	170	24
	250-2000µm	0.8	<4	11	<8	<9	<7	<32*	<10*
	<250µm	23.5	<4	110	48	37	37	230	32
	53-2000µm	1.8	<4	<7	<7	<9	<4	<31	<10
	5-53µm	45.3	<6	870	340	300	280	1800	240
	5-53µm (duplicate)	45.3	<5	760	330	280	250	1600	220
	<5µm	63.2	<13	1200	430	370	380	2300	310
	<5µm (duplicate)	63.2	<11	1100	420	360	340	2300	300

Appendix A: PCDD/Fs congener pattern (Continued)

Sample ID/Depth (ft bgs)	Fraction	Moisture Content %	2,3,7,8- TCDD (ng/kg)	2,3,7,8- TCDF (ng/kg)	1,2,3,7,8- PeCDF (ng/kg)	2,3,4,7,8- PeCDF (ng/kg)	1,2,3,4,7,8- + 1,2,3,6,7,8- HxCDF (ng/kg)	Aggregate Indicator Congener Concentration (ng/kg)	Estimated Total TEQ (ng/kg)
RL-246+00-SW265 0-0.8	Bulk soil	17.9	46	3200	1400	1100	1500	7200	970
	250-2000µm	9.6	29	1200	490	460	610	2800	400
	<250µm	51.5	43	2500	980	880	1000	5400	760
	53-2000µm	2	34	6100	2100	1800	1700	12000	1500
	5-53µm	49.1	38	2000	900	770	1000	4700	660
	<5µm	57.3	54	2800	1100	970	1300	6200	870
RL-246+00-SW265 0.8-1.1	Bulk soil	1	17	6900	2700	2400	2300	14000	1900
	250-2000µm	2	36	9100	4100	3200	3100	19000	2600
	<250µm	30	19	4000	1800	1400	1300	8600	1100
	53-2000µm	1	14	4300	2700	1800	2300	11000	1400
	5-53µm	39.5	15	3600	1600	1400	1500	8100	1100
	<5µm	53.7	21	4900	2100	1800	2000	11000	1400
RL-246+00-SW265 1.1-3.1	Bulk soil	4.7	<4	230	100	79	110	510	68
	<250µm	40	<8	300	100	87	71	560	78
	53-2000µm	1	<4	170	72	58	66	360	49
	5-53µm	34.7	<4	240	99	80	92	520	68
	<5µm	54.7	<9	350	88	72	63	570	77