

ATTACHMENT G

***TECHNICAL MEMORANDUM,
DISTRIBUTION OF FURANS AND DIOXINS ON SOIL FRACTIONS
FROM THE TITABAWASSEE RIVER FLOODPLAIN***

TOXICOLOGY & ENVIRONMENTAL RESEARCH AND CONSULTING
THE DOW CHEMICAL COMPANY

DRAFT PROTOCOL

1803 BUILDING, MIDLAND, MICHIGAN 48674

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

KEY NUMBERS

PLANNED DATES

FILE #:	EXPERIMENTAL START: July, 2006
STUDY ID:	EXPERIMENTAL TERMINATION:
PTR #:	ESTIMATED FINAL REPORT: December, 2006
CAS #:	GLP STUDY: No

SPONSOR: The Dow Chemical Company
Midland, Michigan 48674

TESTING FACILITY: The Dow Chemical Company
Toxicology & Environmental Research and Consulting
1803 Building
Midland, Michigan 48674

REQUIRED SIGNATURES:

STUDY DIRECTOR: _____
LEAD SCIENTIST _____ DATE

MANAGEMENT APPROVAL: _____
DATE

SPONSOR or DESIGNEE: _____
DATE

MANAGEMENT ASSIGNED STUDY PERSONNEL:

Technical Reviewer:

ADDITIONAL STUDY CONTACTS:

Document Management:

A. TITLE

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

B. INTRODUCTION

Understanding the fate, transport and bioaccessibility of hydrophobic organochlorines in soils and sediments may be an important component of the information necessary to make risk management decisions. 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.

This laboratory study will be conducted to develop a method to fractionate soil samples and to determine the distribution of PCDD/Fs in soil fractions from the Tittabawassee River floodplain. Two soil samples from the Tittabawassee floodplain will be collected from areas previously identified to contain elevated levels of PCDD/Fs. Soil samples will be fractionated into different size fractions, e.g., sand, silt and clay, according to standard methods of soil analysis (Day, 1965). The distribution of PCDD/Fs in each fraction will be determined. The correlation between the distribution of PCDD/Fs and the organic carbon (e.g. total organic carbon and black carbon) of each fraction will be elucidated.

The soil fractionation method will be developed and validated using the two soil samples collected. Once the approach has been validated it will be used to characterize a series of soil samples from the Tittabawassee floodplain. The location of the soil samples will be identified in the upcoming Geomorphology investigation (i.e. ATS) currently planned for the summer of 2006. Sample locations will be representative of observed geomorphic features, targeting four depositional features per study area and collecting four samples per feature.

C. OBJECTIVES

Specific objectives of this laboratory study include:

1. Develop an approach for fractionating floodplain soil samples into sub-domains based upon grain size, e.g., sand, silt and clay;
2. Apply the fractionation method to two separate samples from the Tittabawassee floodplain known to contain elevated levels of PCDD/Fs;
3. Characterize floodplain soils and their sub-domains for total organic carbon/total organic matter, black carbon content, elemental analysis (carbon/hydrogen/nitrogen elemental ratio, C/H/N), and specific surface area;
4. Determine the distribution of PCDD/Fs in bulk soil samples and in each sub-fraction.

D. HYPOTHESES

The following hypotheses will be tested in the 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.

E. TEST MATERIAL

Test Material Name

Tittabawassee floodplain soil

Chemical Name

Polychlorinated dibenzo-*p*-dioxin/dibenzofurans

Synonyms

PCDD/Fs

Supplier, City, State (Lot, Reference Number)

PCDD/Fs standards for calibration will be purchased from a qualified commercial vendor.

Purity/Characterization (Method of Analysis and Reference)

Manufacturing product information of the PCDD/Fs standards will be retained.

Other Chemicals and Reagents

All other chemicals and solvents to be used in the experiment will be reagent grade and purchased from commercial sources. Unless otherwise indicated, Milli-Q[®] water will be used in preparation of test solutions and reagents. Milli-Q[®] water is a deionized water, purified through a Milli-Q[®] water treatment system (Millipore Corporation, Bedford, Massachusetts).

F. TEST SYSTEM

Soil

Soil samples will be collected from two agreed upon locations along the Tittabawassee River floodplain. These samples will be collected from areas agreed upon that contain elevated levels of PCDD/Fs. The exact sampling locations will be agreed upon between Michigan Department of Environmental Quality (MDEQ) and Dow. From each sampling location, soil samples from 0-2 in below surface will be taken after the overlying grass has been removed. Soil samples will be sealed in 4-L plastic jars and transported into laboratory and stored in a refrigerator at 4°C.

Soil samples will be sieved through 2 mm sieve after collection to remove large objects such as gravels, leaves and grass roots, sealed in 4-L plastic jars and stored in a refrigerator at 4°C. Soil samples will be fractionated into different size fractions, i.e., sand, silt and clay. The mass distribution of different fractions and the distribution of PCDD/Fs in each fraction will be 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}), will be determined.

G. EXPERIMENTS

Method Development for the Fractionation of Soil

Soil Fractionation

Two fractionation schemes as shown in Figure 1 will be used for the method development. Scheme A separates the soil samples into two fractions by sieving: <250 µm and 250–2000 µm. The fraction of <250 µm was previously used to feed rats to determine the relative bioavailability of PCDD/Fs in soils. The objective of this scheme is to obtain further characterization of the fraction of <250 µm.

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: gravel (> 2000 µm), sand (50–2000 µm), silt (2–50 µm) and clay (< 2 µm). This scheme will focus on fractionating the soil into the three grain sizes (i.e., sand, silt, and clay) using different approaches to identify which technique is suitable for generating sufficient sub-fractions for further analyses.

One option is to fractionate soil samples according to the Society of Agronomy standard method (Day, 1965) based on sedimentation and wet-sieving. According to this method, soil suspension (7%, dry soil/suspension) in water will be prepared. Clay particles (< 2 µm) will be separated through repetitive resuspension and sedimentation. Silt (2–47 µm) particles will be separated from sand (> 47 µm) by wet-sieving the residue on a 47µm sieve. 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 and water, respectively, μ is the dynamic viscosity of water, g is the acceleration of gravity, and d is the particle diameter. The disadvantage of the sedimentation method is that this might not give a clear-cut separation according to particle diameter because of flocculation and compression during sedimentation. The initial height of a

particle in the water column is another factor that hinders the clear-cut 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, resuspension and sedimentation will need to be repeated until the yield of fine particles is negligible.

Note that a stainless steel sieve with an opening of 53 μm will be used in this study because a sieve with an opening of 47 μm as stated in the method by Day (1965) is not currently available. Current American Society for Testing and Materials (ASTM) standard test sieves only provide sieves with opening of 45 and 53 μm . This will not pose any negative effect on the study.

An alternative for the fractionation is dry-sieving and the use of cyclone. Soil samples will be air-dried and soil aggregates will be crushed manually. A 53 μm sieve will be used to separate sand ($> 53 \mu\text{m}$) from silt and clay particles. A micro-feeder (MF-2, Siboto) and a 5 μm cut-off stainless steel cyclone will be utilized to separate particles with diameters below 53 μm to silt (5-53 μm) 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 will separate particles with aerodynamic diameters as low as 5 μm . Particles with diameters less than 5 μm will be collected in a Teflon bag. Particles with diameter of 5 to 53 μm will be collected in a reservoir below the cyclone.

Characterization of soil sub-domains

Total organic carbon (f_{oc}), black carbon contents (f_{bc}), elemental analysis (Carbon/Hydrogen/Nitrogen elemental ratio), specific surface area and the concentrations of PCDD/Fs will be determined for the bulk soil and the sand, silt, clay fractions.

Analytical Methods

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

The degree of aromaticity of the organic matter in soil and soil fractions can be assessed by measuring elemental ratio of C/H/N. An elemental analyzer will be used to determine the carbon weight percent and elemental atomic ratio of C/H/N. The samples will be acidified before C/H/N elemental measurement to remove the inorganic carbon in the soil samples. The elemental carbon content from this C/H/N

analysis is the total organic carbon content (f_{oc}) of the sample. 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)., This analysis will be done in a commercial laboratory.

Black Carbon Content (f_{bc})

The black carbon content (f_{bc}) in each of the soils and soil fractions will be determined using combustion techniques (Gustafsson *et al.*, 1997). Briefly, aliquots of dry sample will be weighed and combusted under air for 24 h at 375°C, so that the labile organic matter will be oxidized but the black carbon fraction in the sample will be retained. The organic carbon content of the sample after combustion at 375°C (f_{oc}^{375}) will be determined following the above procedure. The black carbon content (f_{bc}) will be 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 will be operationally defined (*i.e.*, intact in air combustion at 375°C for 24 h).

Specific Surface Area Analysis

The specific surface area for each of the sediments and sediment fractions will be analyzed using nitrogen gas physisorption method. The sediment surface area will be estimated based on B.E.T. (Brunauer, Emmett, Teller multilayer adsorption model) isotherms of nitrogen gas. This analysis will be done in a commercial laboratory.

PCDD/Fs in Solid Samples

The analysis will be conducted by the Trace Laboratory in the Environmental Analytical Chemistry Laboratory at The Dow Chemical Company (Midland, Michigan) following a modified EPA 1613b procedure. The total of each homolog (tetra- through octa- chlorodibenzo-p-dioxin/furans) and total WHO-TEQs will be determined for each soil and soil fraction. The detailed analytical method will be included in the final report.

H. DATA AND REPORTING

Experimental data will be compiled and evaluated in accordance with the following aspects:

- Soil-bound PCDD/Fs concentrations in bulk floodplain soil samples and their distribution in size separated soil fractions (e.g. sand, silt, clay);
- Total organic carbon (f_{oc}) and total organic matter, black carbon (f_{bc}) contents, elemental analysis (C/H/N elemental ratio), specific surface area in bulk soil samples and their distribution in size separated sediment particle fractions;
- Relationship between soil-bound PCDD/Fs concentrations and total organic carbon, black carbon contents and other soil characteristics.

I. FINAL REPORT

A final report of the definitive study will be submitted to the study sponsor and will include but not be limited to the following:

1. Name and address of the facility performing the study and the dates on which the study is initiated and completed;
2. Objectives and procedures stated in the approved protocol, including any changes in the original protocol;
3. Statistical methods employed for analyzing the data;
4. Description of test and/or control substance (e.g., lot number, purity, physical characteristics, and method of preparing test concentrations);
5. Description of the analytical methods used;
6. A description of the test concentration used and duration of the studies;
7. A description of all circumstances that may have affected the quality or integrity of the study;
8. Location of raw data and specimens;
9. List and signatures of study personnel.

J. STUDY ARCHIVES

The data, protocol, protocol changes/revisions, and final report will be archived at Toxicology & Environmental Research and Consulting, The Dow Chemical Company, Midland, Michigan.

K. SAFETY

All personnel involved in the study will be advised of the safety precautions to follow when handling the test material. Chemical safety information will be made available.

L. SCHEDULE FOR STUDY

A tentative schedule is listed below. The actual schedule will be pending on the approval by Michigan Department of Environmental Quality (MDEQ).

Protocol Finalized:	July, 2006
Protocol Implementation Initiated:	July, 2006
Final Report:	December 2006

M. REFERENCES

- (1) Day, P. R. (1965). Method for separation of clay, silt and sand fractions. In Black, C. A., Evans, D. D., White, J. L., Ensminger, L. E. and Clark, F. E., Eds, *Method of soil analysis. Part 1 Physical and mineralogical properties, Including statistics of measurement and sampling*. Vol. **9**. American Society of Agronomy. Madison, Wisconsin, USA, 550-552.
- (2) Marshall, T. J. and Holmes, J. W. (1979). *Soil Physics*, Cambridge University Press.
- (3) Nelson, D. W. and Sommers, L. E. (1982). Total carbon, organic carbon, and organic matter. In Page, A. L., Miller, R. H. and Keeney, D. R., Eds, *Method of soil analysis. Part 2 Chemical and microbiological properties*. Vol. **9**. American Society of Agronomy, Soil Science Society of America. Madison, Wisconsin, USA, 539-577.
- (4) Gustafsson, Ö., Haghseta, F., Chan, C., Macfarlane, J. and Gschwend, P. M. (1997). Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environmental Science and Technology* **31**: 203-209.

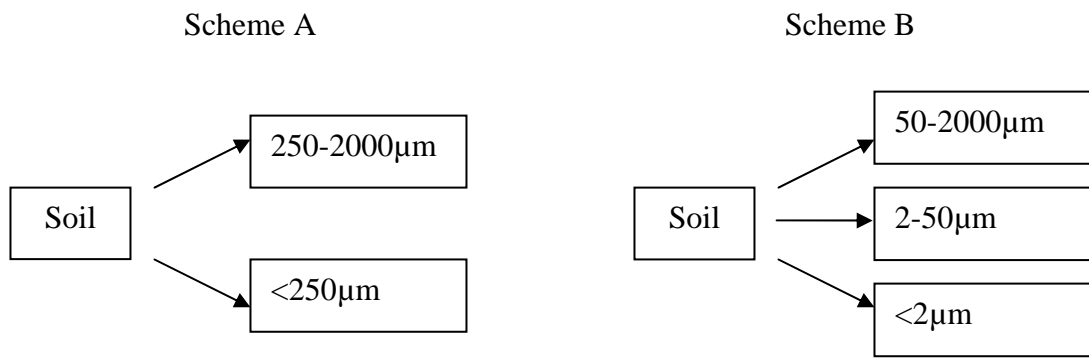


Figure 1 Fractionation schemes