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Sampling and Analysis Plan in Support of Bioavailability Study, Midland Area Soils

FINAL DRAFT

Prepared for

The Dow Chemical Company

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(Revised October 2006)

CH2MHILL

Contents

Attachment

Tables (located at the end of each section, following text)

Figures (located at the end of each section, following tables)

Abbreviations and Acronyms

µm	micrometer
BC	black carbon
BSAP	Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study
C/O	carbon/oxygen
CFR	Code of Federal Regulations
dioxin	polychlorinated dibenzo-p-dioxin
Dow	The Dow Chemical Company
furan	polychlorinated dibenzo-p-furans
GC/MS	gas chromotograph/mass spectrometer
H/C/N	hydrogen/carbon/nitrogen
HOC	hydrophobic organic chemical
IDW	investigation-derived waste
ISAP	Independent Science Advisory Panel
K_{ow}	lipophicity
LC/MS	liquid chromotograph/mass spectrometer
MDEQ	Michigan Department of Environmental Quality
MS	matrix spike
MSD	matrix spike duplicate
PCB	polychlorinated biphenyl
PCOI	potential constituent of interest
QAPP	quality assurance project plan
QC	quality control
SAP	sampling and analysis plan
SOC	soil organic carbon
SOM	soil organic matter
SOP	standard operating procedure

SVOC	semivolatile organic compound
TEQ	toxicity equivalent, used to report the *toxicity-weighted masses* of mixtures of furans and dioxins
TIC	tentatively identified compound
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound

SECTION 1

Introduction

This sampling and analysis plan (SAP) describes the sampling approach and procedures for characterizing the distributions of physical and chemical parameters in surface soil in the vicinity of The Dow Chemical Company (Dow) Plant in Midland, Michigan. The objectives of the sampling program are as follows:

- Characterize the distribution of physical and chemical parameters that are reported to influence bioavailability to identify the range of soils to be used for future bioavailability studies.
- Develop additional information on the nature and extent of polychlorinated dibenzo-p-dioxins (dioxin) and polychlorinated dibenzo-p-furans (furan) in Midland area surface soil.
- Determine whether additional Dow-related hazardous substances are present in Midland area surface soil.
- Develop and implement a process so chemical results for samples obtained on residential properties remain confidential until site-specific cleanup criteria are developed.

The sampling approach presented in this SAP is based on modifications to the *Midland Representative Soils Sampling Analysis Plan in Support of Bioavailability Study* (BSAP) (CH2M HILL, 2006) resulting from comments received from the Michigan Department of Environmental Quality (MDEQ) and the U.S. Environmental Protection Agency (USEPA). The approach described herein reflects collaboration between Dow, MDEQ, and USEPA to reach a consensus approach that meets the stated objectives. The sampling approach was agreed to during a series of phone conversations and key meetings held on April 20 and May 9, 2006. Subsequent modifications were made to this SAP based on comments received from MDEQ on June 20, July 3, July 14, and October 11, 2006.

1.1 Study Location

The area covered by this study is a portion of the city of Midland and the surrounding community that may have been impacted by offsite releases of hazardous substances from the Dow Plant. The study area encompasses residential, commercial, and industrial properties surrounding the Dow Plant, as shown in Figure 1-1.

1.2 Sampling and Analysis Plan Organization

This SAP is organized as follows:

- **Section 1** presents an introduction to the Midland study area and identifies the project objectives.

- **Section 2** presents the investigation approach and sampling design, describes the sample collection methods, and presents the procedures to be used in assuring confidentiality of sampling locations and sample results.
- **Section 3** describes the methods to be used in evaluating the data collected during this investigation.
- **Section 4** summarizes the data validation and management procedures.
- **Section 5** provides a schedule for the work described in this SAP.
- **Section 6** lists references cited in this SAP.

Insert Figure 1-1
11 X 17

SECTION 2

Sampling Design

The investigation approach for the soil sampling program is based on the conceptual site model for release, aerial transport, and deposition of potential hazardous constituents from the Dow Plant as presented in the *Midland Area Soils Remedial Investigation Work Plan* (CH2M HILL, 2005a). This conceptual site model considers potential releases from a variety of potential point and nonpoint sources located on the Dow Plant such as emissions from waste incinerators, power plants, production facilities, and fugitive dust.

2.1 Sampling Design

The basic sampling design approach consists of samples collected along radial transects extending from the Dow Plant site into the surrounding community. This design was developed primarily based on the conceptual site model of aerial dispersion and providing additional information about the distribution of hazardous substances in the study area. In addition, the design will provide representative information on soil characteristics in support of a possible future bioavailability study as well as providing information on the possible presence of hazardous substances other than dioxins and furans.

The basic elements of the design are as follows:

- **Origin of transects**: Potential major point and nonpoint sources (for example, incinerator complex, power plants, brine electrolysis, and track-out) were considered to create a centralized origin for transects within the Dow Plant. The origin location was established by MDEQ.
- **Number of transects**: The number of transects was established by MDEQ considering coverage requirements and MDEQ statistical sampling guidance (MDEQ, 2002), meteorological data, and land use patterns in the study area resulting in a total of 23 radial transects. Transects are arrayed such that soil in the dominant downwind directions are sampled more densely than soil in the upwind direction. Wind rose data from meteorological station No. 72639 were used to identify the prevailing wind directions, with the goal of concentrating sampling in directions that are downwind 75 percent of the time. This resulted in 17 transects located in the downwind direction and six transects located upwind, as shown in Figure 2-1.
- **Length of transects**: The transects extend a minimum of 9,400 feet outward from the origin with a minimum distance of 3,000 feet beyond the Dow Plant boundary into the surrounding community. To assure sufficient lateral coverage into residential areas (needed to support the bioavailability study), every other transect in the dominant wind direction extends approximately 10,000 to 11,000 feet beyond the Dow Plant boundary.
- **Sample stations along transects**: Soil samples will be collected within defined sample stations (sometimes referred to as sample "boxes") at regularly spaced intervals of approximately 950 feet along each transect, beginning just beyond the Dow Plant

boundary and extending to the end of the transect. The designated distance between sample stations was determined by MDEQ.

- **Sample stations**: Sample stations consist of a nominal 300-foot by 300-foot box. The sizes and dimension of the boxes were modified in collaboration between Dow and MDEQ ensure that the study objectives were met. (Adjustments are described in the following section.)

- **Selection of samples for analysis**: Where multiple properties are present, samples will be collected from up to five different properties. All of these samples will be analyzed for soil parameters that may affect bioavailability; however, only one sample from each sample station will be selected for laboratory analysis for dioxins furans and other hazardous substances. Selection of the sample for analysis will be subject to a procedure that will ensure the anonymity of the sample selected. Where only a single property (or property owner) is present within a sample station, only one sample will be collected and submitted for laboratory analysis. These samples also will be subjected to a procedure that will ensure the anonymity of the results obtained from the laboratory. This procedure is described in Section 2.4 and Attachment A.

- **Samples to evaluate variability**: The representativeness of the single sample location per box approach will be evaluated using collocated samples obtained at random locations within 10 percent of the sample stations.

- **Sample depth**: Two sample intervals may be collected at each sample location (a sample location is defined as the specific physical location where a soil sample is collected): one representing the upper 1 inch of soil, and the other representing soil between 1 and 6 inches below grade. The sample intervals obtained at each sample location will be determined by the type of analytical data to be gathered at that location, as described in Section 2.3.

The sampling approach listed above was used to develop the final locations and dimensions of each of the sample stations. Adjustments to the sample stations were necessary to account for actual conditions in the study area. MDEQ and Dow met on May 9, 2006, and reached an agreement on the locations and sizes of each of the sample stations based on the following adjustments:

- Sample stations were adjusted to group together properties of similar land use.

- Sample stations were adjusted to assure the inclusion of multiple properties within the sample station to help protect the anonymity of the property owners. Where possible, a minimum of nine properties were grouped within a sample station.

- In cases where only one or two property parcels were present in proximity to the sample station, the station was adjusted to be fully on one of the properties. Preference was given to Dow or public property to help facilitate access for sampling.

- Sample stations were eliminated in cases where the locations were fully within developed industrial and or commercial property and no viable soils were available for sampling.

- Sample stations were eliminated from the Tittabawassee River floodplain.

- Sample stations were eliminated from Midland Cogeneration Venture cooling water ponds because sediment samples are not representative of soil conditions in the community and any potential hazardous substances that might be present are subject to different fate and transport mechanisms than surface soils, which are the focus of this study.

In addition, modifications to sample stations on Transects R, S, and T were made based on MDEQ comments received on July 14, 2006, in order to ensure a sufficient number of parcels were available in each sample station. After making these adjustments, 145 sampling stations were defined and are shown on Figure 2-2. A list of the parcels within each sample station is provided in Table 2-1.

2.2 Target Analytes

The target analytes for this investigation include soil parameters which may impact bioavailability (soil parameters), dioxins and furans, and additional hazardous substances (chemicals) that may be considered as potential constituents of interest (PCOIs) in future remedial investigation activities. The chemicals and parameters selected for analysis are based on the sample station's position relative to the Dow Plant and the station's dominant land use, as listed below:

- Analysis of soil parameters that may impact bioavailability will be conducted on the 0- to 1-inch interval soil samples taken at all stations except for those that consist of fully developed industrial or commercial properties because the surface soils in these areas are highly disturbed or not present. MDEQ and Dow agreed to sample station locations on May 9, 2006. Not all of the parameters (such as black carbon) may be used to classify soils. The decision on which parameters that will be useful for soil classification will be determined once the data have been collected and evaluated.
- Additional chemical analyses will be conducted on the 0- to 1-inch and 1- to 6-inch interval samples for the sample locations selected at sampling stations in close proximity to the Dow Plant (the first two sampling stations along each transect closest to the plant).
- Dioxin and furan analysis will be conducted on the 0- to 1-inch interval samples selected for analysis from all sampling stations, and on the 1- to 6-inch interval samples taken at sampling stations in close proximity to the Dow Plant.

The target analyte groups for each sample station are listed by transect letter and sample station number on Table 2-1. The individual compounds and analyses associated with each target analyte group are described in the subsections below.

2.2.1 Soil Parameters That May Impact Bioavailability

Studies to date have shown that the bioavailability of hydrophobic organic chemicals (HOC) such as dioxins and furans in soil is highly variable, depending not only on a chemical's lipophicity (K_{ow}), but also molecular steric conformation and soil characteristics. The following primary soil parameters have been reported to influence the bioaccessibility/bioavailability of dioxin and furans (Qiu and Davis, 2004):

- **Soil organic carbon (SOC):** SOC is a subdomain of soil organic matter (SOM) and is a measure of the sorption capacity of a soil for HOCs.
- **Specific surface area:** Surface area has been reported to be a significant factor affecting the bioavailability of dioxins and furans. A large surface area and high aromaticity enables the formation of π-π interactions (Lyytikäinen et al., 2003). These factors favor stronger binding to soil and sediment, thus decreasing desorption and bioavailability of the chemical. In general, surface area is related to particle size (that is, smaller particle size generally correlates to a larger specific surface area).
- **Particle size:** Particle size has been reported to be a significant factor affecting the bioavailability of dioxins and furans. As noted above, particle size is related to specific surface area, with smaller soil particle sizes favoring stronger binding to soil and thus decreasing desorption and bioavailability.
- **Hydrogen/Carbon/Nitrogen (H/C/N):** The H/C/N ratio is a measure of the aromaticity of a soil. Increasing H/C/N levels favor stronger binding to soil and sediment, and thus decreasing desorption and bioavailability of the chemical.
- **Black carbon (BC):** BC, a subdomain of SOM, has much higher affinity to planar HOCs than amorphous organic carbon, and has been found to be the predominant repository of many HOCs. BC particles that have sizes ranging from a few microns to above 100 micrometers (μm) are highly aromatic in structure and exhibit relatively low oxygen to organic carbon and H/C/N atomic ratios and low contents of oxygen-containing functional groups (Song et al., 2002). Comparable to diagenetically aged coal, shale, and cenospheres, BC also has a high carbon/oxygen (C/O) ratio and is responsible for strong HOC sorption (and limited bioavailability) because of its high specific surface areas and relatively reduced chemical nature. It has been proposed that the BC and possibly other distinct subfractions of bulk organic carbon can influence the bioavailability of HOCs (Bucheli and Gustafsson, 2001).

The parameters that will be analyzed as part of this study and the concentrations and levels of the parameters that affect bioavailability are listed in Table 2-2.

2.2.2 Additional Hazardous Substances

MDEQ and Dow have agreed upon an expanded 40 Code of Federal Regulations (CFR) Part 261 Appendix IX target analyte list for soil sampling at the Dow Midland Plant. This list of chemicals, provided as Table 2-3, includes a variety of volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), metals, pesticides, and polychlorinated biphenyls (PCBs).

Evaluating Tentatively Identified Compounds

The ion current chromatograms of multicompound analytical methods based upon gas chromatograph/mass spectrometer (GC/MS) or liquid chromatograph/mass spectrometer (LC/MS) (for example, USEPA 8260 and 8270) can contain information on nontarget analyses. Qualitative and quantitative information about the substances responsible for nontarget peaks in such chromatograms can be included in the laboratory data reports if the peaks are handled using the procedure for tentatively identified compounds as described in USEPA Methods 8260B and 8270C (Section 7.6.2 in both methods).

Compounds detected will be identified and quantified as tentatively identified compounds (TICs) if they have peak areas equal to or greater than 10 percent of the nearest (retention time) internal standard. All such peaks will be reported in special section of the laboratory data report for each sample.

For nontarget peaks meeting the 10 percent threshold, the mass spectrum will be compared to referenced spectra in the current National Institute of Standards and Technology library, using a computer search routine. If the spectral match has a fit of 80 percent or better, the substance name representing the best fit will be reported as the tentative identity of the compound. If the spectral fit is less than 80 percent, the peak will be reported as "Unknown RRT x.xxx", where x.xxx is the relative retention time in minutes. In either case, an estimated concentration will be calculated by comparing the peak area to that of the internal standard, using a response factor of 1.00. The estimated concentration will be shown on the laboratory data report.

2.2.3 Dioxin and Furan Analysis

All samples collected from the 0- to 1-inch interval and samples collected from the 1- to 6-inch interval from the first two sampling stations along each transect closest to the Dow Plant will be analyzed for the 17 dioxin and furan congeners listed in Table 2-4.

2.3 Sample Collection Procedures

The following sample collection procedures will be used at each designated sample location:

- Identify appropriate area for sample collection using the following guidelines:
  - Residential property: Samples will be preferentially collected from a visually undisturbed location in the central area in the front yard. The front of the house is preferable as it will likely be subject to less disturbances and be more easily accessible to the sampling team. Sample locations that will be avoided to the extent practical include gardens, recently landscaped areas, recently disturbed areas (based on visual inspection), and areas with evidence of disposal activities.
  - Commercial and industrial property: Samples will be preferentially collected from undeveloped or vegetated areas, such as wood lots and grassy areas. Sample locations that will be avoided to the extent practical include unpaved parking lots, industrial process areas, recently landscaped areas, and areas with evidence of disposal activities.

- Public property: These properties include parks, schools, and highway medians. Samples will be preferentially collected from undeveloped or vegetated areas, such as wood lots and grassy areas. Sample locations that will be avoided to the extent practical include unpaved parking lots, recently landscaped areas, and areas with evidence of disposal activities.

- Surface materials, sod, and/or vegetation will be removed from the selected sampling location as described in Field Standard Operating Procedure (SOP) 2.1 (CH2M HILL, 2005b).
- Two sample intervals may be collected at each location: one representing the upper 1 inch of soil, and the other representing soil between 1 and 6 inches below grade (see Section 2.2). In accordance with the Midland soil sampling program conducted in 1996 (Dow, 2000), each sample will be made up of aliquots taken from the required sample depth intervals at 15 equally spaced subsample locations along the circumference of a 6-foot-diameter circle that has been deployed within the identified sample area. Hand tools such as stainless steel spoons, trowels, or other easily cleaned or disposable material will be used to collect the subsamples.
- The 15 aliquots will be mixed in a bowl and be transferred to sample containers to permit analysis for all analytical suites, except VOCs. The sample containers for VOC analysis will be filled without mixing by placing soil from one centrally located subsample location directly into the VOC sample container.
- Cleaned or disposable hand tools, bowls, and spoons will be used to mix and transfer the soil sample to appropriate sample containers.
- Excess soil not used to fill sample jars will be returned to the sample locations. Potting soil will be placed in the sample holes to bring the surface back to grade. Sod will be replaced and grass seed will be planted as necessary to restore vegetation.

2.3.1 Field Quality Control

Field quality control (QC) samples will be collected or prepared to assist in assessing data use. These QC samples will include field duplicates, laboratory QC samples (for matrix spikes [MS] and matrix spike duplicates [MSD]), equipment blanks, temperature blanks, and trip blanks (for samples requiring VOC analysis). Field QC samples will be collected in accordance with Section 2.5 of the quality assurance project plan (QAPP) (CH2M HILL, 2005c).

Field duplicate samples will be collected and analyzed at a minimum frequency of 1 per 10 samples, and extra sample volumes for MS/MSD will be collected and analyzed at a minimum frequency of 1 per 20 samples. Trip (VOC analysis, only) and equipment blanks will be collected at a minimum frequency of one per day of sampling.

2.3.2 Sample Containers and Preservation

Analytical methods, sample bottle requirements, preservatives, and hold times associated with soil parameters, dioxin and furan, and additional chemical analyses are provided in Table 2-5.

2.3.3 Equipment Decontamination

The field team will decontaminate reusable sampling equipment prior to commencement of sampling, between sample locations, and upon completion of the field activity. Separate sample processing equipment (that is, bowls, spoons, and trowels) will be dedicated to one location per day, and materials that come into direct contact with sample materials will be decontaminated or disposed of. Disposable equipment will be used whenever possible to avoid potential cross contamination and reduce generation of decontamination fluids.

The field sampling team will decontaminate sampling equipment at the end of each sampling day at the field warehouse (this equipment will have been only used at one sampling location) as follows:

- Transfer equipment to the decontamination station (plastic-covered area with full containment of all fluids).
- Wash all equipment surfaces that contacted the potentially contaminated soil with detergent solution (Alconox or other laboratory-grade detergent), using a brush as needed to remove particulate matter and surface films.
- Rinse with potable water.
- Maintain decontaminated equipment in a position and location where it will not come into contact with contaminants.
- Transfer decontamination fluids to a sealable container, such as tubs, for later disposal.

2.3.4 Containment and Disposal of Investigation-Derived Waste

The procedures for the containment and disposal of investigation-derived waste (IDW) that will be generated during the field sampling activities will depend on the type and source of waste. Types of IDW are as follows:

- Excess soil
- Decontamination fluids
- Disposable equipment (for example, paper towels, gloves, core liners)

Excess soil will be returned to the location where it was obtained. Decontamination fluids, if generated, will be discharged at the field warehouse. Disposable equipment will be placed in garbage bags and be disposed as solid waste.

2.4 Sample Management Procedures

The sample management procedures for each sample station vary based upon the configuration, number of properties within the station, and location of the station. All sample stations will be subjected to a procedure designed to protect the anonymity of the property owner from which the samples are actually analyzed. Procedures for the various circumstances are described in Attachment A, Blinding Protocol for Sampling and Analysis in Support of the Bioavailability Study, Midland Area Soils. If any discrepancy is identified between the SAP, QAPP, and the Blinding Protocol, the Blinding Protocol will take precedence.

Insert Table 2-1 (excel) – 15 pages

TABLE 2-2
Soil Physical and Geochemical Parameters of Interest
Sampling and Analysis Plan in Support of Bioavailability Study

Parameter[a]	Estimated Range
Soil particle size distribution	Not determined, no data set to estimate ranges
Specific surface area (SA)	Not determined, no data set to estimate ranges
Soil organic carbon content (SOC)	0.5 to 15% (approximately 58% of f_{om})
Black carbon content (BC)	1 to 20% of the total organic carbon
Ratio of hydrogen/carbon/nitrogen (H/C/N)	Not determined, no data set to estimate ranges

[a] Qiu and Davis, 2004

TABLE 2-3
List of Additional Chemicals
Sampling and Analysis Plan in Support of Bioavailability Study

Parameter
Acenaphthene
Acenaphthylene
Acetone
Acetophenone
Acetonitrile
2-Acetylaminofluorene; 2-AAF
Acrolein
Acrylonitrile
Aldrin
Allyl Chloride
4-Aminobiphenyl
Aniline
Anthracene
Antimony
Aramite
Arsenic
Barium
Benzene
Benzo[a]anthracene; Benzanthracene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[ghi]perylene
Benzo[a]pyrene
Benzyl alcohol
Beryllium
alpha-BHC
beta-BHC
delta-BHC
gamma-BHC; Lindane
Bis (2-chloroethoxy)methane
Bis (2-chloroethyl)ether
Bis (2-chloro-1-methylethyl) ether
Bis (2-ethylhexyl)phthlate
Bromodichloromethane
Bromoform; Tribromoethane
4-Bromophenyl phenyl ether
Butylbenzylphthalate
Cadmium
Carbon disulfide

TABLE 2-3
List of Additional Chemicals
Sampling and Analysis Plan in Support of Bioavailability Study

Parameter
Carbon tetrachloride
Chlordane
p-Chloroaniline
Chlorobenzene
Chlorobenzilate
p-Chloro-m-cresol
Chloroethane
Chloroform
2-Chloronapthalene
2-Chlorophenol
4-Chlorophenylphenylether
Chloroprene
Chromium
Chrysene
Cobalt
Copper
m-Cresol
o-Cresol
p-Cresol
Cyanide
2,4-D; 2,4-Dichlorophenoxyacetic acid
4,4'-DDD
4,4'-DDE
4,4'-DDT
Diallate
Dibenz[a,h]anthracene
Dibenzofuran
Dibromochloromethane
1,2-Dibromo-3-chloropropane; DBCP
1,2-Dibromoethane; Ethylenedibromide
Di-n-butylphthalate
o-Dichlorobenzene
m-Dichlorobenzene
p-Dichlorobenzene
3,3'-Dichlorobenzidine
trans-1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethylene

TABLE 2-3
List of Additional Chemicals
Sampling and Analysis Plan in Support of Bioavailability Study

Parameter
trans-1,2-Dichloroethylene
2,4-Dichlorophenol
2,6-Dichlorophenol
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Dieldrin
Diethylphthalate
Thionazin
Dimethoate
p-(Dimethylamino)azobenzene
7,12-Dimethylbenza[a]anthracene
3,3-Dimethylbenzidine
alpha,alpha-Dimethylphenethylamine
2,4-Dimethylphenol
Dimethylphthalate
m-Dinitrobenzene
4,6-Dinitro-o-cresol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Dinoseb
Di-n-octylphthalate
1,4-Dioxane
Diphenylamine
Disulfoton
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Ethylbenzene
Ethylmethacrylate
Ethylmethanesulfonate
Famphur
Fluoranthene
Fluorene
Heptachlor
Heptachlor epoxide
Hexachlorobenzene

TABLE 2-3
List of Additional Chemicals
Sampling and Analysis Plan in Support of Bioavailability Study

Parameter
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachlorophene
Hexachloropropene
2-Hexanone
Indeno(1,2,3-cd)pyrene
Isobutyl alcohol
Isodrin
Isophorone
Isosafrole
Kepone
Lead
Mercury
Methacrylonitrile
Methapyrilene
Methoxychlor
Methyl bromide; Bromomethane
Methyl chloride; Chloromethane
3-Methylcholanthrene
Methylene bromide; Dibromomethane
Methylene chloride; Dichloromethane
Methyl ethyl ketone; MEK
Methyl iodide; Iodomethane
Methyl methacrylate
Methyl methanesulfonate
2-Methylnaphthalene
Methyl parathion; Parathion
4-Methyl-2-petanone
Naphthalene
1,4-Naphthoquinone
1-Naphthylamine
2-Naphthylamine
Nickel
o-Nitroaniline
m-Nitroaniline
p-Nitroaniline
Nitrobenzene
o-Nitrophenol
p-Nitrophenol

TABLE 2-3
List of Additional Chemicals
Sampling and Analysis Plan in Support of Bioavailability Study

Parameter
4-Nitroquinoline-1-oxide
N-Nitrosodi-n-butylamine
N-Nitrosodiethylamine
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodipropylamine
N-Nitrosomethylethyl-1-amine
N-Nitrosomorpholine
N-Nitrosopiperidine
N-Nitrosopyrrolidine
5-Nitro-o-toluidine
Parathion
Polychlorinated biphenyls; PCB
Polychlorinatedibenzo-p-dioxins; PCDD
Polychlorinatedibenzofurans; PCDF
Pentachlorobenzene
Pentachloroethane
Pentachloronitrobenzene
Pentachlorophenol
Phenacetin
Phenanthrene
Phenol
p-Phenylenediamine
Phorate
Pronamide
Propionitrile
Pyrene
Pyridine
Safrole
Selenium
Silver
Silvex; 2,4,5-TP
Styrene
Sulfide
Sulfotepp
2,4,5-Trichlorophenoxyacetic acid
2,3,7,8-Tetrachlorodibenzo-p-dioxin
1,2,4,5-Tetrachlorobenzene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane

TABLE 2-3
List of Additional Chemicals
Sampling and Analysis Plan in Support of Bioavailability Study

Parameter
Tetrachloroethylene
2,3,4,6-Tetrachlorophenol
Thallium
Tin
Toluene
o-Toluidine
Toxaphene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethylene
Trichlorofluoromethane
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
1,2,3-Trichloropropane
o,o,o-Triethylphophorothioate
sym-Trinitrobenzene
Vanadium
Vinyl acetate
Vinyl chloride
Total Xylenes
Zinc

TABLE 2-4
List of Dioxin and Furan Congeners
Sampling and Analysis Plan in Support of Bioavailability Study

Analyte	CAS Number
1,2,3,4,6,7,8-Heptachlorodibenzofuran	67562-39-4
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	35822-46-9
1,2,3,4,7,8,9-Heptachlorodibenzofuran	55673-89-7
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	39227-28-6
1,2,3,4,7,8-Hexachlorodibenzofuran	55684-94-1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	57653-85-7
1,2,3,6,7,8-Hexachlorodibenzofuran	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	19408-74-3
1,2,3,7,8,9-Hexachlorodibenzofuran	72918-21-9
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321-76-4
1,2,3,7,8-Pentachlorodibenzofuran	57117-41-6
2,3,4,6,7,8-Hexachlorodibenzofuran	70648-26-9
2,3,4,7,8-Pentachlorodibenzofuran	57117-31-4
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6
2,3,7,8-Tetrachlorodibenzofuran	51207-31-9
Octachlorodibenzodioxin	3268-87-9
Octachlorodibenzofuran	39001-02-0

TABLE 2-5
Required Analytical Method, Sample Containers, Preservation, and Holding Times
Sampling and Analysis Plan in Support of Bioavailability Study

Analysis	Preparatory/ Analytical Method	Sample Matrix[a]	Container[b]	Preservative[c]	Holding Time[d]
Soil Parameters That May Impact Bioavailability					
Soil particle size	ASTM D2217-85 Wet Preparation ASTM D422 Size separation (sieve)[e] Particle size distribution above and below 250 µm will also be included	S	16-oz glass (500 grams)	< 10°C	NA
Specific surface area	BET nitrogen gas physisorption (static pressure technique)[f]	S	2 or 4-oz glass (10 grams)	< 10°C	NA
Soil organic carbon content	Combustion[f]	S	4-or 8 oz glass (10 grams	< 10°C	NA
Black carbon content	Combustion[f]	S	4-or 8-oz glass (5 grams)	< 10°C	NA
Ratio of hydrogen/carbon/ nitrogen	Elemental analyzer[f] (Prior to analysis samples acidified to remove inorganic carbon)	S	2 or 4-oz glass (2 grams)	< 10°C	NA
Dioxins and Furans					
Dioxins and furans	SW-846 8290/EPA Method 1613	W	1-L amber glass	Cool 4°C	30/45 days[g]
		S	8-oz glass (100 grams)		
Additional Chemicals					
Volatile organic compounds	SW-846 5030B/8260B	W	40-mL, glass	HCl, pH < 2, cool to 4°C	14 days
	SW-846 5035/8260B	S	10 g pre-weighed 40-mL, glass	Methanol, cool to 4°C	Field preserved, 14 days to analysis
Semivolatile organic compounds	SW-846 3510C/3520C/ 8270C	W	1-L amber glass	Cool 4°C	7/40 days[h]
	SW-846 3550B/ 8270C	S	4-oz glass (30 grams)	Cool 4°C	14/40 days[i]
Organochlorine pesticides	SW-846 3510C/3520C/ 8081A	W	1-L amber glass	Cool 4°C	7/40 days[h]
	SW-846 3550B/8081A Cleanup – 3620B	S	4-oz glass (30 grams)	Cool 4°C	14/40 days[i]

TABLE 2-5
Required Analytical Method, Sample Containers, Preservation, and Holding Times
Sampling and Analysis Plan in Support of Bioavailability Study

Analysis	Preparatory/ Analytical Method	Sample Matrix[a]	Container[b]	Preservative[c]	Holding Time[d]
Organophosphorous pesticides	SW-846 3510C/3520C/ 8141A	W	1-L amber glass	Cool 4°C	7/40 days[h]
	SW-846 3550B/8141A	S	4-oz glass (30 grams)	Cool 4°C	14/40 days[i]
Herbicides	SW-846 3510C/8151A	W	1-L amber glass	Cool 4°C	7/40 days[h]
	SW-846 3550B/8151A	S	4-oz glass (30 grams)	Cool 4°C	14/40 days[i]
Polychlorinated Biphenyls	SW-846 3510C/3520C/8082	W	1-L amber glass	Cool 4°C	7/40 days[h]
	SW-846 3550B/8082 Cleanup – 3665A	S	4-oz glass (30 grams)	Cool 4°C	14/40 days[i]
Metals (total)	SW-846 3010A/3020A-SW6010B Series	W	500-mL polyethylene	HNO_3, pH < 2 Cool 4°C	6 months
	SW-846 3050-SW6010B /7000 Series	S	2-oz glass (10 grams)	Cool 4°C,	
Mercury	SW-846 7470A	W	500-mL polyethylene	HNO_3, pH < 2 Cool 4°C	28 days
	SW-846 7471A	S	2-oz glass (10 grams)	Cool 4°C,	
Cyanide	SW-846 9010B/9012A	W	1-L polyethylene	pH>12 NaOH Ascorbic Acid as needed (.6g)	14 days
		S	4-oz glass (30 grams)	Cool 4°C	
Sulfide	SW-846 9030B	W	1-L glass/polyehtylene	pH>12 NaOH and Zinc acetate, Cool 4°C	7 days
		S	4-oz glass (30 grams)	Cool 4°C	
Total Organic Carbon	EPA 415.1/SW-846 9060	W	250-mL glass	H_2SO_4 or HCl pH < 2, Cool 4°C	28 days
		S	2-oz glass (10 grams)	Cool 4°C	
Percent Moisture	EPA 160.3/ASTM D2216	S	2-oz glass (20 grams)	None	NA

TABLE 2-5
Required Analytical Method, Sample Containers, Preservation, and Holding Times
Sampling and Analysis Plan in Support of Bioavailability Study

Analysis	Preparatory/ Analytical Method	Sample Matrix[a]	Container[b]	Preservative[c]	Holding Time[d]

Sample container and volume requirements will be specified by the analytical laboratory performing the tests. Three times the required volume should be collected for samples designated as MS/MSD samples.

Minimum sample volumes are included in parentheses

a Sample matrix: S = surface soil, subsurface soil, sediment; W = surface water.
b All containers will be sealed with Teflon®-lined screw caps.
c All samples will be stored promptly at 4°C in an insulated chest.
d Holding times are from the time of sample collection.
e 30 days to extraction for water, 45 days for analysis.
f Dane and Topp, 2002.
g Brunauer et al., 1938.
h 7 days to extraction for water, 40 days for analysis.
I 14 days for extraction for soil, 40 days for analysis.

°C = degrees Centigrade
mL = milliliter
L = liter
oz = ounce
NaOH = sodium hydroxide
H_2SO_4 = sulfuric acid
BET =Brunauer-Emmett-Teller
EPA = U.S. Environmental Protection Agency
ASTM = American Society for Testing and Materials
NA = not applicable
HNO_3 = nitric acid

Insert Figure 2-1

Insert Figure 2-2

SECTION 3

Data Evaluation Procedures

3.1 Soil Parameters That May Impact Bioavailability

The quantification of soil physical and geochemical properties potentially influencing bioavailability is intended to identify representative soils for use as feedstock in possible future bioavailability studies that will be used estimate relative bioavailability of dioxins and furans in study area soils.

Analytical results for the soil properties will be used to calculate best estimates of the ranges of values for each soil property. This analysis also will provide the basis for recommendations for colleting soils for use in future bioavailability studies that are representative of the soils observed within the study area. Meeting the sampling objectives will require both statistical and spatial evaluation of each of the soil properties as well as the concentrations of dioxins and furans in Midland area soils. Data evaluations will be limited to individual soil properties, consisting of the following procedures:

- Statistical distributions for each soil property of interest will be examined through graphical displays (probability plots of observed values against normal and lognormal theoretical values for the sample size). Conventional goodness-of-fit tests (Shapiro-Wilks and/or Shapiro-Francia tests for sample sizes less than and greater than 50 observations, respectively) to establish appropriate methods to estimate ranges of values for the soil properties within the study area also will be applied in the examination of soil properties of interest. Goodness-of-fit distribution test results will determine which equations are appropriate to provide statistical estimates of interest (ranges, median with confidence intervals, and/or upper bounds of soil property concentrations). If probability plots exhibit distinct breaks over the range of values, individual value-groupings will be plan-view mapped in conjunction with other spatial evaluations.
- Spatial distribution of the soil properties will be performed through plan-view mapping of results. Soil properties exhibiting apparent random distribution of values throughout the area will be considered homogeneous. Soil properties exhibiting localized clusters of elevated or reduced levels will be considered heterogeneous with potentially different subpopulations of concentration levels within the study area. Outputs from the evaluations will include summary statistics of each factor over the study area and the relative homogeneity of each factor and maps supporting application of single or multimodal estimates of factor concentrations. Soil properties exhibiting nonnormal behavior and/or spatially clustered results will be evaluated within spatially localized areas to provide more accurate estimates of concentrations within areas exhibiting localized distributions which differ in other areas.
- If one or more of the soil properties exhibit multimodal and/or spatially heterogeneous behavior, correlations among soil properties will be evaluated to determine which (if any) soil properties coincide spatially. If soil properties covary and exhibit locally

different levels of factor concentrations, populations within the study area will be identified as potentially independent areas for collection of soils for use in bioavailability studies.

- Because the nature of the distribution and relationships of the measures potentially affecting bioavailability is unknown at this time, it is not possible to determine precisely how these groupings will be developed. There are, however, a number of multivariate methods that can be used to further generalize and characterize results. The preliminary univariate and spatial distributions of the bioavailability measures will be supplemented with multivariate methods to determine which measures covary and to what extent they covary. Cluster analyses can then be used to segregate different groups (across the multivariate sample space) to identify individual locations that are more and less similar. These groupings can then be mapped to determine if the groupings represent spatially distinct areas within the study area or suggest study-areawide heterogeneity.

The information on the statistical and spatial distribution of the study parameters will be used to group soils based on their characteristics for the purpose of selecting soils that will be used in a future bioavailability study. The following objectives will be used to guide selection of soils that will be collected for use in the bioavailability study.

- Test soils that are representative of the range of bioavailability parameters measured throughout the study area. Ideally, it is desired to select soils that are representative of low, medium, and high levels of the factors that may influence bioavailability.
- Test soils that are representative of dioxin/furan concentrations found throughout the study area. Soils selected for the bioavailability study should have dioxin/furan concentrations that are representative of the range concentrations that are present within the study area.

The final basis for the selection of soils to be used in the bioavailability study along with the methodology and procedures for collection of the samples will be documented in the future bioavailability work plan that will be submitted to MDEQ for review and approval. This information is not provided in this SAP because the basis for selection of the soils is not yet known.

3.2 Additional Hazardous Substances Results

Data resulting from this portion of the evaluation will provide pre-remedial investigation information on the presence or absence of a broad range of hazardous substances (chemicals) that may be associated with the Dow Plant. If all proposed samples are collected, the resulting sample set will consist of analytical results for both the 0- to 1-inch and 1- to 6-inch sample intervals at 40 locations proximal to the Dow Plant. This data set will be sufficient for the following:

- Evaluate the statistical distributions of analytes detected in each sample interval
- Evaluate the spatial distribution of detected analytes in each sample interval
- Determine whether the distributions of detected analytes in the different sample intervals are statistically similar

The results of these analyses are not intended to be used to conclude whether or not any contaminant detected resulted from historic manufacturing operations at the Dow Plant, complete identification of Dow-related PCOIs, or provide detailed evaluation of potential risk. The following subsections describe the evaluations that will be conducted.

3.2.1 Statistical Distributions

The initial summary of the analytical results will rely upon descriptive statistics for each analyte and sample interval group. The statistical measures reported for each analyte will include the following:

- Number of samples
- Number of detected results
- Frequency of detections (ratio of detected results to total number of samples)
- Range of detected concentrations
- Range of reporting limits for nondetected results
- Standard summary statistics of mean, median, standard deviation, and coefficient of variation
- Preliminary point-interval estimate (for example, mean/median plus confidence intervals)

The statistical information will be presented in tables, which will be organized to clearly identify whether an analyte is present or absent in the designated sample interval.

3.2.2 Spatial Distribution

Plan-view mapping will be used to evaluate the spatial distribution of detected analytes.

3.2.3 Sample Interval Comparisons

Evaluations of both surface and subsurface soils, independently, will rely upon standard summary statistics, as described above. Comparison of the 40 paired surface (0- to 1-inch) and subsurface (1- to 6-inch) sets of results will consist of two steps. First, the pooled set of paired surface and shallow subsurface results will be summarized in the same way. Here, the summary tables will be used to establish which analytes can be reliably compared between the two sample depths. Reliability of comparisons depends, primarily, upon the frequency of detection. Three different cases and applicable evaluation methods are described, as follows:

1. The simplest case occurs for the analytes that are detected in all samples. Those analytes will be compared using conventional paired T-tests and/or the nonparametric analogue of the Mann-Whitney test comparing two populations. Results from the tests will be summarized, listing the analytes for which no statistically significant differences in depths were detected, analytes that were significantly higher in surface samples, and analytes that were significantly lower in surface samples.

2. The second simple case, which precludes comparisons, consists of analytes for which detection frequencies are zero. Statistical comparisons between concentrations of an analyte detected at the two depths would be meaningless because any differences would simply represent differences in laboratory quantitation.

3. The more difficult case includes those analytes for which frequencies of detection lie between 0 and 100 percent. Analytes with extremely low frequencies of detection may be compared strictly on that basis: relative frequency of detection of a given analyte in surface and subsurface samples. Presumably, if there are statistically significant differences in detection frequency, the case would have been made that, to some extent, there are vertical differences in the distribution of the analyte—the substance of the difference can only be evaluated with improved detection limits.

Evaluation results will be summarized as a list of analytes, grouped by case and statistical test result, defining the case and the presence or absence of statistically significant differences in analyte concentration [case 1] or analyte detection frequency [case 3] in surface and shallow subsurface soils.

3.3 Dioxin and Furan Results

Existing information on the concentration and distribution of dioxins and furans in the Midland area soil is limited. To supplement the existing data and begin to develop a better understanding of the distribution and concentrations of these contaminants, samples of surface soils collected and selected for analysis from all of the sampling stations will be analyzed for furans and dioxins. If access is granted by property owners for all sample areas, the investigation will yield results for over 145 locations within the study area. The data will provide useful information for an initial evaluation of both the statistical and relative spatial distribution of dioxin and furan concentrations in surface soils in the Midland area.

Data evaluations will be limited to statistical distribution testing and mapping of toxicity equivalent (TEQ) concentrations, similar to those evaluations described for bioavailability parameters and the additional target analyte chemicals. Where two interval sample data are collected, results for 0- to 1-inch interval samples also will be compared to results for 1- to 6-inch interval samples to determine whether the two intervals are significantly different or can be treated as a single interval.

None of these evaluations require detailed property location or ownership information and can be conducted using the blinded sample identification numbers.

3.4 Effects of Access Constraints

Implementation of this study and the utility of the data obtained depend on success in gaining access to the proposed sample locations. For sample locations not on Dow-owned property, access agreements will be required from owners of public and private property. Dow will describe the confidential aspect of the study and indicate that the property owner has the option of obtaining analytical results from their sampling station if a sample is collected from their property. Given the potential that access may be denied to a number of properties, Dow and MDEQ will review the access agreements obtained in the context of the sample design prior to initiating these field investigations.

The proposed sampling has been designed to obtain data that can be used to characterize soil properties with reasonable confidence over the study area and indicate the presence and level of dioxins and furans and other contaminants in Midland area soils. Once access efforts have been conducted and completed, potential limitations to the sampling design resulting from lack of access will be evaluated with respect to both number and location of properties giving access. Constraints on the number of locations granted access may adversely affect the statistical confidence in interpretation of results. Similarly, access constraints, limiting spatial coverage of the study area, could adversely affect the resulting information on the analytes of interest.

If either sample size or spatial distribution or the combination of sample size and distribution appears to severely limit attainment of project objectives, Dow will meet with MDEQ to discuss potential alternatives.

3.5 Data Gaps

Following the collection of data and subsequent analysis, it may be determined that data gaps exist that may need to be addressed prior to finalizing the bioavailability work plan. Any data gaps identified that affect the ability to select representative soils for use in the bioavailability study will be communicated to MDEQ prior to submission of the work plan in order to identify actions necessary to fill the data gaps. Actions that might be identified include collecting additional samples or conducting additional or different laboratory analyses.

Samples collected to develop additional information on the nature and extent of dioxins and furans will be incorporated into the development of the remedial investigation work plan, and any data gaps identified will be incorporated into sampling proposed as part of that plan. Similarly, sampling to determine whether additional Dow-related hazardous substances are present in Midland area surface soil will be incorporated into the development of the remedial investigation work plan.

SECTION 4

Data Management and Validation

All data collected under this SAP will be managed in accordance with the QAPP (CH2M HILL, 2005c); however, most of the soil properties specified for this SAP are not standard chemical analyses and do not lend themselves to certain types of quality assurance specified in the QAPP (for example, matrix spikes and method blanks cannot be performed for particle size distribution or BC). All analytical results and laboratory reports will be reviewed for accuracy and validated where feasible. The data will then be accessible for evaluation, interpretation, and reporting activities.

SECTION 5

Schedule

Implementation of this SAP can be affected by weather and the time needed to obtain access to a sufficient number of properties. The schedule shown in Table 5-1 has been constructed to identify the key dependencies and time frames.

TABLE 5-1
Schedule
Sampling and Analysis Plan in Support of Bioavailability Study

Date	Action
June 1, 2006	Submit SAP to MDEQ for review and approval.
July 25, 2006	Submit revised SAP to MDEQ addressing MDEQ comments.
August 4, 2006	MDEQ review of SAP.
August 4, 2006	Upon MDEQ review of SAP, initiate mailing of access agreements for parcels within sampling stations.
August 7, 2006	Submit approved SAP to Independent Science Advisory Panel (ISAP) for review.
September 1, 2006	ISAP provides comments on SAP.
September 1 to October 20, 2006	MDEQ review and approval. Finalize SAP and prepare to implement sampling program.
October 23 to November 22, 2006	Field sampling.

There must be access to sufficient properties to achieve minimum investigation objectives and surface soils must be accessible (that is, no snow cover) for sampling be completed on this schedule.

The investigation report will be submitted to MDEQ within 60 days of completion of sampling, analytical work, data validation, data summary, and evaluation. The schedule above is predicated on a number of assumptions over which Dow has no control. Efforts have been made through meetings, conference calls, and electronic communications to prepare a SAP that will be approvable by MDEQ without modification. Based on input from MDEQ, it was assumed that the Independent Science Advisory Panel (ISAP) review would be limited to the verification that the appropriate bioavailability parameters were selected. Review comments from ISAP were assumed to be provided within 30 days.

SECTION 6

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Attachment 1

Blinding Protocol for Sampling and Analysis Plan in Support of Bioavailability Study