

The Dow Chemical Company Part II - Remedial Investigation Report

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Prepared by URS Corporation

### URS

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#### Attachment

Attachment A Ecological Screening Evaluation Support Documentation



#### Appendices

- Appendix A May 2012 Interim Response Activity Designed to Meet Criteria
- Appendix B June 2012 Site-Specific Leachability Study Summary Report
- Appendix C January 2012 Composite Sampling Pilot Study Summary Report
- Appendix D Annual Work Plans and Associated Documentation
- Appendix E Implementation Annual Reports
- Appendix F MDEQ Correspondence
- Appendix G Midland Area Soils Project Database



#### List of Acronyms and Abbreviations

%	percent
AOC	Administrative Settlement Agreement and Order on Consent
bgs	below ground surface
BHC	benzenehexachloride
CMI	Corrective Measures Implementation
COC	contaminant of concern
COI	constituent of interest
COM	Community
CSM	conceptual site model
DCC	direct contact criteria
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DOS	Dow on-site
Dow	Dow Chemical Company
DU	decision unit
EcoSSLs	Ecological Soil Screening Levels
EDA	Exploratory Data Analysis
EE/CA	Engineering Evaluation and Cost Analysis
ESL	Ecological Screening Level
ESLB	Ecological Screening Level Benchmark
FAQs	frequently asked questions
FS	Feasibility Study
FWS	U.S. Fish and Wildlife Service
GIS	Geographic Information System
GSI	groundwater surface water interface
HMW	High Molecular Weight
IA	Industrial.
IB	Industrial.
IRA	Interim Response Activity
IRDC	Interim Response Activity Work Plan Designed to Meet Criteria
LANL	Los Alamos National Laboratory
LCMR	Limited Commercial, Manufacturing and Research
License	Part 111 Hazardous Waste Management Facility Operating License
LMW	Low Molecular Weight
LULC	Land Use Land Classification
MAS	Midland Area Soils
MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
MRA	Midland Resolution Area
MSU	Michigan State University
NOAA	National Oceanic and Atmospheric Administration
PAH	polynuclear aromatic hydrocarbon



Part I	Remedial Investigation Work Plan
Part II	Remedial Investigation Report
Part III	Remedial Action Plan/Corrective Measures Implementation
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofuran
PCOI	potential constituent of interest
ppb	parts per billion
ppt	parts per trillion
QA	Quality Assurance
QC	Quality Control
RA-3	Residential
RA-4	Residential
RAP	Remedial Action Plan
RB	Residential
RC	Regional Commercial or restrictive covenant
RCRA	Resource Conservation and Recovery Act
RI	Remedial Investigation
RIWP	Remedial Investigation Work Plan
RL	reporting limit
RSL	Regional Screening Level
SOW	Scope of Work
SSAL	site-specific action level
SVOC	Semivolatile organic compounds
TAL	target analyte list
TCDD	tetrachlorodibenzo-p-dioxin
TEF	toxic equivalency factor
TEQ	toxic equivalent
UMDES	University of Michigan Dioxin Exposure Study
URS	URS Corporation
USDA	U.S. Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	volatile organic compound
WHO	World Health Organization



#### **1.0 Introduction**

Pursuant to its Part 111 Hazardous Waste Management Facility Operating License (License), The Dow Chemical Company (Dow), with oversight from the Michigan Department of Environmental Quality (MDEQ), has investigated the City of Midland Area Soils (MAS). The purpose of this final Remedial Investigation Report (Part II) for the off-site MAS is to:

- Summarize the results of the Target Analyte List (TAL) screening for relevant human health exposure pathways other than direct contact;
- Summarize and conclude the results of the leachability study completed for the soil to groundwater pathways;
- Document the development of the residential site-specific action level (SSAL) for dioxins and furans in surface soil;
- Summarize the results of the TAL screening performed to identify potential non-dioxin contaminants of concern for the ecological exposure pathway;
- Document the activities completed as part of the Public Participation Plan;
- Document the decision rules and design sampling;
- Summarize the Implementation Annual Reports for the three years of design sampling activities conducted for the soil direct contact exposure pathway; and
- Present the final nature and extent of the Midland Resolution Area (MRA).

The final Remedial Action Plan/Corrective Measures Implementation (RAP/CMI) (Part III), and associated Completion Report will describe the types of remedy used to address current and reasonably anticipated future use and document the completion of remedy for current land use; thereby fulfilling Dow's obligations with respect to the historic airborne releases that have migrated off-site from the Michigan Operations Facility.



#### 2.0 Human Health Soil Exposure Pathway Evaluation

A significant effort has been undertaken to identify primary contaminants of concern (COCs) for human health exposure pathways in relation to MAS. The purpose was to develop a broad TAL of potential COCs, and then narrow that list, through further evaluation and study, to the COCs for the MAS.

The following steps were completed as part of the TAL screening effort:

- TAL development;
- Initial evaluation of TAL based on fate and transport and similar information;
- Determine if TAL compounds, in addition to dioxins and furans, are present at sampling areas adjacent to the Michigan Operations site at levels that require further investigation;
- Analyze for contaminants other than dioxins and furans in MAS;
- Screen TAL according to screening criteria; and
- Review and further reduce remaining TAL categories through collaborative meetings with Michigan Department of Environmental Quality (MDEQ) and United States Environmental Protection Agency (USEPA).

In addition, an evaluation of the dioxin/furan Toxic Equivalency (TEQ) results was performed during this process.

#### 2.1 Human Health Pathway Screening Evaluation

Part I presented the methodology of the human health screening evaluation. Part I presented the data sets used for the screening evaluation and described the summary statistics used. A table of basic summary statistics was prepared for non-dioxin data of the combined data set. These tables included common statistical parameters, such as mean, standard deviation, minimum and maximum detected values, and minimum and maximum reporting limits (RLs) where substances were not detected. These tables were presented in the approved *May 25, 2012 Interim Response Activity Plan Designed to Meet Criteria* (IRDC) (Appendix A).

Part I also presented the TAL pathway specific screening criteria for soil. MDEQ Part 201 Residential Soil Criteria were selected whenever available (MDEQ, 2011). USEPA Regional Screening Levels (RSLs) for Residential Soil were selected whenever MDEQ screening criteria



were not available (USEPA, 2011). Part I also presented the background values used to evaluate metals.

As per MDEQ request, the results for certain classes of analytes were totaled and compared to appropriate criteria. These classes of analytes included endrins, benzenehexachlorides (BHCs), heptachlors, dichlorodiphenyldichloroethane [DDD], dichlorodiphenyldichloroethylene [DDE], dichlorodiphenyltrichloroethane [DDT], endosulfans, chlordanes, and parathions. DDD, DDE, and DDT were also evaluated as individual analytes. For polycyclic aromatic hydrocarbons (PAHs), each result from the seven carcinogenic PAHs (benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene) were multiplied by their respective relative potency factor (RPF), and then summed to achieve the PAH toxicity equivalent quotient (TEQ) (USEPA, 1993). If a sample result was not detected, one half the reporting limit was assumed in the total value. Tables that show the total results for each class of analytes were provided in the approved IRDC (Appendix A).

#### 2.2 TAL Data Screening Categories

As discussed in Part I, screening categories ("Groups") were developed as part of the screening effort to group and organize the non-dioxin constituents to facilitate the data review process. The screening categories are briefly described below, and each constituent, through the screening process, was placed into one of the "Groups."

Below Background (for metals only; compare to background values when available):

- Group A1 Analytes with all detected concentrations and RLs of nondetects below the Statewide Default Background Level.
- Group A2 Analytes with all detected concentrations and RLs of nondetects below the Regional Background Screening Level.

Nondetect Evaluation (for analytes not detected in all collected samples):

• Group B1 – Analytes that were 100% non-detected and all RLs met the MDEQ target detection limits.



- Group B2 Analytes that were 100% non-detected and all off-site sample RLs met the MDEQ target detection levels.
- Group B3 Analytes that were 100% non-detected and all RLs were less than or equal to all Part 201 criteria and USEPA criteria for the given analyte.

Identify Criteria (for detected analytes without Part 201 Criteria and USEPA Criteria):

- Group C1 Analytes that were detected at a frequency less than or equal to 5%, with no Part 201 criteria and USEPA criteria.
- Group C2 Analytes that were detected at a frequency greater than 5%, with no Part 201 criteria and USEPA criteria.

Criteria Comparison (for detected analytes with Part 201 Criteria or USEPA Criteria):

- Group D1 Analytes that were screened-out based on pathway-specific or other evaluation (no analytes were grouped into this category).
- Group D2 Analytes that were detected at a frequency of less than or equal to 5%, and all detected concentrations and RLs of nondetects were less than or equal to Part 201 criteria and/or USEPA criteria.
- Group D3 Analytes that were detected at a frequency greater than 5%, and all detected concentrations and RLs of nondetects were less than or equal to Part 201 criteria and/or USEPA criteria.
- Group D4 Analytes that were not detected at concentrations greater than Part 201 criteria and/or USEPA criteria, but some RLs of nondetects exceeded the criteria.
- Group D5 Analytes that were detected at a frequency of less than or equal to 5%, and one or more detected concentrations were greater than one or more of the Part 201 criteria and/or USEPA criteria.
- Group D6 Analytes that were detected at a frequency of greater than 5%, and 1 or more detected concentrations were greater than one or more of Part 201 criteria and/or USEPA criteria.

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Groups D4, D5, and D6 underwent further evaluation. Some analytes in these categories were eliminated as follows:

- Group E1 Analytes that were eliminated through a spatial (map) review of the data (e.g., the sample results were isolated and/or not spatially connected to Michigan Operations, evidencing that the source is something other than Dow).
- Group E2 Analytes that were evaluated and eliminated based on leach testing results (i.e., the analyte only exceeded leach-based cleanup criteria, but site-specific analysis showed that the analyte was not actually leaching in material amounts).
- Group E3 If this evaluation is necessary, an analyte may be eliminated if it is determined that it was not sourced by Dow.

Each analyte was categorized and screened as discussed above and the results were shown in the approved IRDC (Appendix A).

#### 2.2.1 Results of Category Discussions

Screening categories C1, C2, D4, D5, and D6 were retained for further consideration and each of the analytes were evaluated through a series of meetings and conference calls that were attended by various MDEQ, USEPA, Dow, and URS. During these meetings, analytes were eliminated from the TAL based on a review of the following information:

- Statewide and/or regional background concentrations reported by MDEQ, supplemented by United States Geological Survey (USGS) and Agency for Toxic Substances and Disease Registry (ATSDR);
- Fate and transport parameters;
- Spatial distribution (distribution of detections not indicative of an aerial release); and
- Consideration of reported no observed adverse effect level (NOAEL) values.

The resulting status of each analyte is shown on Figure 2-1. All of the supporting documentation was included in the approved IRDC (Appendix A).



#### 2.2.2 Findings of TAL Screening

The TAL evaluation identified the COCs for the relevant exposure pathways. The TAL analysis also ruled out a number of potential exposure pathways, including volatilization pathways. The screening results for these pathways for non-dioxin analytes are discussed in more detail below. The results are presented in Table 5-2 in the approved IRDC (Appendix A).

As stated in Part I, the groundwater medium is not included in this report since surface and nearsurface soils are the media affected by air emissions and subsequent deposition. Furthermore, because dioxins and furans do not volatilize and do not leach in material amounts into ground or surface water, only the direct contact protection pathway was considered relevant for the IRDC (URS, 2012).

Human health exposure pathways for surface water and sediment are incomplete and there are no exposure points for these two media. Surface water and sediments associated with the Tittabawassee River and its Floodplain will be addressed as a part of the January 2010 Administrative Settlement Agreement and Order on Consent (AOC). The AOC specifies the steps for the Remedial Investigation, Feasibility Study and/or Engineering Evaluation and Cost Analysis (EE/CA), and the Response Design to be taken by Dow, the USEPA, and the MDEQ to evaluate current conditions and assess response options for the Tittabawassee River/Saginaw River & Bay Site.

The following were the potentially relevant soil exposure pathways considered for the MAS project:

- Ingestion and dermal contact with soil (direct contact protection);
- Soil volatilization to indoor air inhalation;
- Soil-to-ambient air inhalation of volatiles and particulates;
- Soil-to-groundwater leaching (drinking water protection);
- Soil-to-groundwater leaching to surface water (surface water interface protection); and
- Soil-to-groundwater leaching dermal contact (groundwater contact protection).

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Soil exposure was evaluated by comparing the soil analytical data to the appropriate residential or non-residential Part 201 generic cleanup criteria (March 25, 2011) (MDEQ, 2011), or by comparing to site-specific cleanup criteria (see Section 4.0) developed for dioxins and furans.

#### 2.3 Soil Direct Contact Exposure Pathway

As discussed above, the TAL evaluation confirmed that dioxins and furans were the COCs driving the presumptive remedy for the MAS to address the direct contact pathway. Aside from dioxins and furans, arsenic was the only TAL analyte that had any sample results that exceeded the residential direct contact pathway. The approved IRDC provides a statistical demonstration of the correlation found between the dioxin/furan TEQ and arsenic (Appendix A). This evaluation demonstrated that soil that may exceed the generic direct contact criteria (DCC) for arsenic also exceeded the proposed SSAL for dioxin/furan TEQ. This relationship was further confirmed by DEQ analysis of retained Midland soil samples for arsenic. No soil samples with TEQ less than the SSAL (see Section 4.0) contained arsenic at levels above the generic DCC. Based on the correlation between the two analytes, any location that indicates that a presumptive remedy is necessary based on a dioxin/furan TEQ concentration, would also address the potential presence of arsenic. Therefore, even though arsenic was retained as a COC, samples will only require analysis for dioxin/furan TEQ to determine the need for a presumptive remedy.

#### Soil Volatilization to Indoor Air Inhalation

The volatilization from soil into indoor air pathway is an incomplete exposure pathway for the MAS project. There is no exposure point present as no residences are located above or adjacent to volatile contaminated soil or groundwater. As part of the TAL screening effort, a comparison of analytical results to relevant indoor air criteria demonstrated that only one detected concentration for hexachlorobenzene exceeded the criteria in an on-site sample (DOS-8), demonstrating that there were no exceedances in off-site MAS.

#### 2.4 Soil to Ambient Air Pathway

Contaminants in soil can volatilize to ambient air or be dispersed as dust particles in the ambient air. Human receptors can be exposed to contaminants by inhaling these vapors or particulates. The Part 201 Volatilization to Ambient Air and Residential Inhalation of Particulate Soil criteria was used to evaluate this exposure pathway in the screening effort.



Hexachlorobenzene was the only analyte with a detected concentration that exceeded the criteria for this pathway. Hexachlorobenzene was detected in 35 samples out of a total of 227 samples collected. Sixteen detections occurred on-site. Only one detected concentration exceeded the volatilization to ambient air pathway criteria (17,000  $\mu$ g/kg). This detected concentration was the maximum detected concentration that occurs on-site at DOS-8 (32,000  $\mu$ g/kg). The maximum detected off-site concentration was 193  $\mu$ g/kg. This off-site maximum detected concentration was on-site at DOS-8 (32,000  $\mu$ g/kg). The volatilization conservatively represents soils in the MRA and did not exceed the soil volatilization to ambient air pathway criteria.

#### 2.5 **Protection of Drinking Water (Soil Leaching to Groundwater Pathway)**

Analytical results were screened against the Part 201 Residential Drinking Water Protection criteria to evaluate the exposure pathway that is protective of the fate and transport pathway of soil contaminants leaching into groundwater that is used as drinking water. A review of all analytes that had concentrations that exceeded the protection of drinking water pathway criteria was performed in 2011-2012 during working meetings and conference calls between MDEQ, USEPA, Dow and URS.

A site-specific leachability study was conducted that included evaluation of the following seven analytes that had concentrations that exceeded the protection of drinking water exposure pathway: arsenic, boron, selenium, strontium, hexachlorobenzene, pentachlorophenol, and methylene chloride. Section 3.0 presents a description of the leachability study and the results.

#### 2.6 Soil Leaching to Groundwater (Dermal Contact with Groundwater)

Analytical results were compared to the Part 201 Residential Groundwater Contact Protection criterion to evaluate the need for further evaluation of this exposure pathway. This exposure pathway considers dermal contact with constituents in groundwater that leached in from the soil. Hexachlorobenzene was the only analyte with a detected concentration that exceeded the criteria for this pathway. Hexachlorobenzene was detected in 35 samples out of a total of 227 samples collected. Sixteen detections occurred on-site. Only one detected concentration exceeded the groundwater contact protection pathway criteria (350  $\mu$ g/kg). This detected concentration was the maximum detected concentration which occurred on-site at DOS-8 (32,000  $\mu$ g/kg). The



maximum detected off-site concentration was 193  $\mu$ g/kg. This off-site maximum detected concentration conservatively represents soils in the study area and did not exceed the dermal contact with constituents that have leached from the soil to groundwater. Based on this, no further evaluation is necessary for the protection of dermal contact with groundwater exposure pathway.

### 2.7 Soil Leaching to Groundwater Which Vents to Surface Water (GSI Protection)

Analytical data results were compared to the Soil Groundwater Surface Water Interface (GSI) Protection Criteria to identify potential COCs for the GSI pathway. A site-specific leachability study was conducted that included evaluation of the following 11 analytes that had concentrations that exceeded the Groundwater Surface Water Interface Protection exposure pathway: hexachlorobutadiene, total cyanide, arsenic, chromium VI, selenium, hexachlorobenzene, fluoranthene, pentachlorophenol, methylene chloride, toluene and total xylenes.

The approved IRDC (Appendix A) presents the detailed results of the human health TAL screening. Analytes that were not included in the leachability study that had detected concentrations that exceed the Soil Protection of GSI Pathway were eliminated based on their spatial distribution and were also documented in this table. A detailed description of the leachability study and the results is presented in Section 3.0.

#### 2.8 Exposure to Soil Impacts via Surface Runoff

The potential for exposure to contaminated soil via surface runoff was a potentially relevant pathway for the MAS. Generic numerical criteria do not exist for evaluating the impact of contaminated soil runoff to surface waters. This exposure pathway was considered on a case-by-case basis in the event that a non-residential property shared a property boundary with a residential property. During the 2014 implementation activities, non-residential properties were sampled and the results were compared to the residential dioxins and furans SSAL of 250 ppt. After the 2014 non-residential sampling activities, a few non-residential properties and undeveloped woodlands were not sampled and were added to the long-term monitoring program. RAP (Part III) presents the long-term monitoring program.



#### 2.9 Summary

The screening of TAL compounds for the MAS project for the human health soil exposure pathways resulted in identification of the direct contact to soil as the relevant human health exposure pathway for the release. The COCs identified for this exposure pathway were dioxins and furans and arsenic.

The remaining hazardous substances evaluated either do not exceed the cleanup criteria or were eliminated from further consideration based on a comparison to background, an evaluation of fate and transport parameters, or review of spatial distribution in the study area. Some of the sampling locations represent localized releases at or directly adjacent to the Midland Plant that are being addressed as part of the Midland Plant Facility Corrective Action Program. The design sampling plan to address the COCs for the soil direct contact exposure pathway is discussed in Section 7.0.

#### Figure 2-1 Summary of Non-dioxin Data Screening Process Part II - Remedial Investigation Report The Dow Chemical Company, Michigan Operations

A1 <sup>1</sup> Metals Screen-out by Statewide Default Background	<u>A2 <sup>1</sup></u> Metals Screen-out by Regional Background Screening Levels	B1 <sup>1</sup> Screen-out by all NDs; RLs met MDE target detection levels	B2 <sup>1</sup> Q Screen-out by off-site NDs; RLs me MDEQ target detection levels	<u>B3 <sup>1</sup></u> Screen-out by all NDs; all RLs ≤ all Part 201/EPA criteria	<u>C1 ²</u> No criteria; detected ≤ 5%	<u>C2 <sup>2</sup></u> No criteria; detected > 5%	D1 <sup>1</sup> Screen-out by other reasons	<u>D2 <sup>1</sup></u> Detected ≤ 5%; screen-out by Part 201/EPA criteria	D3 <sup>1</sup> Detected > 5%; screen-out by Part 201/EPA criteria	D4 <sup>2</sup> Not detected above Part 201/EPA criteria; but have elevated RLs for NDs	D5 <sup>2</sup> Detected ≤ 5%; one or more detected concentrations > Part 201/EPA criteri	<u>D6<sup>2</sup></u> Detected > 5%; one or more detected a concentrations > Part 201/EPA criteria	Eliminate through a review of spacia distribution	E2 Eliminate based on leach testing results	E3 Eliminate - Groundwater Screening (DW & GSI Pathways)	Eliminate - analyte not sourced by Dow
(none)	Barium	Silvex (2,4,5-TP)	bis(2-Chloroisopropyl)ether	Endrin ketone	Delta BHC	Calcium	(none)	2,4,5-T (Trichlorophenoxyacetic Acid)	2,4-D (Dichlorophenoxyacetic Acid)	Thallium	alpha-BHC	Cyanide, Total	Delta BHC	Hexachlorobutadiene		
	Cadmium	3,3'-Dichlorobenzidine	Hexabromobenzene	Heptachlor	Endrin aldehyde	Potassium	_	Endrin	Beryllium	PCBs, Total	Gamma BHC (Lindane)	Mercury	Endrin aldehyde	Lithium	Arsenic Methylene chloride	
	Magnesium	4,4'-Methylene bis(2- chloroaniline)	Hexabromobiphenyl	(E)-alpha,beta-2,3,4,5,6- Heptachlorostyrene	4-Bromophenyl phenyl ether	Thorium	_	Mirex	Sodium	Aldrin	Hexachlorobutadiene	Aluminum	4-Bromophenyl phenyl ether	Fluoranthene	Pentachlorophenol	
	Manganese	2-Chloroethyl vinyl ether		(E)-beta-2,3,4,5,6- Hexachlorostyrene	4-Chlorophenyl phenyl ether	Titanium	_	1,2,4-Trichlorobenzene	Tin	Beta BHC	1,2-Dichlorobenzene	Antimony	4-Chlorophenyl phenyl ether	Zinc	Total Cyanide	
		Ethyl tert-Butyl Ether		(Z)-alpha,beta-2,3,4,5,6- Heptachlorostyrene	Octachlorostyrene	Endosulfan sulfate	_	2,4,5-Trichlorophenol	4,4'-DDD	Dieldrin	Acrylonitrile	Arsenic	Octachlorostyrene	Boron	Selenium	
		Isopropyl Ether		(Z)-beta-2,3,4,5,6- Hexachlorostyrene	1,1-Dichloropropene	Sulfide		Azobenzene	4,4'-DDE	Toxaphene	Chlorobenzene	Boron	1,1-Dichloropropene	Strontium	Toluene	
		Methyl-t-butyl ether		1,2,3-Trichlorobenzene	Propionitrile, Ethyl Cyanide	1,2,3,4-Tetrachlorobenzene		Benzyl alcohol	4,4'-DDT	Tris(2,3- dibromopropyl)phosphate	Tetrachloroethene	Chromium	Propionitrile, Ethyl Cyanide	Hoveeblarebastope	Total Vilance	
		t-Butanol	-	1,2,4,5-Tetrachlorobenzene		1,2,3-Trimethylbenzene	-	Dimethyl phthalate	Chlordane, Total	1,2-Diphenyl-hydrazine		Chromium VI	Calcium	Hexachiorobenzene	Chromium VI	
		tert-Amyl Methyl Ether	-	1,4-Naphthoquinone	-	Methyl lodide (lodomethane)	_	Isophorone	Endosulfan, Total	1,3-Dinitrobenzene	-	Cobalt	Potassium	-	on on on one of the other	
		Vinyl acetate	-	1-Naphthylamine	-	p-Isopropyltoluene	-	n-Nitrosodiphenylamine	Heptachlor epoxide	2,2'-Oxybis(1-Chloropropane)	]	Copper	Thorium	-		
			_	2,3,4,5,6-Pentachlorostyrene			_	Propachlor	Methoxychlor	2,4,6-Trichlorophenol		Iron	Titanium			
				2,4-Dimethylphenol				1,3,5-Trimethylbenzene	2,3,4,6-Tetrachlorophenol	2,4-Dichlorophenol	]	Lead	Endosulfan sulfate			
				2,6-Dichlorophenol 2-Acetylaminofluorene	-			2-Chlorotoluene 2-Hexanone	2-Methylnaphthalene Acenaphthene	2,4-Dinitrophenol 2,4-Dinitrotoluene	-	Lithium Molybdenum	Sulfide 1,2,3,4-Tetrachlorobenzene	-		
				2-Chloronaphthalene	-			Chloroform	Acenaphthylene	2,6-Dimethylphenol	-	Nickel	1,2,3-Trimethylbenzene	-		
				4-Nitrophenol	-			Cyclohexane	Anthracene	2-Chlorophenol	-	Silver	p-lsopropyltoluene	-		
				4-Nitroquinoline-1-oxide	-			Dichlorodifluoromethane	Benzo(a)anthracene	2-Naphthylamine	1	Strontium	Thallium			
				4-tert-Butylphenol				Methyl Ethyl Ketone (2- Butanone)	Benzo(b)fluoranthene	2-Nitroaniline	]	Vanadium	PCBs, Total	-		
				Alpha, Alpha Dimethylphenethylamine				Methyl Isobutyl Ketone (4- Methyl-2-Pentanone)	Benzo(g,h,i)perylene	2-Nitrophenol		Zinc	Aldrin			
				alpha-2,3,4,5,6-	-			n-Butylbenzene	Benzo(k)fluoranthene	3,3'-Dimethylbenzidine	-	Benzo[a]pyrene	Beta BHC	-		
				Benzyl dichloride	-			Styrene	Benzoic acid	3-Methylcholanthrene	-	Dibenzofuran	Dieldrin	-		
				Heptachlorostyrene	_			ten-Butyibenzene	bis(2, sthutheus), phthalate	4,o-Dinitro-z-methylphenol	_		Toxaphene	-		
				Disprienti-A					bis(2-ethylnexyl) phthalate	4-Aminobiphenyi		Hexachiorobenzene	dibromopropyl)phosphate			
				Caprolactam	-				Carbazole	4-Chloro-3-methylphenol		Pentachlorophenol	1,2-Diphenyl-hydrazine			
				cis-Nonachlor Di-n-octylphthalate	-				Chrysene Di-n-butyl phthalate	4-Chloroaniline 4-Nitroaniline	-	Phenanthrene 1,3-Dichlorobenzene	1,3-Dinitrobenzene 2,2'-Oxybis(1-Chloropropane)			
				Ethyl methanesulfonate	-				Fluorene	5-Nitro-o-toluidine	-	1,4-Dichlorobenzene	2,4,6-Trichlorophenol	-		
				Famphur					Indeno(1,2,3-c,a)Pyrene	7,12- Dimethylbenz(a)anthracene		Benzene	2,4-Dichlorophenol			
				Hexachlorocyclopentadiene	-				o-Phenylphenol	Aniline	-	Bromomethane	2,4-Dinitrophenol	1		
				Hexachlorophene Hexachloropropene	-				Phenol Pyrene	Aramite (Total) Benzidine	-	Methylene Chloride Naphthalene	2,4-Dinitrotoluene 2,6-Dimethylphenol	-		
				Isodrin	_				1,2,4-Trimethylbenzene	Bis(2-Chloroethoxy) methane	_	Toluene	2,6-Dinitrotoluene	_		
				Isosafrole Methapyrilene	-				Acetone Isopropylbenzene	Bis(2-Chloroethyl) ether Chlorobenzilate	-	Xylenes, Total	2-Chlorophenol 2-Naphthylamine	-		
				O,O,O-Triethyl	-				N-Propylbenzene sec-Butylbenzene	Chlorpyrifos Cresol, Total	-		2-Nitrophenol	-		
				O,O-Diethyl O-2-Pyrazinyl Phosphorothioate (Thiopazin)	-				Tetrahydrofuran	Diallate (total of cis and trans	-		3,3'-Dimethylbenzidine	-		
				Theopholetineate (Thionazin)						loomoroy						
				o,p'-DDD o-Toluidine	-				·	Dibenz(a,h)anthracene Diethyl phthalate	-		3-Methylcholanthrene 4,6-Dinitro-2-methylphenol	-		
				Parathion, Ethyl (Parathion)	-					Dimethoate	-		4-Aminobiphenyl	-		
				Pentachlorobenzene	-					Dinoseb	-		4-Chloro-3-methylphenol	-		
				Pentachloronitrobenzene	-					Diphenylamine	-		4-Chloroaniline	-		
				p-Phenylenediamine	-					Disulfoton	_		4-Nitroaniline	-		
				Ronnel	-					Hexachloroethane Kepone	-		5-Nitro-o-toluidine 7,12- Dimethylhenz(a)apthroppe	-		
				Svm-Trinitrobenzene	-					Methyl methanesulfonate	-		Aniline	-		
				trans-Nonachlor	-					Nitrobenzene	_		Aramite (Total)	-		
				1,1,1,2-Tetrachloroethane						n-Nitrosodiethylamine			Benzidine			
				1,1,1-Trichloroethane						n-Nitrosodimethylamine	_		Bis(2-Chloroethoxy) methane			
				1,1-Dichloroethane	_					N-Nitroso-di-n-butylamine			Bis(2-Chloroethyl) ether	_		
				2,2-Dichloropropane						n-Nitrosomethylethylamine	-		Chlorpyrifos	-		
				4-Chlorotoluene Bromobenzene						n-Nitrosomorpholine n-Nitrosopiperidine			Cresol, Total Diallate (total of cis and trans			
				Bromodichloromethane						n-Nitrosopyrrolidine	-		Isomers) Dibenz(a,h)anthracene			
				Carbon disulfide						p-Dimethylaminoazobenzene	-		Dimethoate			
				Chlorobromomethane						Pentochlorethane	-		Dinoseb			
				Chloroethane cis-1,2-Dichloroethene						Phenacetin Phorate	-		Diphenylamine Disulfoton			
				cis-1,3-Dichloropropene	_					Pyridine			Hexachloroethane	+		

Figure 2-1 Summary of Non-dioxin Data Screening Process Part II - Remedial Investigation Report The Dow Chemical Company, Michigan Operations

A1 <sup>1</sup>	A2 <sup>1</sup>		B2 <sup>1</sup>	B3 <sup>1</sup>	C1 <sup>2</sup>	C2 <sup>2</sup>	<u>D1 1</u>	D2 <sup>1</sup>	D3 <sup>1</sup>	D4 <sup>2</sup> Not detected above Part 201/EPA	$\underline{D5^2}$	E1 <sup>3</sup>	E2	E3	E4
Default Background	Background Screening Levels	target detection levels	MDEQ target detection levels	Part 201/EPA criteria	No criteria; detected ≤ 5%	No criteria; detected > 5%	Screen-out by other reasons	201/EPA criteria	201/EPA criteria	criteria; but have elevated RLs for NDs	concentrations > Part 201/EPA criteria concentrations > Part 201/EPA criteria	distribution	results	(DW & GSI Pathways)	Dow
			Ī	Dibromochloromethane						Tetraethyl Dithiopyrophosphate		Methyl methanesulfonate			
			-							(Surotepp)					
				Dibromomethane						1,1,2,2-Tetrachloroethane		Nitrobenzene			
			Ī	Ethyl methacrylate Isobutanol						1,1,2-Trichloroethane 1,1,2-Trichlorotrifluoroethane		n-Nitrosodiethylamine n-Nitrosodimethylamine			
			-	n-Butanol						1.1-Dichloroethene		N-Nitroso-di-n-butylamine			
			-	historianoi								N-Nicoso-Grin-Dutylamine			
				trans-1,2-Dichloroethene						1,2-Dibromo-3-chioropropane		n-initrosodi-n-propylamine			
			1	trans-1,3-Dichloropropene						1,2-Dibromoethane (EDB)		n-Nitrosomethylethylamine			
			-	Trichlorofluoromethane						1.2-Dichloroethane		n-Nitrosomorpholine			
				Trihalomethanes, Total						1,2-Dichloropropane		n-Nitrosopiperidine			
										1,3-Dichloropropene, Total		Parathion, Methyl			
										1,4-Dioxane		p-Dimethylaminoazobenzene			
										2-Propanol Acetonitrile		Pentochlorethane Phenacetin			
										Acrolein Allyl Chloride (3-Chloropropene)		Phorate Pvridine			
										Carbon totrachlarida		Safrola			
										Chloroprene (2-Chloro-1,3-		Tetraethyl Dithiopyrophosphate			
										Butadiene)		(Surrotepp)			
										Ethyl Benzene		1,1,2,2-Tetrachloroethane			
										Ethyl ether Ethylene oxide		1,1,2-Trichloroethane 1,1,2-Trichlorotrifluoroethane			
										Methyl methacrylate		1.1-Dichloroethene			
										Methylacrylonitrile		1,2-Dibromo-3-chloropropane			
										trans-1,4-Dichloro-2-butene		1,2-Dibromoethane (EDB)			
										Trichloroethene (TCE)		1,2-Dichloroethane			
										Vinyl chloride	]	1,2-Dichloropropane 1,3-Dichloropropane			
												1,3-Dichloropropene, Total			
												1,4-Dioxane			
												Acetonitrile			
												Allyl Chloride (3-Chloropropene)			
												Carbon tetrachloride			
												Chloroprene (2-Chloro-1,3- Butadiene)			
												Ethyl Benzene Ethyl ether			
												Ethylene oxide			
												Methyl methacrylate Methylacrylonitrile			
												trans-1,4-Dichloro-2-butene			
												Trichloroethene (TCE)			
												alpha-BHC			
												1,2-Dichlorobenzene			
												Acrylonitrile Chlorobenzene			
												Tetrachloroethene Cyanide, Total			
												Mercury			
												Antimony			
												Cobalt			
												Copper Iron			
												Lead Molybdenum			
												Nickel Selenium			
												Silver			
												Benzo[a]pyrene			
												Fluoranthene			
												Phenanthrene 1,3-Dichlorobenzene			
												1,4-Dichlorobenzene Benzene			
												Bromomethane Methylene Chloride			
												Naphthalene			
												Xylenes, Total			
Notes:															
Figure 5-4 serves as a companio Screen-out	on figure to this table.	· · · · · · · · · · · · · · · · · · ·													
Eliminate May require additional ovelvation										······					
Requires additional evaluation						·				·					
<sup>1</sup> Anayltes in categories A1, A2, <sup>2</sup> Analytes in categories C1, C2	B1. B2, B3, D1, D2, and D3 scree D4, D5, and D6 were initially retain	ened-out from further evaluation base	ed on the screening category th eries of meetings and conference	ney were placed. ce calls (held in May through July 1	2011) attended by MDEO_EPA	and Dow staff									
<sup>3</sup> Analytes from categories C1, C	2, D4, D5, and D6 (shaded in gra	ay) were placed in category E1 when	the analyte was determined to	be eliminated from further evaluat	ion based on the results of the n	neetings and conference calls.								;   	



### 3.0 Leachability Study

Based on the TAL screening effort completed for the MAS project, analytical results from previous studies performed in 2005, 2006 (CH2M Hill, 2007), and 2010 (URS, 2011b) were identified above MDEQ Residential Generic Groundwater Drinking Water Protection (DW) and soil GSI protection criteria. A Work Plan was submitted July 1, 2011 detailing a proposed soil sampling study to determine the level at which the compounds of interest (COIs) leach from samples representative of the soils in the Midland area (URS, 2011a).

#### 3.1 Background

The screening and preliminary results of the TAL were presented in the 2010 Field Pilot Characterization Plan Summary Report that was submitted August 26, 2011 (URS, 2011b). A summary of the COI screening of analytical results is presented in the IRDC (Appendix A). As shown in Appendix A, a number of analytes were not detected or were detected below generic MDEQ criteria or applicable background levels, and therefore have been eliminated as COIs and excluded from the TAL.

The following list of COIs were identified for the leachability study through the TAL screening effort:

- Arsenic
- Boron
- Chromium (Hexavalent)
- Total Cyanide
- Fluoranthene
- Hexachlorobenzene
- Hexachlorobutadiene
- Lithium
- Methylene Chloride
- Pentaclorophenol
- Selenium
- Strontium
- Toluene



- Total Xylene
- Zinc

Figure 3-1 presents the Leachability Study Process Flowchart and summarizes the steps of the leach study, including the identification of COIs, which is Step 1 of the flow chart.

This section details the results of the samples collected to determine if COIs in MAS can be expected to leach at concentrations that exceed MDEQ residential DW and GSI criteria. The process for determining if the COIs listed above should be excluded from the TAL is presented on Figure 3-1 as Steps 2 and 3.

#### **3.2** Deviation from Leach Study Work Plan (Additional Analytes)

The final COI list for the leachability study presented above was agreed upon during discussions with the MDEQ in conference calls conducted May through October 2011. Because the Work Plan and *2010 Field Pilot Characterization Plan Summary Report* were submitted before the final meeting, the final COI list differs from the lists submitted in those reports (URS, 2011b). During the final meeting on October 6, 2011, mercury, silver, benzidine, and ethylene dibromide were eliminated from further consideration, as well as the six analytes the MDEQ had placed on hold pending MDEQ review (acrylonitrile, ethyl cyanide propionitrile, octachlorostyrene, 1,2,3-trimethylbenzene, methylene iodide, and thorium). Lithium was the only COI added to the final list during the October 6, 2011 meeting.

#### **3.3** Soil Sampling Activities

The July 1, 2011 Work Plan provided the strategy and scope of work to address the key elements required to complete sampling for leach testing in the Study Area. The following section summarizes the activities that were performed in order to successfully complete sampling.

Sample collection and analysis is presented on Figure 3-1 as Step 2 of the Leachability Study Process Flowchart.

#### 3.3.1 Soil Work Summary

Soil samples were collected in November 2011 from select locations and submitted for both totals analysis and leach testing for the leach study COIs. The soil sampling and leach testing activities were conducted in areas on or around the Michigan Operations facility where relevant

# URS

default cleanup criteria for soil were exceeded in soils and are believed to be representative of the study area as a whole. These areas included:

- The highest results (generally in or near the plant site);
- Areas where limited data are available (generally to the southwest of the plant site); and
- Areas that are representative of the areas predominantly downwind from historic releases from the plant site.

This methodology allowed the total results to be correlated with results from leaching analyses. These resulting patterns identified the potential of COIs to leach to groundwater within the study area.

Furthermore, the MDEQ generic GSI protection criteria for soils used in the initial screening process are based on calculated cleanup criteria derived from conservatively assumed surface water hardness and pH data of approximately 100 mg/L and 8.2 units, respectively. In September 2011, four surface water samples were collected from the main water bodies/open drains in the study area to evaluate site-specific hardness and pH data. The surface water hardness and pH data from representative locations were utilized to calculate facility-specific criteria when applicable. For the detailed information documenting the field activities, sampling, and Quality Assurance and Quality Control (QA/QC) associated with the soil study, refer to the June 1, 2012 *Site-Specific Leachability Study Summary Report*, attached to this report as Appendix B.

#### 3.3.2 Results and Discussion

Total soil concentration and soil leachate concentration results were used to evaluate the potential of the selected COIs in MAS to leach to groundwater at levels greater than the generic residential DW and GSI criteria. A summary of the results of the leachate study sampling effort and comparison to criteria are shown on Table 3-1. Leach testing results were compared to generic residential MDEQ DW and GSI criteria to estimate the potential for soils to leach at concentrations that may cause impact to groundwater. For metals, if a background level was higher than the generic criteria, the background level was used in place of the criteria (as indicated on Table 3-1 for arsenic, cyanide, lithium, and selenium). For zinc, the GSI facility-specific criteria used were derived using the MDEQ GSI and GSI protection criteria spreadsheet



(MDEQ, 2011). The facility-specific criteria were calculated using site-specific pH and hardness data collected from nearby receiving waters and the most conservative criteria were selected. The surface water results and MDEQ calculation worksheets can be found in the June 1, 2012 *Site-Specific Leachability Study Summary Report* (Appendix B).

#### 3.3.3 COI Evaluations

As summarized on Figure 3-1, COIs were eliminated from the TAL if all total soil results were below criteria, or if the COI had total soil results greater than criteria, all of the leachate results for that COI were below criteria. COIs were considered to have the potential to leach to groundwater if co-located soil and leachate results were identified above relevant criteria. For those COIs, further evaluation was conducted to determine if the COI warranted inclusion in the TAL for the site. A detailed discussion of the results for each analyte was presented in the June 1, 2012 *Site-Specific Leachability Study Summary Report* (Appendix B). The conclusions of the report are reviewed below.

#### 3.3.4 Soil Leachability Study Conclusion

Pursuant to the Leachability Study Process outlined in Figure 3-1, 11 compounds were excluded from further consideration because they were not detected in either soil or Synthetic Precipitation Leaching Protocol (SPLP) leachate above the DW or GSI criteria. These include:

- Boron
- Hexavalent Chromium
- Total Cyanide
- Fluoranthene
- Hexachlorobenzene
- Lithium
- Methylene Chloride
- Selenium
- Strontium
- Toluene
- Total Xylenes



Additional evaluation was conducted for the remaining four (4) compounds (arsenic, hexachlorobutadiene, pentachlorophenol, and zinc) to determine if the compound should be retained for the TAL. The lines of evidence presented in Section 3.0 of the June 1, 2012 *Site-Specific Leachability Study Summary Report* (Appendix B) for each of these compounds successfully demonstrated that detected concentrations of the COIs included in this study in MAS are not leaching into area groundwater above the DW and/or GSI pathway. Dow recommended that all of the COIs included in this study be eliminated from additional consideration and excluded from the TAL. This report was discussed in detail with MDEQ in June 2013 and the next section presents the outcome of that meeting.

#### 3.4 Shallow Groundwater Study

The June 1, 2012 *Site-Specific Leachability Study Summary Report* (Appendix B) presented the results of the leach study. A review of the Summary Report findings was conducted during a meeting between MDEQ, USEPA, Dow, and URS on June 27, 2013. As discussed during the June 27, 2013 meeting, Column E2 in Figure 2-1 presents the analytes that were eliminated as a COI based on the findings of the leach study.

During the June 27, 2013 meeting, the COIs that were not eliminated based on the findings of the leachability study were retained for further evaluation through shallow groundwater screening and are as follows:

- Arsenic
- Chromium (Hexavalent)
- Cyanide (Total)
- Methylene Chloride
- Pentachlorophenol
- Selenium
- Toluene
- Xylene (Total)

A Work Plan was submitted September 19, 2013 detailing a proposed shallow groundwater study to verify and support the results of the leach study for COIs in soils in the Midland Area (URS,



2013). The objective of this study was to determine if the COIs in soil were leaching into the shallow groundwater at concentrations above generic MDEQ Residential DW and GSI Cleanup Criteria. The sampling activities took place September, October, and November 2013, with collection of eighteen (18) additional groundwater samples in June and August of 2014 for Total Cyanide.

This section details the results of the shallow groundwater samples collected to determine if COIs in MAS have leached at concentrations that exceed MDEQ residential DW and GSI criteria. The process for determining if the COIs listed above should be excluded from the TAL is presented on Figure 3-1 as Steps 2 and 3.

#### 3.4.1 Shallow Groundwater Sampling Activities

The September 19, 2013 Work Plan provided the strategy and scope of work to address the key elements required to complete shallow groundwater sampling to confirm leach testing results in the Study Area. The following section summarizes the activities that were performed in order to successfully complete sampling.

Sample collection and analysis is presented on Figure 3-1 as Step 2 of the Leachability Study Process Flowchart.

#### 3.4.2 Shallow Groundwater Work Summary

Shallow groundwater samples were collected in September, October and November 2013 from select locations and submitted for totals analysis for the shallow groundwater COIs (Section 3.1). The groundwater sampling activities were conducted in both new and existing shallow wells with screen intervals installed within the uppermost saturated soil unit, where the groundwater is present and where there is no other known source present. A series of four new shallow wells were installed at the Southwest Plant Perimeter, along Poseyville Road and the southern boundary of Poseyville Landfill (see Figure 3-2). Existing wells that were sampled included shallow groundwater wells along the Northeast Plant Perimeter (see Figure 3-3). These areas included:

• Locations that are representative of areas predominantly downwind from historic releases from the Midland Plant site; and



• Locations closest to properties that use groundwater as a drinking water source.

The results were then compared to MDEQ residential DW and GSI criteria shown in Table 3-1.

#### 3.4.3 Field Activities

The following sections detail the well installation and sampling procedures that were utilized for the MAS field activities. Samples were collected in accordance with USEPA and MDEQ protocols as outlined in the Work Plan.

#### **3.4.3.1** Well Installation and Development

The well installation and development activities implemented for this effort were completed in September 2013 and are described in the Work Plan for Limited Groundwater Sampling and Screening (URS, September 2013). Figures 3-2 and 3-3 present the wells that were installed for this effort.

#### 3.4.3.2 Shallow Groundwater Sampling

Shallow groundwater samples were collected in each of the wells listed below and presented in Figures 3-2 and 3-3. Three rounds of shallow groundwater samples were collected over a three month timeframe from September – November 2013; with some additional sampling for total cyanide in June and August 2014.

Northeast Plant Perimeter	Southwest Plant Perimeter
4363	5385
6176	8817
MW-10 (MW-6175 Area)	8818
4355	8874
6177	8875

Static water level (SWL) readings were obtained prior to purging to the nearest hundredth of a foot using a clean electric water level indicator.

Groundwater samples collected for analyses were representative of the ground water moving in the aquifer, in the uppermost saturated zone and in communication with the unsaturated zone. These samples represent the zone where leached contaminants from soils impacted by aerial deposition would be present. Sampling procedures assured that the COI concentrations were



representative of natural groundwater and not the stagnant water in the well casings, using both low flow and fixed volume purging. These two methods are described below.

#### 3.4.3.3 Low-flow Purging

Low-flow purging, commonly referred to as minimal drawdown or low stress purging is essentially a means of collecting a groundwater sample from a well that is the most representative of actual groundwater in the formation. This is effectively completed by removing water from the well slow enough that the formation can re-charge the well at least as fast as the pumping rate and monitoring water quality parameters to achieve stabilization of the readings.

To assure formation water was being pumped, the pump intake or inlet tubing is set within the lower half of the screen interval, and the pumping rate is adjusted so that the static water level readings eventually stabilize. This assures that groundwater is recharging the well at an equivalent rate to pumping. Flow rate and static water level readings were recorded on the field data sheets.

While purging, the following water quality measurements were made using a flow-through cell and multi-parameter field meter:

- Dissolved oxygen;
- Temperature;
- Specific conductivity;
- pH;
- Reduction / Oxidation potential; and
- Turbidity.

Stabilization is generically defined when the values measured meet the criteria listed in the table below. When these criteria are met, formation water is obtained and sampling may proceed. Knowledge of site geology, well installation, and sampling methodology is helpful in evaluating deviations from the generic stabilization criteria. Deviations from the generic criteria are noted on individual field data sheets. Sampling proceeded after the point at which all parameters stabilized, however the pumping rate during sampling remained consistent with the purging rate



(pump speed was not increased) to maintain stability with the aquifer. Groundwater samples collected in this manner were not filtered prior to analysis.

#### **Generic Stabilization Criteria**

Parameter	Generic Stabilization Criteria
Dissolved Oxygen	+/- 10% or < 0.3 mg/L
Specific Conductivity	+/- 3%
рН	+/- 0.1 SU
Reduction / Oxidation potential	+/- 10 mV
Turbidity	< 20 NTU or +/- 10%

#### 3.4.3.4 Fixed Volume Purging

In locations where transmissivity of the aquifer limits the recharge rate to the well (either due to low hydraulic conductivity or limited saturated thickness), fixed-volume purging was used. For low-volume recovery wells, fixed-volume purging includes removing all of the water within the well casing, commonly referred to purging to dryness. Groundwater samples were collected within 24 hours of purging to dryness. Wells with sufficiently low transmissivity require purging to dryness more than once. Groundwater samples collected in this manner were filtered prior to analysis.

#### 3.4.3.5 Sample Collection and Analyses

Each sample was assigned a unique sample identification number consistent with the previous 2010 Dow sampling effort and current project needs. Grab was the only sample type collected. Each sample location had a unique identification that relates to the location of the sample. Each sample was uniquely identified by location designation. Sample labels were affixed to each sample at the time of collection. The label included the following information at a minimum:

- Sample location designation;
- Date and time sampled;
- Preservatives added (as required);
- Sampler's initials; and
- Required analysis.



Environmental samples were shipped using standard chain-of-custody procedures.

Environmental soil samples were analyzed for the analytes listed in Section 1.1. These analyses included select metals using USEPA Method 6020 and 218.7; select chlorinated herbicides using USEPA Method 8151; cyanide using USEPA Method 9014 or 9012A; and select volatile organic compounds using USEPA Method 8260B.

#### 3.4.3.6 Quality Assurance/Quality Control

The sampling activities included implementation of quality assurance/quality control (QA/QC) protocols for environmental samples. The QA/QC measures are summarized below:

- Trip Blanks
- Matrix Spike and Matrix Spike Duplicate (MS/MSD)
- Temperature Blanks
- Method Blanks
- Lab Control Samples
- Evaluation of Sample Surrogate Recoveries

#### 3.4.4 Shallow Groundwater Study Conclusion

Shallow groundwater concentration results were used to evaluate if the COIs (listed in Section 3.1) are leaching into the shallow groundwater at concentrations above generic MDEQ Residential DW and GSI cleanup criteria. As presented in Figure 3-1, Step 4 of the Leachability Study Process Flowchart summarizes the procedure for evaluating the results of each COI and determining if the COI should be excluded from the TAL.

Laboratory testing for the groundwater concentrations of COIs identified for study during this investigation were required to achieve a reliable level of detection equivalent to or less than the relevant groundwater criteria. This objective was met.

A summary of the results of the shallow groundwater study sampling effort and comparison to criteria are shown on Tables 3-2 thru 3-5. Shallow groundwater results were compared to generic residential MDEQ DW and GSI criteria to determine if the COIs are leaching to shallow groundwater at concentrations that may cause impact to groundwater.



#### 3.5 Shallow Groundwater Results

For those COIs with co-located soil and leachate results identified above relevant criteria, further evaluation, including analyzing for the COIs in shallow groundwater was conducted to determine if the COI warrants inclusion in the TAL for the site.

With the exception of total cyanide, all COI samples analyzed for in shallow groundwater fall into one of two categories:

- Not detected in shallow groundwater; or
- Detected in shallow groundwater at concentrations that do not exceed criteria.

Both of these categories and total cyanide are discussed in further detail below.

#### 3.6 Substances Not Detected in Shallow Groundwater

The following analytes were not detected in any of the shallow groundwater samples collected during this effort:

- Methylene Chloride
- Toluene
- Total Xylenes
- Pentachlorophenol

These analytes were not detected in either the Dow or MDEQ data sets. The detection limits were less than or equal to the relevant criteria. Based on the non-detected results, together with the conclusions for each of the analytes in the *Site-Specific Leachability Study Report* (Appendix B), and the discussion of these results on March 13, 2014 between Dow, MDEQ, and URS, these four analytes were eliminated from further evaluation for the soil to groundwater pathways.

#### 3.7 Substances Detected Below Criteria

Shallow groundwater sample results indicated that the following analytes were detected in some samples:



- Arsenic
- Chromium VI
- Selenium

As shown in Tables 3-2 through 3-5, while these metals were detected in shallow groundwater, none of the detections exceeded relevant criteria. Based on this and the conclusions from the *Site-Specific Leachability Summary Report* (Appendix B), these metals were eliminated from further evaluation for the soil to groundwater pathway.

#### 3.8 Total Cyanide

Total cyanide was not detected at a RL of 5.0  $\mu$ g/L in thirty-six (36) of the fifty-five (55) shallow groundwater samples collected during this effort, representing eight (8) of the ten (10) total wells included in the study. The remaining nineteen detections occurred in two of the ten wells sampled as part of this project. One detection at MW-5385 exceeded the Residential Drinking Water Cleanup Criteria of 200  $\mu$ g/L, but this result was not replicated in either a split of the sample nor in subsequent sampling events. All of the concentrations measured at the two wells where cyanide was detected exceeded the GSI Protection Cleanup Criteria of 5.2  $\mu$ g/L. Three of the detections range from 5.5 to 6.5  $\mu$ g/L, very close to the GSI Protection Cleanup Criteria. One of the results with a concentration of 5.5  $\mu$ g/L also identified the presence of cyanide in a corresponding blank sample and another sample at 32  $\mu$ g/L analyzed by MDEQ identified matrix interference.

For the two wells where cyanide was detected, it was consistently detected at MW-4355 in eleven (11) out of twelve (12) total samples. In split samples, both Dow and MDEQ laboratories detected cyanide at well 4355 ranging from 6.5 to 18  $\mu$ g/L.

Cyanide was detected in MW-5385 inconsistently in only four (4) of the fourteen (14) total samples collected. In split samples from MW-5385, the Dow contract lab identified 560  $\mu$ g/L of cyanide in September 2013, while MDEQ measured 32  $\mu$ g/L, also noting matrix interference. Additional split sampling conducted in October of 2013 and August of 2014 resulting in no further detections by the Dow contract lab at a RL of 5  $\mu$ g/L and concentrations measured by MDEQ were 14 to 18  $\mu$ g/L.



The following lines of evidence were developed as a result of the shallow groundwater study:

- The detection frequency for cyanide in the shallow groundwater study area was 33% and all detections occurred in two (2) out of the total 10 wells sampled for the study;
- Of the two wells, cyanide was consistently detected in only one (1) of the wells; and
- Cyanide was detected at a concentration greater than the Generic Residential Drinking Water Cleanup Criteria in only one out of 55 samples.

Based on these lines of evidence, cyanide in groundwater does not appear to be from wide spread aerial dispersion and subsequent leaching to groundwater but rather a local condition affecting a small area. Cyanide is eliminated from the TAL for the MAS project. Cyanide presence at MW-4355 will be further evaluated as part of the site corrective action program.

#### 3.9 Conclusion

The results of this leachability study have been reviewed for the leach study COIs. Pursuant to the Leachability Study Process outlined in Figure 3-1, the remaining eight (8) compounds retained for further evaluation have been excluded from additional consideration because they were not detected in shallow groundwater above the DW or GSI criteria, or their distribution is not reflective of leaching from soil as a result of historical aerial releases. These include:

- Arsenic
- Hexavalent Chromium
- Total Cyanide
- Methylene Chloride
- Pentachlorophenol
- Selenium
- Toluene
- Total Xylenes

The lines of evidence presented for total cyanide at remaining wells successfully demonstrate that detected concentrations of cyanide and all other COIs included in this study in MAS are not



leaching into area groundwater above the DW and/or GSI pathway and all of the COIs included in this study were eliminated from additional consideration and excluded from the TAL.





Note: Leach testing results in soil were compared to generic residential MDEQ DW and GSI protection criteria to estimate the potential for soils to leach at concentrations that may cause impact to groundwater. For metals, if a background level was higher than generic criteria, the background level was used in place of the criteria. For zinc, the GSI facility-specific criteria used were derived using the MDEQ GSI protection criteria spreadsheet (MDEQ, 2011).

Shallow groundwater testing results were compared to generic residential MDEQ DW and GSI criteria to determine if COIs have leached to groundwater from soil at concentrations that may cause impacts to groundwater.

Acronyms: COIs = Constituents of Interest DW = Drinking Water GSI = Groundwater/Surface Water Interface TAL = Target Analyte List






# 4.0 Summary of the Basis for the Residential Site-Specific Action Level

This section presents the basis for the residential property SSAL developed and approved for dioxin/furan TEQ. This documentation was provided in the approved IRDC (Appendix A). The SSAL serves as the threshold trigger level for requiring presumptive response activities at a particular residential property. The approved SSAL is 250 ppt TEQ. For the City of Midland, a SSAL for dioxin/furan TEQ of 250 ppt TEQ (based on the 2005 World Health Organization (WHO) toxic equivalency factor (TEFs) [Van den Berg et al, 2006]) is protective of the public health, safety and welfare and appropriately takes certain updated and site-specific information into account while leaving a protective margin of safety. This action level serves as a "site-specific cleanup criterion" as described in Part 201 of Michigan's Natural Resources and Environmental Protection Act.

The SSAL is a site-specific criterion that applies in lieu of the MDEQ's default generic DCC for dioxin/furan TEQ of 90 ppt. The default and site-specific parameter inputs and equations are shown below:

Parameter Inputs		MDEQ Default	Site- Specific
TR	target risk (unitless)	1.00E-05	1.00E-05
AT	averaging time (days)	25550	25550
CF	conversion factor (ng/kg)	1.00E+12	1.00E+12
SF	cancer slope (mg/kg-day)-1	7.50E+04	7.50E+04
EFi	ingestion exposure frequency for soil and dust (days/yr)	350	260
IF	age-adjusted soil ingestion factor (mg-yr/kg-day)	114	114
AEi	ingestion absorption efficiency (unitless)	0.5	0.38
EFd	dermal exposure frequency for soil and dust (days/yr)	245	260
DF	age-adjusted soil dermal factor (mg-yr/kg-day)	353 <sup>a</sup>	353
AEd	dermal absorption efficiency (unitless)	0.03	0.032
SDCF	soil and dust contribution factor (unitless)		0.5
EFi-dust only	ingestion exposure frequency for dust only (days/yr)		90
EFd-dust only	dermal exposure frequency for dust only (days/yr)		90
RDSF	relative dust:soil concentration factor (unitless)		0.5
Parts per trillion (ppt) TEQ <sup>b</sup>		9.0E+01	2.6E+02

Note:

MDEQ originally used an age-adjusted DF of 2,442 mg-yr/kg-day when the generic direct contact criterion of 90 ppt TEQ was

developed. However, MDEQ has since adopted and promulgated an updated DF of 353 mg-yr/kg-day.

<sup>&</sup>lt;sup>b</sup> TEQ is calculated based on the 2005 WHO TEFs ([Van den Berg et al, 2006], see Table 4-1 in Part I).



$$MDEQ\_Algorithm = \frac{TR \times AT \times CF}{SF \times \left[ \left( EF_i \times IF \times AE_i \right) + \left( EF_d \times DF \times AE_d \right) \right]}$$

$$Site - Specific \_ Algorithm = \frac{TR \times AT \times CF}{SDCF(EF_i \times IF \times AE_i) + SDCF(EF_i \times IF \times AE_i \times RDSF) + (EF_{i-dustonly} \times IF \times AE_i \times RDSF)} + (SDCF(EF_d \times DF \times AE_d) + SDCF(EF_d \times DF \times AE_d \times RDSF) + (EF_{d-dustonly} \times DF \times AE_d \times RDSF)$$

The SSAL was based on the following modifications to the exposure variables that MDEQ used to calculate the state-wide generic cleanup criterion in order to better reflect the best available information.

#### • <u>Relative Dust: Soil Concentration Factor (RDSF)</u>

Based on data from the University of Michigan's Dioxin Exposure Study (UMDES), concentrations of dioxins in house dust in the City of Midland are consistently lower than in composited outdoor soil samples surrounding the house. Specifically, the UMDES linear regression model indicates that indoor house dust dioxin concentrations are between 19% and 35% of the outdoor soil concentrations. Paired dust and soil TEQ values from the UMDES study are not available at this time. An evaluation of unpaired summary statistics indicates that the dust:soil concentration ranges up to approximately 50% (fractional TEQ concentration 0.30 - 0.54). Therefore, the default dust:soil concentration ratio of 1 is too high. The fractional concentration of TEQ for dust from soil in the site-specific equation is 0.5, to better represent site-specific information.

• Exposure Frequency (EF) and Soil: Dust Contribution Factor (SDCF)

The MDEQ generic direct contact calculation assumes incidental ingestion of contaminated soil 350 days per year based on the rationale that incidental ingestion of indoor dust can occur on "indoor" weather days, replacing the outdoor soil ingestion assumed for those days. This value also assumes that dioxin concentrations in outdoor soil and indoor dust are the same. It is appropriate to adjust for the site-specific relationship between indoor dust and outdoor soil in Midland, taking into consideration site-specific weather data. Based on local weather data, soil exposure frequency (incidental ingestion and dermal contact) of 260 outdoor days per year and a dust exposure frequency of 350 days per year are appropriate. Soil and dust exposure each



contribute half of the soil/dust exposure for the 260 outdoor days (hence a SDCF of 0.5), and the other 90 days (indoor days) are 100% dust exposure. Therefore, Midland-specific weather data is being used to adjust the  $EF_i$  (for soil and dust) from 350 to 260 days per year with the addition of an "indoor"  $EF_i$  (dust only) of 90 days per year. The  $EF_d$  (for soil and dust) is being adjusted from 245 days to 260 days per year with the addition of an "indoor"  $EF_d$  (dust only) of 90 days per year.

• Ingestion Absorption Efficiency (AE<sub>i</sub>)

The current generic  $AE_i$  for dioxin is set at 50%. Dow has conducted site-specific rat and juvenile swine studies to determine the relative bioavailability (RBA) of dioxin in Midland soil. MDEQ's evaluation of the studies determined that both animal studies appear equally valid, and therefore has suggested that a midpoint value of the studies be used. Accordingly, the  $AE_i$  is reduced from the default of 50% to 38%.

• <u>Age-Adjusted Soil Dermal Factor (DF)</u>

When MDEQ calculated the generic DCC of 90 ppt TEQ, MDEQ used an age-adjusted soil dermal factor (DF) of 2,442 mg-yr/kg-day, which was the default value at that time. Subsequently, MDEQ has adopted an updated default DF of 353 mg-yr/kg-day, which it has used for all subsequent DCC calculations for many compounds. This updated DF is based primarily on MDEQ's adoption of lower soil adherence factors (AF) for the DF calculation, from an AF of 1.0 mg/cm<sup>2</sup> for both children and adults, to new values of 0.2 mg/ cm<sup>2</sup> for children and 0.07 mg/ cm<sup>2</sup> for adults. These changes are consistent with the recommendations of USEPA in its dermal risk assessment guidance. The updated DF of 353 mg-yr/kg-day is used for this site-specific calculation.

• Dermal Absorption Efficiency from Soil (AE<sub>d</sub>)

The AE<sub>d</sub> represents the fraction of the contaminant that is assumed to penetrate the skin after contact. For dioxin, the generic value is currently set at the compound-based value of 3%, representing an upper bound value of two study approaches supporting values of 0.95 and 2.5%. MDEQ has previously recognized that both approaches appear equally valid, and therefore has suggested that a midpoint value of 1.75% be used in place of 3%. Dow has provided information showing the relatively high percentage of organic content in Midland soil, which further supports using a value less than the upper bound value of 3%, and lends additional site-specific support to MDEQ's earlier suggestion to use



1.75%. However, the USEPA dermal guidance recommends the soil dermal absorption rate be divided by the feed absolute bioavailability value (USEPA, 2004). Therefore, the value recommended as the best available information for dermal absorption efficiency is the 0.0175 soil dermal absorption rate divided by the feed absolute bioavailability value (ABS<sub>GI</sub>) of 0.55, which results in a relative bioavailability rate of 0.032. The ABS<sub>GI</sub> value of 0.55 was derived from the rat feed results from the pilot bioavailability study (Dow, 2005).

Adoption of all of the above changes results in a calculated dioxin action level of greater than 250 ppt TEQ. The SSAL that was approved for the City of Midland is 250 ppt TEQ. A SSAL of 250 ppt TEQ is protective of the public health, safety, and welfare and appropriately takes updated and site-specific information into account, while leaving a margin of safety. The SSAL only applies to residential properties (and "residential-like" properties, such as daycare centers). For non-residential properties within the MRA, the State's generic soil DCC for non-residential properties of 990 ppt TEQ will be applied.



# 5.0 Ecological Soil Exposure Pathway Screening and Evaluation

A significant effort has been undertaken to identify potential COCs in relation to MAS for the ecological pathway. The purpose was to build upon the process used to identify the COCs for the human health exposure pathways to screen the analytical results from the extensive on and off-site sampling results for over 200 compounds and identify COCs for the ecological pathway. This information was reviewed with MDEQ in a series of collaborative meetings.

The following steps were completed as part of this task:

- Screen TAL according to generic ecological screening criteria;
- Develop ecological screening categories based on results of generic screen;
- Determine the appropriate site-specific ecological receptors;
- Calculate site-specific ecological benchmarks, as necessary; and
- Review results of screening evaluation by category through collaborative meetings with MDEQ and U.S. Fish and Wildlife Service (FWS).

The MRA is an urban environment. In a meeting on April 4, 2014 with MDEQ, FWS, Dow and URS, avian receptors were proposed as the primary ecological receptors of interest, specifically the Northern Cardinal and the American Robin. In a meeting on May 16, 2014, MDEQ approved the use of avian receptors for the MAS ecological screening pathway evaluation. Therefore, identification of ecological screening level benchmarks (ESLB) for avian receptors was the focus of the ESLB selection process once the preliminary screen was completed.

# 5.1 Ecological Pathway Screening Evaluation

The ecological exposure pathway was evaluated for the MAS using a similar screening process as human health evaluation and the ecological screening methodology was presented in Part I. The ESLB represent media-specific concentrations that are protective of ecological receptors. The medium of interest is off-site urban soil. Chemicals for which soil concentrations are equal to or less than the chemical-specific ESLB were excluded from further evaluation as it was concluded they pose no unacceptable risks. Exceedance of an ESLB did not indicate that an unacceptable risk was present, but rather that further evaluation was warranted.

Part I presented the data sets used for the screening evaluation and described the summary

statistics used for the initial evaluation. A table of basic summary statistics was prepared for non-dioxin data of the combined data set. These tables included common statistical parameters, such as mean, standard deviation, minimum and maximum detected values, and minimum and maximum RLs where substances were not detected. Tables 5-1 and 5-2 present the summary statistics for each non-dioxin analyte.

Part I also presented the TAL screening criteria, background values, and the selection of ESLB. Part I Attachment A presented the hierarchal scheme used for the selection of a single avian ESLB from multiple sources for application in the site-specific MAS ecological pathway screening evaluation.

As per MDEQ request, the results for certain classes of analytes were totaled and compared to appropriate criteria. These classes of analytes included LMW and HMW PAHs, endrins, BHCs, heptachlors, DDx (DDD, DDE, DDT), endosulfans, chlordanes, and parathions and are presented in Table 5-3. DDD, DDE, DDT were also evaluated as individual analytes.

# 5.1.1 TAL Data Screening Results and Results of Category Discussions

After a series of meetings held between MDEQ, FWS, Dow and URS, a screening approach similar to the human health screening categories was proposed by FWS on September 23, 2013 and was accepted as the path forward in a meeting held on April 8, 2014 (see Part I).

Screening categories were identified as part of the screening effort to group and organize the non-dioxin constituents to facilitate the data review process. The screening categories are presented in Table 5-4, and each constituent, through the screening process, was placed into one of the twelve categories. The full screening process and the hierarchy of each step are illustrated on the ecological screening flowchart shown in Figure 5-1.

The screening results of the ecological evaluation are presented by category in Tables 5-5 through 5-15 for Categories 1 through 11, respectively. These tables provide the results of the evaluation conducted for each analyte during a series of meetings and conference calls that were attended by MDEQ, FWS, Dow, and URS. Supporting documentation is provided in Tables A1 through A12 in Attachment A of this report.

During the working meetings, further evaluation and discussion occurred for each category of analytes. Justification for elimination was presented for each analyte and reviewed during the meetings. When it was determined that analytes required further discussion, additional work was performed and included at least one of the following evaluations:

- Avian NOAEL-based ESLB development Part I Attachment A presents the memorandum that served as the basis for the NOAEL calculation. The supporting documentation for the analyte-specific ESLB calculations is provided in Attachment A of this report. Detected results and RLs were then compared to the NOAEL-based ESLB.
- Spatial Review A spatial (map) review of the data was conducted to determine if the sample results were isolated and/or not spatially connected to Michigan Operations, evidencing that the source is something other than Dow.
- Avian lowest observed adverse effect level (LOAEL)-based ESLB development Part I Attachment A presents the memorandum that served as the basis for the LOAEL calculation. The supporting documentation for the analyte-specific ESLB calculations is provided in Attachment A of this report. Detected results and RLs were then compared to the LOAEL-based ESLB.
- USGS Background evaluation MDEQ provided the results of a USGS background evaluation (USGS Data Series 801 (Smith, et al., 2013)). Detected results and RLs were then compared to the background (mean + 1 standard deviation) (see Table 5-16).
- Totals evaluations (total BHCs, total heptachlors, etc.) As per MDEQ request, the results for certain classes of analytes were totaled and compared to appropriate criteria (see Table 5-3).
- Target Detection Limit (TDL) evaluation If the TDL provided in MDEQ guidance (MDEQ, 2004) was higher than the maximum RL, the TDL was compared to the ESLB.
- Analyte was determined to not be sourced by Dow or the sample location was associated with a known off-site source not related to the MAS historical release, see Table 5-17.
- Uncertainty analysis The uncertainty analysis is intended to identify and evaluate key uncertainties so that a level of confidence can be considered when risk management decisions are made. In general, uncertainty is addressed by evaluating the likelihood that risk was over-estimated or under-estimated and identifying and discussing the major



sources of uncertainty so that the results can be properly interpreted.

Analytes were eliminated based on one or more lines of evidence discussed above with MDEQ's concurrence. The uncertainty analysis is presented below.

## 5.1.2 Uncertainty Analysis

Within the multiple steps of calculating ESLBs, assumptions were made which introduce some degree of uncertainty into the estimated values. Assumptions can be categorized into three groups:

- Data collection and evaluation;
- Exposure assessment; and
- Toxicity assessment.

The uncertainties associated with each of these are discussed below in qualitative terms. There is generally not enough information for most uncertainties to assign numerical values to the uncertainty. Quantitative estimates of uncertainty were included where appropriate.

## 5.1.3 Data Collection and Analysis

Data were collected from locations assumed to be representative of areas where historical deposition most likely occurred. However, uncertainty may be introduced through biases in sampling. For example, samples collected in areas suspected of contamination tend to overestimate exposure because the data are not randomly collected. This subsequently contributes to bias in statistical estimates of exposure, which assume random sample collection. Furthermore, due to the historical nature of the release it is likely that some soils in the study area have been disturbed between the time of release and the current sampling activities. This random variability of samples and lack of homogeneity of the media may result in either an over-or under-estimate of actual exposure concentrations.

Samples were analyzed using USEPA methodologies, and were subjected to data review and validation procedures. However, sample analysis is subject to uncertainties associated with precision and accuracy, and detection of chemicals at low concentrations. Differences between how accurately measured concentrations reflect actual concentrations could lead to an overestimate or underestimate of exposures and potential risks.

When evaluating data, the ESLB was compared with RLs, primarily to confirm that RLs were lower than ESLBs. The concern is that chemicals may be present at concentrations that have the potential to cause adverse effects, but are not detected by the analytical method used. The RL is the lowest concentration at which an analyte can be detected in a sample with a reasonable degree of accuracy and precision. The RL is a laboratory-specific number, which varies between labs and may also change with time. The method detection limit (MDL) is a laboratory-specific number, dependent (among other things) on the instrumentation used by a laboratory and the skill of the operator. When a chemical is detected by the instrument, but at a concentration lower than the RL, it is concluded that the chemical is present but the accuracy and precision is uncertain and the value is qualified as estimated.

Soil samples were collected during several different investigations at different periods in time and analyzed by different laboratories. For some analytes, RLs vary greatly between sampling efforts, largely due to laboratory-specific differences in the RL that was achievable. The largest RLs may not be representative of the majority of the data. For example, the 2010 MDEQ data set included data results with high RLs that often exceeded the ESLBs. The frequency of RLs above and below the ESLBs was considered in categorizing chemicals (see Part I) and group decision making with respect to retaining or eliminating chemicals for further evaluation. This categorization and decision-making approach was developed as part of the project to consider uncertainties regarding sample analysis and detection limits, thereby minimizing uncertainty in the overall evaluation.

# 5.1.4 Exposure Assessment

In calculating ESLBs, an exposure model was developed using assumptions for the receptors of interest, the Northern Cardinal and American Robin. Assumptions include patterns of behavior leading to exposure and intake of various media (e.g., soils, plants, invertebrates). Uncertainties include:

Selection of receptors requires an understanding of the complex interactions in an ecosystem, including abiotic processes and interactions between organisms. Uncertainties are associated with the representativeness of the selected receptors as sensitive species and as key organisms in the functioning of the ecosystem. These factors



were considered when the American Robin and Northern Cardinal were selected as receptors of interest. In a meeting on April 4, 2014 with MDEQ, FWS, Dow and URS, avian receptors were proposed as the primary ecological receptors of interest, specifically the Northern Cardinal and the American Robin. In a meeting on May 16, 2014, MDEQ approved the use of avian receptors for the MAS ecological screening pathway evaluation.

- Generalized and conservative assumptions were made about the behavior of the receptor in the environment in terms of diet composition, activity, mobility, and seasonality. It was assumed that the receptors of interest are year-round residents and inhabit and feed exclusively in the area under investigation; an area or seasonal use factor was not applied at the screening level. The conservativeness of the assumptions will likely overestimate actual exposures. However, this approach is inherent in the conservative nature of a screening evaluation.
- Assumptions regarding diet composition and ingestion rates can significantly influence the calculation of the ESLB. Ingestion rates were either based on empirical data (robin) or based on widely accepted allometric equations (cardinal). In addition, both the American Robin's and Northern Cardinal's diets fluctuate seasonally. Although the diet composition and ingestion rates were based on well-documented information, the assumptions could underestimate or overestimate potential exposures.
- A significant route of exposure is the incidental ingestion of soil. Assumptions were made regarding soil ingestion rates based on the foraging behavior of each receptor. As a ground-feeder, the American Robin was assumed to ingest soil incidentally while feeding at a rate of 5% of its diet. The Northern Cardinal is primarily a seed and fruit eater, and was assumed to ingest soil at a rate of 2% of its diet. Soil ingestion rates could be greater than or less than assumed.
- The concentration of chemicals in dietary items was estimated using uptake assumptions from the literature. However, chemicals exhibit complex behavior in the environment and the form in which they exist can significantly alter their toxicological properties, as well as their fate and transport characteristics and bioavailability. The characteristics of the medium in which they are present can also substantially affect bioavailability, and the



level to which potential receptors might be exposed. The assumptions applied could underestimate or overestimate potential exposures.

## 5.1.5 Toxicity Assessment

Generally, the available scientific information is insufficient to provide a thorough understanding of all the potential toxic properties of the subject chemicals on bird species. Toxicity reference Values (TRVs) were selected from available online databases and the published literature. The uncertainties are as follows:

- The foremost uncertainty is the lack of available data for describing toxic effects to birds. The absence of avian TRVs for some chemicals is discussed in greater detail below.
- No toxicological data were found specific to the American Robin or the Northern Cardinal. Therefore, TRVs were based on surrogate species. Differences in sensitivities to chemicals between surrogate test species and receptor species is not known. This could lead to either an overestimate or underestimate of potential toxicity.
- The relationship between toxic effects observed in the laboratory may not reflect the conditions of exposure in the wild where a number of ameliorating or exacerbating environmental conditions may apply.
- Differences between the life-stage of the laboratory surrogate and the critical life-stage of the receptor in the wild contributes to uncertainty.
- Differences between the duration of laboratory studies and the likely duration of exposure to receptors in the wild contribute to uncertainty.
- Much of the avian toxicity data were limited to acute studies reported as lethal doses (LD). The LD50 is the estimated dose which results in 50% lethality of test individuals. This is the least preferred toxic endpoint (chronic NOAELs and LOAELs are preferred), but for many chemicals was the only endpoint identified. Where only LD50 values were available, the LD50 was divided by a factor of 10 to estimate a chronic LOAEL, and by 100 to estimate a chronic NOAEL. If a chronic LOAEL was available, but no NOAEL, a chronic NOAEL was calculated by dividing by a factor of 5. Actual uncertainty factors can vary widely, and the application of the uncertainty factors described could under- or overestimate actual toxicity levels.



• The use of single-chemical test data that do not account for multiple exposures or additive, synergistic and antagonistic interactions between the chemicals present in soil may under-estimate or over-estimate potential toxicity. This was partially addressed by summing similar classes of analytes, including LMW PAHs, HMW PAHs, endrins, BHCs, heptachlors, DDx (DDD, DDE, DDT), endosulfans, and parathions, to account for exposure to similar chemicals.

## **Total Endrins**

For most of these chemicals, the summed concentrations remained below ESLBs. No further evaluation was recommended. An exception was total endrins. Total endrins are comprised of endrin, endrin aldehyde, and endrin ketone. According to ATSDR (1996), endrin was historically used as a pesticide to control insects, rodents, and birds. It has not been produced or sold for general use in the United States since 1986. Little is known about the properties of endrin aldehyde (an impurity and breakdown product of endrin) or endrin ketone (a product of endrin when it is exposed to light).

A NOAEL-based ESLB of 2.62  $\mu$ g/kg was used to evaluate total endrins. This is based on the most conservative ESLB among the three endrin compounds (endrin aldehyde), and does not reflect potentially lower toxicity that may be associated with an endrin mixture (the toxicity of both endrin and endrin ketone were estimated at about half that of endrin aldehyde). Total endrins were detected in only five (5) of 128 total samples collected, all of which were located off-site. Four (4) of the five (5) samples had detected concentrations that were greater than the NOAEL ESLB, ranging from 9.79 to 16.5  $\mu$ g/kg. In addition, 64 samples had RLs that exceeded the NOAEL ESLB. There were no detected concentrations that exceeded the LOAEL ESLB for endrins (26.2  $\mu$ g/kg) and RLs only exceeded the LOAEL ESLB at four (4) sample locations (2 on-site and 2 off-site). The two off-site sample locations with RL exceedances were B1-01 and C-02, which are both associated with off-site sources not related to the historical MAS release.

Dow Midland did not produce endrin; nor is the site suggested as a potential source of endrins as all detections occurred off-site. Off-site detections above the NOAEL ESLB contribute to uncertainty in assessing potential risks to endrins. But based on the low frequency of detection, spatial distribution, and because all detected concentrations were below the LOAEL ESLB, no



further evaluation of endrins is warranted.

## **Essential Nutrients**

Essential nutrients, specifically magnesium, calcium, potassium, and sodium, were not considered to be of ecological concern. Essential nutrients are required elements for maintaining normal health in plants and animals and are generally toxic only at very high levels. When present at low concentrations (i.e., only slightly elevated above naturally occurring levels), they need not be considered in a quantitative risk assessment (USEPA 1989). Homeostatic mechanisms in organisms tend to protect against excessive quantities of essential nutrients. In addition, because of the interrelationship of nutrients (e.g., the presence of excess calcium may precipitate a deficiency of other essential nutrients), maximum toxicological levels are difficult to define (USEPA 1989, NAS 1980).

## Analytes Not Detected with Limited Toxicity Data

There is one category of chemicals (Category 4), which is comprised of chemicals that were not detected in any soil samples and had no ESLB available and no ESLB could be calculated due to the absence of relevant toxicity data. Physical/chemical properties that describe the chemicals fate and transport in the environment were used as lines of evidence to evaluate these analytes. Several physical-chemical properties and fate and transport characteristics of a chemical were used to qualitatively evaluate these chemicals. If potential exposure pathways are incomplete or insignificant, it can be concluded that uncertainty is low in the absence of toxicological data or reportable concentrations of the chemical of interest.

Volatility – The more volatile a chemical, the less likely it is to persist in surface soils the zone of greatest potential ecological exposure. Lyman (1995) provides a generalization that is useful in qualitatively describing a chemical's propensity towards volatilization using its Henry's Law constant where:

Volatilization Potential				
H (atm m <sup>3</sup> /mol)	Volatilization Potential			
$< 3 \times 10^{-7}$	Chemical is less volatile than water			
$3 \ge 10^{-7}$ to $10^{-5}$	Chemical volatilizes slowly			

 $> 10^{-3}$ 

Volatilization Potential				
H (atm m <sup>3</sup> /mol)	Volatilization Potential			
$> 10^{-5}$ to $< 10^{-3}$	Volatilization is significant			

Chemicals that have rapid or significant volatilization are unlikely to be retained in
surface soil and therefore unlikely to represent complete or significant exposure
surface son and, meterore, university to represent complete of significant exposure
pathways through the food chain. Therefore, uncertainty is low in the absence of an
ESLB when these chemicals are not detected.

Volatilization is rapid

- Bioaccumulation potential A chemical's potential to accumulate in biotic tissue is of concern when evaluating higher trophic level receptors such as the Northern Cardinal and American Robin because they are largely exposed in their diet through food-chain transfer. One indicator of bioaccumulation potential is the octanol-water-partitioning coefficient (K<sub>ow</sub>). This coefficient describes a chemical's propensity to adhere to lipids (octanol) and, as such, is an indicator of a chemical's potential to bioaccumulate. The document *Assessment and Control of Bioconcentratable Contaminants in Surface Waters* (USEPA 1991) used a log K<sub>ow</sub> of > 3.5 as a threshold value to target organic chemicals with greatest potential to bioaccumulate. Although developed for surface waters, the concept is equally applicable to terrestrial systems as well. Using this as a guideline, if the log K<sub>ow</sub> of a chemical is less than or equal to 3.5, the chemical is less likely to be a bioaccumulative chemical of concern, and the uncertainty is reduced that the chemical poses a potential risk through food chain exposures, which are important to the evaluation of the Northern Cardinal and American Robin. Thus, uncertainty is considered low for a chemical that has no ESLB but the log K<sub>ow</sub> is 3.5 or less.
- Another indicator of bioaccumulation potential is the soil organic carbon-water partitioning coefficient,  $K_{oc}$ . This is the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution. Donnelly et al. (1994) suggested relative mobility in soils based on a chemical's  $K_{oc}$  as follows:



Soli Mobility Defined by Affinity for Organic Carbon				
K <sub>oc</sub>	Log K <sub>oc</sub>	Mobility Class		
> 2000	>3.3	Immobile		
500 - 2000	2.7-3.3	Low Mobility		
150 - 500	2.2-2.7	Intermediate Mobility		
50 - 150	1.7-2.2	Mobile		
< 50	<1.7	Very Mobile		

Soil Mobility Defined by Affinity for Organic Carbon

 $K_{oc}$  values are useful in predicting the mobility of organic soil contaminants; higher  $K_{oc}$  values correlate to less mobile organic chemicals while lower  $K_{oc}$  values correlate to greater mobility. More mobile contaminants are less likely to be persistent over time in surface soils. Conversely, chemicals with a higher  $K_{oc}$  may be retained for longer periods (not considering potential degradation).

 Degradation – Some chemicals attenuate naturally through biological, chemical, or physical processes in the environment. Biodegradation (at least for some chemicals) can be examined through general descriptions of degradability and/or quantitative information regarding degradation rates and half-lives in soils for the chemical or chemicals of similar structure. The uncertainty is considered low in the absence of an ESLB when chemicals are readily biodegraded and not detected.

Table A13 in Attachment A considers one or more of the above physical/chemical properties and fate and transport characteristics for the analytes not detected with limited toxicity data based largely on excerpts from the National Institutes of Health, National Library of Medicine Hazardous Substances Data Bank (HSDB) – (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB). Other sources were searched when information was unavailable from HSDB. In general, uncertainty is considered low for most of these analytes. However, there was a subset of chemicals listed below that had no physical/chemical properties or fate and transport characteristics identified:

- (E)-alpha,beta-2,3,4,5,6-Heptachlorostyrene
- (E)-beta-2,3,4,5,6-Hexachlorostyrene
- (Z)-alpha,beta-2,3,4,5,6-Heptachlorostyrene



- (Z)-beta-2,3,4,5,6-Hexachlorostyrene
- 2,3,4,5,6-Pentachlorostyrene
- alpha-2,3,4,5,6-Hexachlorostyrene
- beta, beta-2, 3, 4, 5, 6-Heptachlorostyrene

These constituents are likely related to metabolic and degradation/transformation products associated with octachlorostyrene (see HSDB 2014). The lack of any toxicological or chemical/physical information limits an interpretation of these analytes. They were not detected in any samples collected, providing one line of evidence that suggests these analytes are unlikely to be present. Octachlorostyrene was only detected in three (3) of 99 samples: each of the detections was found at locations of known other off-site sources and was recommended for elimination based on detection frequency and spatial distribution. It is therefore concluded that the uncertainty for these octachlorostyrene-related constituents is low in the absence of ESLBs.

# 5.2 Conclusions of Ecological TAL Screening Evaluation

At the conclusion of these working meetings, all non-dioxin analytes were eliminated or were addressed by the uncertainty analysis and subsequently eliminated from the TAL. Dioxins and furans were carried forward into Category 12. The TAL evaluation confirmed that dioxins and furans are the COCs for the MAS ecological exposure pathway. Dioxins and furans will be considered in the Natural Resources Damages Assessment (NRDA).

Figure 5-1 Dow Midland Area Soils Ecological Screening Flowchart The Dow Chemical Company, Michigan Operations





# 6.0 Public Participation Plan

Public involvement in the RI process for the MAS project included opportunities for members of the public to obtain information and to provide their input or voice concerns. A variety of communication tools were used during the project which includes press releases, dedicated informational websites, a formal public hearing and comment process, advertised sessions where project staff were available to the public, as well as public repositories of information.

In February 2012, MDEQ announced that conceptual agreement had been reached with Dow and that they would establish a public comment period for the IRDC. During this public comment period, a public meeting was held and Dow and the MDEQ presented information regarding the project background and development of the IRDC. This meeting also included a question and answer session. At the closure of the public comment period, MDEQ provided their approval, a summary of responses to comments, and the basis for their approval. The IRDC and annual Work Plans were made available to the public via the Grace A Dow Memorial Library, in Midland, Michigan. These documents were also available for download from the publically available website, discussed below.

During the initial stages of the project, an open house was hosted for the property owners involved in Phase I (2012) to answer specific questions about the implementation of the program and allow them to meet the project team. As the project continued, a number of public availability sessions were held to allow members of the public to come and express concerns or obtain information from both project staff and MDEQ.

A number of informational flyers were provided to the public with general information including the overall program, sampling, remedy, post remedy lawn care, and a compiled list of frequently asked questions (FAQs). Newsletters were mailed to property owners within the MRA each year to provide project updates and additional information. A publically available website, <u>http://www.midlandresolution.com</u>, was established for the public to provide easy access for obtaining the general information about the program, and to view informational flyers and newsletters, project updates, and access relevant documents. The website also provided an avenue for the public to send an e-mail directly to the project team. Also posted on the website was a video of the public meeting and links to the USEPA and MDEQ websites.

The Midland Resolution Center, located at 1008 Jefferson Avenue, was open to the public during normal business hours (8 AM to 5 PM), or by appointment. A toll-free telephone hotline was also available 24 hours a day to allow the public to express their concerns or obtain additional information. During the project, several informal availability sessions were held at the Midland Resolution Center to provide an opportunity for members of the public to obtain inperson one-on-one meetings with project members.

At the completion of the project, pursuant to Operating License Condition XI.L.2, MDEQ will provide notice to the public of its draft decision on the RAP/CMI (Part III) to persons on the facility mailing list and an opportunity for a public hearing.



# 7.0 Study Area

The study area for the MAS project is called the Midland Resolution Area (MRA). The MRA covers approximately 1,700 total acres. Part I provides a detailed description of the primary land uses and zoning within the MRA. Of the 1,700 acres, approximately 425 acres are in residential or residential-like land use. Approximately 1,275 acres are in industrial/commercial land use. The MRA includes portions of the City of Midland where land use is primarily residential and others near Michigan Operations where a limited number of residential properties (some not conforming with existing zoning) are intermixed among predominantly commercial or industrial uses. Figure 7-1 presents the initial MRA boundary. The predominantly residential areas are in large part located to the north of the facility, in addition to a second smaller area to the east of the facility. Figures 7-2 and 7-3 present an overview of the two (2) predominantly residential areas within the MRA. Figure 7-4 presents an overview of the area with predominantly industrial/commercial land use within the MRA. The MRA is largely contiguous to Michigan Operations to the north and east of the faceline. The boundaries of the MRA are generally:

- Bound to the north by East Nelson Rd. and Eastlawn Rd.;
- Bound to the west by Rodd St.;
- Bound to the east by Waldo Ave; and
- Bound to the south by East Patrick Rd and East Indian St.

The concentration of dioxin in the soil in the remainder of the City of Midland beyond the MRA is, based on current data, below the residential SSAL (see Section 4.0) and will not require any work under this MAS project. However, the final boundary for the MRA was adjusted, based on soils data generated during implementation of the work and the physical features of the area. Section 10.0 presents the final MRA.

Implementation of the presumptive remedy began in areas that are the closest to Michigan Operations and then progressed outwards in bands across the MRA in subsequent years. Some residential properties close to the plant site were addressed during the second year of work rather than the first year (note that these properties previously received or were offered interim response activities [IRAs] to control exposure in 2005).

The MRA was subdivided into large property grouping, based on the number of properties that may be reasonably addressed within one construction season (April-October). The intent was for all field activities – from sampling and analysis to implementation of the remedy – for the property grouping to be addressed within one construction season. Changes to the schedule through the Adaptive Management Process (Section 9.0 in the approved IRDC [Appendix A]) were made during the project; when improvements or efficiencies could be made; or when other factors made it appropriate to do so.

Figure 7-5 shows the property groupings designated by current block designation for implementation (A, B, and C). These property groupings were selected based on distance from the site. For example, the plan for Year 1 implementation (discussed further in Section 9.0) is shown on Figure 7-5 as the "A" property grouping. The table below presents details for each property grouping, including the total number of properties, number of residential properties, and acreage.

Property	Total Number of Decision Units	Residential Decision Units	Total Area	Residential Acres
Year 1 (A)	174	171	51	Housing = 40 Parks & Rec = 10 Public/Semi-Public = 1
Year 2 (B)	871	860	234	Housing = 214 Parks & Rec = 18 Public/semi-public = 2
Year 3 (C)	660	600	292	Housing = 165 Parks & Rec = 78 Public/semi-public = 49

# 7.1 Current Land Use

The MRA includes approximately 1,750 total properties that are broken generally into the following land uses: residential properties, residential-like properties (park, school), and non-residential (commercial, industrial, public).

The properties designated as residential-like properties include daycares, schools for children, and parks with playgrounds (see Part I). These properties are being addressed as residential based on the assumption that exposures are similar to or consistent with those at residential properties. All remaining areas are classified as "non-residential." Figure 7-6 shows general land use areas within the MRA.



Dow offered a voluntary property purchase program for 50 residential properties located in the Resolution Area near the fenceline both east and north of Michigan Operations. The land use in these areas has become increasingly industrial/commercial and this program offered the property owners an option to sell their home and move to a residential area. If a property owner of a rental home participated in the program, Dow provided the renter(s) with relocation support.

Dow retained a real estate and communications services company, Community Interaction Consulting, Inc. ("CIC") to administer the program on Dow's behalf. CIC representatives provided assistance to property owners throughout the process. Upon acquisition of the properties, Dow had the structures on each property removed. Dow then donated the acquired properties to Midland Tomorrow, the nonprofit economic development entity serving Midland County.

The approved IRDC (Appendix A) presented MRA outlier areas and during Year 3, boundary verification activities were performed to confirm the outer extent of the MRA boundary which in part addressed the outlier areas. Sections 9.0 and 10.0 discuss these activities.

# 20 Midland Resolution Area 110 **Dow Chemical** Michigan Operations THE THIN 戦争 Legend Midland Resolution Area

Dow Facility Boundary















# 8.0 Sampling Design

# 8.1 Depth of Sampling

# 8.1.1 Sampling for Release Characterization

Soil sampling specifically designed to provide data for subsequent screening evaluations to establish COIs, included the 2005/2006 Dow On-Site (DOS) Samples, 2006 CH2M Hill Samples, and the *2010 Field Characterization Pilot Study* (2010 Dow and MDEQ split samples). The data were subjected to a rigorous screening, described in detail in Part I.

# 8.1.2 Sampling for Nature and Extent Characterization

Seventeen (17) dioxin and furan congeners were analyzed for the three (3) data sets (2005/2006 DOS data set, 2006 CH2M Hill data set, and 2010 Dow and MDEQ split sample data set), and the results for these congeners were used to calculate dioxin TEQ for each individual sample using the 2005 WHO TEFs (Van den Berg et al, 2006, see Table 4-1 in Part I). The calculated dioxin TEQs were then used for subsequent data and statistical evaluation.

A table of summary statistics for dioxin TEQs by depth and by data set is presented in Table 8-1. The majority of the dioxin TEQ data were originated from the 2006 CH2M Hill data set, and 2010 Dow and MDEQ data set. The number of samples from the 2005/2006 DOS set was very small (n=28), and it was evident that the dioxin TEQs were as much as two orders of magnitude higher than the other two sets. Thus, the 2005/2006 Dow DOS data set (i.e., inside the Dow's plant) was deemed to be non-representative of the dioxin concentrations existing in the City of Midland soils (i.e., outside the Dow's plant). The following evaluation and discussion excluded the dioxin TEQs obtained from the 2005/2006 DOS sampling event.

# 8.1.3 Generalized Horizontal Extent of Dioxin and Furan Impacts

In 2006, CH2M Hill collected surface soil samples from the communities within the City of Midland on 23 transects radiating from Michigan Operations (but outside the facility boundary). These transects were labeled from A to W (Transect P and Q had no data), with the majority of them radiating to the northerly and easterly directions to reflect prevailing winds. There were between one and twelve stations in each transect, and each station was approximately 300 feet by 300 feet. The sampling locations of these transects are shown in Figure 4-2 of Part I. Because the exact locations for a number of samples were initially "blinded," the number of available data



points was actually less than what is shown in Figure 4-2 of Part I. The data set was "unblinded" in June 2012 upon approval of the May 25, 2012 IRDC (as discussed in Section 4.0 of Part I).

A qualitative inspection of the dioxin TEQ values for surface samples along each transect indicated a general downward spatial trend when the sample locations were moving further away from Michigan Operations. This general observation appeared to be more prominent for Transects B, C, E, I, and M. For example, for Transect B, the dioxin TEQ concentration for Station B-001 was reported to be 379 ppt. The dioxin TEQ concentration continued an apparent monotonic decline along Transect B until it reached 75 ppt at Station B-009. (Note: At the time of this evaluation, Stations B-010 and B-011 were "blinded.") For Transect M, if one excluded the first station (Station M-001), the dioxin TEQ concentration declined from 915 ppt at Station M-002 to 44 ppt at Station M-011.

## 8.1.4 Vertical Extent of Dioxin and Furan Impacts

Table 8-2 shows the summary statistics of the combined 2006 CH2M Hill data set and 2010 Dow and MDEQ data set by depth for dioxin TEQs, and Figure 8-1 shows the box-and-whisker plot of this combined data set. Data from 0 to 1 inch below ground surface (bgs) had the largest number of samples (n=361), followed by 1 to 6 inch bgs (n=173) and 6 to 12 inch bgs (n=138). The number of samples collected from greater than 1 foot bgs was also large (n=154), with the deepest depth at 4 feet bgs. It should be noted that data from the two deeper levels were exclusively collected from the 2010 event.

As shown in Figure 8-1, the highest dioxin TEQs appeared to be observed in the 1 to 6 inch bgs level, with a mean of 303 ppt and a median of 155 ppt. Given the data were positive skewed and not normally distributed, a non-parametric multiple comparison test using the Steel-Dwass method at a 5 percent significance level was performed to compare the four depth levels. The Steel-Dwass test is a non-parametric version of Tukey multiple comparison test, for which the alpha is sized for all differences among the means of different groups. The statistical outputs and results of this test are also shown in Figure 8-1.

The result of the multiple comparison test showed that the top two depth levels (0 to 1 inch bgs and 1 to 6 inch bgs) were not significantly different from each other. However, concentrations decreased in the third depth level (6 to 12 inch bgs), which appeared to be different and lower in



concentration from the top two depth levels. A continued decrease in concentration was identified in the fourth depth level (>1 foot bgs).

As detailed in Section 4.0, a SSAL of 250 ppt was calculated and approved for dioxins and furans for the direct contact exposure pathway. Table 8-2 also shows percentage of dioxin TEQs exceeding 250 ppt and exceeding 300 ppt. Based on the percentage of exceedance, it appeared that the top three depths levels (i.e., from 0 to 12 inches bgs) have some exceedances. The fourth depth level, >1 foot bgs, had very limited exceedances. All the locations with samples >250 ppt at a depth >1 foot bgs have identified historic surface disturbances from industrial activity and possible filling based on a review of historical aerials (see Attachment 1 of the *2010 Field Pilot Characterization Summary Report* [URS, August 2010]). Two locations are specifically known to have had filling take place, where cleaner materials have been placed over historic land surfaces. Based on the observed distribution of contaminants and what is known about the history of these areas, concentrations of dioxins and furans above 250 ppt are not evidenced or expected to be present in the deeper MAS (greater than one foot from surface).

## 8.1.5 Determination of Small Scale Variability of Dioxins and Furans

Variograms were developed to evaluate the pattern and scale of spatial variability in dioxin TEQ concentrations. A variogram provides a means of quantifying the commonly observed relationship that samples close together tend to have more similar (correlated) values than samples far apart. The pattern of spatial correlation exhibited in a variogram helps to understand how homogeneous or heterogeneous the field of measurements (i.e., data set) is.

The 2010 Field Characterization Pilot Study Summary Report (URS, 2010) provides a discussion of key components of a variogram, the data used to develop variograms for this study, and the actual variograms that were developed. The main findings are discussed below.

## 8.1.6 Findings of Variogram Analysis

The calculated points on the variograms in Figures 8-2 through 8-4 show a large degree of scatter around a fitted model. This is a reflection of significant random variability or noise (including potential measurement errors) between samples located close together (short-scale variability).

A nugget in a variogram is a measure of short-scale spatial variability, including random measurement error. Discrete points for a variogram plat are calculated using available sample data. A "best-fit" line is then drawn to fit these points. The nugget is estimated by the intercept of this line on the y-axis.

The nugget estimated for this study accounted for some 40% of the total variability in the longrange variogram. This is a further indication of sample measurements with significant shortscale variability. Given this significant short-scale variability in MAS, measuring concentrations at individual sample locations would be highly variable. Measuring average concentrations over a larger area such as a property would help reduce the influence of the short-scale variability and hence would be more reliable.

# 8.2 Design Sampling Methodology

# 8.2.1 Response Action Addressing Residential Land Use

The remedial objective for the MRA for residential and residential-like properties was to reduce the dioxin and furan TEQ in impacted areas to a concentration that is below the SSAL. The objective was achieved by implementing a presumptive remedy for any area that has dioxin and furan TEQ concentrations greater than the SSAL in the top six inches of soil as determined by incremental composite sampling. A phased approach that involved sampling and analysis to identify properties where a presumptive remedy was warranted was used to methodically work through the properties located within the MRA. Part III presents the details of the remedy.

The sampling and analysis was accomplished through incremental composite sampling, following methods that were optimized by the results of a pilot study documented in the *Composite Sampling Pilot Study Summary Report* (URS, 2012), included as Appendix C. The samples collected were analyzed for dioxins and furans. Decision rules establish standards for determining whether or not the presumptive remedy was warranted for a property and are discussed in further detail later in this section. The Decision Rules guided the use of analytical results to identify properties that were either below or equal to the SSAL or required implementation of the presumptive remedy.



## 8.2.2 Decision Unit

A decision unit (DU) is an area for which an individual remedial decision is made. A DU is equivalent to an exposure area or may represent an agglomeration of exposure areas with similar characteristics. Typically, a DU consisted of one residence. A DU extended to the farther of the property line, an adjoining fence, curb line, pavement edge, or the top edge of a drainage ditch or creek, including outlawns associated with the property that were not owned by the property owner but were functional parts of the owner's property, provided that separate sampling access for these areas is obtained. Wooded areas above a specified size (as defined in Section 7.4.3.1 in the approved IRDC [Appendix A] and discussed in Section 8.2.5 below) were not included as part of the results of soil testing at each DU to determine if the presumptive remedy was warranted at that DU.

## 8.2.3 Obtaining Access from Current Property Owners

Dow used best efforts to obtain appropriate access from property owners to conduct sampling on their property. For the purposes of the design sampling activities, best efforts were defined as follows: an initial letter, a first and second follow-up telephone call, certified letter, and an in-person visit. A meeting was requested with the current property owner to review the proposed actions and to obtain an access agreement and permission to permit Dow to conduct sampling activities and the remedial work (if applicable) specified in the approved IRDC (Appendix A). An example agreement form (Midland Soils Sampling Agreement Form) was presented in Attachment D of the IRDC (Appendix A). Dow and its contractors worked closely with property owners to inform them of the planned process, the implications of the field implementation, in addition to providing the results of the sample analysis.

## 8.2.4 Soil Testing

Sampling was based on current land use, physical attributes of the property and DU area size. Individual DUs that were in residential use include both single and multi-family dwellings. Properties that were being treated as residential-like include such categories as parks, schools for children, daycare centers, and playground areas, as discussed in Part I, and other public areas on a case-by-case basis.



## 8.2.5 Sample Collection

Samples obtained from an individual DU were collected from a number of locations (increments) and combined into a single sample (composite) representative of the entire DU. This technique is commonly referred to as incremental composite sampling (IS). The increment collection locations within each DU were generated using a systematic random approach. In the systematic-random pattern, a random starting point was generated and then subsequent increment locations were established on an even spacing within the remainder of the DU. Samples were collected from DUs in a manner consistent with detailed sampling methods discussed in the approved IRDC (Appendix A) and the January 2012 *Incremental Composite Sampling Pilot Study Report*.

Three replicate incremental composite samples were obtained from each DU, with the number of increments based on its area. The area for a DU was determined as the area not covered by buildings, large immovable features (decks or pools) and paved areas. A single composite was obtained from ten (10) increment locations for DUs less than or equal 1/4-acre. A single composite from twenty (20) increment locations was obtained for DUs greater than 1/4-acre, but less than 1 acre.

Specific sample plans were developed for DUs that were larger than one acre on a case-by-case basis prior to sampling each year. Properties were divided and sampled separately as multiple decision units (where splitting the DU is logical) or individually with 30 increments per DU.

Some properties within the MRA have densely wooded areas within the property boundaries. Exposure and land use were different for wooded areas than exposure and land use for mowed and maintained lawns and required separate evaluation as described below.

The minimum lot size that can be developed by building a structure as a residence within the City of Midland is 7,200 square feet (sq ft). Wooded areas less than 7,200 sq ft on active residential lots were considered de minimis and were sampled as part of the residential DU. Wooded areas comprising an entire parcel (or nearly so), with no active residential use were identified as non-residential, and were addressed according to Section 7.4.6 of the approved IRDC (Appendix A).



Wooded areas larger than 7,200 sq ft on an individual parcel with a current land use of residential or residential-like were considered non-residential areas, due to their limited use for the purposes of this project; and were addressed as a separate DU. Samples were collected from this area upon approval of the property owner.

A property owner provided permission for sampling for the residential DU, woodland DU or both at their discretion. These options for sampling were discussed with the owner during individual meetings, as described in Section 7.4.2 of the approved IRDC (Appendix A).

Quality assurance for soil testing (including replicate and split sampling procedures) was used to validate analytical methods, but was not included in remedial decisions. Specific procedures were outlined within the Quality Assurance Project Plan (QAPP, Attachment C of the approved IRDC [Appendix A]). Laboratory sub-sampling was performed in accordance with Section 7.4.3.2 of the approved IRDC (Appendix A).

# 8.2.6 Analytical Methods

A method was developed by Dow analytical chemists by adaptation of existing USEPA Method 8280 for rapid determination of polychlorinated dibenzo-p-dioxins (PCDDS) and dibenzofurans (PCDFs) in soil by high resolution gas chromatography/high or low resolution mass spectrometry (HRGC/HRMS or HRGC/LRMS). It is specific to the MAS. This method was developed to decrease the time necessary for each laboratory analysis. The Standard Operating Procedure (SOP) for Method 8280 was submitted to MDEQ and USEPA on June 29, 2011 and was approved for use on October 21, 2011. A copy of the SOP was included as Attachment B to the IRDC (Appendix A).

This is referred to as the Method 8280 MAS Site-Specific Fast Analysis method and it was the principal means used for laboratory analyses. Additional methods, such as USEPA Method 1613b with additional chromatographic column confirmation, were performed as required. In cases where interferences are identified, analytical options and performance criteria are discussed in detail in the Method 8280 MAS Site-Specific Fast Analysis Method Quality Assurance Project Plan (QAPP). The QAPP is contained in Attachment C of the approved IRDC (Appendix A).
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## 8.2.7 Response Actions Addressing Non-Residential Land Use

Measured concentrations of dioxin and furan TEQ beyond the Dow Plant site within the MRA were below MDEQ generic non-residential DCC (990 ppt TEQ). With a limited exception described below, concentrations of dioxins and furans TEQ on non-residential property in the Resolution Area did not require additional evaluation under the approved IRDC (Appendix A). Current delineation of non-residential land use was based on a preliminary review of the properties. As the work progressed, site visits or surveys were conducted as necessary to verify that non-residential properties (e.g., businesses) were not currently also used as a residence or in a manner which constituted residential-like use (as described in Part I). Additionally, non-residential properties bordering residential properties were evaluated for the potential for soil and sediment erosion and transport by surface water runoff. A non-residential property was addressed as a residential-like manner.

Property currently used for non-residential purposes but located in a zoning district that allows residential uses were considered for potential future use. These properties were addressed in one of the following ways, as appropriate to the circumstances. In most cases, long-term monitoring for land use changes will be used as a means to track non-residential properties. Dow and the City of Midland are entering into a contract that will provide notification to Dow of changes in ownership or land use since a number of local and state requirements alert the City to those changes. Restrictive covenants will be implemented for Dow-owned property to limit land use to non-residential (as described in Part III). In limited cases, the property was sampled and addressed as a residential property. Limited sampling of some non-residential property occurred to more clearly define and limit appropriate boundaries for application of institutional controls, or to define the boundary of the MRA.

Discrete samples from three Dow-owned properties that fell within the land use area that was predominantly industrial/commercial exhibited detected concentrations of dioxin and furan TEQ that exceeded the MDEQ generic non-residential DCC of 990 ppt TEQ. Figure 8-5 presents the sample locations that were collected in 2010. All were located near the Michigan Operations Facility. A sample location at Site 1 exhibited a detected concentration greater than 990 ppt TEQ (1,150 ppt TEQ). However, the 95% upper confidence level (UCL) for the analytical



results in the 0-6" depth range at this site is 558 ppt TEQ. Therefore, no further action was necessary to address this sample. Site F1 had two detected concentrations that were greater than 990 ppt TEQ (1,770 and 1,130 ppt TEQ). However, the 95% UCL for the analytical results in the 0-6" depth range at this site was 575 ppt TEQ. Therefore, no further action was necessary to address this sample location.

In an area that was formerly a rail track spur, a discrete sample from location B1-03R10 1"-6", obtained from Site B-01 on 11/12/2010 had a measured concentration of roughly 10,600 ppt TEQ. A number of additional discrete soil samples were obtained from Site B-001 in July 2011, with a resulting 95% UCL of 1,384 µg/Kg. Dow submitted the Work Plan for Site B-001 Remediation Project to MDEQ for review on September 27, 2011. This work plan proposed targeted remedial activities for this site where the 95% UCL exceeded 990 ppt TEQ. Response Actions were implemented per that Work Plan beginning on October 5 and were completed November 11, 2011. Dow submitted the Work Plan Addendum for Site B-001 Remediation *Project* on November 9, 2011 to address the MDEO approval stipulation that Dow must propose a plan and schedule to investigate concentrations of dioxins and furans along the former rail spur to the north of Austin Street to determine if additional remediation is necessary. The Addendum was incorporated as Attachment H of the approved IRDC (Appendix A). This investigation was completed during 2012. Dow obtained property access and collected one incremental composite sample and two replicate samples from each of four DUs (across three parcels). Each of the parcels are currently zoned 1A Industrial and the use is consistent with the zoning. Two of the three parcels were treated as individual DUs. The third parcel consisted of two DUs:

- The first DU was approximately 60-ft wide by 200-ft long buffer roughly centered along the former rail line; and
- The second DU consisted of the remaining property for that parcel.

The results were presented as Table 2-5 of the *Year 1 (2012) Implementation Annual Report* (Appendix E). All three replicates from the former rail line DU were tested by 1613b and a 95% UCL was determined for that DU. All dioxin and furan TEQ concentrations identified on these properties were less than the generic MDEQ non-residential direct contact criterion; therefore, no further action was required to address Site B-001.

# URS

## 8.2.8 Decision Rules for Residential Land Use

This section sets forth the decision rules for the response actions and how the information obtained were used to inform them. For each DU, soil testing results were used to determine if the presumptive remedy was warranted.

As shown on Figure 8-6, the first of the three composites collected in a single DU were tested at the laboratory by Method 8280 MAS. If the result determines a concentration greater than 250 ppt TEQ, Dow completed the presumptive remedy for the DU as specified in the approved IRDC (Appendix A) or demonstrated the concentration is below the SSAL of 250 ppt TEQ by testing of all three replicates using EPA Method 1613b with a DB-5ms (or equivalent) column. Method 8280 MAS concentrations measured greater than 220 ppt TEQ and less than or equal to 250 ppt TEQ resulted in testing of all three replicates by EPA Method 1613b using a DB-5ms (or equivalent) column. All 1613b analysis may have involved a second column confirmation as was determined to be appropriate by Dow. If a second column confirmation analysis was performed, those results were used for remedial decisions, as described below. A 95% Upper Confidence Limit (UCL) was developed from the three analytical results. The 95% UCL was compared to the SSAL of 250 ppt TEQ. If the 95% UCL was less than or equal to 250 ppt TEQ, performance of the presumptive remedy at the property was not necessary. If the 95% UCL was greater than 250 ppt TEQ, performance of the presumptive remedy at that DU.

As shown on Figure 8-7, for properties where the property owner provided information establishing that the existing lawn has been significantly landscaped or fill placed across much of the property, the standard decision rules established above were supplemented to verify that impacted soils were not present in the upper 12" of soil. Additional evaluation was necessary if the upper 6" is less than 250 ppt TEQ. In that case, one of the 0-12" samples (Section 7.4.3.1 of the Approved IRDC [Appendix A]) was tested at the laboratory by Method 8280 MAS, and a concentration for the 6-12" interval was determined (see Note 1 on Figure 8-7). If the result indicated that concentrations of the 0-6" and 6-12" intervals were less than or equal to 220 ppt TEQ (30 ppt less than action level), soil testing was completed and cleanup of the property was not necessary. If the result determined a concentration greater than 250 ppt TEQ, Dow completed a remedy for the DU as specified in the approved IRDC (Appendix A) or



demonstrated the concentration is below the SSAL of 250 ppt TEQ by testing of all three replicates using EPA Method 1613b with a DB-5ms (or equivalent) column. Concentrations of either interval determined to be greater than 220 ppt TEQ and less than or equal to 250 ppt TEQ resulted in testing of all three replicates for the interval with the highest concentration by USEPA Method 1613b with additional column confirmation analyses, and subsequent derivation of a 95% UCL (see Note 2 of Figure 8-7). If the 95% UCL was greater than 250 ppt TEQ, performance of the presumptive remedy was implemented as specified in the approved IRDC (Appendix A) at that DU. If the detected concentration at the DU was less than or equal to the SSAL, dust accumulated in the dwelling(s) duct work did not require a remedy. If the detected concentration at the DU was greater to dust accumulated in the dwelling(s) duct work was performed as per Section 7.4.7.1 of the approved IRDC (Appendix A).

## 8.2.9 Communication of Results to Property Owner

Dow provided written notification of the results of soil testing to the individual property owners in a timely manner. The written communication briefly described the next steps for the property owner based on the testing results. Written notification included contact information for both MDEQ and Dow representatives who were available to discuss the information reported to the property owners. Example letters that were used to communicate results to the property owners were presented in Attachment E in the IRDC (Appendix A).

### 8.2.10 Properties with No Further Action

Based on the result of the decision rules and the property-specific samples, it was determined whether the property requires remedy or if no further action was warranted. For properties where no further action was warranted, Dow provided the property owners with written notification of the results of soil testing and that no further action was necessary on their property by Dow. MDEQ reviewed the information provided by Dow before it was sent to the property owners and also sent letters to the property owners confirming that no further action is necessary for these properties.

## 8.2.11 Properties with Remedy

Those properties that require remedy based on the result of the decision rules and the propertyspecific samples will be discussed in Part III.



## 8.2.12 Decision Rules for Non-Residential Property

As discussed above, current data indicated that non-residential property in the MRA, with two exceptions described above where more data was needed, was below the non-residential DCC and, therefore, no further evaluation or remedial action was necessary. This section sets forth remedial decisions for two exceptions: 1) the rail track spur area discussed above, and 2) densely wooded areas greater than 7,200 sq ft (based on zoning code, see Section 7.4.3.1 of the approved IRDC [Appendix A]) with no active residential use. At each DU, soil testing results were used to determine if the presumptive remedy was warranted at such properties.

One composite sample and two replicates were collected from these non-residential properties and were tested at the laboratory by Method 8280 MAS. If results of testing indicated that a concentration less than or equal to 990 ppt TEQ for the DU, either the DU was demonstrated to be below an appropriate action level for non-residential use incorporating appropriate site-specific exposure assumptions or a presumptive remedy was implemented as specified in Section 7.4.7 of the approved IRDC (Appendix A).

Figure 8-1 One-way Analysis of WHO-TEQ 2005 (ppt) By Depth Interval



## Quantiles

Level	Minimum	10%	25%	Median	75%	90%	Maximum
(1) 0 in - 1 in	2.5	29.26	61.85	123	285.5	495.6	2750
(2) 1 in - 6 in	2.9	20.64	62.3	155	377	564	10500
(3) 6 in - 1 ft	0.49	5.814	22.025	85.3	231	569.2	1310
(4) > 1 ft	0.231	2.111688	8.295368	35.59355	92.96923	212.2579	806.5071

### **Means and Std Deviations**

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
(1) 0 in - 1 in	361	221.142	294.852	15.519	190.62	251.66
(2) 1 in - 6 in	173	303.207	817.180	62.129	180.57	425.84
(3) 6 in - 1 ft	138	195.723	282.452	24.044	148.18	243.27
(4) > 1 ft	154	76.793	109.450	8.820	59.37	94.22

#### Nonparametric Comparisons For All Pairs Using Steel-Dwass Method q\* Alpha

0.05

**q\*** 2.56903

Level	- Level	Score Mean Difference	Std Err Dif	Z	p-Value
(2) 1 in - 6 in	(1) 0 in - 1 in	23.270	14.26754	1.63097	0.3611
(3) 6 in - 1 ft	(2) 1 in - 6 in	-38.455	10.26321	-3.74687	0.0010*
(4) > 1 ft	(3) 6 in - 1 ft	-41.934	9.89749	-4.23685	0.0001*
(3) 6 in - 1 ft	(1) 0 in - 1 in	-48.259	14.43111	-3.34412	0.0046*
(4) > 1 ft	(2) 1 in - 6 in	-91.600	10.47394	-8.74550	<.0001*
(4) > 1 ft	(1) 0 in - 1 in	-137.013	14.32274	-9.56613	<.0001*

Figure 8-2 Omni-directional Short-Range Variogram



Figure 8-3 North-South Directional Long-Range Variogram



Figure 8-4 East-West Directional Long-Range Variogram





# **Decision Rules**



# Figure 8-6. Decision Rules for Residential or Residential–Like Decision Units

\*EPA Method 1613b analyses conducted using a single DB-5ms (or equivalent) GC column. A second column may be added as appropriate.

# **Decision Rules**



**Figure 8-7.** Decision Rules for Residential or Residential –Like Decision Units with Extensive Landscaping \* EPA Method 1613b analyses conducted using a single DB-5ms (or equivalent) GC column. A second column may be added as appropriate. Notes 1 & 2 See Page 2 Page 1 of 2

# **Decision Rules (notes)**

<u>Note 1:</u>

$$[6-12''] = \left(\frac{[0-12'']}{0.5'}\right) - [0-6'']^{8280MAS}$$

If 
$$[0-12"] < [0-6"]$$
  $[6-12"] = \left(\frac{[0-12"]^{8280MAS}}{0.5'}\right) - [0-6"]^{1613b}_{95\% \text{ UCL}}$ 

If 
$$[0-12"] > [0-6"]$$
  $[6-12"] = \left(\frac{[0-12"]_{95\% UCL}^{1613b}}{0.5'}\right) - [0-6"]^{8280MAS}$ 

**Figure 8-7.** Decision Rules for Residential or Residential –Like Decision Units with Extensive Landscaping \* EPA Method 1613b analyses conducted using a single DB-5ms (or equivalent) GC column. A second column may be added as appropriate.



# 9.0 Implementation of Design Sampling

This section presents an overview of the Implementation Annual Reports for each of the three years of design sampling for the MAS project. Work plans for each of the three years were submitted and approved prior to implementation of proposed activities. The Year 1 Implementation Work Plan was presented as Section 8.0 of the approved May 25, 2012 IRDC (Appendix A). The Work Plans for Years 2 and 3 of implementation are presented in Appendix D. Annual Reports were submitted for each year of implementation detailing the results of each year of activities. The Implementation Annual Reports are presented in Appendix E.

During the three years of implementation, access was obtained to property that previously had denied access or where owners had not responded. The sections below summarize the final total number of DUs that were sampled, and results of that sampling for each of the corresponding areas shown in Figure 7-5.

The results of the remedy implementation activities will be presented in the RAP (Part III).

## 9.1 Year 1 Implementation (2012)

Year 1 implementation began in June 2012 upon approval of the May 25, 2012 IRDC (Appendix A). Work in Year 1 was implemented on a DU-by-DU basis and focused on the properties closest to the Midland facility within the MRA. The Year 1 implementation plan initially addressed 106 properties (Phase I); however, because the implementation effort was completed ahead of schedule, 57 additional properties were added in August 2012 (Phase II). The addition of Phase II was approved by MDEQ on July 23, 2012.

Table 9-1 presents the properties included in the Year 1 Implementation activities. These areas are also shown on Figures 9-1 and 9-2. The following table provides a breakdown by outcome.

Totals	Number of DUs
Year 1 DUs with Access Requested	171
Year 1 DUs Sampled	168
Year 1 DUs with No Access (declined or no response)	3
Number of Properties with No Further Action	140
Number of Properties where Remedy was Completed	28

The documentation of the completion of the presumptive remedy is provided in Part III.



## 9.2 Year 2 Implementation (2013)

Year 2 was implemented in accordance with the 2013 Work Plan and Adaptive Management Plan dated February 15, 2013 and approved by MDEQ on May 3, 2013. Year 2 implementation was completed in three phases, the first of which (Phase I) began in Fall 2012 as an early start to the 2013 work. Phase I 2013 was proposed to MDEQ in a letter submitted via email on September 6, 2012. MDEQ provided their approval of the early kickoff to 2013 implementation via email on September 13, 2012. Year 2 focused on the properties moving sequentially outwards from the Midland facility within the MRA, in three phases:

- Phase I (approved 2012 and initiated in the fall of 2012);
- Phase II (initiated in the Spring of 2013); and
- Phase III (initiated in the Summer of 2013).

Table 9-2 presents the properties included in the 2013 implementation activities. These areas are also shown on Figure 9-3.

The following table provides a breakdown by outcome.

Totals	Number of DUs
Year 2 DUs with Access Requested	860
Year 2 DUs Sampled	848
Year 2 DUs with No Access (declined or no response)	12
Number of Properties with No Further Action	774
Number of Properties where Remedy was Completed	74

The documentation of the completion of the presumptive remedy is provided in Part III.

## 9.3 Year 3 Implementation (2014)

Year 3 was implemented in accordance with the 2014 Work Plan and Adaptive Management Plan dated March 14, 2014 and approved by MDEQ on June 27, 2014. 2014 Phase I implementation began in September 2013. These efforts were proposed to MDEQ in a letter submitted via email on September 19, 2013. MDEQ provided a partial approval on September 25, 2013, with their final approval with modifications of the 2013 Additional Work on October 14, 2013. Year 3 implementation was completed in four phases, the first of which (Phase I) began in Fall 2013 as an early start to the 2014 work:



- Phase I final phase of MRA;
- Phase IA non–residential properties apart from residential neighborhoods;
- Phase II non-residential properties in residential neighborhoods; and
- Phase III MRA boundary confirmation.

2014 Phase I focused on the properties moving sequentially outwards from the Midland facility within the MRA. Tables 9-3 and 9-4 present the properties included in the 2014 implementation activities. These areas are also shown on Figure 9-4.

In accordance with Section 9.0 Adaptive Management of the IRDC, Dow proposed to perform additional work to verify the boundary of the MRA during 2014 Phase III. Along portions of the western and northeastern boundary, further testing was necessary to verify the location of the MRA boundary. Figure 9-5 shows the areas where boundary verification was completed. The 2014 Phase III boundary verification activities included the following:

- Northeast MRA boundary (I-008 and I-010);
- Western MRA boundary; and
- Non-residential properties.

The results of the Phase III boundary verification activities are discussed in detail in Section 10.0.

## 9.4 Non-Residential Property Sampling

During 2014, a limited number of non-residential properties adjacent to contiguous residential property blocks were incorporated into the sampling program during 2014 Phase IA and Phase II. There are two types of non-residential properties, being: (1) non-residential property in residential neighborhoods and (2) non-residential properties apart from residential neighborhoods.

## 9.4.1 Non-Residential Property in Residential Neighborhoods

These properties were included into the sampling program because they are largely surrounded by or located within predominantly residential areas. While the property use is non-residential today long term land use may reasonably be residential use. Therefore, although the generic



MDEQ DCC for dioxins and furans is 990 ppt TEQ for non-residential land use, the decision rules for implementation of remedy were consistent with those identified in Section 8.2.8 of this report.

## 9.4.2 Non-Residential Property Apart From Residential Neighborhoods

These properties are located outside residential areas, and long term use is not likely to become residential (see Figure 2-2). These properties (parcels 14-14-30-010, 14-13-10-800 and a portion of the Michigan Department of Transportation (MDOT) right-of-way) were included into the 2014 Phase IA sampling program to address specific property-specific needs:

- Samples were obtained from portions of the MDOT right-of-way to address a large construction project; and
- Samples were obtained from 14-14-30-010 and 14-13-10-800 to evaluate the northeast boundary of the MRA, as described in Sections 2.2 and 4.3 of this report.

The decision rules for these properties were consistent with the Section 7.5 of the approved 2012 IRDC (Appendix A).

Year 3 implementation began with Phase I in October 2013. The following table provides a breakdown by outcome.

Totals	Number of DUs
Year 3 DUs with Access Requested	652
Year 3 DUs Sampled	619
Year 3 DUs with No Access (declines or no response)	33
Number of DUs with No Further Action	587
Number of DUs where Remedy was Completed	32

The table below summarizes the current status of the work completed over the three years of implementation and includes all properties in the original MRA proposed in 2012, as well as the boundary verification areas.



Totals	Number of DUs
DUs with Access Requested	1683
DUs Sampled	1635
DUs with No Access (declines or no response)	48
Number of DUs with No Further Action	1501
Number of DUs where Remedy was Completed	134

Documentation of the completed remedies is provided in Part III.













# 10.0 Final Extent of MRA

Dow is obligated to conduct corrective action to address off-site contamination pursuant to the approved *IDRC* (Appendix A). The MRA was established to include all properties where corrective action may be necessary due to the historical aerial release. The MRA was initially defined using data that existed at the time the project was started in 2012. Since then, approximately 1,780 additional samples were collected and analyzed to establish the extent of contamination and to determine where remedial action was necessary. The final MRA boundary has been verified and encompasses the area where properties have the reasonable possibility to be greater than 250 ppt dioxin and furan TEQ from aerial releases from the site. This was accomplished by including property that has been addressed or will be addressed (e.g. institutional controls) for all future land use. At the conclusion of the MAS project, Dow's obligations will have been fulfilled and the historical airborne release has been addressed with remedial actions that are appropriate.







Figure 10-3 Isomer Fingerprint as a Component of TEQ



Figure 10-4 Isomer Fingerprint as a Component of TEQ



Figure 10-5 Isomer Fingerprint as a Component of TEQ



Figure 10-6 Isomer Fingerprint as a Component of TEQ Original Sample 515 East Buttles Street Typical Midland Soils Fingerprint

50%



Figure 10-7 Isomer Fingerprint as a Component of TEQ





# 11.0 Extent of Contamination

The practical purpose of the MRA boundary was to establish an area that encompassed the extent of contamination beyond which no remedy was necessary. The final boundary was defined when the available incremental compositing data demonstrated that areas beyond the boundary are less than 250 ppt TEQ. This was accomplished when a buffer of three properties in a row, moving outward from the Michigan Operations plant, were sampled and results were below the SSAL (taking physical features and age of property development into account). Roadways were not counted as a "property" for this purpose, but were used to delineate the final boundary if clean properties were on either side.

During the 2006 CH2M Hill sampling activities, transect sampling areas E-007, I-008 and I-010 were sampled and each exhibited a detected concentration of dioxin and furan TEQ at a level greater than 250 ppt in a discrete sample. E-007 is located north of the currently defined MRA. The specific location of this area is identified in Figure 4-2 of Part I. I-008 is located along the east boundary of the currently defined MRA, and I-010 is roughly <sup>1</sup>/<sub>4</sub>-mile to the east of the boundary, also shown in Figure 4-2 of Part I.

The outlier area was assessed following the same decision rules that were presented in Section 7.4.4 of the IRDC (Appendix A). Of the 14 properties in E-007, samples from 13 of them were obtained and the results were all significantly less than the SSAL. Dow has not been able to obtain access from the one remaining property in the southwest corner of the E-007. Over 90% of the properties sampled in the E-007 area were less than the SSAL; therefore, this area is beyond the extent of contamination and was removed from the MRA.

A significant portion of the current northeast boundary of the MRA does not contain residential property. Because widespread sampling that took place within residential areas did not occur here, this portion of the current boundary was further considered as described in Section 7.7 of the IRDC (Appendix A). Additional sampling in properties north and east of the current MRA as depicted in Figure 10-1 was originally planned to be proposed to verify the boundary under either of the following circumstances:



- Either I-008 or I-010 to the northeast are confirmed to be greater than the SSAL (section 7.2 of the IRDC); or
- Remedy is required for the properties located generally between Swede Rd, Carolina and Iowa Streets.

Outlier areas I-008 and I-010 are each owned by The Dow Chemical Company. Each of these outlier areas was split into two approximately 1-acre DUs for the purposes of sampling. Results of composite sample testing from the I-008 or I-010 DUs are less than the SSAL, therefore, no further action is required. The areas along the north and east MRA boundary are large tracts of non-residential land owned by Dow and not likely to be developed for residential use in the future. These areas have been presumptively included within the MRA.

Remedies were required for some properties located between Swede Road, Carolina, and Iowa Streets, and additional sampling was completed to verify the location of the northeastern boundary (during 2014 Phase III). These areas are shown on Figure 10-2. In areas directly north of the MRA, additional areas along Ashman Road were used to verify the boundary, as properties closer to the MRA were developed more recently, and bias due to the known age relationship had to be overcome. Of the 121 DUs proposed as part of the boundary verification program in the northern area, access to conduct sampling was received for approximately 101 of the DUs (approximately 84%). All results were less than the SSAL, including the properties immediately north of the MRA boundary and the properties along Ashman Street. Based on these results, this area is beyond the extent of contamination which confirms the location of the northeastern boundary, as shown on Figure 10-2.

Along the eastern MRA boundary, all the property sampled east of Longview Road, including a City of Midland Park and residential properties along Waldo Road were all found to be below the SSAL. This block of properties provides a buffer of well over three properties in a row, moving outward from the Michigan Operations plant, that have results below the SSAL. Included in this area are undeveloped woodlands and non-residential properties are surrounded by sampled properties with results below the SSAL. Based on these results, this area is beyond the extent of contamination and the eastern boundary may be moved to the west of its original location to that shown in Figure 10-2 as the yellow line.



Along the northern boundary, the area extending from the western property line of the residential lots west of Virginia Street to the north side of Carpenter Street, shown on Figure 10-2, had a single DU with a result greater than 250 ppt TEQ. The source of contamination at this DU was not related to the historical aerial release, as described in greater detail below. Other than this single DU, the remaining properties provide a buffer of well over three properties in a row, moving outward from the Michigan Operations plant, that have results below the SSAL. There are 24 non-residential properties along South Saginaw Road that have not been sampled; however, there is a buffer of three properties in a row on either side of this area with sample results below the SSAL.

Along the western boundary of the initial MRA, there were two DUs with results greater than the SSAL located at the perimeter of the boundary. Additional verification was necessary and these areas are shown on Figure 10-2. Additional sampling was performed outside of the MRA to verify the location of the MRA boundary in these areas. Over 90% of the 82 DUs granted access for sampling. Two additional properties were identified in this area with results above the SSAL; however, the source of contamination at all of the DUs that were greater than the SSAL outside the proposed MRA boundary was not related to the historical aerial release, as described in greater detail below.



# 12.0 Property Building Age

Dioxin and furan TEQ concentrations were compared to the year of building construction within the MRA. The analysis suggests there is a correlation between the dioxin and furan TEQ concentration and building age, with the TEQ concentration increasing with building age up to 1947 (approximately 66 years). Prior to 1947, the correlation is inconsistent and the dioxin and furan TEQ concentration does not appear to increase with building age (URS, 2014).

As part of boundary verification activities, MDEQ requested that Dow select areas with older building age to confirm the boundary wherever possible. Most boundary verification areas included properties with sufficient building age; however, directly north of the MRA, additional areas along Ashman Road were used to verify the boundary in place of properties closer in to the MRA that were developed more recently. Where the final MRA boundary is proposed to be moved in closer to the Michigan Operations plant, the data used to support this adjustment was from properties with development ages near 1947. This conservative evaluation was completed so that the potential age bias did not impact the final extent of the MRA.


## 13.0 Properties with Fill Contaminated by Other Sources

When determining the dioxin and furan TEQ, the concentrations of different congeners are measured and a weighted average is calculated (a total of eleven congeners of dioxins and furans are measured as part of the MAS 8280 method). Different sources of contamination have varying amounts of dioxin and furan congeners, which can be used to identify contamination sources. By comparing the relative contribution of each of the different types of dioxin and furan congeners for each DU, it is possible to determine how similar the distribution pattern for that DU is to other contamination in the area, or whether it is from another source (see Buekens, A., et al., 2000; Uchimiya, M. et al., 2007; and Sundqvist, K.L. et al., 2009). As a result of the historical aerial release, a comparison of the numerous samples collected demonstrated a common distribution pattern of dioxin and furan congener concentrations, much like a chemical 'fingerprint.' However, the results of several properties indicated a source of contamination that was not representative of the historical aerial release (e.g., the dioxin and furan fingerprint was different). Based on further evaluation conducted for each of these properties that included a review of any available property history documentation, it was concluded that these properties had fill contaminated by another source.

Specifically, there were five DUs outside of the proposed final MRA boundary along the western edge that had samples with a total TEQ greater than the SSAL. Every other property in this area had results below the SSAL. The 'fingerprint' of these five samples is significantly different than that of other properties throughout the MRA. Figures 10-3 through 10-7 compare the 'fingerprints' of each of the individual DUs that are beyond the final MRA boundary that were greater than the SSAL, with results from properties randomly selected across the MRA. Each of these five properties outside of the MRA consistently had significantly higher concentrations of certain furans, particularly 2,3,7,8-TCDF; 2,3,4,7,8-PCDF; and 1,2,3,4,7,8-HCDF, which is inconsistent with the pattern that represents the historical aerial release and is representative of fill that was contaminated by another source. Although these properties were remediated because the results were greater than the SSAL, the source of contamination was not a result of the historical aerial release. Therefore, this western area is excluded from the final MRA boundary.



Based on the soil sampling results, the final MRA boundary is presented on Figure 10-1. Figure 10.1a presents the final MRA boundary with properties where remedy was completed.



## 14.0 References

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