FORM EQP 5111 ATTACHMENT TEMPLATE B5
ENVIRONMENTAL MONITORING PROGRAMS

This document is an attachment to the Michigan Department of Environment, Great Lakes, and Energy's (EGLE) *Form EQP 5111, Operating License Application Form for Hazardous Waste Treatment, Storage, and Disposal Facilities.* See the instructions for Form EQP 5111 for details on how to use this attachment. All references to Title 40 of the Code of Federal Regulations (40 CFR) citations specified herein are adopted by reference in R 299.11003.

The administrative rules promulgated pursuant to Part 111, Hazardous Waste Management, of Michigan's Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (Act 451), R 299.9611 establishes requirements for the environmental monitoring programs for hazardous waste management facilities. Owners and operators of hazardous waste treatment, storage, or disposal facilities must develop an environmental monitoring program capable of detecting a release of hazardous waste or hazardous waste constituents from the facility to groundwater, air, or soil.

This license application template addresses requirements for an environmental monitoring program for hazardous waste management units and the hazardous waste management facility for the Dow Silicones Corporation (Dow Silicones) facility. The template includes either a monitoring program description or a demonstration for a waiver from the monitoring requirements in accordance with R 299.9611(3)(a) and (b) and R 299.9611(4) as indicated below:

Groundwater Monitoring Program *(Check as appropriate)*

☒ R 299.9612 detection monitoring program and sampling and analysis plan for one or more units
☐ Waiver for one or more units

If appropriate, both boxes may be checked if different monitoring programs and waivers apply to the units at the facility.

Ambient Air Monitoring Program (Check as appropriate)

☐ Monitoring program and sampling and analysis plan

☒ Waiver

Annual Soil Monitoring Program (Check as appropriate)

☐ Monitoring program and sampling and analysis plan

☒ Waiver

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B5 ENVIRONMENTAL MONITORING PROGRAMS

The Dow Silicones facility will comply with the requirements for a groundwater monitoring program by implementing the program described in this section. This program was developed to satisfy the requirements of R 299.9612 and R 299.9629 and 40 CFR §§264, except 40 CFR §§264.94(a)(2) and (3) and 264.94(b) and (c).

This module presents the environmental monitoring programs that will be implemented following license renewal in 2022. The monitoring programs include:

- Groundwater monitoring
  - Detection monitoring (deep monitor wells)
  - Supplemental monitoring (shallow monitor wells)
  - Corrective action monitoring (site interceptor system (SIS), 604 area vaults, and quench pond)
- Surface water monitoring
- Landfill leachate monitoring

Dow Silicones requests a continuation of the waivers for air and soil monitoring; see Sections B5.B and B5.C.

Reporting

Quarterly Environmental Monitoring: The licensee shall provide the results of all environmental monitoring required by this license to the Division in accordance with Condition II.I.3. of this license. The results shall be provided as follows:

The licensee shall submit Quarterly Environmental Monitoring Reports to the Division. At a minimum, the report shall include the following information:

(1) A narrative summary of the quarter's sampling events.

(2) Data tables with the monitoring data obtained during the quarter.

(3) Indication of any increased frequency beyond what is required by the license.

(4) Program specific quarterly evaluations listed in Module B5 of this license.

Beginning in 2022 the licensee shall provide the results of environmental monitoring required by this license to the Division either by a Report as specified in Appendix B5-3 of this license or by updating an Environmental Monitoring Information System (EMIS) if approved by the Division.

Annual Environmental Monitoring Report: The licensee shall submit an Annual Environmental Monitoring Report to the Division no later than March 1 for the previous calendar year's activities. At a minimum, the report shall include the following information:

(i) A narrative summary of the previous calendar year's sampling events, including the dates of the sampling events, and the identification of any significant problems with respect to sampling and analysis plan (SAP) defined procedures.

(ii) Data tables with the monitoring data obtained during the calendar year that has not been previously provided in a Quarterly Environmental Monitoring Report.

(iii) Program specific quarterly and annual evaluations listed in Module B5 of this license.

B5.A GROUNDWATER MONITORING PROGRAM

[R 299.9611(2)(b) and (3), R 299.9612, and R 299.9629 and 40 CFR, Part 264, Subpart F, except 40 CFR §§264.94(a)(2) and (3), (b), and (c), 264.100, and 264.101]

The groundwater monitoring program includes detection monitoring (deep monitor wells); supplemental monitoring (shallow monitor wells); and corrective action monitoring (site interceptor system (SIS), 604 area vaults and quench pond). The SIS is an interim response activity that encompasses the regulated units (800/1000 Block Landfill, 806 Tank Farm, 801 Building and 809 Container Storage Building) listed in **Table B5-1,** as well as most other areas of the Dow Silicones facility.

B5.A.1 Unit-Specific Groundwater Monitoring Program

Table B5.A.1 Groundwater Monitoring Program

Dow Silicones will conduct monitoring of groundwater associated with specific units listed in **Table B5-1**. The hydrogeological basis for determining the groundwater monitoring program is provided in Module B3, Hydrogeologic Report.

B5.A.2 Groundwater Monitoring Program Waiver

[R 299.9611(3)]

Dow Silicones does not request a waiver of the groundwater detection, corrective action, or supplemental monitoring programs.

B5.A.3 General Groundwater Monitoring Requirements

[R 299.9612 and 40 CFR §§264.97 and 264.91(b)]

The Dow Silicones facility will comply with the requirements for a groundwater monitoring program by implementing the program described in this section. This program was developed to satisfy the requirements of R 299.9612 and R 299.9629 and 40 CFR §§264.98 and 264.99, except 40 CFR §§264.94(a)(2) and (3) and 264.94(b) and (c). The basis for determining the groundwater monitoring program for each unit is provided in Template B3, Hydrogeologic Report, of this application that was prepared in accordance with R 299.9506.

B5.A.3(a) Groundwater Monitoring Sampling and Analysis Plan
[R 299.9611(2)(a)]

A sampling and analysis plan for groundwater monitoring at Dow Silicones facility is included in this section. The SAP was prepared in accordance with the requirements specified in R 299.9611(2)(a). All sampling and analyses performed pursuant to this application will be consistent with the SAP. All samples for the purpose of environmental monitoring will be collected, transported, stored, and disposed by trained and qualified individuals in accordance with the QA/QC procedures and processes outline in this module.

Table B5-2 presents the sampling frequencies for this groundwater monitoring program, including:

- Deep monitoring wells
- Shallow monitoring wells and manholes
- Site Interceptor System
- 604 Vaults
- Quench Ponds

Surface Water and Landfill Leachate Sampling Frequency is discussed in Sections B5.D and B5.E, respectively.

Deep Monitoring Wells

Groundwater in the Regional Aquifer has been sampled semi-annually from the deep monitoring wells listed in **Table B5-2** since 1994. Dow Silicones will continue to sample these wells semi-annually, as required in 40 CFR 264.98(d). Water levels are measured in each well at each sampling event, prior to sampling.

Shallow Monitoring Wells

Ground water in the shallow saturated zones is sampled semi-annually from the five shallow monitoring wells and three manholes listed in **Table B5-2**. Water levels are measured in each well at each sampling event, prior to sampling.

Site Interceptor System (SIS)

The (SIS is sampled quarterly for pH, certain metals, certain VOCs and fluoride, as well as biennially for a RCRA Appendix IX scan (excluding PCBs, dioxins and furans). Sampling details for the SIS are shown in **Table B5-2**.

604 Vaults

The 604 area vaults are sampled semi-annually as shown in **Table B5-2**.

Quench Ponds

The quench pond wells are sampled semi-annually as shown in **Table B5-2**.

Static Water Level and Purging

Each monitoring well has a permanent, top-of-casing reference mark on the rim of the well casing. The elevations of these marks relative to USGS benchmark at the Midland plant were determined by survey. The elevations of the deep and shallow monitoring wells are re-surveyed every three years and any corrections determined and recorded. The elevations of the manholes, staff gauges and piezometers used to monitor hydraulic gradients in the SIS are surveyed annually.

Water levels are measured prior to purging to ensure the levels are not affected by the purging. The device used to measure the water levels is rinsed with distilled water between well locations.

Static water levels are measured in a well each time the well is sampled. In wells where the static water level is below the top of the casing, the distance from a permanent, top-of-casing reference mark on the rim of the well casing to the static water level is measured to within 0.01 foot with a conductivity sensor well probe or with a chalked steel tape. To ensure accurate measurement, the well probe or steel tape is lowered into the well alongside the reference mark. The elevation of the static water level is calculated by subtracting the distance from the fixed datum to the static water level from the elevation of the fixed datum. This will determine the elevation of the static water level to an accuracy of 0.01 foot.

DMW-9 is the only well in this monitoring program in which the static water level is above the top of the casing. During spring, summer, and fall DMW-9 is equipped with a pressure gauge which reads pressures from 0 to 100 inches of water. During the winter the gauge on DMW-9 is removed and the well is plugged so the gauge is not damaged by ice. The elevation of the static water level is measured by closing all of the valves at the well head, attaching a pressure gauge, allowing the pressure to stabilize, and then measuring the artesian pressure and the distance from the center line on the pressure gauge to a fixed datum, typically the top of the casing. The water level is calculated by first converting the units of the pressure measurement to feet of water.

Sampling Equipment

The deep monitoring wells have dedicated sampling equipment to reduce the possibility of cross contamination of a well. The dedicated sampling equipment is used to purge and sample the wells. Sampling equipment may be repaired or replaced with equivalent equipment as necessary.

Deep monitoring wells DMW-4A and DMW-6A have permanent electric submersible pumps. All of the piping is 1-inch diameter stainless steel, and only Teflon® tape was used on the joints.

Monitoring wells DMW-10, DMW-11 and DMW-12 have dedicated Well Wizards from QED Environmental Systems, Inc. These pumps are positive displacement bladder pumps with Teflon® bladders and Teflon® lined tubing. The pumps are equipped with a fill and discharge cycle control mechanism to vary the flow rate and bladder cycling time. The intakes are at the bottom of the pumps, which two feet above the top of the well screen. Inflatable packers are placed 5 feet above the bottom of the pumps to reduce the required purge volumes.

Monitoring well DMW-9 is a flowing well and does not have any sampling equipment. Instead, the natural artesian head is used to purge and sample the well. The well head device at DMW-9 is shown with the well log in the Hydrogeologic Report.

The shallow monitoring wells (listed in **Table B5-2**) have dedicated PVC bailers with polypropylene rope. The manholes included in the shallow monitoring well program are sampled using a disposable bailer or sampled using a peristaltic pump and disposable tubing.

- The SIS is sampled using a disposable bailer.
- The 604 Vaults are sampled using disposable bailers at each vault.
- The Quench Pond wells are sampled using dedicated bailers at each well.

Purging

The volume of water purged prior to sampling equals 3 times the submerged casing volume plus the porous portion of the filter pack (except at DMW-9, which is a flowing well).

Monitoring wells DMW-10, DMW-11, and DMW-12 all contain inflatable packers that are inflated to the proper pounds per square inch (PSI) as documented on the field forms and confirmed to hold that pressure for five minutes prior to purging the well. The packers are all located 12 feet above the bottom of the well. Therefore, the length of the casing to be purged is 12 feet, and the required purge volume is 6 gallons. DMW-4 and DMW-6A do not have packers and the total purge volume necessary is removed using the dedicated permanent submersible pumps. The volume of water purged prior to sampling equals three times the submerged casing volume plus the porous portion of the filter pack.

DMW-4A requires a second sample to be collected after an additional hour of purging. This second sample is analyzed only for dissolved lead and zinc.

For DMW-9, the depth to the water is zero feet, and the purge volume is only dependent on the well depth. The length from the top of the casing to the bottom of the screen is approximately 235 feet and the casing is 2 inches in diameter, so the required purge volume for DMW-9 is set at 123.5 gallons (235 x 0.49). This well is normally capped.

Samples are collected directly into the sample bottles. The transfer to the sample bottles is performed as gently as possible to reduce the exposure of the sample to the air. Samples from the Well Wizard bladder pumps are collected with the flow pressure throttled back, allowing a gentle discharge of the sample into the sample bottle.

Deep monitoring wells are purged as described above. The volume purged is either directly measured with a graduated container or calculated by using a flow rate over time calculation. When the actual purge volume is calculated by the pumping rate, the pumping rate is checked periodically throughout the purge time.

Ground water purged from the deep monitoring wells is not hazardous (see Module B3, Hydrogeologic Report) and the available data in the Hydrogeologic Report) and is disposed of on the ground, away from the well casing. If a deep monitoring well does pump dry before purging

three casing volumes, the well is allowed to stabilize and sampled within 24 hours. Purge water is discharged to the ground away from the well location.

Shallow monitoring wells are low yielding wells that typically do not produce three casing volumes plus the filter pack volume of water when bailed. The shallow monitoring wells are bailed dry with dedicated bailers and sampled within 24 hours and typically allowed to stabilize overnight. The bailer is pulled in and out of the water gently to minimize the aeration of the groundwater in the well. Purge water withdrawn from the shallow monitoring wells is placed in a container and disposed of in the Dow Silicones chemical sewers.

During purging of the well, the first two bailers are slowly lowered into the well. The first bailer is lowered until approximately one half of the bailer is submerged and then the bailer is withdrawn from the well. The water removed from the first bailer is visually checked for the presence of light non-aqueous phase liquids (LNAPL), and the presence or absence of visible LNAPL is noted on the field form (Appendix B5-1). The second bailer is slowly lowered all of the way to the bottom of the well and then slowly withdrawn from the well. The water removed from the second bailer is visibly checked for dense non-aqueous phase liquids (DNAPL), and the presence or absence of visible DNAPL is also noted on the field form (Appendix B501).

Sample Parameters and Basis

Table B5-2 presents the sampling parameters for this groundwater monitoring program, including:

- Deep monitoring wells
- Shallow monitoring wells
- Site Interceptor System
- 604 Vaults
- Quench Ponds

Dow Silicones may request additions or deletions to the sampling parameters in order to improve the effectiveness of the program or to delete parameters that are no longer necessary. Such requests will be supported by data and are subject to approval by the EGLE.

Deep Monitoring Wells

Deep monitoring wells are analyzed for primary monitoring parameters, secondary monitoring parameters, and tracking monitoring parameters (cations/anions). The primary monitoring parameters are chemicals found in the landfill leachate with concentrations greater than 0.5 mg/L. Lead is also a primary monitoring parameter because the landfill is licensed for lead containing wastes, although lead is generally not detected or has low concentrations in the landfill leachate. The secondary monitoring parameters, other than tracking parameters, are chemicals sometimes detected in landfill leachate. The cations and anions are tracking parameters used to develop Stiff diagrams.

Shallow Monitoring Wells

Shallow monitoring wells are analyzed for secondary monitoring parameters and tracking monitoring parameters (major cations/anions). The secondary monitoring parameters are

chemicals found in the landfill leachate with concentrations greater than 0.5 mg/L. Lead is also a secondary monitoring parameter because the landfill is licensed for lead containing wastes. The cations and anions are tracking parameters used to develop Stiff diagrams.

Site Interceptor System (SIS)

The SIS is analyzed biennially for the Appendix IX list (excepting PCBs dioxins and furans) at the request of the EGLE. The SIS is analyzed quarterly for parameters listed in **Table B5-2**, which are based on the previous monitoring program.

604 Vaults

The 604 vaults drains are analyzed for chemicals associated with the processes formerly used at the vaults.

Quench Ponds

The quench pond wells are analyzed for chloride, which was produced by the quenching process.

Sample Collection Procedure

[40 CFR 264.97(d)(1)]

The sample collection procedures described in this section are designed to generate samples and data that are representative of conditions at the site at the time of the sampling. These procedures document sample collection so that future users can re-evaluate the data, if necessary.

Sample Withdrawal

Sampling with a bailer from DMW-4 and DMW-6A is not feasible as the submersible pumps cannot be temporarily removed. Inflatable packers are used while purging deep monitoring wells DMW-10, DMW-11, and DMW-12, therefore, bailers cannot be used for sampling these wells. The natural artesian head is used to collect the sample from DMW-9, eliminating contact of the sample with extra sampling equipment.

In the shallow monitoring wells, the dedicated bailers are gently lowered into the water in the well, and samples are collected by gently pouring the water into the sample bottles. The manholes included in the shallow monitoring well program are sampled using a peristaltic pump or disposable bailer that is lowered into the manhole to collect water.

All samples for dissolved metals are filtered at the time of sampling, before contacting the nitric acid preservative. Metals filtration is done in the field using a peristaltic pump, silicon tubing, and a 0.45 micron in-line filter. New tubing and a new inline filter are used for each sample location, and the groundwater is allowed to pass through the filter for approximately 10 seconds prior to sample collection. These items are single-use and are then properly disposed of. (**Table B5-2** identifies which samples are filtered.)

Sample bottles are filled for volatiles first, then other required constituents. Samples for volatile organics are collected in glass vials, filled just to overflowing, ensuring that no air bubbles pass through the sample as the vial is being filled. Each vial is sealed with a clean Teflon® lined septum and caps such that no headspace or entrapped air bubbles are present in the sample.

Separate portions of the sample are drawn off for the analysis of unstable parameters such as pH. These portions are drawn off and analyzed after the samples for laboratory analyses have been collected and preserved. None of the probes used for in-field analyses will come in contact with the water samples collected for laboratory analyses.

Sample Blanks – Quality Control

Refer to Quality Control Table in **Table B5-2**.

When the sample bottles are prepared prior to shipment to the field, one complete set of sample bottles is selected, filled with de-ionized water, and labeled "trip blank". The trip blanks are transported to the field and sent to the laboratory for analyses along with the other sample bottles.

Documentation of Sample Collection

The procedures used in the field to collect the samples are documented so that future users of the data can review and re-evaluate any possible bias introduced by these procedures. Customized field data entry forms are used for each well/location to assure that the sampling procedures are thoroughly documented. Customized forms are in **Appendix B5-1**. These forms provide thorough documentation and aid in efficient sample collection.

No monitoring program design can foresee all of the modifications that are required by changing field conditions, and field samplers may be confronted with field conditions that make it impossible to follow the designated sample collection procedures. If this occurs, the field sampler will note these changes on the field data entry form to document the actual procedures used during the sample collection. The field sampler completing a sampling event fills in all of the information on the field data entry forms and notes any deviations from the sample procedures. The field sampler then signs the forms, and the forms are retained to document the actual sampling procedures used.

Field Measurements

The pH and specific conductivity of the groundwater samples are measured in the field immediately after collecting the groundwater samples. A separate portion of the sample is drawn off for these analyses to avoid any contamination of the laboratory samples by the probes. The multi-parameter sonde is calibrated once a day prior to sampling. Calibration records are available upon request.

Analytical Procedures and Quality Control [40 CFR 264.97(d)(3)]

The analytical procedures are listed in Table B5-3. These analytical procedures include the target method detection limits used in reporting the data. Analytical methods may be revised in accordance with applicable future federal or state guidelines. Detection limits may vary based on the presence of interference in a sample, required dilutions or other analytical limitations.

Sample Preservation, Shipment and Chain of Custody [40 CFR 264.97(d)(2)] & [40 CFR 264.97(d)(4)]

Preservation techniques are used to retard the chemical and biological changes that may take place after a sample is collected. Samples collected in this monitoring program are placed in coolers with ice or cold packs immediately upon collection and then transported to the appropriate analytical laboratory where they are stored at 4.0° C until analysis. Samples are preserved as specified by the analytical method. Preservation techniques are summarized in **Table B5-3**. Sample preservation may be revised in accordance with applicable future federal or state guidelines or changes in analytical methods. Samples are shipped and delivered to the laboratory.

The chain of custody program documents the possession and handling of individual samples from the field collection through laboratory analysis. This program includes sample labels which identify the sample, the field data entry forms that record data about the collection of each sample, a chain-of-custody record to document the possession of all samples after collection, and laboratory logbooks that contain information about the analyses of the sample in the laboratory. An example chain of custody form is in **Appendix B5-2**. An equivalent form may be used.

B5.A.3(b) Description of Wells

[R 299.9612 and 40 CFR §264.97(a), (b), and (c)]

Deep Monitoring Wells (Detection Monitoring)

The wells that are used to monitor the Regional Aquifer are DMW-4A, DMW-6A, DMW-9, DMW-10, DMW-11, and DMW-12. The locations of these wells are shown on **Figure B5-1** and the monitoring well construction summary is included in **Table B5-4**.

Monitoring wells DMW-9 and DMW-11 are located up-gradient from the regulated unit and are used to collect samples that are representative of the ground water in the Regional Aquifer before it flows under the regulated unit. Monitoring wells DMW-4A, DMW-6A, DMW-10 and DMW-12 are screened in the Regional Aquifer at the point of compliance, just down-gradient of the regulated units, and are used to collect samples representative of the ground water passing the point of compliance.

The deep monitoring wells were designed for groundwater monitoring, and all of these wells are capable of yielding groundwater samples that are representative of the saturated zone in which they are screened.

Shallow Monitoring Wells and Manholes (Supplemental Monitoring)

The five shallow wells plus three manholes surrounding the landfill that are used for monitoring are SMW6-1, SMW6-2, SMW7-1, SMW7-2, SMW28-1, MH28-11, MH28-12, and MH10-15. These manholes are part of the SIS that collects shallow groundwater. The manholes are used to replace some shallow monitoring wells that became mostly dry after the SIS was installed. These wells are screened in the shallow surface sand that veneers the Lakebed Clay.

The locations of the shallow wells are shown on **Figure B5-1** and the monitoring well construction summary is included in **Table B5-4**.

The shallow monitoring wells were designed for groundwater monitoring, and all of these wells are capable of yielding groundwater samples representative of the saturated zone in which they are screened. The SIS collects shallow groundwater and the SIS manholes provide samples representative of shallow groundwater collected upstream of the manhole.

Site Interceptor System (SIS) (Corrective Action Monitoring)

The SIS is an interim response measure comprised of a system of drainage tiles surrounding the Midland plant site. See **Appendix B2-1** (Drawing Y1-86188) for details on SIS location. The samples are collected from a lift station at the lowest point of the SIS (southwest part of the site near Building 121) before the SIS flow mixes with other flows. Samples from this location are representative of the SIS water at the downstream end of the SIS.

Water levels are monitored at manholes along the SIS, staff gauges in Lingle Drain, and piezometers located in pairs on either side of the SIS. The locations are identified in **Table B5-2**. Drawing YI86188 in Appendix B2-1 illustrates the SIS and the monitoring locations.

604 Area Vaults (Corrective Action Monitoring)

Samples are collected from perimeter French drains installed around three former process vaults located near the 604 Building. The locations are identified as 7710, 7800, and 8015, corresponding to the names of the vaults (see **Figure B5-1** for locations). The drains remove shallow groundwater to the wastewater sewer for treatment. The water in these drains is representative of groundwater impacted by former processes at these vaults. The vault drains are an interim response measure, and well construction does not apply.

Quench Ponds (Corrective Action Monitoring)

Three shallow monitoring wells, designated as 25n-1, 25n-2 and 25n-3, have been installed in the 2500 Block in the area formerly occupied by the quench ponds. The Quench Pond wells have stainless steel screens and PVC risers and compatible with the groundwater conditions.

The locations of the quench pond shallow wells are shown on **Figure B5-1**.

B5.A.3(c) Procedure for Establishing Background Quality
[R 299.9612 and 40 CFR §264.97(a)(1) and (g)]

Background values for the volatile organic primary parameters listed in **Table B5-2** are the laboratory detection limits for each parameter. The background data for the inorganic primary and secondary monitoring parameters in DMW-9 and DMW-11, the up-gradient background wells, are summarized (range, mean, standard deviation and mean plus three standard deviations) in **Table B5-7**. Historical intra-well background data for down-gradient deep monitoring wells are summarized in **Table B5-7**. These summaries are based on the groundwater quality data through 2021, excluding statistical outliers.

B5.A.3(d) Statistical Procedures

[R 299.9612 and 40 CFR §§264.97(h) and 264.97(i)(1), (5), and (6)]

This section presents the statistical methods used to evaluate deep monitoring well data. Statistical evaluations are completed for the deep monitoring wells screened at the point of compliance, which is the Regional Aquifer down-gradient of the regulated unit. Separate statistical tests are conducted for each primary and secondary monitoring parameter in each well.

Data from the supplemental and corrective action ground water monitoring programs are evaluated graphically, with Stiff diagrams, or qualitatively.

Statistical Procedures for Primary Monitoring Parameters

Dow Silicones will determine if a statistically significant increase has occurred compared to background concentrations for each deep monitoring well primary parameter listed in **Table B5-2**. A concentration above the primary parameter's laboratory detection limit is considered potentially statistically significant. If none of the primary monitoring parameters are present at or above their detection limits, then the groundwater has not been affected by the regulated unit and the sampling event is over. If a primary monitoring parameter is present at or above its detection limit in a sample from a deep monitoring well, then that well is re-sampled in quadruplicate, and each of the four samples are analyzed for the detected primary monitoring parameter.

If the primary monitoring parameter is detected in none or only one of the four new samples, then the detection of the primary monitoring parameter during the initial sampling event will be attributed to sample contamination and the sampling event will be over. If the primary monitoring parameter is detected with at least two of the four re-samples above the detection limit, or if at in at least one of the four samples at a concentration more than five times the detection limit for that parameter, then the detection will be considered statistically significant.

In the event of a potentially significant detection, Dow Silicones will proceed with the requirements of 40 CFR 264.98(g) as required by R 299.9612.

Dow Silicones may also resample the well; evaluate laboratory methods; evaluate sampling equipment, well or method; evaluate statistical methods, evaluate data from the up-gradient deep monitoring wells, evaluate sources other than the licensed facility; or otherwise demonstrate that the potentially significant difference in the concentration of the primary parameter was not related to the regulated unit. Dow Silicones also may compare the data to the lowest applicable groundwater criterion developed by EGLE, pursuant to Parts 31 and 201 of PA 451, as amended. Such evaluations will be subject to review by the EGLE.

Statistical Procedures for Secondary Monitoring Parameters

The overall purpose of these intra-well statistical analyses is to evaluate changes in concentrations of secondary monitoring parameters (except for tracking parameters) in groundwater at the compliance wells down-gradient of the regulated unit. The statistical tests include the Shewhart-CUSUM control chart procedure for parameters with normal or normally transformed distributions and non-parametric tests for parameters without a statistical distribution.

The following sections describe updating of the background data and evaluation of the distribution of the intra-well background data; the outlier analysis; and the statistical tests and criteria that will be used.

Intra-Well Background Data Set and Distribution Analyses

The historic background data were initially updated to include secondary parameter data through 2020. The next step in establishing the updated intra-well background data was to identify, if possible, the distribution of the updated data. This evaluation was completed on a parameter by parameter basis for compliance wells DMW-4A, DMW-6A, DMW-10 and DMW-12 for all the available data through December 2020. These intra-well background data are in **Appendix B5-5**.

The historic intra-well background data include multiple samples collected from the same well on the same day. The data from these samples are dependent on each other since they were collected on the same day, and this violates an assumption of the *Shewhart CUSUM Control Chart* method. The second daily measurement was selected and the other daily measurements were not used as intra-well background data so the assumption of independent data was not violated. The initial updated background data in **Appendix B5-5** include all the historic inter-well data and all the subsequent data through 2020, but only the second daily measurement was used for subsequent analyses.

The Chemstat statistical program was used to evaluate the distribution of the updated background data in **Appendix B5-5**. The software uses the Shapiro-Wilk or Shapiro-Francia test (dependent on sample size) to determine, if possible, if the background data are normally distributed or if normality can be achieved with a transformation. If a dataset failed the normality test, a series of transformations was undertaken until a dataset was produced that could pass the normality test. The series of transformations followed the “Ladder of Powers” (Box and Cox 1964). The order of the transformations was to use original data, square-root transformed data, cube-root transformed data, and logarithmically transformed data. If the data were negatively skewed, the Ladder of Powers could be applied in the opposite direction, and the order of transformations would be x^2, x^3, x^4, x^5, and x^6. Non-parametric methods will be used if a statistical distribution could not be identified for a given parameter if $p< 0.05$, or if a parameter was detected in less than 50% of background samples.

Table B5-5 provides a summary of the distributional analysis for the secondary tracking parameters in the compliance monitoring wells.

The background data for the deep monitoring wells are updated every event. The other groundwater monitoring programs do not have specific background data sets. The distribution, outlier tests and upper tolerance limits (UTLs) for the deep monitoring well data will be updated annually in the annual report. The annual reports are subject to written approval by the MDEQ. Approval will be assumed if not received within 30 days of submission of the report to the MDEQ and revised UTLs will be used to evaluate subsequent data.

Screening for Statistical Outliers

Statistical outliers are concentrations that do not conform to the pattern established by the remaining concentrations. The intra-well background data with normal or normalized distributions were evaluated for the presence of potential statistical outliers using a formal test for outliers

(U.S. EPA, 1989; Section 8.2) at a 95% level of confidence. If the background data for a parameter were normalized by transformation, the outlier test was completed on the transformed data. For normally distributed background data, the outlier test was completed on the raw data. If no distribution was confirmed, a formal outlier test was not completed and potential outliers were identified based on a qualitative review of the data.

Once identified, a potential outlier was further evaluated to determine if it was due to a laboratory, sampling/handling error, transcription error, a problem with the well, or to actual groundwater conditions. A potential outlier was removed from the background data set if a valid reason could be determined in accordance with Section 6.2 of U.S. EPA's *Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance*, July 1992 (U.S. EPA, 1992). A few potential outliers were removed from the background data based on a qualitative review. The potential outliers removed from the background data are identified in footnotes to Appendix B5-5.

Statistical Tests for Intra-Well Comparisons

The statistical methods described below are based on the distribution of the data for each secondary monitoring parameter in each compliance well (except DMW-6A). The parametric statistical method for comparing current monitoring data to intra-well background data will be the *Shewhart-CUSUM Control Chart* method for intra-well evaluations. If the distribution of the intra-well background data cannot be established or more than 50% of the data are below detection limits, a non-parametric statistical method will be used. The non-parametric method will compare current monitoring data to non-parametric upper tolerance limits (UTLs) based on intra-well background data. These statistical methods are described in more detail in the following sections. If no statistical test is appropriate because all the intra-well background concentrations are less than detection limits, the current monitoring data will be compared to the respective current detection limits.

Parametric Statistical Method – Shewhart CUSUM Control Charts

Parametric monitoring data from DMW-4A, DMW-6A (when sufficient data are available), DMW-10 and DMW-12 will be compared to intra-well background data using *Shewhart Cumulative Sum (CUSUM) Control Charts* (U.S. EPA, February 1989; Section 7). One of the basic assumptions underlying the use of control charts is that the data being evaluated are normally distributed. Therefore, if the background data then transformed data will be used to construct the control charts. For example, if the background data are log-normally distributed, then the natural logs of the data will be used, If the data are not normally distributed and a transformation cannot be found (see **Table B5-5**), or more than 50% of the data are less than detection limits, then the non-parametric (distribution free) statistical test will be used to evaluate the data for that parameter, as described in the following section.

Data reported as less than a detection limit will be represented as one half of the detection limit for purposes of constructing the control charts.

The standardized Shewhart value, Z_i, represents the distance an individual concentration falls from its background mean in units of standard deviations. This value can be positive or negative,

depending on whether the individual concentration falls above or below the background mean. Z_i values are sensitive to rapid changes in parameter concentrations or decreases pH.

The CUSUM values (Si) are dependent on the Shewhart values. They are cumulative in that they accumulate positive differences which are greater than one standard deviation from the background mean. As a result, the CUSUM value (Si) is sensitive to gradual increases or decreases in concentrations over a long span of time. For example, if several positive Zi values larger than one occur consecutively, the CUSUM value will continue to grow unless concentrations decrease and offset the accumulated value.

Control Charts graph values of Z_i and S_i over time for all the available data and compare them to standard values. Z_i is compared to the Shewhart Control Limit (SCL). S_i is compared to the decision interval, h. The values of SCL and h are included as constants on the charts to facilitate visual evaluation of the data. The control charts will be evaluated for evidence of a statistically significant increase using control limits recommended by the U.S. Environmental Protection Agency (*Statistical Analysis of Ground Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance*. US EPA, July1992; page 78):

SCL	=	4.5, the Shewhart control limit, in units of standard deviations; and
h	=	5, the decision interval value for the CUSUM

Zi values which exceed the SCL of 4.5 will indicate a statistically significant increase.

Values of Si which exceed the h, CUSUM decision interval, indicates a potentially statistically significant increase in concentrations. One possible exception will be events in which an extreme Zi value is obtained, causing the corresponding Si value to exceed the decision interval value in a single event. The CUSUM portion of the Shewhart-CUSUM control chart is designed to identify gradual increases in concentrations over longer periods of time and is not intended to identify extreme changes. Therefore, if an extreme Shewhart value causes a CUSUM value to exceed the decision interval value, the results will be evaluated in light of the specific circumstances and the interpretation of the Shewhart values.

The Shewhart-CUSUM control charts for secondary monitoring parameters with normal or log-normal distributions are in Appendix B5-4. These charts include the available data from the beginning of the monitoring program through 2010. The time covered by the charts varies with parameter, depending on when the parameter was added to the monitoring program.

A potentially statistically significant increase in the current concentration of a secondary parameter shall be identified if the Zi value exceeds the SCL of 4.5 or e value of Si exceeds h, CUSUM decision interval.

Non-Parametric Statistical Method

A non-parametric statistical method will be used to evaluate a given parameter when the updated intra-well background data are not normally distributed, cannot be normalized by a transformation, or have more than 50% of the intra-well data less than detection limits. A non-parametric upper tolerance limit will be used to compare the current concentration for a given parameter to the intra-well background data for the corresponding well. Non-parametric upper tolerance limits were

established as the maximum observed concentration (U.S. EPA, 1992; pages 55 to 56), excluding outliers and detection limits that are elevated relative to current detection limits.

The upper tolerance limits for the updated intra-well background data are in **Table B5-5**. The concentration is potentially significant if it exceeded the non-parametric upper tolerance limit.

Re-Sampling and Re-Evaluation

If the concentration of a secondary monitoring parameter in a well is potentially statistically significant, then that well will be re-sampled in quadruplicate and each of the four samples will be analyzed for the same secondary monitoring parameter. The significance of the results of the quadruplicate samples will be evaluated using either the Shewhart CUSUM charts or the upper tolerance limit, as appropriate to the distribution of the data for the well and parameter being evaluated.

The results of the quadruplicate samples for wells/parameters with parametric distribution will be considered significant if more than half of the Z_i values exceed the SCL (4.5) and the average Z_i in the quadruplicates exceeds the SCL.

The results of the quadruplicate samples for wells/parameters with non-parametric distributions will be considered significant if more than half of the concentrations exceed the tolerance limit and the average concentration of the four samples exceeds the tolerance limit.

If the concentrations of the secondary monitoring parameter in the quadruplicate samples are not potentially statistically significant, then the concentration of the secondary monitoring parameter in the initial sampling event will be attributed to sample contamination or some other cause and the sampling event will be over.

If the concentrations of the secondary monitoring parameter in the quadruplicate samples are significant, Dow Silicones will proceed with the requirements of 40 CFR 264.98(h) as required by R 299.9612. Dow Silicones may also resample the well; evaluate laboratory methods; evaluate sampling equipment, well or method; evaluate statistical methods, evaluate data from the up-gradient deep monitoring wells, evaluate sources other than the licensed facility; or otherwise demonstrate that the potentially significant difference in the concentration of parameter was not related to the regulated unit. Dow Silicones also may compare the data to the lowest applicable groundwater criterion developed by the EGLE pursuant to Parts 31 and 201 of Public Act 451, as amended. These evaluations will be subject to review by the EGLE.

Box, G.E.P. and D.R. Cox. 1964. An analysis of transformations (with discussion). *Journal of Royal Statistical Society Series B*, *26*, 211-252.

Reporting

See **Appendix B5-3**, Environmental Monitoring Report Contents, for detailed reporting contents for each groundwater monitoring program.

Stiff Diagrams

Stiff diagrams are useful for visually describing differences in major ion chemistry in ground water. Stiff diagrams are prepared semi-annually for the shallow and deep monitoring wells and Lingle Drain.

Trend Charts

Dow Silicones will include graphs of the concentrations of selected secondary monitoring parameters in shallow monitoring wells over time in the annual report. The selected parameters are chloride, total phenol, benzene, toluene, ethylbenzene and chlorobenzene. The trend graphs will be prepared for Quench Ponds, 604 Vaults, Shallow and Deep Monitoring Wells and SIS data. Trend charts will be prepared for chemicals with over 50% of reported concentrations above detection limits.

B5.A.4 Detection Monitoring Program – Deep Monitoring Wells

[R 299.9612 and 40 CFR §§264.91(a)(4) and 264.98]

Dow Silicones' groundwater monitoring program satisfies the requirements of R 299.9612 and 40 CFR 264 Subpart F. The purposes of the detection monitoring program are to provide a thorough understanding of the groundwater under the regulated unit and to provide a basis for evaluating changes in the groundwater in the Regional Aquifer over time. The basis for determining the detection monitoring program is provided in Module B3, Hydrogeologic Report prepared in accordance with R 299.9506.

This detection monitoring program evaluates whether hazardous constituents from the regulated units (800/1000 Block landfill, 806 tank farm, 801 Building, and 809 container storage building) have entered the Regional Aquifer under the waste management area. The evaluation is done by comparing measured concentrations of each primary monitoring parameter at the point of compliance wells with detection limits for the organic primary monitoring parameters or background concentrations for inorganic primary monitoring parameters.

The *point of compliance* is defined as "a vertical surface located at the hydraulically down-gradient limit of the waste management area that extends down into the uppermost aquifer underlying the regulated units" (40CFR264.95). The *point of compliance* at Dow Silicones is the upper surface of Regional Aquifer down-gradient of the regulated unit. The deep monitoring wells down-gradient of the regulated (DMW-4A DMW-6A, DMW-10 and DMW-12) units represent the points of compliance. Hazardous waste constituents have not been detected at the point of compliance at the Dow Silicones facility in over 25 years of monitoring.

In addition, this groundwater monitoring program continues to build a database of the chemistry of the groundwater under the Dow Silicones facility. The database may be used to evaluate any future changes in the groundwater. This is accomplished by measuring the concentrations of the secondary parameters in the deep monitoring wells. The concentrations of the secondary monitoring parameters in the deep monitoring wells are compared historical concentrations in the same well (i.e., intra-well comparisons).

Section B5.A.8 presents the Sampling and Analysis Plan for the groundwater monitoring program. **Table B5-2** presents the monitoring schedule and monitoring parameters for each monitoring location.

B5.A.4(a) Indicator Parameters, Waste Constituents, and Reaction Products

[R 299.9506(3)(a) and (f), R 299.9506(4)(a), and R 299.9612 and 40 CFR §264.98(a)]

The deep monitoring wells in the Regional Aquifer have both primary and secondary monitoring parameters. The primary (including indicator parameters) and secondary monitoring parameters (including tracking parameters) are identified in **Table B5-2**.

Primary monitoring parameters are defined as "indicator parameters, for example specific conductance, total organic carbon, total organic halogen; hazardous waste constituents; or reaction products which provide reliable indication of presence of hazardous constituents in groundwater and which, when specified in the facility operating license, are subject to all of the requirements of 40 CFR 264 Subpart F" (R299.9106(s)). The primary parameters are listed in **Table B5-2**.

The primary monitoring parameters are the hazardous wastes constituents that have the greatest potential to impact the Regional Aquifer at the point of compliance. The primary monitoring parameters are organic hazardous waste constituents detected in landfill leachate since monitoring began and with concentrations greater than 0.5 mg/L. Lead is also a primary monitoring parameter because it is a hazardous constituent in the landfill. The primary monitoring parameters will be modified biennially to include all organic chemicals detected in the biennial monitoring of landfill leachate for the 40 CFR 264 Appendix IX parameters. Lead will be retained as a primary monitoring parameter regardless of the results of the Appendix IX analyses of landfill leachate.

Secondary monitoring parameters are defined in Part 111 regulations as "ions such as calcium, sodium, magnesium, iron, chloride, sulfate, bicarbonate, and carbonate, waste constituents; reaction products; or other parameters which provide an indication of the presence of hazardous constituents in groundwater and which are not subject to requirements of 40 CFR 264, Subpart F" (R299.9107(r)). The secondary monitoring parameters are listed in **Table B5-2**. The ions are not waste constituents, reaction products and do not indicate the presence of hazardous constituents and are therefore identified as tracking monitoring parameters.

Tracking monitoring parameters are secondary monitoring parameters that are general inorganic constituents present in groundwater (calcium, sodium, magnesium, potassium, chloride, sulfate, bicarbonate alkalinity and carbonate alkalinity). Concentrations of the tracking parameters are not waste constituents or other parameters that provide an indication of presence of hazardous constituent in groundwater. Concentrations of tracking parameters are not evaluated statistically, but may provide information on the condition of a well or changes in groundwater quality that are not related to the regulated unit. (This definition of tracking parameters is from Comment 10 in MDNRE's Technical Notice of Deficiency dated March 7, 2011.)

Type, Quantity, and Concentrations of Constituents

Only one type of hazardous waste has been placed in the landfill: lead-containing materials. The lead containing wastes exhibit the characteristic of extraction procedure toxicity (D008) due to the presence of lead in the EP toxicity extraction in a concentration in excess of the 5 mg/L limit (R 299.9212(4)).

Leachate from the leachate collection system at the landfill has been analyzed for priority pollutants annually since 1982 in accordance with Dow Silicones facility operating license. Benzene, ethyl benzene, chlorobenzene, 2,4-dimethylphenol, phenol, toluene, and copper have been detected in the leachate at concentrations greater than 0.5 ppm since leachate monitoring began. Although lead-containing wastes have been placed in the landfill, concentrations of lead are generally below or slightly above detection limits in the leachate. The pH of the leachate is typically around 6 to 6.5. Section B5.E describes the monitoring program for landfill leachate.

The materials stored in the container storage area are summarized in Module A2 (Chemical and Physical Analyses). These materials are predominantly silicones and silanes, both containing solvents.

Mobility, stability, persistence of waste constituents, or their reaction products, expected in the unsaturated zone

Table B5-6 summarizes the mobility, stability and persistence of constituents detected in landfill leachate since leachate monitoring began. The tank farm and container storage facilities are equipped with adequate secondary containment and constituents are not expected to be released to or found in the unsaturated zone. Waste constituents in landfill leachate could be released to the unsaturated zone although the landfill is designed to prevent such releases.

Detectability of indicator parameters, waste constituents, or their reaction products in the groundwater

Analytical methods are available for all of the primary parameters, secondary parameters and waste constituents (leachate). **Table B5-3** summarizes normal detection limits.

Concentrations or values and coefficients of variation of proposed parameters in the background groundwater

Table B5-5 summarizes statistics for background (upgradient and historical) groundwater from Deep Monitoring Wells. The data are presented in Appendix B5-5.

Evidence the sampling equipment and well construction materials are compatible with the monitoring parameters

Table B5-4 summarizes monitoring well construction materials. Section B5.A.8(e) summarizes sampling procedures.

The U.S. Environmental Protection Agency (*Nonaqueous Phase Liquids Compatibility with Materials Used in Well Construction, Sampling and Remediation* (Ground Water Issue, July 1995 (EPA/540/S-95/503)) reviewed compatibility of several common well construction materials with

various organic chemicals. The stainless steel wells at Dow Silicones are considered to be compatible with the organic chemicals found in the landfill leachate.

The Illinois State Water Survey (*A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling*. 1983. ISWS Contract Report 327 by Michael J. Barcelona, James P. Gibb and Robin A. Miller) evaluated compatibility of well construction materials for monitoring metals in groundwater. The stainless steel wells at Dow Silicones are expected to be compatible with the relatively non-corrosive groundwater conditions present at the site.

The dedicated sampling equipment, described in Section B5.A.8(e), is primarily made of stainless steel or polyvinyl chloride (PVC), and is also compatible with the monitoring parameters.

B5.A.4(b) Groundwater Monitoring System
[R 299.9612 and 40 CFR §§264.97(a)(2), (b), and (c) and 264.98(b)]

See Section B5.A.3(a)

B5.A.4(c) Background Concentration Values for Proposed Parameters
[R 299.9612 and 40 CFR §§264.98(c) and 264.97(g)(1) and (2)]

See Section B5.A.3(c) and (d) of this Module. **Table B5-5** presents summary statistics for the deep monitoring wells that are used and background concentrations.

B5.A.4(d) Proposed Sampling and Analysis Procedures
[R 299.9506(3)(e) and R 299.9612 and 40 CFR §§264.97(d), (e), and (f) and 264.98(d), (e), and (f)]

See Section B5.A.3(a) and (b) of this Module.

B5.A.5 Supplemental Groundwater Monitoring Program – Shallow Monitoring Wells

The Supplemental Groundwater Monitoring Program includes groundwater from shallow monitoring wells. The purpose of the supplemental monitoring program is to evaluate historic impacts to shallow groundwater from unknown locations, potential releases from active units and to track trends in quality of shallow groundwater. The Supplemental Groundwater Monitoring program is not a detection monitoring program, but does supplement the detection monitoring program. The shallow monitoring wells have been sampled since 1983.

The shallow saturated zone in the Surface Sand has a thin saturated thickness and is not capable of acting as a source of water supply and is not an aquifer. As discussed in the Hydrogeological Report, some of the shallow ground water has been affected by historical practices, and the chemistry of the shallow ground water quality does not represent impacts from the operation of the regulated units. Therefore, the shallow ground water samples are analyzed for the shallow monitoring well secondary and tracking parameters to establish a data base on the ground water chemistry in the shallow saturated zone and to evaluate site-wide groundwater conditions.

B5.A.5(a) Hazardous Constituents to be Monitored in Supplemental Groundwater Monitoring Program

The hazardous constituents included in the supplemental Groundwater Monitoring Program are listed in **Table B5-2**. These are the same as the Detection Monitoring Program parameters (with exception that 2,4-dimethylphenol, arsenic, mercury, and copper are not included). These are all secondary and tracking monitoring parameters. The secondary parameters are based on the results of landfill leachate monitoring since monitoring began and lead-containing wastes disposed of in the landfill or are general groundwater quality tracking parameters.

B5.A.5(b) Concentration Limits

Concentration limits are not used in the supplemental groundwater monitoring program.

B5.A.5(c) Concentration Limit Other than Background

[R 299.9612(d)]

Concentration limits other than background are not used in the supplemental groundwater monitoring program.

B5.A.5(d) Sampling and Analysis Procedures

See Section B5.A.3(a) and (b) of this Module.

B5.A.6 Corrective Action Groundwater Monitoring Program – Site Interceptor System (SIS)

The Site Interceptor System (SIS) is a site-wide interim corrective response measure. The SIS is a subsurface drain that completely circles the Midland Site and intercepts shallow groundwater before the ground water leaves the site. The SIS consists of a trench, backfilled with gravel and drainage media that acts as a collection trough. A perforated collection tile is placed in the bottom of the trench. The outside face of the trench consists of a geosynthetic liner to prevent movement of shallow groundwater past the plant boundary. The collected groundwater is pumped to Dow Chemical's Wastewater Treatment Plant where it is treated prior to discharge to the Tittabawassee River under an NPDES permit. The SIS was completed in 1998. The SIS is described in detail in Section B2.D.1.

The purposes of the SIS Corrective Action Groundwater Monitoring Program are to monitor water quality in the SIS and to monitor the hydraulic effectiveness of the SIS. Water quality is monitored at a lift station at the lowest point of the SIS (southwest part of the site near Building 121; see **Figure B2-1**) before the SIS flow mixes with other flows. Water levels are monitored at manholes along the SIS, staff gauges in Lingle Drain, and piezometers located in pairs on either side of the SIS. Drawing YI86188 in Appendix B2-1 illustrates the SIS and the monitoring locations. The SIS potentially could be impacted by any accidental release from anywhere within the site.

SIS monitoring includes sampling and analyses (Section B5.A.6(a)) and monitoring hydraulic gradients near the SIS (Section B5.A.6(e)). Hydraulic gradients are monitored and evaluated to determine if the SIS is effectively capturing the shallow groundwater.

B5.A.6(a) Hazardous Constituents to be Monitored in Corrective Action Groundwater Monitoring Program

Table B5-2 identifies the constituents included in SIS monitoring. The SIS is monitored quarterly for most of the detection monitoring primary parameters and chemicals detected (1982 – 2021) in the leachate with concentrations above 0.5 mg/L. The SIS is monitored biennially for Appendix IX parameters (except PCBs, dioxins and furans) to detect potential releases from the regulated units and most of the site. Concentrations historically have been below criteria (the former Act 307 Type B criteria) with some minor exceptions.

B5.A.6(b) Concentration Limits

The SIS monitoring is an ongoing corrective response program with no specified concentration limits. The concentrations from biennial samples are compared to criteria developed pursuant to Part 201 – Environmental Remediation of Public Act 451 of 1994, as amended.

B5.A.6(c) Concentration Limit Other than Background

The SIS is an interim response measure with no established background data.

B5.A.6(d) Sampling and Analysis Procedures

See Section B5.A.3(a) and (b) of this Module.

B5.A.6(e) Hydraulic Gradient Monitoring

Hydraulic gradients in shallow groundwater are monitored quarterly to evaluate if the SIS is collecting shallow groundwater before the groundwater discharges from the site. Hydraulic gradients along the west branch of the SIS are monitored by measuring water levels in manholes along the SIS and in paired piezometers located near the manholes and on either side of the SIS. The east branch of the SIS is on both the south and east sides of the site and the upgradient side of Lingle Drain. Hydraulic gradients along the east branch of the SIS are monitored by measuring water levels at manholes along the SIS and staff gauges in Lingle Drain located near the manholes.

The hydraulic gradients at each SIS manhole where water levels are monitored are evaluated to determine if the groundwater gradient is toward the SIS or toward off-site areas or Lingle Drain. If the water elevation in the SIS is less than the water elevation of Lingle Drain or the piezometers, it is concluded that the SIS is functioning properly, and no further action is needed. If the water elevation in the SIS is higher than in Lingle Drain or the piezometers, actions are required. The initial action will include checking the operating components of the SIS to determine the cause. Dow Silicones will develop a specific plan to fix or modify the SIS based on the cause identified in the initial action.

A map of the SIS and monitoring locations is in Appendix B2-1. The sample locations are identified in **Table B5-2**.

B5.A.7 Corrective Action Groundwater Monitoring Program – 604 Area Vaults

The 604 Vaults are below grade concrete vaults ranging in depth from 13.1 to 15.5 feet that were formerly used to house process equipment (see **Figure B5-1**). The 604 Vault area is the site of chlorinated hydrocarbon releases from former processes. Compounds released were carbon tetrachloride, chloroform, 1,2-dichloroethane, 1,4-dichlorobenzene, 1,3-dichloropropane, and toluene. Each vault has a perimeter French drainage system installed in the native clay and flowing to a catch basin that is connected to the wastewater sewer. These drains were installed in 1995-1997. Each catch basin is sampled to monitor for contaminants associated with the manufacturing processes that were used at the vaults.

The purpose of the 604 Area Vault Corrective Action Groundwater Monitoring Program is to monitor groundwater quality in French drains installed as corrective actions for impacts to shallow groundwater associated with former operations at the vaults.

B5.A.7(a) Hazardous Constituents to be Monitored in Corrective Action Groundwater Monitoring Program – 604 Vaults

The vault samples are collected from a system that collects shallow groundwater associated with the former vaults. The constituents are those associated with former use of the vaults. The ranges of most recent data (October 2021) from the three vaults are summarized below:

Carbon tetrachloride ..... 110-32,000 ug/L
Chloroform 290-12,000ug/L
1,4-Dichlobenzene ..... <5-<250 ug/L
1,2-Dichloroethane..... <20-3,100 ug/L
1,3-Dichloropropane ..... <5-<500 ug/L
1,1-Dichloropropylene..... <5-22 ug/L
Toluene..... <5-<500 ug/L

B5.A.7(b) Concentration Limits

The 604 Area Vault Corrective Action Groundwater Monitoring Program has no specified concentration limits.

B5.A.7(c) Concentration Limit Other than Background

This is an ongoing corrective action program with no specific concentration limits.

B5.A.7(d) Sampling and Analysis Procedures

See Section B5.A.3(a) and (b) of this Module.

B5.A.8 Corrective Action Groundwater Monitoring Program – Quench Ponds

The 2500 Block Quench Ponds (see **Figure B5-1** for location) were formerly used to neutralize corrosive chlorosilanes using lime. The major waste byproducts of the quenching operation were neutralized gels, which were disposed of as solid wastes, and brine that was disposed of in the wastewater sewer. Chloride is the major component of the waste brine generated by the

neutralization process formerly used at the Quench Ponds. The purpose of the Corrective Action Groundwater Monitoring Program at the Quench Ponds is to monitor the concentrations of chloride in the shallow groundwater near the former ponds.

B5.A.8(a) Hazardous Constituents to be Monitored in Corrective Action Groundwater Monitoring Program – Quench Ponds

The quench ponds samples are collected from shallow groundwater monitoring wells associated with the former quench ponds. The constituent is chloride, which was produced by the quenching process. The concentrations of chloride in the most recent samples (November 2021) ranged from 130 – 14,000 mg/L.

B5.A.8(b) Concentration Limits

There are no background data associated with the shallow groundwater collected at the former quench ponds.

B5.A.8(c) Concentration Limit Other than Background

This is an ongoing corrective action program with no specific concentration limits.

B5.A.7(d) Sampling and Analysis Procedures

See Section B5.A.3(a) and (b) of this Module.

B5.B AMBIENT AIR MONITORING PROGRAM
[R 299.9611(2)(c) and (4)]

Dow Silicones requests a continuation of the waiver for ambient air monitoring. No hazardous wastes have been disposed in the landfill at this facility since 1984; hence ambient air monitoring is not required at this facility. If Dow Silicones wishes to resume land disposal of lead containing wastes at this facility it will first obtain prior approval from EGLE and submit an ambient monitoring plan. The tank storage units at the 800 Block facility are equipped with inert nitrogen gas blanket systems including nitrogen relief valves which also function as conservation vents to minimize emissions of volatile organic compounds to the atmosphere.

B5.C ANNUAL SOIL MONITORING PROGRAM
[R 299.9611(2)(d) and (4)]

Dow Silicones requests a continuation of the waiver of the annual soil monitoring program.

Lead containing (D008) hazardous waste has not been disposed of in the Licensed Facility landfill since 1984. For this reason, the Director has previously granted a waiver of the requirement for soil monitoring.

If lead containing hazardous waste is disposed of in the landfill at this facility at a future date, Dow Silicones will:

1. Provide prior notification to EGLE of the lead disposal;
2. Obtain prior approval from EGLE for such disposal; and
3. Submit a soil sampling plan for approval by EGLE and resume annual sampling.

See Module B3 for a discussion of the geology beneath the site and potential contaminant fate and transport conditions related to soil.

B5.D SURFACE WATER MONITORING PROGRAM

The purpose of the Surface Water Monitoring Program is to monitoring water quality in Lingle Drain. Lingle Drain flows past the regulated units and potentially could be impacted by shallow groundwater. No concentrations significantly above background concentrations have been observed since monitoring of the drain began in 1989.

B5.D.1 Surface Water Sampling Plan

The location of Lingle Drain is shown on **Figure B5-1**. Lingle drain originates at the outfall from the City of Midland Wastewater Treatment Plant, flows past the Dow Silicones facility and discharges off-site to the Tittabawassee River. Much of the drain is enclosed in an underground pipe.

B5.D.1(a) Surface Water Sampling Locations

Samples are collected from the drain at the outfall of the Midland County Wastewater treatment Plant (MCOF, which is also the origin of the drain and upstream of the regulated unit); upstream of the regulated unit (UPDL) and downstream from the regulated unit (LD1). These locations are identified on **Figure B5-1**. Lingle drain is enclosed in an underground pipe at MCOF and UPDL, and samples are collected from manholes. LD1 is collected from an open channel.

B5.D.1(b) Surface Water Sample Frequency

Samples are collected semiannually. **Table B5-2** presents sampling frequency.

B5.D.1(c) Static Water Level Measurements and Purging

This section is not applicable for Surface Water locations. (Surface water elevations are measured and used to evaluate the SIS, see section B5.A.5.)

B5.D.1(d) Sample Parameters and Basis

The monitoring parameters in Lingle Drain are identified in **Table B5-2**. The monitoring parameters in Lingle Drain are the same as the primary monitoring parameters in the deep monitoring wells plus a scan for volatile organic compounds (VOCs). Data from the shallow groundwater monitoring program are evaluated to determine if parameters present in the shallow groundwater should be added to the surface water monitoring parameter list.

Dow Silicones may request additions or deletions to the sampling parameters in order to improve the effectiveness of the program or to delete parameters that are no longer necessary. Such requests will be supported by data and are subject to approval by the MDNRE

B5.D.1(e) Sample Collection Procedure Surface Water Sample Collection
[40 CFR 264.97(d)(1)]

Lingle Drain flows past the landfill. The part of the drain nearest the landfill is in a pipe. Grab samples of the surface water are collected at the sampling locations listed in **Table B5-2** and shown on **Figure B5-1**. Samples from these locations are representative of the surface water just upstream and just downstream from the regulated unit. In addition, the outfall for the City of Midland Waste Water Treatment Plant, which is upstream of the regulated unit, is also sampled.

Surface water samples are collected using disposable bailer. MCOF and UPDL surface water samples are collected from manholes and LD1 is collected from the open channel. The container is lowered down the center of the manhole or to the center of the drain to collect a representative sample. The surface water sample from LD1 is collected off a dock from the Lingle Drain using disposable sampling device.

Duplicate samples are collected from each surface water sampling location. The duplicate samples are shipped to the laboratory with the initial samples and held pending sample results from the initial samples. The laboratory will analyze the duplicate samples if concentrations of any primary monitoring parameter in the initial samples are detected. Both the initial and duplicate results will be reported if duplicate samples are analyzed.

During each sampling event, one trip blank is analyzed for each volatile parameter to evaluate possible sample contamination from the sample bottles, shipping methods, and laboratory analyses. When the sample bottles are prepared prior to shipment to the field, one complete set of sample bottles is selected, filled with de-ionized water, and labeled "trip blank." The trip blank is transported to the field and sent to the laboratory for analyses along with the other sample bottles. In the laboratory, the trip blank is analyzed for the same volatile organic chemicals as the samples. The presence of any contaminant in the trip blank is noted and attributed to sample contamination. These data are not used to correct the concentration in other samples.

One equipment blank is collected during each sampling event. The equipment blank is collected after standard decontamination procedures are followed to clean the stainless steel sampling container. To collect the equipment blank, the stainless steel sampling container is filled with de-ionized water which is then used to fill the laboratory sampling containers. The equipment blanks are sent to the laboratory for analysis to detect the presence of any contaminant that may be the result of cross-contamination in the sampling container.

The sample collection is documented using customized field data entry forms **Appendix B5-1**.

B5.D.1(f) Field Measurements
[40 CFR 264.97(d)(3)]

The pH of the surface water is measured in the field immediately after collecting the sample. The pH measurement procedure is discussed in Section B5.A.3(a).

B5.D.1(g) Analytical Procedures and Quality Control
[40 CFR 264.97(d)(3)]

The analytical methods and quality control procedures are discussed in Section B5.A.3(a). The method and detection limits are listed in **Table B5-3**.

B5.D.1(h) Sample Preservation, Shipment, and Chain of Custody

The procedures used for sample preservation and shipment are described in Sections B5.A.3a). The chain of custody in **Appendix B5-2** or an equivalent form will be used.

B5.D.1(i) Data Evaluation and Statistical Procedures

To determine if the regulated unit has affected the surface water quality in Lingle Drain a statistical test has been developed to determine if there has been a significant increase in the levels of the monitoring parameters. The background data set consists of the upstream surface water data from the Upstream Lingle Drain (UPDL) and Midland County Outfall (MCOF) for benzene, toluene, ethylbenzene, chlorobenzene, and 2,4-dimethylphenol. These data are used to calculate the background +/- three times one standard deviation. The surface water background data are summarized in **Table B5-7**. The current analytical results from the Lingle Drain downstream of the regulated unit (LD1) are compared with the background value to determine if a significant increase may have occurred due to a release from the regulated unit.

Stiff diagrams of ion concentrations in samples from Lingle Drain are also prepared and evaluated qualitatively.

The historical background data are updated each sampling event. Anomalous data are evaluated qualitatively and are not included if a reason for the anomaly is identified.

Re-sampling and Re-Evaluation

A duplicate sample is collected from each sampling location. The duplicate sample will be held pending receipt of sampling results. If a statistically significant increase is detected in a monitoring parameter(s), the duplicate sample will be analyzed for confirmation purposes. If a statistically significant increase(s) of a parameter(s) is confirmed following the duplicate sample analysis, Dow Silicones will assess whether a discharge to surface waters is occurring, determine the source, and take immediate steps to eliminate a prevent any such discharge.

B5.D.1(j) Reporting

See **Appendix B5-3**, Environmental Monitoring Report Contents, for detailed reporting requirements for each monitoring program.

B5.E LANDFILL LEACHATE MONITORING PROGRAM

B5.E.1 Leachate Sampling Plan

The purpose of leachate monitoring is to identify parameters that should be included in the Detection Monitoring Program, the Supplemental Groundwater Monitoring Program and the Surface Water Monitoring Program. The leachate flowing into the landfill leachate collection

system is monitored before the leachate mixes with other waste streams. The leachate is collected and treated.

B5.E.1(a) Leachate Sampling Location

The leachate is sampled quarterly from the metering manhole, LL, shown in **Figure B5-1** southwest of the landfill.

Leachate flow is presently monitored in three manholes, MH7-11, MH6-30 and MH 28-6. MH7-11 handles most of the flow, and higher flows are directed to the other two manholes.

B5.E.1(b) Leachate Sampling Frequency

The leachate from the landfill is sampled quarterly. Once every two years, the leachate is also sampled and analyzed for a RCRA 40 CFR 264 Appendix IX scan, excluding PCBs, dioxins and furans.

Leachate flow is documented and monthly totals will included in the quarterly report.

B5.E.1(c) Static Water Level Measurements and Purging

This section is not applicable for Leachate Monitoring.

B5.E.1(d) Sample Parameters and Basis

The quarterly leachate monitoring parameters consist of two groups of parameters: fixed parameters (Lead, Mercury, PCBs, pH) and additional organic parameters (Benzene, Ethyl Benzene, Chlorobenzene, Toluene, 2,4-Dimethylphenol, total Phenols). The leachate is analyzed for the fixed parameters regardless of their concentration in previous samples. The additional organic parameters are organic parameters which are present in the leachate and which have been measured at concentrations greater than 0.5 mg/l in the leachate. If an organic parameter is measured at a concentration greater than 0.5 mg/l in the Appendix IX scan, which is run every two years, then that organic parameter is added to the list of additional quarterly organic parameters. If an additional quarterly organic parameter is not detected over two consecutive quarterly samples, then that parameter may be removed from the list of additional quarterly organic parameters.

The Appendix IX list is summarized in **Table B5-3**. Appendix IX list (excluding PCBs, dioxins and furans) is included at the request of the EGLE and replaces the priority pollutant scan used formerly. PCBs, dioxins and furans, have never placed in the land fill. PCBs are included in the quarterly sample analyses.

Dow Silicones may request additions or deletions to the sampling parameters in order to improve the effectiveness of the program or to delete parameters that are no longer necessary. Such requests will be supported by data and are subject to approval by the EGLE.

B5.E.1(e) Sample Collection Procedure
[40 CFR 264.97(d)(1)]

Leachate samples are collected using a peristaltic pump and tubing if the water is too shallow to allow use of bailers. In order to collect a representative sample of the Landfill Leachate, the sample is collected prior to 8 AM, before any landfill truck washing is started for the day., . Since the Leachate sample is analyzed for total metals, the sample is not filtered. The data generated during the sample collection are recorded on the Field Data Entry Form. This form is attached in **Appendix B5-1**.

B5.E.1(f) Field Measurements
[40 CFR 264.97(d)(3)]

The pH of the leachate is analyzed in the field immediately after collecting the leachate sample and recorded on the field form. A separate portion of the sample is drawn off for these analyses to avoid any contamination of the laboratory samples by the pH probe.

B5.E.1(g) Analytical Procedures and Quality Control
[40 CFR 264.97(d)(3)]

The analytical methods and quality control procedures are discussed in Section B5.A.3(a). The method and detection limits for quarterly and biennial leachate monitoring are listed in **Table B5-3**.

B5.E.1(h) Sample Preservation, Shipment, and Chain of Custody

The methods for sample preservation and shipment are described in Sections B5.A.3(a) and **Table B5-3**. The chain of custody form in **Appendix B5-2** or an equivalent form will be used.

B5.E.1(i) Data Evaluation and Statistical Procedures

The Appendix IX leachate data are evaluated to identify analytical parameters for detection monitoring program, supplemental monitoring program and surface water monitoring program. Chemicals that occur with concentration greater than 0.5 mg/L in the Appendix IX landfill leachate samples are added to these other monitoring programs and to subsequent quarterly landfill leach samples.

B5.E.1(j) Reporting

See **Appendix B5-3**, Environmental Monitoring Report Contents for detailed reporting requirements for leachate monitoring program.