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## SECTION III: TECHNICAL AND PROCEDURAL GUIDANCE

### A. Fate and Transport Analysis

Fate and transport analyses required under Act 2 may involve a wide spectrum of predictive assumptions, calculations and simulations, ranging from the simple to the complex, depending on the hydrogeologic characteristics of a site, future use scenarios, and the selection/applicability of a particular cleanup standard.

**Fate and transport analysis or modeling is a necessary part of site characterization and demonstrating attainment of an Act 2 standard.** However, the Chapter 250 regulations governing Act 2 use the term “fate and transport analysis” as opposed to “fate and transport model.” This particular distinction was made because it will not always be necessary to run an analytical or numerical quantitative “fate and transport model” to achieve a standard.

Whether simple or complex, any fate and transport analysis must rely on having and/or obtaining valid data. Reliable field data will be critical in supporting the professional conclusions regarding any predictions of contaminant fate and transport and needs to be considered during the site characterization.

Fate and transport analysis will be used in the Act 2 process to predict contaminant concentrations migrating through the unsaturated zone and the saturated zone, including the impact of soil contamination on groundwater. It will also include an analysis of diffuse groundwater flow into surface water (e.g., a stream) for purposes of determining compliance with surface water quality standards.

Generally, fate and transport analyses under Act 2 may be used for the following purposes:

- To predict the concentrations of one or more contaminants at one or more locations in the future, often at a specific time (e.g., 30 years).
- To assess potential remediation alternatives.
- To evaluate natural attenuation remedies and associated monitoring requirements.
- To assure continued attainment of the relevant standard.
- To estimate groundwater chemical flux used in mass balance calculations for attainment of surface water standards.
- To assess postremediation care requirements and termination.

Furthermore, fate and transport analysis is used in specific ways under the three remediation standards.

### BACKGROUND STANDARD

- To justify reduced duration for monitoring of upgradient release.

- To combine the background groundwater standard with non-background soil standards.
- To assess the impact of transformations in the upgradient plume.

#### **STATEWIDE HEALTH STANDARD**

- To justify reduced duration of attainment monitoring at the point of compliance.
- To complete the equivalency demonstration for soil-to-groundwater attainment.
- To predict the extent of contamination above the standard in off-property nonuse aquifers.
- To demonstrate attainment of the used aquifer standard at a point 1,000 feet downgradient from the point of compliance (POC) for the nonuse aquifer standard.
- To demonstrate compliance with surface water standards where there is diffuse groundwater flow to surface water.

#### **SITE-SPECIFIC STANDARD**

- To identify current completed pathways and related exposures.
- To predict future completed pathways and related exposures.
- To demonstrate pathway elimination.
- To establish numerical site-specific risk-based standards.
- To demonstrate compliance with surface water standards where there is diffuse groundwater flow to surface water.

When applicable, the fate and transport analysis should also consider the degradation of a particular chemical compound(s) into one or several “breakdown” compounds. This can occur in the unsaturated or saturated zone at or below the point of release of a particular compound of concern, or downgradient in the chemical plume. An example may include a scenario involving a release of trichloroethylene from an upgradient source which has entered the saturated zone and migrated downgradient under a site seeking a release under the background standard. The site in question may exhibit dichloroethylene and vinyl chloride in wells on its property, but it also may have never used chlorinated compounds. In this case, the remediator may be able to demonstrate that there was no release of the regulated substance on the property and use fate and transport analysis to demonstrate that the constituents result from breakdown of compounds from the upgradient release.

## 1. Fate and Transport Analysis in the Unsaturated Zone

### a) General

In lieu of using the soil-to-groundwater medium-specific concentrations (MSCs) from Tables 3 and 4 in Appendix A of Chapter 250 as the Statewide health standards (SHS), a person may also perform a site-specific demonstration. The site-specific demonstration can be used to show that contaminant levels in soil exceeding the SHS for one or more contaminants at that site are protective of groundwater. Such a demonstration requires the use of fate and transport models, equations, algorithms, or methods (hereafter “analytical tools”) applied to contaminants in the soil of the unsaturated zone and may also include the use of groundwater fate and transport analytical tools (e.g., using the results of an unsaturated zone transport demonstration as input into a groundwater fate and transport analysis).

The unsaturated zone fate and transport analytical tools may be very simple equations requiring minimal input or may be more complex models requiring much more detailed input. The choice of the analytical tool or tools used in making site-specific demonstrations for contaminants in unsaturated zone soil should be appropriate to the circumstances of the site. At a minimum, the analytical tools used in making demonstrations in the unsaturated zone should include certain contaminant-specific and site-specific parameters. Other parameters may also be necessary depending on the analytical tools being used and the overall goal of the demonstration. In addition, the analytical tools and parameter input values themselves are subject to certain conditions.

### b) Minimum Contaminant-Specific and Site-Specific Requirements

With very few exceptions, the analytical tools currently available for unsaturated zone contaminant fate and transport demonstrations are based on equilibrium partitioning equations. The equations that have been used in estimating the soil-to-groundwater MSCs and the soil buffer distances in Tables 3 and 4 in Appendix A of the regulations are equilibrium partitioning equations. These equations can be used in a variety of different types of analytical tools. Depending on the analytical tool being used, other parameter input values may be necessary. At a minimum, input values are needed for each of the following parameters for any unsaturated zone analytical tool:

#### i) Contaminant-Specific Requirements for All Analytical Tools

- $K_{oc}$  in L/kg or mL/g (for organic compounds only): this is the organic carbon partition coefficient. Values for this parameter for listed organic regulated substances can be found in Table 5A in Appendix A of the regulations or in scientific literature. For organic compounds not listed in Appendix A of the regulations, values can be found in literature.  $K_{oc}$  estimation methods (based on other parameters such as aqueous solubility, octanol-water

partition coefficient, bioconcentration factor, and molecular structure) are also available in literature.

- $K_d$  in L/kg or mL/g (primarily for inorganic contaminants and, in some instances, organic compounds): this is the soil-to-water partition coefficient. Values for this parameter for listed inorganic regulated substances can be found in Table 5B in Appendix A of Chapter 250. Some  $K_d$  values for inorganic contaminants can also be found in scientific literature. In many instances, it may be necessary to estimate  $K_d$  values based on soil analytical data at a particular site. This can be done by using total contaminant concentrations in soil in conjunction with leachable concentrations. Generally, the  $K_d$  values for organic compounds are estimated from  $K_{oc}$  values and the fraction of organic carbon in soil ( $f_{oc}$  - which is discussed later) or by using total contaminant concentrations in soil in conjunction with leachable concentrations. If  $K_d$  values are estimated in this manner, it is not necessary to include or use a  $K_{oc}$  value for the organic compound.
- $C_{soil}$  in mg/kg: This is the dry weight concentration of a regulated substance or contaminant in soil which is determined through use of the site characterization data (if the demonstration is being done to show that groundwater is protected under current site conditions) or which is used as input (on a trial-and-error basis) to estimate a concentration in soil that would be protective of groundwater.

## ii) **Site-Specific Requirements for All Analytical Tools**

- $\theta_w$  (dimensionless): This is the water-filled porosity of the unsaturated zone soil. Appropriate values for this parameter generally range from 0.05 to 0.15 for sandy soils to 0.26 to 0.45 for clays. A default value of 0.2 has been used in the estimation of the soil to groundwater MSCs in Tables 3 and 4 in Appendix A of the Chapter 250 regulations.
- $\rho_b$  in kg/L or g/mL: This is dry bulk density of unsaturated zone soil. Appropriate values for this parameter generally range from 1.3 to 2.0 for silts and clays to 1.6 to 2.2 for sandy soils to 1.8 to 2.3 for gravelly soils. A default value of 1.8 has been used in the estimation of the soil to groundwater MSCs in Tables 3 and 4 in Appendix A of the regulations.
- $f_{oc}$  (dimensionless): This is the fraction of organic carbon in unsaturated zone soil. This parameter applies only to demonstrations being done for organic compounds where the  $K_{oc}$  values for the compounds are being used. For demonstrations for organic compounds where  $K_d$  is being estimated or determined by a means other than use of  $K_{oc}$ , this parameter is not needed.

Typical values for this parameter range from 0.001 to 0.006 for subsurface soils to 0.01 to 0.03 for topsoil. A default value of 0.0025 has been used in the estimation of the soil to groundwater MSCs in Table 3b in Appendix A of the regulations. A value of 0.005 has been used in estimation of the soil to groundwater buffer distances in Table 3B in Appendix A of the regulations.

### iii) **Additional Requirements**

The simplest unsaturated zone analytical tools are those that estimate contaminant concentrations in unsaturated zone soil pore water from equilibrium partitioning equations and utilize these aqueous concentrations as source input into a groundwater fate and transport analysis. Actual transport through the unsaturated zone is not estimated with this type of analytical tool. This type of unsaturated zone analytical tool would require input data for only those parameters discussed above.

Another type of unsaturated zone analytical tool that is commonly used and is more complex is one that estimates the migration of contaminants through the unsaturated zone. These are generally either infinite source or finite source analytical tools. Both are more complicated than the one previously discussed and, as such, require additional parameter input values. Both of these analytical tools require the vertical depth to groundwater or bedrock from the contaminated soil as well as a water recharge rate so that pore water velocity can be estimated. An unsaturated zone finite source analytical tool is particularly useful in demonstrating how long it will take a contaminant to migrate from unsaturated zone soils to groundwater (if at all) and what the contaminant concentration (including the maximum concentration) will be in soil or soil pore water at various depths and at various times as migration occurs. Finite source models generally require input values for additional parameters such as values for  $C_{\text{soil}}$  at different depths from the surface of the unsaturated zone. This can ensure that mass balance constraints are met, i.e., the analytical tool will not estimate migration of a greater mass of contaminant than the amount that was originally in the source soil. The **BUFFER1.XLS** spreadsheet model is available on the DEP website to assist in performing this modeling.

In addition, more complex unsaturated zone analytical tools can take into account other mechanisms that would affect the vertical migration of contaminants toward groundwater. These mechanisms are generally ones that result in loss of the contaminant through time, meaning that additional input values are required. Two loss mechanisms are biodegradation and volatilization. Analytical tools that consider biodegradation require either a degradation rate constant (in units of reciprocal time) or a half-life value (in units of time). In rare circumstances, an analytical tool may consider loss from volatilization. This would require a volatilization rate constant which can be calculated from several other parameters (such as Henry's

constant, vapor pressure, aqueous solubility, other partition coefficients as well as soil property data) or can be estimated using onsite analytical data.

**c) Conditions for Use of Analytical Tools and Parameter Input Values**

Dozens of unsaturated zone analytical tools exist in the public domain, most of which are based on equilibrium partitioning between the solid soil matrix and the soil pore water. As such, most of these analytical tools are very similar with respect to the parameters that require input values. In order to ensure validity of the results of all unsaturated zone demonstrations submitted to the Department, the following conditions should be met:

- Analytical tools used for unsaturated zone transport demonstrations should be based on equilibrium partitioning concepts when possible. Although analytical tools based on other concepts (such as metal speciation and non-equilibrium desorption) exist and may be technically valid, their use could cause significant delays in Department review time.
- The source of all values for all required input parameters ( $K_{oc}$ ,  $K_d$ ,  $C_{soil}$ ,  $\theta_w$ ,  $\rho_b$ ,  $f_{oc}$ ) should be provided. All data used as input for  $C_{soil}$  should be representative of the area for which the demonstration is being made and should meet all site characterization requirements.
- If analytical tools require input values for water recharge rate and vertical depth to groundwater, the sources of those values should be provided.
- Any degradation rate constant or half-life used in any unsaturated zone analytical tool should be based on site-specific data. Well-documented degradation constants and half-life values may be used from the literature or other studies only when it can be shown that the conditions at the site are clearly similar to those from which the degradation rate constant or half-life came. In addition, degradation products which may be toxic (such as those from chlorinated alkenes) should be considered in the demonstration. If these conditions are not met, the degradation rate constant should be assumed to be zero.
- Any unsaturated zone analytical tool that incorporates loss of contaminant from volatilization processes should base the volatilization rate constant on volatilization data for soils existing at the site. Otherwise, loss due to volatilization should be assumed to be zero.
- Any unsaturated zone analytical tool should be used only for soils in the unsaturated zone and should not be used for saturated zone soils or bedrock.
- For any unsaturated zone analytical tool that links to groundwater by means of dilution directly under the area of contaminated soil, the entire aquifer depth directly under the soil should not be used in dilution calculations, i.e., as a mixing zone. The mixing zone should be calculated

based on specific site parameters such as pore water velocity, groundwater velocity and direction, depth of the entire aquifer under the site, and areal extent of soil contamination.

**d) Conclusion**

This guidance is being provided to aid any person who is submitting results of a fate and transport analysis for the unsaturated zone to do so in a manner that will ensure validity of the analysis as well as timely and efficient review by the Department. There are many unsaturated zone analytical tools available in the public and private domains. Some of these are extremely complex, difficult to use, and not readily available to Department staff while others are fairly simple, easy to use, and are readily available to the Department. For unsaturated zone fate and transport analysis submissions that rely on concepts other than equilibrium partitioning (such as metal speciation and non-equilibrium desorption), adequate supporting documentation must be submitted to the Department.

**2. Fate and Transport Analysis in the Saturated Zone**

This section provides guidelines for the application of fate and transport analysis in the saturated zone. As stated above, a “fate and transport analysis” is not necessarily a highly complex computer simulation. It can be a range of analyses, based on physical, structural, chemical and hydraulic factors. It is based on professional judgment and may need to include the use of simulations.

Elements of fate and transport analysis include:

**GROUNDWATER FLOW**

- Direction
- Velocity
- Boundaries

**CHEMICAL FATE AND TRANSPORT MECHANISMS**

- Leaching/dissolving
- Adsorption/desorption
- Matrix diffusion
- Degradation/transformations/reactions
- Volatilization
- Precipitation

- Phase behavior

Depending on the characteristics of the site and the type of standard/remediation selected, the fate and transport analysis can range from the simple to the complex, which can span from qualitative “empirical” or simple conceptual models, up to quantitative simulation (analytical and numerical) models.

Simple descriptive or conceptual models may be either qualitative or quantitative. A particular example under this scenario might be a facility seeking a release of liability under the background standard. This facility (facility “A”) is downgradient from facility “B,” which has caused a release of a contaminant to groundwater. The fate and transport analysis required under Section 250.204(f)(5) of the regulations could conceivably be a simple qualitative demonstration of a conceptual site model which employs the use of monitoring well data/measurements to clearly establish that facility “A” is hydraulically downgradient of facility “B.” Data requirements would include water level measurements from a sufficient number of properly located monitoring wells and establishing the hydraulic gradient. Note, however, that simple scenarios such as this can easily become more complicated by other factors including water level fluctuations, pumping influences of wells, etc., which could require a more detailed quantitative fate and transport analysis.

Another scenario could involve the use of simple extrapolation in predicting groundwater plume movement or its relative stability over time. If groundwater monitoring samples have been collected over a sufficiently long period of time, and the information consists of reliable data, then certain predictions can be made using professional judgment as to aspects of plume behavior. For example, monitoring over a number of years may indicate that the contaminant plume has exhibited no movement over that time. In this case, the use of professional judgment involving simple extrapolation of the data may be a sufficient fate and transport analysis. The conclusion could be made, based on the above merits, that the plume has reached a steady-state condition and would not migrate further downgradient. In this case it may also be possible to determine that downgradient surface water quality criteria may be met even though the concentrations in the groundwater plume exceed the MSCs.

Quantitative fate and transport analysis may be needed in more complex situations, where a demonstration of attainment would require additional data and calculations.

One example might be a facility seeking to demonstrate that very low groundwater velocities in bedrock would preclude contaminated groundwater from the facility from reaching the property boundary/POC. Data requirements in this case would need to include calculation of hydraulic gradient, determination of hydraulic conductivity, estimation/measurement of effective porosity, and calculation of groundwater velocity. Note that this somewhat simple example could evolve into a more detailed quantitative or simulated model given a variety of complicating factors, such as saturated flow in soil, preferential fracture flow, etc. Another example of this type may be a demonstration of groundwater discharge into a natural flow boundary, as in the case of a facility located adjacent to a large river sustained by regional groundwater discharge. While in some cases this might be a qualitative analysis, in other cases there would be a need to

determine both vertical and horizontal gradients to demonstrate the stream is in fact a discharge feature and not losing flow to the surrounding terrain.

Quantitative analysis may involve the use of more complicated fate and transport tools involving various analytical equations up to the more complex numerical simulations of groundwater flow, which collectively can help determine the spread of contamination in a plume and predict its fate and concentration at specific future times and locations. The simpler analytical equations are more appropriate where more uniform aquifer conditions exist and there are no complex boundary conditions. An example might be a facility seeking a release under Act 2 which is underlain by alluvium near a stream. Analytical fate and transport equations can be used to help determine the concentration of a groundwater contaminant at a downgradient location. In many cases the simple empirical examples mentioned above may need to employ analytical equations, as conditions warrant, to account for dilution, attenuation, degradation, and other physical and chemical factors in contaminant fate and transport.

Numerical simulations are the most complex models used under the provisions of fate and transport analysis under Act 2. They generally require use of a computer software model due to the number of simultaneous equations to be solved. They are most applicable where predictions of groundwater contamination need to be made at certain locations in the future (e.g., property boundary, 1,000 feet downgradient from property boundary, etc.), at sites which exhibit more heterogeneous geologic/hydrogeologic characteristics and more complex boundary conditions (which are common in Pennsylvania). As such, they will be useful tools for a variety of sites where such predictions are required to demonstrate attainment of an Act 2 standard.

**a) Groundwater Solute Fate and Transport Modeling (General)**

The Department recommends that those with appropriate academic training and practical experience in the field conduct fate and transport analysis, especially if it involves more complex numerical models.

Except in cases where it is unnecessary to project or predict contaminant concentrations in groundwater at various locations into the future, some sort of quantitative fate and transport analysis such as groundwater modeling will very likely be needed.

Some considerations:

- All models rely on input parameters that vary because of inherent heterogeneity and anisotropy of the aquifer.
- Some of the required input parameters such as dispersivity are not measured and need to be determined by model calibration to accurate isoconcentration contour maps.
- Some important information such as the date of the release and mass involved is often difficult to pin down.

All of the above creates uncertainty that needs to be considered in how the results of any model are used and their reliability. The uncertainty associated with models can and should be reduced by collecting site-specific data for certain input parameters that are representative of subsurface conditions.

Accurate isoconcentration contour maps of each parameter of concern, which are constructed from data collected during the site characterization phase of the remedial action, are especially important. These maps are the calibration targets of the model. Adequate data to determine if a plume exhibits a centerline, and, if so, its location and associated concentrations is fundamental to a fate and transport analysis. It is good practice to install several transects (lines of wells) downgradient from the source and perpendicular to the direction of groundwater flow to accurately find and define any plume centerline and the spread of contamination away from the centerline.

The following data are the minimum input requirements of many models, both analytical and numerical. The following data should be derived from measurements made at the site:

- Source Geometry and Concentration
- Hydraulic conductivity
- Hydraulic gradient
- Natural fraction of organic carbon in the aquifer
- Porosity

The following additional parameters are also often involved:

- Time source active – this is a very important parameter in calibrating any model if transient plume conditions are suspected or involved and can be one of the hardest to pin down unless good historical records are available.
- $K_{oc}$  – this value can be obtained from Appendix A-Table 5A of Chapter 250.
- Lambda – this measure of biodegradation (as first order decay) varies from site to site for each compound and is usually determined by model calibration, or sometimes calculated from plume centerline data. Published values such those in Appendix A, Table 5A of Chapter 250 should not be relied on as default values for site-specific modeling.
- Soil Bulk Density – often estimated as  $(2.65 \text{ g/cm}^3)(1-\text{porosity})$ .
- Dispersion – this parameter is used to simulate the spread of contaminants in one, two, or three dimensions. Values are often initially derived using

several published “rules of thumb” and then adjusted during model calibration to fit plume isoconcentration contours.

After selection of the best values for input parameters, the model is run and compared to the plume geometry portrayed by isoconcentration maps of each parameter of concern. Adjustments may be needed for certain parameters such as lambda, dispersion or others within reasonable ranges to obtain a better match to site data. Measured site data should be utilized in conjunction with initial modeling results to further calibrate the model using to ensure the most accurate predictive results. Modeling efforts associated with a postremediation care plan under an Act 2 standard should include a test of the predictive accuracy of the model by comparing predictions to a future data set sometimes referred to as a “post-audit,” followed by recalibration and retesting, if needed.

Readers are referred to ASTM Standard Guide D 5447-04 (2010) for an overview of the basic elements involved in groundwater flow modeling effort. The same general principles apply to fate and transport modeling. Since the ASTM Standard Guide 5447-04 (2010) is intended as a general guide, covering both analytical and numerical models, all elements discussed may not be applicable to every modeling situation.

**b) Define Study Objectives**

In all cases the site characterization should be conducted with the objective of providing the data necessary to demonstrate attainment of an Act 2 standard. Prior to any computer modeling, an initial conceptual model of local hydrogeologic conditions should be developed. The results of the characterization/initial conceptual site model will influence what kind of fate and transport model, if any, should be used, as well as many of the values for the input parameters to that model. Some models require certain kinds or quantities of data which is good to know ahead of time. To some extent this will be an iterative process. As data are collected and evaluated, the selected Act 2 remediation standard may change, and areas where additional data are needed may be identified.

The acceptable tolerances for model calibration should also be defined in the study objectives.

**c) Data Collection**

The data used for groundwater fate and transport modeling will come from the site characterization, attainment monitoring, and in some cases, values published in scientific literature or Table 5 in Appendix A to the regulations. Examples of data that may need to be obtained from published values include first-order decay coefficients and equilibrium partitioning coefficients. Once obtained, these values may need to be adjusted within reasonable ranges to calibrate a model to site conditions. Examples of data which should be obtained from the site characterization, to name a few, include hydraulic conductivity, gradients, porosity, organic carbon content and chemical concentrations. Some parameters

such as dispersion coefficients, which are not available from the literature or site characterization work, initially need to be estimated according to basic assumptions and then adjusted during model calibration to match actual plume shape and concentration data.

**d) Conceptual Model**

As stated in ASTM D 5447, “the purpose of the conceptual model is to consolidate site and regional hydrogeologic and hydrologic data into a set of assumptions and concepts that can be evaluated quantitatively.” The conceptual model of the site will emerge from the data collected during the site characterization. The site characterization work should be designed to assure that the quantity and kind of data collected will, in the end, be sufficient for justifying and completing the fate and transport analysis. Elements important to developing the conceptual model of the site for any fate and transport analysis include geologic, hydrologic, hydraulic and contaminant data (note that these are common elements of some of the non-numerical conceptual models discussed above). Data collection should be concentrated on the site, but offsite features that influence contaminant fate and transport on the site should not be overlooked.

**i) Geologic Data**

- Thickness, continuity, lithology, and structural features of consolidated geologic formations underlying the site.
- Thickness, texture, density, and organic carbon content of soil and unconsolidated units.
- Information from review of published reports on the geology and soils of the site and nearby areas, or previous work at the site.
- Information from any additional investigation needed to confirm or refine existing data such as wells, borings, and backhoe pits, and possibly geophysical methods.

**ii) Hydrologic Data**

- Water levels, hydraulic gradients and groundwater flow directions, including seasonal variations; determining seasonal variations in hydrologic data are extremely important for conceptual site model development. Seasonal variations in hydrologic data are site dependent and may not exist at every Act 2 site. Conceptual site model development as well as fate and transport analysis should take into account any seasonal variations that may exist at an Act 2 site.
- The presence and magnitude of vertical gradients at the site.

- Recharge and discharge boundaries relevant to the site including groundwater divides, streams, and drains.
- Sources and sinks, e.g., characteristics of any pumping or injection wells, artificial recharge, ponds, etc.
- The presence of any confining units.
- For bedrock aquifers, the degree to which the aquifer system departs from assumptions regarding flow in porous media.
- Data from review of available information as well as drilling of wells, borings and piezometers, and water level measurements over regular intervals.

**iii) Hydraulic Data**

- Hydraulic conductivity and transmissivity data for consolidated and unconsolidated deposits.
- Porosity, effective porosity estimates, and storativity.
- The degree to which the aquifer(s) depart from assumptions of isotropy or homogeneity.
- The degree of interconnection between different aquifer units and leakage characteristics between different water-bearing units.
- Hydraulic data often is not available at the level of detail necessary and may require pumping tests on wells to determine aquifer anisotropy of bedrock systems and values for other hydraulic parameters such as transmissivity. Slug tests may suffice in bedrock wells where anisotropy is not a factor requiring consideration.

**iv) Chemical and Contaminant Data**

- Location, age and current status of source areas to the extent knowable.
- Types of contaminants and their chemical properties such as viscosity, solubility, biodegradability, density, toxicity,  $K_{oc}$  value, decay rate, etc.
- The magnitude and vertical and horizontal extent of contamination in soil and/or groundwater.

- Dissolved oxygen content and other electron acceptors in groundwater, if required by the model.
- Historical plume configuration based on existing monitoring data.
- Determination if the contaminant plume is at steady-state conditions or is continuing to migrate. This is a critical piece of information. Is the mass of contamination increasing, decreasing or relatively constant? This should be determined by monitoring the vertical and horizontal extent of groundwater contamination for a period of time sufficient to reveal the trend. These data will be useful in calibrating the model and making predictive simulations. In some cases, the monitoring data alone may be all that is needed to complete the fate and transport analysis, provided the monitoring record is sufficiently long.
- Review of chemicals used at the facility, which will help identify the chemicals of concern. Sampling soil, soil vapors, and groundwater from appropriately constructed monitoring wells, borings or excavations and checking for any free product will need to be performed. Geophysical methods may be useful to delineate areas needing further investigation or identifying sources.

e) **Model Selection**

When the site characterization is completed, and the conceptual model has been developed, selection of an appropriate model can be made. At sites where there is little variation in conditions over the model domain, with a simple plume geometry or conceptual model, relatively simple analytical models should be employed. At sites where the site characterization has determined significant variation in important parameters, or where more complex questions are being asked, a more sophisticated numerical solution may be needed.

The Department has prepared two spreadsheets that may be useful in completing a fate and transport analysis. All spreadsheets are based on the following equation:

$$C(x, y, z, t) = \left(\frac{C_0}{8}\right) \exp\left\{\frac{x}{2\alpha_x} \left[1 - \left(1 + 4\lambda\alpha_x/v\right)^{\frac{1}{2}}\right]\right\} \operatorname{erfc}\left\{\left[x - vt\left(\sqrt{1 + 4\lambda\alpha_x/v}\right)\right] / 2\sqrt{\alpha_x vt}\right\} \\ \left\{\operatorname{erf}\left[(y + Y/2) / 2\sqrt{\alpha_y x}\right] - \operatorname{erf}\left[(y - Y/2) / 2\sqrt{\alpha_y x}\right]\right\} \left\{\operatorname{erf}\left[(z + Z/2) / 2\sqrt{\alpha_z x}\right] - \operatorname{erf}\left[(z - Z/2) / 2\sqrt{\alpha_z x}\right]\right\}$$

Reference: An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species, P.A. Domenico, 1987, Journal of Hydrology, 91, 49-58.

The two spreadsheets are:

### **QUICK\_DOMENICO.XLS**

The Quick Domenico (QD) application spreadsheet calculates the concentration anywhere in a plume of contamination at any time after a continuous, finite source becomes active. A “User’s Manual for the Quick Domenico Groundwater Fate-and-Transport Model” accompanies the spreadsheet model on the PA DEP website.

### **SWLOAD.XLS**

This spreadsheet uses a rearrangement of the Domenico equation to calculate concentrations at different points in the cross section of a plume at any distance from a continuous finite source at any time. The concentrations are then added and multiplied by the groundwater flux and can be used to estimate the mass loading of a particular contaminant from diffuse groundwater flow to a stream or surface water body.

As mentioned above, these spreadsheets and documentation can be downloaded from the PA DEP web site under “Standards, Guidance and Procedures,” “Guidance and Technical Tools,” “Fate and Transport Analysis Tools.” These spreadsheets will not be applicable to every situation involving modeling. The remediator should thoroughly review the help documents for the spreadsheet programs to determine if the modeling spreadsheets are suitable for the situation.

#### **f) Calibration and Sensitivity**

As stated in ASTM D 5447, calibration is the process of adjusting hydraulic parameters, boundary conditions and initial conditions within reasonable ranges to obtain a match between observed and simulated potentials, flow rates or other calibration targets. In working with sites under Act 2, an obvious calibration target is matching the model output to existing, and, if known, historical geometry and concentration of plume contaminants. The Act 2 final report should include a discussion of calibration targets, and an analysis and significance of residuals (differences between modeled and actual contaminant concentrations).

Sensitivity analysis is an evaluation of which model parameters have the most influence on model results. The parameters to which the model is most sensitive should be identified. Those parameters which have the most influence on model results are those which should be given the most attention in the data collection phase.

**g) Predictive Simulations**

Fate and transport models may be used in the Land Recycling Program (LRP) to make predictions of future contaminant concentrations. Uses may include:

- Predicting the maximum concentrations that will occur at downgradient compliance points (usually property boundaries) for the SHS in the case of both used and nonuse aquifers.
- Predicting whether groundwater contamination above an MSC will extend beyond 1,000 feet in the case of nonuse aquifers, and if it will be at or below the MSC for groundwater in these areas within the next 30 years.
- In cases where the fate and transport analysis indicates that a standard may not be maintained at some time in the future, a postremediation care plan will be needed.
- If postremediation care is required, a “post-audit” of the fate and transport model should be performed. In a post-audit, the fate and transport model’s predictions are compared to continued monitoring data collected during the postremediation care period to check the validity and accuracy of previous model predictions. Monitoring wells for the post-audit must be located at points where they would be sensitive to auditing the model. This may not coincide with the property line compliance point if the plume would not be expected to migrate to the compliance point by the time of the post-audit.
- Post-audits should be performed on the model during the attainment monitoring phase (usually a minimum of two years) as a check on model predictions.

**h) Fate and Transport Model Report**

With the exception of those projects which do not require submission of a fate and transport model, the following general report format should be used to the extent applicable to adequately document the modeling effort:

1.0 Introduction

1.1 General Setting

1.2 Study Objectives - which Act 2 standard is being demonstrated and what is the purpose of the modeling

2.0 Conceptual Model

2.1 Aquifer System Framework

2.2 Groundwater Flow Model

- 2.3 Hydrologic Boundaries
- 2.4 Hydraulic Boundaries
- 2.5 Sources and Sinks
- 3.0 Analytical Model
  - 3.1 Model Selection - justification for use of analytical, numerical or other analysis
  - 3.2 Model Description - name and version of analysis, model assumptions and limitations, name of organization or person which has developed the analysis
- 4.0 Groundwater Flow Model Construction
  - 4.1 Model Grid - state if fixed by model
  - 4.2 Hydraulic Parameters - state source such as field determined or literature. Cite relevant section of Site Characterization report or literature reference.
  - 4.3 Boundary Conditions - state if fixed by model
  - 4.4 Selection of Calibration Targets
- 5.0 Calibration
  - 5.1 Residual Analysis
  - 5.2 Sensitivity Analysis
  - 5.3 Model Verification, if applicable
- 6.0 Predictive Simulations - Indicate relation to applicable Act 2 standard
- 7.0 Summary and Conclusions
  - 7.1 Model Assumptions/Limitations
  - 7.2 Model Predictions
  - 7.3 Recommendations - including planned post-audit activities during postremediation care plan if required

## 8.0 Figures and Tables

### 8.1 Model grid or axes oriented on the site map

### 8.2 Input and output files

## 3. Impacts to Surface Water from Diffuse Flow of Contaminated Groundwater

Sections 250.309 and 250.406 of the regulations provide for determining compliance with surface water quality standards from a diffuse surface or groundwater discharge. The following types of sites that are impacted by diffuse flow of a dissolved groundwater plume into a stream need to be analyzed incorporating the methods and models of DEP's Bureau of Clean Water:

- Some sites selecting the SHS for used aquifers with a total dissolved solids (TDS) concentration of 2,500 mg/L or less;
- All sites selecting the Statewide health nonuse aquifer groundwater standard;
- All sites selecting the SHS for used aquifers with a TDS greater than 2,500 mg/L; and
- All sites selecting the site-specific standard for groundwater.

All discharges involved with a remediation should be in compliance with the provisions of Chapter 93 to demonstrate attainment of the Statewide health and site-specific standards. This includes all applicable antidegradation requirements as outlined by Chapter 93.4(a) including the protection of exceptional value and high-quality waters. Any discharges to surface water should likewise be in compliance with the provisions summarized in Chapter 93.6 (no presence of floating materials and sheens) in addition to dissolved plumes.

### a) Conceptual Framework

In order to understand how to evaluate the impact of diffuse groundwater plumes on surface water quality, several important concepts must be understood. These concepts apply to evaluating impacts of groundwater plumes on surface water regardless of the standard selected.

The first is the concept of "maximum average concentration." Surface water impacts must be evaluated for the time that the "maximum average concentration" in the groundwater plume is discharging into the stream. As a plume in groundwater begins to encroach onto a stream, the average concentration entering the stream will rise, and remain steady, or then fall depending on the nature of the source (continuous or pulse). For a constant source with a decaying contaminant, the maximum average concentration to the stream occurs when the plume has reached a steady-state condition. For a constant source and non-decaying contaminant, the maximum average concentration to the stream occurs when the mass discharging into the stream equals the mass emanating from the source. For

a pulse or slug source, the maximum average concentration will occur at the time the peak concentrations in the pulse (or slug) pass into the stream. The Department has prepared a spreadsheet, SWLOAD5B (SWL5B), which will calculate the “maximum average concentration” for decaying and non-decaying plumes emanating from a constant source.

A second concept to understand concerns what is termed the plume “edge criterion.” The “edge criterion” is the concentration equal or above which the maximum average concentration and associated flow will be determined for the plume in question. This is needed to assure that concentrations below the criterion will not be used and serve to dilute the average concentration and/or increase the flow in the plume to a point where any and all discharges to surface water become acceptable. The “edge criterion” is contaminant specific. The following rules should be used in establishing the “edge criterion.” These rules apply to selection of the “edge criterion” regardless of the standard selected:

- For those compounds on Table III-1 of the technical guidance manual (TGM) which have established surface water criteria, further surface water compliance evaluation is not necessary. Demonstrating that the MSC is met at the POC or groundwater/surface water interface is sufficient to address surface water concerns.
- For all other compounds, further surface water compliance evaluation is necessary.

Maximum average concentrations and flow for input into Pennsylvania’s PENTOXSD surface water mixing model should only be calculated for portions of a groundwater plume that exceed the “edge criterion” for the compound being evaluated. The Department has prepared a spreadsheet, SWL5B, which incorporates the “edge criterion” for calculating inputs to PENTOXSD for decaying and non-decaying plumes emanating from a constant source. If no portion of a plume entering a stream at the time of maximum average concentration exceeds the “edge criterion,” no further demonstration of surface water attainment is needed.

A third concept to understand is that of “maximum modeled or measured concentration.” It is important to understand that the maximum concentration being referred to by this phrase is the maximum concentration in the plume at the time and place that the maximum average concentration is discharging into the stream. Therefore, a measured concentration is inappropriate, and a modeled concentration should be used in cases where:

- The plume has not yet reached the stream;
- The plume is entering the stream, but has not yet reached its maximum average concentration; or
- The number and/or location of wells is insufficient to assure the Department that the maximum concentration has been found.

A fourth concept to understand is where the concentrations should be measured with respect to the Act 2 property line POC. If a plume discharges off the property being remediated before discharging into a stream, then the criteria for waiving a PENTOXSD analysis can be measured at the POC. If the plume discharges into a stream before leaving the property, criteria must be demonstrated along the groundwater/surface water interface where the plume is discharging.

The spreadsheet SWL5B is constructed so that the “maximum modeled concentration” is compared to the “edge criterion” for each compound and a determination is automatically made if a PENTOXSD analysis is needed. By convention, the “edge criterion” in SWL5B is defined as the threshold for waiving a PENTOXSD analysis.

Two final comments need to be made regarding the demonstration of surface water quality attainment. First, worst-case source concentration and flow associated with the source can be input directly into PENTOXSD. Doing this will avoid groundwater modeling or measuring concentrations at the POC or groundwater/surface water interface in many situations.

Secondly, anytime it can be demonstrated conclusively that the maximum concentration in a plume is less than the lowest surface water quality criteria, attainment of surface water quality can be assumed. Surface water quality criteria for specific compounds may be found in Tables 3 and 5 in 25 Pa. Code Chapter 93, Surface Water Quality Standards.

## b) **Mathematical Framework**

The basic mass balance equation to determine the concentration of a contaminant in surface water downstream of a diffuse groundwater contaminant discharge at design flow conditions with background contaminant levels included is:

$$C_{sw} = \frac{(Q_{gw} * C_{gw}) + (Q_{sw} * Y_c * C_{bsw})}{(Q_{sw} * Y_c) + Q_{gw}}$$

where:

$C_{sw}$  = the concentration in surface water of a contaminant of concern downstream of the nonpoint source discharge into the surface water.

$Q_{sw}$  = the quantity of stream flow above the nonpoint source discharge into surface water.

$Q_{gw}$  = the quantity of flow in the groundwater plume discharging into the surface water.

$C_{gw}$  = the maximum average concentration of a contaminant in the groundwater discharging into surface water.

$Y_c$  = the partial mix factor (decimal per cent), derived from using the PENTOXSD model.

$C_{bsw}$  = the background concentration in surface water of a contaminant of concern above the nonpoint source discharge.

The equation for determining the allowable groundwater concentration in a plume discharging to surface water is:

$$C_{gw} = C_x + \frac{Y_c * Q_{sw} * (C_x - C_{bsw})}{Q_{gw}}$$

where:

$C_x$  = the water quality objective (criteria value most of the time, can be site-specific).

Other variables are as listed above at design flow conditions (e.g.  $Q_{7-10}$  or  $Q_{hm}$ ).

For surface water bodies exhibiting tidal effects (e.g. Delaware River estuary) 1% of the  $Q_{7-10}$  and  $Q_h$  flows are acceptably conservative for calculations of  $Q_{sw}$  in estuaries.

### c) **Application**

The general procedure for applying the mathematical framework above to applicable compounds requires estimating the flow and maximum average concentration of the contaminated groundwater plume for each parameter of concern at the groundwater/surface water boundary. These values, in turn, are the discharge flow and discharge concentration values to be evaluated using the Bureau of Clean Water's PENTOXSD model to determine if the groundwater discharge to the stream meets the applicable surface water quality criteria. Users are referred to Technical Guide 391-2000-011 and PENTOXSD for Windows (Version 2.0D) Supplemental Information for information on using the PENTOXSD model.

The analysis will involve incorporating background concentrations in surface water for certain contaminants. Users are referred to TGM 391-2000-022 (Implementation Guidance for the Determination and Use of Background/Ambient Water Quality in the Determination of Wasteload Allocations and NPDES Effluent Limitations for Toxic Substances) for information on how and when to apply background water quality data.

For steady-state plumes which have compliance points at or very near a stream, the groundwater flow and concentrations (mass load) within the plume can and

should be determined from direct measurements. The mass loading of groundwater plumes which have not yet reached the stream boundary, which are not at steady state at the stream boundary, or for which data at the stream boundary are not available, must be estimated in some way (e.g. using groundwater solute transport models, or by assuming, conservatively, that the highest concentrations measured in the plume are representative of those at the stream boundary).

The general guidelines and example problems presented below in this guidance apply to single source discharge analysis. If there is more than one source of a pollutant in a stream reach, it may be necessary to evaluate the cumulative impact of these sources. The stream reach is determined by the site-specific travel times, stream flow, discharge flow dilution and potency of the pollutant as it moves downstream. The term that describes this process is “multiple source discharge.” The Bureau of Clean Water recommends that the Equal Marginal Percent Reduction (EMPR) method of allocation be used for these situations.

EMPR is a two-step process:

- **Baseline Analysis:** this step evaluates each contributor individually to determine if it would exceed the water quality objective by itself. This step evaluates the contributor’s currently modeled load and compares it to the water quality objective. If the modeled load is greater than the water quality objective, the modeled load is reduced to the water quality objective. A baseline value is determined for every contributor. This baseline value is either the currently modeled load or the water quality objective. This step assures that no contributor would cause an exceedance of the water quality objective by itself.
- **Multiple Analysis:** this step evaluates the cumulative impact of multiple sources on the stream. The analysis is carried out by systematically moving downstream, adding the baseline pollutant loads, and determining if the water quality objective is met at all locations. Through this process the critical reach of the stream can be found and any further necessary reductions from the baseline values can be made to meet the water quality objective at all points in the stream. Any further reductions from the baseline are made on an equal percentage basis.

Further information regarding the EMPR process can be found in the Technical Reference Guide for the Wasteload Allocation Program for Dissolved Oxygen and Ammonia-Nitrogen on the Bureau of Clean Water web page.

**d) Statewide Health Standard in Aquifers with 2,500 mg/L TDS or Less**

For certain compounds that have SHSs established in Chapter 250, simply demonstrating attainment of the residential or nonresidential SHS MSC for groundwater in used aquifers with TDS less than or equal to 2,500 mg/L at the point of compliance, or at the groundwater/surface water interface when the plume discharges to surface water prior to or instead of passing through the property line POC, will satisfy the surface water criteria attainment

demonstration. This is because either the MSC is equal to or below the lowest surface water quality criterion (LSWC) or the compound in question does not have any corresponding surface water criteria at this time. These compounds are listed in Table III-1.

For all other compounds, surface water compliance analysis is required to the compound's edge criterion. These are compounds where the MSC exceeds the LSWC. In some cases, the LSWC may be much lower than the laboratory PQL. In this case, please contact the Act 2 site project officer for further guidance.

Regardless of the standard selected, whenever the maximum concentration of a regulated substance in groundwater discharging to a stream at the time of maximum mass loading to the stream is quantified at a level lower than the LSWC, further demonstration of compliance with surface water criteria is not required.

It is also important to note that if the fate and transport modeling or actual in-stream sampling show that surface water quality criteria are exceeded, the remediator may be able to demonstrate that the site-specific standard can be attained by addressing the applicable exposure pathways. This would result in a waiver of the provisions of Chapter 93 Water Quality Standards as described in Section 250.406(c)(2) of the regulations.

e) **Examples**

i) **Example 1: Groundwater Source Very Near or Adjacent to Surface Water Discharge**

A site with an accumulation of gasoline as a separate phase liquid lies immediately adjacent to a small stream. Separate phase liquid is being collected by an interceptor/skimmer system that prevents its discharge to the stream. However, a dissolved phase hydrocarbon plume with maximum concentrations of certain compounds near their solubility limit is entering the stream. The remediator has selected the site-specific standard for these contaminants and must determine if surface water criteria are met without any treatment or removal of the dissolved phase plume. Because the groundwater concentrations exceeding the lowest surface water quality criteria are entering the stream, a PENTOXSD analysis is required.

Because the site is located very near the surface water discharge point, no opportunity for dispersion or decay of the groundwater plume prior to its discharge is expected. Data from the site characterization and attainment monitoring wells is assumed here to allow an accurate estimate of the quantity and concentration of the groundwater plume entering the stream, without any need for fate and transport modeling of groundwater. The following characteristics of the groundwater plume have been determined:

Plume (source) width: 100 feet

Plume depth: 10 feet

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW ≤ 2,500 TDS**

SUBSTANCE	CAS Number
ACENAPHTHYLENE	208-96-8
ACEPHATE	30560-19-1
ACETALDEHYDE	75-07-0
ACETONITRILE	75-05-8
ACETOPHENONE	98-86-2
ACETYLAMINOFLUORENE, 2-(2AAF)	53-96-3
ACROLEIN	107-02-8
ACRYLIC ACID	79-10-7
ALACHLOR	15972-60-8
ALDICARB	116-06-3
ALDICARB SULFONE	1646-88-4
ALDICARB SULFOXIDE	1646-87-3
ALLYL ALCOHOL	107-18-6
ALUMINUM	7429-90-5
AMETRYN	834-12-8
AMINOBIHENYL, 4-	92-67-1
AMITROLE	61-82-5
AMMONIUM SULFAMATE	7773-06-0
ANILINE	62-53-3
ANTHRACENE	120-12-7
ARSENIC	7440-38-2
ASBESTOS	12001-29-5
ATRAZINE	1912-24-9
AZINPHOS-METHYL (GUTHION)	86-50-0
BARIUM AND COMPOUNDS	7440-39-3
BAYGON (PROPOXUR)	114-26-1
BENOMYL	17804-35-2
BENTAZON	25057-89-0
BENZO(G,H,I)PERYLENE	191-24-2
BENZOIC ACID	65-85-0
BENZOTRICHLORIDE	98-07-7
BENZYL ALCOHOL	100-51-6
BERYLLIUM	7440-41-7
BETA PROPIOLACTONE	57-57-8
BIPHENYL, 1,1-	92-52-4
BIS(2-CHLOROETHOXY)METHANE	111-91-1
BIS(2-CHLOROISOPROPYL)ETHER	108-60-1
BIS(CHLOROMETHYL)ETHER	542-88-1
BISPHENOL A	80-05-7
BROMACIL	314-40-9

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW ≤ 2,500 TDS**

SUBSTANCE	CAS Number
BROMOCHLOROMETHANE	74-97-5
BROMOMETHANE	74-83-9
BROMOXYNIL	1689-84-5
BROMOXYNIL OCTANOATE	1689-99-2
BUTADIENE, 1,3-	106-99-0
BUTYL ALCOHOL, N-	71-36-3
BUTYLATE	2008-41-5
BUTYLBENZENE, N-	104-51-8
BUTYLBENZENE, SEC-	135-98-8
BUTYLBENZENE, TERT-	98-06-6
CAPTAN	133-06-2
CARBARYL	63-25-2
CARBAZOLE	86-74-8
CARBOFURAN	1563-66-2
CARBON DISULFIDE	75-15-0
CARBOXIN	5234-68-4
CHLORAMBEN	133-90-4
CHLORIDE	7647-14-5
CHLORO-1, 1-DIFLUOROETHANE, 1-	75-68-3
CHLORO-1-PROPENE, 3- (ALLYL CHLORIDE)	107-05-1
CHLOROACETALDEHYDE	107-20-0
CHLOROACETOPHENONE, 2-	532-27-4
CHLOROANILINE, P-	106-47-8
CHLOROBENZENE	108-90-7
CHLOROBENZILATE	510-15-6
CHLOROBUTANE, 1-	109-69-3
CHLORODIFLUOROMETHANE	75-45-6
CHLOROETHANE	75-00-3
CHLORONITROBENZENE, P-	100-00-5
CHLOROPHENOL, 2-	95-57-8
CHLOROPRENE	126-99-8
CHLOROPROPANE, 2-	75-29-6
CHLOROTHALONIL	1897-45-6
CHLOROTOLUENE, O-	95-49-8
CHLOROTOLUENE, P-	106-43-4
CHLORPYRIFOS	2921-88-2
CHLORSULFURON	64902-72-3
CHLOROTHAL-DIMETHYL (DACTHAL) (DCPA)	1861-32-1

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW ≤ 2,500 TDS**

SUBSTANCE	CAS Number
CHROMIUM, TOTAL	7440-47-3
COPPER	7440-50-8
CRESOL, DINITRO-O-4,6-	534-52-1
CRESOL(S)	1319-77-3
CRESOL, O-(METHYLPHENOL, 2-)	95-48-7
CRESOL, M (METHYLPHENOL, 3-)	108-39-4
CROTONALDEHYDE	4170-30-3
CROTONALDEHYDE, TRANS-	123-73-9
CUMENE (ISOPROPYL BENZENE)	98-82-8
CYANAZINE	21725-46-2
CYCLOHEXANE	110-82-7
CYCLOHEXANONE	108-94-1
CYFLUTHRIN	68359-37-5
CYROMAZINE	66215-27-8
DI(2-ETHYLHEXYL)ADIPATE	103-23-1
DIALLATE	2303-16-4
DIAMINOTOLUENE, 2-4-	95-80-7
DIBENZOFURAN	132-64-9
DIBROMO-3-CHLOROPROPANE, 1,2-	96-12-8
DIBROMOBENZENE, 1,4-	106-37-6
DIBROMOETHANE, 1,2- (ETHYLENE DIBROMIDE)	106-93-4
DIBROMOMETHANE	74-95-3
DICAMBA	1918-00-9
DICHLORO-2-BUTENE, 1,4-	764-41-0
DICHLORO-2-BUTENE, TRANS-1, 4-	110-57-6
DICHLOROACETIC ACID	79-43-6
DICHLOROBENZENE, P	106-46-7
DICHLORODIFLUOROMETHANE (FREON 12)	75-71-8
DICHLOROETHANE, 1,1-	75-34-3
DICHLOROETHYLENE, 1,1-	75-35-4
DICHLOROETHYLENE, TRANS-1,2-	156-60-5
DICHLOROPHENOL, 2,4-	120-83-2
DICHLOROPHENOXYACETIC ACID, 2,4- (2,4-D)	94-75-7
DICHLOROPROPANE, 1,2-	78-87-5
DICHLOROPROPIONIC ACID, 2,2- (DALAPON)	75-99-0
DICHLORVOS	62-73-7

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW ≤ 2,500 TDS**

SUBSTANCE	CAS Number
DICYCLOPENTADIENE	77-73-6
DIFLUBENZURON	35367-38-5
DIISOPROPYL METHYLPHOSPHONATE	1445-75-6
DIMETHOATE	60-51-5
DIMETHOXYBENZIDINE, 3,3-	119-90-4
DIMETHRIN	70-38-2
DIMETHYLAMINOAZOBENZENE, P-	60-11-7
DIMETHYLANILINE, N,N-	121-69-7
DIMETHYLBENZIDINE, 3,3-	119-93-7
DINITROBENZENE, 1,3-	99-65-0
DINOSEB	88-85-7
DIOXANE, 1,4-	123-91-1
DIPHENAMID	957-51-7
DIPHENYLAMINE	122-39-4
DIQUAT	85-00-7
DISULFOTON	298-04-4
DITHIANE, 1,4-	505-29-3
DIURON	330-54-1
ENDOSULFAN	115-29-7
ENDOSULFAN SULFATE	1031-07-8
ENDOTHALL	145-73-3
EPICHLOROHYDRIN	106-89-8
ETHEPHON	16672-87-0
ETHION	563-12-2
ETHOXYETHANOL, 2- (EGEE)	110-80-5
ETHYL ACETATE	141-78-6
ETHYL ACRYLATE	140-88-5
ETHYL DIPROPYLTHIOCARBAMATE, S- (EPTC)	759-94-4
ETHYL ETHER	60-29-7
ETHYL METHACRYLATE	97-63-2
ETHYLENE CHLORHYDRIN	107-07-3
ETHYLENE GLYCOL	107-21-1
ETHYLENE THIOUREA (ETU)	96-45-7
ETHYLP-NITROPHENYL PHENYLPHOSPHOROTHIOATE	2104-64-5
FENAMIPHOS	22224-92-6
FENVALERATE (PYDRIN)	51630-58-1
FLUOMETURON	2164-17-2
FLUORIDE	16984-48-8

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW ≤ 2,500 TDS**

SUBSTANCE	CAS Number
FLUOROTRICHLOROMETHANE (FREON 11)	75-69-4
FONOFOS	944-22-9
FORMIC ACID	64-18-6
FOSETYL-AL	39148-24-8
FURAN	110-00-9
FURFURAL	98-01-1
GLYPHOSATE	1071-83-6
HEXACHLOROETHANE	67-72-1
HEXANE	110-54-3
HEXAZINONE	51235-04-2
HEXYTHIAZOX (SAVEY)	78587-05-0
HMX	2691-41-0
HYDRAZINE/HYDRAZINE SULFATE	302-01-2
HYDROQUINONE	123-31-9
IPRODIONE	36734-19-7
IRON	7439-89-6
ISOBUTYL ALCOHOL	78-83-1
ISOPROPYL METHYLPHOSPHONATE	1832-54-8
KEPONE	143-50-0
LITHIUM	7439-93-2
MALATHION	121-75-5
MALEIC HYDRAZIDE	123-33-1
MANEB	12427-38-2
MANGANESE	7439-96-5
MERPHOS OXIDE	78-48-8
METHACRYLONITRILE	126-98-7
METHAMIDOPHOS	10265-92-6
METHANOL	67-56-1
METHOMYL	16752-77-5
METHOXYCHLOR	72-43-5
METHOXYETHANOL, 2-	109-86-4
METHYL ACETATE	79-20-9
METHYL ACRYLATE	96-33-3
METHYL CHLORIDE	74-87-3
METHYL ETHYL KETONE	78-93-3
METHYL HYDRAZINE	60-34-4
METHYL ISOCYANATE	624-83-9
METHYL METHACRYLATE	80-62-6
METHYL METHANESULFONATE	66-27-3

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW ≤ 2,500 TDS**

SUBSTANCE	CAS Number
METHYL PARATHION	298-00-0
METHYL STYRENE (MIXED ISOMERS)	25013-15-4
METHYL TERT-BUTYL ETHER (MTBE)	1634-04-4
METHYLCHLOROPHOXYACETIC ACID (MCPA)	94-74-6
METHYLENE BIS(2-CHLOROANILINE), 4,4'-	101-14-4
METHYLNAPHTHALENE, 2-	91-57-6
METHYLSTYRENE, ALPHA	98-83-9
METRIBUZIN	21087-64-9
MOLYBDENUM	7439-98-7
MONOCHLOROACETIC ACID	79-11-8
NAPHTHYLAMINE, 1-	134-32-7
NAPHTHYLAMINE, 2-	91-59-8
NAPROPAMIDE	15299-99-7
NITRATE-NITROGEN (TOTAL)	14797-55-8
NITRITE-NITROGEN (TOTAL)	14797-65-0
NITROANILINE, O-	88-74-4
NITROANILINE, P-	100-01-6
NITROGUANIDINE	556-88-7
NITROPHENOL, 2-	88-75-5
NITROPHENOL, 4-	100-02-7
NITROPROPANE, 2-	79-46-9
NITROSODIETHYLAMINE, N-	55-18-5
NITROSO-DI-N-BUTYLAMINE, N-	924-16-3
NITROSO-N-ETHYLUREA, N-	759-73-9
OCTYL PHTHALATE, DI-N-	117-84-0
OXAMYL (VYDATE)	23135-22-0
PARAQUAT	1910-42-5
PARATHION	56-38-2
PEBULATE	1114-71-2
PENTACHLOROENZENE	608-93-5
PENTACHLOROETHANE	76-01-7
PENTACHLORONITROENZENE	82-68-8
PERCHLORATE	7790-98-9
PHENACETIN	62-44-2
PHENOL	108-95-2
PHENYL MERCAPTAN	108-98-5
PHENYLENEDIAMINE, M-	108-45-2
PHENYLPHENOL, 2-	90-43-7

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW ≤ 2,500 TDS**

SUBSTANCE	CAS Number
PHORATE	298-02-2
PHTHALIC ANHYDRIDE	85-44-9
PICLORAM	1918-02-1
PROMETON	1610-18-0
PRONAMIDE	23950-58-5
PROPANIL	709-98-8
PROPANOL, 2- (ISOPROPYL ALCOHOL)	67-63-0
PROPAZINE	139-40-2
PROPHAM	122-42-9
PROPYLBENZENE, N-	103-65-1
PROPYLENE OXIDE	75-56-9
PYRENE	129-00-0
PYRIDINE	110-86-1
QUINOLINE	91-22-5
QUIZALOFOP (ASSURE)	76578-14-8
RDX	121-82-4
RONNEL	299-84-3
SIMAZINE	122-34-9
STRONTIUM	7440-24-6
STRYCHNINE	57-24-9
STYRENE	100-42-5
SULFATE	7757-82-6
TEBUTHIURON	34014-18-1
TERBACIL	5902-51-2
TERBUFOS	13071-79-9
TETRACHLOROENZENE, 1,2,4,5-	95-94-3
TETRACHLOROETHANE, 1,1,1,2	630-20-6
TETRACHLOROPHENOL, 2,3,4,6-	58-90-2
TETRAETHYL LEAD	78-00-2
TETRAETHYLDITHIOPYROPHOSPHATE	3689-24-5
TETRAHYDROFURAN	109-99-9
THIOFANOX	39196-18-4
THIRAM	137-26-8
TIN	7440-31-5
TOLUDINE, M-	108-44-1
TOLUDINE, O-	95-53-4
TOLUDINE, P-	106-49-0
TRIALATE	2303-17-5
TRICHLORO-1,2,2-TRIFLUOROETHANE, 1,1,2-	76-13-1

**Table III-1: Compounds Excluded from Further Surface  
Water Evaluation on Attainment of NR SHS for  
GW  $\leq$  2,500 TDS**

SUBSTANCE	CAS Number
TRICHLOROACETIC ACID	76-03-9
TRICHLOROBENZENE, 1,3,5-	180-70-3
TRICHLOROETHANE, 1,1,1-	71-55-6
TRICHLOROPHENOL, 2,4,5-	95-95-4
TRICHLOROPHENOXYACETIC ACID, 2,4,5- (2,4,5-T)	93-76-5
TRICHLOROPHENOXYPROPIONIC ACID, 2,4,5- (2,4,5-TP)	93-72-1
TRICHLOROPROPANE, 1,1,2-	598-77-6
TRICHLOROPROPANE, 1,2,3-	96-18-4
TRICHLOROPROPENE, 1,2,3-	96-19-5
TRIETHYLAMINE	121-44-8
TRIETHYLENE GLYCOL	112-27-6
TRIFLURALIN	1582-09-8
TRIMETHYLBENZENE, 1,3,4- (TRIMETHYLBENZENE, 1,2,4-)	95-63-6
TRINITROGLYCEROL (NITROGLYCERIN)	55-63-0
TRINITROTOLUENE, 2,4,6-	118-96-7
VANADIUM	7440-62-2
VINYL ACETATE	108-05-4
VINYL BROMIDE (BROMOETHENE)	593-60-2
WARFARIN	81-81-2
ZINEB	12122-67-7

Conductivity: 1.90 ft/day

Gradient: .01 ft/ft

Groundwater flow represented by plume: 1,900 ft<sup>3</sup>/day =  
14,000 gallons/day

Average concentrations in groundwater at surface water interface ( $\mu\text{g/L}$ ):

- Benzene: 12,000
- Toluene: 52,000
- Ethylbenzene: 1,500
- Total xylenes: 9,000

Using benzene for this example, the maximum average groundwater concentration is 12,000 µg/L and the plume flow is 14,000 gallons/day or 0.014 million gallons/day (MGD).

Assuming all groundwater discharges to the stream, an evaluation of the plume discharge to the stream can now be made with the above data using PENTOXSD for each of the contaminants. The approach is described and shown below for benzene:

Figures III-1 and III-2 are printouts from the PENTOXSD model for Example 1. PENTOXSD shows that the recommended effluent limit for benzene in this case is 181 µg/L, which is less than the 329 µg/L maximum effluent groundwater concentration daily limit expected for benzene calculated for this example. Therefore, a release of liability cannot be granted in this case until the maximum effluent groundwater concentration daily limit is reduced to at least 181 µg/L and other parameters in the example are shown to be at acceptable levels.

**ii) Example 2: Groundwater Source at Distance from Surface Water Discharge – Steady-State Conditions**

In this example, all conditions are the same as for Example 1 except the source is 100 feet from the stream. Additionally, one well is located 40 feet from the source in a downgradient direction toward the stream containing benzene at a concentration of 6,500 µg/L. Assume that wells cannot be drilled at the groundwater/surface water interface because of existing buildings and other obstacles. However, enough onsite and offsite data have been collected to reasonably calibrate a model and establish that the plume is at or near steady-state conditions. A groundwater solute transport model is chosen by the remediator to estimate the flow and concentration of the contaminants into the river. For purposes of this example, the QD and SWL5B spreadsheet applications will be used. A plan view model such as QD is being used because it is difficult or impossible to calibrate a cross-sectional model such as SWL5B using isoconcentration map data. Isoconcentration contours are usually developed and drawn in the plan-view or horizontal dimension. Once the model input parameters are finalized using the plan view model, they are easily transferred for use into the cross-sectional model. The Department does not require the use of these particular models; however, if another surface water loading model is used, the rules incorporated into selection of SWL5B's "edge criterion" for establishing the portion of the plume flow and average concentration must be used.

In order to complete the analysis, input values for the following additional parameters required by the model were developed during the site characterization phase. Those parameters and how they were determined for this example are as follows (See Figure III-3 for the actual values):

Longitudinal and Transverse Dispersion – fitted to plume data (isoconcentration map) using QD

Vertical Dispersion – set to 0.0001 because the entire plume is assumed to discharge into the stream and any vertically dispersed contamination would enter the stream.

Lambda – starting values may be found from Appendix A, Table 5A, Chapter 250 (and converted to the correct units).

Time – 11 years-established from historical records. Note that this is fixed at  $1 \times 10^9$  days in SWL5B to assure that output is at steady-state conditions. This assures that SWL5B will yield the maximum average concentration for plumes emanating from a constant source.

Porosity – determined by laboratory analysis of undisturbed samples.

Dry Bulk Density – estimated at  $2.65 * (1 - \text{porosity})$ .

K<sub>oc</sub> – from Appendix A, Table 5, Chapter 250.

Fraction Organic Carbon – Can be estimated (Section III.A.1.b.ii).

**Figure III-1: Example 1 – PENTOXSD Model Inputs**

Input Data

**General Data**

General | Stream | Discharge and Parameters

Stream Code	RMI	Elevation (ft)	Drainage Area (sq mi)	Slope (ft/ft)	PWS With (mgd)	Apply FC
▶ 25409	10.000	500	4	0	0	<input checked="" type="checkbox"/>
25409	0.001	400	10	0	0	<input checked="" type="checkbox"/>

Record: 1 of 2

Print | < Back | Next > | Save | Analyze | Cancel | Export

Input Data

**Discharge and Parameter Data**

General | Stream | Discharge and Parameters

RMI	Name	Permit Number	Existing Disc Flow (mgd)	Permitted Disc Flow (mgd)	Design Disc Flow (mgd)	Reserve Factor	AFC PMF	CFC PMF	THH PMF	CRL PMF	Disc Hard (mg/L)	Disc pH
▶ 10.000	Example 1 creek	0000000	0.01436	0	0	0	0	0	0	0	100	7

Parameter Name	Disc Conc (µg/L)	Trib Conc (µg/L)	Disc Daily CV	Disc Hourly CV	Stream Conc (µg/L)	Stream CV	Fate Coef	FOS	Crit Mod	Chem Trans	Max Disc Conc (µg/L)
▶ BENZENE	12000	0	0.5	0.5	0	0	0	0	1	NA	0

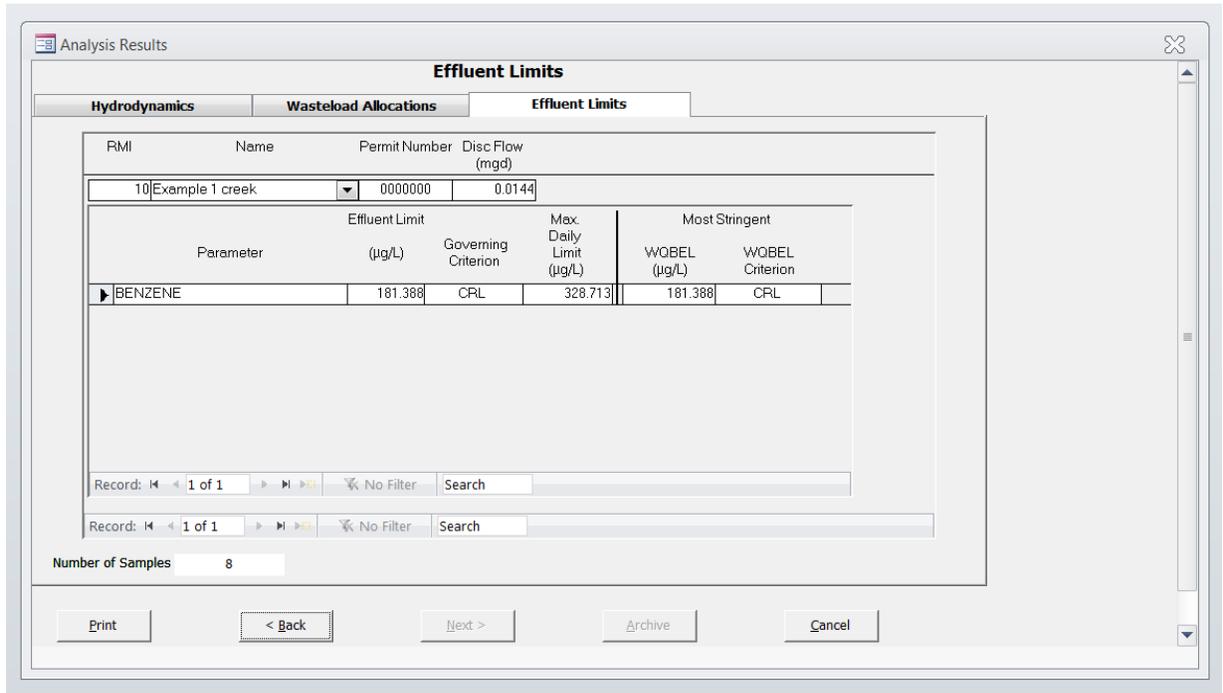
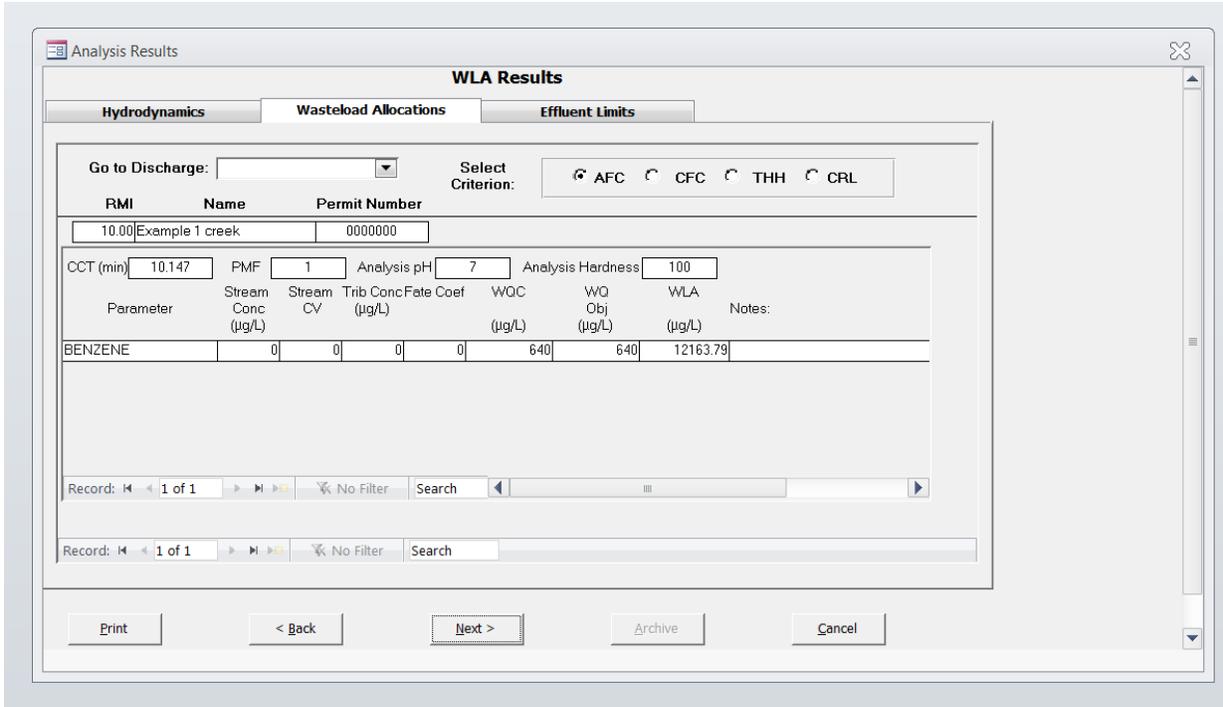
Record: 1 of 1

Design Condition	CMT
▶ Q7-10	0.00
Qh	0.00

Record: 1 of 2

Print | < Back | Next > | Save | Analyze | Cancel | Export

Figure III-2: Example 1 –PENTOXSD Model Output



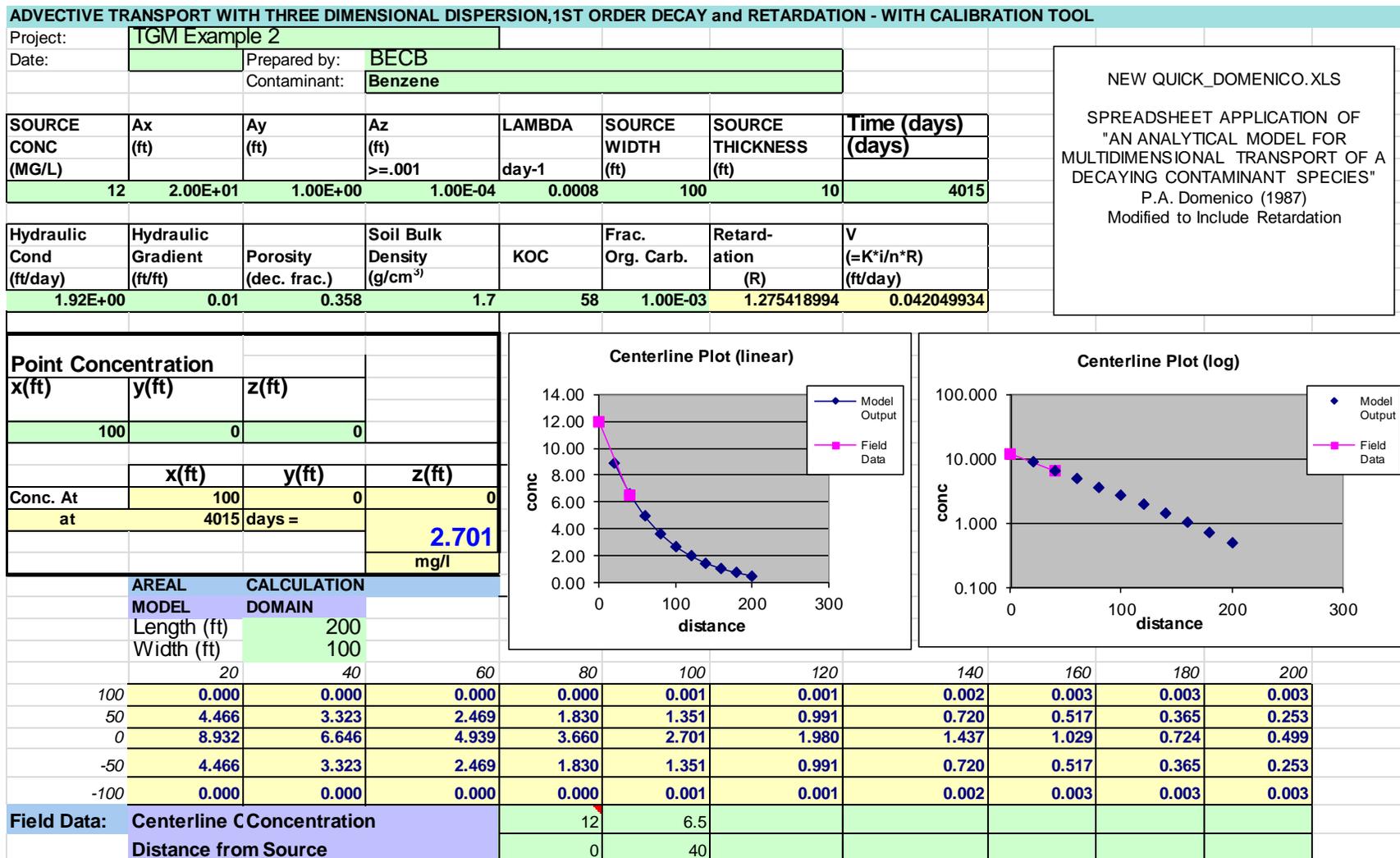
Once a satisfactory output matching the overall plume geometry at 11 years was achieved using QD, the flow and transport terms of QD, except for time, were input into SWL5B. The output from QD and SWL5B is shown in Figures III-3 and III-4.

The model indicates that the maximum average concentration in groundwater is 1.28 mg/L for benzene and the total flow through the plume is 0.00026 MGD. The model output indicates that PENTOX is required as the next step. These values (after any necessary conversion) then become the input values for existing discharge flow and discharge concentration of benzene in PENTOXSD. Note that the average concentration in the benzene plume is lower than in the first example because of first-order decay and dispersion. However, note also that, because the plume has dispersed, the cross-sectional flow is somewhat greater.

Documentation for using SWL5B to estimate plume flow, concentrations and mass loading is provided on the LRP web page under “Guidance and Technical Tools.”

Figures III-5 and III-6 are printouts from the PENTOXSD model run for Example 2. In this case, the recommended effluent limit for benzene is 9,953 µg/L, which is greater than the effluent groundwater concentration daily limit expected of 1,994 µg/L. Therefore, attainment of surface water criteria for benzene has been demonstrated. If attainment of the other parameters in the example with surface water criteria were also demonstrated, a release of liability would be conveyed.

Figure III-3: Example 2 – Quick Domenico Model Output





**Figure III-5: Example 2 – PENTOXSD Model Inputs**

Input Data

**General Data**

General | **Stream** | Discharge and Parameters

Stream Code	RMI	Elevation (ft)	Drainage Area (sq mi)	Slope (ft/ft)	PWS With (mgd)	Apply FC
▶ 25409	10.000	500	4	0	0	<input checked="" type="checkbox"/>
25409	0.001	400	10	0	0	<input checked="" type="checkbox"/>

Record: 1 of 2 | No Filter | Search

Print | < Back | Next > | Save | Analyze | Cancel | Export

Input Data

**Discharge and Parameter Data**

General | Stream | **Discharge and Parameters**

RMI	Name	Permit Number	Existing Disc Flow (mgd)	Permitted Disc Flow (mgd)	Design Disc Flow (mgd)	Reserve Disc Flow (mgd)	AFC PMF	CFC PMF	THH PMF	CRL PMF	Disc Hard	Disc pH
▶ 10.000	Example 2 creek	0000000	0.00026	0	0	0	0	0	0	0	100	7

**Parameter Data**

Parameter Name	Disc Conc (µg/L)	Trib Conc (µg/L)	Disc Daily CV	Disc Hourly CV	Stream Conc (µg/L)	Stream CV	Fate Coef	FOS	Crit Mod	Chem Trans	Max Disc Conc (µg/L)
▶ BENZENE	1278	0	0.5	0.5	0	0	0	0	1	NA	0

Record: 1 of 1 | No Filter | Search

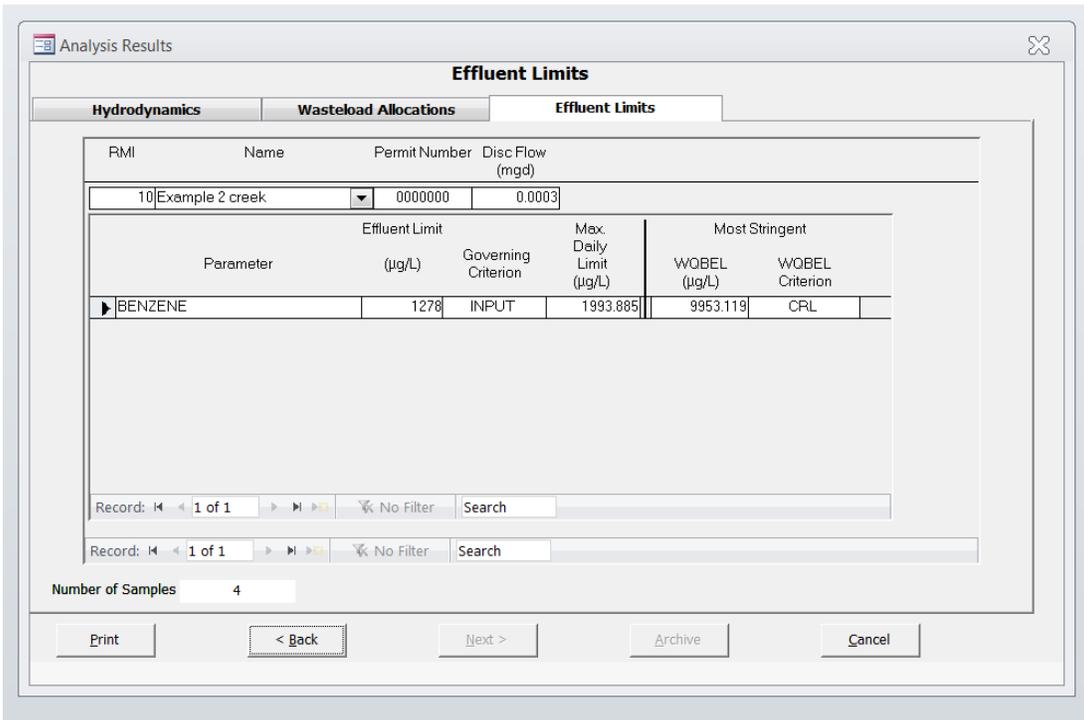
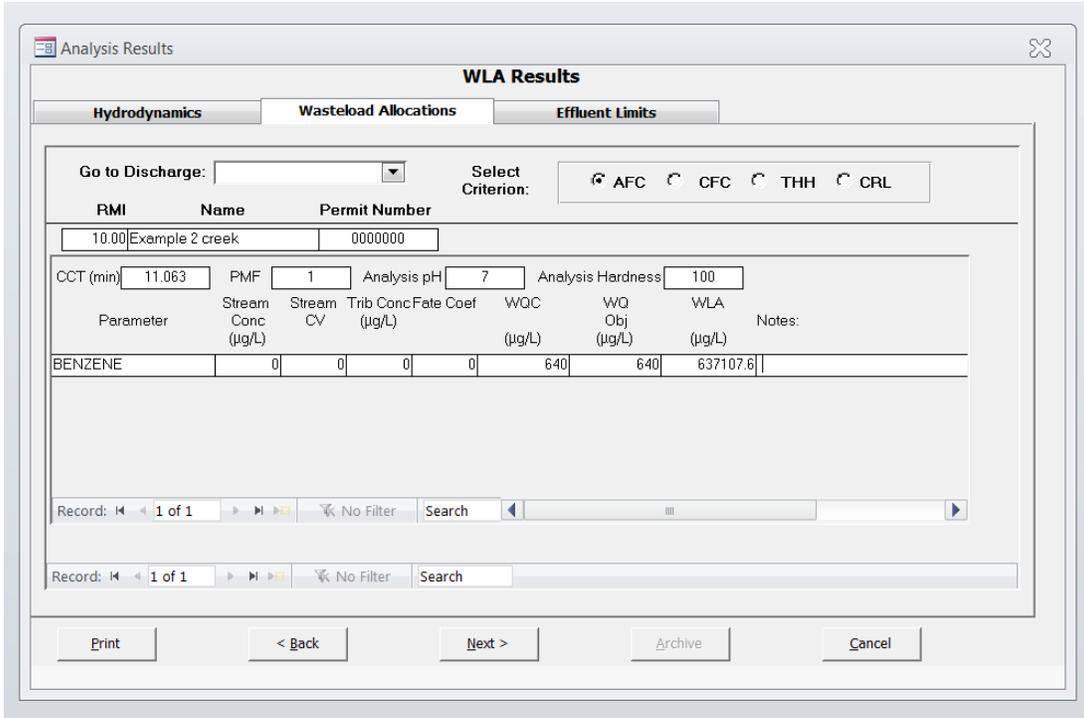
**Discharge Mixing Data**

Design Condition	CMT
▶ Q7-10	0.00
Qh	0.00

Record: 1 of 2 | No Filter | Search

Print | < Back | Next > | Save | Analyze | Cancel | Export

**Figure III-6: Example 2 – PENTOXSD Model Output**



## **B. Guidance for Attainment Demonstration with Statistical Methods**

### **1. Introduction**

The requirement to apply statistical methods to verify the cleanup of a site is emphasized in Act 2. Sections 302, 303 and 304 of Act 2 (35 P.S. §§ 6026.302-304) require that attainment of a standard be demonstrated by the collection and analysis of samples from affected media (such as surface water, soil, groundwater in aquifers at the point of compliance) through the application of statistical tests set forth in regulation. The Act also requires the Department to recognize those methods of attainment demonstration generally recognized as appropriate for that particular remediation.

Statistical methods are emphasized because there is a practical need to make decisions regarding whether a site meets a cleanup standard in spite of uncertainty. The uncertainty arises because we are able to sample and analyze only a small portion of the soil and groundwater at a site, yet we have to make a decision regarding the entire site.

The purpose of this section is to provide guidance for the use of statistics to demonstrate that a site has attained a cleanup standard under Act 2. It is intended to address certain key issues pertinent to the sampling and statistical analysis under Act 2, to provide references for proper statistical analysis and, if necessary, to provide examples of applying statistical procedures in detail. It is not intended to address every statistical issue.

For statistical attainment issues not addressed directly in this manual or in 25 Pa. Code Chapter 250, a person may consult the latest ITRC and EPA documents for additional guidance. The 2013 ITRC document *Groundwater Statistics and Monitoring Compliance* and EPA guidance documents (EPA 1992b, 1992c, 1996, 2002b, 2009) are particularly helpful. They provide detailed statistical procedures for demonstration of attainment and data analysis.

For groundwater characterization, remediators should consult Appendix A of this manual “Groundwater Monitoring Guidance” which provides general information on groundwater monitoring and sampling issues, such as monitoring well construction, locations and depths of monitoring wells, and well abandonment procedures. The Groundwater Monitoring Guidance provides a good summary of various statistical methods used for groundwater characterization.

For conducting statistical analyses, remediators may wish to utilize EPA’s ProUCL Statistical Software for Environmental Applications. This free program is available on EPA’s website and accompanied with a Technical Guide. ProUCL is able to run most of the statistical applications summarized in this section of the TGM.

Other standard statistics-related tests may be used to perform the procedures to demonstrate attainment as appropriate. If necessary, professional services should be obtained.

When we consider applying statistical methods to demonstrate the attainment of a risk-based cleanup standard, it is important to realize that three components may influence the overall stringency of this cleanup standard:

- The first component is the magnitude, level, or concentration that is deemed protective of human health and the environment. The development of risk-based cleanup standards is addressed in the regulations and Department's risk assessment guidances.
- The second component of the standard is the sampling that is done to evaluate whether a site is above or below the standard.
- The final component is how the resulting data are compared with the standard to decide whether the remedial action was successful (a statistical analysis).

Persons overseeing cleanup must look beyond the cleanup level and explore the sampling and statistical analysis that will allow evaluation of the site relative to the cleanup level. This guidance is intended to address statistical analysis and sampling components that may affect the stringency of cleanup standards.

## **2. Data Review for Statistical Methods**

Preliminary data review for statistical analysis (also known as exploratory data analysis in the DEP Groundwater Monitoring Guidance Manual; PA DEP, 2001) includes the use of graphical techniques and calculation of summary statistics. By reviewing the data both numerically and graphically, one can learn the "structure" of the data and identify limitations for using the data. Graphical methods include histograms, probability plots, box charts, and time-series plots to visually review the data for trends or patterns. EPA and most statistical texts recommend that time-series data should be graphed. This visual approach allows for a quick assessment of the statistical features of the data. Calculations of summary statistics are typically done to characterize the data and make judgments on the central tendencies, symmetry, presence of outliers, etc. Preliminary data review is critical in selecting additional appropriate mathematical procedures.

Graphical and parametric statistical procedures discussed here are included in many introductory statistics textbooks (e.g., Iman and Conover, 1983 and Ott, 1988) and are available in many computer statistics packages.

### **a) Summary Statistics**

Basic summary statistics can be used to characterize groundwater monitoring data. Summary statistics include median, interquartile range (IQR), mean, standard deviation, and range. Median and IQR are determined from percentiles. Median is the 50th percentile and IQR is the 25th to 75th percentile. Median indicates the "center" of data values. The mean is another measure of center but only if data are normally or symmetrically distributed. Mean and standard deviation are required values with parametric procedures. Range is the minimum to maximum values. Procedures for such summary statistics are found in introductory statistics texts.

## b) **Graphical Procedures**

Refer to ITRC (2013) for a general reference on graphical procedures.

**Histogram** - A histogram is a graphic display of frequency distribution. The area within the bar represents the relative density of the data.

**Boxplots** - A boxplot summarizes a data set by presenting the percentile distribution of the data. The “box” portion indicates the median and interquartile range (IQR). IQR is the middle 50 percent of data. Difference in the size of box halves represents data skewness.

Normal and symmetrical distributions will have equal size box halves. Extreme outliers are displayed as individual points that are recognized easily. Boxplots can be constructed by hand; however, many computer statistical packages will prepare them.

The boxplot of a lognormal distribution will have noticeably different-sized box halves. Lack of IQR overlap for different data sets will indicate a probable significant difference. Boxplots of seasonally grouped data can be used to detect data seasonality.

**Time Series Plots** - A time series plot displays individual data points on a time scale. A monthly scale can help to identify seasonal variation. A yearly scale also can identify possible trends. Superimposing data from multiple sampling locations may provide additional information. Improved trend information is often available with data smoothing.

**Control Charts** - Control charts are used to define limits for an analyte that has been monitored at an uncontaminated well over time. This procedure is a graphical alternative to prediction limits.

A common technique is the Shewhart-CUSUM control chart that plots the data on a time scale. Obvious features such as trends or sudden changes in concentration levels could then be observed. With this method, if any compliance well has a value or a sequence of values that lie outside the control limits for that analyte, it may indicate statistically significant evidence of contamination.

The control chart approach is recommended only for uncontaminated wells, a normal or lognormal data distribution with few nondetects, and for a dataset that has at least eight independent samples over a one-year period. This baseline is then used to judge the future samples. See the EPA Guidance (EPA, 2009, Chapter 20).

## 3. **Statistical Inference and Hypothesis Statements**

A statistical procedure that is designed to allow the extrapolation from the results of a few samples to a statement regarding the entire site is known as statistical inference.

Statistical inference allows decision making under uncertainty and valid extrapolation of information that can be defended and used with confidence to determine whether the site meets the cleanup standard.

The goal of statistical inference, the process of extrapolating results from a sample to a larger population, is to decide which of two complementary hypotheses, null hypothesis and alternative hypothesis, is likely to be true.

In general, statistical inference procedures include the following steps:

- (1) A null hypothesis and its alternative hypothesis are drawn up. The null hypothesis is developed in such a way that the probability of Type I error can be determined. The Type I error is an error that we falsely reject the null hypothesis, when the null hypothesis is true. Type I error is also known as false positive error.
- (2) Decide the level of significance,  $\alpha$ . This controls the risk of committing a Type I error.
- (3) Establish a decision rule for each scale of decision making that is derived from step 4 of the Data Quality Objectives (DQO) process. (See Section III.G for more information on the DQO process).
- (4) Determine the sample size,  $n$ . This is the number of environmental samples needed to make decision. Obtain data through the implementation of sampling and analysis plan.
- (5) Apply the decision rule to the data. The null hypothesis is rejected or not rejected. Rejection of the null hypothesis implies acceptance of the alternative hypothesis.

Section 250.707(d)(1) of the regulations has specified the ground rules of hypothesis statements under Act 2. For demonstration of attainment of Statewide health or site-specific standards, the null hypothesis ( $H_0$ ) is that the true site arithmetic average concentration is at or above the cleanup standard, and the alternative hypothesis ( $H_a$ ) is that the true site arithmetic average concentration is below the cleanup standard. When statistical methods are to be used to determine that the background standard is exceeded, the null hypothesis ( $H_0$ ) is that the background standard is achieved and the alternative hypothesis ( $H_a$ ) is that the background standard is not achieved.

To understand the rationale of hypothesis testing, let us consider a nonstatistical hypothesis testing example - the process in which an accused individual is judged to be innocent or guilty in a criminal court. Under our legal system, we feel that it is a more grievous mistake to convict an innocent man than to let a guilty man go free. Therefore, the accused person is presumed to be innocent under our legal system. The burden of proof of his guilt rests upon the prosecution. The prosecutor must present sufficient evidence to the jury in order to convict the defendant, while the defendant's lawyer would want to throw any reasonable doubt into the evidence presented by the prosecutor in order to get an acquittal verdict for the defendant. Using the language of hypothesis

testing, we want to test a null hypothesis ( $H_0$ ) that the accused man is innocent. That means that an alternative hypothesis ( $H_a$ ) exists, that the defendant is guilty. The jury will examine the evidence and decide whether the prosecution has demonstrated sufficiently that the evidence is inconsistent with the null hypothesis ( $H_0$ ) of innocent. If the jurors decide that the evidence is inconsistent with  $H_0$ , they reject that hypothesis and therefore accept the alternative hypothesis ( $H_a$ ) that the defendant is guilty.

Similar to the above legal process example, because we feel that it is a more serious mistake to declare a contaminated site to be uncontaminated than to declare an uncontaminated site to be contaminated under the Statewide health and site-specific standards, we choose the following null hypothesis statement: the true site arithmetic average concentration is at or above the cleanup standard. The null hypothesis is assumed to be true unless substantial evidence shows that it is false. The demonstration of attainment must be presented with sufficient evidence in order to show that the postremediation condition at the site is not consistent with the null hypothesis. We use “true site arithmetic average concentration” here because arithmetic average concentration is representative of the concentration that would be contacted at a site over time and toxicity criteria that are used to develop cleanup standards are based on long-term average exposure. The arithmetic average is appropriate regardless of the type of statistical distribution that might best describe the sampling data. We do not use geometric average concentration because the geometric mean of a set of sampling data bears no logical connection to the cumulative intake that would result from long-term contact with site contaminants.

It should be noted that the above hypothesis statements referring to the arithmetic average concentration does not force everyone to use 95% upper confidence limit (UCL) to infer the true site arithmetic average concentration. Methods other than the 95% UCL, such as tests for percentiles or proportions, also may be used provided that a person can document that high coverage of the true population mean occurs, (i.e., the value used in a method equals or exceeds the true site arithmetic average concentration with high probability).

For the background standard, the null hypothesis ( $H_0$ ) is that the background standard is achieved and the alternative hypothesis ( $H_a$ ) is that the background standard is not achieved. The background standard is not risk-based. These hypothesis statements will allow some site concentrations to be higher than some background reference-area measurements without rejecting the null hypothesis. These hypothesis statements are consistent with EPA guidance documents (EPA, 2009). If we reverse the hypothesis statements and presume that the background standard is not achieved, we would require most site concentrations to be less than the reference measurements in order to declare a site to be clean. In considering the cost of remediation, both the Department and EPA believe that this requirement is unreasonable.

#### **4. Selection of Statistical Methods**

##### **a) Factors Affecting the Selection of Statistical Methods**

The selection of statistical methods for use in assessing the attainment of cleanup standards depends on the characteristics of the environmental media. In soils,

concentrations of contaminants change relatively slowly, with little variation from season to season. In groundwater, the number of measurements available for spatial characterization is limited and seasonal patterns may exist in the data. As a result of these differences, separate procedures are recommended for the differing problems associated with soils and groundwater.

The selection of statistical methods also depends on remediation standards. There are three types of remediation standards under Act 2: background standards, Statewide health standards, and site-specific standards. Background standards are developed using background data. Many SHS and site-specific standards are risk-based standards that are concentration limits based on risk assessment methodologies. At some sites, a site-specific standard might use an engineering control, such as capping a site to eliminate pathways. The cap must be designed to meet certain engineering specifications prescribed in numerical levels. A background standard is not a single number, but rather a range of numbers. A statistical method used to demonstrate the attainment of the background standard is used to compare the distribution of data for a background reference area to the distribution of data for the impacted area. Different statistical methods are used to demonstrate the attainment of a risk-based concentration limit.

As a result of the above factors, recommended statistical approaches are addressed separately based on environment media and remediation standards. The flowchart in Figure III-7 provides a summary of recommended statistical methods described in the Chapter 250 regulations. Since Act 2 also requires the Department to recognize those methods of attainment demonstration generally recognized as appropriate for a particular remediation, the Department will also accept other appropriate statistical methods that meet the performance standards described in Section 250.707(d)(2) of the regulations.

Statistical methods generally can be classified into two categories: parametric procedures and nonparametric procedures. The selection of a parametric or a nonparametric procedure depends on the distribution of the data, the percentage of nondetects, and the database size. However, both procedures have assumptions that must be met to be considered valid analyses.

**Parametric Procedure** - Assumptions of parametric procedures include a specific data distribution such as normal (also known as Gaussian or the bell-shaped curve) or lognormal (normality achieved by log-transforming the data), and data variances that are similar. In addition, the data are assumed to be independent.

**Nonparametric Procedure** - Assumptions for nonparametric tests also are important. Nonparametric procedures assume equal variances and that the type (shape) of distribution of the population is the same. In other words, nonparametric methods do not require a specific type of data distribution, which is different from assuming a normal distribution when using parametric statistics.

Nonparametric procedures may be preferred because they:

- are free from normal distribution assumptions, thereby eliminating the need for normality tests and data transformations;
- are resistant to effects of outliers; and
- are usable when censored (i.e., less than detection values) data are present.

**b) Recommended Statistical Procedures**

In consideration of the factors described above, Section 250.707 of the regulations provides recommended statistical procedures that can be used to demonstrate attainment of cleanup standards. The following discussions provide background information of these recommended methods.

Unless otherwise specified or approved by the Department, systematic sampling (grid sampling) designs should be used in developing the sampling and analysis plan for demonstrating attainment of soil cleanup standards. (See 25 Pa. Code § 250.703(c)). Systematic random sampling is a grid sampling design with a random starting point. Systematic random sampling provides better coverage of the soil study area than simple random sampling. Limitations and procedures to implement systematic sampling can be found in Sections 5.3 and 6.5 of EPA guidance (EPA, 1989b). A square grid and a triangular grid are two common patterns used in systematic sampling. To avoid grid pattern corresponding to patterns of contamination, EPA (EPA 1992c) recommended the use of unaligned grid sampling design (Gilbert, 1987, p. 94). Unaligned grid sampling design maintains the advantage of uniform coverage while incorporating an element of randomness in the choice of sampling locations. To obtain an unbiased estimate of the variance of the mean, the multiple systematic sampling approach (Gilbert, 1987, p. 97) may be needed.

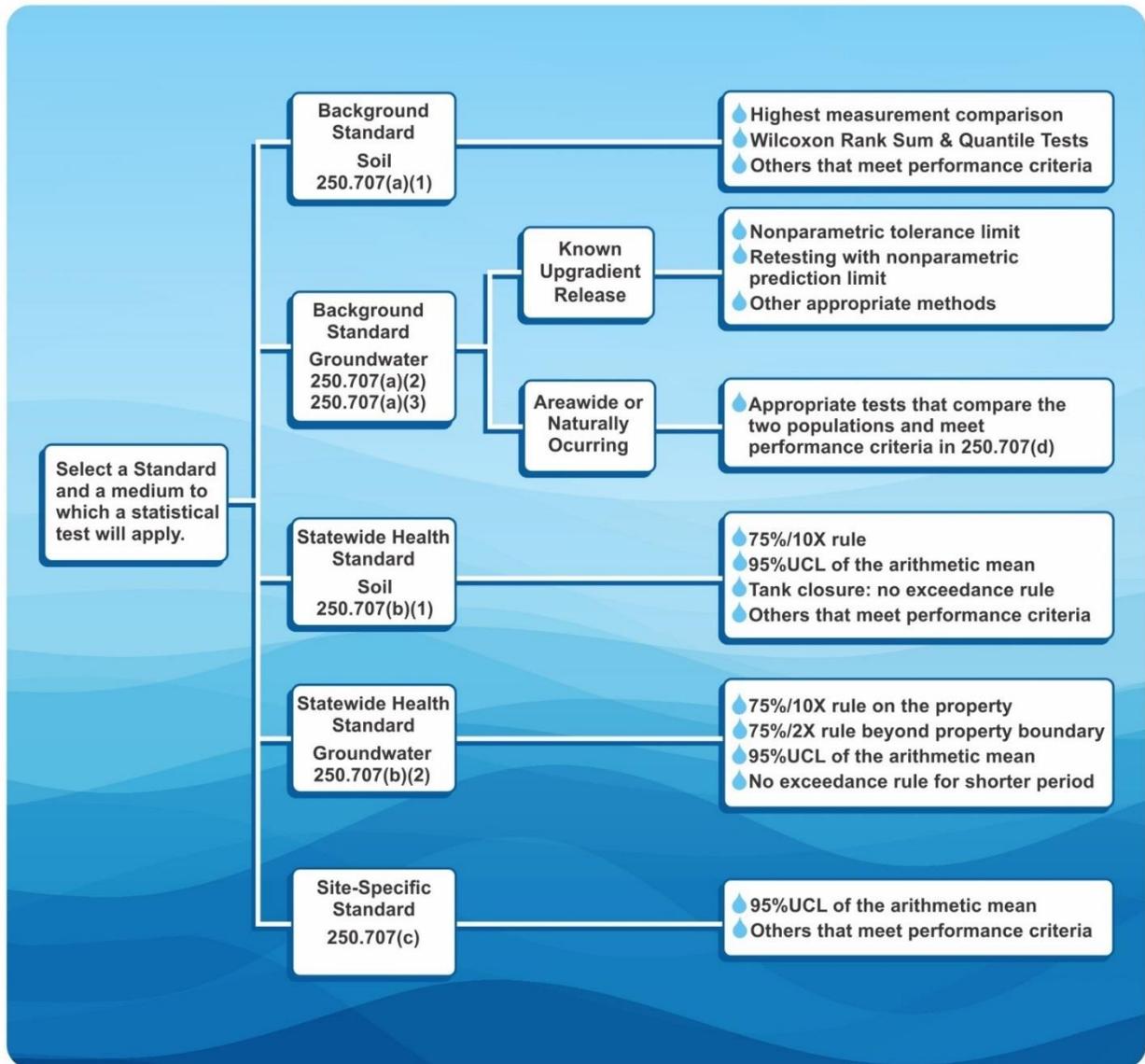
To generate a grid sampling design, a computer random number generator or a random number table may be used. To assist remediators with systematic random sampling, a spreadsheet program which creates a grid covering a soil study area is provided on the LRP web page.

**i) Soil Risk-Based Standards**

For risk-based standards, the selection of statistical parameters, such as mean, median or an upper percentile, to use in the statistical assessment decision depends on the toxicity criteria. Mean and median are useful for cleanup standards based on carcinogenic or chronic health effects and long-term average exposure. Upper proportion or percentile should be used if the health effects of the contaminant are acute or worst-case effects. Because the SHS values are based on the evaluation of carcinogenic or chronic health effects and long-term average exposure, the Cleanup Standards Scientific Advisory Board (CSSAB) has recommended that mean or median should be the statistical parameter of choice. The

regulations allow the remediator to use the 75%/10X rule or the 95% UCL of arithmetic mean to demonstrate attainment of the SHS in soils. The 75%/10X rule is valid ONLY for the SHS. For UST release sites that have only localized (soil) contamination as defined in the storage tank program's Underground Storage Tank Closure Guidance, and where the confirmatory samples taken in accordance with this TGM result in fewer samples being taken than otherwise required [including the sampling procedure for petroleum contaminated soils outlined in Section 250.707(b)(1)(iii)(B) of the regulations], all sample results must meet the SHS. For the site-specific standard, the regulations recommend the use of the 95% UCL of the arithmetic mean to demonstrate attainment in soils. Sections 250.707(b) and (c) of the regulations discuss statistical tests appropriate to demonstrating compliance of surface soils with the Statewide health and site-specific standards.

Figure III-7: Flow Chart of Recommended Statistical Methods



**(a) 75%/10X Rule**

The 75%/10X rule is a statistical ad hoc rule that tests whether the true site median concentration is below the cleanup standard. This rule requires that 75% of the samples collected for demonstration attainment be equal to or below the risk-based cleanup standard and that no single sample result exceeds the risk-based standard by more than ten times. (See 25 Pa. Code § 250.707(b)(1)(i)).

For the 75%/10X rule, the number of sample points required for each distinct area of contamination is specified in Section 250.703(d) of the regulations and is as follows:

- For soil volumes equal to or less than 125 cubic yards, at least eight (8) samples.
- For soil volumes up to 3,000 cubic yards, at least twelve (12) sample points.
- For each additional volume of up to 3,000 cubic yards, an additional twelve (12) sample points.
- Additional sampling points may be required based on site-specific conditions.

This recommendation of 8 to 12 samples at minimum is based on a simulation study using lognormal distributions (CSSAB 1996). Because the heterogeneity of a volume of soil increases as the volume increases, the number of samples required to accurately demonstrate attainment would also increase.

In a situation where compliance with two different SHS MSCs are required, such as an MSC for surface soil and another MSC for subsurface soil, two separate attainment tests, each applying the 75%/10x rule, would be required (0-2 feet and 2-15 feet).

It should be noted that the 75%/10X rule should not be used to demonstrate attainment of the site-specific standard. The site-specific standard is based on site-specific risk assessment methodology, including the assumption that a receptor's long-term exposure is related to the true site arithmetic average concentration of a contaminant. Therefore, the 75%/10X rule is not appropriate for the site-specific standard.

**(b) The 95% Upper Confidence Limit (UCL) of Arithmetic Mean**

Using 95% UCL of the arithmetic mean as described in Sections 250.707(b)(1)(ii) and 250.707(c) of the regulations is well documented in various EPA risk assessment or statistical

guidances (EPA, 1989, 1992c, 1996, 2002a). It should be noted that this statistical test may be applied to each distinct area of contamination for demonstration of attainment at a site. Site characterization data may not be suitable for inclusion in determining a 95% UCL for attainment demonstration.

The following formula can be used for calculating sample size (number of discrete soil samples) needed to estimate the mean:

$$n_d = \sigma^2 \{ (Z_{1-\beta} + Z_{1-\alpha}) / (C_s - \mu_1) \}^2$$

where  $\alpha$  is the false positive rate;  $\beta$  is the false negative rate;  $Z_{1-\alpha}$  and  $Z_{1-\beta}$  are the critical values for the normal distribution with probabilities of  $1-\alpha$  and  $1-\beta$ ;  $C_s$  is the cleanup standard;  $\mu_1$  is the value of population mean under the alternative hypothesis for which the specific false negative rate ( $\beta$ ) is to be controlled;  $\sigma$  is an estimate of true standard deviation of the population.

Please note that the above equation may generate exceedingly large sample size numbers (e.g.,  $\gg 50$ ). When some adjustments of the sample size are necessary based on practical and cost considerations, a person may use the equation to generate a smaller sample size by increasing the false negative rate or the detection difference  $C_s - \mu_1$ . Professional judgment should be used in calculating sample size versus the reliability of the statistical test. The false positive rate must not be greater than 0.20 for a nonresidential site or 0.05 for a residential site (25 Pa. Code § 250.707(d)(2)(vii)).

Procedures to calculate 95% UCL of arithmetic mean are provided in Sections III.B.6 and III.B.7 of this TGM.

The following decision rule is used to determine if a site meets the cleanup standard:

- If 95% UCL of arithmetic mean is greater than or equal to  $C_s$ , conclude that the sample results do not meet the cleanup standard.
- If 95% UCL of arithmetic mean is less than  $C_s$ , conclude that the sample results meet the cleanup standard.

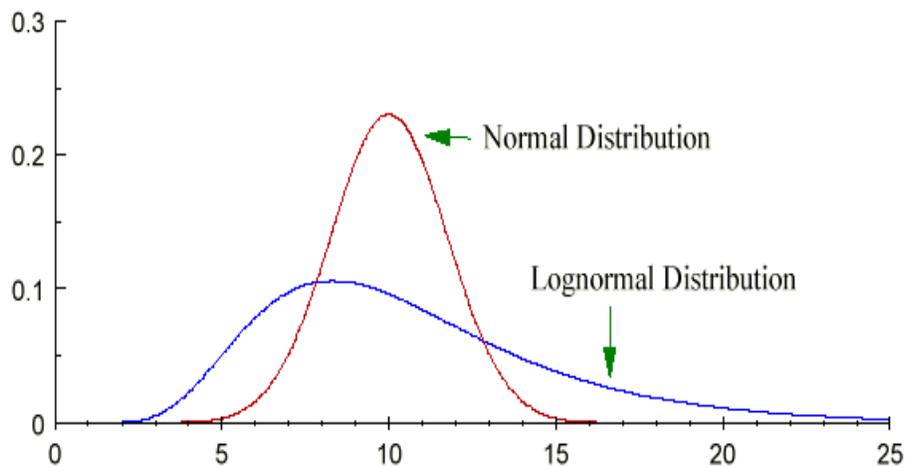
Note that this rule uses the 95% UCL of the arithmetic mean to estimate the limit of the population mean. The decision rule is consistent with the hypothesis statements.

The primary assumptions of this method are independence of the data, and sample mean is approximately normally distributed or data are lognormally distributed. Examples of normal and

lognormal distributions are shown in Figure III-8. When the population is normally distributed, the sample mean is normally distributed, no matter the sample size. However, if the population distribution is unknown, Central Limit Theorem states that the distribution of sample means of random samples with fixed sample size (n) from a population with an unknown distribution will be approximately normally distributed provided the sample size (n) is large. This means that moderate violation of the assumption of normality for the population is acceptable when sample size is large.

For sample sizes up to 50, EPA recommends using Shapiro Wilk test for testing normality (EPA, 2009). Other tests for normality, such as Shapiro-Francia test and other goodness-of-fit tests are discussed in EPA's Unified Guidance (EPA, 2009). To test the independence of data, ordinary-runs test (Gibbons, 1990) can be used.

**Figure III-8: Examples of Normal Distribution and Lognormal Distribution**



An important consideration regarding the 95% UCL of arithmetic mean is the use of composite sampling approach. Unless composite sampling is considered inappropriate (such as for volatile organic compounds (VOCs)), data from composite sampling can be more cost-efficient to estimate population mean and population variance than discrete sampling (Edland et al., 1994; Patil et al., 1994). Composite sampling can reduce the laboratory analysis cost. Composite sampling may be considered, if appropriate, to obtain the 95% UCL of arithmetic mean. Equations to calculate the 95% UCL of arithmetic mean for composite sampling are available (Edland et al., 1994; Patil et al., 1994).

**(c) No Exceedance Rule**

For cleanup of releases of petroleum products where full site characterization has not been conducted and remediation is guided by visual observation and/or field screening, the no exceedance rule must be used as described in Section 250.707(b)(1)(iii) of the regulations as follows:

For sites where there is localized contamination as defined in the document “Closure Requirements for Underground Storage Tank Systems” (DEP technical document No. 263-4500-601), samples shall be taken in accordance with that document.

For sites with contamination that does not qualify as localized under that document, samples shall be taken from the bottom and sidewalls of the excavation in a biased fashion that concentrates on areas where any remaining contamination above the SHS would most likely be found. The samples shall be taken from these suspect areas based on visual observation and the use of field instruments. If a sufficient number of samples has been collected from all suspect locations and the minimum number of samples has not been collected, or if there are no suspect areas, then the locations to meet the minimum number of samples shall be based on a random procedure. The number of sample points required shall be determined in the following way:

- For 250 cubic yards or less of excavated contaminated soil, five samples shall be collected.
- For each additional 100 cubic yards of excavated contaminated soil, one sample shall be collected.
- For excavation involving more than 1,000 cubic yards of contaminated soil, the Department will approve the confirmatory sampling plan.
- Where water is encountered in the excavation and no obvious contamination is observed or indicated, a minimum of two of the soil samples identified above shall be collected just above the soil/water interface. These samples shall meet the MSC determined by using the saturated soil component of the soil-to-groundwater numeric value.
- Where water is encountered in the excavation and no obvious contamination is observed or indicated, a minimum of two water samples shall also be collected from the water surface in the excavation.

All sample results shall meet the SHS.

For sites where there is a release to surface soils resulting in excavation of 50 cubic yards or less of contaminated soil, samples shall be collected as described above, except that two samples shall be collected.

**ii) Groundwater Risk-Based Standards**

Statistical tests appropriate to demonstrating compliance with groundwater standards are presented in Section 250.707(b)(2) of the regulations. Groundwater cleanup activities generally include site investigation, groundwater remediation, a post-treatment period allowing the groundwater to stabilize, sampling and analysis to assess attainment, and possible post-cleanup monitoring. Different statistical procedures are applicable at different stages in this cleanup process. The statistical procedures used must account for the changes in the groundwater system over time due to natural or man-induced causes. The specific statistical procedures used depend on the goals and quality of the monitoring data. The methods selected should be consistent with the goals of the monitoring. For example, a remediator may want to use regression analysis to decide when to stop treatment of groundwater. Regression analysis can be used to detect trends in contaminant concentration levels over time, to determine variables that influence concentration levels, and to predict chemical concentrations at future points in time. After terminating groundwater treatment, a remediator may want to use time trend analysis or plotted data to find if the groundwater has stabilized. After the groundwater has reached a steady state, the remediator may compare monitoring well concentrations to background reference well concentrations to determine whether the post-cleanup contamination concentrations are acceptable compared to the cleanup standards and may perform trend analysis or use plotted data to determine whether the post-cleanup contamination concentrations are likely to remain acceptable.

Once the groundwater has stabilized, it is recommended to use the 95% UCL of the mean (EPA, 2002a) or the following CSSAB ad hoc rule to compare with groundwater risk-based standards: In monitoring wells beyond the property boundary, the attainment criteria would be 75% of the sampling results from any given well below the standard with no individual value being more than 2 times the standard (75%/2X rule). This rule would have to be met in each individual monitoring well.

To use the CSSAB ad hoc rule, eight samples from each compliance well must be obtained during eight consecutive quarters. A shorter sampling period (25 Pa. Code § 250.704(d)) requires the use of the no exceedance rule (25 Pa. Code § 250.704(d)(3)) with written approval of the Department.

### iii) Soil Background Standards

The determination of attainment of soil background standards is based on a comparison of the distributions of the background concentrations of a regulated substance with the concentrations in an impacted area. The regulations allow a remediator to use highest measurement comparison, combination of Wilcoxon Rank Sum (WRS) test and Quantile test, or other appropriate methods to demonstrate attainment of background standards (25 Pa. Code §250.707(a)(1)). No matter which method is used, the regulations require that the minimum number of samples to be collected is ten from the background reference area and ten from each cleanup unit. This requirement of ten samples is to ensure that any selected statistical test has sufficient power to detect contamination. The regulations do not specify the false negative rate because it is more appropriate to determine the false negative rate on a site-specific basis. For the background standard, the false negative rate is the probability of mistakenly concluding that the site is clean when it is contaminated. It is the probability of making a Type II error.

Background soil sampling locations must be representative of background conditions for the site, including soil type and depth below ground surface. Randomization of sampling at background reference and onsite locations must be comparable. EPA (EPA, 1992c) recommends that samples be collected from background reference areas and cleanup units based on a random-start equilateral triangular grid. When a triangular grid may miss the pattern of contamination, EPA recommends the use of an unaligned grid (Gilbert, 1987, p. 94) to determine the sampling locations.

#### (a) Wilcoxon Rank Sum Test

This procedure (also known as Mann-Whitney U test) is a nonparametric test for differences between two independent groups. See EPA, 2009, ITRC (2013) and Section 250.707(a)(1)(ii) of the regulations.

For the WRS test, the EPA states that Noether's formula may be used for computing the approximate total number of samples to collect from the background reference area and in the cleanup unit (EPA 1992c).

$$N = \frac{(Z_{1-\alpha} + Z_{1-\beta})^2}{12c(1-c)(Pr-0.5)^2(1-R)}$$

(Noether's formula) = total number of required samples.

where

$\alpha$  = specified Type I error rate

$\beta$  = specified Type II error rate

$Z_{1-\alpha}$  = the value that cuts off (100 $\alpha$ )% of the upper tail of the standard normal distribution

$Z_{1-\beta}$  = the value that cuts off (100 $\beta$ )% of the upper tail of the standard normal distribution

$c$  = specified proportion of the total number of required samples,  $N$ , that will be collected in the reference area

$m$  = number of samples required in the reference area  
 $= c \times N$

$Pr$  = specified probability greater than 1/2 and less than 1.0 that a measurement of a sample collected at a random location in the cleanup unit is greater than a measurement of a sample collected at a random location in the reference area. This value is specified by the user. See Section 6.2.2 of EPA, 1992c for methods to determine  $Pr$ .

$R$  = expected rate of missing or unusable data

$n$  = number of samples required in the cleanup unit =  
 $N - m$

The underlying assumptions for the WRS test are random sampling, independence assumption of selecting sampling points, and that the distributions of the two populations are identical in shape and dispersion. The distributions need not to be symmetric. When applied with the Quantile test, the combined tests are most powerful for detecting true differences between two population distributions. When using the combined test, caution should be exercised to ensure that the underlying assumption of equal variance is met. An appropriate test for dispersion, such as Levene's test can be used. Unequal dispersion of data due to higher concentration of contaminant at the site should be properly addressed.

Procedures and an example of using the WRS test are in Section III.B.8.

#### **(b) Quantile Test**

The Quantile test (Johnson et al. 1987), described in Sections 250.707(a)(1) and 250.707(a)(1)(ii) of the regulations, is performed by first listing the combined reference-area and

cleanup-unit measurements from smallest to largest, as was done for the WRS test. Then, among the largest  $r$  measurements (i.e.,  $r$  is the number of measurements) of the combined data sets, a count is made of the number of measurements,  $k$ , that are from the cleanup unit. If  $k$  is sufficiently large, then we conclude that the cleanup unit has not attained the reference-area cleanup standard. The Quantile test is more powerful than the WRS test for detecting when only one or a few small portions of the cleanup unit have concentrations larger than those in the reference area. Also, the Quantile test can be used when a large proportion of the data is below the limit of detection. See Chapter 7 of the EPA attainment guidance (EPA, 1992c). See ProUCL Version 4.0 (2007) for further details.

For Quantile test, EPA recommends using look-up tables to determine the number of measurements that are needed from the background reference area and the cleanup unit (Section 7.2 of EPA, 1992c).

Procedures and an example of using the Quantile test are in Section III.B.9 of this TGM. The null hypothesis ( $H_0$ ) and alternative hypothesis ( $H_a$ ) statements for the Quantile test are:

$$H_0: \varepsilon = 0, \Delta/\sigma = 0$$

$$H_a: \varepsilon > 0, \Delta/\sigma > 0$$

where

$\varepsilon$  = the proportion of the soil in the cleanup unit that has not been remediated to background reference levels

$\Delta/\sigma$  = amount (in units of standard deviation,  $\sigma$ ) that the distribution of  $100\varepsilon\%$  of the measurements in the remediated cleanup unit is shifted to the right (to higher measurements) of the distribution in the background reference area

The underlying assumptions for Quantile test are random sampling, independence assumption of selecting sampling points, and that the distributions of the two populations have the same dispersion (variance).

#### iv) **Groundwater Background Standards**

Background conditions include two general categories. The first is naturally occurring background or area-wide contamination. The second is background associated with a release of regulated substances at a location upgradient from the site that may be subject to such patterns and trends.

For naturally occurring background or area wide contamination, it is recommended that a minimum of 12 samples be collected from any combination of upgradient monitoring wells, provided that all data collected are used in determination of background concentrations. This same number of samples must then be collected from monitoring wells impacted by a release on the site during the same sampling event. In both cases, this sampling may be accelerated such that all samples are collected as quickly as possible, so long as the frequency does not result in serial correlation in the data. The resulting values may be compared using nonparametric or parametric methods to compare the two populations, such as using the combination of WRS test and Quantile test described previously. When comparing with the background results, the sampling results in the onsite plume may not exceed the sum of the arithmetic average and three times standard deviation calculated for the background reference area (25 Pa. Code §250.707(a)(1) § 250.707(a)(3)(vii)).

For background associated with a release of regulated substances at a location upgradient from a property, the background groundwater concentrations will be determined at the hydrogeological upgradient property line of the property, or a point hydrogeologically upgradient from the upgradient property line that is unaffected by the release (25 Pa. Code §250.204(f)(8)).

Attainment of the background standard must be demonstrated wherever the contamination occurs. Some mass of a particular contaminant may be added to groundwater on the property. However, that additional mass cannot result in concentrations which exceed the concentration measured at the property line, nor can it be used to allow releases on the property. In some cases, contaminants may degrade in groundwater (e.g. chlorinated solvents). In situations such as these where biodegradation is occurring, the total contaminant mass must not increase at the POC for the site. Background concentrations are not related to a release at the site (Section 103 of Act 2).

In the event contamination migrates off the property, concentrations at the downgradient property boundary must be equal to or less than the background concentrations measured where groundwater enters the property. If a release on-property has occurred, the plume migrating beyond the property boundary must also meet the background standard (25 Pa. Code § 250.203(a)).

For background associated with an upgradient release of regulated substances, allows the use of the nonparametric tolerance limit procedure (25 Pa. Code § 250.707(a)(2). The nonparametric tolerance limit procedure requires at least 8 samples from each well over 8 quarters to have sufficient power to detect contamination. When the nonparametric upper tolerance limit is established for upgradient data, data from downgradient compliance wells can be compared to the limit. A

resampling strategy must be used when an analyte exceeds the nonparametric upper tolerance limit. The well is retested for the analyte of concern, and the value is compared to the nonparametric upper prediction limit. These two-phase testing strategies can be very effective tools for controlling the facility-wide false positive rate while maintaining a high power of detecting contamination.

## 5. Additional Information on Statistical Procedures

This section provides an overview regarding various other statistical methods available to use to determine if a cleanup activity is successful. The EPA Addendum (EPA, 1992a), EPA Groundwater Attainment (EPA, 1992b), EPA Soil Reference-Based Standards Attainment (EPA, 1992c), EPA QA/G-9 (EPA, 1996), and EPA Unified Guidance (2009) describe and provide examples for both the parametric and nonparametric methods. See additional discussions in Helsel and Hirsch (1992), Conover (1980), Gilbert (1987), and Davis and McNichols (1994, Parts I and II), and ITRC's Groundwater Statistics and Monitoring Compliance (2013). It is important to note that EPA's ProUCL, free statistical software for environmental applications, can run all of the tests summarized in the following sections.

### a) Interval Tests

**Statistical Intervals** - Statistical interval tests can be used independently for comparing with a numerical value or in combination with other tests for comparing populations. Statistical intervals include three main types: tolerance intervals, prediction intervals, and confidence intervals. Which ones are used depend on the goals of the data analysis.

**Tolerance Intervals** - Tolerance intervals will typically be the most useful interval test. They are used to determine the extent of data that is within a standard (like an MCL) or ambient level. Parametric tolerance intervals can be computed by assuming a lognormal distribution.

**Prediction Intervals** - Prediction intervals are used to determine if the next one or more samples are within the existing data distribution at a certain confidence level. The prediction interval contains  $100 * (1 - \alpha)$  percent of the distribution. A smaller  $\alpha$  value will include a larger range of data. Prediction intervals are used for intrawell (single well) comparisons, and with comparison of a compliance well with a background well.

**Confidence Intervals** - Confidence intervals contain a specified parameter of the distribution (such as the mean of the data) at a specified confidence level. Confidence intervals do not address extreme values. The step-by-step procedures to calculate the upper confidence of mean are provided in Sections III.B.6 and III.B.7.

## b) **Tests for Comparing Populations**

The following tests are some of the EPA's recommended tests for analysis of groundwater data between upgradient and downgradient well groups, downgradient wells and a health-based standard, or of intrawell (single well) comparisons. This does not include all potentially satisfactory statistical tests.

**Analysis of Variance (ANOVA)** - ANOVA includes a group of procedures used for comparing the means of multiple (3 or more) independent groups such as upgradient wells and downgradient wells. The ANOVA methods are used to determine if there is statistically significant evidence of contamination at downgradient wells compared to an upgradient well, or groups of wells.

The one-way ANOVA method is described with examples in Section 17 of the EPA Unified Guidance (EPA, 2009). This is the EPA recommended procedure for comparing data that do not violate the assumptions of normal distribution and approximately equal variances.

However, as the number of wells (or groups) increases at a site, the power of ANOVA to detect individual instances of contamination decreases. For this reason, tolerance and prediction intervals with retesting provisions are often much better procedures to use.

**Kruskal-Wallis Test** - If assumptions of the one-way ANOVA test are "grossly" violated, the nonparametric Kruskal-Wallis test is used for more than 2 independent groups of data. It can be used for comparison of upgradient water quality to water quality from many downgradient wells in one procedure. Alternatively, if the wells are grouped by some characteristic (e.g., depth, geology, location, season), comparisons among other groups can be made.

If the null hypothesis (no change) is rejected by Kruskal-Wallis (i.e., the test statistic exceeds the tabulated critical value), then pairwise comparisons should be made to determine what wells are contaminated (see Gilbert (1987), Section 18.2.2; the EPA Addendum (1992a), Section 3.1; and the EPA Unified Guidance (2009), Section 17.1.2). The underlying assumptions are the distributions of the independent populations are identical in shape (variance), but the distributions need not to be symmetric.

**t-test** - The t-test is a parametric, ANOVA type of test used to assess differences in means of two independent groups. This test assumes normal distributions and equal variances for both groups. The t-test is best limited to situations where the data sets are too small to use nonparametric procedures. For example, if background water quality is limited to two or three samples, the t-test can be used to test for differences between background and compliance data.

## c) **Trend Tests**

**Considerations** - When monitoring data have been collected over several years or more, trend tests allow the determination of the change in distribution of data over

time. In addition to water quality trends, a time series of monitoring data may contain characteristics of seasonality and serial correlation. Other complicating factors include changes in laboratories or procedures involving the sampling and analysis of the analyte.

Seasonality and serial correlation interfere with trend tests either by reducing the power to detect trends or giving erroneous probabilities. Correction for seasonality is available for tests presented here. Serial correlation exists if a data point value is at least partially dependent on nearby data point values. For a given data set, serial correlation decreases with increasing temporal distance between samples. Harris, *et al.* (1987) reported difficulty detecting serial correlation in 10 years or less of quarterly groundwater data. Therefore, correction is not recommended for quarterly data. Serial correlation correction is available for the Seasonal Kendall trend test (Hirsch and Slack, 1984), but has reduced power with small data sets and is not recommended for a monthly time series that is less than 5 years.

**Parametric Trend Tests** - Parametric trend tests are based on regression methods and allow compensation for exogenous effects (outside influences). Regression analysis between two variables can be used to calculate the correlation coefficient ( $r$ ). The closer  $r$  is to one, the closer the relationship is between the two variables. A t-test of correlation can be done on  $r$  to see if it is significant (see Davis, 1987, Chapter 2; EPA, 1996, Section 4.3.2; EPA, 2009).

Mixed (i.e., parametric and nonparametric methods) methods also are available when removing the effects of exogenous variables. Helsel and Hirsch (1992) present a thorough review of trend analysis. Methods for detecting trends also are presented in Chapter 16 of Gilbert (1987).

Because regression techniques are based on the assumption of a normal distribution of the data, a nonparametric approach may have to be used.

**Nonparametric Trend Tests** - The Mann-Kendall trend test is a nonparametric test for monotonic (steadily upward or downward) trend. (Gilbert, 1987; Section 4.3.4 of EPA, 1996; Section 17.3.2 of EPA, 2009).

This test requires constant variance in data. Non-constant variance may be changed to constant variance with a power transformation. Logarithm transformation is usually most appropriate. This transformation does not affect the test statistic. Decision rules, exact test tables, normal approximation formulas, and correction for ties can be found in Helsel and Hirsch (1992); Gilbert (1987) and many introductory statistics texts. When a trend is present, the slope of fitted line can be estimated using Sen's estimator (see Gilbert, 1987; Section 4.3.3 of EPA, 1996; Section 17.3.3 of EPA, 2009).

The Seasonal Kendall trend test is a seasonally corrected Mann-Kendall trend test. This should be applied when time series graphs or boxplots of data indicate the presence of seasonal variation. See Chapter 17 of Gilbert (1987).

The following sections present the methodology of several statistical tests which may be utilized in the course of demonstrating attainment of an Act 2 standard. Again, it is worthwhile to note that statistical computer software, such as EPA's ProUCL, has been developed to perform these tests.

## 6. Calculation of UCL of Mean When the Distribution of the Sampling Mean is Normal

The following is a step-by-step description of the approach used to calculate confidence limits of an arithmetic mean when the distribution of the sampling mean is normal. For data sets of lognormal distribution, the approach in Section III.B.7 should be used instead.

1. Calculate the sample mean by dividing the sum of the total readings by the total number of readings:

$$\bar{X} = (X_1 + X_2 + X_n)/n$$

2. Calculate the sample variance ( $S_b^2$ ) by taking the sum of the squares of each reading minus the mean and dividing by the degrees of freedom (df, the total number of samples minus one):

$$S_b^2 = [(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + \dots + (X_n - \bar{X})^2]/(n-1)$$

3. Calculate the standard deviation ( $S_b$ ) by taking the square root of the variance ( $S_b^2$ ):

$$S_b = \sqrt{(S_b^2)}$$

4. Calculate the standard error of the mean ( $S_x$ ). Standard error is inversely proportional to the square root of the number of samples (increasing n from 4 to 16 reduces  $S_x$  by 50%) where  $S_x$  equals  $S_b/\sqrt{n}$ . [Note: The above procedure is for simple random samples. For systematic sampling, the calculation of standard error should follow instructions in Section 6.5 of EPA soil attainment guidance (EPA, 1989b). For multiple systematic sampling, the equation to calculate unbiased estimate of variance is also available (Gilbert, 1987, p. 97).]
5. Since the concern is only whether the upper limit of a confidence interval is below or above the Act 2 regulatory threshold (RT), the lower confidence limit (LCL) need not be considered. The upper confidence limit (UCL) can be calculated using the one-tailed (one-sided) t values with n-1 degrees of freedom (df) derived from a table of the student's t distribution,  $t_{1-\alpha, n-1}$  (Table III-3).
6. The 95% UCL ( $\alpha=0.05$ ; one-sided) is calculated by using the following formula and substituting the values determined above plus the appropriate t value obtained from the student's t table where UCL equals  $\bar{X} + t_{1-\alpha, n-1} * S_x$ .

The UCL number resulting from this formula will indicate with a 95% probability that it is either above or below the Act 2 regulatory threshold (RT) developed for the regulated substance subjected to the test.

## 7. Calculation of UCL of Mean of a Lognormal Distribution

Following is a step-by-step description of the approach used to calculate confidence limits of an arithmetic mean when the distribution of the data set is lognormal. This method is used in risk assessment by EPA (EPA, 1992d).

1. Transform all sample data  $X_i$  to  $Y_i$  ( $i = 1, 2, \dots, n$ ) using the natural logarithm function:

$$Y_i = \ln X_i$$

2. Calculate the arithmetic mean of transformed data by dividing the sum of the transformed data by the total number of data:

$$\bar{Y} = (Y_1 + Y_2 + \dots + Y_n)/n$$

3. Calculate the variance ( $Sy^2$ ) of transformed data by taking the sum of the squares of each data minus the mean and dividing by the degrees of freedom (df, the total number of samples minus one):

$$Sy^2 = [(Y_1 - \bar{Y})^2 + (Y_2 - \bar{Y})^2 + \dots + (Y_n - \bar{Y})^2]/(n-1)$$

4. Calculate the standard deviation ( $Sy$ ) by taking the square root of the variance ( $Sy^2$ ):

$$Sy = \sqrt{(Sy^2)}$$

5. Since the concern is only whether the upper limit of a confidence interval is below or above the Act 2 regulatory threshold (RT), the lower confidence limit (LCL) need not be considered. The UCL can be calculated using the one-tailed (one-sided)  $H_{1-\alpha}$  values associated with sample size  $n$  from the table of  $H_{1-\alpha}$  for computing a one-sided upper 95% confidence limit on a lognormal mean.

6. The 95% UCL ( $\alpha=0.05$ ; one-sided) is calculated by using the following formula and substituting the values determined above plus the appropriate  $H_{1-\alpha}$  value obtained from the table of  $H_{1-\alpha}$  where UCL equals

$$\exp\left(\bar{Y} + 0.5 * Sy^2 + Sy * H_{1-\alpha} / \sqrt{n-1}\right)$$

The UCL number resulting from this formula will indicate with a 95% probability that it is either above or below the Act 2 regulatory threshold (RT) developed for the regulated substance subjected to the test.

Note: The  $H_{1-a}$  tables can be found in “Selected Tables in Mathematical Statistics, Volume III, American Mathematical Society,” pp. 385-419, C. E. Land, 1975. A subset of Land’s tables also can be found in “Statistical Methods for Environmental Pollution Monitoring,” Tables A10-A13, R. O. Gilbert, 1987. The value of  $H_{1-a}$  depends on  $S_y$ ,  $n$ , and the confidence level  $\alpha$ . If  $H_{1-a}$  is required for values of  $S_y$  and  $n$  not given in the tables, Land (1975) indicated that four-point Lagrangian interpolation appeared to be adequate with these tables.

The equation used in four-point Lagrangian interpolation is:

$$y = f(x) = \frac{y_1(x-x_2)(x-x_3)(x-x_4)}{(x_1-x_2)(x_1-x_3)(x_1-x_4)} + \frac{(x-x_1)y_2(x-x_3)(x-x_4)}{(x_2-x_1)(x_2-x_3)(x_2-x_4)} + \frac{(x-x_1)(x-x_2)y_3(x-x_4)}{(x_3-x_1)(x_3-x_2)(x_3-x_4)} + \frac{(x-x_1)(x-x_2)(x-x_3)y_4}{(x_4-x_1)(x_4-x_2)(x_4-x_3)}$$

where  $y_1 = f(x_1)$

$y_2 = f(x_2)$

$y_3 = f(x_3)$

$y_4 = f(x_4)$

The interpolation procedure may include four interpolation steps which are performed along the columns of the table and one interpolation step performed along the rows of the table. The following example illustrates the procedure to apply the four-point Lagrangian interpolation:

$H_{1-A}$ Table	Sample Size, $n$			
	3	5	7	10
0.1	2.750	2.035	1.886	1.802
0.2	3.295	2.198	1.992	1.881
$S_y$ 0.3	4.109	2.402	2.125	1.977
0.4	5.220	2.651	2.282	2.089

The above table only provides values for sample sizes of 3, 5, 7, and 10, and  $S_y$  values of 0.1, 0.2, 0.3 and 0.4. To interpolate a value for a sample size of 6 and an  $S_y$  value of 0.25, the first step is to interpolate a value corresponding to an  $S_y$  of 0.25 and a sample size of 3 using the four-point Lagrangian interpolation equation, where

$x = 0.25$

$$x_1 = 0.10 \quad y_1 = 2.750$$

$$x_2 = 0.20 \quad y_2 = 3.295$$

$$x_3 = 0.30 \quad y_3 = 4.109$$

$$x_4 = 0.40 \quad y_4 = 5.220$$

The result of this interpolation step is  $y = f(0.25) = 3.667$ .

The second step is to interpolate a value corresponding to  $S_y$  of 0.25 and a sample size of 5 using the four-point Lagrangian interpolation equation, where

$$x = 0.25$$

$$x_1 = 0.10 \quad y_1 = 2.035$$

$$x_2 = 0.20 \quad y_2 = 2.198$$

$$x_3 = 0.30 \quad y_3 = 2.402$$

$$x_4 = 0.40 \quad y_4 = 2.651$$

The result of this interpolation step is  $y = f(0.25) = 2.295$ .

The third step is to interpolate a value corresponding to an  $S_y$  of 0.25 and a sample size of 7 using the four-point Lagrangian interpolation equation, where

$$x = 0.25$$

$$x_1 = 0.10 \quad y_1 = 1.886$$

$$x_2 = 0.20 \quad y_2 = 1.992$$

$$x_3 = 0.30 \quad y_3 = 2.125$$

$$x_4 = 0.40 \quad y_4 = 2.282$$

The result of this interpolation step is  $y = f(0.25) = 2.055$ .

The fourth step is to interpolate a value corresponding to an  $S_y$  of 0.25 and a sample size of 10 using the four-point Lagrangian interpolation equation, where

$$x = 0.25$$

$$x_1 = 0.10 \quad y_1 = 1.802$$

$$x_2 = 0.20 \quad y_2 = 1.881$$

$$x_3 = 0.30 \quad y_3 = 1.977$$

$$x_4 = 0.40 \quad y_4 = 2.089$$

The result of this interpolation step is  $y = f(0.25) = 1.927$ .

The last step is using the results obtained from steps 1 - 4 to perform another four-point Lagrangian interpolation to generate a value corresponding to an  $S_y$  of 0.25 and a sample size of 6, where

$$x = 6$$

$$x_1 = 3 \quad y_1 = 3.667$$

$$x_2 = 5 \quad y_2 = 2.295$$

$$x_3 = 7 \quad y_3 = 2.055$$

$$x_4 = 10 \quad y_4 = 1.927$$

The resulted interpolation value is 2.087.

## 8. Procedure and Example for Conducting the Wilcoxon Rank Sum Test

### Procedure

For each cleanup unit and pollution parameter, use the following procedure to compute the WRS test statistic and to determine on the basis of that statistic if the cleanup unit being compared with the background reference area has attained the background standard.

1. Collect the  $m$  samples in the reference area and the  $n$  samples in the cleanup unit ( $m + n = N$ ).
2. Measure each of the  $N$  samples for the pollution parameter of interest.

3. Consider all N data as one data set. Rank the N data from 1 to N; that is, assign the rank 1 to the smallest datum, the rank 2 to the next smallest datum, and the rank N to the largest datum.
4. If several data are tied, i.e., have the same value, assign them the midrank, that is, the average of the ranks that would otherwise be assigned to those data.
5. If some of the reference-area and/or cleanup-unit data are less-than data (i.e., data less than the limit of detection) consider these less-than data to be tied at a value less than the smallest measured (detected) value in the combined data set. Assign the midrank for the group of less-than data to each less-than datum. For example, if there were 10 less-than data among the background reference and cleanup-unit measurements, they would each receive the rank 5.5, which is the average of the ranks from 1 to 10. The assumption that all less-than measurements are less than the smallest detected measurement should not be made lightly because it may not be true for some pollution parameters, as pointed out by Lambert et al. (1991). However, the development of statistical testing procedures to handle this situation are beyond the scope of this document.
  - i. The above procedure is applicable when all measurements have the same limit of detection. When there are multiple limits of detection, the adjustments given in Millard and Deveral (1988) may be used.
  - ii. Do not compute the WRS test if more than 40% of either the reference-area or cleanup unit measurements are less-than values. However, still conduct the Quantile test.
6. Sum the ranks of the n samples from the cleanup unit. Denote this sum by WRS.
7. If both m and n are less than or equal to 10 and no ties are present, conduct the test of  $H_0$  (cleanup standard attained,  $Pr = 1/2$ ) versus  $H_a$  (cleanup standard not attained,  $Pr > 1/2$ ) by comparing WRS to the appropriate critical value in Table A.5 in Hollander and Wolfe (1973). Then go to Step 12 below.
8. If both m and n are greater than 10, go to Step 9. If m is less than 10 and n is greater than 10, or if n is less than 10 and m is greater than 10, or if both m and n are less than or equal to 10 and ties are present, then consult a statistician to generate the required tables.
9. If both m and n are greater than 10 and ties are not present, compute Equation A3-1 and go to Step 11.

$$Z_{rs} = \frac{WRS - n(N+1)/2}{\sqrt{mn(N+1)/12}} \quad (A3-1)$$

10. If both m and n are greater than 10 and ties are present, compute

$$Z_{rs} = \frac{WRS - n(N+1)/2}{\sqrt{(nm/12) \left[ N+1 - \sum_{j=1}^g t_j(t_j^2 - 1) \right] / (N(N-1))}} \quad (A3-2)$$

- i. where g is the number of tied groups and  $t_j$  is the number of tied measurements in the jth group.
11. Reject  $H_0$  (cleanup standard attained) and accept  $H_a$  (cleanup standard not attained) if  $Z_{rs}$  (from Equation A3-1 or A3-2, whichever was used) is greater than or equal to  $Z_{1-\alpha}$ , where  $Z_{1-\alpha}$  is the value that cuts off 100 $\alpha$ % of the upper tail of the standard normal distribution.
12. If  $H_0$  is not rejected, conduct the Quantile test.

#### EXAMPLE

#### TESTING PROCEDURE FOR THE WILCOXON RANK SUM TEST

1. Suppose that the number of samples was determined using the following specification:

$\beta$  = specified Type II error rate = 0.30

$\alpha$  = specified Type I error rate = 0.05

c = specified proportion of the total number of required samples, N, that will be collected in the reference area = 0.50

Pr = specified probability greater than 1/2 and less than 1.0 that a measurement of a sample collected at a random location in the cleanup unit is greater than a measurement of a sample collected at a random location in the reference area = 0.75

R = expected rate of missing or unusable data = 0.10

For these specifications we found that  $m = n = 14$  based on Noether's formula.

2. Rank the reference-area and cleanup-unit measurements from 1 to 28, arranging the data and their ranks as illustrated. Measurements below the limit of detection are denoted by ND and assumed to be less than the smallest value reported for the combined data sets. The data are lead measurements (mg/kg).
3. The sum of the ranks of the cleanup unit is

$$WRS = 3 + 7 + \dots + 27 + 28 = 272.$$

4. Compute  $Z_{rs}$  using Equation A3-2 because ties are present. There are  $t = 5$  tied values for the  $g = 1$  group of ties (ND values). We obtained:

$$Z_{rs} = \frac{272 - 14(28 + 1) / 2}{\sqrt{(14 * 14 / 12) [28 + 1 - 5(5 * 5 - 1) / (28(28 - 1))]}}$$
$$= \frac{69}{21.704} = 3.18$$

5. From the table of  $z$  (Table III-4) we find that  $Z_{1-\alpha} = 1.645$  for  $\alpha = 0.05$  ( $\alpha = 0.05$ , the Type I error rate for the test, was specified in Step 1 above). Since  $3.18 > 1.645$ , we reject the null hypothesis  $H_0: Pr = 1/2$  and accept the alternative hypothesis  $H_a: Pr > 1/2$ .

6. Conclusion:

The cleanup unit does not attain the cleanup standard of  $Pr = 1/2$ . This test result occurred because most of the small ranks were for the reference area and most of the large ranks were for the cleanup unit. Hence, WRS was large enough for  $H_0$  to be rejected.

Example - Wilcoxon Rank Sum Test

Reference Area		Cleanup Unit	
Data	Rank	Data	Rank
ND	3		
ND	3	ND	3
ND	3		
ND	3		
39	6		
		48	7
49	8		
		51	9
53	10		
59	11		
61	12		
65	13		
67	14		
70	15		
72	16		
75	17		
		80	18
		82	19
		89	20
		100	21
		150	22
		164	23
		193	24
		208	25
		257	26
		265	27
		705	28
		WRS = 272	

**9. Procedure and Example for Conducting the Quantile Test**

Table Look-Up Procedure

A simple table look-up procedure for conducting the Quantile test when  $m$  and  $n$  are specified *a priori* is given in this section. It is assumed that  $m$  and  $n$  representative measurements have been obtained from the reference area and the cleanup unit, respectively. The procedure in this section is approximate because the Type I error rate,  $\alpha$ , of the test may not be exactly what is required. However, the difference between the actual and required levels will usually be small. Moreover, the exact  $\alpha$  level may be computed.

The testing procedure is as follows:

1. Specify the required Type I error rate,  $\alpha$ . The available options in this document are  $\alpha$  equal to 0.01, 0.025, 0.05 and 0.10.
2. Turn to Table A.6, A.7, A.8, or A.9 in Appendix A of EPA 1992 guidance document (EPA, 1992c) if  $\alpha$  is 0.01, 0.025, 0.05, or 0.10, respectively.
3. Enter the selected table with  $m$  and  $n$  (the number of reference-area and cleanup-unit measurements, respectively) to find
  - values of  $r$  and  $k$  needed for the Quantile test.
  - actual  $\alpha$  level for the test for these values of  $r$  and  $k$  (the actual  $\alpha$  may differ slightly from the required  $\alpha$  level in Step 1)
4. If the table has no values of  $r$  and  $k$  for the values of  $m$  and  $n$ , enter the table at the closest tabled values of  $m$  and  $n$ . In that case, the  $\alpha$  level in the table will apply to the tabled values of  $m$  and  $n$ , not the actual values of  $m$  and  $n$ . However, the  $\alpha$  level for the actual  $m$  and  $n$  can be computed using the following equations:

$$\alpha = \frac{\sum_{i=k}^r \binom{m+n-r}{n-i} \binom{r}{i}}{\binom{m+n}{n}} \quad (\text{A4-1})$$

$$\text{where } \binom{a}{b} \equiv \frac{a!}{b!(a-b)!}$$

and  $a! = a * (a - 1) * (a - 2) * \dots * 3 * 2 * 1$

5. Order from smallest to largest the combined  $m + n = N$  reference-area and cleanup-unit measurements for the pollution parameter. If measurements less than the limit of detection are present in either data set, assume that their values are less than the  $r$ th largest measured value in the combined data set of  $N$  measurements (counting down from the maximum measurement). If fewer than  $r$  measurements are greater than the limit of detection, then the Quantile test cannot be performed.
6. If the  $r$ th largest measurement (counting down from the maximum measurement) is among a group of tied (equal-in-value) measurements, then increase  $r$  to include that entire set of tied measurements. Also increase  $k$  by the same amount. For example, suppose from Step 3 we have  $r = 6$  and  $k = 6$ . Suppose the 5th through 8th largest measurements (counting down from the maximum measurement) have the same value. Then we would increase both  $r$  and  $k$  from 6 to 8.

7. Count the number,  $k$ , of measurements from the cleanup unit that are among the  $r$  largest measurements of the ordered  $N$  measurements, where  $r$  and  $k$  were determined in Step 3 (or Step 6 if the  $r$ th largest measurement is among a group of tied measurements).
8. If the observed  $k$  (from Step 7) is greater than or equal to the tabled value of  $k$ , then reject  $H_0$  and conclude that the cleanup unit has not attained the reference area cleanup standard ( $\varepsilon = 0$  and  $\Delta/\sigma = 0$ ).
9. If  $H_0$  is not rejected, then do the WRS test. If the WRS test indicates the  $H_0$  should be rejected, then additional remedial action may be necessary.

#### EXAMPLE

#### TABLE LOOK-UP TESTING PROCEDURE FOR THE QUANTILE TEST

1. We illustrate the Quantile test using the measurements listed in the example of Section III.B.8. There are 14 measurements in both the reference area and the cleanup unit. Suppose we specify  $\alpha = 0.05$  for this Quantile test.
2. Turn to Table A.8 in EPA 1992 guidance (EPA, 1992c; because the table is for  $\alpha = 0.05$ ). We see that there are no entries in that table for  $m = n = 14$ . Hence, we enter the table with  $n = m = 15$ , the values closest to 14. For  $n = m = 15$  we find  $r = 4$  and  $k = 4$ . Hence, the test consists of rejecting the  $H_0$  if all 4 of the 4 largest measurements among the 28 measurements are from the cleanup unit.
3. The  $N = 28$  largest measurements are ordered from smallest to largest in the Example of Section III.B.8.
4. From the Example of Section III.B.8, we see that all 4 of the  $r = 4$  largest measurements are from the cleanup unit. That is,  $k = 4$ .
5. Conclusion:  
  
Because  $k = 4$ , we reject the  $H_0$  and conclude that the cleanup unit has not attained the cleanup standard of  $\varepsilon = 0$  and  $\Delta/\sigma = 0$ . The Type I error level of this test is approximately 0.05.

Note: The exact Type I error level,  $\alpha$ , for this test is not given in Table A.8 in EPA 1992 guidance (EPA, 1992c) because the table does not provide  $r$ ,  $k$ , and  $\alpha$  for  $m = n = 14$ . However, the exact  $\alpha$  level can be computed using Equation (A4-1).

The remediator is reminded that the Quantile Test can be run using EPA's ProUCL free statistical software, version 4.0.

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USEPA 2009, Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities. Office of Resource Conservation and Recovery. EPA 530-R-09-007.

**Table III-2: Random Number Table**

67 35 39 82 14	21 81 21 96 81	65 41 49 04 80	38 34 13 03 15	96 42 55 62 54
43 25 59 81 92	29 54 98 87 58	77 38 02 09 27	06 83 23 00 90	63 39 04 52 72
93 16 47 22 58	33 01 43 61 70	10 55 75 64 68	40 17 24 98 10	53 93 00 31 43
76 77 01 14 64	62 38 18 48 04	77 42 32 38 34	34 34 91 42 14	98 51 98 29 05
69 46 32 94 85	32 27 87 78 37	73 39 25 48 92	91 57 68 52 55	11 08 99 13 55
79 92 47 00 30	13 95 52 30 16	41 45 60 80 42	90 05 38 89 84	04 33 13 21 72
84 35 41 19 11	63 65 09 06 44	43 71 87 58 78	95 27 91 41 54	10 42 38 55 83
18 57 74 64 75	42 79 88 46 32	90 31 29 09 90	07 59 89 22 74	50 05 90 43 37
14 18 29 77 76	54 35 67 41 92	09 28 91 97 68	05 60 09 22 47	04 96 99 06 24
49 02 18 20 81	94 15 81 23 52	28 84 83 75 19	13 55 96 13 70	49 79 66 85 27
49 44 95 16 39	39 13 83 99 97	38 48 63 01 40	03 95 68 71 39	36 99 24 29 55
62 07 74 32 26	41 64 83 37 57	55 37 51 98 24	99 16 02 88 85	13 65 61 81 59
75 35 06 72 07	45 22 98 59 25	90 22 41 03 96	33 89 33 58 78	01 32 36 92 82
12 50 08 09 64	33 54 62 98 24	41 72 97 33 34	11 73 67 33 79	95 62 31 23 87
16 95 18 38 50	33 78 48 00 83	01 43 77 97 26	74 84 53 05 49	29 75 77 02 32
76 23 56 61 20	15 68 82 18 28	35 82 40 18 40	31 78 53 98 45	21 87 21 31 95
74 26 53 14 97	14 09 11 22 65	74 81 52 44 80	03 86 84 78 02	55 45 90 71 49
93 69 54 96 15	66 92 23 22 51	38 42 26 71 37	01 70 87 82 47	97 83 49 24 10
85 99 75 39 81	83 56 56 87 09	32 47 40 14 72	95 74 21 08 69	47 94 65 84 88
86 43 28 23 92	54 05 55 03 89	12 57 75 16 83	36 93 99 23 59	67 24 69 74 30
22 91 19 64 96	84 66 44 09 48	80 12 65 25 43	76 36 68 27 47	52 35 61 03 33
65 82 01 56 34	08 22 38 56 21	68 55 13 18 97	45 90 91 27 25	92 06 69 84 31
51 41 63 38 07	27 96 11 21 06	24 45 33 45 37	44 40 67 80 81	39 80 77 98 43
97 80 96 04 25	30 36 44 40 25	84 23 42 79 14	41 11 64 23 14	38 29 48 18 65
89 63 32 14 59	33 78 24 52 88	02 79 97 35 74	67 96 31 61 18	00 44 59 88 88
54 14 28 53 79	48 05 74 00 98	15 74 72 91 47	45 90 66 55 38	99 60 85 09 01
77 14 06 84 47	46 88 91 03 36	75 64 77 72 11	96 46 87 33 07	29 48 37 86 66
67 33 09 75 00	76 85 28 80 71	36 29 40 32 52	52 72 89 43 05	89 50 25 84 26
75 48 93 50 88	27 76 21 90 66	48 55 88 37 76	57 00 14 83 60	67 20 35 37 18
75 86 22 20 23	27 17 67 16 38	16 33 28 72 13	47 84 57 36 12	75 86 75 23 51
40 41 19 44 32	22 13 31 25 77	28 93 89 37 04	52 71 49 87 72	32 30 69 94 36
70 94 88 25 57	99 94 82 56 91	38 22 09 52 01	84 00 60 04 91	53 10 10 51 94
42 06 41 49 47	44 71 23 61 25	64 16 16 04 48	20 65 84 89 71	43 89 73 79 80
90 55 23 36 61	93 34 69 43 83	38 03 93 00 03	13 04 77 54 90	61 26 88 01 26
22 71 21 14 59	41 29 51 06 96	62 92 63 96 16	62 48 56 86 21	16 58 33 07 41
65 63 59 60 55	36 77 10 63 48	11 60 55 27 52	73 11 95 03 79	46 12 07 26 52
74 20 65 77 78	83 37 34 09 07	47 57 86 13 47	91 17 32 50 29	72 25 87 96 71
12 16 90 59 89	14 66 72 99 45	88 86 45 48 35	26 30 34 73 46	78 29 91 46 44
52 14 41 65 84	73 55 53 00 76	43 83 09 28 13	82 07 62 72 74	60 34 43 69 26
19 87 80 56 89	83 28 45 99 87	37 02 53 39 74	08 91 23 30 13	59 59 10 57 10
29 13 62 89 16	81 78 54 60 92	31 01 04 83 60	16 42 66 81 37	42 39 74 64 40
37 30 72 00 39	53 83 30 75 48	44 30 38 98 76	94 55 60 35 12	22 82 36 18 48
66 17 13 28 82	64 10 76 67 69	53 39 05 71 22	35 13 39 97 27	48 26 94 74 53
86 41 73 49 70	03 41 05 77 28	37 71 01 30 86	36 42 65 97 78	09 34 36 56 01
56 52 43 82 45	20 20 45 49 83	52 73 63 70 47	89 93 77 32 26	73 70 50 75 10
17 89 69 72 84	80 48 78 32 51	66 12 29 79 90	25 11 33 37 44	25 47 18 40 74
11 29 91 99 26	43 90 15 09 64	20 54 89 91 59	01 93 40 33 04	46 91 86 33 90
96 68 63 61 19	29 71 05 42 14	05 84 10 36 27	60 49 40 84 92	29 23 10 45 05
29 12 44 07 75	41 74 25 36 05	49 36 50 27 64	37 51 92 47 32	05 02 21 20 71
79 00 54 24 24	32 03 96 86 98	90 65 41 87 39	29 39 75 07 20	14 94 28 87 23

## EXAMPLE

### USING THE RANDOM NUMBER TABLE (TABLE III-2)

Assume we need to select 10 random numbers with four digits between 0000 and 6000. We need to select a starting point on the table and a path to be followed. The common way to locate a starting point is to look away and arbitrarily point to a starting point. Suppose the number we located this way was 3848. (It is located in the upper left corner of the block that is in the third large block from the left and the third large block down.) From here we will proceed down the column, then go to the top of the next set of columns, if necessary. The first selected number is 3848. Proceeding down the column, we find 5537 next. This is the second selected number. The number 9022 is next. This number is discarded. Continue down this column, the selected 10 random numbers will be 3848, 5537, 4172, 0143, 3582, 3842, 3247, 1257, 2445, and 0279. (The numbers 9022, 7481, 8012, 6855 and 8423 were discarded because they are greater than 6000.)

**Table III-3: Student's t-Distribution for Selected Alpha and Degrees of Freedom**

	$\alpha$ for determining t $1-\alpha, n-1$								
	one-tailed	0.450	0.250	0.200	0.100	0.050	0.025	0.010	0.005
	$\alpha$ for determining t $1-\alpha/2, n-1$								
two-tailed	0.900	0.500	0.400	0.200	0.100	0.050	0.020	0.010	0.005
df	1	0.158	1.000	1.376	3.078	6.314	12.706	31.821	63.657
	2	0.142	0.816	1.061	1.886	2.920	4.303	6.925	9.925
	3	0.137	0.765	0.978	1.638	2.353	3.182	4.541	5.841
	4	0.134	0.741	0.941	1.533	2.132	2.776	3.747	4.604
	5	0.132	0.727	0.920	1.476	2.015	2.571	3.365	4.032
	6	0.131	0.718	0.906	1.440	1.943	2.447	3.143	3.707
	7	0.130	0.711	0.896	1.415	1.895	2.365	2.998	3.499
	8	0.130	0.706	0.889	1.397	1.860	2.306	2.896	3.355
	9	0.129	0.703	0.883	1.383	1.833	2.262	2.821	3.250
	10	0.129	0.700	0.879	1.372	1.812	2.228	2.764	3.169
	11	0.129	0.697	0.876	1.363	1.796	2.201	2.718	3.106
	12	0.128	0.695	0.873	1.356	1.782	2.179	2.681	3.055
	13	0.128	0.694	0.870	1.350	1.771	2.160	2.650	3.012
	14	0.128	0.692	0.868	1.345	1.761	2.145	2.624	2.977
	15	0.128	0.691	0.866	1.341	1.753	2.131	2.602	2.947
	16	0.128	0.690	0.865	1.337	1.746	2.120	2.583	2.921
	17	0.128	0.689	0.863	1.333	1.740	2.110	2.567	2.898
	18	0.127	0.688	0.862	1.330	1.734	2.101	2.552	2.878
	19	0.127	0.688	0.861	1.328	1.729	2.093	2.539	2.861
	20	0.127	0.687	0.860	1.325	1.725	2.086	2.528	2.845
	21	0.127	0.686	0.859	1.323	1.721	2.080	2.518	2.831
	22	0.127	0.686	0.858	1.321	1.717	2.074	2.508	2.819
	23	0.127	0.685	0.858	1.319	1.714	2.069	2.500	2.807
	24	0.127	0.685	0.857	1.318	1.711	2.064	2.492	2.797
	25	0.127	0.684	0.856	1.316	1.708	2.060	2.485	2.787
	26	0.127	0.684	0.856	1.315	1.706	2.056	2.479	2.779
	27	0.127	0.684	0.855	1.314	1.703	2.052	2.473	2.771
	28	0.127	0.683	0.855	1.313	1.701	2.048	2.467	2.763
	29	0.127	0.683	0.854	1.311	1.699	2.045	2.462	2.756
	30	0.127	0.683	0.854	1.310	1.697	2.042	2.457	2.750
	40	0.126	0.681	0.851	1.303	1.684	2.021	2.423	2.704
	60	0.126	0.679	0.848	1.296	1.671	2.000	2.390	2.660
	120	0.126	0.677	0.845	1.289	1.658	1.980	2.358	2.617
	$\infty$	0.126	0.674	0.842	1.282	1.645	1.960	2.326	2.576

**Table III-4: Table of z for Selected Alpha**

$\alpha$	$Z_{1-\alpha}$
0.450	0.124
0.400	0.253
0.350	0.385
0.300	0.524
0.250	0.674
0.200	0.842
0.100	1.282
0.050	1.645
0.025	1.960
0.010	2.326
0.0050	2.576
0.0025	2.807
0.0010	3.090

## **C. Storage Tank Program Guidance**

### **1. Corrective Action Process**

The corrective action process (CAP) for storage tanks regulated under The Storage Tank and Spill Prevention Act (35 P.S. §§ 6021.101-6021.2104) (“Storage Tanks Act”) was established in 25 Pa. Code Chapter 245 Subchapter D on August 21, 1993 (23 Pa.B. 4033) and revised on December 1, 2001(31 Pa.B. 6615). These regulations provide a streamlined and flexible approach to corrective action. In cases where interim remedial actions (e.g., excavation of contaminated soil) can adequately address a release, the person performing the cleanup is only required to submit one report (site characterization) to the Department. Where localized contamination is associated with the closure of a regulated storage tank system, the Department has offered a standardized closure report form, which may be used to satisfy the site characterization report requirements. The regulation is flexible in that it authorizes the Department to modify or combine elements of the CAP based on the complexity of the release. For example, a responsible party may submit the site characterization report and remedial action plan as one report in some instances.

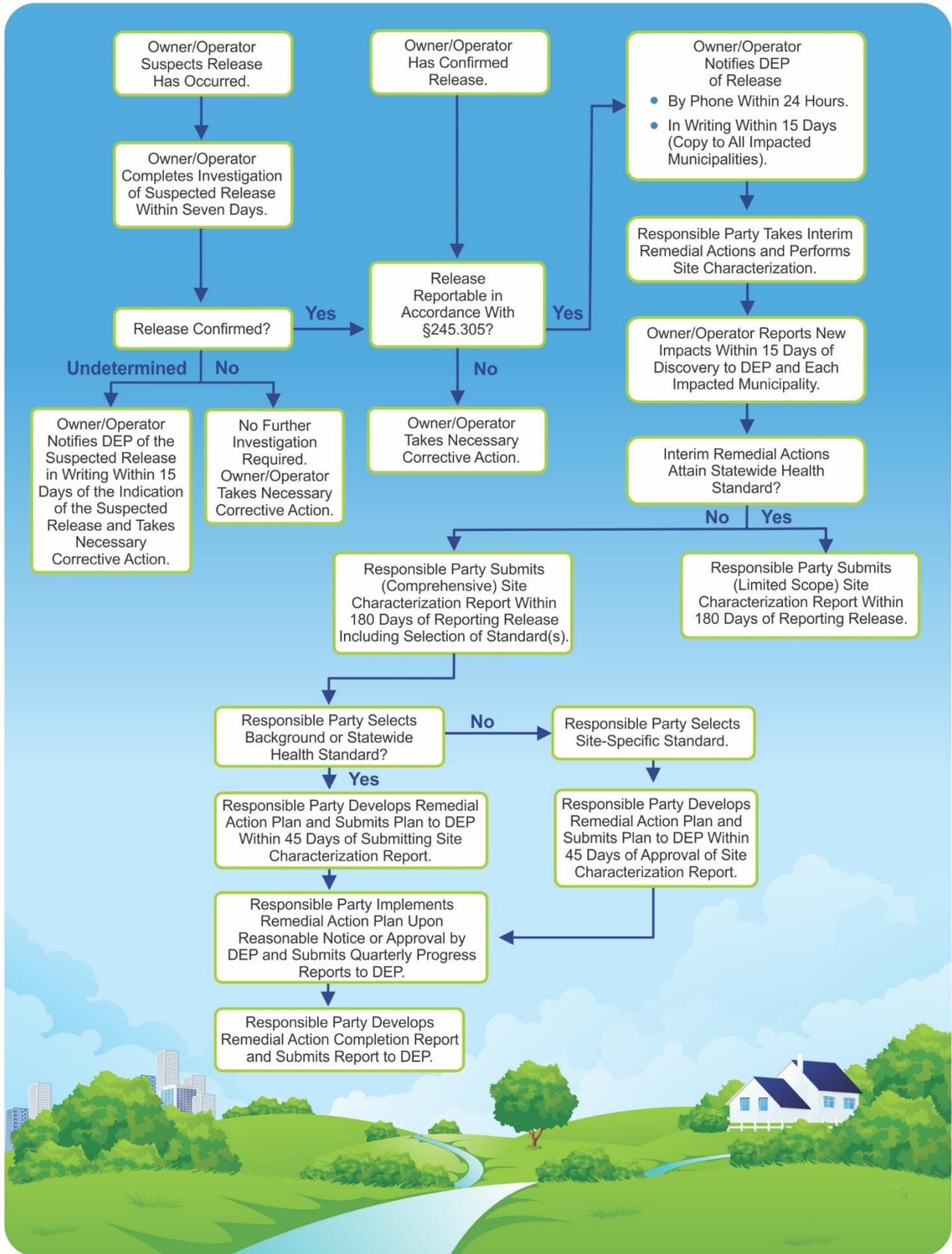
The CAP regulations allow Act 2 cleanup standards to be used to demonstrate remediation of releases from regulated storage tanks. In order to facilitate cleanups, the Department has identified those regulated substances, or “chemicals of concern,” that should be quantified by the laboratory for commonly encountered petroleum products. These substances and the accompanying methodologies should be utilized to demonstrate attainment for storage tank remediations as well as other remediations involving petroleum products. Only these substances need to be analyzed and evaluated when petroleum products are released if they are not contaminated by other sources. These analytical requirements appear in the *Site Assessment Sampling Requirements at Regulated Storage Tank System Closures* booklet number 2630-BK-DEP4699 and as Table III-5 in this manual. The Department does not recommend analysis for indicator parameters such as total petroleum hydrocarbons, as they have no standards established by Act 2.

For remediations conducted under the CAP, the person performing the remediation must demonstrate attainment of an Act 2 standard (25 Pa. Code § 245.313(b)). Upon approval by the Department of the report demonstrating attainment, the person is eligible for Act 2 liability protection.

### **2. Corrective Action Process Checklist**

The flow chart in Figure III-9 shows the major steps and the decision-making process that responsible parties must follow when a release from a regulated storage tank is confirmed. This process was designed to be as flexible as possible in order to accommodate the wide range of specific circumstances associated with releases. The following are the major steps of the process:

**Figure III-9: The Regulated Storage Tank Corrective Action Process Flowchart**



- If a release is confirmed, owners or operators must notify the DEP regional office responsible for the county in which the release occurred, by telephone in accordance with Section 245.305 of the regulations, within 24 hours of confirmation of a release. In addition to basic facility and owner information, the notice must provide, to the extent information is available:
  - the regulated substance involved;
  - the quantity of the regulated substance involved;
  - when and where the release occurred;
  - the affected environmental media;
  - impacts to water supplies, buildings, sewer or other utility lines;
  - interim remedial actions planned, initiated, or completed; and
  - a description of the release.
- Within 15 days of the telephone notice, the owner or operator must follow up with a written notification to the appropriate DEP regional office and any municipality impacted by the release. This written notice must include the same information as provided in the telephone notification and also should include any new information obtained within the 15 days.
- The owner or operator must provide follow-up written notification to the Department and any impacted municipality regarding new impacts to environmental media or water supplies, buildings or sewer or other utility lines, not previously reported, within 15 days of their discovery.
- The Department has prepared a form, number 2630-FM-BECB0082, which can be used to satisfy the written notification requirements. In situations where the release is small, contained and immediately cleaned up, this form may be all that is necessary to complete the CAP.
- Also, upon confirmation of a release, responsible parties must immediately initiate interim remedial actions. These are required response actions from the time a release is confirmed until the time a formal long-term remedial action plan is implemented. Interim remedial actions help maintain or restore public health and safety and prevent the additional release of a regulated substance to the environment and the spread of contamination.

Interim remedial actions may be all that are necessary to adequately address certain releases. These releases may involve spills and overfills, and cases where a release is confined to the excavation zone of an underground tank.

While all appropriate interim remedial actions must be taken in order to bring a release under control, the first priority at any release site is to identify and eliminate any threat to the health and safety of onsite personnel or nearby residents. See Section 245.306 of the regulations for requirements for interim remedial actions. These interim actions can include:

- checking for and venting product vapors from sewer lines or buildings that have been impacted;
- calling emergency personnel such as local fire and public safety officials for assistance where fire, explosion or safety hazards exist;
- relocating residents until potentially explosive vapors have been reduced to safe levels;
- restricting access to the site by nonessential personnel and establishing a buffer area around the site;
- recovering free product leaking into subsurface structures such as basements and sewers.

Attention should be turned to preventing any further release of the regulated substance to the environment either concurrently with these emergency actions, or as soon as any immediate threats to human health and safety have been eliminated or reduced to acceptable levels. This may include:

- scheduling and conducting the necessary tests to identify and confirm all sources of the release;
- removing product from the storage tanks;
- removing the storage tanks;
- excavating product-saturated soils when practicable;
- recovering free product on the water table;
- recovering product from the excavation;
- placing booms in, or interceptor trenches along, streams, gullies or drainageways where surface water has been impacted or may be impacted; and
- identifying and sampling affected water supplies or water supplies with the potential to be affected, and reporting sampling results to the Department and water supply owner within five days of receipt from the laboratory.

Interim remedial actions planned, initiated or completed are to be indicated during the telephone notification and updated in the 15-day initial and any subsequent written notification as required in Section 245.305 of the regulations. A more detailed discussion of interim remedial actions conducted at the site of the release is to be included in the site characterization report. This report is required to be submitted to the Department within 180 days of reporting a release.

- Any responsible party that affects or diminishes a water supply as a result of a release must restore or replace the affected or diminished water supply at no cost to the owner of the supply (35 P.S. § 6021.1303(b)). A water supply is affected if a measurable increase in a concentration of one or more contaminants occurs (e.g., benzene or MTBE) in the water supply. A water supply is diminished if the quantity of water provided by a water supply is decreased. For example, a water supply well may lose flow as a result of groundwater pumping during a remediation effort. (See definition of “affect or diminish” in 25 Pa. Code § 245.1). The requirement to restore or replace an affected or diminished water supply remains with the responsible party regardless of attainment of an Act 2 standard.

The responsible party must provide a temporary water supply (e.g., bottled water or water tank) to residents whose water supply is affected or diminished by the release no later than 48 hours after the responsible party receives information, or is notified by the Department, that a water supply has been affected or diminished (25 Pa. Code § 245.307(c)).

The responsible party must provide a permanent water supply within 90 days after the responsible party receives information, or is notified by the Department, that a water supply has been affected or diminished (25 Pa. Code § 245.307(d)). A permanent water supply may include a well or hookup to a public water supply or treatment system. Where the responsible party provides the affected party with access to a public system, the responsible party is not required to pay for the quantity of water being supplied.

- Responsible parties must properly handle, store and manage excavated contaminated soil which commonly results from tank closures and interim remedial actions (25 Pa. Code § 245.308). In general, petroleum contaminated soil is a residual waste regulated under the Solid Waste Management Act (SWMA) (35 P.S. §§ 6018.101-6018.1003) and must:
  - be stored in accordance with the Department’s residual waste management regulations (25 Pa. Code Chapter 299) relating to standards for storage of residual waste;
  - be completely and securely covered for the duration of the storage period, with an impermeable material of sufficient strength, anchoring or weighting to prevent tearing or lifting of the cover, infiltration of precipitation or surface water, and exposure of the soil to the atmosphere;

- be stored in a manner to prevent public access to the storage area, including use of fencing, security patrols or warning signs; and
  - not present a threat to human health or the environment and must either be undergoing active treatment or disposed of within 90 days from the first day of storage. Active treatment includes methods such as enhanced bioremediation in piles, soil vapor extraction and low-temperature thermal desorption. Active treatment does not include letting the soil pile sit in place.
- At the same time as the interim remedial actions are taking place, responsible parties must conduct a site characterization to determine the extent and magnitude of contamination which has resulted from the release. The CAP regulations provide the objectives of any site characterization and a list of elements that may be necessary or required to be conducted (25 Pa. Code § 245.309). This manual also provides information which should be considered when conducting site characterization work at storage tank release sites. A site characterization report must be submitted to the appropriate DEP regional office within 180 days of confirming the release (25 Pa. Code § 245.310(a)). It is very important that the site characterization report identify the Act 2 cleanup standard selected for the remediation. Interpretations of geologic and hydrogeologic data should be prepared by a professional geologist licensed in Pennsylvania.
  - Where interim remedial actions (e.g., removal of contaminated soil) have attained the SHS, and soil is the only medium of concern, the responsible party may submit a site characterization report to DEP limited to the elements in Section 245.310(b) of the regulations. In this case, the site characterization report should describe the entire CAP from site characterization to demonstration of attainment of the SHS.
  - Where soil contamination no more than three feet from the tank system is the only contamination observed during the closure of a storage tank system, the responsible party may submit the appropriate Storage Tank System Closure Report Form to satisfy the requirements of the site characterization report identified in Section 245.310(b) of the regulations. A completed closure report form, including adherence to the confirmatory sampling protocol in the closure guidance document appropriate for either aboveground or underground storage tank systems, will be adequate to demonstrate that the requirements of the SHS have been met. Note that the confirmatory sample locations in the closure guidance do not apply if the contamination has extended more than three feet from any part of the tank system. Also, because only limited sampling is required in localized contamination situations, the most conservative medium-specific concentrations (MSCs) are used as action levels. The most current action levels are provided in Tables 3 and 4 in DEP Booklet number 2630-BK-DEP4699.
  - Where a site-specific standard is being pursued and a risk assessment report is required under Section 250.405 of the regulations, the report should be submitted to the appropriate DEP regional office with the site characterization report and

should contain those elements as described under the site-specific standard of this manual.

- If the comprehensive site characterization report indicates that the interim remedial actions did not adequately address the release, and the background or SHS is selected, responsible parties must develop and submit a remedial action plan to the appropriate DEP regional office within 45 days of submission of the site characterization report. In cases where the site-specific standard is chosen, the remedial action plan is due 45 days after the Department's approval of the site characterization report (25 Pa. Code § 245.311).
- The responsible party must implement the remedial action consistent with the schedule in the remedial action plan upon reasonable notice or approval of the remedial action plan by DEP. Remedial action progress reports must be submitted quarterly to the appropriate DEP regional office (25 Pa. Code § 245.312).
- When the standard(s) established in the remedial action plan has/have been achieved, the responsible party must submit a remedial action completion report. The remedial action completion report must demonstrate that the requirements of one or more of the Act 2 standards have been met and include, if applicable, a postremediation care plan (25 Pa. Code § 245.313).
- In order to receive Act 2 liability protection, the cleanup standards for all regulated substances stored in the tank system, as identified in the site characterization report, must be achieved.
- Petroleum-contaminated media and debris associated with certain underground storage tanks (e.g., soil and groundwater, but not free product) that fail the test for D018-D043 TCLP only and are subject to the federal corrective action regulations under 40 CFR Part 280 are specifically excluded as hazardous waste (40 CFR § 261.4(b)(10)). This exclusion does not apply to contaminated media and debris from aboveground tanks, farm and residential motor fuel underground storage tanks of less than 1,100-gallon capacity, as well as heating oil underground storage tanks used for consumptive purposes at the property where located (i.e., tanks not regulated under 40 CFR Part 280). Petroleum-contaminated media and debris that are classified as hazardous waste are subject to the deed notice requirements of SWMA (35 P.S. § 6018.405).
- While the CAP regulations specify when the Department is to receive the site characterization report, remedial action plan and remedial action progress reports, the regulations also provide the Department with the flexibility to shorten or extend the timeframes based on the circumstances of a particular release.
- In addition, the CAP regulations establish Department review timeframes for site characterization reports, remedial action plans and remedial action completion reports. These reports are deemed approved if the Department does not take an action within those timeframes unless the Department and the responsible party

agree in writing to an alternative timeframe. The review timeframes are as follows:

- The Department will review a site characterization report submitted under Subsection 245.310(b) within 60 days of receipt, or a site characterization report submitted under Subsection 245.310(a) selecting the site-specific standard within 90 days of receipt.
- Site characterization reports submitted under Subsection 245.310(a) for the background or Statewide health standard will be reviewed within 60 days of receipt of a remedial action plan designed to attain those standards. The review will include the remedial action plan.
- Site characterization reports and remedial action plans for the background or Statewide health standard which are submitted together will be reviewed within 60 days of receipt.
- A remedial action plan designed to attain the site-specific standard will be reviewed within 90 days of receipt by the Department.
- Remedial action completion reports for the background and Statewide health standard will be reviewed within 60 days of receipt. A remedial action completion report demonstrating attainment of the site-specific standard will be reviewed within 90 days of receipt.

Responsible parties are strongly encouraged to properly identify the report or plan being submitted in order to facilitate review of reports and plans by the Department. Figure III-10 is a cover sheet which can be used with CAP submissions.

### **3. Use of the Short List of Regulated Substances for Releases of Petroleum Products**

Petroleum products contain many regulated substances. However, it is not always practical to examine all the regulated substances in a petroleum product. The Department has developed a “short list” of regulated substances for various petroleum products (Table III-5) to be analyzed to demonstrate attainment under any of the Act 2 cleanup standards when a release of these petroleum products occurs and is uncontaminated by other sources.

The Department will accept use of the short list to demonstrate attainment of the SHS if the following conditions are also met:

1. For soil media, no free liquids are left in the soil based on visual observation, and the soil does not create an odor nuisance. The location and level of odor remaining in soil must not result in an odor complaint to the Department, since odor is an indicator which may be attributed to residual free product.
2. For groundwater media, no free-floating product exists at the point of compliance (property line). Free-floating product must be recovered to the maximum extent

practicable and any remaining product cannot pose an unacceptable risk to human health or the environment.

The rationale for the application of these conditions is that the SHS numeric values cannot exceed their saturation and solubility limits in soil and groundwater, respectively. Since the Department is accepting an attainment demonstration for the short list of regulated substances rather than all regulated substances contained in a particular petroleum product, these conditions are necessary to assure that all SHSs applicable to the petroleum product are met.

If the remediator chooses to use the short list, and meets these conditions, then the Remedial Action Completion Report approval will stipulate that Act 2 liability coverage is for the short list substances only.

The short list of petroleum products may be periodically revised as determined necessary by the Department. For sites in the CAP for which a site characterization report has been received, attainment demonstration will be made using the previous list of substances. Sites which commence investigations to characterize or verify releases after the date the new list becomes effective should use the new list for characterization and attainment demonstration purposes to avoid a disapproval.

#### **4. Maximum Extent Practicable**

EPA has approved Pennsylvania's UST program in 25 Pa. Code Chapter 245 as consistent with federal law (68 FR 53520 (September 11, 2003)). EPA regulations under 40 CFR § 280.64 require owners and operators to remove "free product" to the maximum extent practicable (MEP) as determined by the implementing agency. Section 280.64(b) requires owners and operators to use abatement of "free product" migration as a minimum objective for the design of the free product removal system. The Department equates "free product," as the EPA uses the term, to be equivalent to "separate phase liquid" (SPL) as the Department has used that term in the past. Thus, to meet the corrective action requirement for underground storage tanks in Pennsylvania, a remediator must demonstrate the following two requirements, based upon technical data:

- SPL has been removed to the MEP, and
- the release has been demonstrated to attain an Act 2 cleanup standard.

Figure III-10: Corrective Action Process Report/Plan Cover Sheet

# CHAPTER 245 STORAGE TANK ACT

(check all that apply to the enclosed submission)

- Site Characterization Report – Section 245.310(b)
- Site Characterization Report – Site-Specific Standard
- Site Characterization Report – Statewide Health or Background Standard
- Site Characterization Report PLUS – Statewide Health Standard
- Remedial Action Plan – Statewide Health or Background Standard
- Remedial Action Plan – Site Specific Standard
- Remedial Action Progress Report
- Remedial Action Completion Report – Statewide Health or Background Standard
- Remedial Action Completion Report – Site-Specific Standard
- Post Remediation Care Plan Report
- Environmental Covenant

**Table III-5: Short List of Petroleum Products**

<b>PRODUCT STORED</b>	<b>PARAMETERS TO BE TESTED IN SOIL</b>	<b>ANALYTICAL METHOD (reported on a dry weight basis)</b>	<b>PARAMETERS TO BE TESTED IN WATER</b>	<b>ANALYTICAL METHOD<sup>1</sup></b>
Leaded Gasoline, Aviation Gasoline, and Jet Fuel	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5- Dichloroethane, 1,2- Dibromoethane, 1,2- Dibromide)	EPA Method 5035/8021B or 5035/8260B	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5- Dichloroethane, 1,2- Dibromoethane, 1,2-(Ethylene)	EPA Method 5030B/8021B, 5030B/8260B or 524.2
	Lead (total)		EPA Method 6010B or 7420	Lead (dissolved)
Unleaded Gasoline	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether (MTBE) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8260B	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether (MTBE) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8260B or 524.2
Kerosene, Fuel Oil No. 1	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8260B	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8260B or 524.2
Diesel Fuel, Fuel Oil No. 2	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8260B	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) (Isopropylbenzene) Methyl tert-Butyl Ether Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8260B or 524.2

**Table III-5: Short List of Petroleum Products (cont.)**

<b>PRODUCT STORED</b>	<b>PARAMETERS TO BE TESTED IN SOIL</b>	<b>ANALYTICAL METHOD (reported on a dry weight basis)</b>	<b>PARAMETERS TO BE TESTED IN WATER</b>	<b>ANALYTICAL METHOD<sup>1</sup></b>
Fuel Oil Nos. 4, 5 and 6, and Lubricating Oils and Fluids	Benzene Naphthalene	EPA Method 5035/8021B or 5035/8260B	Benzene Naphthalene	EPA Method 5030B/8021B, 5030B/8260B or 524.2
	Fluorene Anthracene Phenanthrene Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(a)pyrene Benzo(g,h,i)perylene	EPA Method 8270C or 8310	Phenanthrene Pyrene Chrysene	EPA Method 8270C, 8310 or 525.2
Used Motor Oil	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) Naphthalene	EPA Method 5035/8021B or 5035/8260B	Benzene Toluene Ethyl Benzene Cumene (Isopropylbenzene) Naphthalene	EPA Method 5030B/8021B, 5030B/8260B or 524.2
	Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Benzo(g,h,i)perylene	EPA Method 8270C or 8310	Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Benzo(g,h,i)perylene	EPA Method 525.2
	Lead (total)	EPA Method 6010B or 7420	Lead (dissolved)	EPA Method 6020, 7421, 200.7, 200.8, or 200.9
Mineral Insulating Oil	PCB-1016 (Aroclor) PCB-1221 (Aroclor) PCB-1232 (Aroclor) PCB-1242 (Aroclor) PCB-1248 (Aroclor) PCB-1254 (Aroclor) PCB-1260 (Aroclor)	EPA Method 8082	PCB-1016 (Aroclor) PCB-1221 (Aroclor) PCB-1232 (Aroclor) PCB-1242 (Aroclor) PCB-1248 (Aroclor) PCB-1254 (Aroclor) PCB-1260 (Aroclor)	EPA Method 8082 or 508A
	Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5035/8021B or 5035/8260B	Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5-	EPA Method 5030B/8021B, 5030B/8260B or 524.2
Other Petroleum Products  Blended Petroleum Products  Unknown Petroleum Products  Other Regulated Substances	Contact the DEP Regional Office responsible for the county in which the tank is located			

<sup>1</sup> Samples from potable water supplies must be analyzed using a method applicable to drinking water.

**Notes:**

When reporting nondetects (ND), the data must be accompanied by a numerical quantitation limit that takes into account dilution, sample preparation, and matrix effects.

The responsible party has the obligation to ensure that the analytical methodologies and techniques employed are suitable to provide data that meets the minimal data quality objectives outlined and referenced in this document.

Laboratories must document that samples meet all applicable preservation requirements.

As the implementing agency, the Department considers MEP under 40 CFR § 280.64 as the extent of removal necessary to prevent migration of SPL to uncontaminated areas and prevent or abate immediate threats to human health or the environment.

It is important to note that removing SPL to the MEP is not required under Chapter 250. Although removal is not required, if groundwater and/or soil is impacted above a standard, then removing SPL may greatly assist the remediator in attaining a standard. A dissolved phase plume may not be stable if there is a migrating SPL body. Migrating SPL is an SPL body and its associated phases that are documented to be spreading or expanding laterally or vertically into previously uncontaminated areas. Residual and mobile SPL and related terms are discussed further in Section V.D. of this guidance.

In the majority of cases, releases at regulated storage tank sites are liquids with a density less than water, or light non-aqueous phase liquids (LNAPLs). Recent advances in the understanding of LNAPL behavior have illustrated that in some cases, continued attempts to reduce LNAPL to a measured thickness in a monitoring well (e.g., 0.01 ft. or less) may not be practicable. Even in cases where the presence of LNAPL is the only reason for remediation, continued recovery of LNAPL may provide little positive impact on the environment.

## **5. Management of Light Nonaqueous Phase Liquids (LNAPL) under Act 32**

LNAPL typically has been viewed as SPL that is less dense than water and can be measured in a well or on a water surface. Even when measurable LNAPL is not detected within a well, LNAPL can remain trapped in nearby soils or bedrock. Depending on site conditions and how conditions can change, this residual LNAPL may remain trapped or become mobile. Therefore, it is important to keep the following in mind:

- The absence of measurable LNAPL in a well does not definitively establish the absence of mobile LNAPL at a site.
- The presence of measurable LNAPL in a well does not definitively establish the size, volume, thickness, or recoverability of LNAPL at the site or in the vicinity of the well.
- The measured LNAPL thickness in a well may not be indicative of the actual LNAPL thickness or volume within the formation.
- The presence of recoverable LNAPL in a well may only indicate that mobile LNAPL exists in the immediate vicinity of that well.
- The observation that LNAPL is no longer accumulating at a significant or appreciable rate in a well may only indicate that the LNAPL in the vicinity of the well is no longer mobile under the present conditions.
- The mass of residual LNAPL remaining in the soil and/or rock matrix after recovery to the MEP may be orders of magnitude larger than the amount of mobile LNAPL that was recovered at the site.

- LNAPL may spread in many directions not necessarily coincident with groundwater gradients (including but not limited to structural influences, preferential pathways, permeability contrasts, and pumping well influences). See “Sources and Pathways” in Section III.C.5(i).
- LNAPL migration rates may not be the same as the groundwater flow rates.
- Some mobile LNAPL is persistent and can be bailed, but quantities removed may be relatively small. Product bailing alone rarely achieves significant LNAPL recovery.

LNAPL exists in residual and non-residual (mobile) phase, so some LNAPL may remain at the site after reaching removal to the MEP. Although the remaining LNAPL may take years to degrade, the low recoverability along with a demonstration of low risk posed by the LNAPL source may make recovery of remaining LNAPL infeasible or unnecessary. In such instances, evaluating the site for terminating LNAPL recovery is warranted. Information necessary to determine when LNAPL removal meets the MEP is identified below.

**a) Site Characterization and LNAPL Conceptual Site Model**

Section 245.309 of the regulations requires completion of a site characterization. A complete and concise site characterization is an important step in identifying the presence, properties, distribution and migration of LNAPL. Simple visual observations during site work and interpretation of analytical results can help identify the presence of LNAPL. The characterization of a site with LNAPL includes the development of an appropriate LNAPL Conceptual Site Model (LCSM). The level of detail required for a given LCSM is site-specific and based on the complexity of environmental conditions at each site. As the corrective action progresses, the LCSM should be regularly re-evaluated in light of additional site/LNAPL data, pilot test data, remedial technology performance metrics, and monitoring data. A complete and up-to-date LCSM allows the best possible decisions about application and operation of remedial technologies to be made and when removal actions are no longer necessary. Documents that should be used to guide the development of an LCSM are included in the list of references in Sections III.C.6 and V.F. The LCSM may require revisions as site conditions change due to remediation and other site factors. Table III-6 is a worksheet that can be used when preparing an LCSM.

Older LNAPL cases which pre-date this guidance may require additional assessment to update the LCSM for the purposes of making MEP decisions. Results from an updated LCSM may provide additional information about LNAPL recovery potential for the site. While technologies may appear costly or overly complex, the use of these technologies may assist responsible parties, consultants, and staff to develop the most cost-effective decision regarding LNAPL recovery or case closure. Information needed to characterize LNAPL at a site and develop a thorough LCSM typically includes, but is not limited to:

- **Delineation:** LNAPL does not necessarily form a “pancake” on the groundwater surface, but shares the pore space in the vadose zone, the capillary fringe, and/or beneath the water table within the smear zone. Different industry standard practices can be used to identify LNAPL trapped in soils or bedrock (ranging from shake test to Laser-Induced Fluorescence (LIF) in conjunction with core photography).
- **Sources and Pathway:** Geologic or manmade features such as fractures in bedrock or clay and fill material adjacent to underground utilities may also contain LNAPL and may serve as pathways for enhanced migration of SPL vapor and dissolved phases. These features include fractures in bedrock or clay and fill material adjacent to underground utilities, old foundations, and old tank system cavities. Their presence may significantly increase risk by accelerating potential migration to receptors. Monitoring well placement should consider the movement and storage of LNAPL in these features as part of the site characterization.
- **Volume:** Where possible, the volume (or plausible volume range) of LNAPL within the subsurface should be established to allow the development and selection of an appropriate recovery strategy as well as a basis for the risk evaluation. Historic records for the site should be reviewed to identify past releases that may have contributed to the volume of LNAPL.
- **Age and Chemical/Physical Character:** LNAPL and groundwater can be analyzed to identify or verify the type of product as well as assess if the product poses a risk to receptors. As LNAPL weathers, the physical and chemical properties of the LNAPL can change. Weathered LNAPL can be more viscous and therefore less mobile and less recoverable than unweathered LNAPL. LNAPL properties can also assist in determining a probable date or timeframe for the product release. Knowing the amount of time the product has been present compared to the known impacts (or lack thereof) can provide valuable insight on whether case closure is advisable.
- **LNAPL Migration:** LNAPL moving into previously uncontaminated areas indicates that LNAPL is migrating. It is a condition requiring immediate recovery as per Section 245.306(a)(3)(ii) of the regulations. The potential for mobile LNAPL to migrate may depend on geologic conditions, changing hydraulic or LNAPL gradients as well as precipitation and groundwater recharge. The presence of other contaminants may impact migration of LNAPL.

**Table III-6: LNAPL Conceptual Site Model (LCSM) Worksheet**

**LCSM - describes the physical properties, chemical composition, occurrence and geologic setting of the LNAPL body from which estimates of flux, risk and potential remedial action can be generated (definition taken from ASTM E2531-06).**

Site Characterization	Yes	No	N/A	Comments
1. Do you know the past and present site use?				
2. Do you know the geology of the site (i.e., soil and bedrock characteristics)?				
3. Do you know the hydrogeology of the site?				
3.a. Unconfined aquifer?				
3.b. Confined/Semi-confined aquifer?				
3.c. Perched aquifer?				
4. Is the source known?				
4.a. If yes, what is the source and quantity released?				
5. Has the vertical and horizontal extent of the LNAPL body been delineated?				
5.a. If yes, have direct and/or indirect indicators been used to detect presence of LNAPL trapped in soils and/or bedrock?				

<b>Site Characterization</b>	<b>Yes</b>	<b>No</b>	<b>N/A</b>	<b>Comments</b>
6. Has dissolved phase or vapor phase plume data been evaluated?				
6.a. Do any dissolved concentrations in groundwater approach their effective solubility?				
7. Have the physical (density, viscosity, interfacial tension, vapor pressure) and chemical properties (constituent solubilities and mole fractions) of the LNAPL been determined?				
8. Have potential migration pathways been identified (i.e. fractures in bedrock and clay, karst features, utilities)?				
9. Are there complete or potentially complete exposure pathways present (potable wells, surface water, vapor intrusion, etc.)?				
10. Are there ecological receptors impacted by the LNAPL body?				
11. Has sufficient gauging data been gathered to determine if LNAPL is mobile?				
11.a. Has gauging taken place during drought or after heavy precipitation events?				
12. Has LNAPL transmissivity been determined?				

<b>Site Characterization</b>	<b>Yes</b>	<b>No</b>	<b>N/A</b>	<b>Comments</b>
13. Has a qualitative assessment of Natural Source Zone Depletion (NSZD) been completed?				
14. Does characterization indicate that the LNAPL is no longer migrating?				

- **LNAPL Mobility:** LNAPL needs to exist at saturations greater than its residual saturation in order to be mobile. It is the mobile portion of the LNAPL body that is typically recovered by LNAPL extraction and recovery technologies. However, the presence of mobile LNAPL in a well does not necessarily indicate that the LNAPL body is migrating. Gauging or recovery data from drought and heavy precipitation events may provide mobility data.
- **LNAPL Recoverability/Transmissivity:** LNAPL Transmissivity (LNAPL Tn) is a useful metric for determining the recoverability of mobile LNAPL. Since LNAPL Tn accounts for multiple LNAPL properties such as density, viscosity, and LNAPL saturation, LNAPL Tn can be more useful than just the measured thickness for determining LNAPL recoverability (ASTM E2856). However, LNAPL Tn can vary over time due to subsurface conditions such as groundwater fluctuations, corrective action implementation (reduced LNAPL saturation), or weathering of LNAPL.

LNAPL Tn tests should be performed at sites where LNAPL is present to aid in determining the recoverability of the LNAPL. LNAPL Tn tests can also be completed over time to document the progress of LNAPL recovery efforts. The ASTM Standard E2856 discusses several LNAPL Tn test methods and how to select the most appropriate method for site conditions. More information about LNAPL Tn may be found in the references to this section, particularly ASTM Standard E2856.

Characterization of LNAPL is found through direct and indirect indicators. Both types of indicators determine where and how much LNAPL is on the property and are especially important if the release history is unknown. The level of detail needed when using these methods is commensurate with the complexity of the site.

Some direct methods of detecting the presence of LNAPL include:

- Direct push technologies that can measure for the presence of LNAPL such as LIF, Rapid Optical Screening Tool LIF, Membrane Interface Probes and cone penetrometers.
- Observation of LNAPL presence in wells, borings, or test pits.
- Field screening tests such as staining, odors, Organic Vapor Analyzers, Photo Ionization Detectors, Flame Ionization Detectors, shake test using oleophyllic dyes, paint filter test (EPA method 9095B), and paper towel tests.
- Ultraviolet light boxes and soil cores.
- Soil and rock core lab analysis.

- Core photography under UV light, pore fluid saturations, soil properties, fluid properties, and LNAPL fingerprinting.

LIF is used to collect real-time, in-situ field screening of residual and nonaqueous phase hydrocarbons in undisturbed vadose, capillary fringe and saturated subsurface soils and groundwater. Detailed information regarding this technology can be found at EPA's Contaminated Site Clean-Up Information website.

LNAPL presence in wells, borings or test pits indicates that LNAPL is in the surrounding formation. In unconfined conditions, the LNAPL could rise and fall with the fluctuation of the water table. However, it is not a reliable indicator of vertical and lateral extent in the formation or for determining the volume of the release. The absence of LNAPL in a well does not necessarily mean the source is eliminated; it may be trapped deeper in the formation by a high-water table.

Some indirect indicators of LNAPL presence in the formation include:

- A persistent dissolved phase plume.
- Dissolved phase groundwater concentrations that are close to the effective solubility of the LNAPL that was released.
- Total Petroleum Hydrocarbons (TPH) concentrations (EPA Method 418.1) that are greater than the Carbon Saturation (Csat) in a given soil type.

Other potential indirect indicators of LNAPL presence are found in EPA's petroleum vapor intrusion guidance document (510-R-15-001, Table 3, p. 52, 2015).

**b) Is the LNAPL Body Migrating?**

Removal of LNAPL must be conducted to prevent the spread of contamination into previously uncontaminated zones. Following a release, LNAPL can move at higher rates than groundwater due to a large LNAPL hydraulic head. The LNAPL can be upgradient of the release point due to the mounding effect. Removal of the source will shorten the time until the LNAPL body stops migrating.

In order to demonstrate that an LNAPL body is not migrating, the Department requires an evaluation of migration potential. The following can be used to make this determination. A more detailed description of each follows the list. This list is not all inclusive. Some methods that may be used to demonstrate that LNAPL is not migrating include:

- Monitoring results

- LNAPL velocity
- Recovery rate
- Age of the release
- Tracer test

Monitoring results are most important in evaluating migration potential. Assuming that there is an adequate monitoring network and sufficient temporal data, there are several factors that are evidence for a stable footprint, which include a stable or decreasing thickness of LNAPL in monitoring wells, sentinel wells outside of the LNAPL zone that remain free of SPL, and a shrinking or stable dissolved phase plume.

Calculating the potential LNAPL velocity using Darcy's Law is also important in the evaluation. The key parameter is LNAPL conductivity, which may be estimated from bail-down tests, or from the measured LNAPL thickness, soil capillary parameters and a model that assumes static equilibrium. The American Petroleum Institute (API) Interactive LNAPL Guide is one tool that may be used to estimate the LNAPL velocity using this model. It is important to recognize that use of Darcy's Law would be precluded for some site conditions, such as a fractured bedrock site.

The recovery rate that is observed as LNAPL is removed from a well is important to the evaluation. Although not directly correlated to LNAPL migration, declining recovery rates would generally indicate reduced potential for LNAPL to migrate.

The age of the release, when known, aids in determining migration potential. If a relatively long time has transpired since the release, there is reduced potential for migration due to smearing of LNAPL within soil and weathering of LNAPL through dissolution, volatilization, and biodegradation.

Tracer tests using hydrophobic dye can also be used for this evaluation. The dilution rate of the dye gives an indication of the rate of movement of the LNAPL. Monitoring wells need to have at least 0.2 feet of LNAPL for this method to work.

**c) Remedial Action Plan (RAP)**

After a complete Site Characterization as outlined in Section 245.309 of the regulations has been completed and when LNAPL recovery continues, a RAP addressing the technologies and methods to remediate both the LNAPL and the dissolved phase portion of the contamination is required under Section 245.311 of the regulations. The RAP should specify remediation goals and endpoints that can be obtained with the most cost-effective solutions/technologies currently proven to remediate the identified contaminants.

If the RAP recommends the ceasing of or no LNAPL recovery, the RAP should clearly list the lines of evidence that demonstrate the LNAPL is not recoverable, is stable, is not migrating and poses no risk to human health and the environment. Once the soil and dissolved phase in groundwater have met attainment under the selected remediation standard, a Remedial Action Completion Report (RACR) can be submitted.

**d) Demonstrating LNAPL Meets MEP Criteria**

To determine when LNAPL recovery is no longer necessary or if a case with LNAPL can be recommended for closure, several lines of evidence should show that LNAPL has been recovered to the MEP and that the remaining LNAPL is not migrating and poses no risk. These lines of evidence should also show that natural attenuation processes are continuing, further demonstrating that the LNAPL body is stable and not migrating. Lines of evidence should be documented in the RAP and RACR for the Storage Tanks Act and in the Cleanup Plan and/or FR for Act 2. Lines of evidence may include the following:

- An estimate, or supportable estimated range, of the total volume of LNAPL released and present in the subsurface. Volume estimates help determine dissolved plume longevity and the potential to migrate to new areas.
- A discussion, including supporting data, regarding the importance of site-specific soil structure, geology/hydrostratigraphy with an emphasis on the possible existence of macropores, fractures, or conduits in karst. All potential pathways for migration should be analyzed to ensure LNAPL migration to new areas is not occurring.
- A discussion with supporting data that establishes whether LNAPL at the site is a function of groundwater level or confined conditions. Since LNAPL thicknesses are often exaggerated under confined conditions, the LCSM must provide adequate characterization of hydrostratigraphy to determine if confining layers are present.
- A demonstration that constituents in the vapor phase do not present a risk to potential receptors. All potential pathways for vapor migration should be analyzed to ensure migration to new areas is not occurring.
- Documentation that demonstrates the areal extent of the LNAPL plume at the site is stable or decreasing. Monitoring of LNAPL thickness in wells over time is needed to determine stability.
- Documentation that demonstrates the areal extent of the dissolved phase plume at the site is stable or decreasing.
- Documentation that shows concentrations of chemicals of concern are below the standards attained and dissolved plume is undergoing attenuation.

- An evaluation that shows the effective solubility of remaining LNAPL and dissolved-phase concentrations are below the standards attained.
- LNAPL Tn data that documents LNAPL recoverability over a range of aquifer conditions. If LNAPL Tn as measured by ASTM E2856 is below 0.1 ft<sup>2</sup>/day, then hydraulic recovery is not feasible. If values exceed 0.1 ft<sup>2</sup>/day, demonstrate that LNAPL body is not migrating or that Tn values have been decreasing with recovery efforts and have reached asymptotic conditions.
- A qualitative assessment of natural attenuation.
- A description of the removal methods and technologies which have been used and/or evaluated. Evaluation of the results of product removal including whether data shows asymptotic recovery trends through seasonal water table variations. Data that demonstrates the technologies and additional recovery are not effective.
- Supporting data which contains current site and area maps that show all current receptors, preferential pathways (such as utilities), basements, drinking water wells, and surface water bodies including High Quality and Exceptional Value streams, wetlands, and sensitive ecological areas.
- Documentation that the NSZD (ITRC, LNAPL-1, 2009) of the LNAPL body and natural attenuation of the dissolved-phase plume are continuing at the site and are expected to further mitigate risk from the release.

**e) Closure of Sites with LNAPL**

For purposes of this guidance, recovery to MEP is considered complete if the following have been demonstrated:

- LNAPL remains onsite, but the following have been achieved:

Receptor evaluation demonstrates that remaining LNAPL, dissolved phase constituents, and associated vapors are not a risk to human health or the environment, and the following:

- i. Natural Source Zone Depletion of the LNAPL body and natural attenuation of the dissolved-phase plume are documented as occurring at the site and are expected to further mitigate risk from the release;
- ii. Multiple lines of evidence demonstrate that LNAPL had been recovered to MEP;

- iii. For sites with active LNAPL recovery, evaluation of corrective actions performed at the site shows asymptotic recovery trends through seasonal water table variations; and
- iv. Remaining LNAPL is not recoverable or has low mobility/recoverability (as evidenced by LNAPL Tn tests).

Situations do exist in which LNAPL can justifiably remain at a site after case closure. However, the Department should have a full understanding of the site-specific geological, hydrogeological, and receptor risk factors before closing a case with measurable LNAPL.

If an institutional or engineering control is needed to attain a standard, then an environmental covenant would be needed.

Note: A closed case may be re-opened if significant previously unidentified environmental problems related to the original release (for example, additional LNAPL, extensive saturated soils, or an impacted receptor) are discovered.

## **6. References**

ASTM E2856, Standard Guide for Estimation of LNAPL Transmissivity.

EPA. 2015. Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites. EPA 510-R-15-001.

ITRC (Interstate Technology & Regulatory Council) 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL. LNAPL-1. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team. [www.itrcweb.org](http://www.itrcweb.org)

EPA. Contaminated Site Clean-Up Information. <http://clu-in.org/characterization/technologies/lif.cfm>

## D. Mass Calculations

The following sections demonstrate methods to calculate groundwater and soil mass utilizing site specific measurements of contaminants and volume of the specific soil or liquid plumes.

### 1. Groundwater Mass Calculation

#### Calculate Water Volume (WV)

Water Volume(WV-ft<sup>3</sup>) = Length of plume(L) x Average Thickness of plume(H) x Average Width of plume(W) x porosity(n)

#### Calculate Water Mass (WM)

Water Mass(WM-lb.) = Water Volume(WV-ft<sup>3</sup>) x 62.5 lb./ft<sup>3</sup>

#### Calculate Mass of Contaminant

Water Mass(WM-lb.) x Contaminant Concentration(C-ppm)/ 10<sup>6</sup> = Contaminant Mass(lb.)

### 2. Soil Mass Calculation

These soil mass calculations provide a way of quantifying contaminants in soil that under an Act 2 remediation would track the estimations of the mass of contaminants removed from public exposure as a measure of program success. Contaminants removed from public exposure can be any one or a combination of excavation and disposal, treatment or pathway elimination measures. The mass calculations would not include areas of the site where site characterization found concentrations to be at or below the applicable standard. This area remains unchanged and thus there is no reduction in exposure as part of the remediation.

$$M(x) = D_{(soil)} \times V_{(total)} \times C_{ave.}(x)$$

#### Where:

M(x) = The mass of a specific contaminant in soil (lb)

D<sub>(soil)</sub> = Density of soil, assume to be a default value of 110 lb/ft<sup>3</sup>

V<sub>(total)</sub> = Volume based on the soil site characterization data with respect to the horizontal and vertical depth of the soil samples collected in areas above the applicable standard. The volume sum of each plot would equate to the total volume.

C<sub>ave. (x)</sub> = The soil contaminant concentration would be the arithmetic mean concentration of the contaminant throughout the soil column. This is the free and absorbed phase of the soil contaminant in areas above the applicable standard and expressed in lb<sub>contaminant</sub>/lb<sub>soil</sub> (ppmw = ppm/10<sup>6</sup>).

## **E. Long-Term Stewardship**

### **1. Introduction**

Long-term stewardship is generally accepted as the establishment and maintenance of physical and non-physical controls that are necessary to maintain the effectiveness of an approved remedy at cleanup sites where remaining regulated substances do not allow for the unrestricted use of the property. It also includes any long-term obligations (e.g., sampling, operation and maintenance, etc.) that ensure the effectiveness of the remedy after completion of the response action.

This section provides general guidelines on the methodology of long-term stewardship, which includes the use of a postremediation care plan. The plan shall be submitted as part of the final report and approved by the Department. The approved postremediation care plan will become a condition of attainment of the chosen standard(s) under Act 2. The plan shall identify the activities that will be conducted after closure and the frequency of those activities.

Answer the questions from the matrix in Table III-7, relative to your chosen standard(s), to determine when a postremediation care plan is required. The proposed postremediation care requirements shall be included in the cleanup plan for Department approval, as specified in Section 250.410(b)(5) of the regulations.

If any of the answers in the following matrix are yes, relative to the selected standard(s), a postremediation care plan shall be included as part of the final report.

### **2. Uniform Environmental Covenants Act**

On Dec. 18, 2007, the Uniform Environmental Covenants Act (UECA) (27 Pa. C.S. § 6501-6517) was signed into law, and was subsequently implemented via Chapter 253, adopted November 19, 2010 (40 Pa.B. 6654). UECA provides a standardized process for creating, documenting and assuring the enforceability of activity and use limitations (AULs) on contaminated sites. Under UECA, an environmental covenant will be required whenever an engineering or institutional control is used to demonstrate the attainment of an Act 2 remediation standard. Environmental covenants are legal documents affecting property rights so remediators are encouraged to seek legal counsel with respect to the contents of the environmental covenant. For the purposes of Act 2, environmental covenants will take the place of deed notices in relation to any restrictions required to attain or maintain the standard.

A model environmental covenant is provided on the LRP website. The model is provided as an example of what type of information should be provided in an environmental covenant. However, it is important to note that each site is unique, so the content of each covenant will vary from site to site.

At some sites additional AULs may be put in place but not included in the environmental covenant, because they are not needed for attainment/maintenance of an Act 2 cleanup standard. Environmental covenants are difficult to modify, so land use restrictions not associated with the attainment/maintenance of an Act 2 standard may unnecessarily impede the ability to redevelop a property. Thus, a mechanism other than an

environmental covenant is recommended for any additional AULs on a site. Regardless, the submitted postremediation care plan should only review the mechanisms required to attain/maintain an Act 2 cleanup standard. Only those AULs that are necessary to attain and/or maintain the selected standard are required for inclusion within the environmental covenant. In addition, the property owner's consent and signature are required to implement an environmental covenant (27 Pa. C.S. § 6504).

**Table III-7: Postremediation Care Decision Matrix**

<b>Background</b>			
		Yes	No
1.)	Is an ENGINEERING CONTROL(s) needed to <u>attain and/or maintain</u> the background standard? § 250.204(g)		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to <u>maintain</u> the background standard? § 250.204(g)		
3.)	Does the FATE & TRANSPORT analysis indicate that the background standard may be exceeded at the point of compliance in the future? § 250.204(g)		
4.)	Does the remedy rely partially or completely on NATURAL ATTENUATION resulting in the need for periodic reporting to the Department? § 250.204(g)		

<b>Statewide Health</b>			
1.)	Is an ENGINEERING CONTROL(s) needed to <u>attain and/or maintain</u> the Statewide health standard? § 250.312(e)		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to <u>maintain</u> the Statewide health standard? § 250.312(e)		
3.)	Does the FATE & TRANSPORT analysis indicate that the Statewide health standard, <u>including the solubility limitation in § 250.304(b)</u> , may be exceeded at the point of compliance in the future? § 250.312(e)		
4.)	Does the remedy rely partially or completely on NATURAL ATTENUATION resulting in the need for periodic reporting to the Department? § 250.312(e)		
5.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will a postremedy use be relied on to eliminate complete exposure pathways, as set forth in § 250.311(e)(2) or § 250.312(b)?		
6.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will mitigation measures be implemented, as set forth in § 250.311(f)(1-4)? [If yes, follow guidelines in § 250.312(b)(1-3) for reporting requirements.]		

**Site-Specific**

1.)	Is an ENGINEERING CONTROL(s) needed to <u>attain and/or maintain</u> the Site-specific standard? § 250.411(d)		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to <u>maintain</u> the Site-specific standard? § 250.411(d)		
3.)	Does the FATE & TRANSPORT analysis indicate that the Site-specific standard may be exceeded at the point of compliance in the future? § 250.411(d)		
4.)	Does the remedy rely partially or completely on NATURAL ATTENUATION resulting in the need for periodic reporting to the Department? § 250.411(d)		
5.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will a postremedy use be relied on to eliminate complete exposure pathways, as set forth in § 250.311(e)(2)?		
6.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will mitigation measures be implemented, as set forth in § 250.311(f)? [If yes, follow guidelines in § 250.411(f)(1-3) for reporting requirements.]		

### 3. Institutional versus Engineering Controls

An institutional control, by definition of Act 2, is a measure taken to limit or prohibit certain activities that may interfere with the integrity of a remedial action or result in exposure to regulated substances at a site. These include, but are not limited to, fencing or restrictions on the future use of the site (35 P.S. § 6026.103).

An engineering control, by definition of Act 2, is a remedial action directed exclusively toward containing or controlling the migration of regulated substances through the environment. These include, but are not limited to, permanent capping of contaminated soils with parking lots or building slab construction, leachate collection systems, groundwater recovery trenches, and vapor mitigation systems.

Example: A groundwater use restriction, as documented in an environmental covenant, is an institutional control. An impermeable cap that prevents volatilization to the atmosphere, controls contaminant migration via run-off and leaching to groundwater, and limits dermal contact is an engineering control.

Institutional and engineering controls serve as AULs because they restrict the use of a property. Institutional controls cannot be used to attain the background or Statewide health standards (35 P.S. §§ 6026.302(b)(4) and 6026.302(e)(3)). Engineering and/or institutional controls may be used to maintain all three standards. *Attaining* a standard refers to steps or actions taken to complete the requirements, and therefore demonstrate attainment, of an Act 2 standard. *Maintaining* a standard refers to steps or actions taken to ensure the requirements of a standard that have already been completed continue to be met in the foreseeable future. Table III-7 provides a decision matrix of postremediation care requirements for each Act 2 standard.

Example of attaining vs. maintaining a cleanup standard: A property with a discharge of regulated substances to the groundwater is able to *attain* the SSS under current conditions because drinking water is supplied by the municipality. The SSS is then *maintained* in the future by implementing an environmental covenant stating that groundwater is not to be used on the property without treatment approved by the Department.

### 4. Postremediation Care Plan

The postremediation care plan should include the following:

- The reason(s) that the postremediation care plan is necessary (See 25 Pa. Code §§ 250.204(g), 250.312, 250.411(d), and 250.708).
- A schedule of operation and maintenance of the controls. Include a description of the planned maintenance activities and frequencies at which they will be performed and future plans for submission of proposed changes.
- Information regarding the submission of monitoring results and analysis, or as otherwise approved by the Department, that demonstrates the effectiveness of the remedy. Include a description of the planned monitoring activities and frequencies at which they will be performed. Monitoring activities in this case

may include inspection and reporting requirements related to engineering controls.

- The proposed method for reporting any instances of nonattainment of the selected standard(s).
- The proposed measures to be taken to correct nonattainment conditions as they occur. A postremediation care plan containing any language proposing any potential future changes to the remedy will require the approval of the Department at the time of the proposed change.
- Information regarding the maintenance of records at the property where the remediation is being conducted for monitoring, sampling and analysis. Include the name, address and telephone number of the person or office to contact about the site during the postremediation care period. This person or office shall keep an updated postremediation care plan during the postremediation care period.
- Documentation of a plan to maintain the mitigated ecological resource, report of success or failure of the mitigation measure, and demonstration of sustaining the measures up to five years from final report approval.
- If requested by the Department, documentation of financial ability to implement the remedy and the postremediation care plan.

## **5. Postremediation Monitoring**

In some situations, postremediation monitoring may be required as part of the postremediation care plan. For example, postremediation monitoring is conducted to determine any changes in groundwater quality after attainment of a standard(s). Unless otherwise instructed by the Department, analytes to be included are those which were monitored during assessment and remediation monitoring. All monitoring activities should incorporate quality control and quality assurance provisions consistent with the Chapter 250 regulations and policies.

Well locations for postremediation monitoring are generally selected from existing monitoring wells used in the characterization and remediation phases. Where a source of contamination is removed prior to impacting groundwater, postremediation monitoring should continue at locations that will detect any residual contamination in the unsaturated zone that might migrate to the groundwater.

### **a) Duration**

In most cases, postremediation monitoring requirements will be developed on a case-by-case basis. The factors determining the duration of postremediation monitoring are the same factors that determine whether a postremediation care plan is necessary.

**b) Frequency**

As stated in Section 250.204(g) of the regulations, postremediation monitoring will take place on a quarterly basis unless otherwise approved by the Department. The interval between sampling events should be short enough to allow for response and correction of any problems that may cause nonattainment at the point of compliance.

Factors that could influence the need for an alternative postremediation monitoring schedule include site size, groundwater velocity, contaminant characteristics and the vulnerability of a site to pulses of contaminant migration during precipitation events.

**c) Cessation of Postremediation Monitoring**

Postremediation monitoring may be terminated when monitoring provisions set forth in the postremediation care plan are met, the engineering controls are no longer needed, and it can be documented by fate and transport analysis that the standard will not be exceeded in the future.

**6. Postremediation Care Attainment**

Remediators can end postremediation care if they can demonstrate through a documented fate and transport analysis that the selected standard(s) will be met, and will continue to be met in the future, after removal of engineering controls. An amendment to the postremediation care plan shall be submitted for approval by the Department. The postremediation care plan shall be amended whenever changes in operating plans or facility design, or events that occur during postremediation care, affect the currently approved postremediation care plan.

## **F. One Cleanup Program**

In March 2004, PA DEP and EPA Region 3 entered into a Memorandum of Agreement (MOA) that outlines a procedure where sites remediated according to the LRP may also satisfy requirements of several federal laws: the Resource Conservation and Recovery Act (RCRA) (42 U.S.C. § 6901, et seq.), the Comprehensive Environmental Response Compensation Liability Act (CERCLA) (42 U.S.C § 9601, et seq.), and the Toxic Substances Control Act (TSCA) (15 U.S.C. § 2601, et seq.).

### **1. Purpose**

DEP and EPA sought to promote the One Cleanup Program initiative by working together to achieve cleanups that protect human health and the environment by making greater use of all available authorities and selecting the optimum programmatic tools to increase the pace, effectiveness, efficiency, and quality of cleanups. In effect, entering into the One Cleanup Program can provide a remediator with a “one-stop shop” for state and federal standards guiding the cleanup of brownfield sites.

### **2. Provisions and Applicability**

EPA has reviewed and evaluated the LRP and has determined that the LRP, as implemented under the MOA, includes each of the four elements of a state response program listed in CERCLA Section 128(a)(2):

- Timely survey and inventory of brownfield properties.
- Oversight and enforcement authorities adequate to ensure that a response action will protect human health and the environment.
- Mechanisms and resources to provide meaningful opportunities for public participation.
- Mechanisms for approval and a requirement for verification and certification that the response activity is complete.

The One Cleanup Program applies only to remediation of properties conducted pursuant to Act 2 provisions. As determined by PA DEP and USEPA, the following properties are not eligible to enter in the program:

- Permitted hazardous waste management units.
- Properties proposed in the Federal Register to be placed on the National Priorities List.
- Properties that have been placed on the National Priorities List.
- Properties that have been permitted under the SWMA and the PA Clean Streams Law for which cleanup standards are different than those of the LRP.

### **3. Implementation**

Under the MOA, DEP and EPA have agreed to work in a coordinated manner to avoid possible duplication of efforts at properties, while ensuring that remediation of properties continues in a timely fashion. DEP will notify EPA when properties are being addressed under the LRP via written documentation for properties in Comprehensive Environmental Response, Compensation and Liability Information System (CERCLIS) that are being addressed under the LRP.

Participation in the One Cleanup Program entails some additional notification and public involvement requirements upon submittal of the NIR and cleanup plan (see Section II.A.3(a)).

For all RCRA Corrective Action Facilities being remediated under the LRP, the remediator will provide EPA with copies of reports. DEP and EPA will work in teams to accomplish cleanup goals in an appropriate and efficient use of both agencies' resources. EPA will review reports submitted to DEP under the LRP to determine if the site data meets RCRA Corrective Action obligations. If EPA determines that the site characterization or final decision is not sufficient to characterize the nature and extent of contamination, the EPA and DEP intend to work together to resolve the matter. If EPA determines the proposed cleanup objectives and corrective measures are sufficient, EPA plans to proceed with remedy selection procedures, including providing opportunity for public comment and review. Once the remedy is implemented and EPA determines that the media cleanup measures are met and corrective measures are satisfied, EPA will, where appropriate, acknowledge that the remediator has completed its Corrective Action obligations.

RCRA facilities enrolled in the One Cleanup Program may be subject to UECA requirements (Section III.E.2 of this TGM). As such, a model covenant for any activity and use limitations which may be in effect for these facilities is located on the DEP website on the 'One Cleanup Program' webpage.

### **4. Benefits**

In summary, by entering into the One Cleanup Program, site owners or operators may be able to satisfy federal RCRA obligations and obtain liability relief under the Act 2 program. Interested parties can review the historic MOA, RCRA Corrective Action Baseline Facilities that have entered the One Cleanup Program, and other useful information on the PA DEP website on the One Cleanup Program tab.

Any owner, operator, or remediator interested in entering the One Cleanup Program should consult with their assigned DEP Project Officer about opportunities and eligibility requirements.

## **G. Data Quality and Practical Quantitation Limits**

### **1. Data Quality Objectives Process, Sampling, and Data Quality Assessment Process**

An important issue regarding sampling and statistical analysis is the quality assurance (QA) management considerations associated with these activities. Steps for the QA management process, in general, can be divided into three phases: planning, implementation and assessment. During the planning phase, a sampling and analysis plan is developed based on Data Quality Objectives (DQO). The implementation phase includes sampling execution and sample analysis. The assessment phase includes Data Quality Assessment (DQA) (See 25 Pa. Code § 250.702(a)).

To help remediators design scientific and resource-effective sampling programs, EPA provides guidance on developing DQO (EPA 1993). The DQO process allows a person to define the data requirements and acceptable levels of decision errors, before any data are collected. The DQO process should be considered in developing the sampling and analysis plan, including the QA plan.

As stated in the EPA guidance (EPA 1993), the DQO process includes the following seven steps:

- State the problem.
- Identify the decision.
- Identify inputs to the decision.
- Define the spatial and temporal boundaries of the decision.
- Develop a decision rule.
- Specify limits on decision errors.
- Optimize the design for obtaining data.

Step 4 of the DQO process, defining the spatial and temporal boundaries of the decision, is particularly important, because it prevents pooling and averaging data in a way that could mask potentially useful information. Activities in this step include:

- Define the domain or geographic area within which all decisions must apply. Some examples are property boundaries, operable units, and exposure areas.
- Specify the characteristics that define the population of interest. Identification of multiple areas of concern—each with its own set of samples and descriptive statistics—will help to reduce the total variability if the areas of concern (AOCs) are defined so that they are very different in their contaminant concentration profiles. For example, the top 2 feet of soil are defined as surface soil. Another example is to define contaminated soil that has been impacted by SPL as SPL-impacted soil.

- When appropriate, divide the population into strata that have relatively homogeneous characteristics. This helps to reduce the variability in each data set.
- Define the scale of decision making. The scale of decision making is the smallest area, volume, or time frame of the media in which decision errors are to be controlled. This is also the unit that will be assumed to generate a “statistical unit” of possible measurements which allows the assessment and control of decision errors. Examples are remediation units, exposure units, and hot spots.
- Determine the time frame to which the study data apply. It may not be possible to collect data over the full time period to which the decision will apply. Therefore, a decision should be made regarding the most appropriate time frame that the data should reflect.
- Determine when to collect samples. Conditions at the site may vary due to seasons, weather or other factors. Therefore, a decision should be made regarding the most appropriate time period to collect data that will reflect the conditions that are of interest.
- Identify any practical constraints on data collection, such as seasonal or meteorological conditions, unavailability of personnel, time, or equipment.

At the completion of the DQO process, information obtained from the DQO process can be used to develop a sampling and analysis plan, including a QA/QC plan.

After the environmental data have been collected and validated in accordance with the sampling and analysis plan (including the QA/QC plan), data must be assessed to determine whether the DQOs are met. This is the DQA process. EPA has developed guidance on DQA (EPA, 1996).

The DQA process involves the following five steps (EPA, 1996):

- Review the DQOs and sampling design.
- Conduct a preliminary data review.
- Select the statistical test.
- Verify the underlying assumptions of the statistical test.
- Perform the statistical hypothesis test and draw conclusions that address the data user’s objectives.

A properly implemented DQA process can help to determine if planning objectives were achieved. The discussions in the statistics Section (III.B) will address key statistical issues that are pertinent to Act 2 and are encountered during these DQO and DQA processes.

## 2. Preliminary Data Review

Preliminary data review should be performed whenever data are used. By reviewing the data both numerically and graphically, one can learn the “structure” of the data and identify limitations for using the data. Graphical methods include histograms, probability plots, box charts, and time-series plots to visually review the data for trends or patterns. Calculations of summary statistics are typically done to characterize the data and make judgments on the central tendencies, symmetry, presence of outliers, etc. These statistical methods are defined and explained in more detail in the statistical section of this guidance. (Section III.B)

Chemical concentrations should initially be compared to laboratory blank concentrations. If the blank samples contain detectable levels of common laboratory contaminants, then the sample results should be considered as positive results only if the concentrations in the sample exceed 10 times the maximum amount detected in the blank. If the concentration is less than 10 times the blank contaminant level, it is concluded that the chemical was not detected in the sample and the blank-related chemical concentration is considered to be the quantitation limit for the chemical in that sample. If all samples contain levels of a common laboratory contaminant that are less than 10 times the level of contamination noted in the blank, then completely eliminate that chemical from the set of sample results. Some common laboratory contaminants include acetone, 2-butanone (methyl ethyl ketone), methylene chloride, toluene, and phthalate esters. This evaluation is typically done during the laboratory data review process and anything that meets the criteria to be included in data evaluation will typically be marked with a “B” qualifier. The “B” flag is placed on data that is considered valid but could be affected by the presence of the same compound in the blank sample.

If the blank samples contain constituents other than common laboratory contaminants, then the sample results should be considered as positive results only if the concentrations in the sample exceed five times the maximum amount detected in any laboratory blank. As with the common laboratory contaminants, if the concentration is less than five times the blank constituent level, it is concluded that the constituent was not detected in the sample and the blank-related chemical concentration is considered to be the quantitation limit for the chemical in that sample. Again, if all samples contain levels of a constituent other than common laboratory contaminants that are less than five times the level of contamination noted in the blank, then completely eliminate that chemical from the set of sample results. As with common laboratory contaminants, this evaluation is typically done during the laboratory data review process, and anything that meets the criteria to be included in data evaluation will typically be marked with a “B” qualifier.

The details describing the five and 10 times the blank concentration evaluation is described in many EPA laboratory methods.

## 3. Practical Quantitation Limit (25 Pa. Code § 250.4)

Practical quantitation limit (PQL), as defined in Act 2 (35 P.S. § 6026.103), is the lowest limit that can be reliably achieved under normal laboratory conditions. Many of the SW-846 (EPA’s hazardous waste test methods) analysis methods previously listed

estimated quantitation limits (EQL) or method detection limits (MDL) to ensure that laboratories were providing the data required to meet the needs of the data-user. However, as technology has improved, the need to define a minimum value to be reached has been reduced. The EQL was the limit set at the time the method was written as an estimated value that could be detected using the given method. MDL is a value that is calculated using statistics on laboratory data to provide the lowest value that can be detected. The MDL is instrument-specific.

Some laboratory methods do continue to list EQL and/or MDL values; however, most laboratories can now consistently achieve reporting limits (RL) or limits of quantitation (LOQ) that are much lower than the EQL or MDL values defined in the method. These RLs and LOQs are the lowest value that can be reliably quantified given a specific method. Detections that fall between the RL and the MDL are “J” values. This indicates that it is above the level that the instrument can reliably identify (MDL), but is below the value that can be reliably quantified (RL) and is an estimate. “J”-flagged values are valid data and can be used for screening, etc.

For the purposes of Act 2, if a laboratory’s RL value is above a constituent’s corresponding MSC value due to a technological issue, remediators should contact their regional project officer to discuss how to proceed. It is important to note that PQL values should not be used for screening data (e.g. for a risk assessment or a VI evaluation) and only apply for the purposes of attaining the standard.

## **H. Site-Specific Human Health Risk Assessment Guidance**

### **1. Introduction**

This Section provides general guidelines on the methodology of risk assessment and the risk assessment report for human health evaluation under Act 2. Regulations regarding risk assessment are in Chapter 250, Subchapter F. This section of the guidance document does not address issues related to ecological risk assessment. Ecological risk assessment is addressed in Section III.I.

Prior to performing a risk assessment, it is important to clearly define the problem that is to be addressed, the objectives of the study, and how the results will be used to meet these objectives. This initial step is critical to ensure a successful outcome (accurate, protective, timely, cost-effective evaluation) and that the level of effort is commensurate with the scope of the problem.

Risk assessment procedures have been well defined in various EPA guidance documents. The process does not need to be reiterated in this document. Instead, certain key issues pertinent to site-specific evaluations under Act 2 are discussed subsequently.

For risk assessment issues not directly addressed in this document, remediators may consult the most recent EPA and ASTM guidelines, such as those listed on Table III-11, for additional guidance. For petroleum release sites, the risk assessment methodology in ASTM E 1739-95 (2015) (Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites) may be consulted for further guidance.

A suggested outline for the risk assessment report is provided in Section II.B.3(g)(v) of this manual. The outline is intended to provide guidance on minimum requirements for the report.

### **2. When to Perform a Risk Assessment**

Remediators selecting the site-specific standard established by Section 304 of Act 2 (35 P.S. § 6026.304) should submit a risk assessment report to the Department for review and approval unless no present or future complete exposure pathways exist as demonstrated in the fate and transport analysis in the site-specific remedial investigation. The exposure scenarios (e.g., residential, industrial, recreational), which will define the exposure pathways, must be based on site-specific land use considerations (see 35 P.S. §§ 6026.301(a)(3) and 6026.304(1)(2)). The pathways, which describe the mechanism by which receptors may be exposed to a source, are also site-specific. Detailed guidance on land use determination and identification of exposure scenarios and pathways are addressed in Section III.H.3(b)(i) of this document and references cited therein. A risk assessment only needs to be performed if complete exposure pathways for human receptors exist under current or potential future conditions. If engineering or institutional controls that are to be implemented will eliminate all exposure pathways, a risk assessment report is not required (see 25 Pa. Code § 250.405(b)).

A baseline risk assessment report is not required if the Department, in its remedial investigation report or cleanup plan approval, determines that a specific remedial

alternative that eliminates all pathways, other than a no-action remedial alternative, can be implemented to attain the site-specific standard (25 Pa. Code § 250.405(c)). A baseline risk assessment is an evaluation of risk prior to, or in the absence of, a remedial measure. When the remedial measure has been completed, a residual risk assessment that evaluates risks posed by postremediation contamination, if present, is required in order to demonstrate attainment of the site-specific standard.

### **3. Risk Assessment for Human Health (25 Pa. Code § 250.602(c))**

A risk assessment for human exposure from contaminated sites consists of the following four steps:

- (1) Site characterization
- (2) Exposure assessment
- (3) Toxicity assessment
- (4) Risk characterization that evaluates if the risks meet the human health protection goals specified in Subsections 304(b) and (c) of Act 2.

The following discussions address key issues pertinent to these four steps of risk assessment for human exposure:

#### **a) Site Characterization [§ 250.602(c)(1)]**

##### **i) Chemicals of Concern**

The initial steps of the site characterization are to review the analytical data and to select the chemicals of concern that are identified in distinct areas of contamination at the site. Under Act 2 there are two possible situations in determining the chemicals of concern in a baseline risk assessment under the site-specific standard: (1) strictly using the site-specific standard, or (2) a combination of standards using site-specific and Statewide health, site-specific and background, or all three standards. These situations are discussed separately below.

In the first situation of using only the site-specific standard, the chemicals of concern can be screened using the EPA Regional Screening Level (RSL) screening procedures. The purpose of this screening procedure is only for potential reduction of the number of chemicals carried through the risk assessment. Those chemicals on the site whose maximum concentration exceeds the RSL values for carcinogenic effects ( $10^{-6}$ ) or the RSL values (HQ=0.1) for noncarcinogenic effects should be retained in the risk assessment. Chemicals on the site at maximum concentration below the RSL values for carcinogenic effects or the RSL values for noncarcinogenic effects may be dropped from the risk assessment unless other contaminant-specific or site-specific considerations suggest that the inclusion of these constituents in the risk assessment is more appropriate

to determine the total risk of the site. Chemicals that are not retained in the risk assessment may be considered having minimal influence on total risk. (Note that it is not permissible under the SSS to perform screening using SHS MSCs.)

The second situation uses a combination of the site-specific standard with one or both of the other two standards. The chemicals of concern to be addressed in the risk assessment should include those chemicals that cannot be addressed using either the SHS or the background standard. The chemicals of concern identified for evaluation in the risk assessment may then be screened using the same RSL screening procedures mentioned above.

Three other factors should be considered when deciding to retain constituents for the risk assessment. Specifically, these factors include the constituent's toxicity, mobility and persistence. Toxicity is a driving force when determining if exposure to a site poses any adverse impact to human health or the environment. Some constituents may be frequently detected at a site, but may be considered relatively innocuous or toxicologically inert. These constituents should not be retained for the risk assessment. In contrast, some constituents may be infrequently detected, but may be relatively more toxic than most constituents. Regardless of the constituent's frequency of detection, its presence (assuming it is not anomalous) may deem it necessary to be retained as a constituent of concern.

The mobility of a constituent dictates what receptors on and off site may be potentially affected and consequently whether the constituent should be retained in the assessment. Physical and chemical properties of a compound control its transport and fate in the environment. For example, these attributes determine whether a constituent will readily volatilize into the air or be transported via advection or diffusion through the soil, groundwater and surface water. These characteristics also describe a chemical's tendency to adsorb onto soil/sediment particles, in turn altering its mobility through the environment.

Finally, the persistence of a chemical in the environment determines whether further receptors would be impacted. The persistence of a chemical in the environment depends on factors such as microbial content of soil and water and the ability of these organisms to degrade the chemical. In addition, chemical and photochemical degradation may contribute to the elimination of a particular compound. Although the parent compound may be eliminated, the byproducts of the degradation of that compound must also be considered and evaluated. These chemical-specific factors will also be used to determine whether a constituent and its byproducts are retained for the risk assessment.

In general, liability protection is not afforded under the site-specific standard for those chemicals that are not identified as contamination at a site and for which attainment has not been demonstrated.

**ii) Conceptual Site Model**

Development of a conceptual site model is an important step in identifying additional data needs in site characterization and in defining exposure. A conceptual site model identifies all potential or suspected sources of contamination, types and concentrations of contaminants detected at the site, potentially contaminated media, potential exposure pathways and receptors. Many components of exposure (such as the source, receptors, migration pathways and routes of exposure) are determined on a site-specific basis. The conceptual site model provides a systematic way to identify and summarize this information to ensure that potential exposures at the site are accounted for accurately.

The conceptual site model may be graphical, tabular or narrative but should provide an accurate understanding of complete exposure pathways for the site. Examples of conceptual site models may be found in EPA, ITRC, or ASTM guidance documents. It is recommended that the development of the conceptual site model be coordinated with the regional project officer to ensure that potential pathways and receptors are adequately and appropriately addressed prior to performing the assessment.

**b) Exposure Assessment [§§ 250.603 and 250.604]**

The exposure assessment determines or estimates (qualitatively or quantitatively) the magnitude, frequency, duration and routes of exposure. The assessment is typically performed in three steps:

- (1) Characterization of the exposure setting including:
  - the physical setting
  - potential exposed populations
- (2) Identification of complete exposure pathways which includes:
  - sources and receiving media
  - fate and transport in the release media
  - exposure points and exposure routes

The information on sources, fate and transport (including biodegradation), exposure points and exposure routes are then integrated to determine the potential

exposure pathways. Complete pathways exist when all components are present. Information for complete pathways should be summarized.

(3) Quantification of exposure of the receptor including:

- environmental concentration
- intake

The exposure assessment process is well defined in various guidance documents, as cited in Section III.H.4, and is not reiterated here. This section discusses some key issues pertaining to performing the site-specific exposure assessments.

**i) Exposure Scenarios and Exposure Pathways**

Exposure Pathways: The exposure pathway describes the mechanism by which receptors (individuals, populations, and ecological receptors) may be exposed to the source. Pathways consist of a source, receptor, route of exposure and a transport mechanism, if the exposure point is not the same as the source. The analysis of the fate and transport of the chemical can help to predict future exposures, to link sources with currently contaminated media, and to identify exposure pathways. The intent of the fate and transport analysis at this stage is to identify media that are receiving or may receive site-related chemicals. Further guidance on fate and transport analysis can be found in Section III.A of this guidance document.

As discussed above, the conceptual site model is useful in defining potential exposure pathways. However, only complete pathways should be advanced through the assessment process. The effects of engineering or institutional controls that are to be implemented, which will eliminate exposure pathways, must be considered for the conceptual model development. The EPA provides guidance referenced in Section III.H.4 of this manual on potential pathways for given land use scenarios.

Realistic current and future land use scenarios (e.g., residential, industrial, agricultural, etc.) provide the basis for selecting the controlling exposure scenarios/pathways. Guidance on land use considerations can be found in the EPA OSWER Directive: *Land Use in The CERCLA Remedy Selection Process* (1995) as well as earlier EPA guidance on exposure assessments as referenced above. Sources and types of information that may aid in determining the reasonably anticipated future land use include, but are not limited to:

- Current land use.
- Zoning laws.
- Zoning maps.

- Comprehensive community master plans.
- Local land use authorities.
- Local officials.
- Population growth patterns and Bureau of Census projections.
- Accessibility of site to existing infrastructure (such as transportation and public utilities).
- Institutional controls currently in place.
- Site location in relation to urban, residential, commercial, industrial, agricultural and recreational areas.
- Federal/State land use designation (such as state parks).
- Historical or recent development patterns.
- Cultural factors (such as historical sites).
- Natural resources information.
- Stakeholder input - allows for all affected parties to define land use.
- Location of onsite or nearby wetlands.
- Proximity of site to a floodplain.
- Proximity of site to critical habitats of endangered or threatened species.
- Geographic and geologic information
- Location of wellhead protection areas, recharge areas, and other areas identified in the state's Comprehensive Groundwater Protection Program.

These types of information should be considered when developing the assumptions about future land use.

Some direct pathways, such as direct ingestion of soil or groundwater and direct inhalation of volatiles and/or particulates from soil, are fairly well established and can be used routinely where they have been identified as complete pathways. At issue would be defining appropriate exposure

factors (such as intake rate for the given population) since these factors exhibit a range of possible values. Typically, the choice of factors (high-end exposure vs. average exposure) is defined by the level of conservatism desired.

Dermal contact (with soil or groundwater), on the other hand, is less well defined, particularly in terms of estimating intake (the mass of substance in contact with the body per unit body weight per unit time) and, more importantly, absorbed dose (intake multiplied by an absorption factor to account for mass actually in the body). This pathway is best addressed at a site-specific level when identified as relevant. Although there is some guidance (EPA, 1991c), professional judgment may play a significant role in estimating dermal exposure. The rationale behind these judgments (and indeed professional judgments wherever they are used) and, as far as possible, documented evidence in support of these judgments should be clearly provided.

Some indirect pathways are also best addressed on a site-specific basis because of the inherent uncertainty associated with defining the transport from the source to the receptor. In the case of vapor intrusion into a trench, for example, actual data from direct measurements, i.e., a monitoring approach, would be preferred to the use of models which have been shown to be imprecise. Vapor intrusion into an enclosed space is discussed in detail in Section IV of this manual.

Other indirect pathways (e.g., soil leaching to groundwater and subsequent ingestion of groundwater) can be addressed by simple analytical models. Although site-specific data inputs to these models are typically favored as producing a more realistic estimate of exposure, site-specific data may not be accessible. The use of a combination of default and site-specific parameters may be used provided the rationale for the choice of values is included.

Receptors and Human Exposure Factors: Receptors should be defined on a site-specific basis taking into account future land use considerations. Guidance on potential receptors for given land use are provided in EPA guidances (EPA 1989a, 1991a,b). Care should be taken to identify potential sensitive subpopulations (e.g., children) as appropriate for site-specific conditions.

Section 250.603 of the regulations specifies requirements to select exposure factors. A risk assessment may use site-specific exposure factors in accordance with EPA's Final Guidelines for Exposure Assessment, 1992 (57 FR 22888-22938) or exposure factors used in the development of the SHSs identified in Subchapter C of the regulations. Site-specific exposure factors shall be clearly justified by supporting data (see 25 Pa. Code § 25.603(b)).

Human exposure factors may be divided into receptor physiologic parameters (e.g., body weight, skin surface area); contact rate (e.g., consumption of water, soil ingestion rate); and time activity patterns (e.g., time spent indoors/outdoors, time spent at work). Some of these variables, particularly the physiologic parameters, have been well characterized but others such as time/activity patterns are less well documented. All parameters are subject to variability (true heterogeneity) and/or uncertainty (ignorance about a measurement). Thus, a range of values may be available for any given parameter. The choice will depend to some extent on the problem and the level of conservatism desired. Typical sources for these parameters are the EPA Exposure Factors Handbook (2011) and the American Industrial Health Council (AIHC) Exposure Factors Sourcebook (AIHC, 1994).

Fate and Transport Parameters and Models: Constituents of concern can both migrate (via leaching, advection, dispersion) and transform (via biodegradation, hydrolysis, photolysis) in the environment. These migration and transformation processes must be considered when determining environmental concentration under indirect exposure (see 25 Pa. Code §§ 250.204(a), 250.312(a), 205.408(a)). A range of fate and transport models (from simple analytical to complex numerical) are available to account for these processes. However, the level of site-specific data needed to make proper use of the models also increases with the level of sophistication of the model (i.e., the increase of model technical capabilities). A tiered approach, based on level of model complexity, is best, i.e., using the least resource intensive method to achieve the objective of the evaluation. The selected model should adequately represent the physical setting (e.g., the geometric configuration of hydrogeological systems, soil profiles, river widths and depths, etc.) and migration and transformation processes that affect the problem. Input parameter values should be representative of field conditions. The choice of model and input parameters will need to be justified as appropriate for given site-specific conditions. Justifications should include why a model is appropriate when limitations of the selected model are considered. In addition, some measure of model validation may be required. This may be as simple as corroborating the conservative assumptions with field measurements. For guidance on selection of groundwater models refer to Section III.A of this manual.

The use of monitoring methods may also be appropriate for defining environmental fate, as in the case of natural attenuation. All supporting data should be provided to support such an evaluation. For specific guidance regarding the use of monitoring methods, check EPA, ITRC, and other references listed in III.H.3(f).

Generic vs. Site-Specific Considerations: In general, risk assessments should be based upon realistic exposure scenarios using current or planned future land use, incorporating any changes from early response actions known or planned. Site-specific information on exposure pathways,

receptors and exposure factors, including actual data, should be used to the maximum extent possible.

However, not all exposure parameters need to be site-specific. Certain generic human physical parameters (e.g., body weight) that do not vary significantly in the general human population, and thus from site to site, are such exceptions. Default values, from single point estimates to distributions for these parameters, are available from such sources as the EPA Exposure Factors Handbook (EPA, 2011) and the AIHC Exposure Factors Sourcebook (AIHC, 1994). Default values of single point estimates for these parameters are also available from Subchapter C of the regulations.

Factors affecting the choice of exposure scenario (land use), complete exposure pathways, the distribution of contaminants in the media, the characteristics of the media, and the activity patterns and demographics of the surrounding populations should be considered, whenever possible, as site-specific. For example, if the planned future land use is industrial, the appropriate population would be adults and default physiological information may be obtained from the above named sources. However, if the concern is for a residential land use, children may be the population of concern. Default physiological information is still available from the above sources but the actual values would be different because the site-specific considerations dictate a different land use and receptor population.

It is possible that a sensitive subpopulation may be of concern (e.g., pregnant women, subsistence fishermen) in certain situations. Some data for these populations may be available from national or regional surveys incorporated in the above sources, but in some instances the data may need to be generated. The choice of data should be supported in the peer review literature and proved to be appropriately applied. For information generated on a site-specific basis, proper QA/QC measures should be exercised and the data should be generated with the understanding of the regulatory agency as to how the information will be used.

## ii) **Exposure Characterization**

Exposure characterization is the quantification step in the process. In the forward calculation of risk, both the environmental concentration and the intake must be determined. In the reverse calculation of site-specific standards, an acceptable concentration is derived based on intake and a predetermined level of risk.

Exposure Point Concentration: This is the concentration expected to be contacted over the exposure period. Since risk assessments are typically performed for a chronic exposure scenario, i.e., the contact period is long (typically 30-70 years), an upper confidence limit on the mean is used. It is important, therefore, to assess the potential fate of the material in the environment to provide the best estimate of its environmental

concentration over time. In some instances, short-term exposure is to be evaluated, in which case some other metric (e.g., maximum concentration) may be more appropriate. EPA OSWER Directive 9285.7-081 provides guidance on the concentration term.

Intake: Three types of variables are associated with defining intake: chemical related variables, i.e., the concentration term and its associated fate and transport parameters; variables that describe the exposed population such as physiologic parameters, contact rate and time/activity patterns; and an assessment-determined variable, i.e., the period over which the exposure is averaged.

Since most exposure factors exhibit both variability and uncertainty, EPA encourages the development of a range of exposure (and risk) descriptors. The use of probabilistic analysis (such as Monte Carlo simulations) is one way to account for variability and uncertainty. However, these evaluations are resource intensive and may be inappropriate for simple sites. Deterministic evaluations, i.e., point estimates, are useful alternatives. If single point estimates are developed, it is recommended that a most likely exposure (MLE) be quantified in addition to the typical high-end exposure (comparable to the reasonable maximum exposure or RME used in the generation of the SHSs). In this way, a range of exposures can be provided as context for risk management decisions. Thus, even within the site-specific evaluation, a tiered approach may be useful (i.e., from point estimates to ranges) depending on the level of sophistication required to address the problem at hand.

### iii) **Good Exposure Assessment Practices**

As a fundamental practice, the methods and data used in the exposure assessment should clearly support the conclusions within the known and stated bounds of uncertainty. Documentation is a core principle of a good exposure assessment. Hawkins, Jaycock and Lynch (1992) provided eight general practices that make for good exposure assessments. Burmaster and Anderson (1994) further defined good practice as it relates to probabilistic assessments. It is suggested that exposure assessments be consistent with these practices as appropriate.

### c) **Toxicity Assessment [Section 250.605]**

The purpose of toxicity assessment is to collect and weigh the available evidence regarding the potential for particular contaminants to cause adverse effects in exposed individuals and to provide an estimate of the relationship between the extent of exposure to a contaminant and the increase likelihood and/or severity of adverse effects.

The carcinogenic and noncarcinogenic (systemic) effects of each chemical of concern at the site should be evaluated.

For toxicity assessment, the person should use appropriate toxicity values from one of the following sources, in the order indicated:

- i) Integrated Risk Information System (IRIS)/Office of Pesticide Programs (OPP) Human Health Benchmarks for Pesticides;
- ii) United States Environmental Protection Agency, National Center for Environmental Assessment (NCEA) Provisional Peer-Reviewed Toxicity Values (PPRTV).
- iii) Other sources
  - (a) Health Effects Assessment Summary Tables (HEAST)
  - (b) Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles.
  - (c) California EPA, California Cancer Potency Factors and Chronic Reference Exposure Levels.
  - (d) EPA criteria documents, including drinking water criteria documents, drinking water health advisory summaries, ambient water quality criteria documents and air quality criteria documents.

If no toxicity values are available from the sources identified above, the person may develop, for the Department's review in the risk assessment report, toxicity values from appropriately justified surrogates or chemical-specific toxicity values with consideration of the following:

- Available data should first be evaluated to determine the likelihood that the agent is a carcinogen. If the chemical is determined to be likely or possibly a human carcinogen, then a toxicity value (slope factor) should be calculated based on the most recent and available information from peer reviewed journals. EPA has developed its most recent approach for defining carcinogens and developing slope factors in the Proposed Guidelines for Carcinogen Risk Assessment (EPA, 1996b). This approach should be applied when determining whether a chemical is a carcinogen and determining its slope factors.
- A toxicity factor should also be developed for the potential noncarcinogenic effects based on the most recent and available information from peer reviewed journals. A reference dose is the toxicity value used most often in evaluating noncarcinogenic effects. EPA's Risk Assessment Guidance for Superfund describes the protocol for developing reference doses. Depending on the exposure duration anticipated at the site, a chronic reference dose would be developed for exposure expected to last 7 to 70 years; a subchronic reference dose would be calculated for exposure less than 7 years (EPA, 1989a).

- The toxicity value must be based on peer reviewed literature that includes all relevant sources of data and must be a balanced description of both positive and negative findings on the toxicity of the chemical, the weight of evidence supporting the toxicity value, and the main sources of uncertainty of the toxicity value documented in the risk assessment report's uncertainty section.

The toxicity of lead is not easily defined by the above approach. EPA has developed the Integrated Exposure Uptake Biokinetic (IEUBK) Model to determine cleanup numbers for children exposed to lead in soil under a residential exposure scenario. For adult exposure in either the residential or nonresidential scenario, the IEUBK model does not apply and other models, such as EPA's adult lead model, have been developed to determine the effects of lead on adults and pregnant women. This model or others, as appropriate, may be used to determine site-specific cleanup numbers.

**d) Risk Characterization**

The risk characterization section summarizes the toxicity and exposure assessments into either a quantitative estimate of risk or the development of cleanup concentrations, if needed, for each of the chemicals of concern at the site. The objectives of the risk assessment that were described in the introductory paragraphs of this section should again be defined, and a description of how the results of the report meet those objectives should be provided. The report should exemplify the values of clarity, transparency, reasonableness and consistency as stated in the Policy for Risk Characterization at the Environmental Protection Agency (EPA, 1995b).

The conceptual model for the site should be described and, for each complete pathway, the total cancer risk and non-cancer hazard quotient should be defined. In addition, a cleanup concentration for that pathway should be determined if necessary. In developing cleanup numbers for the site, cumulative excess risk (across all exposure pathways and all chemicals of concern) to exposed populations, including sensitive subgroups, shall not be greater than 1 in 10,000 for known or suspected carcinogens. The risks associated with carcinogens should be cumulative if the same individuals are exposed to these carcinogens consistently. For noncarcinogens (systemic toxicants), cleanup standards shall represent the level to which an exposed human population could be exposed on a daily basis without appreciable risk of deleterious effect. Where several systemic toxicants affect the same target organ or act by the same method of toxicity, the hazard index shall not exceed one (see 25 Pa. Code § 250.402(b)(2)). The risks associated with systemic toxicants also should be cumulative in the toxicity assessment if these toxicants affect the same target organ or act by the same method of toxicity.

To evaluate the short-term and long-term effectiveness of a selected remedy, both the potential risk associated with implementation of the remedy and the risk associated with exposure to the remediated media must be evaluated. The

algorithms that were defined in the exposure assessment should be used to characterize these potential risks.

The risk characterization associated with short-term effectiveness considers the exposure of workers at the site and the exposure of receptors in the vicinity surrounding the site to migrating media during the implementation of the selected remedy. A comparison of a focused list of remedial alternatives may help predict the risks associated with the implementation of the selected remedy or whether the implementation of alternatives may have any significant impact to human health and the environment.

The risk characterization associated with long-term effectiveness demonstrates whether the selected remedy attains the remedial objectives (site-specific cleanup standards) and whether postremedial risks achieve the acceptable levels of risk. There may be times when a specific cleanup level for one constituent may not be attained, but the overall postremedial risk may be within acceptable levels. Evaluation of the postremedial risk is based on a prediction of what the postremedial exposure concentrations would be. For example, a cap would eliminate exposure to surface soils, rendering the risk from surface soils to be negligible. If bioremediation is considered, the remedial objective would be the concentration that provides the basis for characterization of the postremedial risk. If the calculated postremedial risk is within the acceptable range, the selected remedy would be considered a viable solution.

**e) Uncertainty Analysis**

An often-forgotten component of the risk assessment process is the characterization of uncertainty. Uncertainty represents ignorance (or lack of perfect knowledge) about poorly characterized phenomena or models (Burmester and Anderson, 1994). The concept is important and indeed implicit in the risk-based approach, but it is often ignored in practice. For example, the SHSs are acknowledged to be conservative, and one of the rationales for being conservative is to account for the uncertainty inherent in developing the standards. In the site-specific evaluation, it is recommended that a tiered approach to addressing uncertainty be used. In applying the tiered approach, the level of effort should be commensurate with the magnitude of the decision to be made.

At an initial level, point estimates of exposure and risk (or site-specific standards) may be developed that describe both the high-end individual (RME) and a mid-range individual (MLE). If the level of risk is below the level of regulatory concern, the analysis need go no further. At a minimum a qualitative evaluation of the uncertainty should be included indicating what the most uncertain and most sensitive parameters are and their likely impact on the results. It is important to put in perspective any uncertainties inherent in the toxicity assessment as well as the exposure assessment.

At some middle level of effort, statistical estimates (experimental estimates, population variability, estimation error) should be listed and the impact of these

on the results discussed. A more formal sensitivity analysis may be performed to rank the input parameters on the basis of their contribution to the uncertainty.

At the highest level of effort, methods to quantitatively address variability and uncertainty (including but not limited to probabilistic analysis) should be used to carefully determine the overall precision of the risk estimates as they relate to scenarios, models and inputs.

Probabilistic Analysis: Typically, risk assessments have used a deterministic (single point) approach to estimating risk. However, risk is defined as a probability of injury or damage. Further, exposure-related variables are generally recognized as having a range of possible values. Thus, probabilistic analysis is a useful tool for estimating risk since it can account for both variability and uncertainty.

However, probabilistic analysis is resource intensive and may be inappropriate for simple evaluations. Therefore, it is suggested that probabilistic analysis be used as part of a tiered approach to risk assessment in the site remediation process. Guidance relating to how to perform probabilistic analysis can be found in a number of the references listed in Section III.H.4 including the Burmaster document as well as the EPA Risk Assessment Guidance for Superfund.

If an uncertainty analysis includes Monte Carlo simulations, the person should consider the following guidelines as described in EPA's Guiding Principles for Monte Carlo Analysis (EPA, 1997) to ensure high quality science:

- The purpose and scope of the assessment should be clearly articulated in a "problem formulation" section that includes a full discussion of any highly exposed or highly susceptible subpopulations evaluated (e.g., children, the elderly, etc.). The questions the assessment attempts to answer are to be discussed, and the assessment endpoints should be well defined.
- The methods used for the analysis (including all models used, all data upon which the assessment is based, and all assumptions that have a significant impact upon the results) should be documented and easily located in the report. This documentation should include a discussion of the degree to which the data used are representative of the population under study. Also, this documentation should include the names of the models and software used to generate the analysis. Sufficient information should be provided to allow the results of the analysis to be independently reproduced.
- The results of sensitivity analyses should be presented and discussed in the report. Probabilistic techniques should be applied to the compounds, pathways, and factors of importance to the assessment, as determined by sensitivity analyses or other basic requirements of the assessment.
- The presence or absence of moderate to strong correlations or dependencies between the input variables should be discussed and

accounted for in the analysis, along with the effects these have on the output distribution.

- Information for each input and output distribution should be provided in the report. This includes tabular and graphical representations of the distributions (e.g., probability density function and cumulative distribution function plots) that indicate the location of any point estimates of interest (e.g., mean, median, 95th percentile). The selection of distributions should be explained and justified. For both the input and output distributions, variability and uncertainty should be differentiated where possible.
- The numerical stability of the central tendency and the higher end (i.e., tail) of the output distributions should be presented and discussed.
- Calculations of exposures and risks using deterministic (e.g., point estimate) methods should be reported if possible. Providing these values will allow comparisons between the probabilistic analysis and past or screening level risk assessments. Further, deterministic estimates may be used to answer scenario specific questions and to facilitate risk communication. When comparisons are made, it is important to explain the similarities and differences in the underlying data, assumptions, and models.
- Since fixed exposure assumptions (e.g., exposure duration, body weight) are sometimes embedded in the toxicity metrics (e.g., reference doses, reference concentrations, unit cancer risk factors), the exposure estimates from the probabilistic output distribution are to be aligned with the toxicity metric.

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## **I. Site-Specific Ecological Risk Assessment Guidance**

### **1. Introduction**

The objectives of the site-specific ecological risk procedure are to:

- Evaluate the threat posed by regulated substances to species and habitats of concern through a series of steps which progressively focus the assessment with an emphasis on developing site-specific empirical data and a weight-of-evidence.
- Compile a site-specific weight-of-evidence to determine if a substantial impact has occurred to species or habitats of concern.
- Develop the information necessary to determine what remedial action, if any, could be taken to reduce substantial impacts, if present, without causing greater injury to species or habitats of concern than no further action or less disruptive remedial alternatives.

The Department recommends the use of EPA's interim final guidance on Ecological Risk Assessment Guidance for Superfund (EPA, 1997), with some modification, as the process for designing and conducting site-specific ecological risk assessments. To accommodate the provisions of Act 2, points of emphasis and specific modifications of the EPA process are detailed in this document. In addition, other EPA guidance on ecological risk assessment and specific ASTM standards for ecological risk procedures and methods should be utilized as appropriate to achieve the objectives noted above. This approach contains the same fundamental concepts and components found in the Statewide health ecological screen. However, the Statewide health ecological screen cannot be applied to sites attaining the site-specific standard because that process assumes all of the SHS MSCs have been met. If a site is directed to the site-specific ecological risk assessment process in Step 8 of the Statewide health ecological screen, Steps 3 through 8 of the site-specific ecological risk assessment process as described in Section III.I.2 of this guidance should be applied to the evaluation.

### **2. Ecological Risk Assessment Process**

The EPA ecological risk assessment process is comprised of eight steps. At the end of Steps 2 and 7, the qualified investigators determine whether a substantial impact has resulted from regulated substances. The initial screen (Steps 1 and 2) is necessary for all sites which are to attain the site-specific standard.

#### **a) Step 1 - Fundamental Components**

The following items should be evaluated carefully in the context of site-specific conditions:

- Environmental Setting and Site History.

- An evaluation of wetlands via the wetlands mapping tool (national wetlands inventory, NWI) provided by the US Fish and Wildlife Service may be used to help investigate the environmental setting.
- Remediators may use the Pennsylvania Natural Diversity Inventory (PNDI) Environmental Review Tool to search for habitats and species of concern. The PNDI search tool can be accessed at the Pennsylvania Natural Heritage Program's Pennsylvania Conservation Explorer website.
- Site Visits - evaluate receptors and chemical migration pathways.
- Contaminant Fate and Transport - emphasize gradients of contamination.
- Preliminary Ecotoxicity Evaluation - focus on probable site-specific toxicity mechanisms to species or habitats of concern.
- Preliminary Exposure Pathway Analysis - potential for completed pathways to impact species or habitats of concern.
- Review of similar case studies to assist in the Preliminary Problem Formulation (EPA, 1992; EPA, 1997).
- If any habitats or species of concern are identified; separate areas of concern shall be distinguished where relatively distinct risk scenarios are apparent. These areas of concern should be based on an evaluation of distribution patterns of regulated chemicals, habitat changes along contaminant migration pathways, and changes in species of concern across a site.
- Choose a limited number of species or habitats of concern for assessment endpoints (EPA, 1992; Suter, 1993; EPA, 1997).

**b) Step 2 - Preliminary Exposure Estimate and Risk Assessment**

If complete exposure pathways are identified, the regulated party has the option to evaluate the exposure and risk to selected assessment endpoints (Step 1) by either:

- Community-based analysis such as Rapid Bioassessment Protocols for fish or aquatic macroinvertebrates (EPA, 1989) or
- Hazard Quotient Method (EPA, 1997) with emphasis on representative exposure conditions and toxicity data that most directly relate to the assessment endpoints selected in Step 1. Refer to the EPA website for the Region 3 BTAG (Biological Technical Assistance Group) screening tables and the SSL (Soil Screening Levels) tables, as well as the NOAA website for the SQUIRT (Screening Quick Reference Tables) ecological screening values.

In addition, the uncertainty associated with either of these approaches should be discussed.

**i) Decision Point**

It is important that the qualified investigator understand that the Scientific/Management Decision made at the end of the preliminary risk calculation will not set a clean-up goal. Instead, one of the following will be decided:

- The ecological risk assessment should be continued to develop a site-specific clean-up goal, or to reduce uncertainty in the evaluation of risk and impact;
- The preliminary screening is adequate to determine that no substantial ecological risk exists; or
- There is substantial impact (de manifestis) and proceed to remediation that can eliminate or reduce exposure to an acceptable level (Suter, et al., 1995).

All steps are the same from this point whether the site started with the Statewide Ecological Screen or Steps 1 and 2 of this process (flow chart, Figure III-11). The qualified investigator shall follow the steps of the EPA Guidance but take into account factors noted below which shall be emphasized in Pennsylvania under Act 2.

**c) Step 3 - Problem Formulation: Assessment Endpoint Selection and Testable Hypotheses**

Identify Constituents of Potential Ecological Concern (CPECs) with particular emphasis on Table 8 in Appendix A of the regulations.

Further develop Assessment Endpoints that shall be based on evaluation of keystone species and ecological dominants that influence the ecosystem's structure and function as they relate to species or habitats of concern (EPA, 1992; Suter, 1993; EPA, 1997).

The conclusion of this step should integrate the available information into a determination of which exposure pathways are most likely to result in a substantial ecological impact (see Statewide Ecological Screen for discussion) to habitats or species of concern. Only these prioritized pathways are evaluated in detail in the following steps of the process. All hypotheses should be focused on the prioritized pathways and selected assessment endpoints.

**d) Step 4 - Problem Formulation: Conceptual Site Model, Measurement Endpoint Selection, and Study Design**

The focus in this step should be on the prioritized exposure pathways identified in Step 3, emphasizing development of a study design which will determine if there is a causal relationship between a regulated substance and any substantial ecological impact that may be detected at a site.

Regarding bioaccumulation and tissue studies, the regulated party has the option of:

- Utilizing bioaccumulation factors reported in the literature which are most relevant to habitats or species of concern at the site; or
- Measuring bioaccumulation directly through tissues analysis and environmental media analysis.

Note that bioconcentration or bioaccumulation in and of itself is not evidence of environmental injury or a substantial ecological impact. Tissue levels should be related to a toxicity effect in a species of concern in order to be considered relevant in the evaluation.

Since the habitats and species of concern are readily identified and evaluated through field studies, the investigator should emphasize population/community evaluations over less direct measures of potential impact such as laboratory toxicity testing, literature references, or media chemistry, recognizing that a combination of these evaluations is usually conducted. In addition, laboratory toxicity testing should only be conducted with species that may potentially inhabit or survive at the subject site.

The conclusion of this step should describe the measurement endpoints (EPA, 1992; Suter, 1993; EPA, 1997) for the prioritized exposure pathways and provide a clear outline of the study design.

**e) Step 5 - Site Assessment for Sampling Feasibility**

Ensure that the measurement endpoints are present in sufficient quantity or abundance so that sampling and analysis can be collected across a gradient of contamination and include a representative reference area.<sup>1</sup> If necessary, the measurement endpoints should be modified to ensure the study objectives can be met (EPA, 1997).

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<sup>1</sup> Reference area is defined as an area not contaminated by regulated substances originating on the site and used for comparison to the site (EPA, 1997). In addition, a reference area should be near the site and have similar geochemical, physical, and biological conditions, but be uncontaminated with regulated substances from the subject site (i.e., unimpacted by the site).

**f) Step 6 - Site Investigation**

Only persons qualified and experienced in ecological assessment<sup>2</sup> methods can direct field activities or make modifications of methods in the field.

**g) Step 7 - Risk Characterization**

The chemical data should be presented in a manner which illustrates the contamination gradients at the site and areas of substantial environmental impact distinguished, based on the site-specific weight-of-evidence. Hazard quotients and/or population/community analysis data should be summarized on figures with the analytical data. The uncertainties associated with either of these approaches shall be discussed.

Similar to Step 2 of this process, one of two conclusions shall be reached for the site or separate areas of concern within the site (if applicable, see Step 1), based on the site-specific weight-of-evidence. The conclusion shall be:

- There is no substantial ecological impact; or
- There is a substantial ecological impact, and remediation options shall be evaluated (Step 8).

**h) Step 8 - Risk Management**

Risk management is a balancing of factors (Figure III-11). Consistent with current and intended future use, the risk manager should consider the following in determining whether to remediate or allow natural attenuation processes to complete the recovery:

- Only differences of greater than 20% in the density of species of concern or greater than 50% in the diversity and habitats of concern should be regarded as potentially substantive impacts (Suter, 1993; Suter, et al., 1995).
- Where substantive impacts are determined, an evaluation of the risk reduction and restoration options should be completed, taking into account:
  1. Environmental injury caused by any remedy should not exceed the injury caused by regulated substances;
  2. The primary source of the regulated substance release has been or will be removed or controlled;

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<sup>2</sup> Qualified and experienced means: a certified ecologist or hold a college degree in ecology or environmental sciences or natural resources and at least five years of experience conducting ecological field work and risk assessments.

3. That at many sites, risks to native terrestrial organisms are likely to be low because the current or intended future use is for human activity (such as residential, industrial or commercial land use) and consequently the probability of habitats of concern existing on the site is low;
  4. Natural physical and chemical attenuation mechanisms act on the released regulated compounds resulting in degradation or sequestration and consequent reduced bioavailability of remaining chemical residuals;
  5. The substantial acclimation capacity of natural populations to exposure to low or moderate concentrations of chemical residuals;
  6. That most remedial actions cause substantial injury to areas of concern beyond the toxicological impacts, as well as impacts to previously unimpacted areas along the perimeter of the remediation area; and
  7. That natural systems are self-organizing, and an attempt to manage these processes to produce a particular result requires long-term management, and even then can result in undesirable results.
- Implementation of the selected remedy that will reduce the risks and restore the structure and function of the impacted ecological system to a condition which is capable of sustaining species and habitats of concern without substantial adverse effect from residual regulated substances.
  - Sources of regulated substances will be removed and natural attenuation/acclimation processes in relatively small areas will mitigate impacts naturally to the point that they are no longer substantive.
  - The restoration objective is to return the substantially impacted ecological system to a structure and function which is capable of sustaining species and habitats of concern without adverse effects, consistent with planned future use of the site within a reasonable time frame. The restoration objective is not to return to pre-stressed conditions but something that is similar structurally and functionally.

### **3. References**

EPA. 1989. Rapid Bioassessment Protocols for Use in Streams and Rivers. EPA/444/4-89-001.

EPA. 1992. Framework for Ecological Risk Assessment. EPA/630/R-92/001.

EPA. 1997. Interim Final Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments. EPA-540-R-97-006. PB97-963211.

Risk Assessment Subcommittee. 1996. Ecological Health Evaluation -- Screening Procedure for Sites in Pennsylvania. Submitted to the Science Advisory Board.

Suter, II, G.W. 1993. Ecological Risk Assessment. Lewis Publishers. Ann Arbor, MI.

Suter, II, G.W., B.W. Cornaby, C.T. Haddne, R.N. Hull, M. Stack, and F.A. Zafran. 1995. An Approach for Balancing Health and Ecological Risks at Hazardous Waste Sites. Risk Analysis 15(2)221-231.

Figure III-11: Site-Specific Ecological Risk Assessment Procedure

