SEC	TION IV. GENERAL GUIDANCE	IV-2
A. F	Fate and Transport Analysis	IV-2
1.	Fate and Transport Analysis in the Unsaturated Zone	IV-3
2.	Fate and Transport Analysis in the Saturated Zone	IV-8
3.	Impacts to Surface Water from Diffuse Flow of Contaminated Groundwater	IV-17
В. (	Guidance for Attainment Demonstration with Statistical Methods	IV-41
1.	Introduction	IV-41
2.	Data Quality Objectives Process, Sampling, and Data Quality	
	Assessment Process	IV-42
3.	Preliminary Data Review	IV-44
4.	Statistical Inference and Hypothesis Statements	IV-46
5.	Selection of Statistical Methods	IV-48
6.	Additional Information on Statistical Procedures	IV-58
7.	Calculation of UCL of Mean When the Distribution of the Sampling Mean	
	is Normal	IV-60
8.	Calculation of UCL of Mean of a Lognormal Distribution	IV-61
9.	Procedure and Example for Conducting the Wilcoxon Rank Sum Test	IV-65
10.	Procedure and Example for Conducting the Quantile Test	IV-68
C. I	Mass Calculations	IV-79
1.	Groundwater Mass Calculation	IV-79
2.	Soil Mass Calculation	IV-79
D. F	Postremediation Care	IV-80
1.	Introduction	IV-80
2.	Institutional versus Engineering Controls	IV-80
3.	Postremediation Care Plan	IV-80
4.	Postremediation Monitoring	IV-81
5.	Postremediation Care Attainment	IV-82
E. \$	Storage Tank Program Guidance	IV-86
1.	Corrective Action Process	IV-86
2.	Corrective Action Process Checklist	IV-86
3.	Use of the Short List of Regulated Substances for Releases of	
	Petroleum Products	IV-95
F. F	Practical Quantitation Limits	IV-98
G. S	Site-Specific Human Health Risk Assessment Guidance	IV-114
1.	Introduction	IV-114
2.	Risk Assessment for Human Health	IV-115
н. 9	Site-Specific Ecological Risk Assessment Guidance	IV-138

## SECTION IV. GENERAL 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, 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.

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.*, 10 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 standards.

#### **BACKGROUND STANDARD**

- To justify reduced duration for monitoring of upgradient release.
- To combine 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 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.

Fate and transport analysis or modeling is a necessary part of site characterization and demonstrating attainment of an Act 2 standard. However, the 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.

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 (TCE) 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 (DCE) and vinyl chloride (VC) in wells on its property but 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 the Act 2 regulations as the Statewide health standards, 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 Statewide health standard 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 Act 2 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<sub>oc</sub> 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 <u>Table 5a</u> in Appendix A of the Act 2 regulations or in the scientific literature. For organic compounds not listed in Appendix A of the Act 2 regulations, values can be found in the literature. K<sub>oc</sub> estimation methods (based on other parameters such as aqueous solubility, octanol-water partition coefficient, bioconcentration factor, and molecular structure) are also available in the literature.
- K<sub>d</sub> 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 <u>Table 5b</u> in Appendix A of the Act 2 regulations. Some K<sub>d</sub> values for inorganic contaminants can also be found in the 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). It is also possible to estimate  $K_d$  values for organics 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<sub>soil</sub> in mg/kg-This is the dry weight concentration of 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 Act 2 regulations.
- ρ<sub>b</sub> 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 Act 2 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 topsoils. 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 Act 2 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 Act 2 regulations.

## iii) Additional requirements Depending on type of analytical tool

The simplest unsaturated zone analytical tools are those that estimate contaminant concentrations in unsaturated zone soil pore water from equilibrium partitioning equations and then use those 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 which 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 a water recharge rate so that a pore water velocity can be estimated and the vertical depth to groundwater or bedrock from the contaminated soil. 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<sub>soil</sub> 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.

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). Rarely, 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

- desorption non-equilibrium) 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 MECHANISIMS

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

Depending of 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 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) could conceivably be a simple qualitative demonstration of a site conceptual model which employs the use of monitoring well data/measurements to establish that facility "A" is clearly 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 it's relative stability over time. If groundwater monitoring samples have been collected over a sufficiently long period of time, and the information consists of good, valid 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.

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 often do not require the use of a computer and 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 digital computer 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, 1000 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. Additional discussion on numerical models is provided below.

## 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.

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. Several transects (lines of wells) should be installed downgradient from the source and perpendicular to the direction of ground water 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.
- Koc this value can be derived from Appendix A Table 5 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 5 of Chapter 250 should not be relied on as default values for site-specific modeling..
- Soil Bulk Density often estimated as 2.65\*(1-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. Modeling efforts associated with a post-remediation 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 5447-93 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 5447-93 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 site characterization/initial conceptual 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 and, in some cases, values published in scientific literature or Table 5 in Appendix A to the Act 2 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;
- 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, Koc 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) Code Selection

When the site characterization is completed and the conceptual model has been developed, selection of an appropriate computer code 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 three spreadsheets that may be useful in completing a fate and transport analysis. All spreadsheets are based on the following equation:

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

$$\left\{erf\left[\left(y + Y/2\right) / 2\sqrt{\alpha_y x}\right] - erf\left[\left(y - Y/2\right) / 2\sqrt{\alpha_y x}\right]\right\} \left\{erf\left[\left(z + Z/2\right) 2\sqrt{\alpha_z x}\right] - erf\left[\left(z - Z/2\right) / 2\sqrt{\alpha_z x}\right]\right\}$$

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

The three spreadsheets are:

#### QUICK\_DOMENICO.XLS

This spreadsheet calculates the concentration anywhere in a plume of contamination at any time after a continuous, finite source becomes active.

#### FATBACK.XLS

This spreadsheet calculates the steady-state source concentration given the desired or target receptor concentration and location of the receptor. Given a source concentration calculated by Fatback, Quick\_Domenico could be used to establish a site-specific standard for a property line compliance point.

#### 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.

These spreadsheets and documentation can be downloaded from the PA DEP web site at:

http://www.dep.state.pa.us/dep/deputate/airwaste/wm/landrecy/MANUAL/Manual.htm#anchor86714

## 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 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 Statewide health Standard in the case of both used and nonuse aquifers;
- Predicting whether groundwater contamination above an MSC will extend beyond 1000 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.

The following format is modified after that in ASTM D 5447:

- 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 Aguifer System Framework
- 2.2 Groundwater Flow Model
- 2.3 Hydrologic Boundaries
- 2.4 Hydraulic Boundaries
- 2.5 Sources and Sinks
- 3.0 Computer Code
- 3.1 Code Selection-justification for use of analytical, numerical or other analysis

- 3.2 Code 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 <u>250.309</u> and <u>250.406</u> of the Act 2 regulations provide for determining compliance with surface water quality standards from a diffuse surface or groundwater discharge. For some sites selecting the Statewide health groundwater standard for used aquifers with a TDS of 2500 mg/L or less, and all sites selecting the Statewide health nonuse aquifer groundwater standard, Statewide health standard in used aquifers with greater than 2500 mg/L TDS or the site-specific standard for groundwater, this will involve analyzing the impact of a diffuse flow of a dissolved groundwater plume into a stream incorporating the methods and models of the Office of Water Management. All discharges involved with a remediation must be in compliance with the provisions of

Chapter 93 to demonstrate attainment of the Statewide health and site-specific standards.

#### 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, SWLOAD5, 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 simply the concentration above which the maximum average concentration and associated flow will be determined for the plume in question. An "edge criterion" 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 <u>Table IV-1</u> of the TGM which have established surface water criteria, the "edge criterion" equals the Act 2 non-residential groundwater MSC for used aquifers <2500 TDS.
- For compounds on <u>Table IV -2</u> of the TGM, the "edge criterion" equals the SW-846 PQL.
- For compounds on <u>Table IV-3</u>, if the Act 2 SW-846 PQL is below both the Act 2 MSC and the lowest surface water compliance value (LSWC), the "edge criterion" equals the LSWC. If both the LSWC and the Act 2 MSC are below the SW-846 PQL, the "edge criterion" equals 3.18 times the lowest Chapter 16

method detection limit or the lowest surface water criterion, whichever is higher.

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, SWLOAD5, 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" as this phrase is used in connection with <u>Tables IV-1</u>, <u>IV-2</u> and <u>IV-3</u> below. These tables provide for a waiver of a PENTOXSD analysis in cases where the Statewide Health Standard for groundwater is attained if the "maximum modeled or measured concentration" is below certain criteria. 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 that is particularly important in using <u>Tables IV-1</u>, <u>IV-2</u> and <u>IV-3</u> is where the concentrations should be measured with respect to the Act 2 property line POC and the meaning of the phrase "...at the POC or groundwater/surface water interface, as appropriate...". If a plume discharges off the property being remediated before discharging into a stream, then the criteria for waiving a PENTOXSD analysis on each table 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 SWLOAD5 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 SWLOAD5 is defined as the threshold for waiving a PENTOXSD analysis in each table.

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.

### 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:

$$Csw = (Qgw * Cgw) + (Qsw * Yc * Cbsw)$$
$$(Qsw * Yc) + Qgw$$

where:

Csw = the concentration in surface water a contaminant of concern downstream of a the nonpoint source discharge into the surface water.

Qsw = the quantity of stream flow above the nonpoint source discharge into surface water.

Qgw = the quantity of flow in the groundwater plume discharging into the surface water.

Cgw = the maximum average concentration of a contaminant in the groundwater discharging into surface water.

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

Cbsw = 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:

$$\overline{Cgw} = Cx + \frac{Yc * Qsw * (Cx-Cbsw)}{Qgw}$$

where:

Cx = 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. Q7-10 or Qhm).

## 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 Office of Water Management'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 User's Guide 391-2000-012 for information on using the PENTOXSD model. The PENTOXSD model can be downloaded from the Department's web site at:

http://www.dep.state.pa.us/dep/deputate/airwaste/wm/landrecy/manual/Manualcd.htm.

The analysis will involve incorporating background concentrations in surface water for certain contaminants. Users are referred to 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. Table IV-3 also identifies compounds where background water quality concentration is a factor in the analysis.

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 Office of Water Management 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.

At this time the Office of Water Management addresses the impact of multiple sources on a stream on a site-specific case-by-case basis. Sites which have more than one plume on a single property seeking the site-specific standard for the same contaminants, or adjacent properties on the same stream reach with the same contaminants are examples of sites which should be referred to The Office of Water Management for multiple source discharge analysis.

## d) Statewide health Standard in Aquifers with 2500 mg/L TDS or less

For 65 compounds that have Statewide health standards established in Chapter 250, simply demonstrating attainment of the residential or nonresidential Statewide health standard medium-specific concentration (MSC) for groundwater in used aquifers with total dissolved solids (TDS) less than or equal to 2500 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 65 compounds are listed in Table IV-1 along with the nonresidential MSC.

The Department has identified 89 compounds that require a more detailed analysis. These compounds are listed in Tables <u>IV-2</u> and <u>IV-3</u>.

Table IV-2 identifies 24 compounds where the Act 2 MSC is above both the PQL and the LSWC, but the LSWC is below the PQL. Surface water quality attainment will be deemed to be attained when the maximum modeled or measured compliance well concentration of these compounds at the point of compliance and any groundwater/surface water interface, whether prior to or downgradient of the property line POC, is below the PQL. If the maximum

Table IV-1 Compounds Excluded from Further Surface Water Evaluation on Attainment of SHS for  $GW \le 2500 \text{ TDS}$ 

SUBSTANCE	CAS Number
ACENAPHTHYLENE	208-96-8
ACROLEIN	107-02-8
ALUMINUM	7429-90-5
ANTHRACENE	120-12-7
ANTIMONY	7440-36-0
ARSENIC	7440-38-2
BARIUM AND COMPOUNDS	7440-39-3
BENZENE	71-43-2
BENZO(G,H,I)PERYLENE	191-24-2
BERYLLIUM	7440-41-7
BHC, DELTA	319-86-8
BHC, GAMMA (LINDANE)	58-89-9
BIS(2-CHLOROISOPROPYL)ETHER	39638-32-9
BORON AND COMPOUNDS	7440-42-8
BROMOMETHANE (METHYL BROMIDE)	74-83-9
BROMOPHENYL PHENYL ETHER, 4-	101-55-3
CARBON TETRACHLORIDE	56-23-5
CHLORIDE	
CHLOROBENZENE	108-90-7
CHLOROETHANE	75-00-3
CHLOROETHYL VINYL ETHER, 2-	110-75-8
CHLOROPHENOL, 2-	95-57-8
CHLOROPHENYL PHENYL ETHER, 4-	7005-72-3
CHROMIUM, TOTAL	7440-47-3
CUMENE	98-82-8

Table IV-1 Compounds Excluded from Further Surface Water Evaluation on Attainment of SHS for  $GW \le 2500 \text{ TDS}$ 

SUBSTANCE	CAS Number
DIBROMOETHANE, 1,2- (ETHYLENE DIBROMIDE)	106-93-4
DICHLOROBENZENE, P	106-46-7
DICHLOROETHANE, 1,1-	75-34-3
DICHLOROETHANE, 1,2-	107-06-2
DICHLOROETHYLENE, CIS-1,2-	156-59-2
DICHLOROETHYLENE, TRANS-1,2-	156-60-5
DICHLOROMETHANE (METHYLENE CHLORIDE)	75-09-2
DICHLOROPHENOL, 2,4-	120-83-2
DICHLOROPROPANE, 1,2-	78-87-5
DIMETHYL PHTHALATE	131-11-3
DINITROPHENOL, 2,4-	51-28-5
ENDOSULFAN SULFATE	1031-07-8
FLUORIDE	
HEPTACHLOR EPOXIDE	1024-57-3
HEXACHLOROBUTADIENE	87-68-3
HEXACHLOROETHANE	67-72-1
HEXANONE, 2-	591-78-6
IRON	7439-89-6
MANGANESE	7439-96-5
METHYL CHLORIDE	74-87-3
METHYL ETHYL KETONE	78-93-3
METHYL ISOBUTYL KETONE	108-10-1
METHYL TERT-BUTYL ETHER (MTBE)	1634-04-4
NITROPHENOL, 2-	88-75-5

Table IV-1 Compounds Excluded from Further Surface Water Evaluation on Attainment of SHS for  $GW \le 2500 \text{ TDS}$ 

SUBSTANCE	CAS Number
NITROPHENOL, 4-	100-02-7
OCTYL PHTHALATE, DI-N-	117-84-0
PHENOL	108-95-2
PROPANOL, 1-	71-23-8
PROPANOL, 2-	67-63-0
PYRENE	129-00-0
STYRENE	100-42-5
TCDD, 2,3,7,8-	1746-01-6
TETRACHLOROETHYLENE (PCE)	127-18-4
THALLIUM	7440-28-0
TIN	7440-31-5
TRICHLOROETHANE, 1,1,1-	71-55-6
TRICHLOROETHANE, 1,1,2-	79-00-5
TRICHLOROETHYLENE (TCE)	79-01-6
TRICHLOROPROPANE, 1,2,3-	96-18-4
VINYL CHLORIDE	75-01-4

Table IV-2 Compounds Requiring Additional Evaluation for Surface Water Compliance if PQL Exceeded\*

SUBSTANCE	CAS Number	PQL	LSWC lowest ug/l	MSC highest ug/l
BENZO[A]PYRENE	50-32-8	0.07	0.0044	0.2
ВНС, ВЕТА	319-85-7	0.2	0.014	1.4
BROMODICHLOROMETHANE (DICHLOROBROMOETHANE)	75-27-4	5	0.56	100
CHLORODIBROMOMETHANE	124-48-1	5	0.41	100
CYANIDE, FREE	57-12-5	100	5.2	200
ENDOSULFAN, ALPHA	959-98-8	0.3	0.056	500
ENDOSULFAN, BETA	33213-65-9	0.4	0.056	450
ENDRIN	72-20-8	0.9	0.036	2
HEXACHLOROBENZENE	118-74-1	0.2	0.00075	1
HEXACHLOROCYCLOPENTADIENE	77-47-4	10	1	50
MERCURY	7439-97-6	0.2	0.05	2
NITROSO-DIPHENYLAMINE, N-	86-30-6	10	5	530
PCB-1016	12674-11-2	0.2	0.000044	7.2
PCB-1221	11104-28-2	0.2	0.000044	5.2
PCB-1232	11141-16-5	0.2	0.000044	5.2
PCB-1242	53469-21-9	0.2	0.000044	5.2
PCB-1248	12672-29-6	0.2	0.000044	1.4
PCB-1254	11097-69-1	0.2	0.000044	1.4
PCB-1260 (AROCLOR)	11096-82-5	0.2	0.000044	4.3
PHENANTHRENE	85-01-8	10	1	1100
POLYCHLORINATED BIPHENYLS		0.2	0.000044	0.5
SILVER	7440-22-4	7	3.5	100
TRIBROMOMETHANE (BROMOFORM)	75-25-2	5	4.3	100
TRICHLOROPHENOL, 2,4,6-	88-06-2	10	2.1	240

<sup>\*</sup> Any time the highest groundwater concentration in a plume at the POC or the groundwater/surface water interface, as appropriate, is below the LSWC, a PENTOXSD analysis is not required.

Table IV-3 Compounds Requiring Surface Water Compliance Analysis\*

SUBSTANCE	CAS Number	PQL	LSWC lowest µg/l	MSC highest µg/l	APPLY BACKGROUND DATA
ACENAPHTHENE	83-32-9	10	17	3800	
ACETONE	67-64-1	5	3500	10000	
*ACRYLONITRILE	107-13-1	5	0.059	2.7	
*ALDRIN	309-00-2	4	.00013	0.037	
BENZIDINE	92-87-5		0.00012	0.011	
*BENZO[A]ANTHRACENE	56-55-3	10	0.0044	3.6	
*BENZO[B]FLUORANTHENE	205-99-2	10	0.0044	1.2	
*BENZO[K]FLUORANTHENE	207-08-9	10	0.0044	0.55	
*BHC, ALPHA	319-84-6	0.4	0.0039	0.41	
*BIS(2-CHLOROETHYL)ETHER	111-44-4	10	0.031	0.55	
BIS[2-ETHYLHEXYL] PHTHALATE	117-81-7	1	1.8	6	
BUTYLBENZYL PHTHALATE	85-68-7	10	35	2700	
CADMIUM	7440-43-9	0.1	2.2	5	
*CHLORDANE	57-74-9	0.4	0.0021	2	
CHLOROFORM	67-66-3	5	5.7	100	
CHLORONAPHTHALENE, 2-	91-58-7	10	1700	8200	
CHROMIUM III	16065-83-1	1	74		
CHROMIUM VI	18540-29-9	1	10		
*CHRYSENE	218-01-9	10	0.0044	1.9	
COBALT	7440-48-4	7	19	6100	
COPPER	7440-50-8	6	9	1000	yes
CRESOL, P-	106-44-5	10	160	510	
CRESOL, P-CHLORO-M-	59-50-7		30	510	
*DDD,4,4'-	72-54-8	0.2	0.00083	2.7	
*DDE, 4,4'-	72-55-9	0.2	0.00059	7.6	
*DDT, 4,4'-	50-29-3	0.3	0.00059	5.5	

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Table IV-3 Compounds Requiring Surface Water Compliance Analysis\*

SUBSTANCE	CAS Number	PQL	LSWC lowest µg/l	MSC highest µg/l	APPLY BACKGROUND DATA
DIBUTYL PHTHALATE, N-	84-74-2	10	21	10000	
DICHLOROBENZENE, 1,2-	95-50-1	10	160	600	
DICHLOROBENZENE, 1,3-	541-73-1	10	69	600	
*DICHLOROBENZIDINE, 3,3'-	91-94-1	20	0.04	5.8	
*DICHLOROETHYLENE, 1,1-	75-35-4	5	0.057	7	
DICHLOROPROPYLENE, 1,3-	542-75-6		10	26	
*DIELDRIN	60-57-1	1	0.00014	0.16	
DIETHYL PHTHALATE	84-66-2	10	800	5000	
DIMETHYLPHENOL, 2,4-	105-67-9	10	130	2000	
*DINITRO-O-CRESOL, 4,6-	534-52-1	50	13.4	5	
*DINITROTOLUENE, 2,4-	121-14-2	10	0.05	100	
*DINITROTOLUENE, 2,6-	606-20-2	10	0.05	100	
DIPHENYLHYDRAZINE, 1,2-	122-66-7		0.04	3.3	
ETHYL BENZENE	100-41-4	5	580	700	
FLUORANTHENE	206-44-0	10	40	260	
FLUORENE	86-73-7	10	1300	1900	
FORMALDEHYDE	50-00-0	20	440	1000	
*HEPTACHLOR	76-44-8	0.4	0.00021	0.4	
*INDENO(1,2,3-CD)PYRENE	193-39-5	10	.0.0044	3.6	
ISOPHORONE	78-59-1	10	36	100	
LEAD	7439-92-1	1	1.46	5	yes
NAPHTHALENE	91-20-3	10	43	100	
NICKEL	7440-02-0	15	52	100	yes
NITRATE NITROGEN	14797-55-8			10000	yes
NITRITE NITROGEN	14797-65-0			1000	yes
NITRATE/NITRITE NITROGEN			10000		yes
NITROBENZENE	98-95-3	10	17	51	
*NITROSO-DIMETHYLAMINE, N-	62-75-9	20	0.00069	0.013	

SECTION IV - GENERAL GUIDANCE

A. Fate and Transport Analysis

Table IV-3
Compounds Requiring Surface Water Compliance Analysis\*

SUBSTANCE	CAS Number	PQL	LSWC lowest µg/l	MSC highest µg/l	APPLY BACKGROUND DATA
PENTACHLOROPHENOL	87-86-5	0.1	0.28	1	
SELENIUM	7782-49-2	2	4.6	50	yes
SULFATE			250000	500000	
TETRACHLOROETHANE, 1,1,2,2-	79-34-5	0.1272	0.17	0.3	
TOLUENE	108-88-3	5	330	1000	
*TOXAPHENE	8001-35-2	0.8	0.00073	3	
TRICHLOROBENZENE, 1,2,4-	120-82-1	5	26	70	
VANADIUM	7440-62-2	2.5	100	720	
XYLENES (TOTAL)	1330-20-7	5	210	10000	
ZINC	7440-66-6	2	120	2000	yes

<sup>\*</sup> Any time the highest groundwater concentration in a plume at the POC or the groundwater/surface water interface, as appropriate, is below the LSWC, a PENTOXSD analysis is not required.

concentration in groundwater exceeds the PQL, these compounds must be evaluated as those in Table IV-3, described below.

<u>Table IV-3</u> identifies 65 compounds for which surface water compliance analysis is required. These are compounds where either the MSC exceeds the LSWC and both the MSC and LSWC exceed the PQL, or the LSWC is so much lower than the PQL that the Office of Water Management cannot be assured that the LWSC is met if attainment is demonstrated at the level of the PQL.

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. For this reason a remediator may want to consider using other valid analytical methods which have lower PQLs.

#### 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 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 at or near their effective solubility 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 site-specific standard has been selected and groundwater concentrations exceed the lowest surface water quality criteria, 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

Permeability - 2.83 ft/day

Gradient .01 ft/ft

Groundwater flow represented by plume:  $28.3 \text{ ft}^3/\text{day} = 212 \text{ gallons/day}$ 

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

Benzene: 15,000

Toluene 52,000

Ethylbenzene 1,500

Total xylenes 9,000

MTBE 6,900,000

Using benzene for this example, the maximum average groundwater concentration is 15,000  $\mu$ g/L and the plume flow is 212 gallons/day or 0.00033 cfs (0.00021 MGD).

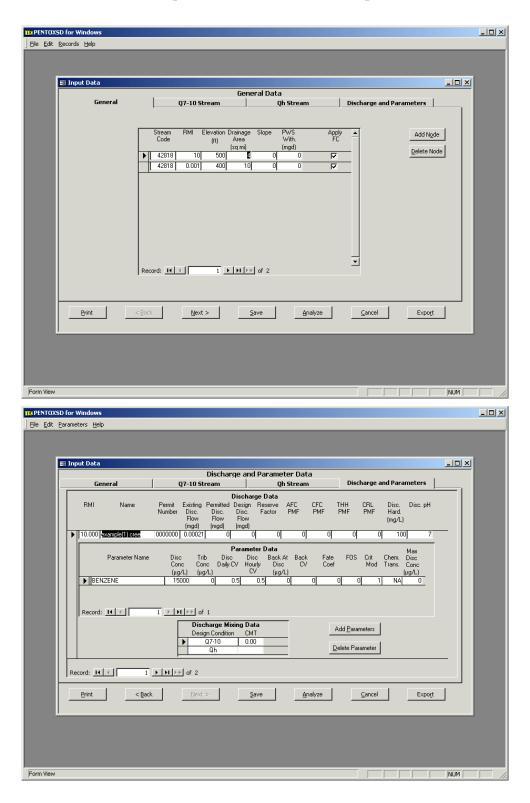
Assuming all groundwater discharges to the stream, an evaluation of the plume discharge to the stream can now be made with the above data using PENTOXSD for each of the contaminants. The approach is described and shown below for benzene:

Figures IV-1 and IV-2 are printouts from the PENTOXSD model for Example 1. PENTOXSD shows that the recommended effluent limit for benzene in this case is 12,323  $\mu$ g/L, which is less than the 15,000  $\mu$ g/L maximum average groundwater concentration for benzene calculated for this example. Therefore, a release of liability cannot be granted in this case until the maximum average groundwater concentration is reduced to at least 12,323  $\mu$ g/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. 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

Figure IV-1
Example 1 -PENTOXSD Model Inputs



\_U× File Help \_\_\_× WLA Results Q7-10 Hydrodynamics Qh Hydrodynamics Wasteload Allocations Go to Discharge: • € CRL О тин C AFC C CFC 10.00 example(1) cree CCT CMT PMF Back.
(min) (min) Conc. WLA Notes: 1 **> > >** > > of 1 1 | | | | | | | | | | | | of 1 Record: 14 < <u>B</u>ack <u>N</u>ext > <u>C</u>ancel <u>P</u>rint <u>S</u>ave Form View \_U× File Help 🔀 Analysis Results \_\_\_× Effluent Limits Results Q7-10 Hydrodynamics Qh Hydrodynamics Wasteload Allocations Effluent Limits Permit Number Disc. Flow 0000000 0.0002 10 example(1) cree Effluent Limit (µg/L) 12322.62 Record: I◀ ◀ 1 ▶ ▶ ▶ ★ of 1 1 ▶ ▶I ▶\* of 1 Record: I◀ ◀ Print < Back <u>S</u>ave <u>C</u>ancel

Figure IV-2
Example 1 -PENTOXSD Model Output

Form View

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 Department's Quick Domenico (QD) and SWLOAD5 (SWL5) spreadsheet applications will be used. A plan view model such as Quick Domenico is being used because it is difficult or impossible to calibrate a cross-sectional model such as SWLOAD5 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 SWLOAD5'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 <u>Figure IV-3</u> for the actual values):

<u>Longitudinal and transverse dispersion</u> – fitted to plume data (isoconcentration map) using QD

<u>Vertical Dispersion</u> – set to 0.0001 because the entire plume is assumed to discharge into the stream and any vertically dispersed contamination would reenter the stream.

<u>Lambda</u> – determined using methods of Buscheck and Alcantar (1995) for steady state plumes.

<u>Time</u> – 11 years-established from historical records. Note that this is fixed at  $1 \times 10^{99}$  days in SWLOAD5 to assure that output is at steady state conditions. This assures that SWLOAD5 will yield the maximum average concentration for plumes emanating from a constant source.

<u>Porosity</u> - determined by laboratory analysis of undisturbed samples.

<u>Dry bulk density</u> - estimated at 2.65\*(1-porosity)

Koc – from Appendix A, Table 5, Chapter 250

Fraction organic carbon - from ASTM D2974-00

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 SWLOAD5. The output from QD and SWLOAD5 is shown in Figures IV-3 and IV-4.

The model indicates that the maximum average concentration in groundwater is 2.35 mg/L and the total flow through the plume is 0.0004 MGD. 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.
ECTION IV - (	GENERAL GUIDANCE

Figure IV-3
Example 2 – Quick Domenico Model Output

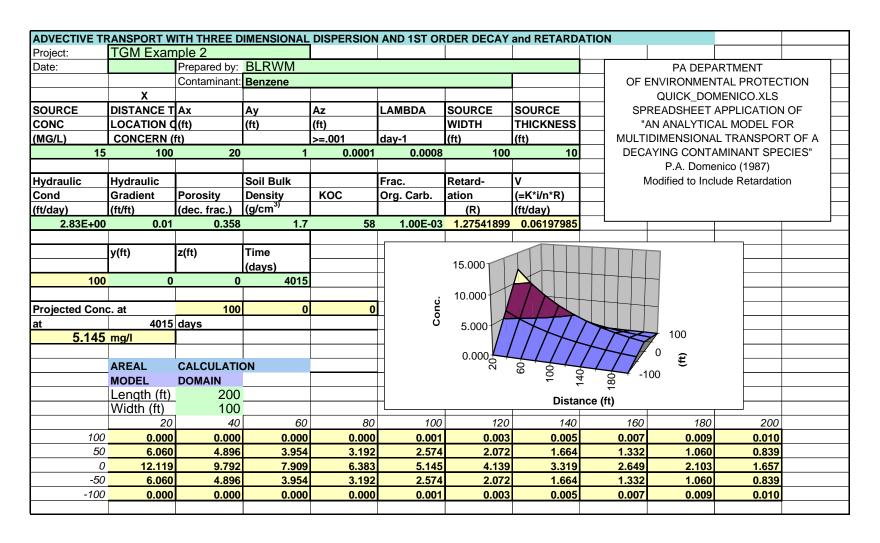


Figure IV-4
Example 2 – SWLOAD Model Output

METHOD FO	R ESTIMATNG FI	OW. AVERA	GE CONC	ENTRATIO	N AND MAS	S LOADING	TO SURFA	CE WATER	FROM GROU	NDWATER				
Project:	SWLOAD5B	2011,717210	102 00110											_
Date:	2/5/2002										PA DEP	ARTMENT		
Contaminant: Benzene		Prepared by: BLRWM				OF E	OF ENVIRONMENTAL PROTECTION							
SOURCE									SWLOAD5B.XLS					
CONC	Ax	Ay	Az	LAMBDA	SOURCE	SOURCE				A	A METHOD FOR ESTIMATING			
(units)	(ft)	(ft)	(ft)			THICKNESS	Time			COMTA	COMTAMINANT LOADING TO SURFACE			
mg/l	>.0001	>.0001	>=.0001	day-1	(ft)	(ft)	(days)				WATER			
15			1.00E-04	0.0008	100		1.00E+99				based on			
											P.A. Domenico (1987)			
Hydraulic	Hydraulic		Soil Bulk		Frac.	Retard-	V			М	Modified to Include Retardation			
Cond	Gradient	Porosity	Density	кос	Org. Carb.	ation	(=K*i/n*R)							
(ft/day)	(ft/ft)	(dec. frac.)	(g/cm <sup>3)</sup>			(R)	(ft/day)							
2.83E+00	0.01	0.358	1.7	58	1.00E-03	1.275419				_				_
								-						
				-94	-75.2	-56.4	-37.6	-18.8	0	18.8	37.6	56.4	75.2	94
Edge Criterio	on (mg/l)	0.005	0	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
Higest modeled conc.		5.173	-1.044	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
			-2.088	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
SURFACE W	ATER LOADING	GRID	-3.132	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
Distance to S	Stream (ft)	100	-4.176	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
Plume View \	Width (ft)	188	-5.22	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
Plume View I	Depth (ft)	10.44	-6.264	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
			-7.308	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
			-8.352	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
PENTOX N	IEEDED		-9.396	0.005	0.193	1.684	4.190	5.104	5.173	5.104	4.190	1.684	0.193	0.005
			-10.44	0.000	0.000	0.002	0.004	0.005	0.005	0.005	0.004	0.002	0.000	0.000
				Average Groundwater Concer		ntration	2.35287	ma/l						
				Average Groundwater Concer		iti ation	2.00201	1119/1						
				Plume Flow			0.00062	cfs	0.0004	MGD				
		Fiuille Flow			0.00002	013	0.0004	שטואו	1					
				Mass Loading to Stream			3553.10 mg/day							
			mass zodanig to otredin				0000.10	mg/day						
		L	1	1	L	l	l		ı					

Documentation for using SWLOAD5 to estimate plume flow, concentrations and mass loading is provided on the Department's web site at <a href="http://www.dep.state.pa.us/dep/deputate/airwaste/wm/landrecy/MANUAL/Manual.htm#anchor86714">http://www.dep.state.pa.us/dep/deputate/airwaste/wm/landrecy/MANUAL/Manual.htm#anchor86714</a>.

Figures IV-5 and IV-6 are printouts from the PENTOXSD model run for Example 2. In this case, the recommended effluent limit for benzene is 6,469.9  $\mu$ g/L, which is greater than the maximum average benzene concentration of 2,353  $\mu$ g/L calculated with SWLOAD5. 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 convey.

Example 2 - PENTOXSD Model Inputs \_UX <u>File Edit Records Help</u> 💴 Input Data \_ O × General Data RMI Elevation Drainage Slope Add Node (sq mi) 500 4 Delete Node 42816 42816 0.001 400 Record: I◀ ◀ 1 ▶ ▶1 ▶\* of 2 <u>C</u>ancel < <u>B</u>ack Print <u>N</u>ext > <u>S</u>ave <u>A</u>nalyze Expo<u>r</u>t Form View NUM TOX PENTOXSD for Window File Edit Parameters Help Discharge and Parameter Data Q7-10 Stream Discharge and Parameters Discharge Data

Existing Permitted Design Reserve AFC CFC
Disc. Disc. Factor PMF PMF
Flow Flow Flow Disc. pH (mg/L) (mgd) (mgd) (mgd) | 00000001 | 0.0004 | 0 | 0 | 10.000 Example 2 Creek Parameter Data | Disc | Trib | Disc | Disc | Back At | Back | Conc | Conc | Daily CV | Hourly | Disc | CV | (μg/L) | (μg/L) | CV | (μg/L) | (μ ▶ BENZENE NA Record: It 1 ▶ ▶I ▶\* of 1 Discharge Mixing Data Add Parameters <u>D</u>elete Parameter Record: I◀ ◀ 1 | | | | | | | | | | | of 2 < Back <u>S</u>ave <u>A</u>nalyze <u>C</u>ancel Export Print

Figure IV-5 Example 2 – PENTOXSD Model Inputs

Example 2 - PENTOXSD Model Output \_\_\_X PENTOXSD for Windows Eile Help 🕮 Analysis Results \_ | X WLA Results Q7-10 Hydrodynamics Qh Hydrodynamics Wasteload Allocations Effluent Limits Go to Discharge: **T**  CRL BMI Permit Number 10.00 Example 2 Creek CCT CMT PMF (min) (min) Back. Conc. WQC (μg/L) WLA Notes: (μg/L) 1.2 6469.948 Record: I 1 | | | | | | | | | | | | of 1 Record: 14 ← Print < <u>B</u>ack Next > <u>S</u>ave ⊆ancel Form View TOX PENTOXSD for Wind \_\_\_× Eile Help 🖺 Analysis Results \_ | × Effluent Limits Results Effluent Limits Q7-10 Hydrodynamics Qh Hydrodynamics Wasteload Allocations Permit Number Disc. Flow 10 Example 2 Creek - 000000000 Effluent Limit (μg/L) 2353 Gov. Crit. Parameter Max. Daily Limit (μg/L) 3671.058 TECH ▶ BENZENE Record: I4 4 1 ▶ ▶I ▶\* of 1 Record: I◀ ◀ 1 > 1 >\* of 1 < Back ⊆ancel Print <u>S</u>ave

Figure IV-6 Example 2 - PENTOXSD Model Output

Form View

## 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 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 the Act 2 regulations, a person may consult the latest EPA documents for additional guidance. EPA guidance documents (EPA 1989b, 1992b, 1992c, 1996) are particularly helpful. They provide detailed statistical procedures for demonstration of attainment and data analysis. Three of these documents are available from the World Wide Web at <a href="http://www.clu-in.org/char1\_edu.cfm">http://www.clu-in.org/char1\_edu.cfm</a>. EPA QA/G-9 (EPA 1996) is available from the World Wide Web at <a href="http://www.epa.gov/quality1/qa\_docs.html">http://www.epa.gov/quality1/qa\_docs.html</a>.

For groundwater characterization, persons should consult the current DEP guidance document "Groundwater Monitoring Guidance Manual" (Section V.F), 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 DEP Groundwater Monitoring Guidance Manual provides a good summary of various statistical methods used for groundwater characterization.

Other references cited in this document and standard texts 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 Act 2 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 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 Section 250.702(a) of the regulations).

To help a person design a scientific and resource-effective sampling program, EPA has provided guidance on developing Data Quality Objectives (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 quality assurance 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 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 separate-phase liquid (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 quality assurance/quality control plan.

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 Section 250.703(c) of the regulations). 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, such as <u>Table IV-4</u>.

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 determined whether the DQOs are met. This is the Data Quality Assessment (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 following discussions will address key statistical issues that are pertinent to Act 2 and are encountered during these DQO and DQA processes.

#### 3. Preliminary Data Review

Preliminary data review (also known as exploratory data analysis in the DEP Groundwater Monitoring Guidance Manual; PaDEP, 1999) includes the use of graphical techniques and calculation of summary statistics. 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. 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, such as SAS and

DataQUEST (EPA QA/G-9D). SAS is available to DEP employees through DER001 network. EPA is developing DataQUEST (EPA QA/G-9D) to support the Data Quality Assessment (DQA) process. DataQUEST (EPA QA/G-9D) will be available from <a href="http://www.epa.gov/quality1/qa\_docs.html">http://www.epa.gov/r10earth/offices/oea/qaindex.htm</a>.

# i) 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.

# ii) Graphical procedures

Refer to Cleveland (1993) or EPA QA/G-9 (EPA, 1996) for a general reference on graphical procedures. The use of boxplots is also described in the EPA Addendum (EPA, 1992a).

**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 do 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. One smoothing procedure showing movement of the "center" of data over time is LOWESS. This procedure is most helpful with data having substantial variability and a long period of record. LOWESS requires computer software.

**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 Interim Final Guidance (EPA, 1989a, Section 7) and the EPA Addendum (EPA, 1992a, Section 6.1) for procedures.

# 4. 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 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 (Ho) is that the true site arithmetic average concentration is at or above the cleanup standard, and the alternative hypothesis (Ha) 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 (Ho) is that the background standard is achieved and the alternative hypothesis (Ha) 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 acquittal verdict for the defendant. Using the language of hypothesis testing, we want to test a null hypothesis (Ho) that the accused man is innocent. That means that an alternative hypothesis (Ha) 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 (Ho) of innocent. If the jurors decide that the evidence is inconsistent with Ho, they reject that hypothesis and therefore accept the alternative hypothesis (Ha) 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 dirty site to be clean than to declare a clean site to be dirty 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 (Ho) is that the background standard is achieved and the alternative hypothesis (Ha) 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, 1992c). 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.

#### 5. 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.

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. Statewide health standards and many site-specific standards are risk-based standards that are concentration limits based on risk assessment methodologies. At some sites, a site-specific standard could be a technology-based standard, 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 (a bright line standard).

As a result of the above factors, recommended statistical approaches are addressed separately based on environment media and remediation standards. The flowchart in <u>Figure IV-7</u> provides a summary of recommended statistical methods described in Act 2 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 <u>250.707(d)(2)</u> of the Act 2 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 know 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, <u>Section 250.707</u> of the Act 2 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.

#### 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 Statewide health standards 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 Act 2 regulations allow the remediator to use the 75%/10X rule or the 95% upper confidence limit (UCL) of arithmetic mean to demonstrate attainment of the Statewide health standard in soils. For UST release sites that have only localized (soil) contamination as defined in the

storage tank program's Closure Guidance, and where the confirmatory samples taken in accordance with this technical guidance document result in fewer samples being taken than otherwise required, all sample results must meet the Statewide health standard. For the site-specific standard, the regulations recommend the use of the 95% upper confidence limit (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.

## (a) 75%/10X rule

The 75%/10X rule is a statistical *ad hoc* rule that tests whether the true site <u>median</u> 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 (<u>See Section 250.707(b)(1)(i)</u> of the regulations).

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 Act 2 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.

It should be noted that the 75%/10X rule should not be used to demonstrate attainment of 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 Section 250.707(b)(1)(ii) and 250.707(c) of the regulations is well documented in various EPA risk assessment or statistical guidances (EPA, 1989b, 1989c, 1992c, 1996). 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., >>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 and 0.05 for a residential site [Section 250.707(d)(2)(vii)].

Procedures to calculate 95% UCL of arithmetic mean are provided in Sections IV.B.7 and IV.B.8.

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<sub>s</sub>, conclude that the area is dirty.
- If 95% UCL of arithmetic mean is less than C<sub>s</sub>, conclude that the area is clean.

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 IV-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 to use Shapiro Wilk W test for testing normality (EPA, 1996). Other tests for normality, such as chi-square test and other goodness-of-fit tests are discussed in Section 4.2 of EPA QA-G9 (EPA, 1996). To test the independence of data, ordinary-runs test (Gibbons, 1990) can be used.

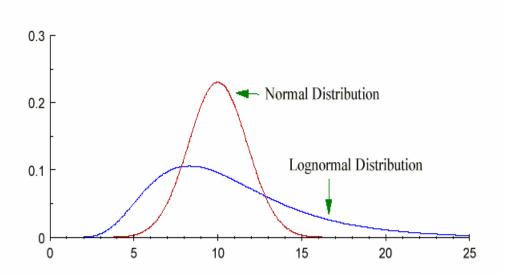


Figure IV-8. Examples of Normal Distribution and Lognormal Distribution

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), data from composite sampling can be more cost-efficient to estimate population mean and population variance than from 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 <a href="Section250.707(b)(1)(iii)">Section250.707(b)(1)(iii)</a> of the regulations as follows:

For sites where there is localized contamination as defined in the document "Closure Requirements for Underground Storage Tank Systems" (<u>DEP technical document No. 2530-BK-DEP2008</u>), 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 Statewide health standard 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, 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 years 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 Statewide health standard.

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 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 person 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 person may want to use time

trend analysis or plots of data to find if the groundwater has stabilized. After the groundwater has reached a steady state, the person 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 plots of 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% upper confidence limit of the mean (EPA, 1992b) 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 being 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, 8 samples from each compliance well must be obtained during 8 consecutive quarters. Shorter sampling period requires the use of the no exceedance rule (Section 250.704(d)(3) of the Act 2 regulations).

# iii) Soil background standards

The determination of attainment of soil background standards is be based on a comparison of the distributions of the background concentrations of a regulated substance with the concentrations in an impacted area. Section 250.707(a)(1) of the regulations allows a person to use highest measurement comparison, combination of Wilcoxon Rank Sum test and Quantile test, or other appropriate methods to demonstrate attainment of background standards. No matter which method is used, Act 2 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 Chapter 6 of the EPA Attainment, Volume 3 (EPA, 1992c), and Section <u>250.707(a)(1)(ii)</u> of the regulations.

For the Wilcoxon Rank Sum (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).

$$N = \frac{\left(Z_{1-\alpha} + Z_{1-\beta}\right)^{2}}{12c(1-c)(Pr - 0.5)^{2}(1-R)}$$
 (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 x 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 Wilcoxon Rank Sum 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 exercise 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 Wilcoxon Rank Sum test are in <u>Section IV.B.9</u>.

# (b) quantile test

The Quantile test (Johnson et al. 1987), described in Section 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 Wilcoxon Rank Sum (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).

For Quantile test, EPA recommends to use 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 <u>Section IV.B.10</u>. The null hypothesis (Ho) and alternative hypothesis (Ha) statements for the Quantile test are:

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

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

where

 $\epsilon$  = 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 $\epsilon$ % 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). See Chapter 4 of EPA QA/G-9 (EPA, 1996) for methods and examples to verify underlying assumptions.

## iv) Groundwater background standards

There are two general categories of background conditions. The first is naturally occurring background or area wide contamination, neither of which is expected to exhibit seasonal patterns or trends. 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 be 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 Wilcoxon Rank Sum test and Quantile test described previously. When comparing with the background results, the sampling results in the onsite plume should not exceed the sum of the arithmetic average and three times standard deviation calculated for the background reference area [Section 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.

Attainment of the background standard must be demonstrated wherever the contamination occurs. There may be some mass of a particular contaminant 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. 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 there has been a release on-property, the plume migrating beyond the property boundary must also meet the background standard.

For background associated with an upgradient release of regulated substances, Section 250.707(a)(2) of the Act 2 regulations allows the use of the nonparametric tolerance limit procedure. The nonparametric tolerance limit procedure requires at least 8 samples from each well over 8 quarters to have sufficient power to detect contamination. Once the nonparametric upper tolerance limit is established for upgradient data, data from downgradient compliance wells can be compared to the limit. A resampling strategy can 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. See Sections 5.2.2 and 5.2.3 of the EPA Addendum (EPA, 1992a) which describes the procedures to use along with recommended coverage and confidence levels.

#### 6. 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 Interim Final Guidance (EPA, 1989a), EPA Addendum (EPA, 1992a), EPA Soil Attainment (EPA, 1989b), EPA Groundwater Attainment (EPA, 1992b), EPA Soil Reference-Based Standards Attainment (EPA, 1992c) and EPA QA/G-9 (EPA, 1996) 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).

## i) 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 (see EPA (1992a) Section 4 or Chapters 6 and 7 of EPA (1989b) for procedures).

**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-  $\alpha$  value) 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 IV.B.7 and IV.B.8.

# ii) Tests for comparing populations

The following tests are outlined in the EPA Interim Final Guidance (EPA, 1989a) and the EPA Addendum (EPA, 1992a). These 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 5.2 of the EPA Interim Final Guidance (EPA, 1989a). 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 Interim Final Guidance (1989a), Section 5.2.2). 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.

## iii) 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, 1992a, Chapter 6; EPA, 1996, Section 4.3.2).

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).

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).

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).

# 7. 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 <a href="Section IV.B.8">Section IV.B.8</a> should be used instead.

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

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

2. Calculate the sample variance ( $Sb^2$ ) 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):

Sb<sup>2</sup> = 
$$[(X_1 - \overline{X})^2 + (X_2 - \overline{X})^2 + ... + (X_n - \overline{X})^2]/(n-1)$$

3. Calculate the standard deviation (Sb) by taking the square root of the variance (Sb<sup>2</sup>):

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

- 4. Calculate the standard error of the mean (Sx). Standard error is inversely proportional to the square root of the number of samples (increasing n from 4 to 16 reduces Sx by 50%) where Sx equals Sb/  $\sqrt{n}$ . [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 IV -5).
- 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  $\overline{X}$  +t<sub>1- $\alpha$ ,n-1</sub>\*Sx.

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.

# 8. 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 Xi to Yi (i = 1,2,...n) using the natural logarithm function:

$$Yi = ln Xi$$

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

$$\overline{Y} = (Y_1 + Y_2 + ... Y_n)/n$$

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<sup>2</sup> = 
$$[(Y_1 - \overline{Y})^2 + (Y_2 - \overline{Y})^2 + ... + (Y_n - \overline{Y})^2]/(n-1)$$

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 upper confidence limit (UCL) can be calculated using the one-tailed (one-sided) H  $_{\rm l-\alpha}$  values associated with sample size n from the table of H  $_{\rm l-\alpha}$  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  $_{l-\alpha}$  value obtained from the table of H  $_{l-\alpha}$  where UCL equals

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

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  $H_{1-\alpha}$  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  $H_{1-\alpha}$  depends on Sy, n, and the confidence level  $\alpha$ . If  $H_{1-\alpha}$  is required for values of Sy 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:

$H_{1-\alpha}$	San				
Table	3	5	7	10	
0.1	2.750	2.035	1.886	1.802	
0.2	3.295	2.198	1.992	1.881	
Sy 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 Sy values of 0.1, 0.2, 0.3 and 0.4. To interpolate a value for a sample size of 6 and an Sy value of 0.25, the first step is to interpolate a value corresponding to an Sy of 0.25 and a sample size of 3 using the four-point Lagrangian interpolation equation, where

$$x = 0.25$$
  
 $x_1 = 0.10$   $y_1 = 2.750$   
 $x_2 = 0.20$   $y_2 = 3.295$   
 $x_3 = 0.30$   $y_3 = 4.109$   
 $x_4 = 0.40$   $y_4 = 5.220$ 

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

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

$$x = 0.25$$
  
 $x_1 = 0.10$   $y_1 = 2.035$   
 $x_2 = 0.20$   $y_2 = 2.198$   
 $x_3 = 0.30$   $y_3 = 2.402$   
 $x_4 = 0.40$   $y_4 = 2.651$ 

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

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

$$x = 0.25$$
  
 $x_1 = 0.10$   $y_1 = 1.886$   
 $x_2 = 0.20$   $y_2 = 1.992$   
 $x_3 = 0.30$   $y_3 = 2.125$   
 $x_4 = 0.40$   $y_4 = 2.282$ 

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

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

$$x = 0.25$$
  
 $x_1 = 0.10$   $y_1 = 1.802$   
 $x_2 = 0.20$   $y_2 = 1.881$   
 $x_3 = 0.30$   $y_3 = 1.977$   
 $x_4 = 0.40$   $y_4 = 2.089$ 

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 Sy of 0.25 and a sample size of 6, where

$$x = 6$$
  
 $x_1 = 3$   $y_1 = 3.667$   
 $x_2 = 5$   $y_2 = 2.295$   
 $x_3 = 7$   $y_3 = 2.055$   
 $x_4 = 10$   $y_4 = 1.927$ 

#### SECTION IV - GENERAL GUIDANCE

The resulted interpolation value is 2.087.

## 9. 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.

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.

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 Ho (cleanup standard attained, Pr = 1/2) versus Ha (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.

$$Zrs = \frac{Wrs - n(N+1)/2}{\sqrt{mn(N+1)/12}}$$
 (A3-1)

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

$$Zrs = \frac{Wrs - n(N+1)/2}{\sqrt{(nm/12)\left[N+1-\sum_{j=1}^{g}t_{j}(t_{j}^{2}-1)/(N(N-1))\right]}}$$
(A3-2)

where g is the number of tied groups and  $t_j$  is the number of tied measurements in the jth group.

- 11. Reject Ho (cleanup standard attained) and accept Ha (cleanup standard not attained) if Zrs (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 Ho 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

$$Wrs = 3 + 7 + ... + 27 + 28 = 272.$$

4. Compute Zrs 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:

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

- 5. From the table of z (<u>Table IV-6</u>) 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 Ho: Pr = 1/2 and accept the alternative hypothesis Ha: 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 Ho to be rejected.

Example - Wilcoxon Rank Sum Test

Referenc	e 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					
<i>7</i> 5	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			

## 10. 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 α 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:

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

where 
$$\left(\frac{a}{b}\right) \equiv \frac{a!}{b!(a-b)!}$$

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

- 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 rth 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 rth 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 rth 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 Ho and conclude that the cleanup unit has not attained the reference area cleanup standard ( $\varepsilon = 0$  and  $\Delta/\sigma = 0$ ).
- 9. If Ho is not rejected, then do the WRS test. If the WRS test indicates the Ho 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 IV.B.9. 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 Ho 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 IV.B.9.
- 4. From the Example of Section IV.B.9, 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 Ho 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).

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Table IV-4. 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 IV-4)

Say, 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 IV-5. Student's t-Distribution for Selected Alpha and Degrees of Freedom

			α for d	leterminin	g t <sub>1-a,n-1</sub>			
one-tailed	0.450	0.250	0.200	0.100	0.050	0.025	0.010	0.005
			α for de	etermining	g t <sub>1-a/2.n-1</sub>			
two-tailed	0.900	0.500	0.400	0.200	0.100	0.050	0.020	0.010
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
df 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	2.0S6	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

B. Guidance for Attainment Demonstration with Statistical Methods

Table IV-6 Table of z for Selected Alpha

α	$Z_{1-lpha}$
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

Background Highest measurement comparison Standard Wilcoxon Rank Sum & Quantile tests Soil Others that meet performance criteria 250.707(a)(1) Nonparametric tolerance limit Known Retesting with nonparametric Upgradient prediction limit Background Release Standard Others appropriate methods Groundwater 250.707(a)(2) Areawide or - Appropriate tests that compare the 250.707(a)(3) Select a Standard **Naturally** two populations and meet performance and a medium to Occurring criteria in 250.707(d) which a statistical test will apply. 75%/10X rule Statewide Health 95%UCL of the arithmetic mean Standard Tank closure: no exceedance rule Soil 250.707(b)(1) Others that meet performance criteria 75%/10X rule on the property Statewide Health 75%/2X rule beyond property Standard boundary Groundwater 95%UCL of the arithmetic mean 250.707(b)(2) No exceedance rule for shorter period Site-Specific 95%UCL of the arithmetic mean Standard 250.707(c) Others that meet performance criteria

Figure IV-7. Flow Chart of Recommended Statistical Methods

#### C. Mass Calculations

#### 1. Groundwater Mass Calculation

<u>Calculate Water Volume (WV)</u>

Water Volume(WV-ft $^3$ ) = 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>)  $\times$  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 & 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(soil) = Density of soil, assume to be a default value of 110 lb/ft<sup>3</sup>

 $V_{\text{(total)}}$  = 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 the each plot would equate to the total volume.

 $C_{\text{ave.}}(x)$  = 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  $lb_{\text{comtaminant}}/lb_{\text{soil}}$  (ppmw = ppm/106).

#### D. Postremediation Care

#### 1. Introduction

This section provides general guidelines on the methodology of postremediation care and the 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 <u>Table IV-7</u>, 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 <u>Section 250.410(b)(5)</u>.

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

#### 2. 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.

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, slurry walls, liner systems, caps, leachate collection systems and groundwater recovery trenches.

Example: A deed restriction prohibiting use of the property in some way is an institutional control. An impermeable cap that prevents volatilization to the atmosphere, controls contaminant migration by run-on and run-off, and limits dermal contact (hydraulic conductivity less than  $1 \times 10^{-7}$  cm/sec) is an engineering control.

Institutional controls cannot be used to attain the background or Statewide health standards. Institutional controls alone cannot be used to attain the site-specific standard. Engineering and/or institutional controls may be used to maintain all three standards.

#### 3. Postremediation Care Plan

The postremediation care plan should include the following:

- The reason(s) that the postremediation care plan is necessary (See Sections 250.204(g), 250.311, 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 quarterly 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.
- 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. Include a description of the corrective measures that may be required for
  all possible nonattainment scenarios.
- 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 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.

#### 4. Postremediation Monitoring

In some situations, postremediation monitoring may be required as part of the postremediation care program. 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 Act 2 regulations and policies.

Well locations for postremediation monitoring are generally selected from existing monitoring wells used in the assessment 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 factors that determine whether a postremediation care plan is necessary.

#### b) Frequency

As stated in <u>Section 250.204(g)</u> 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.

#### 5. Postremediation Care Attainment

A person may terminate postremediation care as approved in the final report if he can demonstrate attainment of the standard(s) without the engineering controls in place, and document by a fate and transport analysis that the standard will not be exceeded in the future. 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.

TABLE IV-7
Postremediation Care Decision Matrix

Background

		Yes	No
1.)	Is an ENGINEERING CONTROL(s) needed to <u>attain and/or maintain</u> the background standard?		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to maintain the background standard?		
3.)	Does the FATE & TRANSPORT analysis indicate that the background standard may be exceeded at the point of compliance in the future?		
4.)	Does the remediation rely on NATURAL ATTENUATION?		
	Statewide Health	•	
1.)	Is an ENGINEERING CONTROL(s) needed to <u>attain and/or maintain</u> the Statewide health standard?		
2.)	Is an INSTITUTIONAL CONTROL(s) needed to maintain the Statewide health standard?		
3.)	Does the FATE & TRANSPORT analysis indicate that the Statewide health standard, including the solubility limitation in section 250.304(b), may be exceeded at the point of compliance in the future?		
4.)	Does the remediation rely on NATURAL ATTENUATION?		
5.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will a post-remedy use be relied on to eliminate complete exposure pathways, as set forth		

	in Section 250.311(e)(2)?		

Ē		
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 section 250.311(f)(v)? [If yes, follow guidelines in section 250.312(b)(1-3) for reporting requirements.]	
	Site-Specific	
1.)	Is an ENGINEERING CONTROL(s) needed to <u>maintain</u> the Site-specific Standard?	
2.)	Is an INSTITUTIONAL CONTROL(s) needed to <u>maintain</u> the Site-specific Standard?	
3.)	Does the FATE & TRANSPORT analysis indicate that the Site-specific Standard may be exceeded at the point of compliance in the future?	
4.)	Does the remediation rely on NATURAL ATTENUATION?	
5.)	If there are ECOLOGICAL IMPACTS identified in the evaluation of ecological receptors that must be addressed, will a post-remedy use be relied on to eliminate complete exposure pathways, as set forth in section 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 section 250.311(f)? [If yes, follow guidelines in section 250.411(f)(1-3) for reporting requirements.]	

#### E. Storage Tank Program Guidance

#### 1. Corrective Action Process

While an informal corrective action process (CAP) existed upon the passage of Act 32, the existing CAP was established in regulation on August 21, 1993, and revised on December 1, 2001. These regulations represent a streamlined and flexible approach to corrective action, and a formalization of the "assessment/remedial" process utilized prior to August 21, 1993. For instance, in cases where interim remedial actions (e.g., excavation of contaminated soil) can adequately address a release, the person performing the cleanup is required to submit only one report (site characterization) to the Department. Where there is limited contamination associated with the closure of an underground 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 waive or combine elements of the corrective action process 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.

The CAP regulations did not establish cleanup standards. With the passage of Act 2, persons can utilize the flexible corrective action process together with the Act 2 cleanup levels to accomplish their remediation goal. Further, in order to facilitate cleanups, the Department has identified those regulated substances or "chemicals of concern" that must be quantified by the laboratory for commonly encountered petroleum products. These substances and the accompanying methodologies are to be utilized to demonstrate attainment for storage tank remediations, as well as other remediations involving petroleum products. It is only these substances that need to be tested for when there is a release of these products, uncontaminated by other sources. These analytical requirements appear in both the "Closure Requirements For Underground Storage Tank Systems" technical document and as <a href="Table IV-9">Table IV-9</a> in this manual. The Department has moved away from requiring analysis for the indicator parameters TRPH and PHC, as they are not standards established by, or under, Act 2.

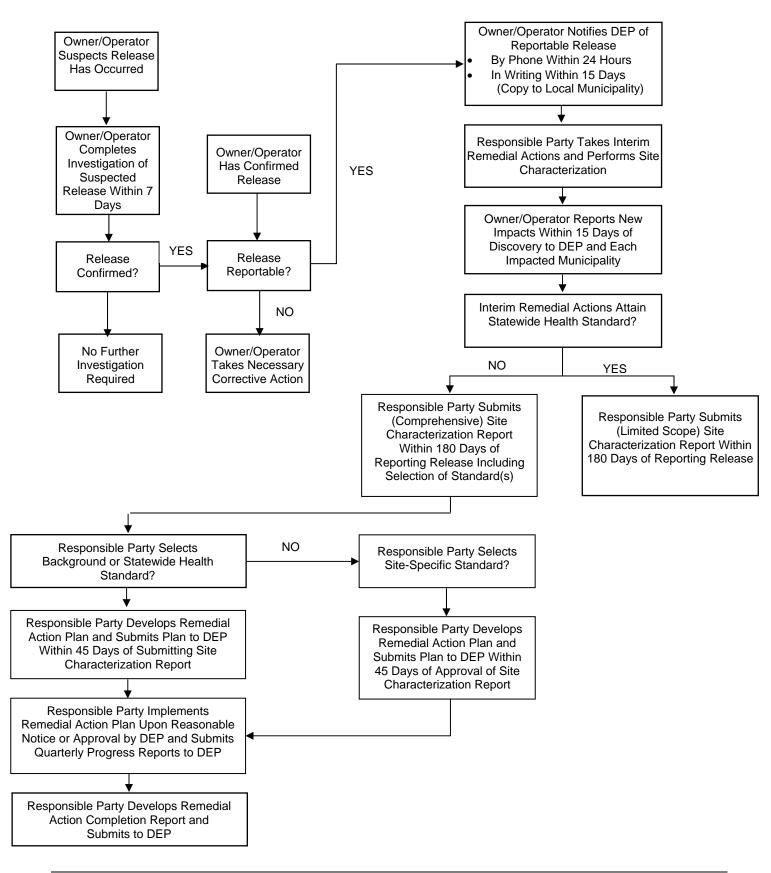
Finally, there have been many questions about the status of "No Further Action" (NFA) letters now that the Act 2 regulations are final. For remediations initiated or continuing after August 16, 1997 (the initial effective date of the Act 2 final rulemaking) under the CAP, the person conducting the remediation must demonstrate attainment of an Act 2 standard. Upon demonstration of attainment, liability protection is provided. NFA letters are not appropriate and will not be issued for doing less than is required under an Act 2 standard.

#### 2. Corrective Action Process Checklist

The flow chart in <u>Figure IV-9</u> shows the major steps and the decision-making process that responsible parties must follow if a release from a regulated storage tank is confirmed to have occurred. This process was designed to be as flexible as possible to accommodate the wide range of specific circumstances that characterize releases.

The following are the major steps of the process:

## FIGURE IV-9 CORRECTIVE ACTION PROCESS



SECTION IV - GENERAL GUIDANCE E. Storage Tank Program Guidance

If a reportable release is confirmed, owners or operators must notify, by telephone, the DEP regional office responsible for the county in which the release occurred within 24 hours of confirming a release. In addition to basic facility and owner information, the notice must describe, 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; and
• interim remedial actions planned, initiated, or completed.
Within 15 days of the telephone notice, the owner or operator must follow up with a written notification to the appropriate DEP regional office, DEP Central 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, "Notification of Reportable Release/ Notification of Contamination," 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 corrective action process.
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.
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 <a href="Section 245.306">Section 245.306</a> 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.

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, attention should be turned to preventing any further release of the regulated substance to the environment. Depending on the circumstances of the release, this may involve:

- arranging for 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;
- recovering free product on the water table;
- recovering product from the excavation;
- establishing booms in or interceptor trenches along streams, gullies or drainageways where surface water has been 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.

In cases involving a reportable release, interim remedial actions planned, initiated or completed are to be indicated in the telephone notification and updated in the 15 day initial and any subsequent written notification. 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.

Act 32 requires that any responsible party who 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. A water supply is affected or
diminished if there is a measurable increase in a concentration of one or more
contaminants (e.g., benzene or MTBE) in the water supply or if the quantity of water
provided by a water supply is decreased. A water supply well may lose flow as a
result of groundwater pumping during a remediation effort.

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.

The responsible party must provide a permanent water supply within 90 days. A permanent water supply includes 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.

The requirement to restore or replace an affected or diminished water supply is strictly an Act 32 issue and remains with the responsible party whether or not liability protection has been afforded to the site for attainment of an Act 2 standard.

- ☐ Responsible parties must properly handle, store and manage excavated contaminated soil which commonly results from tank closures and interim remedial actions. In general, petroleum contaminated soil is a residual waste and must:
  - be stored in accordance with the Department's residual waste management regulations 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 deter public access to the storage area, including use of fencing, security patrols or warning signs;
  - not present a threat to human health or the environment and must be either
    undergoing active treatment or disposed of within 90 days from the first day of
    storage (Active treatment includes treatment methods such as enhanced
    bioremediation in piles, soil vapor extraction and low-temperature thermal
    desorption. Active treatment does not include simply letting the soil pile sit.).
- 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 that has resulted from the release. Section 245.309 of the CAP regulations provides the objectives of any site characterization and a list of elements that may be necessary or required to be conducted. 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 reportable release. It is very important that the site characterization report identify the Act 2 standard selected for the remediation. Interpretations of geologic and hydrogeologic data shall be prepared by a professional geologist licensed in Pennsylvania.

Where interim remedial actions (*e.g.*, removal of contaminated soil) have attained the statewide health standard, and soil is the only medium of concern,, the responsible party may submit a (limited scope) site characterization report to DEP as the final corrective action report in accordance with Section 245.310(b). In this case, the site

characterization report should describe the entire CAP from site characterization to demonstration of attainment of the Statewide health standard.

Where obvious, localized contamination is encountered during the closure of an underground storage tank, the responsible party may submit the closure report form (Attachment 4 in the "Closure Requirements for Underground Storage Tank Systems" document) to satisfy the requirements of the site characterization report identified in Section 245.310(b) of the CAP regulations. A completed closure report form including adherence to the confirmatory sampling protocol in the closure document will be adequate to demonstrate that the requirements of the Statewide health standard have been met. Note that the confirmatory sample locations in the closure document do not apply if the contamination has extended more than three feet from any part of the tank system. Also, because a limited site characterization is required to be conducted in localized contamination situations, the more conservative Statewide health standard must be met. For instance, in soil, the confirmatory sampling will be assumed to be conducted within 2 to 15 feet of the surface. Therefore, the more stringent of the direct contact or highest soil to groundwater numeric values will apply. Where the soil to groundwater values apply, it will be assumed that the aquifer is used with a TDS ≤2500. More stringent standards may apply to samples collected at the soil/water interface [see Sections 250.308(a)(2) and 250.308(a)(4) of the regulations]. Where water is encountered, it will be assumed to be groundwater in a used aquifer with a TDS ≤2500. All sample results must meet the Statewide health standard.

Where a site-specific standard is being pursued and a risk assessment report is required, the report should be submitted to the appropriate DEP regional office within 180 days of confirming the reportable release. The report is to be submitted 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 statewide health standard 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
Upon reasonable notice or approval of the remedial action plan by DEP, the responsible party shall implement the plan. Once the remedial action plan is implemented, remedial action progress reports must be submitted quarterly to the appropriate DEP regional office.
When the standard(s) established in the remedial action plan has/have been achieved, the responsible party shall submit a remedial action completion report. The remedial action completion report shall demonstrate that the requirements of one or more of the Act 2 standards have been met and include, if applicable, a postremediation care plan.

In order to demonstrate that a standard(s) under Act 2 has/have been met and receive the liability protection, the cleanup levels for <u>all</u> regulated substances identified in the list for the product stored must be achieved.
Petroleum contaminated media and debris (material outside the tank, <i>e.g.</i> , 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. This exclusion does not apply to contaminated media and debris from, for example, aboveground tanks, farm and residential motor fuel underground storage tanks of less than 1,100-gallon capacity, and heating oil underground storage tanks. Petroleum contaminated media and debris that are classified as hazardous waste are subject to the deed notice requirements of the Solid Waste Management Act.
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 time frames based on the particular release situation.
In addition, the Department has established review timeframes and deemed approved provisions for site characterization reports, remedial action plans and remedial action completion reports. Deemed approved provisions may be superceded if 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.
If the department fails to meet these timeframes and an extension is not mutually agreed upon, the report or plan is deemed approved. In order to facilitate review of reports and plans by the department, responsible parties are strongly encouraged to

1	properly identify the report or plan which is being submitted. sheet which can be used with CAP submissions.	<u>Table IV-8</u> is a cover
SECTION IV - GENE	RAL GUIDANCE	
E. Storage Tank Prog		

#### Table IV-8

## Corrective Action Process Report/Plan Cover Sheet

### CHAPTER 245 STORAGE TANK ACT

	Closure Report meeting the Site Characterization Report requirements of Section 245.310(b)								
	Site Characterization Report - Section 245.310(b)								
	Site Characterization Report - Site-Specific Standard								
	Site Characterization Report - Statewide Health or Background 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								
(che	Remedial Action Completion Report - Statewide Health or Background Standard								
	Facility ID Number								
	Facility Name								
	Facility Address								
	Preparer Name								
	Preparer Address								

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

Petroleum products contain a large number of regulated substances. However, recognizing that it is not practical to examine all of these regulated substances, the Department has developed what is referred to as the "short list" of regulated substances for groups of petroleum products. This "short list" appears in <u>Table IV-9</u>. It is only these regulated substances or "chemicals of concern" that need to be tested for to demonstrate attainment under any of the Act 2 standards when there is a release of these petroleum products, uncontaminated by other sources.

Further, in demonstrating attainment of the Statewide health standard, the following conditions must also be met:

- For attainment in soil media, there must be no free liquids left in the soil based on visual observation, and the soil must not create any odor nuisance. With regard to the odor nuisance, the soil, by virtue of the location and level of odor, must not result in a complaint to the Department concerning petroleum odors which can, upon investigation, be attributed to petroleum contamination remaining in the soil.
- 2. For attainment in groundwater media, there must be no free floating product at the point of compliance (property line).

The rationale for application of these conditions is that the Statewide health standards are capped at saturation and solubility in soil and groundwater, respectively. Since the Department is only requiring an attainment demonstration for the "short list" of regulated substances and not for all regulated substances contained in a particular petroleum product, these conditions provide further assurance that all Statewide health standards applicable to the petroleum product are met.

This short list of petroleum products may be revised from time to time as determined necessary by the Department. For those sites in the Corrective Action Process or for which a Notice of Intent to Remediate has been filed prior to the date a revised list becomes effective and for which site characterization is underway, attainment demonstration will be made using the old list of substances. Sites which commence investigations to characterize or verify releases after the date the new list becomes effective, whether under the Act 2 regulations or the Storage Tank Corrective Action Process, will use the new list for characterization and attainment demonstration purposes.

<sup>&</sup>lt;sup>1</sup> U. S. EPA. How To Effectively Recover Free Product At Leaking Underground Storage Tank Sites: A Guide For State Regulators. EPA 510-R-96-001. September 1996.

Table IV-9
Short List of Petroleum Products

PRODUCT STORED	PARAMETERS TO BE TESTED IN SOIL	ANALYTICAL METHOD (reported on a dry weight basis)	PARAMETERS TO BE TESTED IN WATER	ANALYTICAL METHOD
Leaded Gasoline, Aviation Gasoline, and Jet Fuel	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-) Trimethyl benzene, 1,3,5- Dichloroethane, 1,2- Dibromoethane, 1,2-	EPA Method 5035/8021B or 5035/8260B	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (Isopropylbenzene) Naphthalene Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,5- Dichloroethane, 1,2- Dibromoethane, 1,2-	EPA Method 5030B/8021B, 5030B/8260B or 524.2  EPA Method 8011 or 504.1
	Lead (total)	EPA Method 6010B or 7420	Lead (dissolved)	EPA Method 6020 or 7421
Unleaded Gasoline	Benzene Toluene Ethyl Benzene Xylenes (total) Cumene (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 Xylenes (total) Cumene (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
Kerosene, Fuel Oil No. 1	Benzene Toluene Ethyl Benzene Cumene (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) 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) 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) 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
Fuel Oil Nos. 4, 5 and 6, and Lubricating Oils and Fluids	Benzene Naphthalene Fluorene Anthracene Phenanthrene Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(a)pyrene Benzo(g,h,i)perylene	EPA Method 5035/8021B or 5035/8260B  EPA Method 8270C or 8310	Benzene Naphthalene Phenanthrene Pyrene Chrysene	EPA Method 5030B/8021B, 5030B/8260B or 524.2 EPA Method 8270C, 8310 or 525.2

E. Storage Tank Program Guidance

# Table IV-9 Short List of Petroleum Products (cont'd)

PRODUCT STORED	PARAMETERS TO BE TESTED IN SOIL	ANALYTICAL METHOD (reported on a dry weight basis)	PARAMETERS TO BE TESTED IN WATER	ANALYTICAL METHOD
Used Motor Oil	Benzene	EPA Method 5035/8021B or	Benzene	EPA Method 5030B/8021B,
	Toluene	5035/8260B	Toluene	5030B/8260B or 524.2
	Ethyl Benzene		Ethyl Benzene	
	Cumene (Isopropylbenzene)		Cumene (Isopropylbenzene)	
	Naphthalene		Naphthalene	
	Pyrene	EPA Method 8270C or 8310	Pyrene	EPA Method 525.2
	Benzo(a)anthracene		Benzo(a)anthracene	
	Chrysene		Chrysene	
	Benzo(b)fluoranthene		Benzo(b)fluoranthene	
	Benzo(a)pyrene		Benzo(a)pyrene	
	Indeno(1,2,3-cd)pyrene		Indeno(1,2,3-cd)pyrene	
	Benzo(g,h,i)perylene		Benzo(g,h,i)perylene	
	Lead (total)	EPA Method 6010B or 7420	Lead (dissolved)	EPA Method 6020 or 7421

Mineral Insulating	PCB-1016 (Aroclor)	EPA Method 8082	PCB-1016 (Aroclor)	EPA Method 8082
Oil	PCB-1221 (Aroclor)		PCB-1221 (Aroclor)	
	PCB-1232 (Aroclor)		PCB-1232 (Aroclor)	
	PCB-1242 (Aroclor)		PCB-1242 (Aroclor)	
	PCB-1248 (Aroclor)		PCB-1248 (Aroclor)	
	PCB-1254 (Aroclor)		PCB-1254 (Aroclor)	
	PCB-1260 (Aroclor)		PCB-1260 (Aroclor)	
	Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-)	EPA Method 5035/8021B or 5035/8260B	Trimethyl benzene, 1,2,4- (Trimethyl benzene, 1,3,4-)	EPA Method 5030B/8021B, 5030B/8260B or 524.2
	Trimethyl benzene, 1,3,5-		Trimethyl benzene, 1,3,5-	

F.	Practical Quantitation Limits

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

			AQUEOL	JS METHODS (	(µg/L)			SOILS	METHODS (mg	/kg)		PC	λL
					DETE	CTION				DETECTION		GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SUIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
ACENAPHTHENE	83-32-9	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
ACENAPHTHYLENE	208-96-8	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
ACEPHATE	30560-19-1												
ACETALDEHYDE	75-07-0	EMSLC	554	HPLC	MDL	44		8315A		MDL	43.7	100	140
ACETONE	67-64-1	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ACETONITRILE	75-05-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ACETOPHENONE	98-86-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
ACETYLAMINOFLUORENE, 2- (2AAF)	53-96-3	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
ACROLEIN	107-02-8		8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ACRYLAMIDE	79-06-1	OSW	8032	GCECD	MDL	0.032						0.1	
ACRYLIC ACID	79-10-7												
ACRYLONITRILE	107-13-1	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ALACHLOR	15972-60-8	EMSLC	505	CGCECD	MDL	0.23						0.7	
ALDICARB	116-06-3	OSW	8321A		MDL	1.4	OSW	8321A		MDL	0.017	4	0.054
ALDRIN	309-00-2	OSW	8081A	CGCECD	MDL	1.4	OSW	8081A	GCECD	MDL	0.0022	4	0.007
ALLYL ALCOHOL	107-18-6	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
AMINOBIPHENYL, 4-	92-67-1	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
AMITROLE	61-82-5												
AMMONIA	7664-41-7												
AMMONIUM SULFAMATE	7773-06-0												
ANILINE	62-53-3	OSW	8131		EQL	23	OSW	8131		MDL	2.3	20	7.3
ANTHRACENE	120-12-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
ATRAZINE	1912-24-9	EMSLC	505	CGCECD	MDL	2.4	OSW	8141	CGCFPD			8	
BAYGON (PROPOXUR)	114-26-1		531.1		MDL	1		8318		MDL	17	3	54
BENOMYL	17804-35-2		8321A		MDL	0.4		8321A		MDL	0.025	1	0.08
BENTAZON	25057-89-0		8151A		MDL	0.2		8151A				0.6	
BENZENE	71-43-2	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BENZIDINE	92-87-5		8270C					8270C					
BENZO[A]ANTHRACENE	56-55-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
BENZO[A]PYRENE	50-32-8		610	HPLC	MDL	0.023	OSW	8270C	CGCMS	EQL	0.66	0.07	0.66
BENZO[B]FLUORANTHENE	205-99-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

			AQUEOL	JS METHODS (	(µg/L)			SOILS	METHODS (mg	/kg)		PG	λΓ
					DETE	CTION				DETE	CTION	GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SUIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
BENZO[GHI]PERYLENE	191-24-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
BENZO[K]FLUORANTHENE	207-08-9	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
BENZOIC ACID	65-85-0	OSW	8270C	CGCMS	EQL	50	OSW	8270C	CGCMS	EQL	3.3	50	3.3
BENZOTRICHLORIDE	98-07-7		8121		EQL	0.06		8121		MDL	0.006	0.06	0.019
BENZYL ALCOHOL	100-51-6	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS	EQL	1.3	20	1.3
BENZYL CHLORIDE	100-44-7	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BHC, ALPHA-	319-84-6	OSW	8081A	GCECD	EQL	0.35	OSW	8081A	GCECD	EQL	1.3	0.4	1.3
BHC, BETA-	319-85-7	OSW	8081A	GCECD	EQL	0.23	OSW	8081A	GCECD	EQL	2.2	0.2	2.2
BHC, DELTA-	319-86-8	OSW	8081A	GCECD	EQL	0.24	OSW	8081A	GCECD	EQL	0.74	0.2	0.74
BHC, GAMMA (LINDANE)	58-89-9		608	GC/ECD	MDL	0.004	OSW	8081A	GCECD	EQL	0.002	0.01	0.002
BIPHENYL, 1,1-	92-52-4												
BIS(2-CHLOROETHOXY)METHANE	111-91-1	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	660
BIS(2-CHLOROETHYL)ETHER	111-44-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
BIS(2-CHLORO-ISOPROPYL)ETHER	39638-32-9	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
BIS(CHLOROMETHYL)ETHER	542-88-1												
BIS[2-ETHYLHEXYL] PHTHALATE	117-81-7		525.2		MDL	0.46	OSW	8270C	CGCMS	EQL	0.66	1	0.66
BISPHENOL A	80-05-7												
BROMACIL	314-40-9		8321A		MDL	0.4		8321A		MDL	0.021	1	0.067
BROMOCHLOROMETHANE	74-97-5	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BROMODICHLOROMETHANE	75-27-4	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BROMOMETHANE	74-83-9	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BROMOPHENYL PHENYL ETHER, 4-	101-55-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
BROMOXYNIL	1689-84-5		8270C					8270C					
BROMOXYNIL OCTANOATE	1689-99-2												
BUTADIENE, 1,3-	106-99-0												
BUTYL ACETATE, N-	123-86-4												
BUTYL ACETATE, SEC-	105-46-4												
BUTYL ACETATE, TERT-	540-88-5												
BUTYL ALCOHOL, N-	71-36-3	OSW	8015B	GCFID	MDL	8	OSW	8015B		MDL	0.23	30	0.73
BUTYLAMINE, N-	109-73-9												
BUTYLATE	2008-41-5		525.2		MDL	0.064						0.2	

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

			AQUEOL	JS METHODS (	(µg/L)			SOILS	METHODS (mg	J/kg)		PC	QL
					DETE	CTION			DETECTION		CTION	GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SUIL
					TYPE	VALUE	1			TYPE	VALUE	(µg/L)	(mg/kg)
BUTYLBENZENE, N-	104-51-8		8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BUTYLBENZENE, SEC-	135-98-8		8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BUTYLBENZENE, TERT-	98-06-6		8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
BUTYLBENZYL PHTHALATE	85-68-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
CAPTAN	133-06-2	OSW	8270C	CGCMS	EQL	50	OSW	8270C	CGCMS			50	
CARBARYL	63-25-2	OSW	8318	HPLC	MDL	1.7	OSW	8318	HPLC	MDL	0.031	5	0.099
CARBAZOLE	86-74-8												
CARBOFURAN	1563-66-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL		10	
CARBON DISULFIDE	75-15-0	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CARBON TETRACHLORIDE	56-23-5	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CARBOXIN	5234-68-4		525.2		MDL	0.4						1	
CATECHOL	120-80-9												
CHLORAMBEN	133-90-4	OSW	8151A		MDL	0.093						0.3	
CHLORDANE	57-74-9		505		MDL	0.14	OSW	8081A	GCECD	EQL		0.4	
CHLORO-1,1-DIFLUOROETHANE, 1-	75-68-3												
CHLORO-1-PROPENE, 3- (ALLYL CHLORIDE)	107-05-1	OSW	8260B	CGCMS	EQL	5	osw	8260B	CGCMS	EQL	0.005	5	0.005
CHLOROACETALDEHYDE	107-20-0												
CHLOROACETOPHENONE, 2-	532-27-4												
CHLOROANILINE, P-	106-47-8	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS	EQL	1.3	20	1.3
CHLOROBENZENE	108-90-7	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CHLOROBENZILATE	510-15-6	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS		0.000	10	0.000
CHLOROBUTANE, 1-	109-69-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CHLORODIBROMOMETHANE	124-48-1	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CHLORODIFLUOROMETHANE	75-45-6												
CHLOROETHANE	75-00-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CHLOROETHYL VINYL ETHER, 2-	110-75-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CHLOROFORM	67-66-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CHLORONAPHTHALENE, 2-	91-58-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
CHLORONITROBENZENE, P-	100-00-5												
CHLOROPHENOL, 2-	95-57-8	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
CHLOROPHENYL PHENYL ETHER, 4-	7005-72-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66

F. Practical Quantitation Limits

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

			AQUEOL	JS METHODS	(µg/L)			SOILS	METHODS (mg	J/kg)		PC	QL
					DETE	CTION				DETECTION		GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SUIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
CHLOROPRENE	126-99-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CHLOROPROPANE, 2-	75-29-6												
CHLOROTHALONIL	1897-45-6		8081A					8081A					
CHLOROTOLUENE, O-	95-49-8												
CHLORPYRIFOS	2921-88-2	OSW	8141A		MDL	0.07	OSW	8141A		MDL	5	0.2	16
CHLORSULFURON	64902-72-3												
CHLORTHAL-DIMETHYL (DACTHAL) (DCPA)	1861-32-1		8081A					8081A					
CHRYSENE	218-01-9	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
CRESOL(S)	1319-77-3		8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
CRESOL, 0- (METHYLPHENOL, 2-)	95-48-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
CRESOL, M (METHYLPHENOL, 3-)	108-39-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
CRESOL, P (METHYLPHENOL, 4-)	106-44-5	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
CRESOL, P-CHLORO-M-	59-50-7												
CROTONALDEHYDE	4170-30-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CROTONALDEHYDE, TRANS-	123-73-9	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CUMENE	98-82-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
CYCLOHEXANE	110-82-7												
CYCLOHEXANONE	108-94-1	OSW	8315	HPLC	MDL	6.9						20	
CYFLUTHRIN	68359-37-5												
CYROMAZINE	66215-27-8												
DDD, 4,4'-	72-54-8	OSW	8081AA	GCECD	MDL	0.05	OSW	8081AA	GCECD	MDL	0.0042	0.2	0.013
DDE, 4,4'-	72-55-9	OSW	8081AA	GCECD	MDL	0.058	OSW	8081AA	GCECD	MDL	0.0025	0.2	0.008
DDT, 4,4'-	50-29-3	OSW	8081AA	GCECD	MDL	0.081	OSW	8081AA	GCECD	MDL	0.0036	0.3	0.011
DECABORANE	17702-41-9												
DI(2-ETHYLHEXYL)ADIPATE	103-23-1		525.2		MDL	0.09						0.3	
DIALLATE	2303-16-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
DIAMINOTOLUENE, 2,4-	95-80-7	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
DIAZINON	333-41-5		525.2		MDL	0.11	OSW	8141A	CGCFPD	EQL	0.1	0.3	0.1
DIBENZO[A,H]ANTHRACENE	53-70-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
DIBENZOFURAN	132-64-9	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DIBROMO-3-CHLOROPROPANE, 1,2-	96-12-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005

F. Practical Quantitation Limits

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

			AQUEOL	JS METHODS (	μg/L)			SOILS	METHODS (mg	J/kg)		PC	QL
						CTION						GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS		MIT	ORG	METHOD	APPARATUS		MIT	WATER	
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
DIBROMOBENZENE, 1,4-	106-37-6												
DIBROMOETHANE, 1,2- (ETHYLENE DIBROMIDE)	106-93-4		524.2		MDL	0.06	osw	8260B	CGCMS	EQL	0.005	0.2	0.005
DIBROMOMETHANE	74-95-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DIBUTYL PHTHALATE, N-	84-74-2	OSW	8270C	CGCMS	EQL	10						10	
DICHLORO-2-BUTENE, 1,4-	764-41-0	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DICHLORO-2-BUTENE, TRANS-1,4-	110-57-6	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DICHLOROBENZENE, 1,2-	95-50-1	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DICHLOROBENZENE, 1,3-	541-73-1	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DICHLOROBENZENE, P-	106-46-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DICHLOROBENZIDINE, 3,3'-	91-94-1	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS	EQL	1.3	20	1.3
DICHLORODIFLUOROMETHANE (FREON 12)	75-71-8	osw	8260B	CGCMS	EQL	5	osw	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROETHANE, 1,1-	75-34-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROETHANE, 1,2-	107-06-2	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROETHYLENE, 1,1-	75-35-4	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROETHYLENE, CIS-1,2-	156-59-2	EMSLC	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROETHYLENE, TRANS-1,2-	156-60-5	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROMETHANE (METHYLENE CHLORIDE)	75-09-2	osw	8260B	CGCMS	EQL	5	osw	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROPHENOL, 2,4-	120-83-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DICHLOROPHENOXYACETIC ACID, 2,4-(2,4-D)	94-75-7	osw	8151A	CGCECD	MDL	0.2	osw	8151A	CGCECD	MDL	0.0001 1	0.6	0.00035
DICHLOROPROPANE, 1,2-	78-87-5	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DICHLOROPROPENE, 1,3-	542-75-6												
DICHLOROPROPIONIC ACID, 2,2- (DALAPON)	75-99-0	OSW	8151A	CGCECD	MDL	1.3	osw	8151A	CGCECD	MDL	0.12	4	0.38
DICHLORVOS	62-73-7	OSW	8141A	CGCFPD	EQL	8	OSW	8141	CGCFPD	EQL	0.4	8	0.4
DICYCLOPENTADIENE	77-73-6												
DIELDRIN	60-57-1	OSW	8081A	GC	MDL	0.44						1	
DIETHANOLAMINE	111-42-2												
DIETHYL PHTHALATE	84-66-2		8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

			AQUEOL	JS METHODS	(µg/L)			SOILS	METHODS (mg	J/kg)		PC	QL
					DETE	CTION				DETE	CTION	GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS		MIT	ORG	METHOD	APPARATUS		MIT	WATER	00.2
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
DIETHYLAMINE	109-89-7												
DIFLUBENZURON	35367-38-5												
DIGLYCIDYL ETHER (DGE)	2238-07-5												
DIMETHOATE	60-51-5	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
DIMETHOXYBENZIDINE, 3,3-	119-90-4		8270C	CGCMS	EQL	100	OSW	8270C	CGCMS			100	
DIMETHYL PHTHALATE	131-11-3	OSW	8270C	CGCMS	EQL	40	OSW	8270C	CGCMS	EQL	0.66	40	0.66
DIMETHYL SULFATE	77-78-1									EQL	1.66		1.7
DIMETHYLAMINOAZOBENZENE, P-	60-11-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
DIMETHYLANILINE, N,N-	121-69-7												
DIMETHYLBENZIDINE, 3,3-	119-93-7												
DIMETHYLHYDRAZINE, 1,1-	57-14-7												
DIMETHYLPHENETHYLAMINE, ALPHA,	122-09-8	osw	8270C	CGCMS				8270C	CGCMS				
ALPHA-													
DIMETHYLPHENOL, 2,4-	105-67-9	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DINITROBENZENE, 1,3-	99-65-0		8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
DINITRO-O-CRESOL, 4,6-	534-52-1	OSW	8270C	CGCMS	EQL	50	OSW	8270C	CGCMS	EQL	3.3	50	3.3
DINITROPHENOL, 2,4-	51-28-5		8270C	CGCMS	EQL	50	OSW	8270C	CGCMS	EQL	3.3	50	3.3
DINITROTOLUENE, 2,4-	121-14-2		8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DINITROTOLUENE, 2,6- (2,6-DNT)	606-20-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
DINOSEB	88-85-7		515.1		MDL	0.33	OSW	8270b	CGCMS			1	
DIOXANE, 1,4-	123-91-1	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
DIOXATHION	78-34-2												
DIPHENAMID	957-51-7		525.2		MDL	0.041						0.1	
DIPHENYLAMINE	122-39-4	OSW	8270C	CGCMS			OSW	8270C	CGCMS				
DIPHENYLHYDRAZINE, 1,2-	122-66-7	OSW	8270C	CGCMS			OSW	8270C	CGCMS				
DIQUAT	85-00-7	EMSLC	549.1	HPLCUV	MDL	0.51						2	
DISULFOTON	298-04-4		8141A	CGFPD	EQL	0.7	OSW	8141A	CGCFPD	EQL	0.035	0.7	0.035
DIURON	330-54-1	OSW	8321A	HPLCMS	MDL	0.4	OSW	8321A	HPLCMS	MDL	0.018	1	0.057
ENDOSULFAN	115-29-7												
ENDOSULFAN I (ALPHA)	959-98-8		8081A	CGCECD	EQL	0.3	OSW	8081A	CGCECD	EQL	1.4	0.3	1.4
ENDOSULFAN II (BETA)	33213-65-9	OSW	8081A	CGCECD	EQL	0.4	OSW	8081A	CGCECD	EQL	1.6	0.4	1.6
ENDOSULFAN SULFATE	1031-07-8	OSW	8081A	CGCECD	EQL	0.35	OSW	8081A	CGCECD	EQL	2.4	0.4	2.4

F. Practical Quantitation Limits

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

			AQUEOL	JS METHODS (	(µg/L)			SOILS	METHODS (mg	J/kg)		PC	λΓ
						CTION						GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS		MIT	ORG	METHOD	APPARATUS		MIT	WATER	
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
ENDOTHALL	145-73-3	EMSLC	548.1	CGCECD	MDL	1.8						6	
ENDRIN	72-20-8		525.2		MDL	0.29	OSW	8081A	CGCECD	EQL	2.4	0.9	2.4
EPICHLOROHYDRIN	106-89-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ETHEPHON	16672-87-0												
ETHION	563-12-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
ETHOXYETHANOL, 2- (EGEE)	110-80-5												
ETHYL ACETATE	141-78-6	ASTM	D3695	GCFID	MDL	1000						3000	
ETHYL ACRYLATE	140-88-5	ASTM	D3695	GCFID	MDL	1000						3000	
ETHYL BENZENE	100-41-4	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ETHYL DIPROPYLTHIOCARBAMATE, S-	759-94-4		525.2		MDL	0.056						0.2	
(EPTC)	759-94-4		525.2		MDL	0.056						0.2	
ETHYL ETHER	60-29-7	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ETHYL METHACRYLATE	97-63-2		8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ETHYL METHANESULFONATE	62-50-0	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
ETHYLAMINE	75-04-7												
ETHYLENE CHLORHYDRIN	107-07-3												
ETHYLENE GLYCOL	107-21-1		8015B					8015B					
ETHYLENE THIOUREA (ETU)	96-45-7		509		MDL	2.7						9	
ETHYLP-NITROPHENYL	2104-64-5	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
PHENYLPHOSPHOROTHIOATE	2104-04-3	USW	02/00	CGCIVIS	EQL	10	USW	6270C	CGCIVIS			10	
FAMPHUR	52-85-7	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
FENAMIPHOS	22224-92-6	EMSLC	525.2		MDL	0.95						3	
FENSULFOTHION	115-90-2	OSW	8270C	CGCMS	EQL	40	OSW	8270C	CGCMS			40	
FENVALERATE (PYDRIN)	51630-58-1												
FLUOMETURON	2164-17-2		8321A		MDL	0.6		8321A		MDL	0.011	2	0.035
FLUORANTHENE	206-44-0	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
FLUORENE	86-73-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
FLUOROTRICHLOROMETHANE	75-69-4	osw	8260B	CGCMS	EQL	5	osw	8260B	CGCMS	EQL	0.005	5	0.005
(FREON 11) FONOFOS	944-22-9		04444					01.11.1					<del>                                     </del>
			8141A	LIDI C	MDI	6.0	00/4	8141A	LIDI C	MDI	6.0	20	20
FORMALDEHYDE	50-00-0		8315A	HPLC	MDL	6.2	OSW	8315A	HPLC	MDL	6.2	20	20
FORMIC ACID	64-18-6		1	I	1	l			I	l	l	1	1

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

		AQUEOUS METHODS (µg/L)						SOILS	PQL				
					DETECTION					DETECTION		GROUND	SOII
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SOIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
FOSETYL-AL	39148-24-8												
FURAN	110-00-9												
FURFURAL	98-01-1												
GLYPHOSATE	1071-83-6	EMSLC	547	HPLCFL	MDL	6						20	
HEPTACHLOR	76-44-8	OSW	8081A	GCECD	EQL	0.4	OSW	8081A	GCECD			0.4	
HEPTACHLOR EPOXIDE	1024-57-3	OSW	8081A	GCECD	EQL	0.32	OSW	8081A	GCECD	EQL	1.4	0.3	1.4
HEXACHLOROBENZENE	118-74-1		612	GCECD	MDL	0.05	OSW	8270C	CGCMS	EQL	0.66	0.2	0.66
HEXACHLOROBUTADIENE	87-68-3		612	GCECD	MDL	0.34	OSW	8270C	CGCMS	EQL	0.66	1	0.66
HEXACHLOROCYCLOPENTADIENE	77-47-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
HEXACHLOROETHANE	67-72-1		524.2		MDL	0.057	OSW	8270C	CGCMS	EQL	0.66	0.2	0.66
HEXACHLOROPROPENE	1888-71-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
HEXANE	110-54-3	ASTM	D3695	GCFID	MDL	1000						3000	
HEXANONE, 2- (METHYL N-BUTYL KETONE)	591-78-6	osw	8260B	CGCMS	EQL	1	osw	8260B	CGCMS	EQL	0.005	1	0.005
HEXYTHÍAZOX (SAVEY)	78587-05-0												
HYDRAZINE/HYDRAZINE SULFATE	302-01-2												
HYDROQUINONE	123-31-9												
INDENO[1,2,3-CD]PYRENE	193-39-5	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
IODOMETHANE	74-88-4	OSW	8260B	CGCMS	EQL	1	OSW	8260B	CGCMS	EQL	0.005	1	0.005
IPRODIONE	36734-19-7												
ISOAMYL ACETATE	123-92-2												
ISOBUTYL ACETATE	110-19-0												
ISOBUTYL ALCOHOL	78-83-1	OSW	8260B	GCMS	EQL	5	OSW	8260B	GCMS	EQL	0.005	5	0.005
ISODRIN	465-73-6	OSW	8270C	CGCMS	EQL	20	OSW	8270C				20	
ISOPHORONE	78-59-1	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
ISOPHORONE DIISOCYANATE	4098-71-9												
ISOSAFROLE	120-58-1	OSW	8270C	CGCMS	EQL	10	OSW	8270C				10	
KEPONE	143-50-0		8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
MALATHION	121-75-5	OSW	8270C	CGCMS	EQL	50	OSW	8141				50	
MALEIC HYDRAZIDE	123-33-1												
MANEB	12427-38-2												
MERPHOS OXIDE	78-48-8												

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

		AQUEOUS METHODS (μg/L)						SOILS	PQL				
	1				DETECTION					DETECTION		GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SOIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
METHACRYLONITRILE	126-98-7	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
METHAMIDOPHOS	10265-92-6												
METHANOL	67-56-1	OSW	8015B	GCFID	MDL	21	OSW	8015B	GCFID	MDL	0.46	70	1.5
METHOMYL	16752-77-5	OSW	8321A		MDL	1.5	OSW	8321A		MDL	0.015	5	0.048
METHOXYCHLOR	72-43-5	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
METHOXYETHANOL, 2-	109-86-4												
METHYL ACETATE	79-20-9												
METHYL ACRYLATE	96-33-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
METHYL CHLORIDE	74-87-3		524.2		MDL	0.13	OSW	8260B	CGCMS	EQL	0.005	0.4	0.005
METHYL ETHYL KETONE	78-93-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
METHYL HYDRAZINE	60-34-4												
METHYL ISOAMYL KETONE	110-12-3												
METHYL ISOBUTYL KETONE	108-10-1	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
METHYL ISOCYANATE	624-83-9												
METHYL MERCAPTAN	74-93-1												
METHYL METHACRYLATE	80-62-6	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
METHYL METHANESULFONATE	66-27-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
METHYL PARATHION	298-00-0	OSW	8141A	CGCFPD	MDL	0.12	OSW	8141A	CGCFPD	MDL	0.06	0.4	0.19
METHYL STYRENE (MIXED ISOMERS)	25013-15-4												
METHYL TERT-BUTYL ETHER (MTBE)	1634-04-4	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
METHYLAMINE	74-89-5												
METHYLCHLOROPHENOXYACETIC ACID (MCPA)	94-74-9	osw	8151A	GCECD	MDL	0.056	osw	8151A	GCECD	EDL	0.043	0.2	0.14
METHYLENE BIS(2-CHLOROANILINE), 4,4'-	101-14-4	osw	8270C	CGCMS			osw	8270C	CGCMS				
METHYLNAPHTHALENE, 2-	91-57-6	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
METHYLSTYRENE, ALPHA	98-83-9												
MEVINPHOS	7786-34-7	OSW	8270C	CGCMS	EQL	10	OSW	8141A	GCFPD	MDL	0.025	10	0.08
MONOCROTOPHOS	6923-22-4	OSW	8270C	CGCMS	EQL	40	OSW	8270C	CGCMS			40	
NAPHTHALENE	91-20-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
NAPHTHOQUINONE, 1,4-	130-15-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
NAPHTHYLAMINE, 1-	134-32-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	

F. Practical Quantitation Limits

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

		AQUEOUS METHODS (μg/L)						SOILS	PQL				
						CTION				DETE	CTION	GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS		MIT	ORG	METHOD	APPARATUS		MIT	WATER	
						VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
NAPHTHYLAMINE, 2-	91-59-8	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
NAPROPAMIDE	15299-99-7		525.2		MDL	0.06						0.2	
NITROANILINE, M-	99-09-2	OSW	8270C	CGCMS	EQL	50	OSW	8270C	CGCMS	EQL	3.3	50	3.3
NITROANILINE, O-	88-74-4	OSW	8270C	CGCMS	EQL	50	OSW	8270C	CGCMS	EQL	3.3	50	3.3
NITROANILINE, P-	100-01-6	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS	EQL		20	
NITROBENZENE	98-95-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
NITROPHENOL, 2-	88-75-5		8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
NITROPHENOL, 4-	100-02-7	OSW	8270C	CGCMS	EQL	50	OSW	8270C	CGCMS	EQL	3.3	50	3.3
NITROPROPANE, 2-	79-46-9	OSW	8260B	GCMS	EQL	5	OSW	8260B	GCMS	EQL	0.005	5	0.005
NITROQUINOLINE-1-OXIDE, 4-	56-57-5		8270C	CGCMS	EQL	40	OSW	8270C	CGCMS			40	
NITROSODIETHYLAMINE, N-	55-18-5	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
NITROSODIMETHYLAMINE, N-	62-75-9	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
NITROSO-DI-N-BUTYLAMINE, N-	924-16-3	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
NITROSODI-N-PROPYLAMINE, N-	621-64-7	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
NITROSODIPHENYLAMINE, N-	86-30-6	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
NITROSO-N-ETHYLUREA, N-	759-73-9												
OCTYL PHTHALATE, DI-N-	117-84-0	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
OXAMYL (VYDATE)	23135-22-0	OSW	8321A		MDL	0.3	OSW	8321A		MDL	0.015	1	0.048
PARATHION	56-38-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCFPD			10	
PCB-1016 (AROCLOR)	12674-11-2	OSW	8082	CGCECD	MDL	0.054	OSW	8082	CGCECD	MDL	0.057	0.2	0.18
PCB-1221 (AROCLOR)	11104-28-2	OSW	8082	CGCECD	MDL	0.054	OSW	8082	CGCECD	MDL	0.057	0.2	0.18
PCB-1232 (AROCLOR)	11141-16-5	OSW	8082	CGCECD	MDL	0.054	OSW	8082	CGCECD	MDL	0.057	0.2	0.18
PCB-1242 (AROCLOR)	53469-21-9	OSW	8082	CGCECD	MDL	0.054	OSW	8082	CGCECD	MDL	0.057	0.2	0.18
PCB-1248 (AROCLOR)	12672-29-6	OSW	8082	CGCECD	MDL	0.054	OSW	8082	CGCECD	MDL	0.057	0.2	0.18
PCB-1254 (AROCLOR)	11097-69-1	OSW	8082	CGCECD	MDL	0.054	OSW	8082	CGCECD	MDL	0.057	0.2	0.18
PCB-1260 (AROCLOR)	11096-82-5	OSW	8082	CGCECD	MDL	0.054	OSW	8082	CGCECD	MDL	0.057	0.2	0.18
PEBULATE	1114-71-2		525.2		MDL	0.08						0.3	
PENTABORANE	19624-22-7												
PENTACHLOROBENZENE	608-93-5	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
PENTACHLOROETHANE	76-01-7	OSW	8260B	GCMS	EQL	5	OSW	8260B	GCMS	EQL	0.005	5	0.005
PENTACHLORONITROBENZENE	82-68-8	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

		AQUEOUS METHODS (μg/L)						SOILS	PC	QL			
					DETE	CTION				DETE	CTION	GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SOIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
PENTACHLOROPHENOL	87-86-5		525.2		MDL	0.034	OSW	8270C	CGCMS	EQL	3.3	0.1	3.3
PERCHLOROMETHYL MERCAPTAN	594-42-3												
PHENACETIN	62-44-2		8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
PHENANTHRENE	85-01-8		8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
PHENOL	108-95-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
PHENYL MERCAPTAN	108-98-5	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
PHENYLENEDIAMINE, M-	108-45-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
PHENYLPHENOL, 2-	90-43-7												
PHORATE	298-02-2	OSW	8270C	CGCMS	EQL	10	OSW	8141A	CGFPD	EQL	0.02	10	0.02
PHTHALIC ANHYDRIDE	85-44-9	OSW	8270C	CGCMS	EQL	100	OSW	8270C	CGCMS			100	
PICLORAM	1918-02-1	OSW	8151A		MDL	0.14	OSW	8151A				0.4	
PICOLINE, 2-	109-06-8	OSW	8270C	CGCMS			OSW	8270C	CGCMS				
POLYCHLORINATED BIPHENYLS (AROCLORS) (PCBS)	1336-36-3		8082					8082					
PRONAMIDE	23950-58-5	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
PROPANIL	709-98-8												
PROPANOL, 1-	71-23-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
PROPANOL, 2- (ISOPROPYL ALCOHOL)	67-63-0	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
PROPHAM	122-42-9		8321A		MDL	0.4		8321A		MDL	0.012	1	0.038
PROPIOLACTONE, BETA	57-57-8	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
PROPIONIC ACID	79-09-4												
PROPIONITRILE (ETHYL CYANIDE)	107-12-0	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
PROPYLBENZENE, N-	103-65-1	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
PROPYLENE IMINE	75-55-8												
PROPYLENE OXIDE	75-56-9	ASTM	D3695	GCFID	MDL	1000						3000	
PYRENE	129-00-0	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
PYRETHRUM	8003-34-7												
PYRIDINE	110-86-1	OSW	8270C	CGCMS			OSW	8270C	CGCMS				
QUINOLINE	91-22-5												
QUINONE (p-BENZOQUINONE)	106-51-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
QUIZALOFOP (ASSURE)	76578-14-8												
RESORCINOL	108-46-3	OSW	8270C	CGCMS	EQL	100	OSW	8270C	CGCMS			100	

SECTION IV - GENERAL GUIDANCE

F. Practical Quantitation Limits

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

		AQUEOUS METHODS (μg/L)						SOILS	PC	QL			
					DETE	CTION				DETE	CTION	GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	SUIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
RONNEL	299-84-3	OSW	8141A	GCFPD	EQL	0.7	OSW	8141A	GCFPD	EQL	0.035	0.7	0.035
SIMAZINE	122-34-9	EMSLC	525.2		MDL	0.045	OSW	8141	CGCFPD			0.1	
STRYCHNINE	57-24-9	OSW	8270C	CGCMS	EQL	40	OSW	8270C	CGCMS			40	
STYRENE	100-42-5	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
SULFIDE	18496-25-8												
SULFUR MONOCHLORIDE	10025-67-9												
TEBUTHIURON	34014-18-1		8321A		MDL	0.5		8321A		MDL	0.021	2	0.067
TEPP	107-49-3	OSW	8141A	GCFPD	EQL	8	OSW	8141A	GCFPD	EQL	0.4	8	0.4
TERBACIL	5902-51-2		525.2	CGCMS	MDL	0.22						0.7	
TERBUFOS	13071-79-9	EMSLC	525.2	CGCMS	MDL	0.096	OSW	8270C	CGCMS			0.3	
TETRACHLOROBENZENE, 1,2,4,5-	95-94-3	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
TETRACHLORODIBENZO-P-DIOXIN, 2,3,7,8- (TCDD Equivalents))	1746-01-6	OSW	8280A	CGCMS	EQL	0.01	osw	8280A	CGCMS	EQL	0.001	0.01	0.001
TETRACHLOROETHANE, 1,1,1,2-	630-20-6	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TETRACHLOROETHANE, 1,1,2,2-	79-34-5		524.2		MDL	0.04	OSW	8260B	CGCMS	EQL	0.005	0.1	0.005
TETRACHLOROETHYLENE (PCE)	127-18-4	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TETRACHLOROPHENOL, 2,3,4,6-	58-90-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
TETRAETHYL LEAD	78-00-2												
TETRAETHYLDITHIOPYROPHOSPHAT E	3689-24-5	osw	8270C	CGCMS	EQL	20	osw	8270C	CGCMS			20	
TETRAHYDROFURAN	109-99-9												
TETRANITROMETHANE	509-14-8												
THIOFANOX	39196-18-4		8321A					8321A					
THIONAZIN	297-97-2	OSW	8270C	CGCMS	EQL	20	OSW	8270C	CGCMS			20	
THIRAM	137-26-8												
TOLUENE	108-88-3	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TOLUIDINE, M-	108-44-1												
TOLUIDINE, O	95-53-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS			10	
TOLUIDINE, P-	106-49-0	_	_				_			_			
TOXAPHENE	8001-35-2	OSW	8081A	CGCMS	EQL	0.81	OSW	8081A	CGCMS			0.8	
TRIALLATE	2303-17-5												
TRIBROMOMETHANE (BROMOFORM)	75-25-2	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005

SECTION IV - GENERAL GUIDANCE

F. Practical Quantitation Limits

Table IV-10
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils
Organics

		AQUEOUS METHODS (μg/L)						SOILS	PC	QL			
					DETE	CTION				DETE	CTION	GROUND	SOIL
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS	LI	MIT	ORG	METHOD	<b>APPARATUS</b>	LI	MIT	WATER	JOIL
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
TRICHLORO-1,2,2-	76-13-1												
TRIFLUOROETHANE, 1,1,2-													
TRICHLOROBENZENE, 1,2,4-	120-82-1	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TRICHLOROBENZENE, 1,3,5-	180-70-3		8121		EQL	120	OSW	8121		EQL	8040	100	8000
TRICHLOROETHANE, 1,1,1-	71-55-6	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TRICHLOROETHANE, 1,1,2-	79-00-5	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TRICHLOROETHYLENE (TCE)	79-01-6	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TRICHLOROPHENOL, 2,4,5-	95-95-4	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
TRICHLOROPHENOL, 2,4,6-	88-06-2	OSW	8270C	CGCMS	EQL	10	OSW	8270C	CGCMS	EQL	0.66	10	0.66
TRICHLOROPHENOXYACETIC ACID,	93-76-5	osw	8151A	GCECD	EDL	0.08	OSW	8151A	GCMS			0.3	
2,4,5- (2,4,5-T)	93-70-3	OSW	6151A	GCECD	LDL	0.06	03	0131A	GCIVIS			0.3	
TRICHLOROPHENOXYPROPIONIC	93-72-1	osw	8151A	GCECD	EDL	0.08	OSW	8151A	GCMS	EQL	0.0002	0.3	0.00028
ACID, 2,4,5- (2,4,5-TP)		OSW	0131A	GOLOD	LDL 0	0.06	03	01317	GOIVIO	LQL	8	0.3	0.00028
TRICHLOROPROPANE, 1,1,2-	598-77-6												
TRICHLOROPROPANE, 1,2,3-	96-18-4	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
TRICHLOROPROPENE, 1,2,3-	96-19-5												
TRIETHYLAMINE	121-44-8												
TRIETHYLPHOSPHOROTHIOATE,	126-68-1	OSW	8270C	CGCMS			OSW	8270C	CGCMS				
O,O,O-	120-00-1	OSW		CGCIVIS									
TRIFLURALIN	1582-09-8		525.2		MDL	0.048	OSW	8270C	CGCMS			0.2	
TRIMETHYLBENZENE, 1,3,4-	95-63-6	osw	8260B	CGCMS	EQL	5	osw	8260B	CGCMS	EQL	0.005	5	0.005
(TRIMETHYLBENZENE, 1,2,4-)		OSVV		CGCIVIO			OSW	0200D	CGCIVIS	LQL	0.003	-	0.005
TRIMETHYLBENZENE, 1,3,5-	108-67-8		524.2		MDL	0.05						0.2	
TRINITROGLYCEROL	55-63-0												
(NITROGLYCERIN)													
TRINITROTOLUENE, 2,4,6-	118-96-7												
VINYL ACETATE	108-05-4	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
VINYL BROMIDE (BROMOETHENE)	593-60-2												
VINYL CHLORIDE	75-01-4		524.2		MDL	0.17	OSW	8260B	CGCMS	EQL	0.005	0.5	0.005
WARFARIN	81-81-2												
XYLENES (TOTAL)	1330-20-7	OSW	8260B	CGCMS	EQL	5	OSW	8260B	CGCMS	EQL	0.005	5	0.005
ZINEB	12122-67-7	_											

SECTION IV - GENERAL GUIDANCE

F. Practical Quantitation Limits

Table IV-11
Analytical Methodologies for Establishing Quantitation Limits in Groundwater and Soils Inorganics

			AQUEO	US METHODS	(µg/L)			SOILS	PQL				
REGULATED SUBSTANCE	CASRN	ORG	METHOD	APPARATUS	DETECTION LIMIT		ORG	METHOD	APPARATUS	DETECTION LIMIT		GROUND WATER	Soil
					TYPE	VALUE				TYPE	VALUE	(µg/L)	(mg/kg)
ALUMINUM	7429-90-5	OSW	6010	ICPAES	EDL	45						50	
AMMONIA	7664-41-7												
ANTIMONY	7440-36-0	OSW	6010	ICPAES	EDL	32						30	
ARSENIC	7440-38-2	OSW	7060	GFAA	DL	1						1	
ASBESTOS	12001-29-5												
BARIUM AND COMPOUNDS	7440-39-3	OSW	6010	ICPAES	EDL	2						2	
BERYLLIUM	7440-41-7	OSW	6010	ICPAES	EDL	0.3						0.3	
BORON AND COMPOUNDS	7440-42-8	OSW	6010	ICPAES	EDL	5						5	
CADMIUM	7440-43-9	OSW	7131	GFAA	EDL	0.1						0.1	
CHROMIUM III	7440-47-3	OSW	7191	GFAA	EDL	1						1	
CHROMIUM VI	18540-29-9	OSW	7196	COLORIM.	EDL	1						1	
COBALT	7440-48-4	OSW	6010	ICPAES	EDL	7						7	
COPPER	7440-50-8	OSW	6010	ICPAES	EDL	6						6	
CYANIDE, FREE	57-12-5	OSW	9014		EDL	100						100	
IRON	7439-89-6	OSW	6010	ICPAES	EDL	7						7	
LEAD	7439-92-1	OSW	7421	GFAA	EDL	1						1	
MANGANESE	7439-96-5	OSW	6010	ICPAES	EDL	2						2	
MERCURY	7439-97-6	OSW	7470A	CVAA	DL	0.2	OSW	7471A	CVAA	DL	0.2	0.2	0.2
NICKEL	7440-02-0	OSW	6010	ICPAES	EDL	15						20	
NITRATE-NITROGEN (TOTAL)	14797-55-8												
NITRITE-NITROGEN (TOTAL)	14797-65-0												
SELENIUM	7782-49-2	OSW	7740	GFAA	EDL	2						2	
SILVER	7440-22-4	OSW	6010	ICPAES	EDL	7						7	
THALLIUM	7440-28-0	OSW	6010	ICPAES	EDL	40						40	
TIN	7440-31-5	<b>EMSLC</b>	200.7	ICPAES	MDL	7						20	
VANADIUM	7440-62-2	<b>EMSLC</b>	200.8	ICPMS	MDL	2.5						8	
ZINC	7440-66-6	OSW	6010	ICPAES	EDL	2						2	

SECTION IV - GENERAL GUIDANCE F. Practical Quantitation Limits

# G. Site-Specific Human Health Risk Assessment Guidance

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

Any person selecting the site-specific standard established by Section 304 of Act 2 should submit a risk assessment report to the Department for review and approval unless no present or future complete exposure pathways exist as demonstrated by a fate and transport analysis. If no complete exposure pathways exist, a risk assessment report and cleanup plan are not required and no remedy is required to be proposed or completed. If complete exposure pathways exist, the fate and transport analysis, which is a part of the exposure assessment, should be documented in the risk assessment report.

Under Act 2, a risk assessment report may include the following:

- a baseline risk assessment report that describes the potential adverse effects under both current and planned future conditions caused by the presence of regulated substances in the absence of any further control, remediation or mitigation measures;
- a risk assessment report that documents which exposure pathways will be eliminated by a pathway elimination measure so that any substantial present or probable future risk to human health or the environment is eliminated;
- a risk assessment to develop a site-specific standards report that describes the methods used to develop concentration levels at which human health and the environment are protected; and
- the comments obtained as a result of a public involvement plan, if any, and the responses to those public comments.

A baseline risk assessment report is not required if the Department, in its remedial investigation report or cleanup plan approval, determines that a specific remediation measure that eliminates all pathways, other than a no-action remedial alternative, can be implemented to attain the site-specific standard. [Section 250.405(c)]. All current or probable future exposure pathways as identified in the fate and transport analysis should be addressed in the risk assessment to develop the site-specific standards report.

#### 1. Introduction

To determine if a site-specific risk assessment for human health evaluation is necessary, a site conceptual model should be developed that defines potential exposure scenarios and pathways. The exposure scenario (*e.g.*, residential, industrial, recreational) which will define the exposure pathways must be based on site-specific land use considerations. 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 IV.G.2.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 future planned conditions. If engineering or institutional controls that are to be implemented will eliminate all exposure pathways, the risk assessment report does not need to include information regarding quantification of exposure, toxicity assessment, risk algorithm and risk calculation as identified in Section II.C.7.b of this manual.

However, before getting into the mechanics of performing the 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 Environmental Protection Agency (EPA) guidance documents. The process will not 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, a person may consult the most recent EPA and ASTM guidelines, such as those listed on <u>Table IV-12</u>, for additional guidance. For petroleum release sites, the risk assessment methodology in ASTM E 1739 (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.C.7.b of the manual. The outline is intended to provided guidance on minimum requirements for the report.

## 2. Risk Assessment for Human Health [Section 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; and
- (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 [Section 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 Region III Risk-Based Concentration (RBC) screening procedures [http://www.epa.gov/reg3hwmd/risk/riskmenu.htm]. 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 RBC values for carcinogenic effects or 1/10th of the RBC values (HQ=0.1) for noncarcinogenic effects should be retained in the risk assessment. Chemicals on the site at maximum concentration below the RBC values for carcinogenic effects or 1/10th of the RBC 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.

In the second situation of using combination of standards, the list of chemicals of concern in the site-specific risk assessment should include those onsite chemicals that comply with neither the Statewide health standard nor the background standard. The chemicals of concern may be further screened or re-included using the same RBC screening procedures mentioned above.

Chemical concentrations should also be compared to 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 ten times the maximum amount detected in the blank. If the concentration is less than ten 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 ten times the level of contamination noted in the blank, then completely eliminate that chemical from the set of sample results. Common laboratory contaminants include acetone, 2-butanone (methyl ethyl ketone), methylene chloride, toluene, and phthalate esters.

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 a any 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.

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 obviously 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 reducing 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.

To document attainment in order to obtain liability protection under Act 2, frequency of detection should not be used as a means for determining whether a constituent is retained for the risk assessment. However, infrequently detected constituents that are anomalies due to sampling, analytical or other problems would not be retained in 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) Site conceptual model

Development of a site conceptual model is an important step in identifying additional data needs in site characterization and in defining exposure. A site conceptual model identifies all potential or suspected sources of contamination, types and concentrations of contaminants detected a 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

site conceptual 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 model may be graphical, tabular or narrative but should provide an accurate understanding of complete exposure pathways for the site. Examples of site conceptual models may be found in EPA or ASTM guidance documents, including Section 4.2 of RAGS Part A (EPA, 1989a) and the ASTM RBCA Tier 2 guidance manual (ASTM, 1995). It is suggested that the development of the site conceptual model be coordinated with the regulatory risk manager to ensure that potential pathways are adequately and appropriately addressed prior to performing the assessment.

# b) Exposure Assessment [Sections <u>250.603</u> and <u>250.604</u>]

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 EPA guidance documents (including primarily EPA 1989a, 1991a,b and 1992b but see also the attached list of select references) 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

<u>Exposure Pathways</u>: The exposure pathway describes the mechanism by which receptors (individuals or populations) 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. The EPA provides guidance (e.g., EPA, 1989a) on fate and transport analysis.

As discussed above, the site conceptual 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 (*e.g.*, EPA, 1989a, 1991a,b, 1996a) 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 (*e.g.*, inhalation of vapors via intrusion into enclosed spaces), are also best addressed on a site-specific basis because of the inherent uncertainty associated with the defining the transport from the source to the receptor. In the case of vapor intrusion into enclosed spaces, 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 (EPA, 1996a; PA RA Subcommittee, 1996). 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.

<u>Section 250.603</u> 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 Statewide health standards identified in Subchapter C of the regulations. Site-specific exposure factors shall be clearly justified by supporting data.

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 (1996d) which is in the process of being updated and the American Industrial Health Council (AIHC) Exposure Factors Sourcebook (AIHC, 1994) also being updated.

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. 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 must 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 will be required. This may be as simple as corroborating the conservative assumptions with field measurements.

For the application of a groundwater model, the following quality assurance and quality control procedures as described in Chapter 6 (relating to Models and Computers in Ground-Water Investigation) of EPA's Ground Water Handbook (EPA, 1991d) should be considered:

- Verification of the mathematical basis of a model by comparing its output with known analytical solutions to specific problems.
- Validation of the applicability of a model to various problem categories by successful simulation of observed field data.
  - i) Calibrating the model using one set of historical records: the aquifer coefficients and other model parameters are adjusted to achieve the best match between model outputs and known data.
  - ii) Attempting to predict a subsequent set of historical records: No adjustments are made except for actual changes. A mismatch means that the model either is not correctly formulated or does not treat all of the important phenomena affecting the actual field situation.

- Benchmarking the efficiency of a model in solving problems by comparison with the performance of other models.
- Critical review of the problem conceptualization to ensure that the modeling
  effort considers all physical, chemical, and biological processes that may affect
  the problem.
- Evaluation of the specifics of the model's application, e.g., appropriateness of the boundary conditions, grid design, time steps, etc. Calibration and sensitivity analysis to determine if the model outputs vary greatly with changes in input parameters are important aspects of this process.

For selection of groundwater models, some important technical capabilities for groundwater models are identified in <u>Table IV-13</u>. Additional guidance on the selection and use of fate and transport models can be found in the EPA and ASTM documents listed in <u>Table IV-14</u>.

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. ASTM is in the process of developing a guide for addressing natural attenuation.

# 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 and air intake) 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, 1989b) and the AIHC Exposure Factors Sourcebook (AIHC, 1994). Both of these data sources are in the process of being updated. A draft update (EPA, 1996d) of the EPA Exposure Factors Handbook, 1989 version (EPA, 1989b) is undergoing final revisions. 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 for a given situation, a sensitive subpopulation may be of concern (*e.g.*, pregnant women, subsistence fishermen). 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 must 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.

Environmental 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 average concentration (or an upper confidence limit on the arithmetic average) 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.

<u>Intake</u>: 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, recent EPA guidance encourages the development of a range of exposure (and risk) descriptors (Habicht memo, EPA, 1992a; Browner, EPA, 1995b; Science Policy Council, EPA, 1995d). 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 so may be inappropriate for simple sites. Deterministic evaluation, *i.e.*, point estimates, are a useful alternative. If single point estimates are developed, however, 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 Statewide health standards). In this way, a range of exposures can thus 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, Jayjock 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 reference doses and cancer slope factors from one of the following sources, in the order indicated:

- a) Integrated Risk Information System (IRIS);
- b) Health Effects Assessment Summary Tables (HEAST);
- c) United States Environmental Protection Agency, National Center for Environmental Assessment (NCEA) provisional values;
- d) Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles;
- e) California EPA, California Cancer Potency Factors; and
- f) United States Environmental Protection Agency 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 that it is 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 the Bower model (Bowers et al., 1994), or the physiologically-based pharmacokinetic model (O'Flaherty, 1995, 1997) developed to determine the effects of lead on adults 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 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 completed pathway, the total cancer risk and noncancer hazard quotient should be defined or a cleanup concentration for that pathway determined. In developing cleanup numbers for the site, cumulative excess risk 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. 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, 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, thus, 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 (Burmaster and Anderson, 1994). The concept is important and indeed implicit in the risk-based approach but is often ignored in practice. For example, the Statewide health standards 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. A qualitative evaluation of the uncertainty should be included at a minimum indicating what the most uncertain and most sensitive parameters are and their likely impact on the results. It is important to put in perspective 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 levels, 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.

<u>Probabilistic Analysis</u>: 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. Although the use of probabilistic analysis for risk assessments associated with site remediation has advanced significantly in the last five years, there are still data gaps which also limit its utility on a routine basis. Recent advances include methods for backcalculating soil cleanup levels (Burmaster et al., 1995 and Burmaster and Thompson, 1995); EPA's guiding principles for Monte Carlo analysis (EPA, 1997) as a result of an EPA sponsored workshop on the issue in May 1996 (EPA, 1996c). Both Regions III and VIII have also recently provided guidance (EPA, 1994, 1995c).

It is suggested that probabilistic analysis be used as part of a tiered approach to risk assessment in the site remediation process.

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 are to 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) are to be documented and easily located in the report. This documentation is to include a discussion of the degree to which the data used are representative of the population under study. Also, this documentation is to include the names of the models and software used to generate the analysis. Sufficient information is to be provided to allow the results of the analysis to be independently reproduced.
- The results of sensitivity analyses are to 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 is to 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 is to 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 is to be explained and justified. For both the input and output distributions, variability and uncertainty are to be differentiated where possible.
- The numerical stability of the central tendency and the higher end (i.e., tail) of the output distributions are to be presented and discussed.
- Calculations of exposures and risks using deterministic (e.g., point estimate) methods
  are to 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.

## f) References for Human Health Risk Assessment

American Industrial Health Council, 1994 Exposure Factors Sourcebook,.

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EPA, 1997. Guiding Principles for Monte Carlo Analysis, EPA/630/R-97/001, March.

Hawkins, N.C., M.A. Jayjock, and J. Lynch, 1992. A rationale and framework for establishing the quality of human exposure assessments. <u>American Industrial Hygiene Association Journal</u> 53:34-41.

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- 1. Interim Final Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part A, Baseline Risk Assessment (RAGS Volume 1 Part A). EPA/540/1-89/002.
- 2. Interim Final Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part B, Development of Risk-based Preliminary Remediation Goals (RAGS Volume 1 Part B), OSWER 9285.7-01B, EPA, Office of Solid Waste and Emergency Response, December 1991.
- 3. Interim Final Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part C, Risk Evaluation of Remedial Alternatives (RAGS Volume 1 Part C). EPA/540/R-92/004.
- 4. Interim Final Human Health Evaluation Manual, Supplemental Guidance, `Standard Default Exposure Factors', OSWER Directive 9285.6-03.
- 5. Interim Final Guidance for Soil Ingestion Rates. OSWER Directive 9850.4.
- 6. Exposure Factors Handbook. EPA/600/8-89/043. (This document is in a process of being updated.)
- 7. Interim Final Guidance for Data Usability in Risk Assessment. EPA/540/G-90/008.
- 8. Superfund Exposure Assessment Manual. EPA/540/1-88/001, OSWER Directive 9285.5-1.
- 9. US EPA Region III Technical Guidance Manual, Risk Assessment, Chemical Concentration Data Near the Detection Limit. EPA/903/8-91/001.
- 10. US EPA Region III Technical Guidance Manual, Risk Assessment, Exposure Point Concentrations in Groundwater. EPA/903/8-91/002.
- 11. US EPA Region III Technical Guidance Manual, Risk Assessment, Selecting Exposure Routes and Contaminants of Concern by Risk-Based Screening. EPA/903/R-93-001.
- 12. US EPA Region III Technical Guidance Manual, Risk Assessment, Assessing Dermal Exposure from Soil. EPA/903-K-95-003.
- 13. Guiding Principles for Monte Carlo Analysis. EPA/630/R-97/001.
- 14. Dermal Exposure Assessment: Principles and Applications (Interim Report). US EPA Office of Research and Development. EPA/600/8-91/011B. NTIS PB92205665.
- 15. Guidelines for exposure assessment; 57 Fed Reg., May 29, 1992, p. 22888-22938.

- 16. Guidelines for Developmental Toxicity Risk Assessment; 56 Fed Reg., December 5, 1991, p. 63798-63826.
- 17. Guidelines for Reproductive Toxicity Risk Assessment; 61 Fed Reg., October 31, 1996, p. 56274-56322.
- 18. Guidelines for the Health Risk Assessment of Chemical Mixtures; 52 Fed Reg., September 24, 1986, p. 34014-34025.
- 19. Proposed Guidelines for Neurotoxicity Risk Assessment; 60 Fed Reg., October 4, 1995, p. 52032-52056.
- 20. Guidelines for Mutagenicity Risk Assessment; 51 Fed Reg., September 24, 1986, p. 34006-34012.
- 21. Proposed Guidelines for Carcinogen Risk Assessment; 61 Fed Reg., April 23, 1996, p. 17960-18011.
- 22. Guidance for Risk Characterization; EPA Science Policy Council, February 1995. (Available at Internet: http://www.epa.gov/ORD/spc/rcguide.htm).
- 23. ASTM E 1739, Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites.
- 24. ASTM E 1689, Standard Guide for Developing Conceptual Site Models for Contaminated Sites.
- 25. ASTM E 978, Standard Practice for Evaluating Mathematical Models for the Environmental Fate of Chemicals.

## TABLE IV-13. Technical Capability Criteria for Groundwater Models

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- Ability to estimate a mixing zone in the uppermost aquifer under a site and model the contaminants in this mixing zone.
- Ability to account for contaminant sorption with the aquifer solids including the ability to account for mass transfer or kinetic limitations in contaminant sorption and desorption.
- Ability to account for soil and bedrock heterogeneity.
- Ability to account for the gas phase transport.
- Ability to account for dispersive and advective transport in flowing groundwater.
- Ability to account for special rules described in Act 2, such as 15' direct contact depth.
- Ability to be implemented on a PC hardware/software platform.
- Ease of use/availability of program/level of documentation.
- Ability to account for volatilization.
- Ability to simulate varying recharge conditions (infiltration rates) and varying background groundwater flows.
- Ability to handle degradation.

# TABLE IV-14 Guidances and Resources of Fate and Transport Models and Methodologies

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A person planning to use fate and transport models and methods to estimate exposure concentrations and to develop site-specific standards should give consideration to the following models, methods, and guidances.

# **Equations for Soil-to-Air Volatilization Factor and Particulate Emission Factor:**

These can be found in EPA's "Soil Screening Guidance: User's Guide, Second Edition" Publication 9355.4-23, July 1996, Office of Solid Waste and Emergency Response, Washington, DC 20460.

#### **Groundwater Models:**

Various groundwater models have been identified in the following documents:

- 1. EPA 1988 Superfund Exposure Assessment Manual, EPA/540/1-88/001, OSWER Directive 9285.5-1, Section 3.5.
- 2. EPA, 1988 Selection Criteria for Mathematical Models Used in Exposure Assessments: Ground-Water Models, 600/8-88/075.
- 3. EPA, 1989 Groundwater Modeling: An Overview and Status Report, EPA/600/2-89/028 (NTIS PB89-229497). (Also available from International Ground Water Modeling Center, Institute for Ground-Water Research and Education, Colorado School of Mines, Golden, Colorado 80401.)
- 4. National Academy of Sciences 1990. (NAS) Ground Water Models: Scientific and Regulatory Applications. National Academy Press, Washington, DC.
- 5. EPA, 1994 Ground Water Modeling Compendium, Second Edition EPA-500-B-94-003. 1994. Resource Management and Information Staff, Office of Solid Waste and Emergency Response, Washington, DC 20460.
- 6. van der Heijde, P. M. 1994 Identification and Compilation of Unsaturated/ Vadose Zone Models. EPA/600/R-94/028. 1994. R.S. Kerr Environmental Research Laboratory, Office of Research and Development, EPA, Ada, OK.
- 7. EPA, 1993. Compilation of Ground-Water Models. EPA/600/R-93/118. Office of Research and Development, Washington, DC 20460.

Additional information regarding groundwater models may be obtained from the following sources:

- 1. EPA, Center for Exposure Assessment Modeling (CEAM), 960 College Station Road, Athens, Georgia 30605-2700; telephone (706)546-3549; Internet address: ftp://ftp.epa.gov/epa\_ceam/wwwhtml/ceamhome.htm
- 2. EPA, Robert S. Kerr Environmental Research Laboratory, Center for Subsurface Modeling Support (CSMOS), P. O. Box 1198, Ada, Oklahoma 74820; telephone (405)436-8586; Internet address: http://www.epa.gov/ada/csmos.html
- 3. International Ground-Water Modeling Center (IGWMC), Institute for Ground-Water Research and Education, Colorado School of Mines, Golden, Colorado 80401. Internet address: http://www.mines.edu/igwmc/

Any person planning to select and run computer models in analyzing contaminant migration should consult the following EPA or ASTM documents for guidance:

- 1. EPA. 1988. Selection Criteria for Mathematical Models Used in Exposure Assessments: Ground-Water Models, 600/8-88/075 1988.
- 2. EPA. 1994. Ground Water Modeling Compendium, Second Edition EPA-500-B-94-003. Resource Management and Information Staff, Office of Solid Waste and Emergency Response, Washington, DC.
- 3. EPA. 1994. Assessment Framework for Ground Water Modeling Applications, EPA-500-B-94-004. July 1994. OSWER Directive 9029.00. Office of Solid Waste and Emergency Response, Washington, DC.
- 4. EPA. 1992. Quality Assurance and Quality Control in the Development and Application of Ground-Water Models, EPA/600/R-93/011. Office of Research and Development, Washington, DC 20460.
- 5. ASTM E 978, Standard Practice for Evaluating Mathematical Models for the Environmental Fate of Chemicals.

#### **Surface Water Models:**

Useful surface water models are identified in the following documents:

- 1. Section 3.4 of EPA. 1988. Superfund Exposure Assessment Manual", EPA/540/1-88/001, OSWER Directive 9285.5-1.
- 2. EPA. 1987. Selection Criteria for Mathematical Models Used in Exposure Assessments: Surface Water Models, Office of Health and Environmental Assessment. EPA/600/8-87/042.
- 3. EPA. 1985. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water-Part I, EPA/600/6-85/002a. Environmental Research Laboratory, EPA, Athens, GA 30613.

4. EPA. 1985. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water-Part II, EPA/600/6-85/002b. Environmental Research Laboratory, EPA, Athens, GA 30613.

In addition, the Department utilizes the following computer models to develop water quality-based effluent limitations:

- 1. Water Quality Analysis Model (WQM6.3)
- 2. Lake Tropic Analysis Program
- 3. Pennsylvania Single discharge Wasteload Allocation Program for Toxics and Other Substances (PENTOXSD), Release 1.0.

Additional information regarding specific surface water models may be obtained from EPA, Center for Exposure Assessment Modeling (CEAM), 960 College Station Road, Athens, Georgia 30605-2700; telephone (706)546-3549; Internet address: ftp://ftp.epa.gov/epa\_ceam/wwwhtml/ceamhome.htm. Specific questions regarding the Department's computer codes should be referred to Bureau of Watershed Conservation, Department of Environmental Protection, P.O. Box 8555, Harrisburg, PA 17105-8555; telephone: (717)787-9637.

#### Air Models:

Useful available air models are identified in the following documents:

- 1. Section 3.3 of EPA's "Superfund Exposure Assessment Manual", EPA/540/1-88/001, OSWER Directive 9285.5-1. April 1988.
- 2. "Interim Final Air/Superfund National Technical Guidance Study Series (NTGS). Volume V: Procedures for Air Dispersion Modeling at Superfund Sites." Office of Air Quality Planning and Standards, EPA, Research Triangle Park, NC 27711. (Available through Internet at: http://www.epa.gov/scram001/).
- 3. "Guideline for Air Quality Models (Revised)" (GAQM), 40 CFR Part 51, Appendix W. (Available through Internet at: http://www.epa.gov/scram001/).

Any person planning to select and run computer models in analyzing air contaminant migration should consult the following guides:

- 1. "Guideline for Air Quality Models (Revised)" (GAQM), 40 CFR Part 51, Appendix W. (Available through Internet at: http://www.epa.gov/scram001/).
- 2. "Interim Final Air/Superfund National Technical Guidance Study Series (NTGS). Volume V: Procedures for Air Dispersion Modeling at Superfund Sites." Office of Air Quality Planning and Standards, EPA, Research Triangle Park, NC 27711. (Available through Internet at: http://www.epa.gov/scram001/).

The models identified in GAQM may be downloaded directly from EPA SCRAM Electronic Bulletin Board at (919)541-1447 or through Internet at http://www.epa.gov/scram001/. Additional information regarding air models may be obtained from the following sources:

- 1. The Support Center for Regulatory Air Models (SCRAM), EPA. (919)541-5384. Internet address: http://www.epa.gov/scram001/.
- 2. Air Quality Modeling Section, Bureau of Air Quality Control, Department of Environmental Protection, P. O. Box 8468, Harrisburg, PA 17105-8468; telephone: (717)787-9495.

# H. Site-Specific Ecological Risk Assessment Guidance

## 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; and
- 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 Ecological Screen. Consequently, a site-specific ecological evaluation shall be consistent with the Statewide Ecological Screen.

The EPA ecological risk assessment process is comprised of eight steps. At the end of Steps 2 and 7, the qualified investigators (See the <u>Statewide Health Ecological Screening Process Rationale</u> in Section V.D) determine whether a substantial impact has resulted from regulated substances. The initial screen (Steps 1 and 2) is only necessary for sites which have not gone through the ecological screening process under the Statewide health standard as described in Section II.B.5 of this manual.

## INITIAL SCREEN (TWO STEPS)

#### Step 1 - Fundamental Components

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

- Environmental Setting and Site History.
- Site Visits Evaluate receptors and chemical migration pathways.
- Contaminant Fate and Transport emphasize gradients of contamination.

SECTION IV - GENERAL GUIDANCE

H. Site-Specific Ecological Risk Assessment Guidance

- 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 species or habitats of concern.
- Review of similar case studies to assist in the Preliminary Problem Formulation (EPA, 1992; EPA, 1997).
- 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, separate areas of concern shall be distinguished where relatively
  distinct risk scenarios are apparent.
- Choose a limited number of species or habitats of concern for assessment endpoints (EPA, 1992; Suter, 1993; EPA, 1997).

## Step 2 - Preliminary Exposure Estimate and Risk Assessment

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<sup>2</sup> and toxicity data that most directly relate to the assessment endpoints selected in Step 1.

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

#### **Decision Point**

The qualified investigator must 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 cleanup 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

<sup>&</sup>lt;sup>2</sup> The qualified investigator shall use a mean exposure concentration or other reasonable exposure point concentration estimate, not the maximum concentration detected.

• 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 IV-10). 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.

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

Identify CPECs with particular emphasis on Table 8 in Appendix A of the regulations (included as <u>Table II-2</u> of this manual).

Further develop Assessment Endpoints 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 shall 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 shall be focused on the prioritized pathways and selected assessment endpoints.

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

The focus in this step shall 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 shall be related to a toxicity effect in a species of concern to be considered relevant in the evaluation.

Since the habitats and species of concern are readily identified and evaluated through field studies, the investigator shall 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.

# 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 background or control area.<sup>3</sup> If necessary, the measurement endpoints should be modified to ensure the study objectives can be met (EPA, 1997).

## Step 6 - Site Investigation

Only persons qualified and experienced in ecological assessment<sup>4</sup> methods can direct field activities or make modifications of methods in the field.

# 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 shall 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).

<sup>&</sup>lt;sup>3</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).

<sup>&</sup>lt;sup>4</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.

## Step 8 - Risk Management

Risk management is a balancing of factors (<u>Figure IV-10</u>). Consistent with current and intended future use, the risk manager shall 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 shall 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 shall be completed, taking into account:
  - 1. Environmental injury caused by any remedy shall 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;
  - 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 attempts 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 prestressed conditions but something that is similar structurally and functionally.

#### 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.
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- Suter, II, G.W. 1993. Ecological Risk Assessment. Lewis Publishers. Ann Arbor, MI.
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Figure IV-10
Site-Specific Ecological Risk Assessment Procedure

