7.0 Statistical Methods

Data gathered to support groundwater monitoring at the Hanford Site are used to evaluate the changes noted in groundwater quality from baseline conditions of the various facilities. The methods used for the statistical evaluations are briefly described in this section. The facilities in this evaluation include

- RCRA interim status liquid and solid waste treatment, storage, and/or disposal units
- RCRA final status liquid and solid waste treatment, storage, and/or disposal units
- Variance allowed for the 216-B-3 Pond System
- Solid Waste Landfill
- Liquid effluent receiving facilities where statistical comparisons of groundwater samples were specified in the groundwater monitoring plans.

The RCRA units with a potential to contaminate groundwater require monitoring as prescribed in 40 CFR 265, WAC 173-303-400 (interim status), and 40 CFR 264 Subpart F and WAC 173-303-645 (final status). Groundwater monitoring activities at most of the RCRA units are currently governed by interim status regulations, except for the 183-H solar evaporation basins and the 300 Area process trenches, which were subject to corrective-action programs in accordance with final status regulations. The Solid Waste Landfill, though not a RCRA hazardous waste site, is statistically evaluated according to requirements of WAC 173-304.

In May 2001, Washington State Department of Ecology (Ecology) issued a guidance letter[(a)] that allows for variance from applying interim status regulations at the 216-B-3 pond system (B Pond) and to denote the requirements for achieving acceptable control limits for the 300 Area process trenches. Prior to receiving approval of a variance, conditions specified in the letter issued by Ecology in May 2001 must be met. The guidance letter[(a)] provides a path to more efficient and cost effective monitoring at these facilities. Statistical methodology adopted for these two facilities is described in Section 7.3. Criteria specified by Ecology and agreements reached with Ecology for the B Pond system are described in Section 7.4

Operations at the 200 Areas Treated Effluent Disposal Facility and the State-Approved Land Disposal Site began during 1995. Another facility, the 4608 B/C ponds (also called the 400 Area process ponds), consists of unlined infiltration ponds that receive wastewater from the 400 Area facilities. These sites are regulated by WAC 173-216. Because these are discharge permit disposal facilities, they require effluent and groundwater monitoring. Upgradient and downgradient comparisons for constituents of concern were performed at these sites in accordance with groundwater monitoring plans.

7.1 RCRA Interim Status Facilities

The primary objectives of RCRA groundwater monitoring are to comply with regulatory requirements and agreements, to assess potential impact on groundwater quality, and to identify near-term corrective measures, if feasible, for the protection of human health and the environment. In accordance with 40 CFR 265 Subpart F (which was incorporated, by

(a) Letter from Dib Goswami (Washington State Department of Ecology, Olympia, Washington) to Marvin Furman (U.S. Department of Energy, Richland, Washington), *Statistical Assessment for the 300 Area Resource Conservation and Recovery Act of 1976 (RCRA) Ground Water Monitoring Plan*, dated May 7, 2001.

reference, into WAC 173-303-400), RCRA projects are monitored according to one of three levels of effort:

- background monitoring
- indicator evaluation
- groundwater quality assessment.

All of the RCRA facilities at the Hanford Site have completed their initial background monitoring programs. A general description of the applicable statistical methods that are appropriate for these interim status facilities is provided in this section.

The statistical method used to summarize background data is the averaged replicate t-test method as described in Appendix B of RCRA Groundwater Monitoring Technical Enforcement Guidance Document (OSWER-9950.1). The averaged replicate t-test method for each contamination indicator parameter during each evaluation period is calculated as

$$t = (\bar{x}_i - \bar{x}_b)/S_b * \sqrt{1 + 1/n_b}$$

where: t = test statistic

x_i = average of replicates from the ith monitoring well

$\sqrt{}_b$ = background average

S_b = background standard deviation

n_b = number of background replicate averages.

The guidance documentation (OSWER-9950.1) states that a test statistic larger than the Bonferroni critical value, t_c, (i.e., $t > t_c$) indicates a statistically significant increase (or decrease, for pH) compared to the background data. This increase or decrease would indicate that contamination may have occurred. These Bonferroni critical values depend on the overall false-positive rate required for each sampling period (i.e., 1% for interim status), the total number of wells in the monitoring network, and the number of degrees of freedom (n_b - 1) associated with the background standard deviation. Because of the nature of the test statistic in above equation, sampling results to be compared to background do not contribute to the estimate of the variance, S_b^2. The test can be reformulated, without prior knowledge of the results of the sample to be compared to background, in such a way that a critical mean, CM, can be obtained

$$CM = \bar{x}_b + t_c * S_b * \sqrt{(1 + 1/n_b)}$$

$$CM = \bar{x}_b \pm t_c * S_b * \sqrt{(1 + 1/n_b)}$$

For pH, a two-tailed critical mean (or critical range) is calculated and a one-tailed critical mean is calculated for specific conductance, total organic carbon, and total organic halides. The critical mean (or range for pH) is the value above which (or above/below in the case of pH) a compared value is determined to be statistically different from background.

In the past, the lack of estimates of background variability for total organic carbon and/or total organic halides precluded the determination of critical means for various RCRA facilities. The calculated critical means were used in the statistical evaluations unless the calculated critical means were not quantifiable. In this case, a limit of quantitation was used as the threshold value for the regulatory decision to determine whether a RCRA facility has affected the groundwater quality beneath the facility. The limit of quantitation and limit of detection are determined quarterly and the most recent updated values are used in statistical evaluations.

Finally, if the calculated critical ranges for pH were too large to be meaningful because of the requirement to use four quarters of data to establish background, the upgradient/downgradient comparison value would be revised to the critical range by using more data. The expansion of the background dataset to include more than 1 year's data provides a better estimate of background mean and background standard deviation. More important, it increases the number of degrees of freedom associated with the background standard deviation. Other things being equal, a smaller t_c value and a narrower critical range for pH would result. This approach is preferred because it complies with both the requirements and the spirit of the regulations.

7.2 RCRA Final Status Facilities

Three levels of groundwater monitoring programs are required by the final status regulations (40 CFR 264 Subpart F and WAC 173-303-645): detection monitoring, compliance monitoring, and corrective action. The 183-H solar evaporation basins and the 300 Area process trenches are monitored in accordance with the RCRA final status requirements. Additionally, four permitted treatment, storage, and disposal facilities (i.e., 1301-N Liquid Waste Disposal Facility, 1324-N/NA Liquid Waste Disposal Facilities, 1325-N Liquid Waste Disposal Facility and Liquid Effluent Retention Facility), as of September 30, 1999, also are regulated under final status requirements. Groundwater monitoring, however, is regulated under interim status requirements in accordance with guidance provided by Ecology.

Evaluation of groundwater monitoring data under interim status involves use of a t-test to compare mean concentrations of the four parameters indicating contamination between upgradient and downgradient wells on the four replicate measurements during each sampling event. This required method is flawed (Davis and McNichols 1994; Cameron 1996) because

- The required pooling of background data is not valid when spatial, temporal, and sampling variability constitute a significant portion of the total variability.
- A static background is assumed because one initial set of background samples is collected and statistically compared to downgradient data collected during later monitoring.
- The background data pool does not incorporate any component of spatial variability when only one upgradient well is used.
- The four indicator parameter selected do not serve well as early warning indicators of incipient contamination of groundwater by leachate from the facility.

In final status monitoring, flexibility is allowed in selecting statistical methods as well as constituents used for statistical comparison. Appropriate statistical methods include analysis of variance, tolerance intervals, prediction intervals, control charts, test of proportions, or other statistical methods approved by the regulator. The important factors to consider when selecting appropriate statistical methods are the distribution(s) of monitoring parameters; the nature of the data; and the proportions of non-detections, seasonal, temporal, and spatial variations. The statistical evaluation procedures chosen for final status facilities will be based on guidance given by EPA (PB98-151047; EPA-530/R-93-003), and the American Society for Testing and Materials (ASTM 1996). Specific statistical methods are to be addressed in the unit-specific permit applications and/or in the groundwater monitoring plans.

7.2.1 Detection-Level Monitoring

In a detection-level groundwater monitoring program, the objective is to detect a potential impact from a regulated unit by testing for statistically significant changes in geochemistry in a downgradient monitoring well relative to baseline levels. These baseline levels could be obtained from upgradient (or background) wells, and the comparisons are referred to as interwell (or between-well) comparisons. Alternatively, if baseline values are obtained from historical measurements from that same well, the comparisons are referred to as intra-well (or within-well) comparisons. Groundwater parameter data (e.g., heavy metals, pH, reaction products, specific conductance, total organic carbon, total organic halides, waste constituents) from downgradient, compliance-point wells will be compared semi-annually with baseline data to determine whether there is a statistically significant increase (or decrease for pH) over baseline concentrations. Final status, detection-level, groundwater monitoring plans for the Liquid Effluent Retention Facility and low-level burial grounds were proposed and presented to Ecology. However, a decision was made to not incorporate the low-level burial grounds into the permit until 2002. Therefore, these sites continue to be monitored in accordance with interim status requirements. Although the Liquid Effluent Retention Facility was included in

the Hanford Site RCRA Permit, groundwater monitoring continued in interim status in accordance with the variance letter granted by Ecology in September 1999.[b] Specifically, the variance letter allowed the monitoring of groundwater in the vicinity of the Liquid Effluent Retention Facility using only two downgradient wells and one upgradient well. In January 2001, one of the downgradient wells went dry and no longer provided groundwater samples representative of the aquifer. As a result, the variance granted earlier is no longer in effect.[c] In addition, Ecology suspended further statistical evaluation of groundwater monitoring results associated with the two remaining yield wells.[c] Currently, Ecology, U.S. Department of Energy, and contractors are working on an alternative monitoring program for the Liquid Effluent Retention Facility.

7.2.2 Compliance-Level Monitoring

A compliance-level, groundwater monitoring program will be established for a RCRA unit if groundwater sampling during detection-level monitoring reveals statistically significant evidence of contamination for constituents of concern at the point of compliance well. In compliance-level monitoring, the objective is to determine whether specified concentration limits (e.g., groundwater protection standards) have been exceeded. This is accomplished by comparing the concentration of a constituent of concern to a concentration limit, such as a risk-based maximum concentration limit; alternative concentration limit; area or natural background; or applicable, relevant, and appropriate requirements. These concentration limits would be applied during compliance monitoring to determine whether corrective action might be necessary.

Maximum concentration limits will be identified for each groundwater monitoring constituent of concern. Alternative concentration limits will be proposed after considering the observed concentrations of chemical constituents in the groundwater that might have originated from the regulated unit in question. The area background, natural background, and other standards that are applicable, relevant, and appropriate will be evaluated when proposing an alternative concentration limit. The parameters monitored, the concentration limits, and the statistical methods were specified in the unit-specific groundwater-monitoring plan and approved by Ecology.

Results of groundwater monitoring indicate that the 300 Area process trenches exceed concentration limits for trichloroethylene, cis-1,2-dichloroethylene, and uranium in some of the downgradient compliance wells. The Washington State Department of Ecology was notified and the site RCRA permit was revised, putting the 300 Area process trenches into corrective action. During FY 2001, the revised groundwater monitoring plan for the 300 Area process trenches that complies with RCRA final status corrective action groundwater monitoring requirements was in place (PNNL-13645). This plan replaces the previous compliance-level plan (WHC-SD-EN-AP-185) that was in effect until August 2001.

7.2.3 Corrective Action

A corrective action program is initiated if a concentration limit at the point of compliance is exceeded. Exceedance is defined as statistically significant evidence of increased contamination [see WAC 173-303-645 (2)(a)(ii)]. Details for the corrective-action

(b) Letter from Stan Leja (Washington State Department of Ecology, Olympia, Washington) to Marvin Furman (U.S. Department of Energy, Richland, Washington), *Variance from Interim-Status Groundwater Monitoring Requirements at the Liquid Effluent Retention Facility*, dated September 22, 1999.

(c) Letter from Dib Goswami and Fred Jamison (Washington State Department of Ecology, Olympia, Washington) to Kevin Leary and Michael Thompson (U.S. Department of Energy, Richland, Washington), *Liquid Effluent Retention Basin (LERF) Unsaturated Zone Monitoring Alternatives Evaluation, Suspension of Groundwater Monitoring Statistical Evaluation Requirements, LERF RCRA Permit Modification, and Leachate Monitoring Performance Criteria*, dated January 24, 2001.

program will be specified in the unit-specific permit application. In conjunction with a corrective-action program, a groundwater monitoring program must be established and implemented to demonstrate the effectiveness of the corrective-action program. In addition, the corrective-action groundwater monitoring program must be at least as effective as the previous compliance monitoring program in determining compliance with groundwater protection standards. The 183-H solar evaporation basins are monitored under a corrective-action plan.

As described earlier, the 300 Area process trenches groundwater monitoring plan that complies with final status corrective-action requirements was submitted and approved by Ecology in fiscal year 2001 (PNNL-13645). This monitoring plan includes well and constituent lists; summarizes sampling, analytical, and quality control requirements; and incorporates the entire interim changes made since the last revision of the groundwater monitoring plan for the 300 Area process trenches. Changes from the previous monitoring plan include updating the discussion on hydrogeology and conceptual model, redesigning the monitoring well network to include 11 wells rather than the previous eight, and adopting a combined Shewhart-CUSUM control chart approach that will track the contamination trends better than the previous plan with reduced costs. A detailed description of the combined Shewhart-CUSUM control chart procedures are presented in the following section.

7.3 Shewhart-CUSUM Control Chart Procedures

The combined Shewhart-CUSUM control chart approach was first referenced by Westgard et al. (1977) and further developed by Lucas (1982). This method is also discussed in a groundwater context by EPA-600/4-88/040, Gibbons (1994), and ASTM (1996) and first adopted into EPA guidance in 1989 (PB89-151047; EPA-530/R-93-003). Statisticians of Washington State University (WSU) evaluated the efficacy of this method for monitoring groundwater quality on behalf of Ecology (Jandhyala and Zhang 1999). In their report, Jandhyala and Zhang endorsed the control chart method of monitoring groundwater quality. There are several advantages in applying the control chart procedure:

- This method can be implemented with a single observation at any monitoring event (i.e., this method is efficient).
- This method is effective; it could be applied to monitor each well individually and yet maintain desired site-wide false positive and false-negative error rates. The spatial variations that adversely affect the ANOVA procedure do not play a role under the control chart procedure. [Note: Due to the elimination of spatial variability, the uncertainty in measured concentrations is decreased making intra-well comparisons more sensitive to a real release (that is, false negatives) and false positive results (ASTM 1996).

The power of the control chart method could be enhanced by the combined Shewhart and CUSUM procedures. The Shewhart procedure is sensitive to sudden shifts and the CUSUM procedure is sensitive to gradual changes in the mean concentrations. A combined Shewhart and CUSUM procedure, therefore, is well designed to detect both types of changes.

The combined Shewhart–CUSUM method can be implemented following a baseline of eight or more independent sampling periods for a given well (ASTM 1996). The method assumes that the groundwater baseline data and future observations will be independent and normally distributed. The most important assumption is that the data are independent. The assumption of normality can usually be met by log-transforming the data or by other Box-Cox transformations. The method is more fully discussed in Lucas (1982), EPA-600/4-88/040, Gibbons (1994), ASTM (1996), and Montgomery (1997).

The method is a sequential testing procedure to test for an upward shift in the mean concentration of a constituent of interest. The Shewhart portion of the test checks for any sudden upward shift in groundwater quality parameters based on a single observation, while

the CUSUM checks for any gradually increasing trend in the groundwater quality parameters. The procedure can be implemented as follows: Let x'_i be a series of independent baseline observations i = 1,…., b (b = 8). Let x_i be a series of future monitoring measurements i = 1, 2, 3….. .

Then, using the baseline data, the following steps are applied:

1. First determine if the x'_i can be assumed to follow a normal distribution with mean m and standard deviation s. If not, transform the x'_i using the appropriate Box-Cox transformation and work with the transformed data.
2. Next use the baseline data to compute the estimates

$$\bar{x}' = \sum_{i=1}^{b} x_i' / b \text{ for } \mu \text{ and } s' = \sqrt{\sum_{i=1}^{b} (x_i' - \bar{x}')^2 / (b-1)} \text{ for } \sigma.$$

3. Determine the upper Shewhart control limit (SCL) for the procedure by calculating SCL = $x' + z_s s'$ where z_s is a percentile from the standard normal distribution used to set the false negative and false positive values of the Shewhart control limit. The value of z_s that is most often suggested for groundwater use is 4.5 by Lucas (1982), EPA-600/4-88/040, PB89-151047, and ASTM (1996). Other values may also be used, depending on the sampling scheme used and whether verification sampling is used to modify the false positive and false negative error rates.
4. Determine the upper CUSUM control limit (CCL), with CCL = $x' + z_s s'$. The value of z_c suggested by Lucas (1982), EPA-600/4-88/040, PB89-151047, is $z_c = 5$. This value can also be adjusted to reach desired false negative and false positive error rates. In practice setting $z_c = z_s = 4.5$ results in a single limits with no compromise in leak detection capabilities (ASTM 1996).
5. Determine the amount of increased shift in the mean of the water quality parameter of interest to detect an upward trend. This value is referenced as k and is usually measured in s units of the water quality parameter. Lucas (1982), EPA-600/4-88/040, and PB89-151047, suggest a value of k = 1 if there are less than 12 baseline observations; and a value of k = 0.75 if there are 12 or more baseline observations.

Using the monitoring data after the baseline measurements have been established:

6. Compute the CUSUM statistic as $S_i = \max\{0, (x_i - ks') + S_{i-1}s'\}$ as each new monitoring measurement, x_i becomes available, where i = 1,2,3,….. and $S_0 = 0$
7. As each new monitoring measurement becomes available, compute the Shewhart and CUSUM tests; a verification sampling will be conducted if either $x_i \geq$ SCL or $S_i \geq$ CCL. A well is declared to be out of control only if the verification result also exceeds the SCL or the CCL. If both $x_i <$ SCL and $S_i <$ CCL, then continue monitoring.
8. As monitoring continues and the process is shown to be in control, the baseline mean and standard deviation should be updated periodically (every year or two) to incorporate these new data. This updating process should continue for the life of the monitoring program.

If resampling is implemented during the monitoring, the analytical result from the resample is substituted into the above formulas for the original value obtained, and the CUSUM statistic is updated. Note in the above combined test that the Shewhart portion of the test will quickly detect extremely large deviations from the baseline period. The CUSUM portion of the combined test is sequential; thus, a small shift in the mean concentration over the baseline period will slowly aggregate in the CUSUM statistic and eventually cause the test to exceed the CUSUM control limit CCL.

Various control limits for the 300 Area process trenches constituents of interest were submitted and approved by Ecology and are presented in Table 7.3 of PNNL-13645.

7.4 Variance Allowed for the 216-B-3 Pond System

In May 2001, Ecology issued a letter[d] providing guidance for groundwater monitoring at the B Pond system because the standard indicator-parameters evaluation and accompanying interim status statistical approach is inappropriate for detecting potential B-Pond-derived contaminants in groundwater at this facility. Ecology specified in this guidance letter that certain criteria must be met prior to receiving approval of a variance from applying interim status regulations.

A proposal that included monitoring network, constituent list, statistical analysis, and reporting for the B Pond system was submitted to Ecology in November 2001. The specific elements of the proposal, as per the variance stated in Ecology's letter,[d] and in agreement with subsequent discussions with Ecology, are as follow:

Well Network

1. The well network (see attached map) will consist of one upgradient well (699-44-39B) and three downgradient wells (699-43-42J, 699-43-44, and 699-43-45).
2. Because data from the relatively new well 699-43-44 are limited, data from nearby well 699-43-43 will be used as a historical surrogate for 699-43-44, per letter direction. To establish the degree of data comparability between the wells, well 699-43-43 will be added to the network, and sampled as long as it remains serviceable. Well 699-43-44 is a replacement for well 699-43-43 which is becoming dry.

Constituents List

The constituents will be the same as presented during the May 17 presentation[e] and are shown in Table 7.4-1. This table will replace Table 5.1 in *Groundwater Monitoring Plan for the Hanford Site 216-B-3 Pond RCRA Facility* (PNNL-13367). As agreed, total organic carbon and total organic halides will be eliminated from the list and the total and dissolved concentrations of cadmium, lead, mercury, and silver will be analyzed annually for 4 years. Analysis for these metals will be discontinued after 4 years if no anomalous concentrations or trends are revealed.

Statistical Analysis

1. Only site-specific parameters (gross alpha, gross beta, and specific conductance) will be subject to statistical evaluations on a semiannual basis.
2. The combined Shewhart-CUSUM control chart method will be applied to the three site-specific parameters. The appropriate baseline period for the data will be identified and baseline data evaluated. Outliers will be addressed to avoid bias in the statistical analysis.
3. American Society for Testing and Materials (ASTM 1996) guidance will be used to evaluate non-detect results and outliers.
4. Normal probability plots will be used to verify normal distribution of data.
5. Input parameter values (k, SCL, and CCL) will be proposed and submitted to Ecology for approval prior to implementation of the groundwater monitoring plan. Power curves illustrating probabilities for false positive and false negative will be submitted.

(d) Letter from Dib Goswami (Washington State Department of Ecology, Olympia, Washington) to Marvin Furman (U.S. Department of Energy, Richland, Washington), *Statistical Assessment for the 300 Area Resource Conservation and Recovery Act of 1976 (RCRA) Ground Water Monitoring Plan*, dated May 7, 2001.

(e) Presentation by D. B. Barnett, Pacific Northwest National Laboratory, to Washington State Department of Ecology, May 17, 2001, Richland, Washington.

Reporting

Groundwater analytical and hydrologic data from nearby facilities, such as the Liquid Effluent Retention Facility, Treated Effluent Disposal Facility, and 216-A-29 ditch, will be examined for results that may lend understanding to the B Pond hydrogeologic system and will be discussed in the Hanford Site annual groundwater report, as appropriate. This discussion will be accompanied by recommendations for modifications of the well network and/or constituent list, as necessary.

7.5 Solid Waste Landfill

Groundwater monitoring at the Solid Waste Landfill is regulated in accordance with WAC 173-304-490, requiring no replicate analyses. Thus, the tolerance interval approach, suitable for individual sample comparisons, was used for performing the required comparisons between upgradient and downgradient wells for determining whether a significant change over background occurred for constituents specified in WAC 173-304-490. The statistical evaluations are described as follows.

7.5.1 Calculating Background Summary Statistics

Summary statistics were recalculated for the WAC 173-304-490(2)(d) constituents using quarterly monitoring data collected from March 1993 to May 2000 from upgradient wells. The results were presented in Table 6.1 of PNNL-13014. Some of the background data are below laboratory's specified method detection limit. Following guidance in PB89-151047, EPA-530/R-93-003, and Ecology (1996b), the following procedures were used in handling the non-detects. In cases where the proportion of non-detects is less than 15%, not detected measurements were replaced by half of their method detection limits, and the usual calculations were performed. In cases where the proportion of non-detects is between 15% to 50%, Cohen's method (Cohen 1959, 1961) was used to estimate the mean and standard deviation (dissolved iron, manganese, and zinc). For total organic carbon, Aitchison's adjustment (Aitchison 1955) was used because the fraction of nondetects exceeds 50% and Cohen's method may not give valid results (PB89-151047, pages 27-34). For ammonium, coliform bacteria, chemical oxygen demand, nitrite, and summary statistics are not calculated because these constituents are essentially not detected.

7.5.2 Testing Assumption of Normality of Data

Background water quality is statistically defined as the 95% upper tolerance interval with a 95% confidence (see Ecology 1996b, page 65). The tolerance interval defines a concentration range (from background well data) that contains at least a specified proportion (coverage) of the population with a specified probability (level of confidence). There are two types of tolerance intervals: parametric and non-parametric. Parametric tolerance interval techniques are valid when the assumption that the data are drawn from a normal (or lognormal) population holds. When data is not normally (or log-normally) distributed, a non-parametric tolerance interval is used to estimate background values.

Parametric tolerance intervals are sensitive to the assumption that the data are normally distributed. The statistical tests used to evaluate whether or not the data follow a specified distribution are called goodness-of-fit tests. A recommended test is the Shapiro-Wilk test for normality of the data (Shapiro and Wilk 1965). It is considered one of the best tests of normality available (Miller 1986; Mandansky 1988). The Shapiro-Wilk test statistic (W) will tend to be large when a probability plot of the data indicates a nearly straight line (i.e., normal distribution). Only when the plotted data show significant departure from normality will the test statistic be small. Hence, if the computed value of W is less than the critical value W_α for a prechosen value of α (e.g., α = 5%) shown in statistical table, the hypothesis of normality is rejected. The Shapiro-Wilk test of normality can be used for sample sizes up to 50. When sample size is larger than

50 (up to 98), a slight modification of the procedure called the Shapiro-Francia test (Shapiro and Francia 1972) can be used instead. Like the Shapiro-Wilk test, the Shapiro-Francia test statistic (W') will be small when the probability plot shows significant bends or curves (i.e., non-normality). Procedures are provided in PB98-151047 (pages 9-12) and Shapiro (1980, pages 20-24).

7.5.3 Re-Establishing Background Levels

Background values were established for the WAC 173-304-490(2)(d) constituents based on the tolerance interval approach using monitoring data collected from upgradient wells (699-24-35 and 699-26-35A) during May 1987 to September 1993. Since then more information has been obtained and the analytical laboratory has changed. Therefore, it is deemed appropriate to revise the original background values to reflect the most current site conditions and improve estimates of background mean and standard deviation. Both the upper and lower limits of the interval (two sided) were calculated for pH. Only the upper limits of the intervals (one sided) were calculated for other constituents.

If a lognormal (or a normal) distribution is a reasonable approximation of the background concentrations, a parametric tolerance interval (TI) of the following form is calculated.

$TI = \bar{x}_b \pm kS_b$ (two-sided), or

$TI = \bar{x}_b \pm kS_b$ (one-sided)

where: $\bar{x}_b$ = Background mean

k = a normal tolerance factor, which depends on the number of background samples (n), coverage (P%), and confidence level (Y). Coverage of 95% and confidence of 95% are used. With n = 60, P = 95%, and Y = 95%, k is 2.022 for a one-sided normal tolerance interval (Gibbons 1991).

S_b = Background standard deviation.

If background concentration do not follow a lognormal or normal distribution, or the proportion of non-detects is greater than 15%, a nonparametric tolerance interval is constructed (Conover 1980). A two-sided nonparametric tolerance interval is just the range of the observed data. An upper one-sided nonparametric tolerance limit is the largest observation. With 56 to 60 background samples for chemical oxygen demand, coliform bacteria, iron, manganese, nitrite, total organic carbon, and zinc (see Table 6.2 of PNNL-13014), the upper one-sided tolerance limit defined by the largest observation contains at least 95% of the background population with 95% probability.

In cases where all of the background values are below the contractually established detection limits or where the proportion of nondetects is more than 15%, a limit of quantitation was also calculated using the fiscal year 2000 field blanks data or based on method detection limits (PNNL-13404, Appendix B). Following guidance (OSWER-9950.1; Ecology 1996b), it was decided that for cases where the calculated upper tolerance limit is below the limit of quantitation, the most recently determined limit of quantitation will be used as the background threshold value (comparison value) between data obtained from background and downgradient compliance wells. This approach uses quality control data to target the limits of quantifiable data and provides a realistic approach for background/compliance well comparisons when upgradient wells yield values that are below the detection limit. In cases where the limit of quantitation is not available (e.g., chemical oxygen demand and coliform bacteria), the contractually required quantitation limits were used as the background threshold values. It should be noted that inconsistent values (i.e., outliers) were tested and removed from the background data sets in the statistical evaluations. The exclusion of extreme observation(s) from the background data sets provides smaller variability and lower comparison values. Thus, it is more conservative. The resulting tolerance limits, limits of quantitation, and background threshold values are also presented in groundwater annual reports (PNNL-13404).

7.5.4 Comparisons with Background Levels

Groundwater monitoring results have been and will continue to be compared on a quarterly basis with background levels determined in accordance to methods presented in Section 6.3.3. In addition, when there is a statistically significant increase for parameters or constituents listed in WAC 173-304-490(2)(d), the owner and/or operator needs to determine whether the groundwater performance standard has been exceeded and initiate the notification process. Results of past groundwater monitoring have detected the following primary chlorinated hydrocarbons in the groundwater beneath the Solid Waste Landfill: 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), carbon tetrachloride, trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,4-dichlorobenzene. These contaminants will be compared with WAC 173-200 groundwater quality criteria. If the criterion is exceeded, Ecology will determine whether corrective action program is required. In that case, a new groundwater monitoring plan will be written.

7.6 Liquid Effluent Receiving Facilities

Operation of the 200 Areas Treated Effluent Disposal Facility and the State-Approved Land Disposal Site began during 1995. These facilities are regulated by WAC 173-216; both require effluent and groundwater monitoring. Another facility, the 400 Area process ponds, is designated also as a WAC 173-216 discharge permit site. The permit was issued on August 1, 1996 and modified on February 10, 1998. The principal groundwater quality regulations (WAC 173-200) emphasize the non-degradation of current groundwater quality. These regulations require "Establishment of an enforcement limit as near the natural ground water quality as practical," and establishment of the point of compliance in the groundwater "...as near the source as technically, hydrogeologically, and geographically feasible."

7.6.1 Preoperational Monitoring

Groundwater quality data from the preoperational phases of the 200 Areas Treated Effluent Disposal Facility and the State-Approved Land Disposal Site were used to establish the background (baseline) values for the potential constituents of concern. In essence, background values were calculated using the parametric tolerance-interval approach discussed above because background water quality is statistically defined as the 95% upper tolerance interval with a 95% confidence (Ecology 1996b, p. 65). The baseline values were provided to the regulator to allow the determination of enforcement limits (specified in the permit) for specific constituents in groundwater.

7.6.2 Operational Monitoring

The objectives of collecting and evaluating the groundwater quality data from operational monitoring are (1) to determine if groundwater quality has changed from the baseline, preoperational conditions; (2) to evaluate the impact, if any, that operation of the facility has on the quality of groundwater in the uppermost aquifer; and (3) to demonstrate compliance with the groundwater enforcement limits set forth in the permit.

Statistical approaches used for preoperational and operational monitoring were described in detail in the groundwater monitoring plans for the 200 Areas Treated Effluent Disposal Facility (PNNL-13032) and State-Approved Land Disposal Site (PNNL-13121).

Table 7.1. Constituent List for the B Pond Facility (modified from PNNL-13367)

Indicator Parameters	
pH	
Specific conductance	
Groundwater Quality Parameters[a]	
Chloride[b]	Phenols
Iron[c]	Sodium[c]
Manganese[c]	Sulfate[b]
Site-Specific Parameters	
Gross alpha	Tritium[d]
Gross beta	Cadmium[e]
Arsenic[d]	Lead[e]
Nitrate[d]	Mercury[e]
Iodine-129[d]	Silver[e]
Field Parameters	
Alkalinity	Turbidity
Dissolved oxygen	Temperature

(a) Sampled annually; all others sampled semiannually.
(b) These constituents are part of a larger suite of anions provided in this analysis.
(c) These constituents are part of a large suite of metals provided by this analysis using inductively-coupled plasma methods.
(d) These constituents are also of Hanford sitewide concern, and are scheduled on a periodic basis in coordination with the sitewide surveillance sampling effort.
(e) Total concentrations, to be discontinued following four years (once annually) of analyses with no anomalous concentrations or trends.