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RCRA Groundwater Data Analysis Protocol for the Hanford Site, Washington

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RESOURCE CONSERVATION AND RECOVERY ACT GROUNDWATER DATA ANALYSIS PROTOCOL FOR THE HANFORD SITE

ABSTRACT

The Resource Conservation and Recovery Act of 1976 *(RCRA) groundwater monitoring program currently involves site-specific monitoring of 20 facilities on the Hanford Site in southeastern Washington. The RCRA groundwater monitoring program has collected abundant data on groundwater quality. These data are used to assess the impact of a facility on groundwater quality or whether remediation efforts under RCRA corrective action programs are effective. Both evaluations rely on statistical analysis of groundwater monitoring data.*

The need for information on groundwater quality by regulators and environmental managers makes statistical analysis of monitoring data an important part of RCRA groundwater monitoring programs. The complexity of groundwater monitoring programs and variabilities (spatial, temporal, and analytical) exhibited in groundwater quality variables indicate the need for a data analysis protocol to guide statistical analysis. A data analysis protocol was developed from the perspective of addressing regulatory requirements, data quality, and management information needs. This data analysis protocol contains four elements: data handling methods; graphical evaluation techniques; statistical tests for trend, central tendency, and excursion analysis; and reporting procedures for presenting results to users.

Two case studies are presented to show how the elements of the data analysis protocol apply to the analysis of water quality data at RCRA-regulated facilities on the Hanford Site. The data analysis protocol serves as a guide for statistical analysis of groundwater quality data; as a means to generate technically sound analysis results; and as a signal to alert scientists, management, and regulators about changing conditions.

Finally, recommendations to enhance the overall effectiveness and efficiency of a groundwater monitoring program are provided in this report.

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1.0 INTRODUCTION

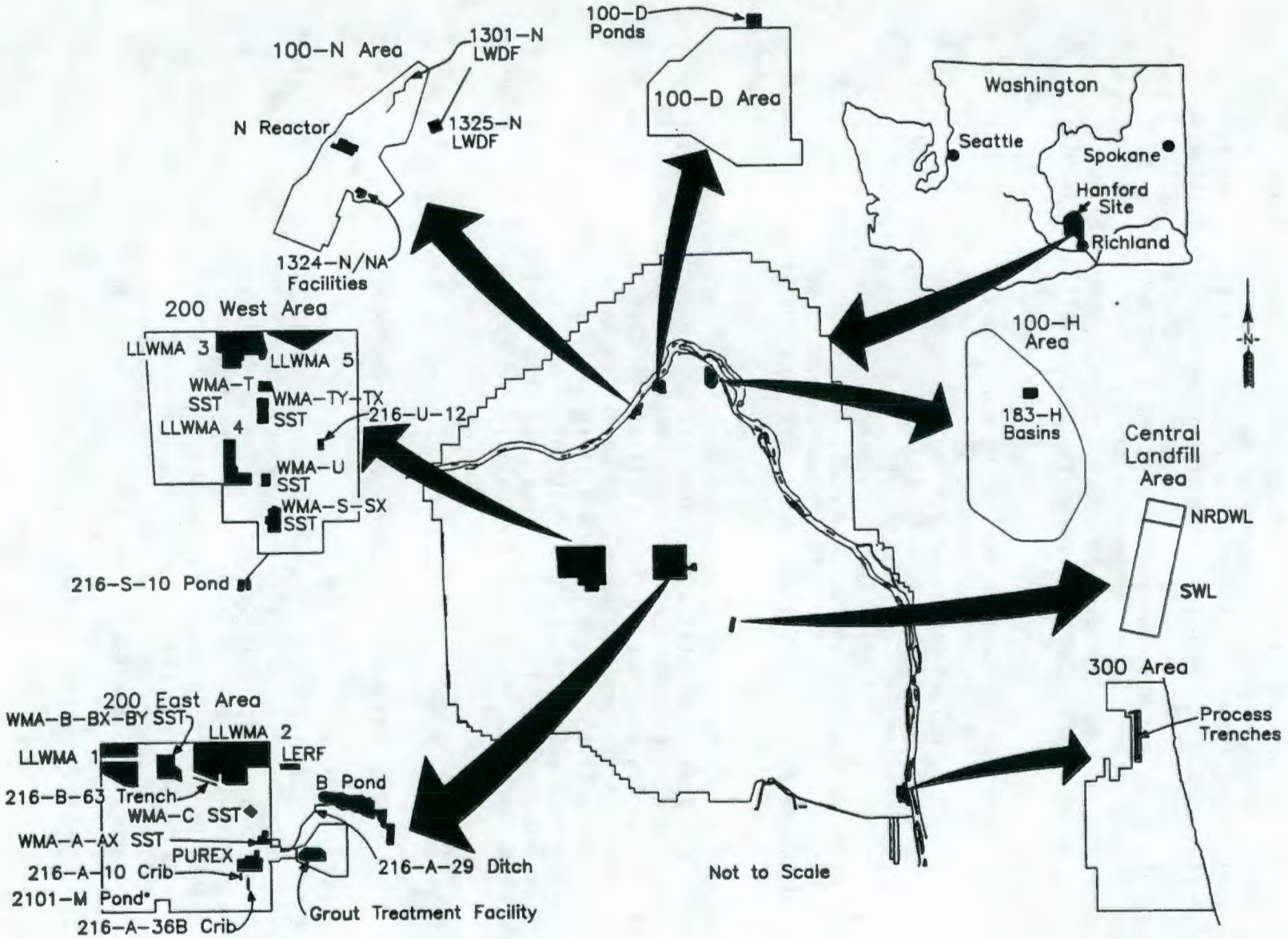
The *Resource Conservation and Recovery Act of 1976* (RCRA) groundwater monitoring program currently involves site-specific monitoring of 20 facilities on the Hanford Site in southeastern Washington (Figure 1-1). The RCRA is implemented under two groundwater monitoring programs to meet state and federal requirements: interim-status and final-status monitoring. The interim-status regulations require the owner/operator of a treatment, storage, and disposal (TSD) facility to implement a groundwater monitoring program capable of determining the facility's impact on the quality of groundwater in the uppermost aquifer beneath the facility. The final-status regulations allow the owner/operator to adopt a phased program to detect, evaluate, and if necessary, correct groundwater contamination at permitted facilities.

Presently, over 250 groundwater monitoring wells have been installed around 20 RCRA TSD facilities on the Hanford Site. The principal chemical constituents analyzed include contamination indicator parameters [40 CFR 265.92(b)(3)], groundwater quality parameters [40 CFR 265.92(b)(2)], drinking water parameters [40 CFR 265.92(b)(1)], and facility-specific parameters. The wells are sampled quarterly and/or semi-annually, and some wells are sampled on a weekly and monthly basis. At least 60,000 analytical results are generated annually for data evaluation and reporting. All results are reported to the Washington State Department of Ecology in quarterly and annual reports.

The need for information on groundwater quality by regulators and environmental managers makes statistical analysis of monitoring data an important part of RCRA groundwater monitoring program. The complexity of groundwater monitoring programs and variabilities (spatial, temporal, and analytical) exhibited in groundwater quality variables indicate the need for a data analysis protocol (DAP) to guide statistical analysis. This report describes a DAP that allows consistent treatment of data and produce technically sound results. The DAP was developed from the perspective of addressing regulatory requirements, data quality, and management information needs.

2.0 ELEMENTS OF A DATA ANALYSIS PROTOCOL

In order for a monitoring program to proceed smoothly and yield data of a known quality, it is essential that a Quality Assurance Project Plan (QAPP) is in place before monitoring activity begins. The QAPP identifies and establishes data quality goals for the monitoring program. It is important that a cooperative effort be undertaken by the scientist, manager, regulator, and user to define the required data quality. These data quality requirements should be based on a common understanding of the intended use of the data, the measurement process, and available resources. As a minimum, requirements should be specified for precision, accuracy, detection, and quantitation limits. Additionally, representativeness, comparability, and completeness of



LERF	Liquid Effluent Retention Facility	PUREX	Plutonium–Uranium Extraction (Plant)
LLWMA	Low–Level Waste Management Area	SST	Single–Shell Tank
LWDF	Liquid Waste Disposal Facility	SWL	Solid Waste Landfill
NRDWL	Nonradioactive Dangerous Waste Landfill	WMA	Waste Management Area

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Figure 1-1. Locations of the RCRA Groundwater Monitoring Projects on the Hanford Site.

data should also be addressed. Once data quality requirements are clearly defined, quality control (QC) procedures can be established for measuring whether these requirements have been met.

In the discussion of statistical methods for analyzing groundwater monitoring data, it is necessary to make the following assumptions: (1) wells in the monitoring network have been properly located; (2) the wells have been properly designed, installed, and developed; and (3) sample collection and handling and laboratory analyses are being conducted according to the appropriate procedures, including field and laboratory QC procedures. The DAP described in this report contains the following four elements:

- *Data handling methods* needed to prepare resulting field and analytical data for a database
- *Graphical evaluation techniques* to detect changes in groundwater quality over time or space
- *Statistical tests* for analysis of trend, central tendency, and extreme conditions (e.g., excursions beyond regulatory limits or standards)
- *Reporting procedures* for presenting results to the end user.

2.1 DATA HANDLING METHODS

To create a database that is easily used for statistical analyses, raw data (field and analytical) must undergo several initial processing steps. These include verification, validation, and entry into a data management system for computerized storage, retrieval, analysis, and compilation.

2.1.1 Data Verification

Verification refers to the process of determining whether procedures, processes, data, or documentation conform to specified requirements (WHC 1990). A procedure for verification is recommended. This procedure should contain a standardized method for governing the receipt, entry into a database, and verification that the database is accurate and complete. It is desirable to use inspection schemes based on acceptance sampling plans such as those provided in American National Standard - Sampling Procedures and Tables for Inspection by Attributes (ANSI/ASQC Z1.4 1981). Audits, surveillances, or technical review are part of the verification activities.

2.1.2 Data Validation

Validation refers to a systematic process of reviewing a body of data against a set of criteria to provide assurance that the data are acceptable for their intended use (WHC 1990). Validation procedures may include review of verification activities, editing, screening for outliers, independent methods to cross-check analytical results, corroboration by other laboratories (interlaboratory comparisons), or analysis of blanks and field-spiked samples

to evaluate the quality of data. Any suspect data should be 'flagged' and a data review process initiated. Personnel should evaluate QC data to assess whether sampling and analysis activities are generating data meeting quality goals established in the QAPP. Any corrections identified in the data verification and validation phase should be entered into the database.

2.1.3 Data Management System

To efficiently manage large quantities of sampling and analytical data a computer-based information system is needed. A primary resource for computerized storage and retrieval, the Hanford Environmental Information System (HEIS), is being developed at the Hanford Site (WHC 1991). When operational, HEIS will provide a means for interactive access to a single, controlled database. In the interim, data are entered into the satellite groundwater database, which is based on Paradox[1]. Various tables for quarterly and annual reports are generated.

2.2 GRAPHICAL EVALUATION TECHNIQUES

One simple and easy way to evaluate data is an appropriately chosen graph. Graphical analysis of data enables one to easily obtain insight into the structure of the data. Most statistical test procedures are based on certain assumptions about the data, and the validity of statistical analyses depends on the validity of these assumptions. Graphical methods are powerful evaluation tools for confirming (or detecting departure from) assumptions. Various plots and their utilities are discussed in the following sections.

2.2.1 Normal Probability Plot

A normal probability plot is used to check whether a sample can reasonably be regarded as having come from a normal population. The plot is constructed so that if data points fall on a straight line, then these data can be assumed as drawn from a normal distribution (Figure 2-1c). By examining the patterns of deviations from linearity, the nature of the mismatch between the sample and the underlying theoretical distributions can be identified (Box and Draper 1987 and Chambers et al. 1983). For example, curvature at both ends indicate 'light-tailed' (short-tailed) or 'heavy-tailed' (long-tailed) distributions. When the left end of the curve is above the fitted line and the right end is below, it can be concluded that these data have a distribution that is longer-tailed than the normal (Figure 2-1b). When the reverse situation is true, it can be concluded that the data have a shorter-tailed distribution than the normal distribution (Figure 2-1a).

Another possibility is that the data are not symmetrically distributed. Convex or concave curvature indicates asymmetry. A concave configuration indicates the data have an asymmetric distribution, such as a log-normal.

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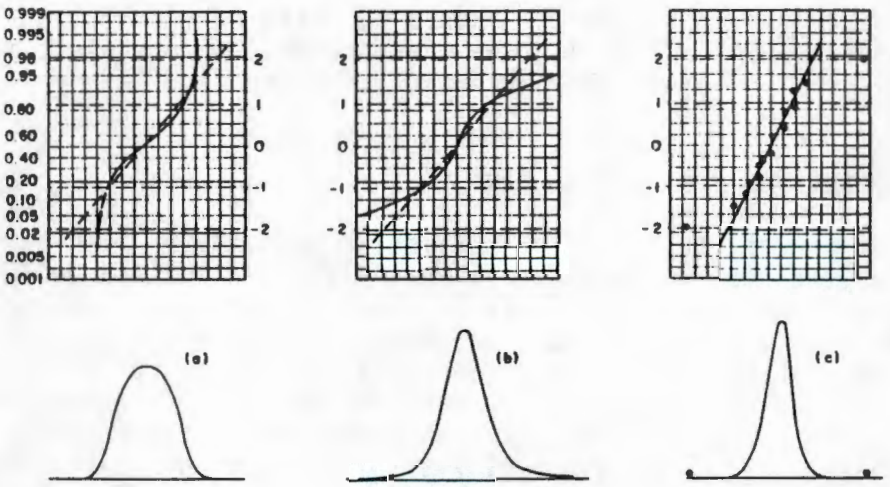
[1]Paradox is a trademark of Borland International.

Figure 2-1a. Light-Tailed Distribution.
2-1b. Heavy-Tailed Distribution.
2-1c. Normal Distribution.
(Box and Draper 1987, pp. 131)



The occurrence of two plateaus on a normal probability plot is also common. This indicates there are two distinct concentration groups or clusters of points (i.e., bimodal distribution). The opposite situation occurs when there is a data gap between two segments of a normal probability plot. This indicates there may be more than one population.

In using the normal probability plot, it is useful to remember that the data are observed values of random variables and hence typically will never lie perfectly on a straight line. Furthermore, when drawing a straight line through the data, the center points should be given more weight than the extremes (Shapiro 1980). That is, the presence of few moderate outliers should not greatly influence the perception of the rest of the data.

2.2.2 Concentrations Versus Time Plot

A plot of concentrations (of a particular constituent of concern) versus time is one of the best methods for observing a water quality behavior over time (Figure 2-2). This plot quickly displays whether there may be increasing or decreasing trends in concentrations; the presence of cyclical (seasonal) patterns; or an outlier observation (anomaly) that does not conform to the pattern established by other observations for that well (Figures 2-3 and 2-4). Adequate data are needed in order to assess seasonal patterns and/or long-term trends. In this report, a minimum of 2 yr of monthly (or quarterly) monitoring data is recommended.

2.2.3 Box-and-Whisker Plot

During some stages of the analysis, it is important to have summary displays of the data. One simple method of summarization is a box-and-whisker plot (Figure 2-5). In this plot, the upper (Q_3) and lower (Q_1) quartiles of the data are shown by the top and bottom of a box and the median (Q_2) is indicated by a line segment within the box. The box covers the middle 50% of the data values. The 'whiskers' extend out to the extremes (minimum and maximum observations). When extremely large or small values occur, they are plotted as individual points. The whiskers extend only to those points that are within 1.5 times the interquartile range. Any point that falls outside the whiskers may be classified as a suspected outlier (Ostle and Malone 1988). When a value is classified as an outlier, it is prudent to check the sampling and analysis records to determine whether the outlier resulted from an error (in transcription, dilution, analytical procedure, etc.). The extreme observation is deleted from the statistical evaluations only when it is in error and the correct value cannot be identified.

Multiple box plots may be used to present the changes in groundwater quality through time or over space (Figure 2-6). This is accomplished by displaying the distributions of concentrations for a particular well over different time periods or that of different monitoring wells monitored in the same time interval.

Figure 2-2. Nitrate Concentration in Well 1-H4-3 (1985 - 1990).

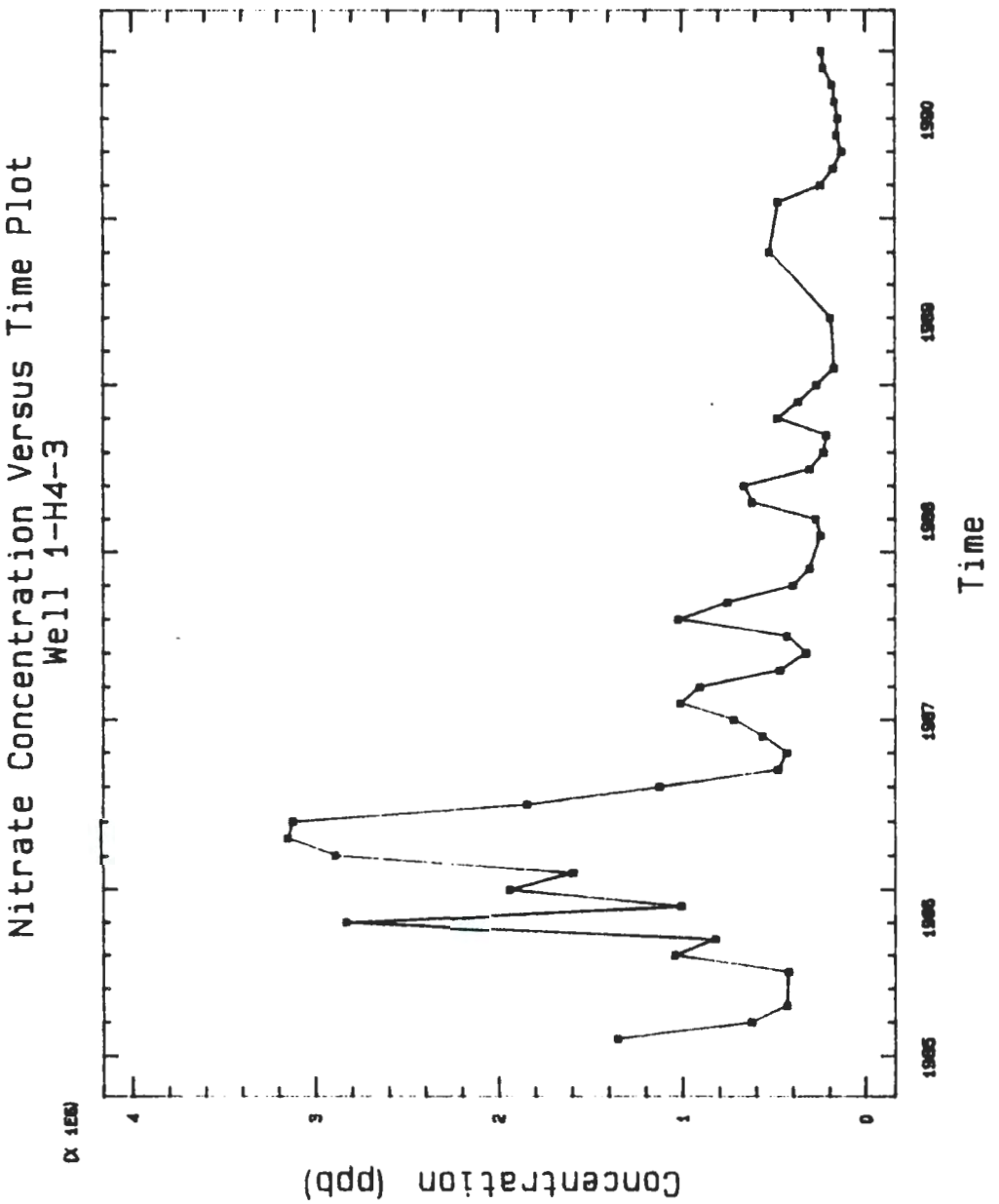


Figure 2-3. Nitrate Concentration and Trend in Well 1-H4-3 (9/86 - 9/88).

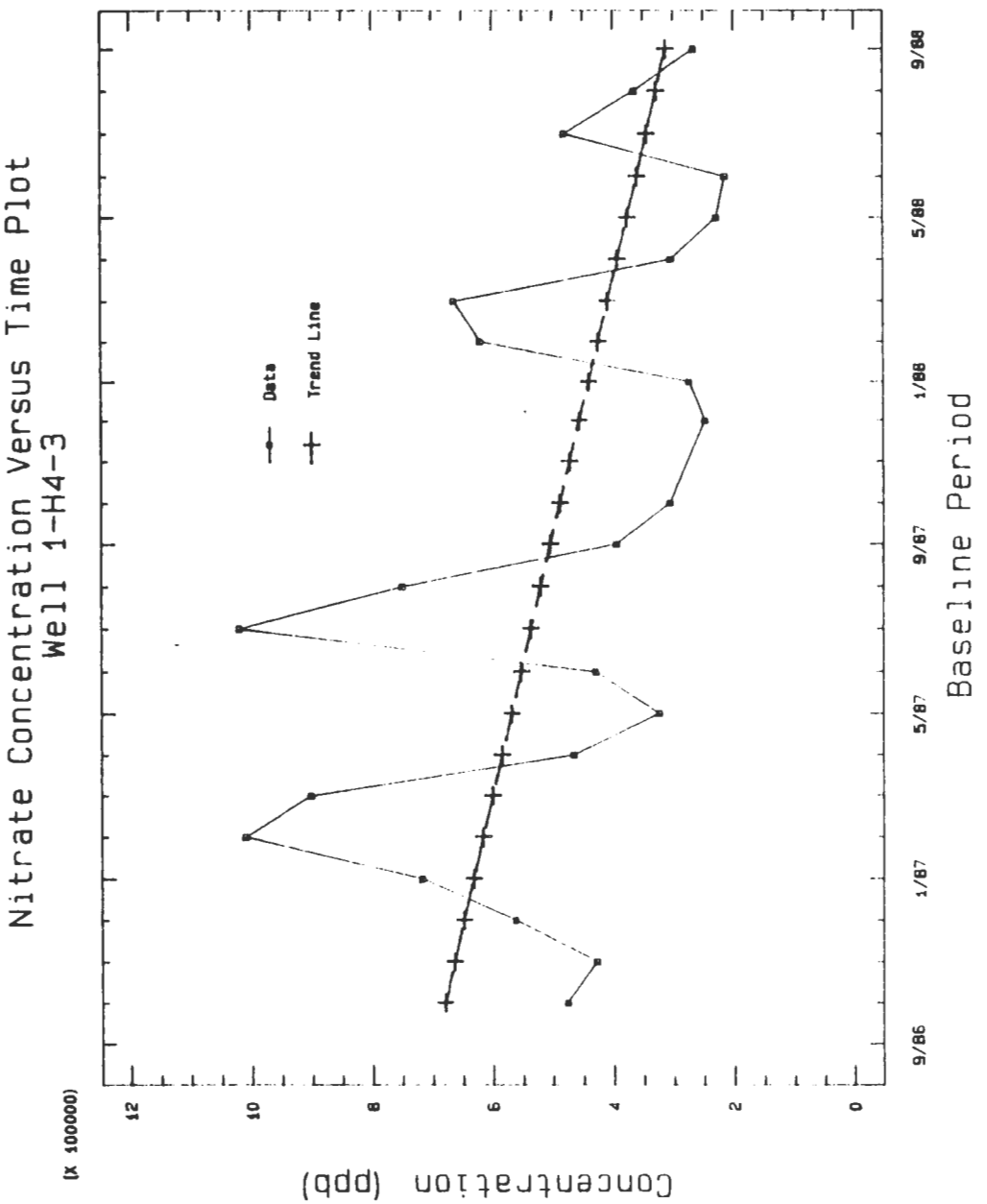


Figure 2-4. Observed and Adjusted Nitrate Concentration in Well 1-H4-3.

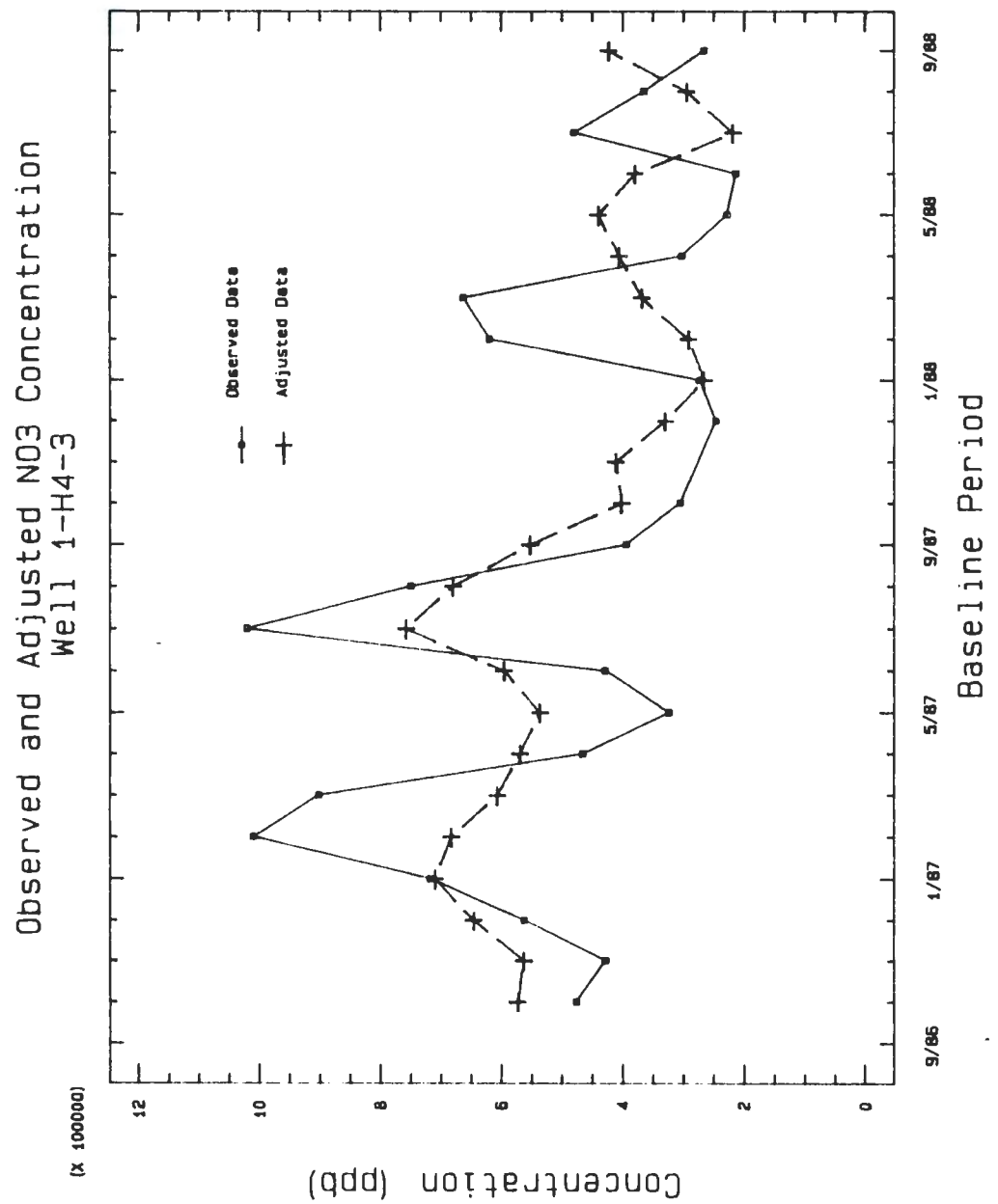


Figure 2-5. Box-and-Whisker Plot.

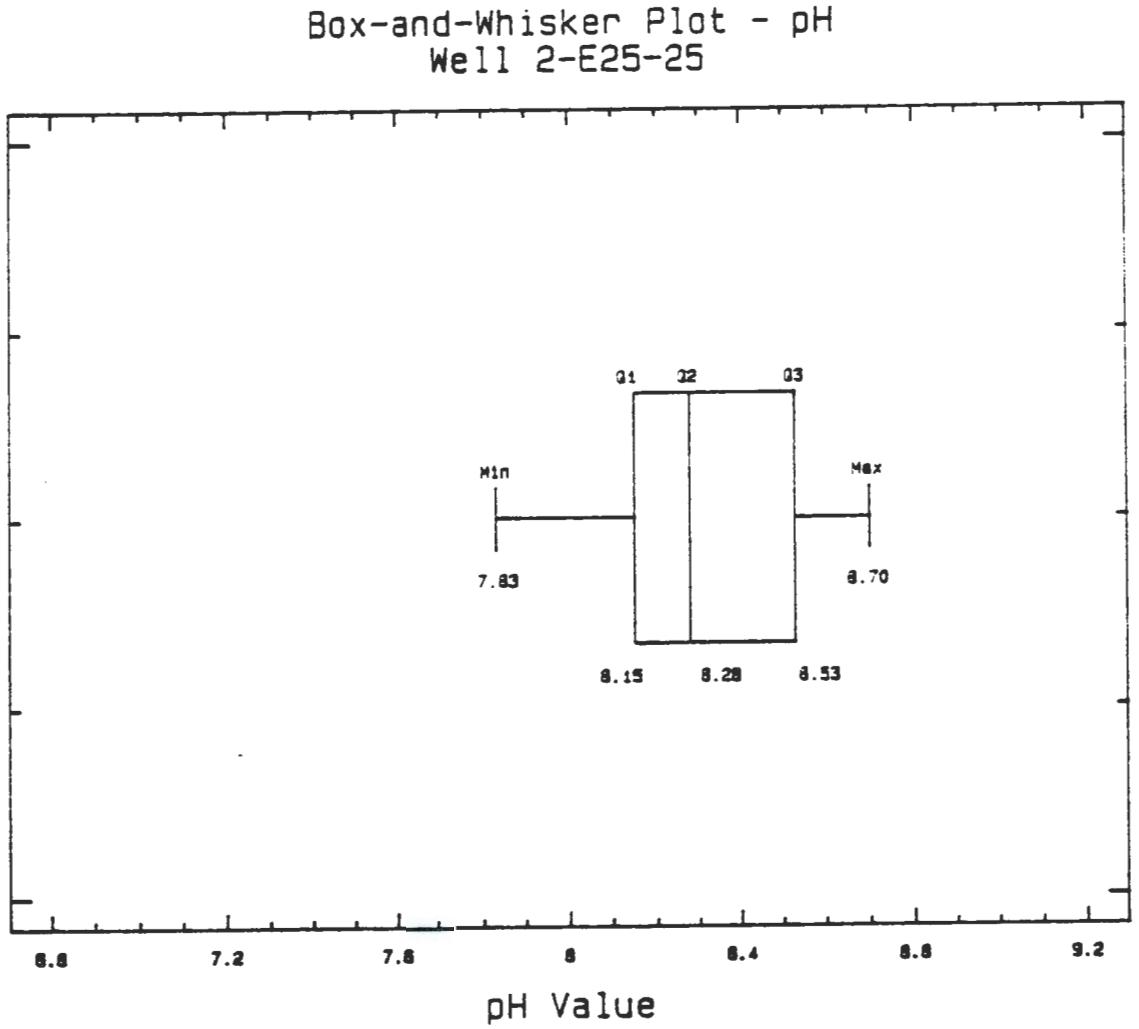
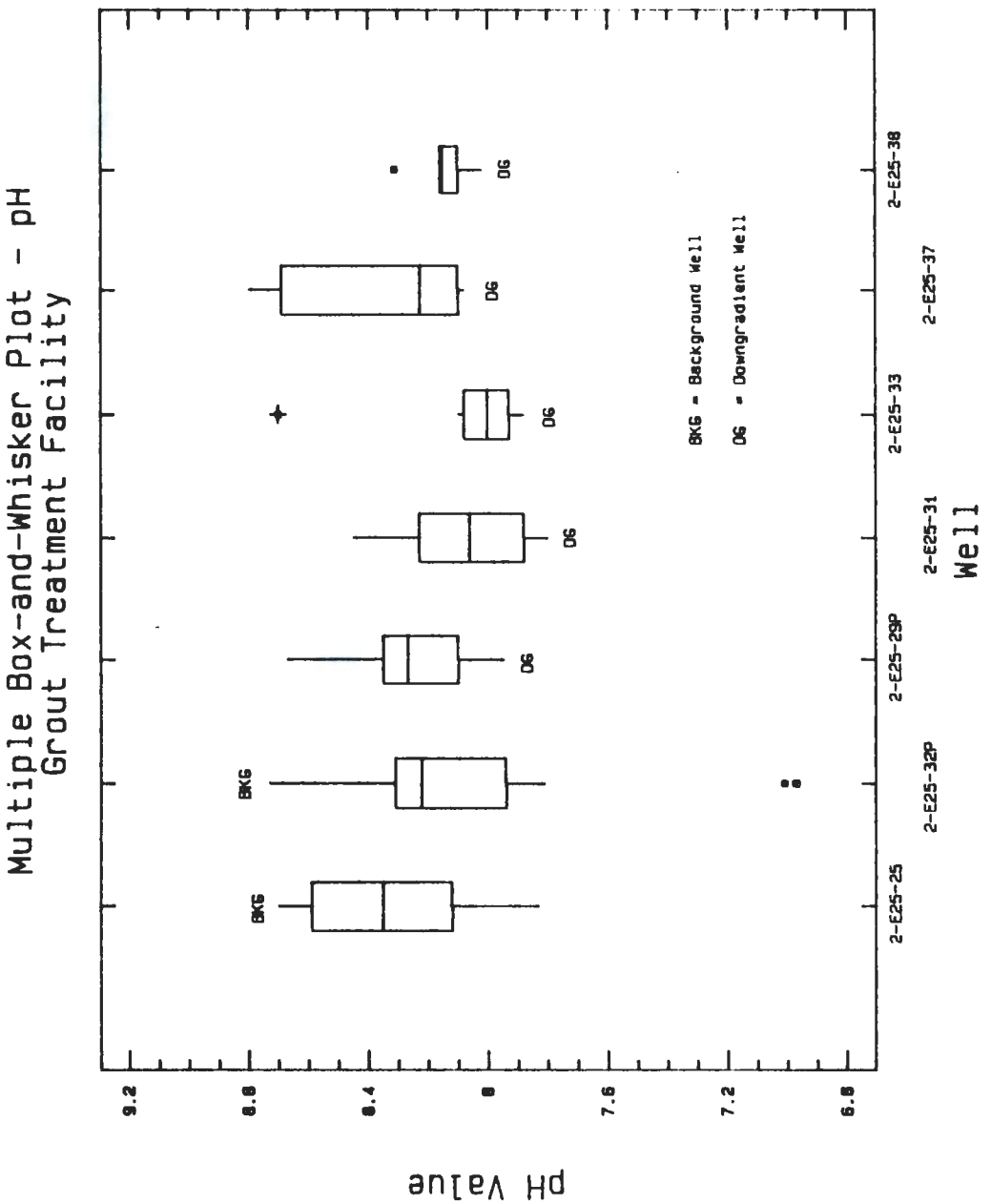


Figure 2-6. Multiple Box-and-Whisker Plot.



2.2.4 Regression Plot

Another method of identifying trends and/or outliers is based on a linear regression model of time (independent variable or X) versus concentrations (dependent variable or Y) (Figure 2-7). In this case, a data point is considered as an outlier if it is outside of the 95% confidence interval of a predicted value for that data using linear regression analysis. For example, to determine if the most recently acquired data is a suspected outlier, use the most recent 20 observations to fit a linear equation. Any value that is outside 2.09 times the standard error of the predicted value $\hat{Y}_x$ for a new value of Y at point X = x is flagged and submitted for further investigation. Note that the multiplier of 2.09 corresponding to a two-tailed (95%) t-value with 19 degrees of freedom. Formulas to calculate prediction interval are given in Snedecor and Cochran (1980). In using the linear regression analysis, the error term is assumed to have a normal distribution. Hence, a regression equation and the residuals must be calculated, then check the normality of the residuals because these residuals estimate the true errors.

2.2.5 Control Charts

Control charts are widely used in industry to detect serious departures from a process mean. A typical control chart for the mean, $\bar{x}$ chart, consists of a center line (CL), corresponding to the process average and two control limits, called the upper control limit (UCL) and the lower control limit (LCL). Process variability can be controlled with a control chart for the range, called an R chart. The $\bar{x}$ and R charts are among the most important and useful statistical process control techniques (Figure 2-8a and 2-8b). The control limits are chosen such that values falling outside them indicate a lack of statistical control. Detailed procedures can be found in statistical text such as Montgomery (1991).

To construct a control chart for a well, there must be no major increasing or decreasing trends in concentration and the variations must be due to random fluctuations about a constant process mean. To detect trends, a concentration versus time plot or a regression plot can be performed as a quick visual examination. A statistical test for detecting trends will be described later (see Section 2.3.3). It is inappropriate to construct a $\bar{x}$ control chart for wells that are contaminated or have shown an increasing trend (EPA 1989a, p. 7-12).

For control charts and statistical tests to work well, the assumption of uncorrelated or independent data has to be satisfied. Unfortunately, this assumption usually is not met because groundwater measurements taken sequentially in time are likely to be positively correlated (autocorrelation). This would give rise to larger than anticipated false-positive rates (i.e., too many false alarms). The Box-Jenkins time series techniques may be used to directly model the correlative structure and apply control charts to the residuals (i.e., the differences between the observed and the predicted values). However, a minimum of 50 observations collected at equally spaced, discrete time intervals are required (Box and Jenkins 1976, p. 33). In the context of groundwater monitoring, at least 5 yr of monthly monitoring data

Figure 2-7. Regression Plot.

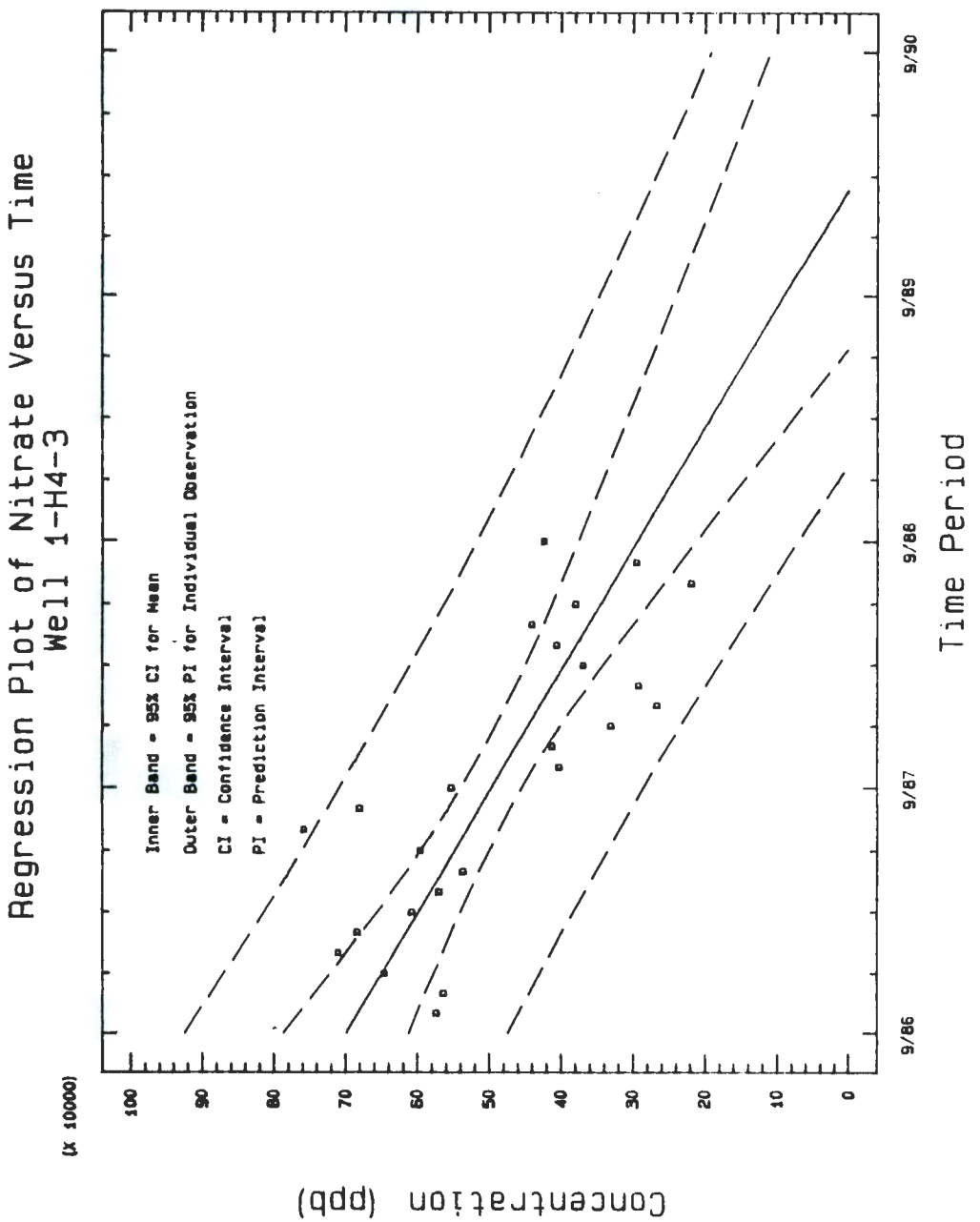
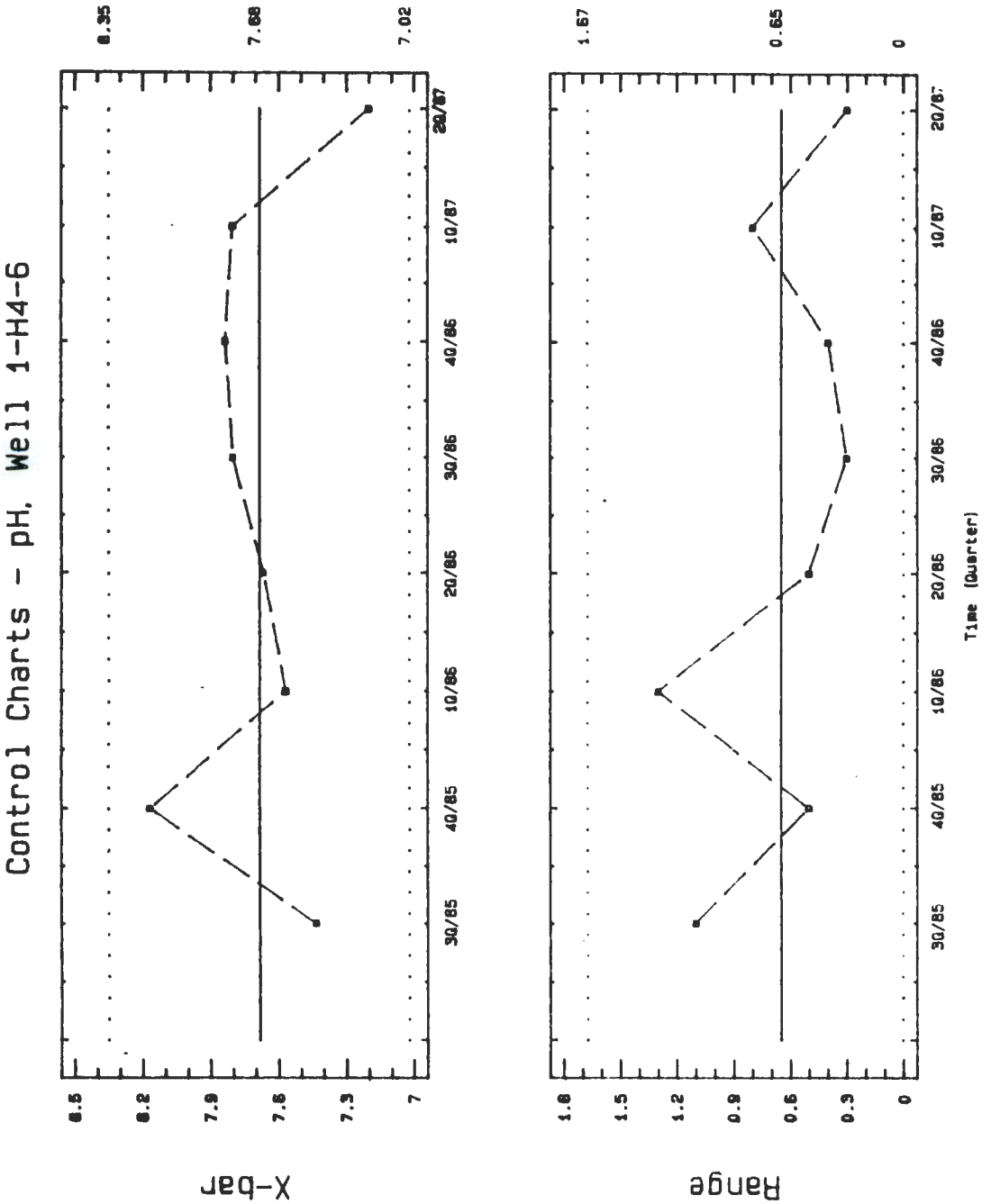


Figure 2-8a. X-Bar Control Chart.
2-8b. Range Chart.



are needed before attempting Box-Jenkins methods. For this reason, Box-Jenkins methods are not recommended in this report. The following two general approaches for dealing with the problem of autocorrelation are recommended instead.

If the presence of autocorrelation is due to the omission of an important factor (regressor), and if that factor can be identified and included in the model, the apparent autocorrelation should disappear. However, when autocorrelation cannot not be removed by adding one or more new regressors to the model, consider averaging the data over longer time periods such that the autocorrelation is insignificant.

Another situation that may decrease the effectiveness of a control chart is seasonality (the presence of temporal cycles) in the data. When seasonality is known to exist in a time series of concentrations, the data must be adjusted prior to constructing control charts in order to account for the seasonal variations. This adjustment requires at least 2 yr of monthly or quarterly monitoring data (EPA 1989a, p. 7-7). One simple and easy method to adjust for seasonality is to subtract the monthly (or quarterly) mean from the observation for that month (or quarter) and add the overall mean (for the 2-yr period). The mathematical formula can be found in the U.S. Environmental Protection Agency (EPA) guidance document (EPA 1989a, p. 7-2 to 7-4).

Finally, a fundamental assumption in developing the control charts is that the underlying distribution of the variable of concern is normal. Studies have been performed to investigate the effect of non-normality on control charts (Burr 1967, Schilling and Nelson 1976). Results of these studies indicate that the normal theory control limits in general are very robust even for nonnormal distributions. In most cases, a sample size of four or five (per time period) is sufficient to ensure reasonable robustness. In the context of groundwater monitoring, a control chart should be established using the quarterly means of monthly data rather than using individual monthly values because it is not possible to calculate variance with only one observation (per month) and it is not practical to sample more frequently because of autocorrelation problems.

2.3 STATISTICAL TESTS

Graphical plots provide visual portrayals of data. Judgement is relied upon in using these plots. The lack of objectivity is one major drawback of the graphical evaluation techniques described in the previous section. Hence, it is always a good idea to supplement the plots with statistical test procedures. This section describes an EPA-recommended approach to handle non-detects (EPA 1989a). It also discusses various statistical analysis methods that may be used to test whether the data are drawn from a normal distribution, the presence of trends, the shift in central tendency, and compliance with regulatory standards.

2.3.1 Non-Detects

One problem frequently encountered in environmental monitoring is the reporting and subsequent statistical analysis of data that are *non-detects* (i.e., a measurement that is less than the limit of detection). It is quite common for an analytical laboratory to report a numerical value (usually the limit of detection) preceded by a '<' sign. This practice often discards potentially useful information. It is recommended that, for statistical analysis purposes, the laboratory reports the actual measured concentrations even if it is less than (LT) the analytical detection limit. In this way, even if the reported data set consists almost entirely of LT values, the mean ($\bar{x}$) and variance (s^2) can be calculated using all the measurements (including the non-detects). The resulting value of $\bar{x}$ should be flagged. However, statistical test results, if known to impact the monitoring status, must be based on quantifiable data.

If actual concentrations are not available and the proportion of non-detects is small (say less than 15%), one may replace these LT values by one-half the detection limit and proceed with the appropriate analysis using these modified values (EPA 1989a, p. 8-3). The results of the statistical analysis are generally not sensitive to the specific choice of the replacement value if a small proportion of the observations are not detected. If more than 15% of the values, say 15% to 50%, are reported as not detected, treat these nondetects as ties and proceed with a nonparametric test. When more than 50% of the data are reported as nondetects, it is preferable to use a method such as test of proportions for the upgradient-downgradient comparisons. The test of proportions may be based on an approximation procedure (EPA 1989a) or an exact procedure for testing the equality of binomial proportions (Nelson 1982), whichever is more appropriate.

2.3.2 Goodness-of-Fit Test on Normality of Data

The statistical tests used for evaluating whether or not the data follow a specified distribution are called 'goodness-of-fit' tests. The hypothesis to be tested is that the data are drawn from a normal (or a lognormal) population. One problem with statistical goodness-of-fit testing is that few tests are useful when the sample size is small (e.g., the chi-square test). One recommended method is Shapiro and Wilk's W-test (EPA 1989a). This test performs well on small sample size and is one of the most powerful tests available for detecting departures from a hypothesized normal (or lognormal) distribution function. Another recommended method is Lilliefors test for normality of data (EPA 1989b). Test procedures for these two tests can be found in Conover (1980).

2.3.3 Trend Analysis

The Mann-Kendall nonparametric test for detecting increasing or decreasing trends is used when there are no cycles or seasonal effects in the data. Seasonal cycles present must be removed before performing the test. The removal of seasonal effects is explained in Section 2.2.5. The Mann-Kendall test for trend is useful because the data need not conform to an

assumption such as normal distribution. Also, non-detects can be treated as ties without invalidating the test because this test uses only the relative magnitudes of the data rather than measured values. Detailed procedures can be found in Gilbert (1987).

When sample size n is less than or equal to 40 and there are no tied data values, the probability values provided in Hollander and Wolfe (1973) can be used as decision rules. In practice, a procedure based on normal distribution yields valid results for n as small as 10 provided a continuity correction factor of 1 is used and there are not many tied data values (Kendall 1975).

If the Mann-Kendall test indicates that a linear trend exists, Sen's method may be used to estimate the true slope (change per unit of time). Sen's method is preferred to the linear regression method because it is not greatly influenced by gross data errors or outliers. Sen's nonparametric estimator of the slope is closely related to the Mann-Kendall test. Computation formulas can be found in Gilbert (1987).

2.3.4 Central Tendency

Interim-Status Groundwater Monitoring Programs--Often a test for a shift in the central tendency is required by federal and state groundwater monitoring regulations. For example, for a TSD facility that is under an interim-status RCRA groundwater monitoring program, a t-test is required to compare means between individual downgradient (or compliance) wells and upgradient (or background) wells [40 CFR 265.93(b)]. A recommended method is the averaged replicate (AR) t-test described in Appendix B of the RCRA Groundwater Monitoring Technical Enforcement Guidance Document (TEGD) (EPA 1986).

Final-Status Groundwater Monitoring Programs--Federal regulations governing final status RCRA groundwater monitoring programs allow more latitude in the application of statistical methods to assess impact on groundwater quality [40 CFR 264.97(h)]. Depending on the nature of data (e.g., proportions of nondetects) and objectives of the monitoring programs (i.e., detection or compliance monitoring), different statistical procedures may be used. The selected statistical methods shall comply with the performance standards as required in 40 CFR 264.97(i).

In a detection-level program, the monitoring objective is to determine the impact of a facility on groundwater quality through comparisons of upgradient and downgradient well data. The recommended method is analysis of variance (ANOVA) (EPA 1989a). Also, for a facility with limited amounts of data, such as in the initial phase of groundwater monitoring, it is advisable to use the ANOVA method. And later, when sufficient data are collected, a tolerance interval or a prediction interval (see discussions in Section 2.3.5) or a control chart approach may be used.

A one-way ANOVA may be used to determine whether differences in mean concentrations among wells are statistically significant; if so, multiple comparison procedures (such as Bonferroni t-statistics) may be used to determine which compliance well is contaminated. There are two types of ANOVA procedures: parametric and nonparametric. Parametric ANOVA assumes that the

data are normally distributed with equal variance and is appropriate when the proportion of nondetects is less than 15%. Test procedures can be found in Snedecor and Cochran (1980). Before applying a parametric ANOVA, the nondetects will be replaced with a value such as one-half the detection limit. If data do not meet the parametric ANOVA requirements, the nonparametric approach such as Kruskal-Wallis test may be utilized (Conover 1980). The Kruskal-Wallis test is an extension of the Mann-Whitney test for two independent samples (i.e., $k = 2$). The Kruskal-Wallis nonparametric ANOVA tests whether the median of the compliance well data is the same as the median of the background data (i.e., $k \geq 2$). A same-point-in-time comparison between background and compliance well data is recommended when using ANOVA (parametric or nonparametric) procedures.

2.3.5 Excursion Analysis

If groundwater sampling during detection-level monitoring reveals a statistically significant increase (or decrease, in the case of pH) over background values, a compliance monitoring program will be initiated. In a compliance monitoring program, the monitoring objective is to determine whether groundwater protection standards have been exceeded. Methods discussed in this section will help facility owner/operator to comply with applicable regulatory requirements.

Statistical evaluation procedures under a compliance monitoring program depend on the type of compliance limit. If the compliance limit is determined from background, the statistical method should compare the concentrations of groundwater from background wells to those from compliance wells. For test of central tendency, parametric or nonparametric ANOVA should be used. An alternative approach to ANOVA is to use tolerance intervals. Tolerance intervals are most appropriate for data that do not exhibit high degrees of spatial variation between background wells and compliance wells. A tolerance interval is constructed using existing data from background wells. The purpose of the tolerance interval approach is to define a concentration range from background well data, within which a large proportion (coverage) of the monitoring data should fall with a high degree of confidence. A coverage of 95% and confidence level of 95% are recommended (EPA 1989a). Data from compliance wells are checked individually for evidence of contamination by simply determining if each data point is within the tolerance interval. If not, this is interpreted as providing statistically significant evidence of contamination. Specific procedures to construct normal or nonparametric tolerance intervals can be found in EPA (1989a) and Conover (1980), respectively.

If the compliance limit is a specified constant such as a maximum concentration limit (MCL) or an alternate concentration limit (ACL), then the appropriate statistical procedures are those that compare the compliance well concentrations with the prescribed fixed limits. In this situation, confidence intervals (on the mean or median concentration for the compliance wells) are the recommended procedures [40 CFR 264.97(h)(5)]. A confidence interval for the mean or median concentration can be constructed individually from the sample data for each compliance well. These confidence intervals are compared with the compliance limit. If the lower confidence limit is above the compliance limit, this indicates noncompliance. Methods to construct

confidence intervals can be found in Gilbert (1987). If the permit requires that a compliance limit is not to be exceeded more than a specified fraction (say 5%) of the time, the recommended procedure is to construct a tolerance interval. For example, a tolerance interval can be constructed (using concentrations from a particular compliance well) in such a way that it will cover at least 95% of the population for that well with 95% confidence. If the upper limit of this interval exceeds the compliance limit, then the concentration of the constituent of concern could exceed the compliance limit more than 5% of the time, indicating noncompliance.

2.4 REPORTING PROCEDURES

Results of statistical evaluations should be presented to the users in a clear, concise, and understandable format so that any action, if warranted, can be initiated in a timely manner. This is especially important if results of statistical evaluation indicate further actions are necessary to comply with the regulations. For example, if concentration of a downgradient well shows a statistically significant increase over background for a contamination indicator parameter (total organic carbon, total organic halogen, pH, or specific conductance), that well has to be immediately resampled to determine if the originally detected increase was a result of laboratory analysis error. If results of the verification sampling confirm the statistically significant increase, then the groundwater monitoring program will be elevated to a higher level (e.g., from detection to compliance monitoring program). This information has to be communicated to the users (managers and regulators). The following procedures provide some general guidance:

a. If results of statistical evaluation have a major impact on the monitoring program(s) and have to be reported to the regulators on a nonroutine basis, the reporting requirements stipulated in the regulations shall be followed. Interim-status regulations are specified in 40 CFR 265.93 (d). Final-status regulations are specified in 40 CFR 264.98 (g) and 40 CFR 264.99 (h) for detection-level and compliance-level monitoring, respectively.

b. If results of the statistical evaluation do not impact the monitoring programs but have to be reported to the regulators on a routine basis (i.e., quarterly or annual report), the reporting requirements stipulated in the regulations shall be followed. Interim-status regulations are specified in 40 CFR 265.94 (a)(b). Data collected for final-status groundwater monitoring programs must be maintained in the facility operating records and submitted for regulatory review based on permit specifications [40 CFR 264.97(j)].

c. If results of statistical evaluation affect only the choice of an appropriate statistical method for subsequent analysis (e.g., test on normality), this information should be documented and kept on file.

The reporting formats that are useful for cases a and b are presented in Tables 2-1 through 2-4. A format suitable for case c is given in a later section when presenting case study results (see Table 3-1).

Table 2-1. Background Contamination Indicator Parameter Data for the Hazardous Waste Management Area (DOE-RL 1991).

Well name	Sample date	Duplicate sample number	Specific conductance umhos/cm 1/700w	Field pH 0.01/8.5s	TOC (ppb) 1000/.	TOXLDL (ppb) 10/.

The column headers consist of: Constituent Name; Analysis Units; and Contractual Detection Limit/Drinking Water Standard (suffix)

Suffix s = based on Secondary Maximum Contaminant Levels in 40 CFR part 143, National Secondary Drinking Water Regulations
w = based on additional Secondary Maximum Contaminant Levels in WAC 248-54, Public Water Supplies
Data flag = # denotes a less than contractual detection limit value.

Table 2-2. Average Replicate Statistics--Background Indicator Parameter Data for Hazardous Waste Management Area (DOE-RL 1991).

Constituent	Well name	Sample date	n	average	Standard deviation	C.V. (%)

Table 2-3. Background Statistics--Contamination Indicator Parameter Data for Hazardous Waste Management Area (DOE-RL 1991).

Constituent	Units	n	Background average	Background standard deviation	Background C.V. (%)
Specific conductance	umhos/cm				
Field pH					
TOC	ppb				
TOXLDL	ppb				

Table 2-4. Critical Means Table for xx Comparisons--Background Contamination Indicator Parameter Data for Hazardous Waste Management Area[a] (DOE-RL 1991).

Constituent	n	df	tc	Average background	Standard deviation	Critical mean

[a]Data collected from xxxx to xxxx for upgradient wells x-xx-xxx and x-xx-xxx. Values calculated based on xx comparisons.

[b]The following notations are used in this table:

df = degrees of freedom (n-1).

n = number of background replicate averages.

t_c = Bonferroni critical t-value for appropriate df and xx comparisons.

3.0 CASE STUDIES

In this section, two case studies are provided. The first case demonstrates various graphical techniques and statistical tests that are suitable for intrawell comparisons. That is, comparing the current concentration for a well with its own past behavior. Topics discussed are; adjusting data for seasonal effects, performing the Mann-Kendall test for long-term trend, calculating Sen's estimator for slope, and constructing control charts for means and ranges. Concentrations of nitrate from well 1-H4-3 and pH from 1-H4-6 were used in the first case study. The second case illustrates various graphical and statistical tests that are appropriate for interwell comparisons. That is, comparing concentrations from downgradient wells with background concentrations. Topics addressed are: identifying potential outliers, testing normality of data, performing parametric and nonparametric ANOVA, and constructing a tolerance interval based on existing data. Data used were pH values from various monitoring wells of a RCRA facility. Flow charts to guide the statistical evaluations for the interim-status and final-status programs are presented in Figures 3-1 and 3-2, respectively. Unless otherwise specified, the statistical software package STATGRAPHICS[2] (Version 4.2) was used to generate the plots and the test statistics.

3.1 CASE STUDY 1 - 183-H FACILITY

Facility Background--The 183-H facility is a RCRA-regulated TSD facility located along the Columbia River in the northern portion of the Hanford Site (see Figure 1-1). This facility is currently in a RCRA interim-status assessment-level monitoring program due to elevated concentrations of nitrate and other constituents in the groundwater. This facility was selected for illustration purposes because it has a fairly continuous record of monitoring results since 1985. The monitoring well (1-H4-3) used is one of two downgradient wells most influenced by the plume from the facility. The chemical constituent selected was nitrate.

Plots to Detect Seasonality and Trend--A concentration versus time plot is presented first (see Figure 2-2). It can be seen that the earlier data (June 1985 through September 1986) were greatly affected by the leakage of nitrate from the 183-H facility. Some of the later data (October 1988 to May 1990) were not sampled regularly (i.e., on monthly intervals). In order to identify seasonal variations and long-term trends, monthly nitrate monitoring data from a 2-yr period (October 1986 through September 1988) were chosen to illustrate various methods described earlier in this report. This 2-yr period is referred to as the baseline period. Nitrate concentrations clearly indicate a definite seasonal pattern together with a decreasing trend (see Figure 2-3). The method described in Section 2.2.5 was applied to the nitrate data resulting in seasonally adjusted data (see Figure 2-4). The residual pattern seen on Figure 2-4 suggests additional factors may need to be considered to completely remove the seasonal effect. The physical process

[2]STATGRAPHICS is a trademark of Statistical Graphics Corporation.

Figure 3-1. Flow Chart Overview for Interim-Status Programs.

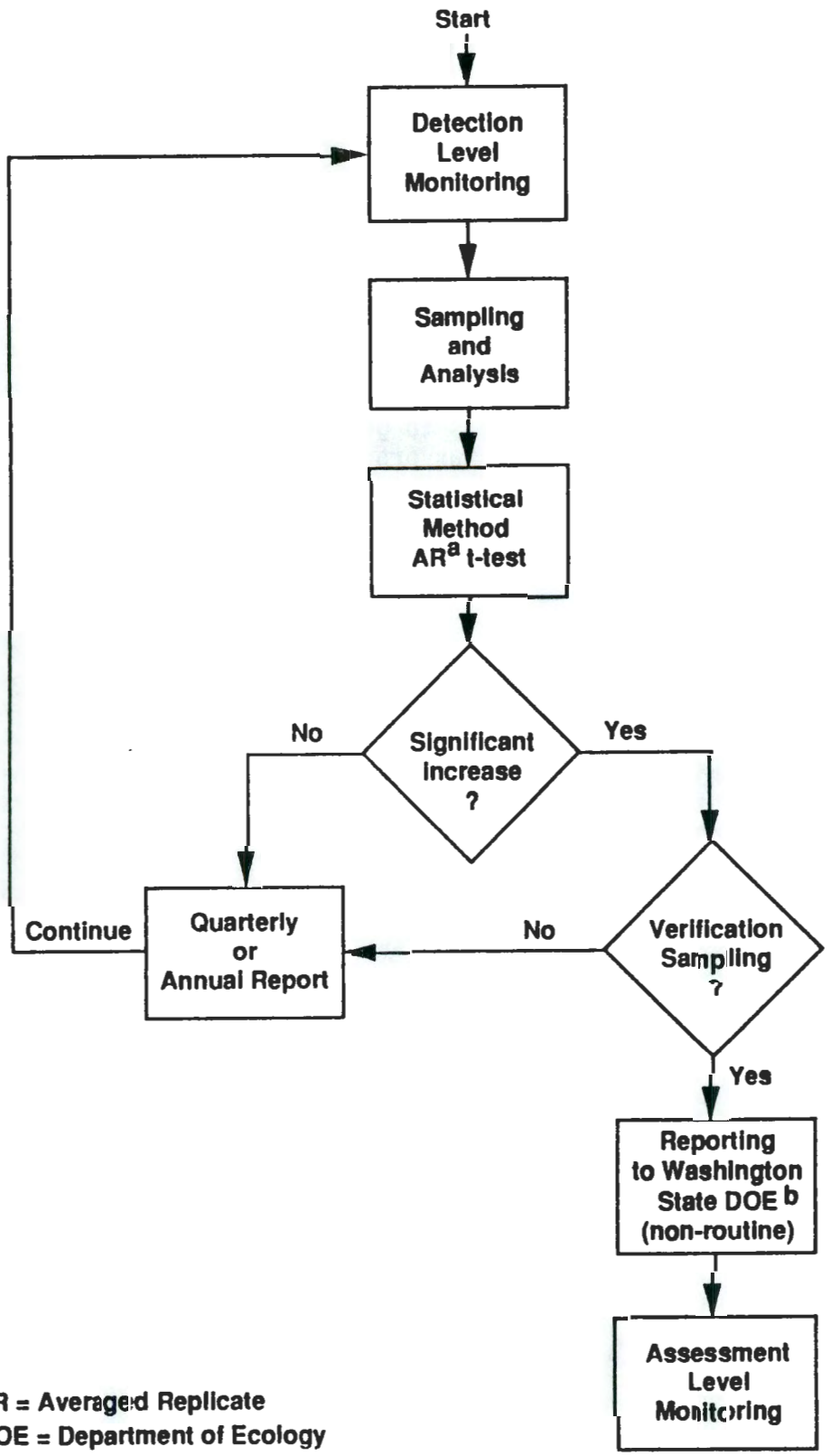
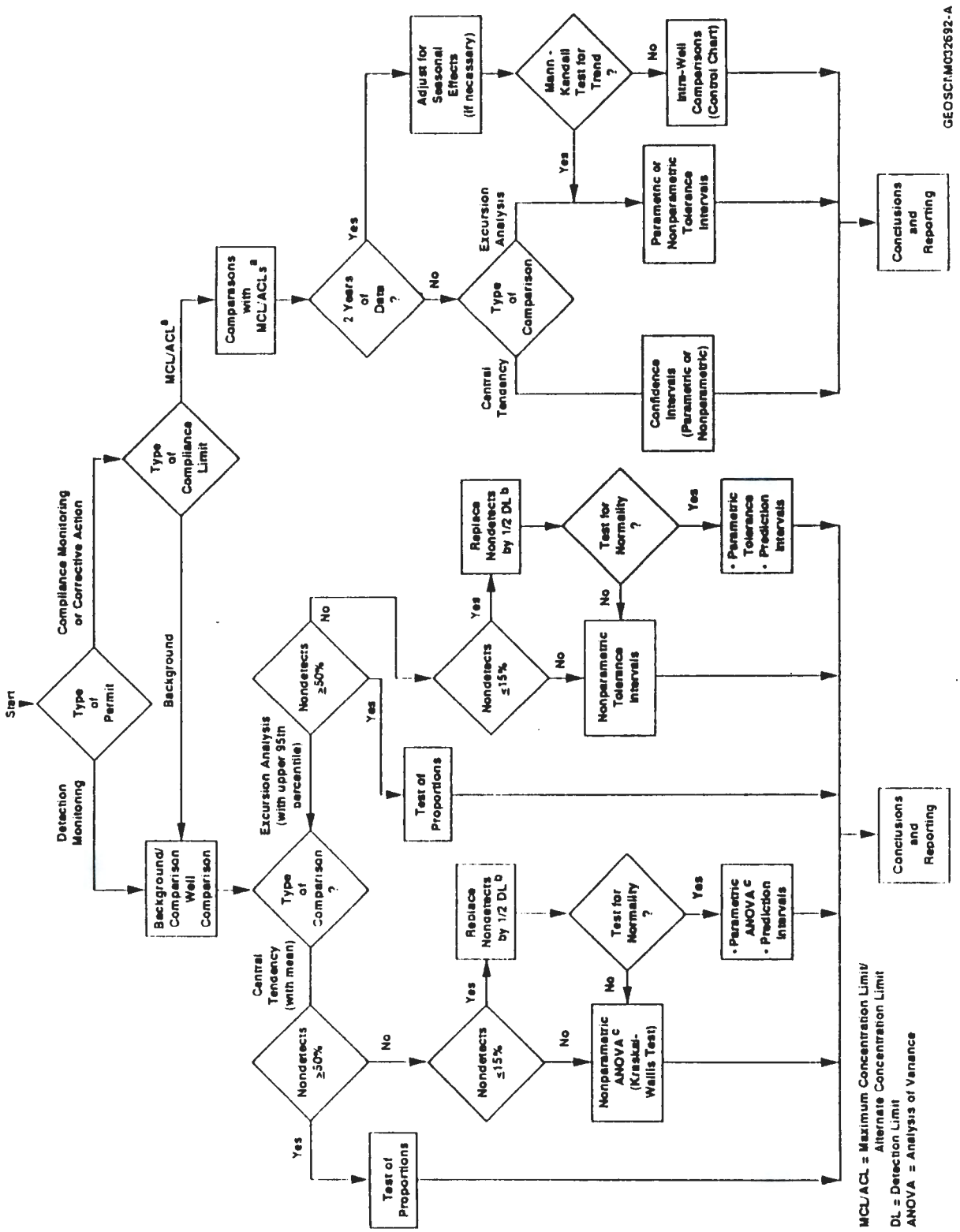


Figure 3-2. Flow Chart Overview for Final-Status Programs.



causing such phenomenon is unknown at this time. The seasonally adjusted nitrate values will be used as 'observations' in subsequent calculations.

Mann-Kendall Test for A Decreasing Trend--The next step is to perform the Mann-Kendall nonparametric test for detecting a decreasing trend using the normal approximation procedures described in Gilbert (1987). The baseline period is 24 months of monitoring data, hence, n = 24. There are $n*(n-1)/2 = 24*23/2 = 276$ differences to be examined for their sign. Lotus 1-2-3[3] was used to calculate the Mann-Kendall statistic S, variance of S (Var(S)), test statistic Z and subsequent Sen's estimator for the slope. Results are presented below:

$$S = \#\text{ of plus signs} - \#\text{ of minus signs}$$

$$= 66 - 210$$

$$= -144.$$

$$Var(S) = [n*(n-1)*(2n+5) - \Sigma\, t_p*(t_p-1)*(2t_p+5)]/18$$

$$= [24*23*48 - 0]/18$$

$$= 1625.33.$$

where $p = 1, \ldots, g$ (the number of tied groups) and t_p is the number of data in the p^{th} group. In above calculation of Var(S), the second term is 0 because there is no tied group, and

$$\sqrt{Var(S)} = 40.32$$

$$Z = (S + 1)/\sqrt{Var(S)}$$

$$= (-144 + 1)/40.32$$

$$= -3.55.$$

Referring to a standard normal table, at $\alpha = 0.01$, $Z_{1-\alpha} = Z_{0.99} = 2.326$. The null hypothesis of no trend is rejected because Z is negative and the absolute value of Z is larger than 2.326. The use of $\alpha = 0.01$ for the trend test is recommended so that control charts can be constructed on as many wells as possible. That is, when α is chosen to be small, it is more difficult for the test to reject the null hypothesis of no trend. Thus, control charts can be constructed on these wells.

[3]LOTUS is a trademark of Lotus Development Corporation.

Least Squares Estimate of Slope--To estimate the linear trend or the true slope (change in nitrate concentrations per month), the least squares estimate by the linear regression method was also used. The resulting equation is:

$$Y = 699{,}094 - 16{,}910.9*X$$
$$= 699{,}000 - 17{,}000*X$$

where Y is the estimated nitrate concentration in units of parts per billion (ppb) and the slope is estimated to be a -17,000 ppb/month. Note that these values are rounded to the nearest 1,000 ppb because the detection limit for nitrate is 500 ppb.

Sen's Nonparametric Estimate of Slope--The slope estimated by the linear regression method will differ greatly from the true slope if there are gross data errors or outliers in the data. Sen's nonparametric estimator of slope is not greatly affected by data errors or outliers and can be computed when data are not normally distributed or are missing. There are $N' = n*(n-1)/2 = 24*23/2 = 276$ slope estimates, Q:

$$Q = (x_j - x_i)/(j - i)$$

where x_j and x_i are seasonally adjusted nitrate values from month j and i, respectively, and where $j > i$. The 276 slopes are ordered from the smallest to the largest. The median of these 276 values of Q is Sen's estimator of slope. Because $N' = 276$ is even, the median of these Q values is the average of the 138^{th} and 139^{th} largest values, which is -17,000 (rounded from -17,015) ppb/month. Note that the two slope's estimates are almost identical. Control charts will not be constructed due to the presence of a decreasing trend.

Regression Plot and Lilliefors Test for Normality on Residuals--A linear regression plot with the 95% confidence interval for the means and the 95% prediction interval for a future observation is presented in Figure 2-7. Lilliefors test for normality of data was applied to the residual nitrate concentrations, the test statistic $D_{max} = 0.102$, which is less than the critical value $W_{0.95} = 0.176$ for $n = 24$. Hence, the assumption of normality is not rejected at level of significance, $\alpha = 0.05$. Seasonally adjusted nitrate concentration of 758,000 ppb (July 1987) is outside the 95% prediction interval (Figure 2-7), this should be served as a flag for further actions to check the validity of the data.

Control Charts--Once the tests for trends for all of the wells have been completed, control charts can be constructed for wells that have no significant trends. It is inappropriate to construct control charts on wells that have shown evidence of a trend because a control chart for the mean will be biased. In that case, there is no constant mean level about which future observations will fluctuate in a random manner. To illustrate how to construct control charts (x-bar chart and range chart) for the quarterly means, pH values from an upgradient well 1-H4-6 of the 183-H facility were selected. A 24-month period was used (July 1985 to June 1987). Original pH values are considered as 'observations' because seasonal adjustment is not necessary.

At the end of the 24-month period, 8 quarterly means $\bar{x}_i$ and 8 ranges R_i were calculated where i = 1, 2, ..., 8. Then, the average of these 8 quarterly means ($\bar{\bar{x}}$) was computed and used as the center line of the x-bar chart. To construct 3-σ control limits, an estimator of the standard deviation σ is needed. This is accomplished by calculating the average of the 8 ranges, $\bar{R}$. The UCL, LCL, and the center line for the x-bar chart are (see Figure 2-8a):

$$\text{UCL} = \bar{\bar{x}} + A_2 * \bar{R} = 7.68 + 1.023 * 0.65 = 8.35$$

$$\text{Center line} = \bar{\bar{x}} = 7.68$$

$$\text{LCL} = \bar{\bar{x}} - A_2 * \bar{R} = 7.68 - 1.023 * 0.65 = 7.02$$

where the values of A_2 are tabulated for various subgroup sizes in Montgomery (1991, Appendix VI). For a subgroup size = 3 (i.e., 3 months in a quarter), A_2 is equal to 1.023.

Similarly, the 3-σ control limits, and the center line for the range chart are (see Figure 2-8b):

$$\text{UCL} = D_4 * \bar{R} = 2.575 * 0.65 = 1.67$$

$$\text{Center line} = \bar{R} = 0.65$$

$$\text{LCL} = D_3 * \bar{R} = 0 * 0.65 = 0$$

Where the values of D_3 and D_4 are tabulated for various subgroup sizes in Montgomery (1991, Appendix VI) and D_4 = 2.575 and D_3 = 0 for a subgroup of 3.

New monthly data should be adjusted for seasonal variations as available (In the case of pH values from 1-H4-6, the seasonal adjustment is not necessary). As new data become available, compute the average pH and pH range for the new quarter and plot them on the x-bar chart and range chart, respectively. Any point falling outside the control limits serves as a signal for further investigation. That is, a request for analytical data evaluation must be initiated. Finally, a format for reporting the statistical evaluation results is presented in Table 3-1.

3.2 CASE STUDY 2 - GROUT TREATMENT FACILITY

Facility Background--The Grout Treatment Facility (GTF) is a treatment and disposal facility regulated under RCRA. The GTF is located east of the 200-East Area in the central portion of the Hanford Site (see Figure 1-1). This facility is currently in a RCRA interim-status detection-level monitoring program.

Statistical Evaluation for Interim-Status Detection-Level Facility--Background concentrations for the contamination indicator parameters were established using data collected August 1988 to February 1989 from two

Table 3-1. Results of Statistical Evaluation for 183-H Facility.

Well	Constituent	Seasonal effects? (Y/N)	M-K test statistic[a]	Critical value[b] (α= 1%)	Trend[c]	Sen's slope estimate	Normal[d] (Y/N)	Control chart?
1-H4-3	Nitrate	Y	-3.55	2.326 (one-sided)	–	-17,000 ppb/month	Y D_{max} = 0.102 (n.s)	N.A.
1-H4-6	pH	N	-1.17	2.576 (two-sided)	0	N.A.	Y D_{max} = 0.140 (n.s.)	$\bar{x}$ chart: UCL = 8.35 Center = 7.68 LCL = 7.02 R chart: UCL = 1.87 Center = 0.65 LCL = 0

[a]Mann-Kendall test statistic for trend.
[b]Critical value is from a standard normal table.
[c]A '+' sign denoting an increasing trend, '-' a decreasing trend, and '0' for no trend.
[d]Based on Lilliefors test for normality at α = 0.05 level of significance.
Y = Yes
N = No
N.A. = Not Applicable
n.s. = not significant.

upgradient wells, 299-E-25-25 and 299-E25-32P. Critical means derived from the averaged-replicate t-test were calculated using these background values (EPA 1986). The critical mean (or range, in the case of pH) is the value to which current and future averages of quadruplicate measurements are compared. If the average from a downgradient well for a parameter exceeds its critical mean/range, that parameter is considered statistically significant over background. If results exceeding the critical mean are confirmed by subsequent verification sampling and analysis, the regulatory program is shifted into an assessment-monitoring program.

Note that in calculating the GTF critical means for total organic carbon and total organic halogen, essentially all of the background values were below the contractually required detection limits; therefore a limit of quantification (LOQ) also was calculated from the laboratory blanks data. Following guidance in the TEGD (EPA 1986, p. 123), for cases where the calculated critical mean is below the LOQ, the LOQ is used as the comparison value between upgradient and downgradient wells. This approach makes use of laboratory quality control data to target the limits of quantifiable data and provides a realistic comparison between upgradient and downgradient wells. Results are reported in the RCRA annual report (DOE-RL 1991). In following sections, GTF pH values were used to illustrate the statistical evaluation methods for a final-status groundwater monitoring program (see Figure 3-2).

Multiple Box-and-Whisker Plot--Spatial variation of pH data is shown by a multiple box-and-whisker plot (see Figure 2-6). The data were collected during August 1988 to June 1991 except for downgradient wells 2-E25-37 and 2-E25-38. These two wells were installed and added to the GTF monitoring network in 1990. There is no apparent shift in the pH concentration, but the assumption of equal variance appears to be violated due to two extremely small pH values in upgradient well 2-E25-32P. There is no evidence that these two values are erroneous; subsequent analysis will be performed twice (i.e., with and without these two values).

Background/Compliance Well Comparisons: Tests for Central Tendency--Assumptions of a parametric ANOVA were checked first. Results of Lilliefors test for normality of data, with and without the outliers, indicate that the pH data can be reasonably approximated by a normal distribution. The assumption of equal variance was rejected by Bartlett's test at $\alpha = 0.05$ when the outliers were included in the data set (p value is 0.006). Hence, Kruskal-Wallis nonparametric ANOVA was used to test whether all wells around the GTF have the same median concentrations of pH. The test statistic is 12.03 with a p value of 0.06. Therefore, the hypothesis of equal medians was not rejected at $\alpha = 0.05$.

Bartlett's test does not reject the assumption of equal variance when the two extremely small values are deleted in the data set (p value is 0.36). Therefore, a parametric ANOVA was used to test for the central tendency. The F-statistic is 2.056 with 6 and 58 degrees of freedom. The hypothesis of equality of means was not rejected at $\alpha = 0.05$ (p value is 0.07). This demonstrates that although the statistical test method chosen varies, the conclusion reached is the same. That is, the facility is not impacting the quality of groundwater.

Background/Compliance Well Comparisons: Excursion Analysis--Sometimes it is desirable to determine a reasonable upper limit (for pH both the upper and lower limits) as a threshold value based on existing data on background wells. This leads to the concept of a tolerance interval. Statistical tolerance intervals are used to estimate these threshold values because they contain a specified proportion, P% (coverage), of the entire sampled population with a specified degree of confidence, $100(1 - \alpha)\%$.

Tolerance interval techniques are sensitive to the assumption that the data are drawn from a normal distribution. If normal distribution is a reasonable approximation of the background concentrations, a parametric tolerance interval can be constructed. Otherwise, a nonparametric tolerance interval is constructed. Two-sided nonparametric tolerance limits are simply the largest and smallest datum of the observed data. Using all pH data from two upgradient wells 2-E25-25 and 2-E25-32P results in a parametric tolerance interval of [7.0, 9.3]. Using the reduced data set, after removal of outliers, results in a narrower tolerance interval, [7.6, 9.0]. None of the individual pH datum from downgradient wells was outside of the tolerance limits. This is interpreted as no evidence of contamination.

Similarly, nonparametric tolerance intervals are [7.0, 8.7] and [7.8, 8.7] for all the data and the reduced data set, respectively. The same conclusion of no evidence of contamination was reached using nonparametric tolerance interval analysis.

Comparisons with Compliance Limit: Excursion Analysis--When the monitoring objective is to determine whether the groundwater protection standard is being exceeded, confidence intervals on the means (for normal distribution) or on the medians (for non-normal distribution) are calculated and compare these intervals with the fixed standard. This type of comparison is appropriate for a RCRA-regulated unit that is in compliance monitoring with a fixed compliance limit. The unit will be in compliance monitoring unless there is statistically significant evidence that the mean (or median) concentration at one or more of the downgradient wells exceed the compliance limit. The following example is for illustration purpose only.

The drinking water standard for pH, based on Secondary Maximum Contaminant Levels, is (6.5, 8.5) (EPA 1990). Using pH data for downgradient wells, two-sided 99% confidence intervals were constructed and compared with the compliance limits. All the calculated confidence intervals are within the compliance limits, the unit remains in compliance. The use of $\alpha = 0.01$ (two-sided) is consistent with the performance standards required of a statistical test [40 CFR Part 264.97(i)].

4.0 CONCLUSIONS AND RECOMMENDATIONS

The RCRA groundwater monitoring program has collected abundant data on groundwater quality. These data are used to assess the impact of a facility on groundwater quality. Statistical techniques discussed in this report (goodness-of-fit test, seasonal adjustment, trend analysis, autocorrelation, control chart, etc.) are also applicable in cases where the effectiveness of the remediation efforts under RCRA corrective action programs needs to be determined. The DAP presented in this report was developed from the perspective of addressing regulatory requirements, data quality, and management information needs. In order to design an effective and efficient groundwater monitoring program that reduces the risks of the Type I and Type II error rates, the following are recommended.

- It is essential that a QAPP is in place before monitoring activity begins. The QAPP identifies and establishes data quality goals for the monitoring program.

- It is essential that sampling and analysis procedures are in place. Data should be collected using consistent collection and measurement techniques. Data should be analyzed in a consistent and technically sound manner. Statistical test results, if known to impact the monitoring status (e.g., from detection to compliance level), must be based on quantifiable data (i.e., measured value $\geq$ LOQ).

- Proper characterization of background concentration levels is critical. The decision on whether a facility is impacting groundwater quality is made by comparing concentrations of downgradient wells with that of background (upgradient) wells. Upgradient wells should be of sufficient number to account for heterogeneity in background groundwater quality.

- In determining whether the remediation effort under RCRA corrective action programs has been successful (e.g., the attainment of background-based cleanup standards), background for a particular constituent of concern should be considered as a statistical distribution of concentration levels. To treat these background-based standards as constants (known without error) may result in excessive or unnecessary remediation (Gilbert and Simpson 1990).

- A 2-yr baseline monitoring period is needed to determine the spatial and temporal variability so that these can be accounted for in the statistical evaluations for trends.

- The number of indicator parameters should be limited to a small set of manifest variables that indicate potential contamination. Inclusion of all potential contaminants in a final-status detection level monitoring program is ineffective (i.e., very poor power) and costly.

- The groundwater monitoring program and the choice of statistical method must be site specific. That is the number and locations of monitoring wells and the chosen statistical method(s) must be adequate so that the likelihood of detecting leakage from the facility is high.

- An integrated approach involving data interpretation, database management, quality assurance/quality control, statistical analysis, and environmental management is needed.

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