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Groundwater Monitoring Plan for the Hanford Site 216-B-3 Pond RCRA Facility

D. B. Barnett
C. J. Chou

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Summary

The 216-B-3 pond system was a series of ponds for disposal of liquid effluent from past Hanford production facilities. In operation since 1945, the B Pond System has been a RCRA facility since 1986, with Resource Conservation and Recovery Act (RCRA) interim-status groundwater monitoring in place since 1988. In 1994, discharges were diverted from the main pond, where the greatest potential for contamination was thought to reside, to the 3C expansion pond. In 1997, all discharges to the pond system were discontinued.

In 1990, the B Pond System was elevated from "detection" groundwater monitoring to an assessment-level status because total organic halogens and total organic carbon were found to exceed critical means in two wells. Subsequent groundwater quality assessment failed to find any specific hazardous waste contaminant that could have accounted for the exceedences, which were largely isolated in occurrence. Thus, it was recommended that the facility be returned to detection-level monitoring.

Exhaustive groundwater analyses during the assessment period indicated that only two contaminants, tritium and nitrate, could be positively attributed to the B Pond System, with two others (arsenic and I-129) of problematic origin. Chemical analyses of shallow soil at the main pond also failed to uncover significant contamination, although records of unplanned releases and waste inventories suggest that contamination could potentially exist at greater depths in the vadose zone.

Based on the observed, minor contamination in groundwater, and the potential for contamination in the soil column, 3 parameters were selected for site-specific, semiannual monitoring: gross alpha, gross beta, and specific conductance. Nitrate, tritium, arsenic, and I-129 will be monitored under the aegis of the sitewide monitoring program. Although the B Pond System will not advance from RCRA interim status to final status until the year 2000, groundwater monitoring for this facility will emulate final status requirements before the official transition. This modification will allow a more sensible and effective screening of groundwater for the facility.

Several statistical testing strategies were evaluated using U.S. Environmental Protection Agency-recommended criteria. Specifically, EPA recommends that the facility-wide false positive rate be kept to ~5% and that adequate statistical power is maintained. Based on comparisons with EPA reference power curves, decision values for the combined Shewhart-CUSUM control chart approach are proposed for the B Pond System for gross alpha and gross beta. Because specific conductance is artificially low in groundwater beneath the facility, this parameter will also be compared with the sitewide background value. This approach will result in a more cost-effective monitoring system without sacrificing detection sensitivity.

Acronyms and Abbreviations

ANOVA	analysis of variance
ASTM	American Society of Testing and Materials
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFEST	Coupled Fluid, Energy and Solute Transport
CRQL	Contractually Required Quantitation Limit
CUSUM	cumulative sum
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy-Richland Operations Office
DQO	Data Quality Objectives
DWS	drinking water standard
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
FY	Fiscal Year
GeoDAT	Geosciences Data Analysis Toolkit
HEIS	Hanford Environmental Information System
MCL	maximum contaminant level
MDA	minimum detectable activity
MTCA	Model Toxics Control Act
NTU	nephlometric turbidity units
PNNL	Pacific Northwest National Laboratory
POC	point of compliance
RCRA	Resource Conservation and Recovery Act
SCL	Shewhart Control Limit
SOW	Statement of Work
TEDF	Treated Effluent Disposal Facility
TOC	total organic carbon
TOX	total organic halogens
TPA	Tri-Party Agreement
TSD	treatment, storage, or disposal
UPR	Unplanned Release of Waste
WHC	Westinghouse Hanford Company

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The authors thank R. O. Gilbert and his colleagues R. F. O'Brien and G. Chen, of the Pacific Northwest National Laboratory Statistics Group for their critical review and indispensable assistance in the application of the Data Quality Objectives process to a complex environmental problem. The document is a far better product because of their efforts. Special thanks are due R. O'Brien for preparing the power curves for evaluating the proposed testing strategy and to V. G. Johnson for his valuable consultation. We also thank P. E. Dresel, M. J. Hartman, and S. P. Luttrell for their critical reviews of the document and many helpful suggestions.

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1.0 Introduction

The 216-B-3 pond system (B Pond System) is a regulated wastewater disposal facility for operations in the 200 East Area of the Hanford Site (Figure 1.1). The B Pond System has been a Resource Conservation and Recovery Act (RCRA) hazardous waste facility since 1986, when a RCRA (Part A) permit application was submitted to the Washington State Department of Ecology (Ecology). Groundwater monitoring has been conducted in accordance with RCRA interim-status requirements since 1988. In 1997, results of RCRA assessment monitoring concluded that groundwater monitoring at this facility should be returned to detection-level monitoring. This document summarizes past and current groundwater monitoring at the B Pond System and describes a new groundwater monitoring plan based on the application of the Data Quality Objectives (DQO [EPA 1994]) process to a conceptual model, and the most recent evaluations of groundwater hydrology and chemistry at the site.

1.1 Objectives and Scope

During fiscal year (FY) 1997, the integrated Hanford Site groundwater monitoring project initiated the DQO planning process to integrate groundwater monitoring projects for the Hanford Site. The DQO process is being used to determine what data are collected, how data will be used to make decisions, and the quantity of data needed to meet criteria specified by the stakeholders. The process thus leads to a groundwater monitoring strategy that will allow the application of technically improved sampling and analysis and statistical evaluation procedures.

The proposed groundwater monitoring plan, developed through the DQO process, departs from requirements as specified in the interim-status regulations (40 CFR 265 and WAC 173-303-400) and emulates final status regulations (40 CFR 264 and WAC 173-303-645) and agreements. This approach provides for a more rational and practical application of groundwater monitoring at the B Pond System rather than simply defaulting to regulatory minimum requirements. Although the federal regulations typically required implementation of a final-status permit by November 1988, the *Hanford Federal Facility Agreement and Consent Order* (Ecology et al. 1994, hereinafter referred to as Tri-Party Agreement or TPA) extended the time period for compliance with final-status provisions to the year 2000 for the B Pond System. It should be noted that the progression as stipulated in the final-status regulations (i.e., from detection-level to compliance-level and to corrective action, if warranted) will be governed by the schedules established in the TPA. Application of the DQO process is presented in Appendix A. This plan controls detection-level groundwater monitoring for only the B Pond System, although coordination with other Hanford Site monitoring networks/programs is described.

1.2 Facility Description and History of Operation

The B Pond System is located east of the 200 East Area and consisted of a main pond and three expansion ponds, all constructed for wastewater disposal (Figure 1.2). The B Pond System began receiving effluent in 1945 at the site of the main pond. The main pond (initially termed the "B-3 Pond") was located in a natural topographic depression, diked on the eastern margin, covered approximately 14.2 ha,

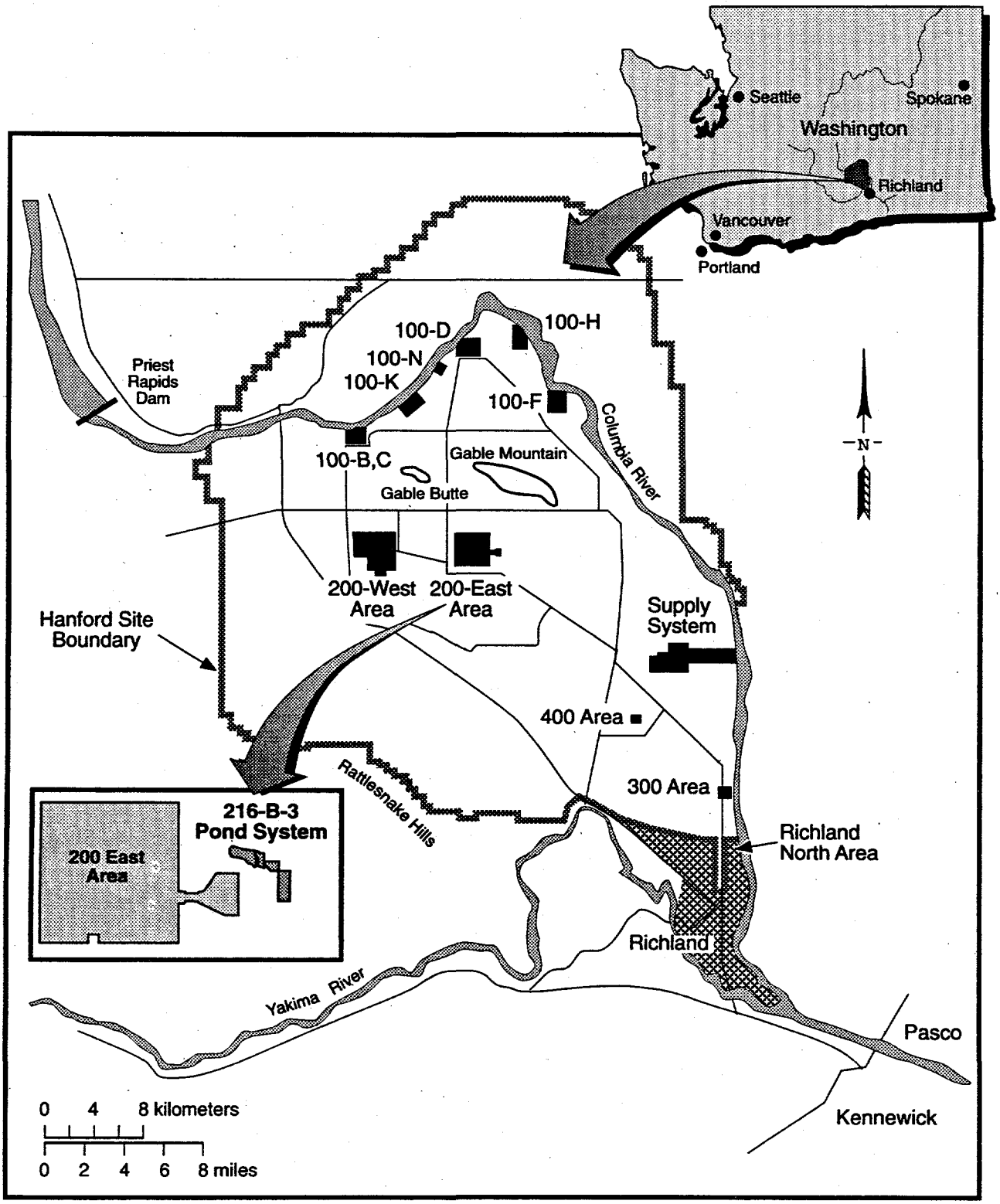

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Figure 1.1. Location of the 216-B-3 Pond System

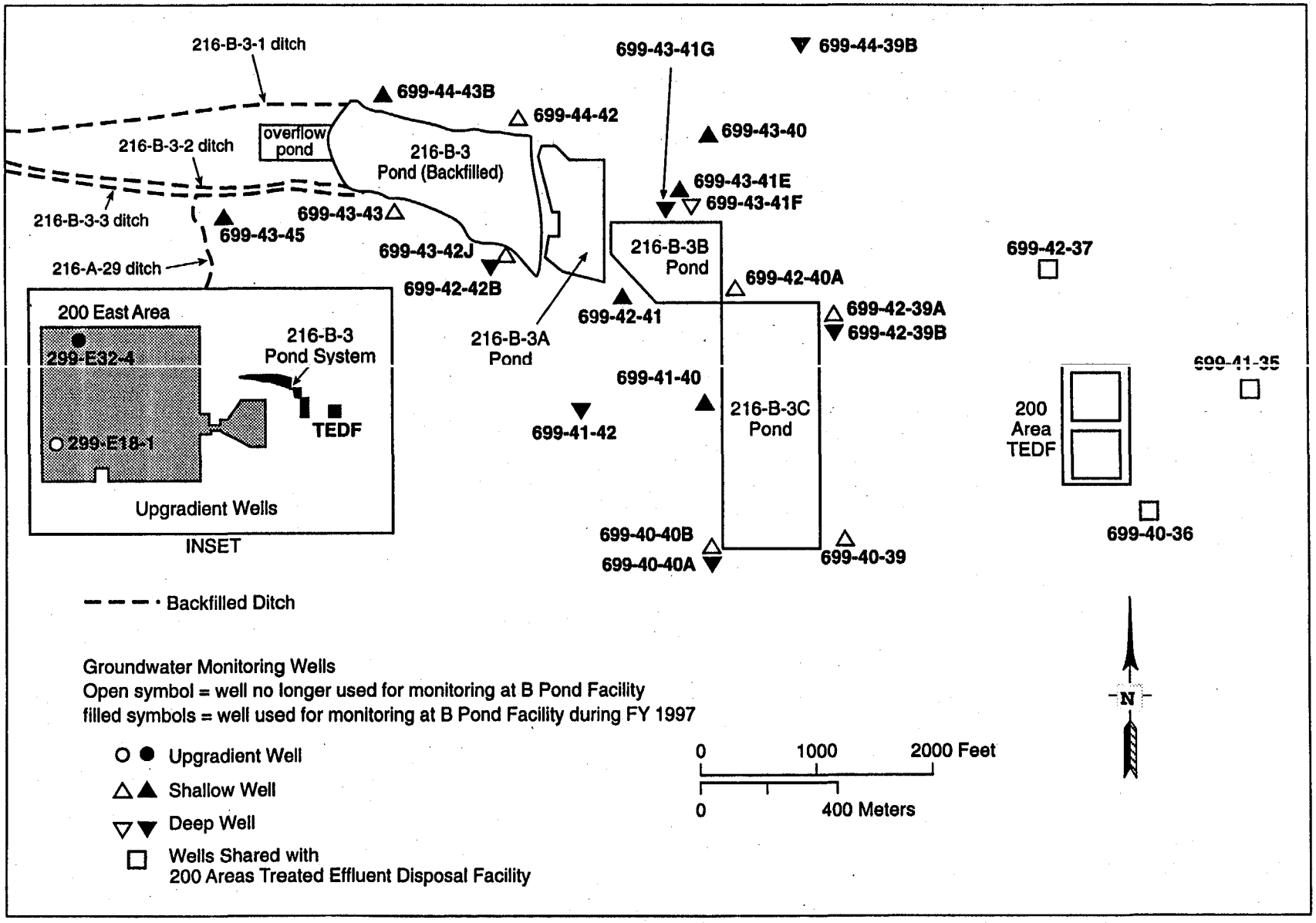

Figure 1.2. Components of the B Pond System and Monitoring Well Network

and had a maximum depth of about 6.1 m. Three expansion ponds (216-B-3A [3A], 216-B-3B [3B], and 216-B-3C [3C] expansion ponds) were placed into service in 1983, 1984, and 1985, respectively. The 3A and 3B expansion ponds are about 4.5 ha in size, and the 3C expansion pond is approximately 16.6 ha. Water discharged to these ponds, primarily the main and 3A ponds, infiltrated into the ground and artificially recharged the underlying aquifer. The main and 3A ponds were connected by an open spillway. The 216-B-3-1, B-3-2, B-3-3, and A-29 ditches were used to convey effluent from the producing facilities in the 200 East Area to the main pond. Details of the operation of these ponds and ditches are presented in DOE-RL (1993b).

Beginning in April 1994, discharges to the main pond/3A pond ceased, and all effluents were rerouted to the 3C expansion pond via a pipeline. Also during 1994, the main pond and 216-B-3-3 ditch were filled with clean soil, and all vegetation was removed from the perimeter as part of interim stabilization activities. Concurrently, the 3A, 3B, and 3C expansion ponds were clean closed under RCRA.

In June 1995, portions of the effluent stream were rerouted to the 200 Area Treated Effluent Disposal Facility ([TEDF]; formerly known as "Project W-049H"). The remaining streams were diverted from the 3C Expansion Pond to the TEDF in August 1997, thus ending all operation of the B Pond System. Historic effluent feeds are described in greater detail by DOE-RL (1993b) and Johnson et al. (1995), and are discussed in terms of potential environmental contamination in Section 3.0. Figure 1.3 illustrates the sequence of important events surrounding operation of the B Pond System.

In the past, the B Plant steam condensate and chemical sewer were discharged to the B Pond System (primarily the main pond). Potential contaminants contained within past waste streams, which may have entered the groundwater, are discussed in DOE-RL (1993b) and are summarized in Section 3.0. The last chemical waste discharge to the B Pond System (main pond) occurred in 1987. Tritium has been discharged to the facility throughout its operational life, though recent quantities have been extremely small.

Discharge volumes to the B Pond System were at a maximum during 1988 (Figure 1.4). Total discharge to the facility since 1945 is estimated to have exceeded 1.0 E+12 liters. For the first 8 months of 1997, until operation ceased, the 3C pond received 487,000,000 liters of effluent. Discharge volumes to the 3C pond are important because of this pond's proximity to potential subsurface contamination beneath the main pond (see Sections 3.0 and 5.0).

1.3 Regulatory Status and History

During 1993, the original RCRA Part A permit application (DOE-RL 1990) was modified to distinguish the three expansion ponds (3A, 3B, and 3C) from the main pond and a segment of the 216-B-3-3 ditch (DOE-RL 1993b). This change allowed clean closure of the expansion ponds to meet the *Hanford Federal Facility Agreement and Consent Order*, Milestone M-17-10 (Ecology et al. 1994). The expansion ponds were also included in a RCRA facility investigation/corrective measures study for the 200-BP-11 operable unit (DOE-RL 1994). The portion of the B-3-3 ditch west of its junction with the 216-A-29 ditch, and the B-3-1 and B-3-2 ditches are RCRA past-practice facilities and are not included in the B Pond System treatment, storage, or disposal (TSD) unit.

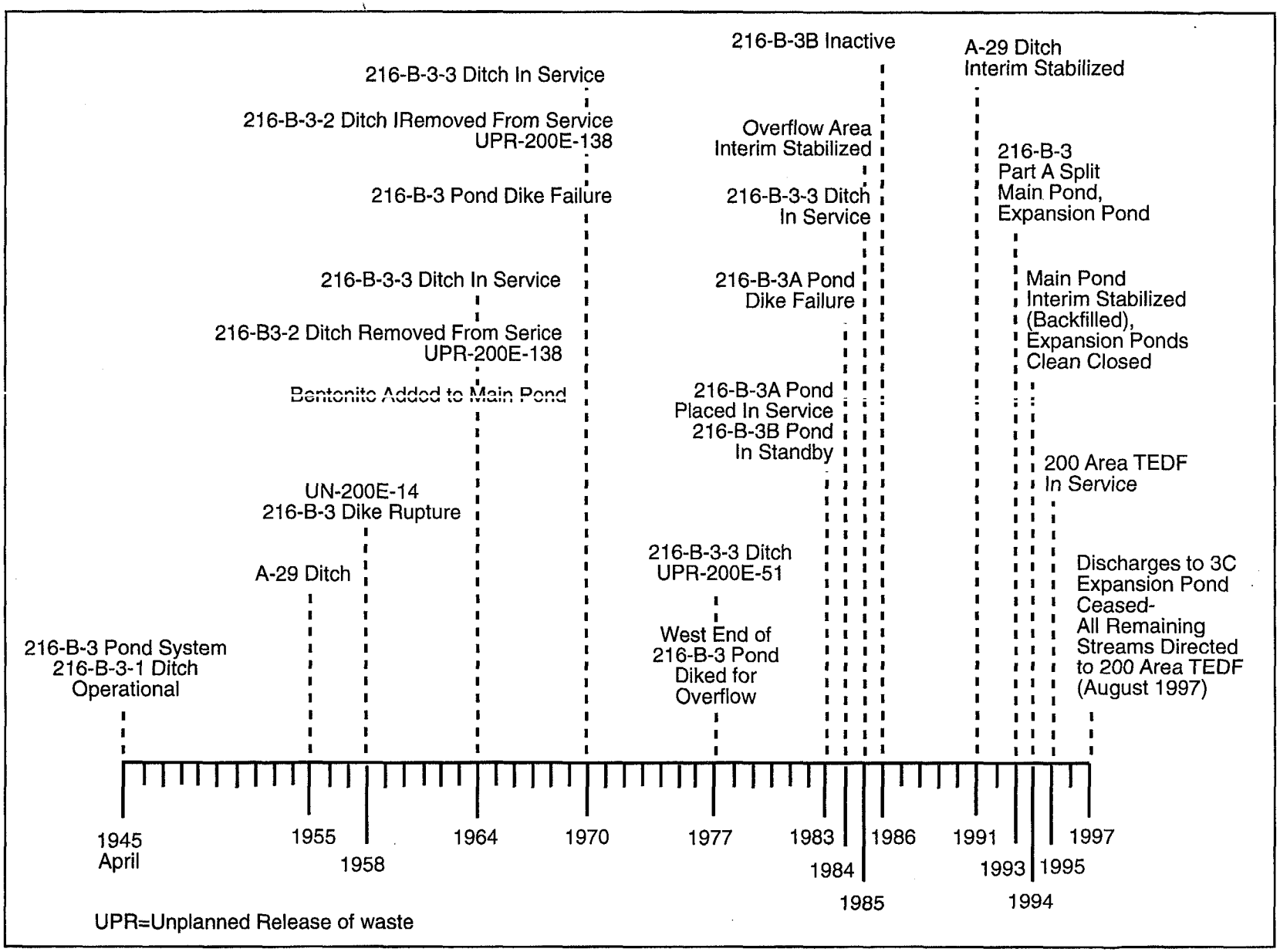

Figure 1.3. Timeline of Significant Events of the B Pond System Operation

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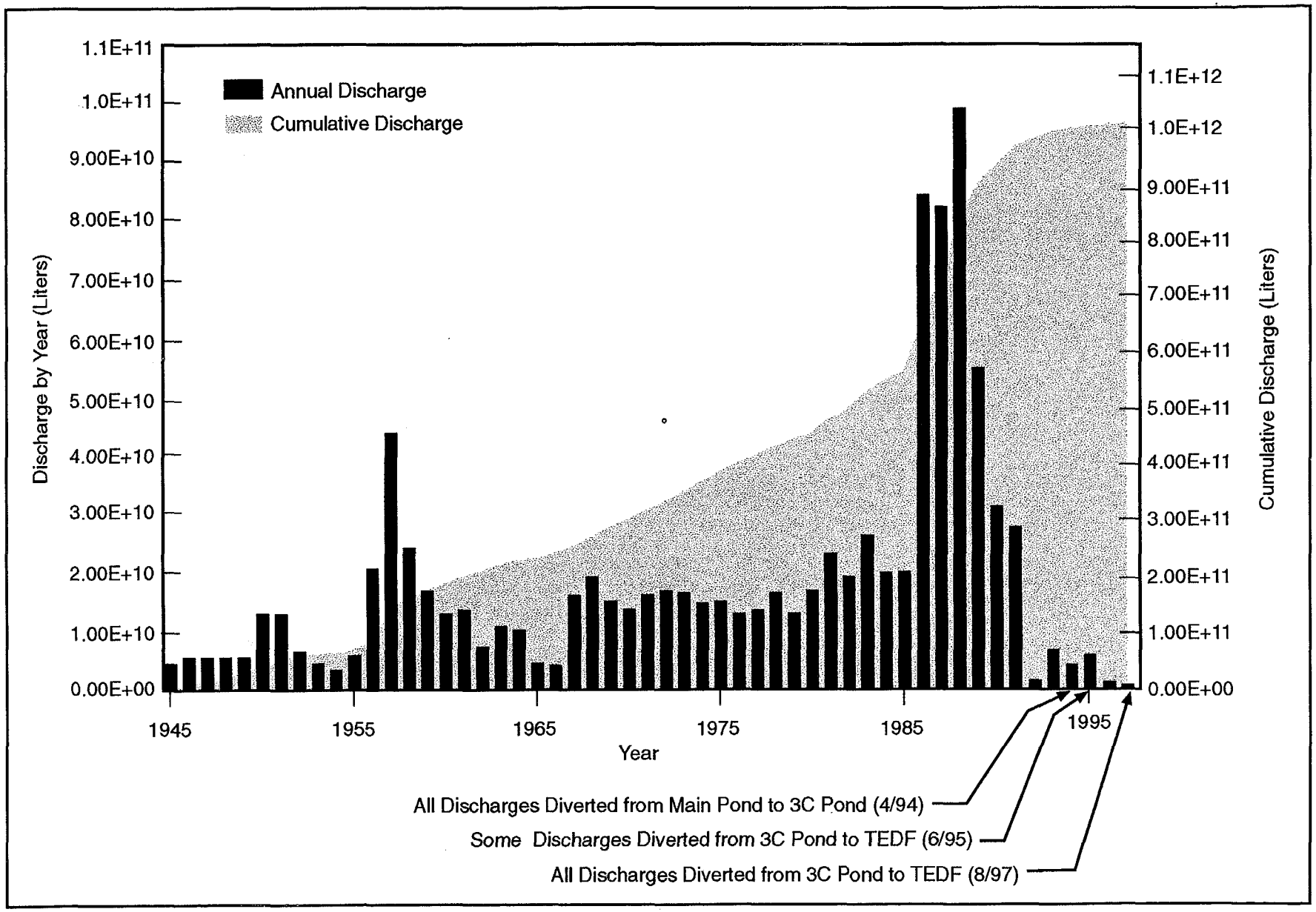

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Figure 1.4. Discharge History and Recent Changes in Disposal Sites at the B Pond System

Activities conducted as part of the closure process for the expansion ponds included soil and sediment sampling, interim stabilization of the main pond and B-3-3 ditch, and decontamination and removal of structures and associated fixed equipment (DOE-RL 1993b). The soil and sediment sampling activities in support of closure was conducted in three phases from 1989 through 1992. The results of all three phases showed little evidence of contamination (DOE-RL 1994). Results of soil sampling and analyses are summarized in Section 3.2.

The *Ground Water Impact Assessment Report for the 216-B-3 Pond System* (Johnson et al. 1995) was released as a requirement of the *Hanford Federal Facility Agreement and Consent Order* (Ecology, U.S. Environmental Protection Agency [EPA], and DOE 1994) Milestones M-17-00A and M-17-00B. This report addressed the impact of continued discharge of uncontaminated water to the 216-B-3C expansion pond of the B Pond System until 1997, and concluded the following:

- Based on groundwater modeling, little change was predicted in the existing flow regime beneath the pond and in the vicinity of the 200 East Area until June 1997 (see Section 2.2.2).
- Remobilization of potential contamination beneath the main pond to groundwater, due to 3C pond operation, is unlikely.
- Effects on existing groundwater contamination plumes from effluent discharge until 1997 would be negligible.

Thus far, these predictions appear to have proven correct.

The B Pond System also falls within the 200-BP-11 source operable unit and the BP-5 and P0-1 groundwater operable units, which are regulated under the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) program (DOE-RL 1994).

1.4 History of RCRA Groundwater Monitoring at the B Pond System

RCRA groundwater monitoring of the B Pond System began in 1988 with an interim-status indicator-parameter-evaluation (detection-level) program. The initial program was described by Luttrell (1989). Groundwater monitoring was elevated from a RCRA detection-level program to an assessment program in 1990 because of elevated total organic halogens (TOX) and total organic carbon (TOC) levels in two downgradient wells. A groundwater quality assessment plan (Harris 1990) was submitted to Ecology in May 1990. The results of groundwater quality assessment, which concluded in 1996, are reported by Barnett and Teel (1997), and are summarized in Section 4.0. The most recent groundwater monitoring plan is found in Sweeney (1995).

A list of the wells in the current and former B Pond System RCRA groundwater monitoring networks and their dates of construction is shown in Table 1.1. Downgradient wells were installed from 1988 through 1992. The locations of these wells are shown in Figure 1.2. Shallow wells indicated in Table 1.1 are those that are screened near or across the water table. Wells designated "deep" or "intermediate" were

Table 1.1. Groundwater Monitoring Wells Used at the 216-B-3 Pond System. Wells inactive since 1995 are indicated in Bold.

Well	Date of Construction	Comments
299-18-1	1988	**Upgradient** monitoring well; dropped in 1996
299-E32-4	1987	**Upgradient** monitoring well
699-40-36	1992	TEDF monitoring well[a]
699-40-39	1989	Shallow well; dropped from monitoring network in 1995
699-40-40A	1991	Deep[b] companion to well 699-40-40B
699-40-40B	1991	Shallow companion to well 699-40-40A; dropped from monitoring network in 1995
699-41-35	1992	TEDF monitoring well[a]
699-41-40	1989	Shallow
699-41-42	1992	Deep
699-42-37	1992	TEDF monitoring well[a]
699-42-39A	1991	Shallow companion to well 699-42-39B; dropped from monitoring network in 1995
699-42-39B	1991	Deep companion to well 699-42-39A
699-42-40A	1981	Shallow; dropped from monitoring network in 1995
699-42-41	1991	Shallow
699-42-42B	1988	Deep companion to well 699-43-42J
699-43-40	1991	Shallow
699-43-41E	1989	Shallow companion to wells 699-43-41F, -41G
699-43-41F	1989	Intermediate-depth companion to wells 699-43-41E, -41G; dropped from monitoring network in 1995
699-43-41G	1991	Deep companion to wells 699-43-41E, -41F
699-43-42J	1988	Shallow companion with well 699-42-42B; dropped from monitoring network in 1995
699-43-43	1988	Shallow; dropped from monitoring network in 1995
699-43-45	1989	Shallow
699-44-39B	1992	Deep
699-44-42	1988	Shallow; dropped from network in 1995
699-44-43B	1989	Shallow

(a) Included in B Pond System monitoring network as a coordinated effort with TEDF until 1995.

(b) The terms "Deep" "Intermediate" and "Shallow" indicate relative position within the aquifer of the screened portions of wells (see Section 1.3).

TEDF = 200 Area Treated Effluent Disposal Facility.

Upgradient wells designated in italic.

screened several meters below the water table, deeper in the aquifer. Ten of the network wells are constructed with screens at the water table. The remaining 15 wells are screened at deeper levels in the aquifer. Four well clusters, involving nine wells, are situated to provide information on vertical components of hydraulic gradient in the aquifer and potential contaminant distribution.

Both upgradient wells were selected so as to be as near the B Pond System as possible, yet outside the hydrologic influence of the facility (see Section 2.2). The maximum number of wells (25) was monitored from 1993 until late 1995. The number of wells in the network was reduced to 13 in 1995 to eliminate redundancy and focus resources on additional hydrochemical analyses in the remaining wells. Three of the wells no longer in the B pond network are part of the TEDF groundwater monitoring network. These three wells were monitored for informational purposes only and were not part of the RCRA-regulated B Pond System network. In 1996, one of two upgradient wells (299-E18-1) was dropped from the network. This well was part of the 2101-M pond facility, which was clean closed. The upgradient well, 299-E32-4, was shared with the still-active Low-Level Burial Grounds facility in the 200 East Area (Figure 1.2).

2.0 Hydrogeologic Summary

Stratigraphy and groundwater hydrology of the B Pond System have been described in several previous studies. The brief description given in this section is a summary of information derived from these earlier reports. The most detailed description of stratigraphic relationships at the B pond facility is presented in DOE-RL (1993b) and DOE-RL (1994). A description of groundwater hydrology and groundwater contamination in the region of the Hanford Site surrounding the B Pond System was presented most recently by Hartman and Dresel (1998). The focus of this summary is the Hanford and Ringold Formations, because these strata comprise the uppermost aquifer and vadose zone in the area of the B Pond System.

2.1 Stratigraphy

The principal geologic units beneath the B Pond System include the Columbia River Basalt Group, the Ringold Formation, and the Hanford formation. A representative stratigraphic column of the B Pond System is shown in Figure 2.1. The uppermost aquifer beneath the B Pond System occurs primarily within sediments of the Ringold Formation, with the Hanford formation comprising the vadose zone. The Columbia River Basalt Group acts as the regional lower boundary for the uppermost unconfined aquifer. Davis et al. (1993) and DOE-RL (1994) provide a general description of the Columbia River Basalt Group in the vicinity of the B Pond System, and reference other reports that discuss this unit in more detail.

Ringold Formation fluviolacustrine sediments consist of (in ascending stratigraphic order): 1) unit A gravel and 2) lower mud sequence. The Ringold unit A gravel ranges in thickness from ~12 m in the area northwest of the main pond to ~30 m in the southern portion. This unit is mainly composed of a silty sandy gravel with secondary lenses and interbeds of gravely sand, sand, and muddy sands to clay/silt (DOE-RL 1994). The Ringold lower mud sequence is not present in the northwestern portion of the B Pond System but is ~24 m thick near the southern extreme of the 3C expansion pond. The lower mud unit consists mostly of various mixtures of silt and clay (DOE-RL 1994). This unit is particularly important to effluent infiltration and groundwater flow patterns near the B Pond System (see Section 2.2).

The Hanford formation ranges in thickness from 40 m beneath the 3C expansion pond to ~50 m at the northwestern corner of the main pond (Davis et al. 1993). The Hanford formation is represented by three facies, in ascending stratigraphic order: 1) lower gravel sequence, 2) sandy sequence, and 3) upper gravel sequence (subdivisions after Lindsey et al. 1992). The upper and lower gravel sequences are not differentiated in those areas where the intervening sandy sequence is absent. The gravel units consist of coarse-grained, basalt-rich, sandy gravels with varying amounts of silt/clay. These gravel units may also contain interbedded sand and or silt/clay lenses, and are notably rich in clay near the western portion of the main pond, as indicated in well logs from this area. The sandy sequence is dominated by sand to gravelly sand with minor sandy gravel or silt/clay interbeds. The sandy sequence is present mainly in the vicinity of the main pond.

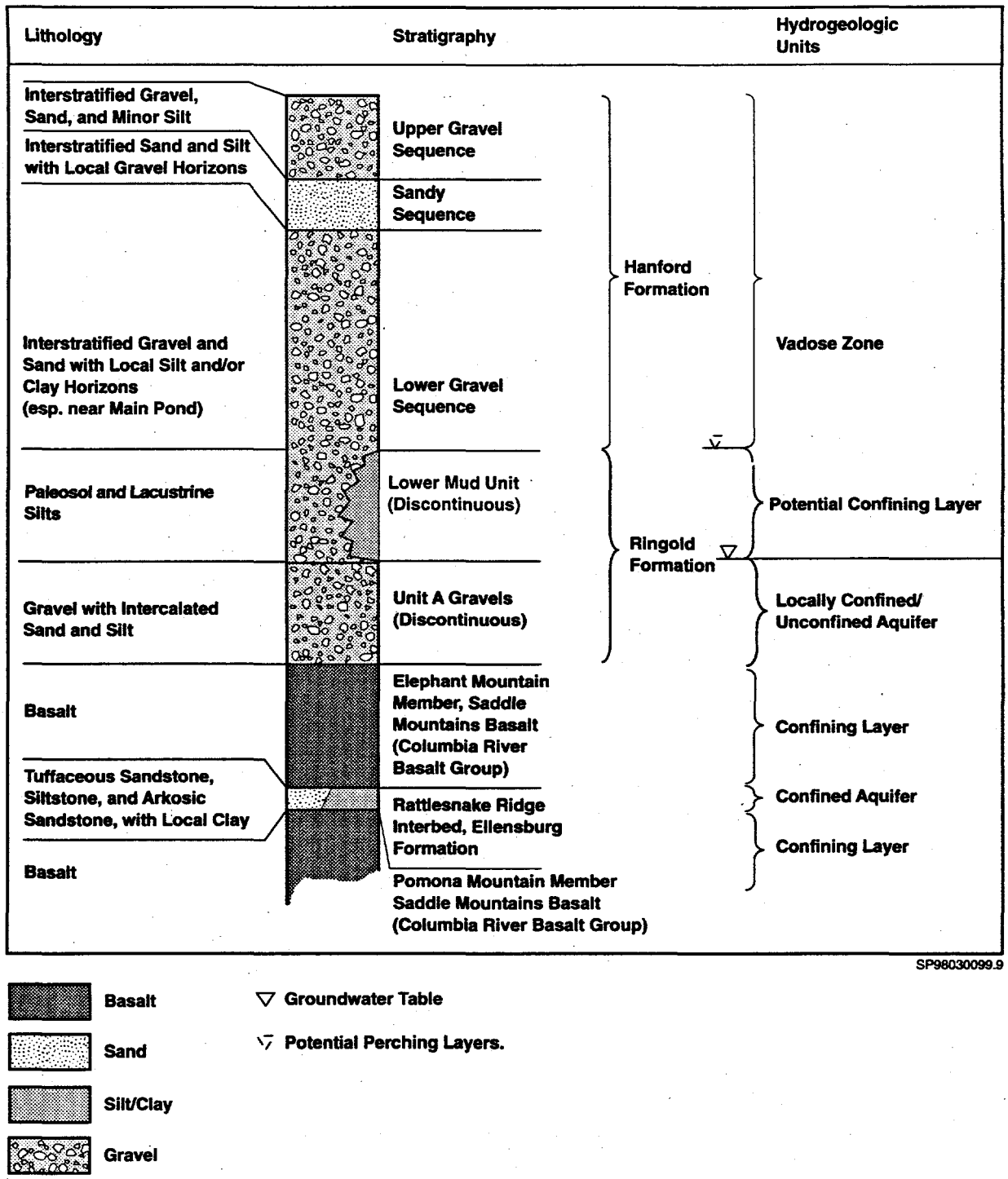


Figure 2.1. Generalized Stratigraphic Column for B Pond System

2.2 Groundwater Hydrology

Measurements of the thickness of the uppermost aquifer at the B Pond System range from ~10 m at well 699-44-43B to >30 m at the southern end of the 3C expansion pond. The water table/potentiometric surface occurs near the Hanford-Ringold contact, with the Ringold Formation comprising the bulk of the uppermost aquifer. This aquifer is typically referred to as unconfined. However, hydrogeologic data suggest that portions of the aquifer may be semiconfined to confined (DOE-RL 1993b). These data suggest that the aquifer is unconfined to the west and north of the main pond and becomes progressively more confined beneath the 3C expansion pond, and southeastward of the facility. The change from unconfined to confined is apparently gradational, and no abrupt transition is evident from the hydraulic head values measured in the confined and unconfined portions of the aquifer. A summary of aquifer test results can be found in DOE-RL (1993b).

The Ringold lower mud unit forms both a confining horizon and potential perching layer for groundwater in the B pond area. An interpretation of the distribution and thickness of this stratum is shown in Figure 2.2. The surface of the lower mud unit is also interpreted to dip gently to the south and southwest in the area immediately south of the main pond and 3C pond (Davis et al. 1993). The presence and configuration of this unit is probably responsible for the lack of correlatable hydraulic response in monitoring wells near the 3C pond to large volumes of effluent diverted to this pond in 1994 (see Section 2.3).

2.2.1 Water Table Interpretation

Potentiometric-surface elevations are currently measured in all active wells in the monitoring network at the time of groundwater sampling. Water levels are also measured in select wells in conjunction with sitewide groundwater monitoring. An interpretation of the potentiometric surface in the vicinity of the B Pond System for June 1997 is shown in Figure 2.3.

Groundwater flows radially outward from a hydraulic mound, the apex of which is approximately located in the vicinity of the 3B expansion pond. Based on June 1997 water-level measurements, the horizontal component of hydraulic gradient near B pond varies from ~0.003 east of the mound apex to 0.006 west-southwest of the former location of the main pond. The mound was created by large volumes of wastewater recharging the uppermost unconfined aquifer, and significantly altered the original groundwater-flow pattern of the area. The apex of the hydraulic mound is interpreted to be displaced somewhat to the east of the principal areas of surface impoundment (i.e., main and 3A ponds). Historic and recent interpretations of the water table/potentiometric surface indicates that the position of the center of the hydraulic mound has remained essentially unchanged for several years. This observation might be attributed to translocation or diversion of the infiltration pathways of the effluent, caused by strata of fined-grained sediments in the vadose zone. Alternatively, the location of the mound may reflect the preferential infiltration of water primarily beneath the 3A pond, because of the application of bentonite to the bottom of the main pond in 1964, and/or accumulation of fine sediment in the main pond.

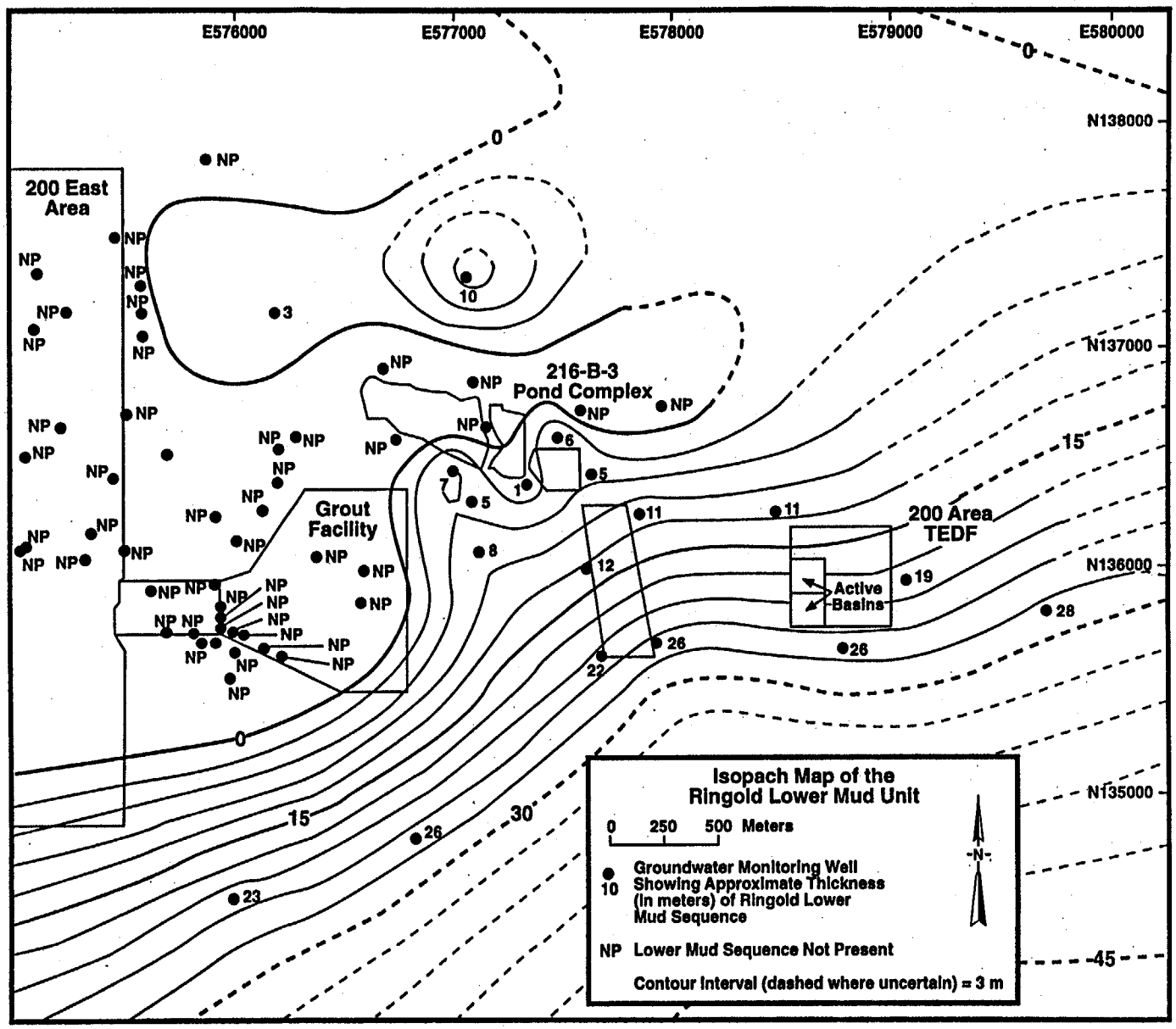


Figure 2.2. Isopach Map of the Ringold Lower Mud Unit

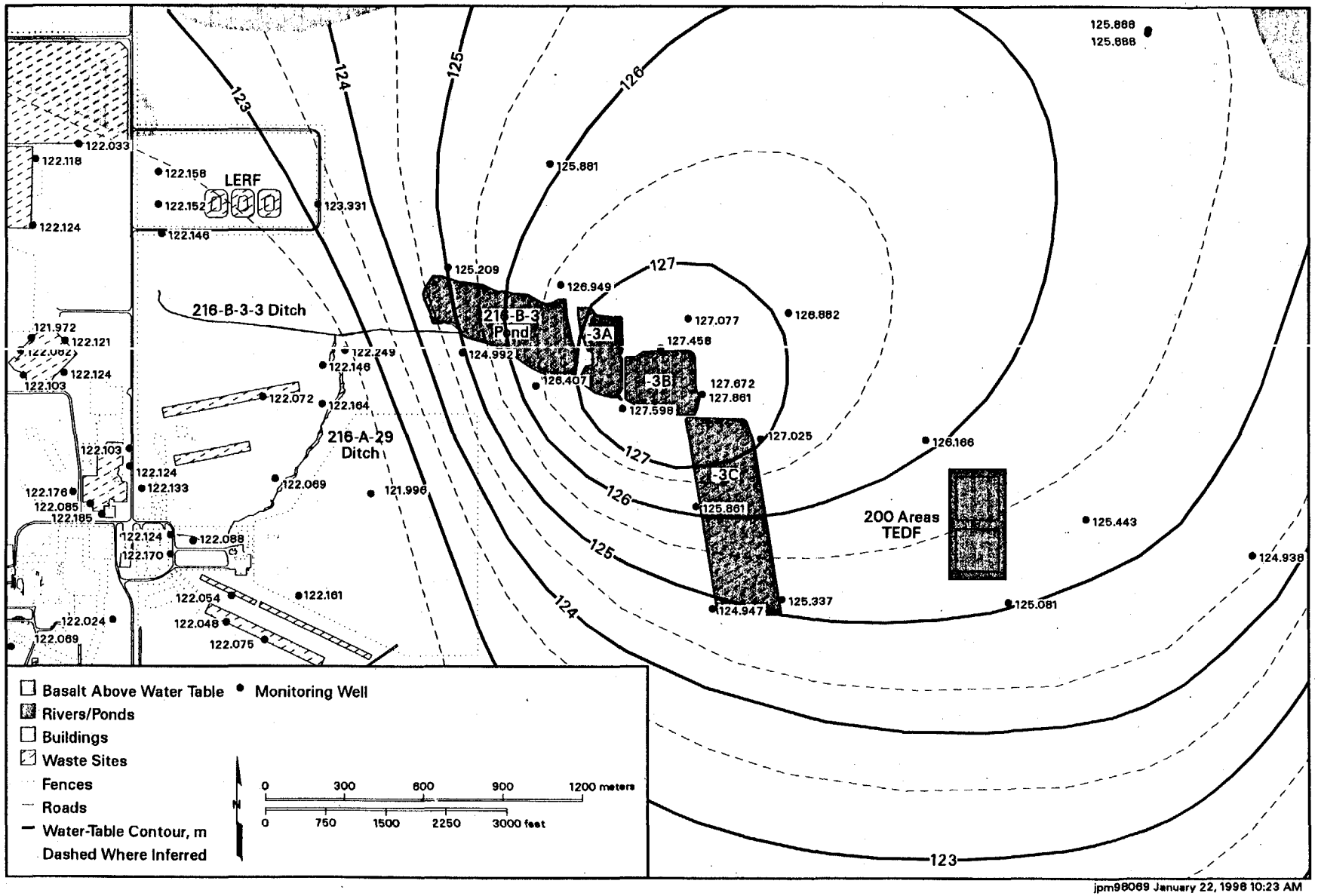


Figure 2.3. Potentiometric Map of the B Pond Area for June 1997

The vertical hydraulic gradient was calculated for four well pairs in the network, representing deep and shallow completions (see Table 1.1). In March 1997, all four pairs indicated a downward hydraulic gradient, ranging from 0.006 at wells 699-42-39A,B well pair to 0.18 at wells 699-43-42J/42-42B. Because the screens in each of these wells are open to several meters of aquifer thickness, potentiometric measurements used for the calculations should be considered gross approximations.

2.2.2 Status of the Groundwater Monitoring Network

Appendix B contains hydrographs for all wells used historically for groundwater monitoring at the B Pond System. Water levels in the 25 wells in the original network have generally declined during the life of the RCRA program. Exceptions to this trend occurred during the early to mid 1990s in some downgradient wells, such as wells 699-40-40A,B, 699-41-42, and wells around the 200 Area TEDF. During the past 1+ years, however, water levels in all wells have resumed a definitively downward trend. In most downgradient wells water levels have dropped dramatically from 1996 to present. Most notably in this category are wells 699-40-40A, 699-42-39A, B, 699-42-40A, 699-42-42B, 699-43-40, 699-43-41E, G, 699-43-43, and 699-44-42.

Table 2.1 summarizes the status of water levels in all wells in the B Pond System network, both active and inactive, and predicts the expected service life (in years) for these wells. The annual rates of decline are calculated using the most recent one year of data available for each well and assumes a linear rate of decline. For most wells, the one-year period ends in June 1997. The years of potential service is calculated by subtracting the depth to water from the well depth, then dividing by the rate of decline. By this method, some wells are estimated to have only a few years of potential service remaining. Wells in the western portion of the network (e.g., well 699-44-42) generally have fewer years of service left than those elsewhere in the network. The water level in well 699-44-42 is calculated to be below the pump intake at present, but may have service extended by lowering of the pump in the well. In early 1998, the water level in well 699-43-45 had dropped to the point where the pump had to be lowered in the well to retain serviceability. Wells shared with the 200 Area TEDF, southeast of the B Pond System, appear to be least affected by the declining water levels.

Projected life of wells at the Hanford Site was modeled by Wurstner and Freshley (1994) using the Coupled Fluid, Energy, and Solute Transport (CFEST) model. In the B Pond System network, seven wells were predicted to be dry before the year 2000. Most of the wells projected to be dry are located near the main pond. By comparison, Table 2.1 estimates that 6 wells will be within 0.3 m of being dry by year 2000. Five of these six wells (699-42-41, 699-43-40, 699-43-42J, 699-43-43, and 699-44-42) coincide with those predicted by Wurstner and Freshley (1994) to go dry during the same time frame.

Johnson et al. (1995) used the VAM3DCG numerical modeling code to predict future water levels in the unconfined aquifer beneath the B Pond System as they respond to diversion of effluent from the main pond to the 3C pond. This model forecasted that the water table beneath the main pond would fall by as much as 1.5 m from 1992 to 1997, and that during the same period a new groundwater mound ~0.5 m in height would develop beneath the 3C pond. In fact, water levels in wells near the main pond have fallen by a substantial amount during the modeled period, though by less than predicted. However, no detectable groundwater mound has developed in the unconfined aquifer beneath the 3C pond.

Table 2.1. Status of Water Levels and Projected Longevity of B Pond System Wells

Well	Measure Date	DTW (m)	WT Elev (m)	Ref Elev (m)	Depth of Well Bottom (m)	Annual Rate of Decline (m)	Approximate Years of Service Left[a]
299-E18-1	12-Jun-97	97.5	122.1	219.5	101.3	0.23	16
299-E26-11	10-Jun-97	59.5	123.3	182.8	62.8	0.09	39
299-E32-4	09-Jun-97	87.0	123.1	210.2	90.8	0.20	19
699-40-36	09-Jun-97	36.1	125.1	161.2	68.0	0.10	316
699-40-39	19-Mar-97	39.8	125.3	165.2	66.5	0.45	60
699-40-40A	09-Jun-97	40.2	124.7	165.0	70.0	0.50	59
699-40-40B	19-Mar-97	40.3	124.9	165.3	61.4	0.54	39
699-41-35	09-Jun-97	33.2	125.4	158.6	62.1	0.08	352
699-41-40	09-Jun-97	40.5	125.9	166.4	54.3	0.68	20
699-41-42	09-Jun-97	71.7	124.5	196.3	85.5	0.64	22
699-42-37	09-Jun-97	32.2	126.2	158.3	48.3	0.29	55
699-42-39A	19-Mar-97	43.1	127.0	170.1	54.8	0.96	12
699-42-39B	09-Jun-97	43.3	126.8	170.2	65.2	0.81	27
699-42-40A	12-Jun-97	38.6	127.7	166.3	51.8	0.87	15
699-42-41	09-Jun-97	45.3	127.6	172.9	47.3	0.48	4
699-42-42B	12-Jun-97	52.3	125.5	177.8	61.9	1.17	8
699-43-40	09-Jun-97	38.2	127.1	165.3	41.2	1.00	3
699-43-41E	09-Jun-97	40.4	127.5	167.9	44.4	0.66	6
699-43-41F	21-Jun-96	39.9	420.2	167.9	53.6	0.11	121
699-43-41G	09-Jun-97	42.0	126.0	168.0	60.5	0.89	21
699-43-42J	12-Jun-97	50.9	414.7	177.3	54.1	0.74	4
699-43-43	06-Jun-97	51.6	125.0	176.6	54.1	0.94	3
699-43-45	06-Jun-97	59.9	401.4	182.2	62.0	0.31	7
699-44-39B	09-Jun-97	29.6	126.9	156.5	36.2	1.20	6
699-44-42	12-Jun-97	49.6	419.0	176.5	52.3	0.78	3
699-44-43B	09-Jun-97	51.6	125.2	176.8	52.6	0.64	2

(a) Linear Calculation based on June 1996 to June 1997 water levels or previous most recent 1 year of data.

No wells are completed above the Ringold lower mud unit (i.e., within the Hanford formation) in the B Pond System network. This region, from the lower mud unit to the surface, was initially within the unsaturated zone. However, it must be assumed that since discharges were diverted to the 3C pond, an artificial, perched aquifer has been created beneath this site and beneath the 200 Area TEDF immediately to the east. Most wells around the B Pond System do display an abrupt rise in water levels from early 1994 to mid 1995 (see Appendix B), but it is uncertain whether this rise is due to the shift of effluent to the 3C pond or is a delayed reflection of earlier discharges to the main pond/3A pond site.

3.0 Summary of Waste Characteristics and Subsurface Contamination

This section identifies known and potential contaminants released to the B Pond System and summarizes results of soil and sediments analyses. Waste streams and unplanned releases to the system are examined as potential contributors of contamination to the soil column. Inorganic and organic chemicals and radionuclides were sampled in mostly shallow soil environments in the B Pond System. Historically, decisions for selecting constituents of concern for B pond groundwater monitoring have been prefaced largely on waste stream characteristics.

3.1 Summary of Waste Stream Characteristics

As noted in Section 1.2, the B Pond System received effluent from several 200 East Area facilities. Descriptions of waste sources, waste streams, process information, and unplanned releases involving the B Pond System are described in several related documents (e.g., WHC 1989, WHC 1990, DOE-RL 1993a, DOE 1993b, DOE-RL 1994). Some of the reports are reiterative, while others improve on previous information. The salient points from these reports, as they apply to potential contamination of the B pond soils or groundwater, are summarized here.

3.1.1 Sources and Potential Sources of Dangerous Wastes

Several sources of waste water and effluent have contributed to B Pond System discharges during the facility's operational life. Discharges from these facilities were routine, scheduled releases and a few unplanned releases. The most important of the facilities include:

- PUREX Plant Chemical Sewer
- B Plant Chemical Sewer
- 242-A Evaporator Steam Condensate and Cooling Water
- 244-AR Vault Cooling Water
- 284-E Powerplant Wastewater
- 241-A Tank Farm Cooling Water
- B Plant Cooling Water
- Purex Plant Cooling Water.

Waste streams from these facilities were conveyed to the main pond through a system of ditches, and pipelines. From the PUREX Plant, the main pond received mixed wastes via the 216-A-29 ditch and the PUREX cooling water line. The B Plant facilities conveyed effluent via the 216-B-2-1, 216-B-2-2, and 216-B-2-3 ditches to the 216-B-3-1, 216-B-3-2, and 216-B-3-3 ditches, which, in turn, emptied into the main pond. These ditches were decommissioned and stabilized (backfilled) over a period of time (see Figure 1.3), mostly as a result of unplanned releases of dangerous wastes (DOE-RL 1993a). During the

final few years of operation, mostly uncontaminated water (essentially river water and condensate with some tritium) from the B Plant and PUREX facilities was conveyed to the main pond, 3A, and 3C ponds via closed pipelines.

Of the eight streams listed above, the largest actual and potential contributors of dangerous waste to the B Pond System are the PUREX and B Plant Chemical Sewers. Table 3.1 lists known and potential hazardous wastes discharged to the B Pond System from these sources. The potential contaminants are those chemicals that were known to be in use at the source facilities, but have not been recorded as present in discharges. Table 3.2 is an estimate of radionuclide inventories discharged to the facility, decayed to 1988 levels. These quantities are based on waste-stream analytical results and known volumes of effluent. Because results of waste stream sampling often produced results below detection limits (MDA) for these radionuclides, most of the inventories are shown as maximum quantities (i.e., less than the given quantity). In many cases, the MDAs were merely multiplied by liquid volumes to derive the inventories in Table 3.2, so as not to underestimate inventories (DOE-RL 1993b).

Corrosive hazardous wastes, such as nitric and sulfuric acid were routinely discharged to the B Pond via the ditches, although attempts were made to neutralize these wastes before they were discharged. Other volumetrically important chemicals discharged to the B Pond System include cadmium nitrate, ammonium fluoride, ammonium nitrate, and sodium hydroxide. Sulfuric acid and sodium hydroxide were the most frequently discharged hazardous wastes. An unplanned release containing 51 kg of cadmium nitrate from the PUREX chemical sewer was sent to the B Pond System in 1977 (DOE-RL 1994). DOE-RL (1993a) reports this release contained only 15 kg of cadmium nitrate. While Westinghouse Hanford Company (WHC) 1990 states that >172,000 kg of cadmium from cadmium nitrate spills has been sent to the B Pond System, DOE-RL (1993b) accounts for only 23 to 39 kg of cadmium nitrate released. Records of dangerous waste discharges to the B Pond System are poor prior to 1983, and information concerning chemical (non-radioactive) releases is sketchy prior to 1987 (DOE-RL 1993b). The last known, reportable discharge of chemical waste (sodium nitrate) occurred in 1987.

Most known radionuclide releases (except tritium) were associated with unplanned releases from the PUREX facility and B Plant. From 1963 to 1970, three of these releases to the B Pond System occurred from operations at these facilities, releasing the estimated quantities of radionuclides, as follows (DOE-RL 1994):

- 1963; 30 Ci of Cs-137 and 0.05 Ci of Sr-90 from B Plant
- 1964; 2500 Ci of "mixed fission products" from PUREX Plant cooling water
- 1970; 1000 Ci of Sr-90 from B Plant Chemical Sewer.

Apparent discrepancies in reported inventories of these radionuclides (such as between Table 3.2 and the above list) may arise from decay status and methods of estimating quantities. For a large portion of the conveyance distance, these releases traveled to the B Pond System main pond via the open, unlined ditches described above and in Section 1.2.

Table 3.1. List of Known and Potential Nonradiological Constituents Discharged to the B Pond System from the PUREX and B Plant Facilities (adapted from DOE-RL 1993b)

Known	Potential	
Aluminum nitrate nonahydrate	Acetic acid	Mercuric nitrate
Ammonium fluoride	Acetone	Nickel ferrocyanide
Ammonium nitrate	Aluminum	Nickel nitrate
Cadmium nitrate	Aluminum nitrate (mono basic)	Periodic acid
Ferrous sulfamate	Ammonia	Phosphoric acid
Hydrazine	Ammonium carbonate	Potassium fluoride
Hydroxylamine nitrate	Ammonium sulfite	Oxalic acid
Nitric acid	Ammonium silcofluoride	Phosphotungstic acid
Potassium permanganate	Boric acid	Shell E-2342
Potassium hydroxide	Calcium chloride	(Naphthalene/paraffins)
Sodium carbonate	Ceric nitrate	Silver Nitrate
Sodium nitrate	Cesium chloride	Sodium bisulfate
Sodium hydroxide	Chromate	Tartaric acid
Sodium nitrite	Citric acid	Tributyl phosphate
Sulfuric acid	Dibutyl butyl phosphonate	Sodium acetate
	DOW Anti-Foam B*	Sodium bismuthate
	(silicon emulsion)	Sodium dichromate
	Di(2-ethylhexyl)phosphoric acid	Sodium ferrocyanide
	Ethylenediaminetetraacetic acid	Sodium persulfate
	Ferric nitrate	Sodium gluconate
	Ferrous sulfate	Sodium fluoride
	Formaldehyde	Sodium thiosulfate
	Hydrochloric acid	Soltrol-170* (paraffins)
	Hydrogen fluoride	Sugar
	Hydrogen peroxide	Tri-n-dodecylamine
	Hydroxyacetic acid	Trichloroethane
	Hydroxyethyl	Trisodium nitrilo triacetate
	Ethylenediaminetetraacetic acid	Strontium fluoride
	Hyflo-super-cel* (contains silica)	Tetrasodium
	Kerosene	Ethylenediaminetetraacetic acid
	Lanthanum nitrate	Trisodium
	Lanthanum-neodymium nitrate	hydroxyethylenthylene-
	Lead nitrate	diaminetriacetic acid
		Zirconyl nitrate

Table 3.2. Inventory of Radiological Constituents Discharged to the B Pond System, Decayed to 1988 Levels (after DOE-RL 1993b)

Radionuclide	Inventory (curies)
Total alpha	$< 1.6 \times 10^{1}$
Total beta	$<3.93 \times 10^{2}$
Tritium	8.29×10^{2}
Ruthenium-106	$<1.34 \times 10^{-4}$
Promethium-147	<1.03
Plutonium-239	$<5.52 \times 10^{-1}$
Strontium-90	$<1.03 \times 10^{2}$
Cesium-137	$<9.49 \times 10^{1}$
Uranium	<2.07
Americium-241	<3.52

Tritium has been a perennial component of B Pond System waste streams. Table 3.2 indicates that nearly 830 Ci (decayed to 1988) of tritium had been discharged up until 1988. Since 1988, an additional ~40 Ci of tritium have been sent to the facility.

3.2 Summary of Soil Contaminant Evaluation

Because of the history of known and potential contaminants discharged to the B Pond System, an evaluation of soil contamination was conducted for the main pond, expansion ponds, and nearby portions of the 216-B-3-3 ditch. This evaluation was conducted in 3 phases from 1989 to 1992. The first phase, completed in 1989, involved shallow soil sampling and analysis of sediments from the main pond, expansion ponds, and 216-B-3-3 ditch (Kramer 1991). Phases 2 and 3 were conducted from 1991 through 1992, and consisted of both shallow and deep vadose-zone sediment sampling and analysis beneath the 3A, 3B and 3C expansion ponds (DOE-RL 1993b). The three expansion ponds are no longer a part of the RCRA-regulated B Pond System. Results of sampling and analysis of these ponds are included to help substantiate inferences about contamination from past practices at the B Pond System as a whole.

The first phase of soil sampling involved 49 soil samples; 20 from the main pond, 9 from adjoining portions of the 216-B-3-3 ditch, and 7, 5, and 8 samples from the 3A, 3B, and 3C expansion ponds, respectively. An additional 10 soil samples were taken from locations around the B Pond System and contingency pond to provide local background values. All samples in this phase were shallow; the average depth of samples taken from the bottom of the main pond was ~10 cm. The analytes were a comprehensive list of organic and inorganic constituents, metals, and radionuclides (gross alpha, beta, and gamma scan) based on known and suspected waste stream constituents (for list, see Kramer 1991).

The results of Phase 1 sampling indicated a notable lack of significant contamination. Cadmium, lead, and mercury were the only metals found above background levels, and these metals were well below toxic levels or Model Toxic Control Act (MCTA) cleanup standards. The maximum results for cadmium, lead, and mercury were, respectively, 22.6 ug/g, 618 ug/g, and 15.6 ug/g, all from the main pond. In general, all metals were "within normal concentration ranges" (Kramer 1991). It should be noted that some of these metal analyses were performed using strong acid digestion procedures (EPA method 3050) instead of the Extraction Procedure Toxicity methods. Thus, some results may have indicated greater concentrations of contaminants than are actually environmentally available.

No contamination by organic compounds could be demonstrated by Phase 1 analytical results. A few low-level results of compounds associated with laboratory contaminants (e.g., acetone, Bis (2-ethylhexyl) phthalate, methyl ethyl ketone) or blank contamination were reported. The report concluded that further sampling for organic analyses was not justified, based on Phase 1 results. Sulfate results were typically *below* background values.

Radionuclide activities in soil as determined from Phase 1 sampling were also surprisingly low. The highest gross alpha and gross beta results (18.4 pCi/g and 718 pCi/g) were measured in samples from the 3C pond. The highest Sr-90 result (4.03 pCi/g) was collected from the B-3-3 ditch. Clearly, results of Phase 1 radionuclide analyses do not indicate a radiological hazard in the shallow soil environment at this facility.

Phases 2 and 3 soil characterization examined only the 3A, 3B, and 3C expansion ponds. Phase 2 sampling was done, in part, to confirm results of Phase 1 sampling, as requested by Ecology. Like Phase 1, Phase 2 focused on sampling shallow soil/sediments. Phase 3 work involved drilling of one borehole through the vadose zone to groundwater in each of the expansion ponds. Results of both Phase 2 and 3 investigations are described in DOE-RL 1993b and DOE-RL 1994.

Phase 2 results indicated that copper, lead, zinc, antimony, and cadmium were above background levels in some samples, but all were below hazardous levels and MTCA cleanup standards appropriate for nonresidential use. Beryllium results in some samples exceeded MTCA method B cleanup standards, but these results were below Hanford Site background levels, and therefore considered not to be at regulated levels. Likewise, all other inorganic and organic constituents were determined to be below regulated levels and not considered hazardous wastes.

Phase 3 soil analytical results further substantiated that very little, if any, contamination exists in the subsurface of the expansion ponds. Samples were collected at 0.6 to 3.0 m intervals (intervals lengthening with depth) until groundwater was reached. Chromium was the only constituent found above background (threshold) levels, but was well below cleanup standards. Beryllium, antimony, mercury, selenium, thallium, and cyanide were detected, but were below either background levels or Contractually Required Quantitation Limits (CRQLs). All investigated (Appendix VIII 40 CFR 261) organic constituents were below detection or CRQL. Gross alpha was highest (42.59 pCi/g) in a sample from 102 ft beneath the 3A pond. The highest gross beta result (8.75 pCi/g) and Sr-90 result (36.5 pCi/g) were found at a depth of 7.5 ft at the 3B pond. A Sr-90 result of 36.1 pCi/g was also produced from the 97 ft depth at the 3A pond.

Based on Phases 1, 2, and 3 soil analytical results, the 3A, 3B, and 3C expansion ponds were clean closed under RCRA. Dispute resolution processes with stakeholders concluded that the greater risk from contamination would probably reside at discharge sites nearest the generating facilities. Hence, further subsurface investigation originally planned for the main pond and B-3-3 ditch was cancelled in favor of investigation (ongoing) of the 216-B-2-2 ditch near the B Plant.

4.0 Summary of Groundwater Chemistry and Groundwater Quality Assessment

Sampling and analysis of groundwater at the B Pond System has been conducted under the RCRA requirements since 1988. During this period, over 60,500 analytical results for various constituents were produced from groundwater samples from the B Pond System well network. The majority of the results were below detection limits. These results, spanning 8 years of monitoring, were evaluated in *Results of RCRA Groundwater Quality Assessment at the 216-B-3 Pond Facility* (Barnett and Teel 1997).

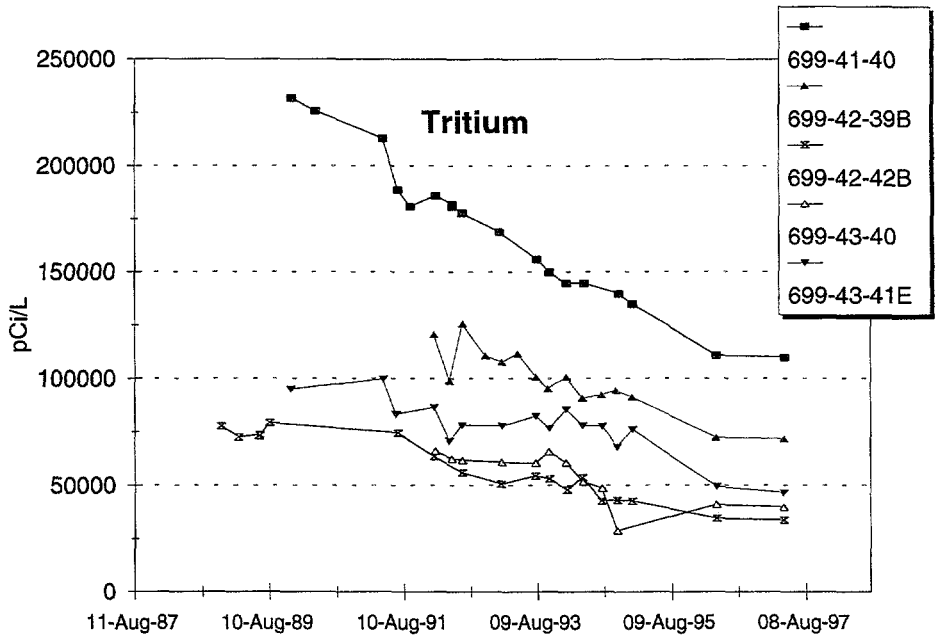
The B Pond System was placed into assessment in 1990 because of elevated TOX and TOC in two wells. From that time until mid 1996, comprehensive sampling and analysis was performed to determine the cause of these anomalies. The assessment report concluded that these occurrences were essentially isolated, and that no hazardous waste could be correlated to TOC or TOX results. Only two organic compounds, which occurred in extremely low concentrations, were identified in the assessment.

The only contaminants consistently detected in groundwater that could be traced to B Pond System operations were tritium (maximum 232,000 pCi/L) and nitrate (maximum 22,500 ug/L). Only tritium occurred in concentrations above drinking water standard (DWS). Concentrations of both tritium and nitrate have generally trended downward since monitoring began at the facility. Figure 4.1 illustrates the trends of tritium and nitrate in wells with the historically highest concentrations of these constituents. Recent analyses for nitrate show a slight departure from the trend of general decline in wells 699-43-41E and 699-42-39B.

Chromium, iron, and manganese have historically exceeded DWS in several wells. Concentrations of these metals have been attributed to well construction and oxidizing conditions in the aquifer. Arsenic has been detected at extremely low levels (far below DWS) in wells near the west end of the Main Pond, but is described by Johnson et al. (1995) as possibly having originated from 200 East Area cribs and trenches prior to the onset of significant hydraulic mounding at the B Pond System.

Measurements of specific conductance (electrical conductivity) in all B Pond System wells have routinely produced results below Hanford Site background values for groundwater. Most of the effluent sent to the facility was water originating from the Columbia River ("raw water") which has a very low dissolved solids load. This effluent significantly diluted groundwater beneath B pond and resulted in specific conductance levels lower than natural background for the aquifer (see discussion in Section 6.9.2).

With the exception of tritium, radionuclide activities in groundwater have been very low at the B Pond System, particularly in light of supposed waste streams. Sitewide monitoring detected I-129 activities in the B Pond System network of up to 4.6 pCi/L in well 699-43-45 in 1997. The highest gross alpha result (21 pCi/L) was taken from well 699-40-36 (shared with the 200 Area TEDF) in 1994. Well 699-42-40A (located between the 3B and 3C ponds—not included in the regular RCRA monitoring network) produced the highest results for gross beta (159 pCi/L in 1983), uranium (12.9 pCi/L in 1983),



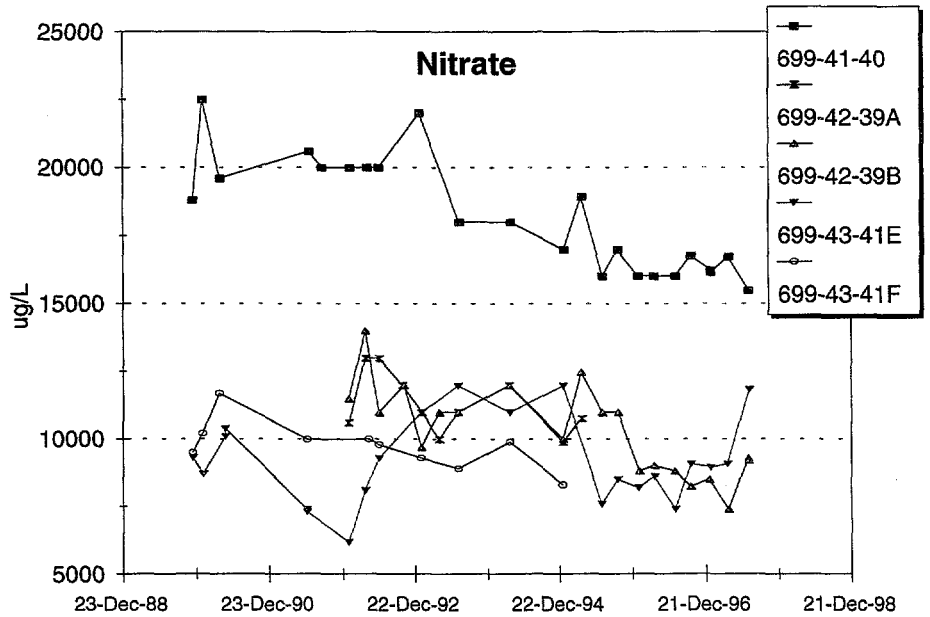
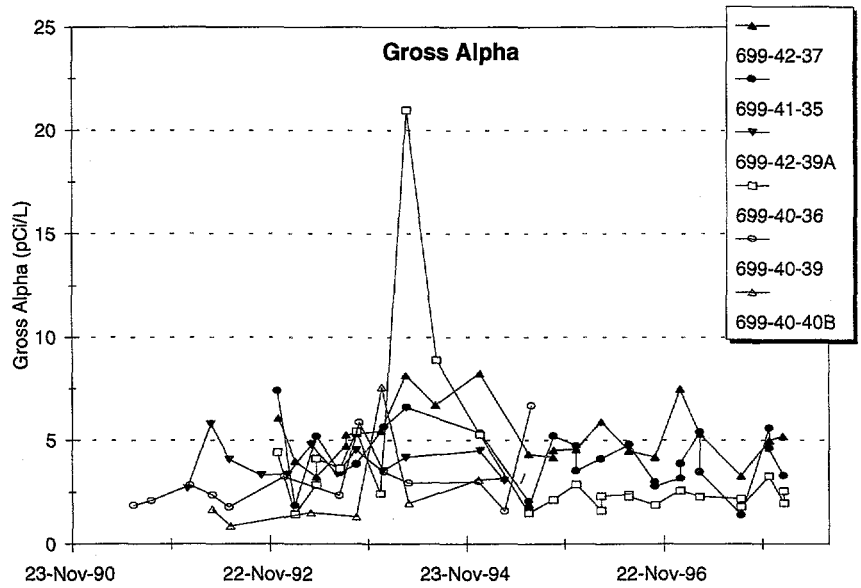


Figure 4.1. Trends for Tritium and Nitrate in B Pond System Wells with Historically Highest Results for Tritium and Nitrate

Sr-90 (16.3 pCi/L in 1985), and Cs-137 (8.68 pCi/L in 1984). Activities of similar magnitudes for these parameters were never reproduced by later analyses from B Pond System wells, so the results from well 699-42-40A are considered problematic. Both gross alpha and gross beta display multiple episodes of relatively elevated concentrations (but still mostly below DWS) in virtually all wells in the network. The most prominent of these episodes occurs from 1993 to 1995, with some slightly elevated results as recently as early 1997. Figure 4.2 illustrates the trends of gross alpha and gross beta in selected B Pond wells with the highest average results for these constituents. Hanford Site background for gross alpha and gross beta concentrations in groundwater are 5.79 pCi/L and 12.62 pCi/L, respectively (Johnson 1993). Like specific conductance, discharge of Columbia River water to the B Pond System has also diluted these parameters beneath the facility and produced concentrations of alpha- and beta-emitting radionuclides which have been mostly below natural background (see discussions in Section 6.9.4 and Appendix D). Background levels of gross alpha and gross beta Columbia River are well below background for groundwater on the Hanford Site (Dirkes and Hanf 1996).

Comparisons of four well clusters monitoring different portions of the uppermost aquifer suggest vertical differences in concentrations of constituents. Figure 4.3 illustrates this trend for tritium in deep/shallow companion wells. With the exception of one group, deeper wells in the groups have produced historically higher concentrations of tritium. This trend is reversed in wells 699-43-41E,F,G, with the shallow well having higher concentrations. Concentrations of other constituents, such as iron, nitrate, manganese, pH, and conductivity, display differences between deep/shallow well pairs, but no consistent pattern is recognizable across all four groups of wells. No obvious differences between shallow/deep well companions were observed for concentrations of total organic carbon or total organic halogens. Reasons for vertical differences in concentrations of constituents are undetermined, but may be due to factors such as well construction, aquifer heterogeneities, variables in transport characteristics, and varying concentrations of constituents in effluent. In the case of tritium, later discharges of effluent were lower in tritium concentrations than earlier discharges, thus possibly accounting for higher concentrations being observed mostly lower in the aquifer. However, the fact that vertical differences in concentrations exist is impetus to consider vertical distribution of potential contaminants in a groundwater monitoring strategy for the facility.



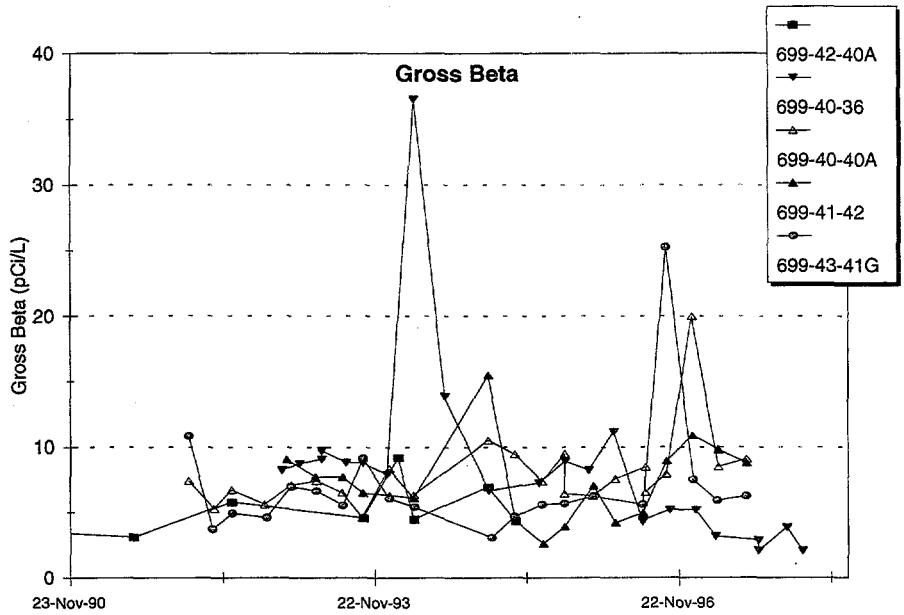


Figure 4.2. Gross Alpha and Gross Beta Trends in B Pond System Wells Having Gross Alpha Averages >3.0 pCi/L and Those Having Gross Beta Averages ≥7.0 pCi/L. Note the coincidence of gross alpha and gross beta highs for well 699-40-36. Well 699-42-40A is an older well that produced significantly higher values (up to 159 pCi/L) for gross beta prior to the period shown.

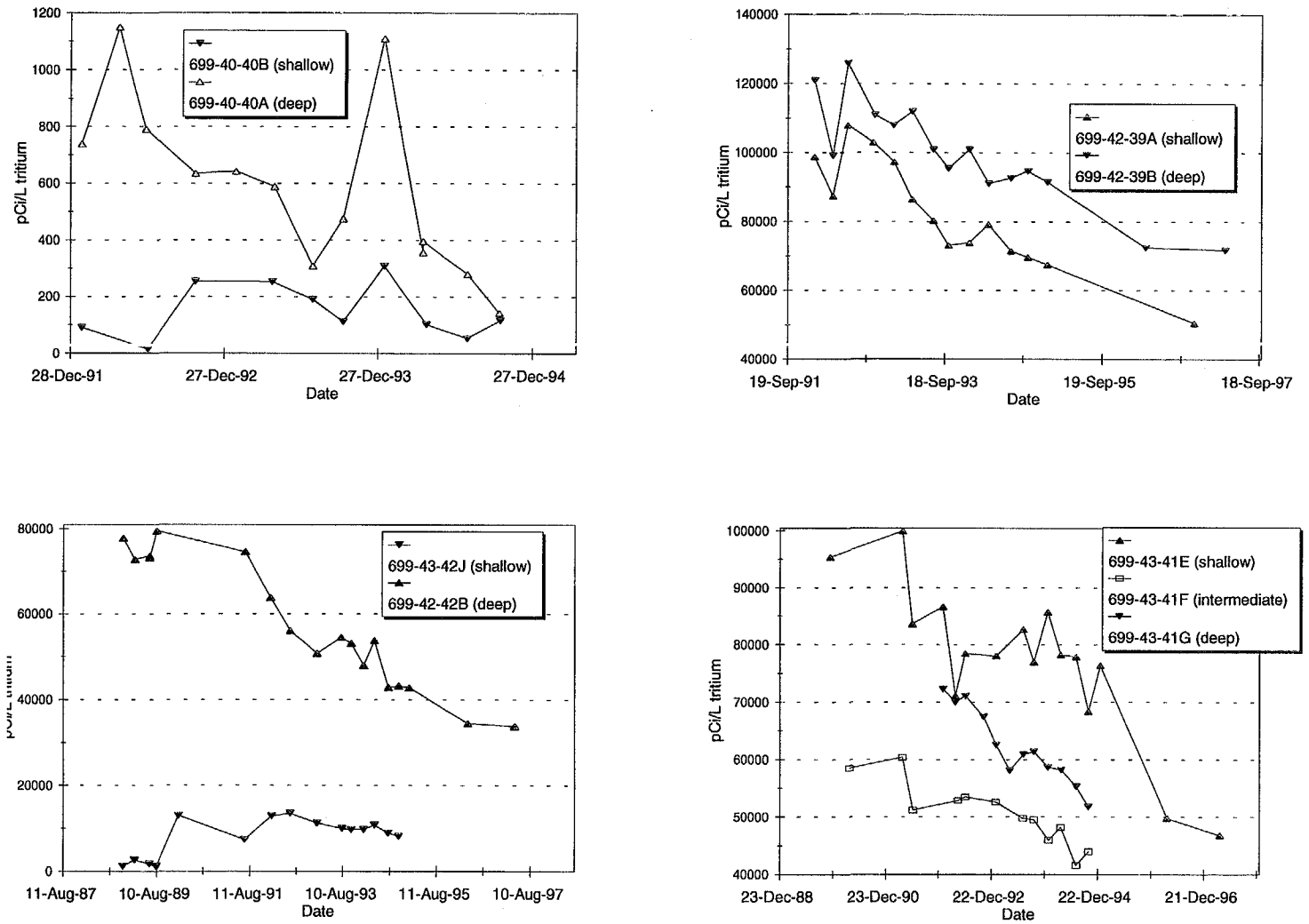


Figure 4.3. Tritium Plots for Deep/Shallow Well Groups in the B Pond System Monitoring Network

5.0 Conceptual Model of Soil and Groundwater Contamination and Constituents of Concern

Although records of waste disposal practices for the B Pond System indicate the potential for contamination at the facility, chemical and radiological analyses of soil and exhaustive groundwater analyses have failed to uncover any substantial contamination in these media by hazardous or radiogenic wastes. As described in the preceding sections, extensive sampling of soils in the shallow subsurface across the B Pond System showed very little contamination, and no hazardous waste components above the MCLs (Kramer 1991). Later work by DOE-RL (1994) also failed to identify any significantly contaminated soils in the three expansion ponds (3A, 3B, 3C); these were subsequently clean closed. From characterization and monitoring performed thus far, it would appear that risks to groundwater from the B Pond System and actual impacts are negligible. Conceptual models of contaminant transport are suggested here to explain apparent disparities between known or suspected disposal practices and actual, observed contamination in soil and groundwater.

5.1 Conceptual Model

Most of the known waste products sent to the B Pond System were conveyed to the facility via open, unlined ditches (see Sections 1.2 and 3.1) from the PUREX and B Plant facilities. In some cases, conveyance distances were >1 km by this method. Recognizing the differences between observed and suspected contamination at the B Pond System, DOE-RL (1994) proposed a conceptual model of the ditch/pond system to explain the movement of contaminated aqueous solutions through the ditches and vadose zone. Figure 5.1 illustrates an explanation of what may happen to liquid effluent as it enters a ditch/pond system from the generating facility. Much of the effluent will infiltrate the permeable Hanford formation within a relatively short distance from the generating facility. Likewise, less mobile contaminants may be adsorbed to sediments beneath the proximal portions of the ditch, with a reduced contaminant load (and effluent volume) eventually reaching the B Pond System. Thus, a vertical and horizontal diminution of contamination will occur progressively from the head of the ditch, nearest the source, to the destination at the main pond of the B Pond System. When the effluent reaches the pond, a further reduction may occur during infiltration to the water table, as shown in the schematic interpretation of Figure 5.2. By these mechanisms, most contamination may not have reached the main pond, and that which did would be further reduced before reaching groundwater.

Unquestionably, contaminated effluent did reach the B Pond System. Contamination, although in minute amounts, has been detected in the shallow soils of all ponds, the vadose zone of the expansion ponds, and in groundwater beneath the facility. However, soil horizons beneath the main pond deeper than a few cm have not been examined. Intermediate-depth soils (between the shallow subsurface and the water table) may host contamination that eventually arrived at the B Pond System, but was forced further down into the vadose zone by later, voluminous, clean-water discharges (see Figure 1.4). Johnson et al. (1995) postulate a scenario for the fate of potential contamination entering the main pond. Figure 5.3 shows that contaminants are expected to segregate vertically in the vadose zone beneath the main pond, with the least mobile contaminants remaining higher in the soil column. Johnson in WHC (1990)

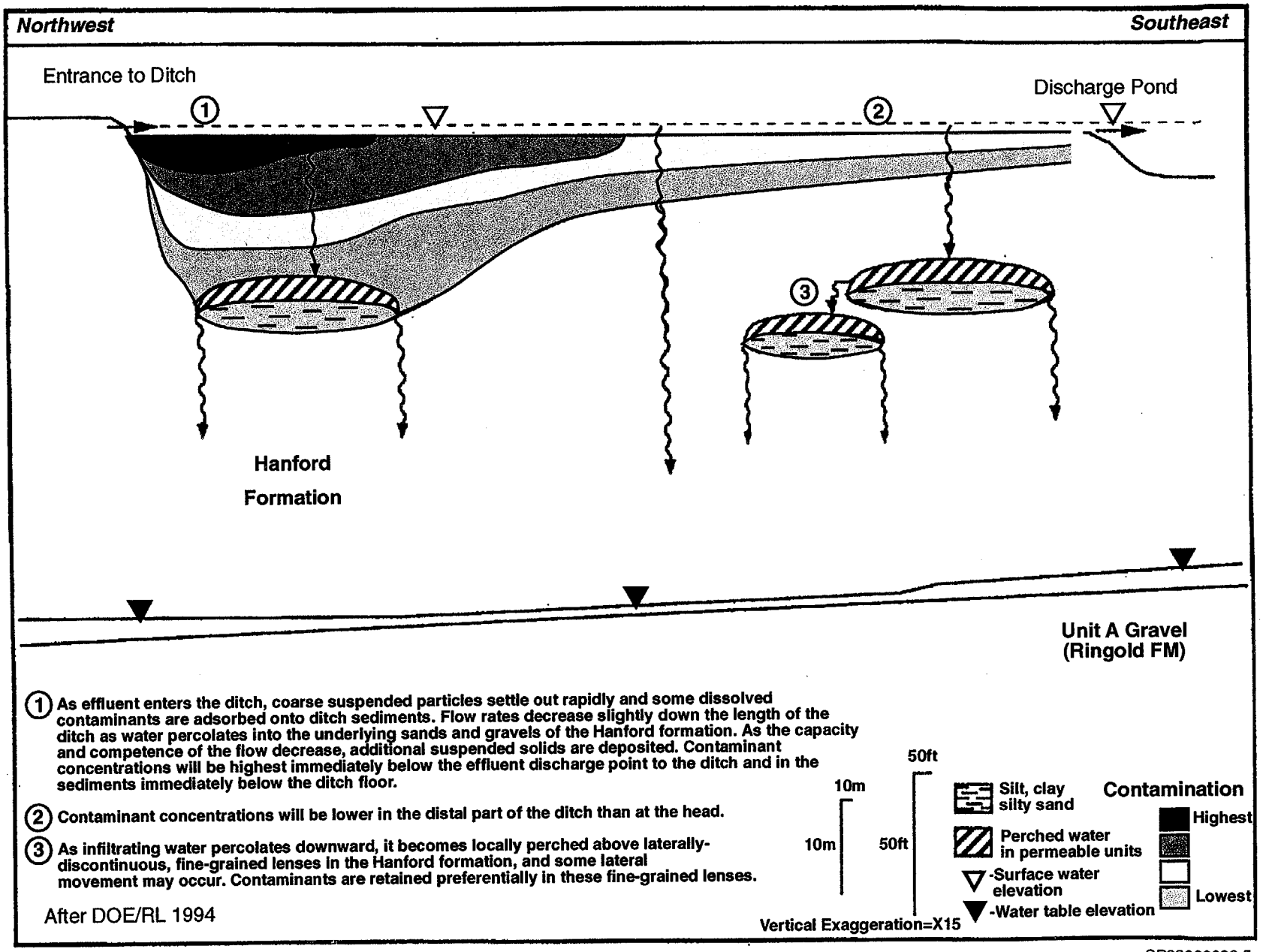


Figure 5.1. Conceptual Model of Effluent Infiltration Within a Ditch/Pond System (after DOE-RL 1994)

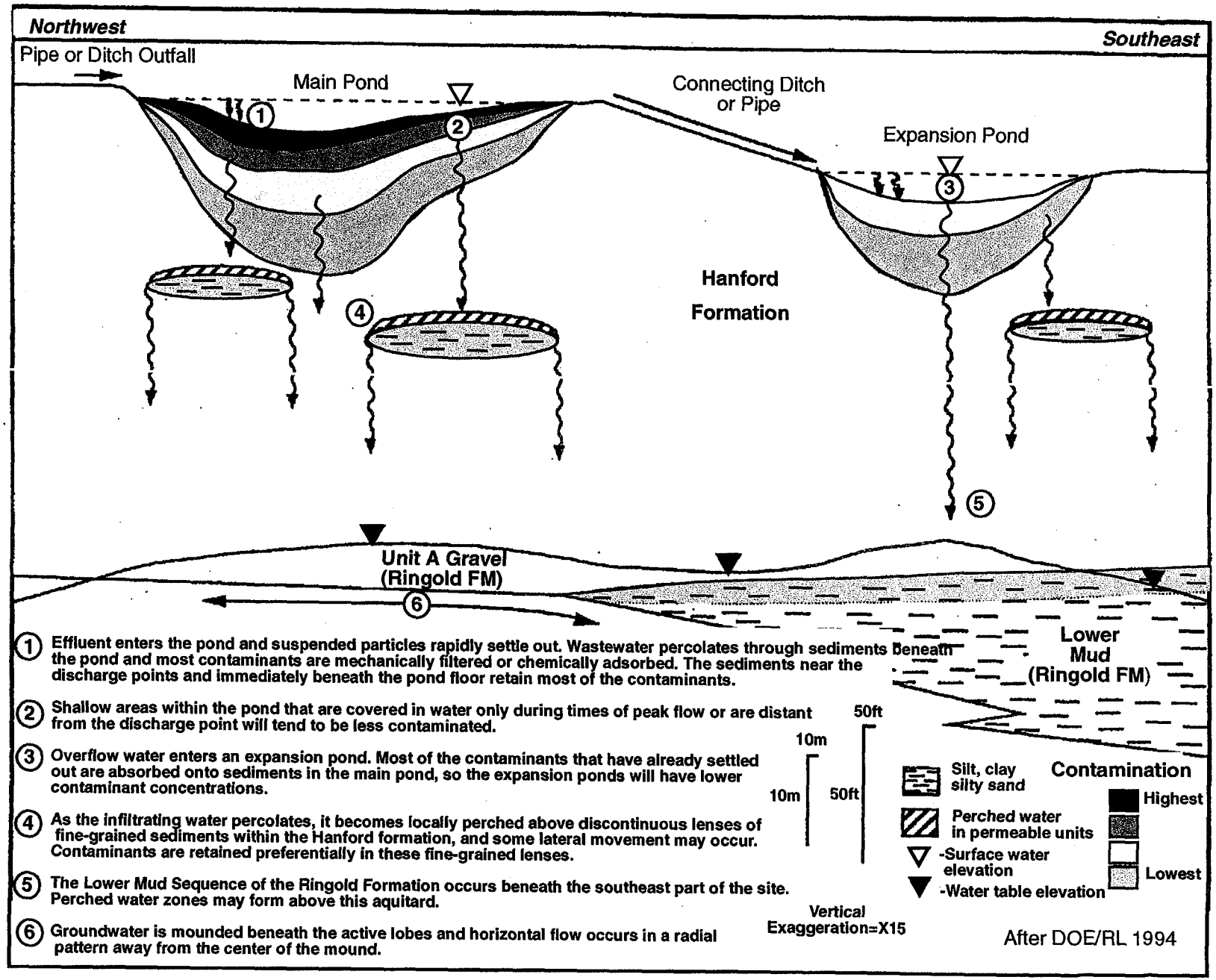


Figure 5.2. Conceptual Model of Infiltration of Effluent at the Main Pond of the B Pond System (after DOE-RL 1994)

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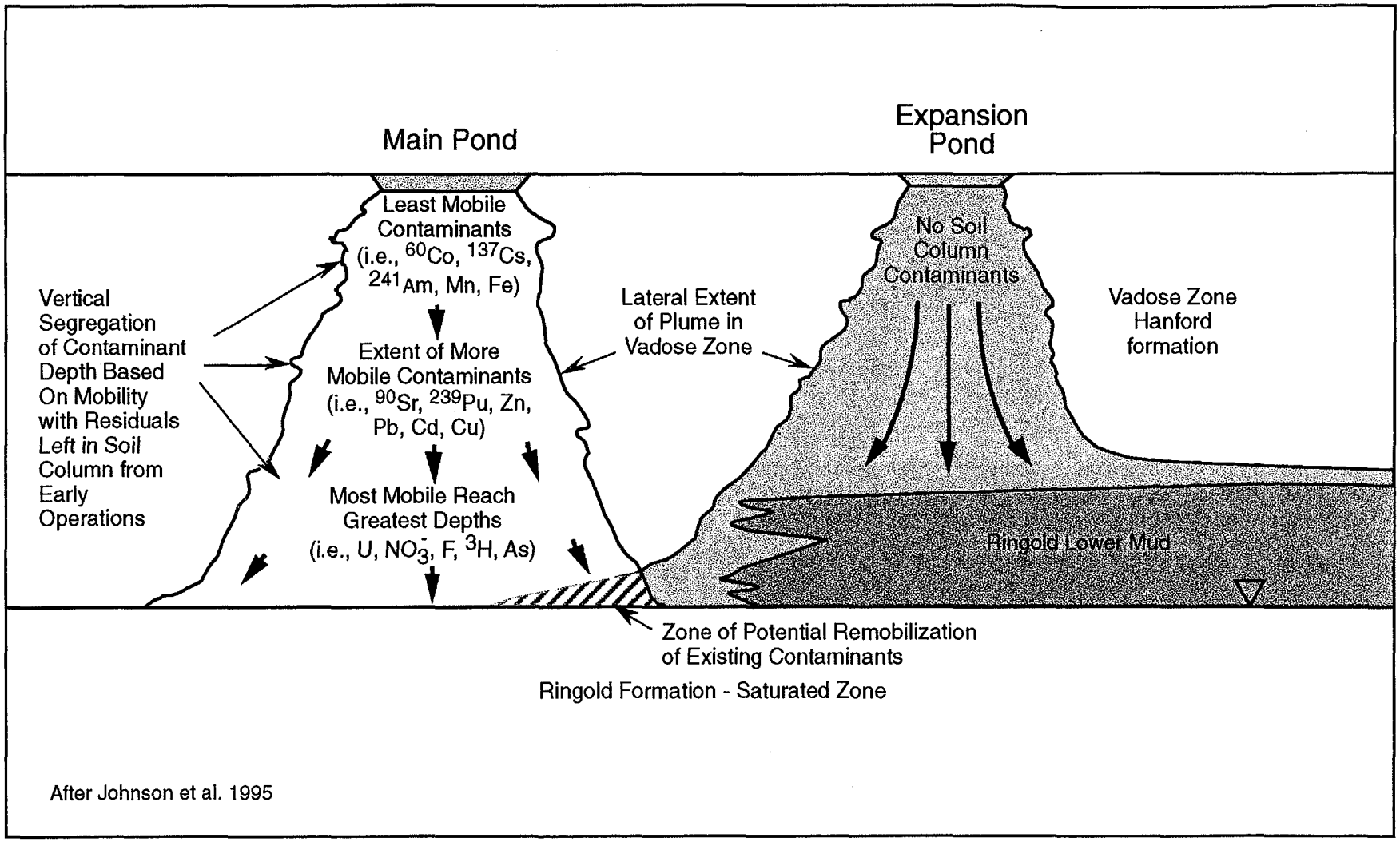

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Figure 5.3. Conceptual Model of Contaminant Distribution Beneath the Main Pond (after Johnson et al. 1995)

calculates that with the assumed contamination loads and effluent volumes sent to the main pond, most radionuclide components (except tritium and uranium) would not reach the water table during the life of the facility.

5.2 Contaminants of Potential Concern

Rationale for further monitoring of groundwater will be based on direct evidence of contamination in soil and groundwater (i.e., analytical results) and the conceptual model for the probable fate of contamination from the source, through the vadose zone, to groundwater. The expansion ponds, 3A, 3B, and 3C, have been cleaned closed and are no longer considered sources of contamination. Discharges to the main pond ceased in 1994, and so ended the primary hydraulic driving force and the potential of further contamination discharging to the facility. Thus, the remaining areas of risk for contamination reaching groundwater are from remobilization of existing contamination in the vadose zone beneath the main pond and/or from contaminants already entrained in groundwater beneath the facility.

As illustrated in the conceptual model represented by Figure 5.3, some minor degree of risk is perceived in the potential for remobilizing contaminants thought to reside in the vadose zone by further infiltration of effluent or precipitation, especially from the adjacent 3C expansion pond. Discharges to the 3C pond were discontinued only recently (August 1997). Thus, because of this recent, nearby activity and the possibility that remnant infiltration (a distinct groundwater mound remains) may still have the potential to move contaminants beneath the main pond, it is prudent to screen groundwater for the most likely contaminants or indicators thereof originating from this region.

Considering all factors of the foregoing discussions on waste profiles and media analyses (Sections 3.0 and 4.0), the most useful indicators for radionuclide detection will be gross alpha and gross beta analysis. These parameters will have the greatest potential for alerting to the presence of the radionuclides species thought to be potentially present in the vadose zone beneath the main pond. Tritium, I-129, nitrate, and arsenic are essentially the only constituents that have been detected in groundwater that cannot be explained as anything but contamination. All four of these constituents are also associated with widespread (sitewide) contamination plumes. Tritium and nitrate show areal distributions that suggest they originate, at least in part, from the B Pond System (see Hartman and Dresel 1998). However, arsenic and I-129 have been observed primarily in wells at the western extremity of the B Pond System network, have not been identified as components of the B Pond System waste stream (Tables 3.1 and 3.2), and thus may originate from other facilities in the 200 East Area (see Section 4.0).

Anionic species, often complexed with radionuclides, predominated the waste streams sent to the B Pond System. Nitrate is still present in groundwater beneath the facility, and has recently shown a reversal in a generally downward trend in two monitoring wells (see Section 4.0). For these reasons, specific conductance of groundwater samples should be measured as part of a B Pond System monitoring program.

In summary, very low levels of contamination are observed in soil and groundwater at the B Pond System. Some higher levels of hazardous and/or radioactive wastes may be potentially present in the vadose zone beneath the main pond. However, if these contaminants are present, they should be virtually

immobile, especially with removal of the hydraulic driving forces (main pond and 3C pond decommissioning). Conceptual models suggest that most of the contaminated effluent directed to the B Pond System infiltrated in the ditches leading to the main pond, probably within the 200 East Area. Most of the contamination that eventually reached the main pond may have been driven into deeper portions of the vadose zone by large volumes of clean water discharged later in the facility's life. This circumstance may also partially account for the virtual lack of contamination in the surficial soils. Tritium, nitrate, arsenic, gross alpha, gross beta, I-129, and specific conductance are chosen as target constituents because these parameters are most likely to expose any residual contamination potentially remaining beneath the B Pond System. Monitoring specific conductance poses a special problem. Because of the dilutive effects of the large volumes of raw river water discharged to the facility, values for this parameter have been artificially depressed below natural background and are not currently in equilibrium with the solid phase of the aquifer. However, this parameter may be a useful indicator for contamination if Hanford Site background levels are exceeded in B Pond System wells (also see Sections 4.0, 6.3, 6.9.2, 6.93, and D.6).

6.0 Groundwater Monitoring Program

This section presents a groundwater monitoring program consisting of monitoring network, sampling and analysis methods, and a statistical approach for data evaluation. The elements of this monitoring program were developed through the DQO process (see EPA 1994), documented in Appendix A, to achieve the following goals in a technically sound and cost-effective manner:

- protect human health and the environment
- comply with regulatory requirements (i.e., WAC 173-303-645 and 40 CFR Subpart F) and agreements (see Section 6.1)
- provide information for groundwater investigation and/or remediation.

RCRA groundwater monitoring efforts proposed for the B Pond System will be consistent with groundwater remediation strategy for the Hanford Site (DOE 1997a) and will be integrated with the site-wide monitoring activities where appropriate.

6.1 RCRA Interim-Status/Final-Status Regulatory Overview

The U.S. Environmental Protection Agency (EPA) promulgated groundwater monitoring and response standards for certain land-based interim-status facilities in 1980 (45 FR 33232, May 19, 1980), codified in 40 CFR Part 265, Subpart F, and permitted facilities in 1982 (47 FR 32350, July 26, 1982), codified in 40 CFR Part 264, Subpart F. Facility owners and operators are required to sample groundwater at specified intervals and to use a statistical procedure to determine whether or not hazardous wastes from these units are contaminating groundwater.

The statistical methods (e.g., the Cochran's Approximation to the Behrens-Fisher t-test, or CABF t-test) and the replicate sampling method used in evaluating groundwater monitoring data, as described in 40 CFR Part 264 (final-status) regulations, have generated criticism because of higher false-positive (resulting in an unnecessary and expensive phase of monitoring) and false-negative decision (resulting in instances where actual contamination would not be detected) error rates.

As a result of these concerns, EPA amended both the statistical methods and the sampling procedures of the regulations by including statistical methods and sampling procedures that are more appropriate for groundwater monitoring (53 FR 39720, October 11, 1988) for the permitted facilities regulated under final status. Although EPA recognized the fact that all the reasons for replacing the Students t-test at a permitted facility should apply equally to an interim-status facility, EPA did not amend the interim-status requirements. This was because EPA expected, by November 1988, the majority of interim-status land disposal facilities should either be permitted (and regulated under final status) or be closed (53 FR 39720, October 11, 1988).

The Hanford Site is designated as a single RCRA facility and has been assigned a single identification number for the purpose of RCRA permitting activity. Because of the complexity of the Hanford Site, most of the RCRA-regulated units are interim-status facilities and will be brought into the Hanford Facility RCRA Permit (Ecology 1994) through a permit modification process. The B Pond System is currently a RCRA interim-status facility, and a closure plan is expected to be submitted to Ecology in the year 2000 that will place the facility in the final status. However, a technically sound and cost-effective detection-level groundwater monitoring that follows the final-status sampling and analysis requirement may be effected now for greater efficiency.

6.2 Objectives of Final-Status RCRA Monitoring

Three stages of *final-status* groundwater monitoring programs are defined in WAC 173-303-645 and in 40 CFR Part 264 with three separate objectives: detection monitoring, compliance monitoring, and corrective action. The *detection* monitoring program [173-303-645(9)] is designed to determine whether a RCRA-regulated unit has adversely affected the groundwater quality in the uppermost aquifer beneath the site. This is accomplished by testing for statistically significant changes in concentrations of constituents of interest in a downgradient monitoring well relative to baseline levels. These baseline levels could be obtained from upgradient (or background) wells, and are referred to as inter-well (or between-well) comparisons. Alternatively, if baseline values are obtained and compared from historical measurements within a downgradient well, the comparisons are referred to as intra-well (or within-well) comparisons. If a statistically significant increase (or pH departure) over baseline condition occurs in a downgradient compliance well, then a compliance monitoring program is initiated. In *compliance* monitoring, downgradient groundwater concentrations of constituents of concern are compared to the concentration limits set forth in the facility's permit. Concentration limits could be those specified in WAC 173-303-645 5(a)(ii) or alternative concentration limits established by Ecology. If concentration limits are exceeded, a corrective action program is initiated. The objective of a *corrective* action program is to protect human health and the environment by removing the dangerous waste constituents, or by treating them in place.

As described in Section 4.0, the only contaminants consistently detected in groundwater that could be confidently ascribed to B Pond System operations were tritium and nitrate. Arsenic and I-129 have also been detected in groundwater at the facility, but the origin of these contaminants is problematic. Tritium, I-129, arsenic, and nitrate are also known to be sitewide contaminant plumes that are widespread, covering tens of square miles with limited areas of high concentration. Currently, remediation through natural attenuation of the sitewide plumes is the proposed interim remedial action (DOE 1997a, page 5-13). Movement of the plumes and changes in concentrations in groundwater are reported. This will provide efficient and cost-effective input to assess the ability of natural attenuation to meet cleanup goals. For the B Pond System, tritium, nitrate, I-129, and arsenic will be monitored in conjunction with sitewide plume tracking. Monitoring data will be used to assess contaminant concentration trends in time and to provide dose/risk impact information for protection of the Columbia River and downstream drinking water systems.

The main pond (B-3 pond) and the 216-B-3-3 ditch were interim stabilized during 1994. At the same time, the three expansion ponds (3A, 3B, and 3C) were clean closed, and are no longer subject to groundwater monitoring. Groundwater quality assessment results from exhaustive investigation (see Section 4.0)

could not demonstrate that hazardous waste from the facility is affecting groundwater. For this reason, it was recommended that the groundwater monitoring program for the B Pond System be returned to indicator-parameter-evaluation (*detection-level*) status (Barnett and Teel 1997). To aid the development of a technically sound groundwater monitoring program, however, a clear understanding of the special conditions at the B Pond System must be obtained.

6.3 Special Conditions at the B Pond System

The peculiar history of effluent discharges to the B pond facility and the resulting hydrologic and hydrochemical conditions require special consideration in the formulation of an appropriate groundwater monitoring program. Discharges to the main pond of the B Pond System began in 1945 and continued until 1994 (see Section 1.1). During most of this period it is probable that some dissolved constituents in the effluents were entering groundwater beneath the facility (DOE-RL 1994). In later years, the effects of relatively pure (low ionic concentrations) Columbia River water (raw water) probably altered the chemistry of the groundwater beneath the facility. At first, dissolved salts derived from infiltration of relatively pure water through evaporate minerals in the vadose-zone strata most likely flushed sulfate, calcium, and other naturally occurring constituents in Hanford Site soils through the vadose zone into groundwater (Thornton 1997; Barnett et al. 1997). These constituents, along with contaminants in the effluent, would have raised levels of dissolved solids, specific conductance, and other related parameters in the groundwater beneath the B Pond System. In the final few years of the main pond's operation, the effluent was essentially free of contamination, and the infiltrating raw water probably had mostly a dilutive effect on groundwater, having depleted most of the soluble salts from the soil (see Section 3.0), and being of intrinsically low ionic strength. At this point, levels of conductivity and dissolved parameters would have been artificially depressed. Johnson (1993) recognized the probable dilutive effects of the effluent on natural groundwater chemistry at the B Pond System, and advised that performance criteria for parameters such as conductivity should take these effects into account. Recent trends in specific conductance in some wells in the B pond network suggest that this parameter is slowly rising, possibly in recovery from artificially lower values. This trend will likely continue until groundwater moving beneath the facility attains equilibrium with solid phases of the aquifer, and natural background conditions are reached.

The hydraulic mound centered east of the main pond (Figure 2.2) was also generated by effluent disposal to the B Pond System, and has persisted for many years. Only in recent years has substantial decline in this mound been observed (see Section 2.3 and Appendix A). The eastward offset of the mound apex is possibly due to patterns of subsurface infiltration and drainage. The driving force for local groundwater flow is centered at the mound apex, and thus, flow is interpreted to be generally radial, away from the apex in all directions. Obviously, subsurface heterogeneities may considerably alter this generality, but estimation of precise patterns of hydraulic gradient, lithologic controls, and groundwater flow is limited by the density of subsurface information (i.e., well coverage). Hence, from a practical standpoint, flow *direction* must be considered to be radically away from the apex of the mound. Interpretation of flow *rate and direction* is aided by contouring of the water table/potentiometric surface, and information about sediment properties.

Figure 2.2 represents an interpretation of the potentiometric surface in the vicinity of the B Pond System using recent information from groundwater monitoring wells. Interpretation of the hydraulic gradient indicates that groundwater flow appears to be relatively constrained to the west and southwest of the main pond, compared with other directions. The position of the mound apex with respect to the main pond indicates that groundwater is flowing generally in a westerly direction beneath the main pond. Therefore, an effective monitoring well network should include a well(s) generally west of (downgradient from) the main pond and the regulated segment of the B-3-3 ditch.

6.4 Chemical Parameters and Dangerous Constituents

The B Pond System received radioactive and nonradioactive process and cooling water from the PUREX Plant, B Plant, and other 200 Area facilities (see Section 3.1). In addition, unplanned releases (spills) may have resulted in significant soil column buildup of Sr-90 and Cs-137 (beta-emitters) in the 216-B-3 pond. Based on the conceptual model depicted for the B Pond System (see Section 5.0), specific conductance, gross alpha, and gross beta were selected as the constituents of interest for the B Pond System. These indicators will be monitored, on a *site-specific* scale, to detect whether chemical/radioactive parameters or dangerous constituents from the regulated unit have impacted groundwater beneath the site. Nitrate, arsenic, I-129, and tritium were identified as contaminants of concern existing in groundwater that could be associated with B pond operations, or possible incursion from nearby facilities (I-129 and arsenic).. Because these constituents are also associated with existing, widespread sitewide plumes, they will be monitored, on a *regional* scale, to track the movement of the plumes.

6.5 Concentration Limits

Concentration limits serve as the compliance standards in case the regulated unit is found to impact the quality of groundwater and the facility enters into compliance-monitoring status. These concentration limits are applied during compliance monitoring to determine whether a corrective action groundwater monitoring program might be necessary.

Concentration limits are *not* proposed for site-specific monitoring parameters (specific conductance, gross alpha, and gross beta) at the B Pond System. These indicator species can only provide an *indication* of the presence of dangerous constituents in the groundwater. They cannot identify the specific constituent(s) that cause the degradation in groundwater quality. The specific constituents would be identified and concentration limits set should compliance monitoring be required. If additional constituents are identified, the groundwater monitoring plan will be revised in accordance with the most updated understanding of the site conditions.

6.6 Point of Compliance

An effective groundwater monitoring network of wells for the B Pond System must account for the peculiar groundwater flow conditions existing at this facility. To ensure interception of any potential contamination the configuration of the network will need to consider not only the degree of areal coverage, but location of potential contamination in the vadose zone and aquifer (from main pond and

B-3-3 ditch operation), and constituents already entrained in the groundwater. More specifically, selection of wells for the revised groundwater monitoring network at the B Pond System is based on:

- Areal distribution of wells in relation to the facility and the hydraulic mound, based on interpretations of groundwater flow directions and rates—flow appears more constrained west of the facility; a relatively uniform spacing is attempted, recognizing that contaminants may potentially still be entrained in groundwater within the bounds of the facility, but with the qualification that the main pond is the most likely source of potential contamination.

- The depth in the aquifer at which the well is screened; as noted in Section 4.0, vertical differences in constituent concentrations are observed and must be accounted for qualitatively in network design.

- The expected life of the well, based on the water level and rate of decline; as discussed in Section 2.2.2, some wells have very limited projected life. Wells in the revised network are selected to optimize the balance between well life and other attributes described here.

- Specific capacity of the well (magnitude of response to pumping); some wells in the historic network were difficult to sample because of poor efficiencies or long purging times. Where possible, these wells were avoided in favor of nearby wells that are otherwise equally acceptable monitoring points.

- Potential for coordination with other monitoring networks (RCRA, sitewide, TEDF).

Using these guidelines, the revised groundwater monitoring network for the B Pond System was derived, as shown in Figure 6.1. The proposed monitoring network for the B Pond System consists of eight wells; the construction details and lithologic logs of these wells are presented in Appendix C. The mounding effect also makes the selection of a true upgradient well for this facility impractical. Therefore, no facility-specific upgradient well is identified, and intra-well comparisons will be performed as described in Sections 6.2 and 6.9.

The point of compliance (POC) is defined in 40 CFR 264.95 and WAC 173-303-645 (6) as a "vertical surface" located at the hydraulically downgradient limit of the waste management area that extends down into the uppermost aquifer underlying the regulated unit. For the B Pond System, the POC will consist of the monitoring wells illustrated in Figure 6.1 (i.e., 299-E26-11, 699-40-36, 699-41-42, 699-42-37, 699-43-43, 699-43-45, 699-44-39B, and 699-40-39). These wells are directly downgradient of the facility, including the regulated portion of the B-3-3 ditch. The wells in Figure 6.1 and/or other wells near the B Pond System (see Figure 1.2) may be used for tracking the plumes of sitewide concern; nitrate, I-129, arsenic, and tritium.

As explained in Section 2.2.2, the groundwater mound that has controlled the hydraulic potential and water levels in wells at the B Pond System is rapidly decaying because of discontinuation of discharges. Eventually, a west-to-east groundwater flow will resume, as before Hanford operations began. As this occurs, some wells in the new network described above may begin to go dry and contamination originating in the 200 East Area will become a concern for groundwater monitoring at the B Pond System. Provisions for an amended configuration to the network will need to be made at that time.

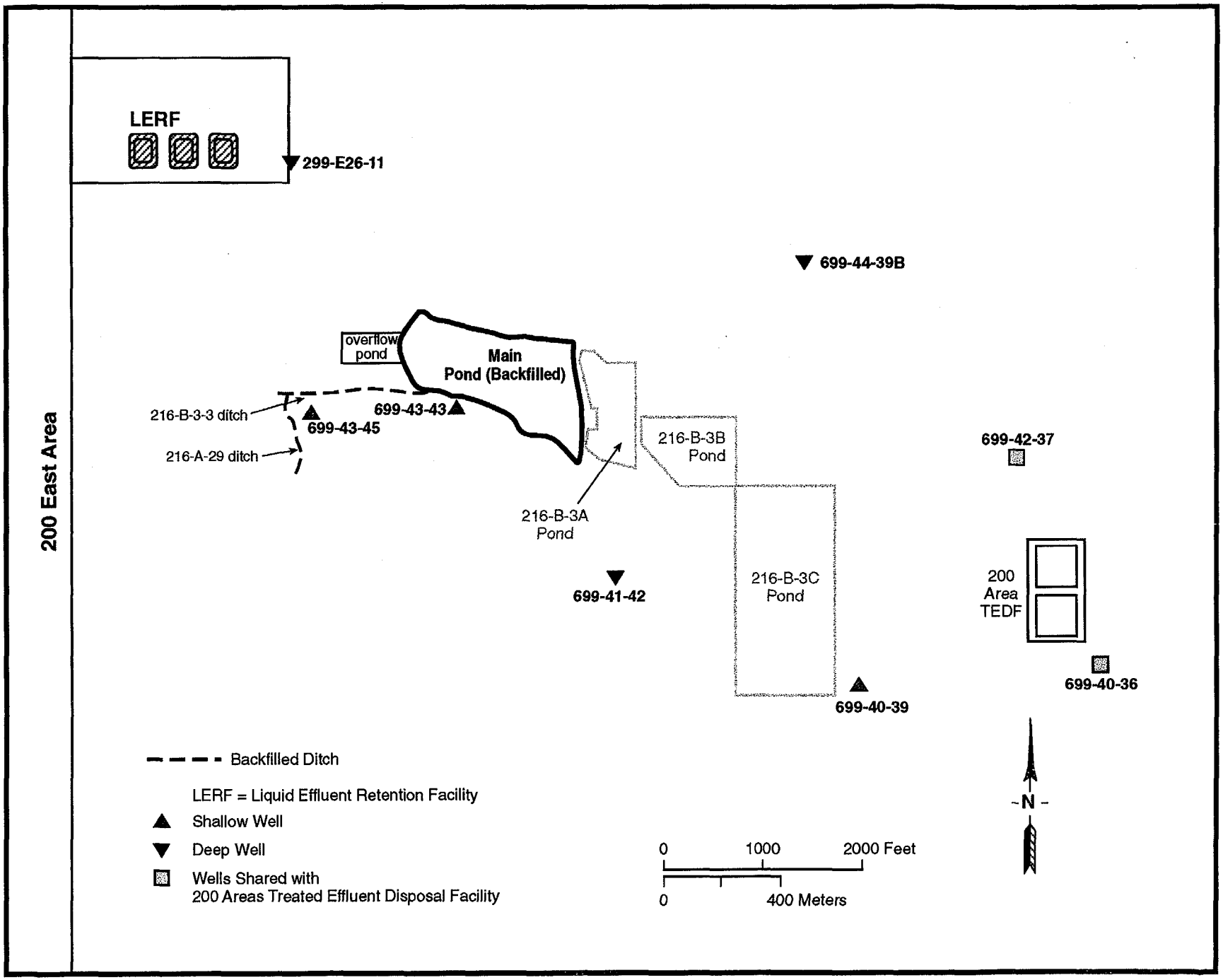

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Figure 6.1. Revised Groundwater Monitoring Network for the B Pond System

6.7 Compliance Period

Typically, groundwater monitoring is required during the active life of the regulated unit and for a period of 30 years following completion of closure activities if not clean closed, although this period may be shortened or extended by the regulatory authority. The compliance period begins when the owner or operator initiates a compliance monitoring program [WAC 173-303-645 (7)(b)]. If the regulated unit undergoes corrective action, then the compliance period will be extended until it can be demonstrated that the applicable limit(s) for constituents in groundwater has not been exceeded for a period of three consecutive years [WAC 173-303-645 (7)(c)].

6.8 Sampling and Analysis

This section describes the sampling and analysis program for the regulated unit, including monitoring parameters, analytical methods, monitoring frequency, and sampling protocols.

6.8.1 Monitoring Parameters

Table 6.1 lists constituents to be analyzed for the regulated unit. This list includes the following:

- the indicator constituents identified in Section 6.4. (Only these constituents of interest to the B Pond System will be used to determine whether statistically significant evidence of contamination has occurred.)

- additional constituents to aid tracking of plume movements (i.e., nitrate, I-129, arsenic, and tritium). Note: these constituents will be coordinated with long-term, sitewide groundwater monitoring efforts.

- additional field parameters routinely acquired at the wellhead (e.g., pH, turbidity, and temperature).

6.8.2 Sampling Frequency

The compliance wells will be sampled for indicator constituents (see column 1 of Table 6.1) at least semiannually during the active life of the regulated unit (including the closure period). Rather than collecting 4 independent samples per sampling event, a single sample will be collected and analyzed (see justification in Section 6.9.1). Samples for nitrate, I-129, arsenic, and tritium will be collected in coordination with long-term sitewide monitoring activities to achieve monitoring objectives in a cost-effective manner.

6.8.3 Sampling Procedures

Groundwater sampling procedures, sample collection documentation, sample preservation and shipment, and chain-of-custody requirements are described in subcontractor operating procedures/manuals

Table 6.1. Constituent List for the B Pond System.

Constituent List		
Indicator Constituents[a]	**Field Parameters**	**Other**
Specific Conductance	PH	Nitrate[b]
Gross Alpha	Turbidity	Tritium[b]
Gross Beta	Temperature	Iodine-129[b]
		Arsenic[b]
(a) Subject to statistical evaluations as described in Section 6.9. (b) Coordinated with long-term sitewide groundwater monitoring activities.		

and in the Quality Assurance (QA) Plan ETD-012, Rev. 0, The Hanford Ground-Water Monitoring Project Quality Assurance Project Plan. Quality requirements for sampling activities, including requirements for procedures, containers, transport, storage, chain of custody, and records requirements, are specified in a Statement of Work (SOW). To ensure that samples of known quality are obtained, the subcontractor is required to use contractor-controlled procedures based on standard methods for groundwater sampling whenever possible. Pacific Northwest National Laboratory (PNNL) will review these procedures for technical quality and consistency. In addition, periodic assessments will be performed by PNNL to further ensure that procedures are followed to maintain sample quality and integrity. A brief description of the sampling requirements is provided below.

Samples are generally collected after three casing volumes are withdrawn or after field parameters pH, temperature and specific conductance have stabilized. Field parameters are measured in a flow-through chamber. Turbidities should be equal to or below 5 NTU (nephlometric turbidity units; 1 NTU = 1 mg/L of solids) prior to sample collection. Sample preservatives are added to the collection bottles in the laboratory prior to their use in the field. Duplicates, trip blanks and field equipment blanks are collected as part of the general quality control program. The sampling and analysis methods and procedures and associated quality control results are described in more detail in Hartman and Dresel (1998).

6.8.4 Analytical Procedures

Procedures for field measurements (pH, specific conductance, temperature, and turbidity) are specified in the manufacturer's manual for each instrument used. The laboratory approved for the groundwater monitoring program will operate under the requirements of current laboratory contracts and will use standard laboratory procedures as listed in the SW-846 (EPA 1986) or an alternate equivalent. Alternative procedures, when used, will meet the guidelines of SW-846, Chapter 10. Analytical methods and quality control for the RCRA groundwater monitoring activities are described in the QA Plan ETD-012, Rev. 0, The Hanford Ground-Water Monitoring Project Quality Assurance Project Plan.

6.9 Statistical Methods

This section proposes statistical evaluation procedures for the B pond detection-level groundwater monitoring program. Statistical evaluation of groundwater monitoring data will comply with requirements set forth in the WAC 173-303-645(8)(h) and (i) final-status regulations. Acceptable statistical methods for a final-status detection-monitoring program includes analysis of variance (ANOVA), tolerance intervals, prediction intervals, control charts, test of proportions, or other statistical methods approved by Ecology [WAC 173-303-645(8)(h)]. The type of monitoring, the nature of the data, the proportions of non-detects, spatial and temporal variations are important factors to consider when selecting appropriate statistical methods. Procedures outlined in the following EPA technical guidance documents and American Society for Testing and Materials (ASTM) standards will be followed:

- *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities - Interim Final Guidance (EPA 1989)*
- *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities - Draft Addendum to Interim Final Guidance (EPA 1992)*
- *Provisional Standard Guide for Developing Appropriate Statistical Approaches for Ground-Water Detection Monitoring Programs (ASTM 1996).*

6.9.1 Approach and Regulatory Basis

As described in Section 6.1, the proposed statistical evaluation method departs from requirements as specified in the interim-status regulations (40 CFR 265 and WAC 173-303-400) and is in compliance with final-status regulations (40 CFR 264 and WAC 173-303-645). Specifically, the requirements of using a t-test (on means) based on quadruplicate measurements of general contamination indicator parameters will not be adopted for the B Pond System for reasons provided below.

The hazardous-waste regulations under RCRA require owners and operators of hazardous-waste facilities to use design features and control features that prevent the release of hazardous waste into groundwater. Regulated units are also subject to the groundwater monitoring and corrective-action standards of 40 CFR Part 264, Subpart F and WAC 173-303-645. These regulations require that a statistical method and sampling procedure approved by the regulator(s) be used to determine whether there are releases from regulated units into groundwater. Default statistical methods and sampling procedures are specified in these regulations; however, alternatives are available as discussed below.

Historically, the default statistical method for detecting release from the regulated unit is *the tests on mean concentrations* between upgradient (background) and downgradient wells. For facilities regulated under the interim-status regulations, a t-test is required to make this determination [40 CFR 265.93(b)]. The owner and operator has the latitude within the interim-status regulations to choose a t-test that will accommodate the data collected. There is much less choice, however, with regard to the data collection

requirement. Four replicate measurements (analyzed on the same sample) must be collected for the general contamination-indicator parameters (specific conductance, pH, total organic carbon, and total organic halide) during each sampling event.

For facilities regulated under the final status regulations, the recommended statistical method (i.e., the default statistical method) at the time of promulgation was ANOVA (EPA 1989, page 4-1 and page 5-3) where the means of different groups of observations are compared to determine whether there are any significant differences among the groups (e.g., background wells and compliance wells). If so, then contrast procedures may be used to determine where the differences lie. Under final-status regulations, two sampling procedures are allowed: 1) a sequence of at least four samples taken at an interval that ensures, to the greatest extent technically feasible, that an independent sample is obtained (i.e., the default sampling procedure); and 2) an alternative sampling procedure proposed by the owner or operator and approved by the regulator(s) that is to be protective of human health and the environment [40 CFR 264.97(g)(1) and (2), WAC 173-303-645 (8)(g)(i) and (ii)].

The minimum number of samples, under the default sampling procedure, that are to be collected each testing period is *four*. This minimum number was selected by the EPA to maintain consistency with the prior requirements (i.e., interim-status requirements using a t-test on means) that specified that the owner or operator must collect one sample from each well and divide it into four replicate samples for laboratory analysis (53 FR 39720). Hence, EPA contended that requiring four samples to be collected from each well for laboratory analysis should not impose an increase in the number of analyses but recognized that there may be an increase in the field sampling costs associated with this sampling procedure. The requirement of four independent samples, therefore, reflected EPA's position (in 1989) of being consistent with interim-status requirements to collect four replicate samples and to use a t-test on mean concentrations as a default statistical method.

The most far-reaching change since 1988 is the extension of groundwater monitoring requirements to solid waste facilities, mandated in the 40 CFR Part 258, Subtitle D regulations. In particular, the solid waste Final Rule of 1991 dropped the four independent samples per monitoring period requirement (only one measurement is required per monitoring event). Another major change included the issuance of an Addendum (EPA 1992) to *Interim Final Guidance on Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities* (EPA 1989). This Addendum reflects more current thinking within the statistics profession and offers a series of currently recommended techniques and updated advice concerning the Interim Final Guidance document (EPA 1992, page 1). One of the revisions is the recommendation of using a two-phased testing strategy (EPA 1992, pages 67-74) that evaluates each sample *individually* rather than relying on a test of the mean concentrations of several independent samples (i.e., the ANOVA procedure). This revision is prompted because the default ANOVA method has proven unsatisfactory for groundwater monitoring applications for the following reasons (see Gibbons 1994, page 260 and EPA 1992, page 67):

1. The ANOVA procedure may have lower power for detecting a narrow plume of contamination that affects only one or two wells in a much larger network (approximately twenty or more comparisons).

2. The ANOVA procedure is more sensitive to spatial variability than to contamination.

3. A significant ANOVA test result will not indicate which well (or wells) is potentially contaminated without further post-hoc comparisons (i.e., comparisons that are found to be of interest after the data were collected).

4. ANOVA procedure is costly. It requires four samples per semiannual event or eight per year versus other methods (e.g., prediction limit, tolerance limit, control limit, etc.) where individual measurement is required per sampling event. In addition, collection of four independent samples at a given well may necessitate a several-month wait if the natural groundwater velocity at that well is low.

In summary, four independent samples may be collected during each monitoring event for facilities regulated under final status because one-way ANOVA can be performed (Davis and McNichols 1994). This requirement was dropped in the solid waste Final Rule of 1991. The EPA 1992 Addendum acknowledges that the one-way ANOVA procedures (parametric and nonparametric) are less attractive. It is desirable to seek alternative strategies (e.g., control charts, tolerance limits, prediction limits, etc.) that allow statistical testing for each new groundwater sample individually as it is collected and analyzed. Furthermore, because each compliance well is compared with the interval limits separately, a narrow plume of contamination can be identified more efficiently than with an ANOVA procedure. That is, no post-hoc comparisons are necessary to find the contaminated wells. The alternative sampling strategy, set out below, is consistent with the EPA 1989 Interim Final Guidance, Addendum to the Interim Final Guidance, and ASTM (1996), but does not require the collection of four independent samples during each monitoring event.

The regulations allow the use of an alternative sampling procedure [40 CFR 264.97(g) (2) and WAC 173-303-645 (8)(g)(ii)] and statistical method, provided they meet the performance standards as specified in 40 CFR 264.97(i) and in WAC 173-303-645(8)(ii). It also should be noted that in referring to "statistical methods" EPA endorsed an approach to groundwater monitoring that evaluates the choice of a level of significance, the choice of a statistical test, the sampling requirement, the number of samples, and the frequency of sampling in their entirety, not by individual components (EPA 1989, page 2-4).

6.9.2 Statistical Evaluation Goals

The goals of statistical evaluation methods proposed for the B Pond System are:

1. to keep the network-wide false-positive rate (across all constituents and wells being tested) at an acceptably low level. (Note that the false-positive rate [or Type I error rate] is the probability that the test will indicate contamination has occurred although no contamination has truly occurred.)

2. to have adequate statistical power to detect real contamination when it occurs.

To achieve the goal of lowering the network-wide false-positive rate, the number of tested constituents should be limited to the most useful indicators (EPA 1992, page 62; Gibbons 1994, page 16); therefore, only the three indicator constituents (see column 1 of Table 6-1) will be subject to statistical evaluations for the B Pond System. Another strategy to lower the overall false-positive rate is to perform

verification sampling to determine whether the statistically significant difference between baseline and compliance-point data is an artifact caused by an error in sampling, analysis, statistical evaluation, or natural variation in groundwater chemistry.

Another goal of the statistical method is to maintain adequate statistical power for detecting contamination. The power of a test depends on several factors, including the background sample size, the type of test proposed, and the number of comparisons (i.e., the false-positive rate). Other factors being equal, the larger the sample size (number of background samples), the larger the statistical power; therefore, the proposed statistical method should use historical groundwater monitoring data (collected under the interim-status) to the greatest extent possible. An evaluation of the power for the proposed testing strategy is presented in Appendix D. The default ANOVA procedures (upgradient/downgradient comparison of the means) are not proposed because the existence of spatial variability invalidates this approach (see following discussions).

There are two general approaches to detecting impact on groundwater quality at a waste disposal facility. The first approach is the traditional upgradient versus downgradient (or inter-well) comparisons where new downgradient monitoring results are compared to a series of n measurements obtained from well(s) that are located upgradient of the facility. The second approach is the intra-well comparisons where new downgradient measurements are compared to their own history (or baseline conditions).

The inter-well comparisons are based on the assumption that the only difference between upgradient and downgradient water quality is the site impact. A high degree of spatial variability is common, and may be complicated by contamination. This condition invalidates upgradient versus downgradient comparison results. A specific conductance time series plot for wells in the proposed B Pond network is presented in Figure 6.2. It can be seen from Figure 6.2 that the mean concentrations vary from ~200 to 375 μmho/cm; however, observations from each well fluctuate little from their respective mean. These features are indicative of the existence of spatial variability because spatial variability affects mean concentrations but typically not the variance, whereas contamination affects both mean concentrations and variance. In contrast, intra-well comparisons completely remove the spatial component of variation from the comparison (i.e., each well is compared to its own history). The intra-well comparisons are, in general, the preferred method for the following reasons (EPA 1989, 1992; ASTM 1996; Gibbons 1994):

- Intra-well comparisons are more sensitive to detect real releases.

- Intra-well comparisons completely eliminate the false-positive indications caused by spatial variability.

However, care must be exercised in selecting a statistical evaluation method. The possibility of previous contamination may make the intra-well comparisons insensitive to detecting changes in groundwater quality on a timely basis. Thus, before selecting a specific statistical method, the conditions that previously existed at the site must be evaluated first.

Because most of the water discharged to the B Pond System in the recent past was river water, which has lower dissolved solids than ambient groundwater, the major chemical composition of groundwater in

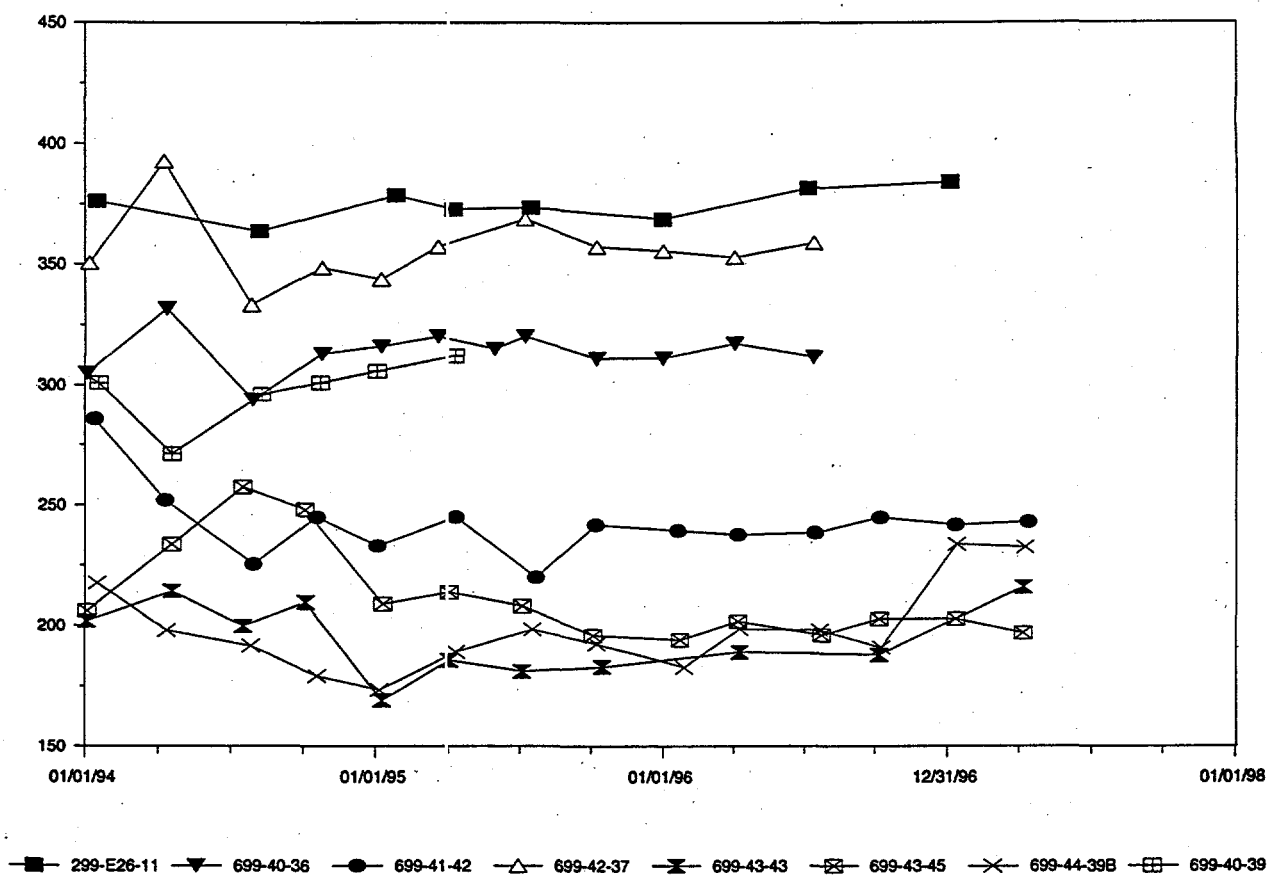

Figure 6.2. Specific Conductance Time Series Plot for B Pond Wells

the 200 East Area has been markedly altered because of dilution. As conditions adjust to the decreased discharge of water, and the change in discharge location (200 Area TEDF), specific conductance will probably increase gradually toward to the ambient natural groundwater background (mean) of ~350 µmho/cm (DOE-RL 1997b; Johnson 1993). Thus, as groundwater returns to a natural background composition intra-well comparisons (for specific conductance) may yield too many false positives. Because of special conditions at the B Pond System, statistical evaluations will use a hybrid approach using intra-well comparisons and Hanford Site background values as follows.

- Specific conductance will be evaluated by comparison to the Hanford site-wide background (DOE-RL 1997b). Intra-well control limits will be used as early warning signals to alert for changing conditions (see Section 6.9.3.2 and Appendix A.5 for actions needed).

- Gross alpha and gross beta will be evaluated by intra-well comparison methods as described by ASTM (1996) and in Section 6.9.4, below.

6.9.3 Evaluation of Specific Conductance Results

As described in previous sections, the property of specific conductance appears to be on an upward trend in groundwater from some B Pond System wells. The upward trend is interpreted as a return to background conditions (see Sections 4.0 and 6.3). Figure 6.3 illustrates this trend in well 299-E26-11. Because this trend likely does not represent an increase caused by contamination, a two-phased approach to statistical evaluation is recommended, as described below.

6.9.3.1 Sitewide Background Comparison

The Hanford Site natural groundwater background value for field-measured specific conductance has been documented in several reports (e.g., DOE 1997b, Johnson 1993). Although the wells used to derive the natural background values are different, the calculated background values are similar. For example, the mean value (± one standard deviation) was 344 ± 83 μmho/cm with a provisional threshold value of 539 μmho/cm in Johnson (1993, Table A-1-2). This threshold value represents the 95% confidence limit on the 95th percentile of the natural background distribution for specific conductance. Alternatively, a mean value of 348 μmho/cm, a 90th percentile of 541 μmho/cm, and a 95th percentile of 614 μmho/cm are provided in DOE-RL (1997b, Table ES-1). Note that these statistics were derived based on assumed lognormal distribution). The sitewide background data set was corrected and modified, as discussed below.

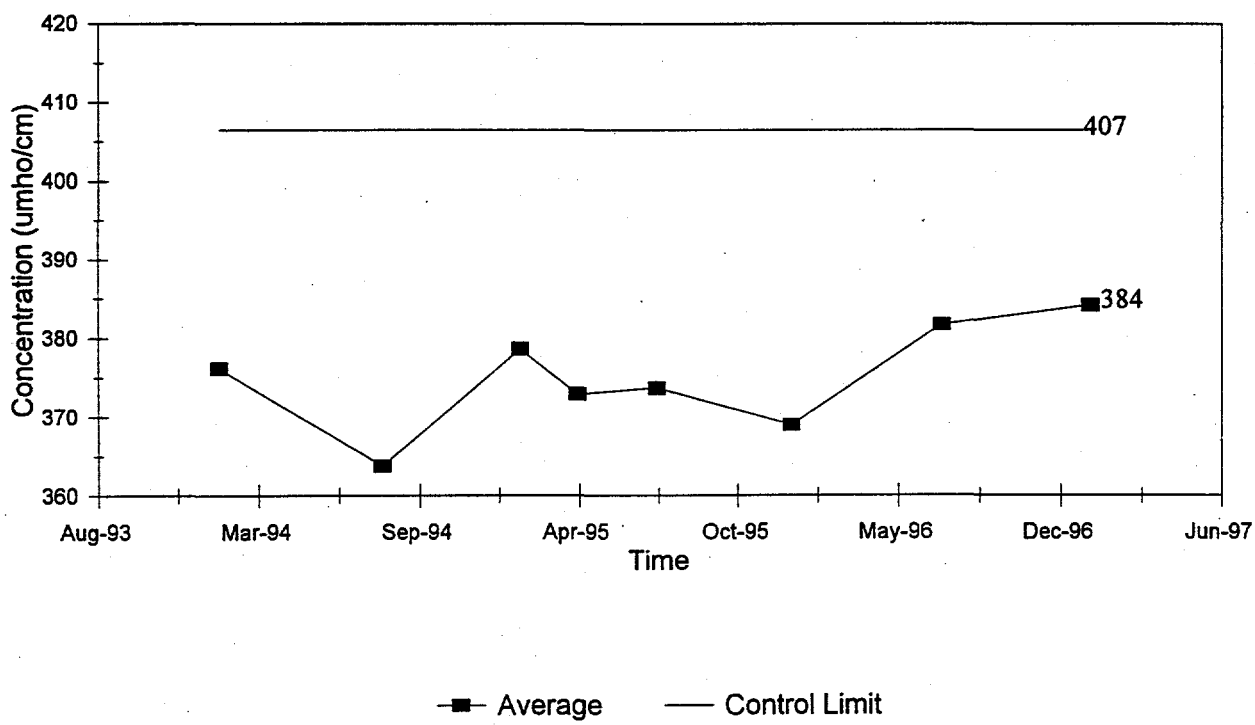

Figure 6.3. Combined Shewhart-CUSUM Control Chart for Specific Conductance in Well-299-E26-11

- The reported maximum value (in Table ES-1, DOE-RL 1997b) of 1,361 μmho/cm, was judged to be unrepresentative of natural background groundwater composition. Upon closer investigation, it was found to be the average of five measurements (528, 520, 499, 429, and 4,830 μmho/cm) obtained from well 699-63-25A during the period from 1/31/91 to 1/9/94.[1] Obviously, the value of 4,830 was a data entry error. A revised average value of 494 μmho/cm was obtained (for well 699-63-25A) after removing the anomalous value of 4,830 μmho/cm.

- In addition, two values as reported in the Hanford sitewide background data were not used. The smallest value of ~150 μmho/cm was obtained from well 699-S40-E14, which is located next to the North Richland wellfield infiltration ponds. The city pumps river water into those ponds to recharge the groundwater. Hence, the datum is not representative of groundwater background. Another value, 662 μmho/cm (which is based on one value) was obtained from well 699-S24-19. This well is located adjacent to the Yakima River. In the past, this well had a compromised completion resulting in communication between aquifers. Thus, it is likely that this well has been impacted by recharge from the Yakima River.

After making adjustments indicated above, the following statistics were obtained: mean value of 346 ± 67 μmho/cm, a 90th percentile of 433 μmho/cm, and a 95th percentile of 465 μmho/cm, and a 95% confidence limit on the 95th percentile of 513 μmho/cm. The value of 513 μmho/cm was chosen to represent *natural background value* because: (1) it is consistent with the definition of background water quality as stated in Ecology (1996a, page 65); and (2) it is also consistent with methods for defining background concentrations as required under the *Model Toxics Control Act Cleanup Regulation,* WAC 173-340 (Ecology 1996b amended). The value of 513 μmho/cm (or its most recent updated value) is the most representative of natural groundwater background conditions for specific conductance, and will be used as the "trigger value" for contamination indication for this parameter at the B Pond System. Verification sampling, however, to confirm the initial exceedence must be conducted before statistically significant evidence of contamination is declared (see Section 6.9.5).

6.9.3.2 Shewhart-CUSUM Intra-Well Comparisons

In addition to comparing with sitewide natural groundwater background, specific conductance results from each well will be plotted and evaluated using the *combined Shewhart-CUSUM control chart*. This method is recommended by EPA (1989 and 1992), ASTM (1996), and statistical professionals (e.g., Gibbons 1994) for intra-well comparisons. This method combines the advantages of Shewhart control chart (sensitive to large and abrupt shifts) with a cumulative sum (CUSUM) control chart (sensitive to small and gradual changes), and allows data from a well to be viewed graphically over time (i.e., to detect changes over time). Discussions of the assumptions, step-by-step procedure, and the performance of this test are presented in Appendix D.

Specific conductance data from each individual well of the B pond network were log-transformed (natural logarithm) and tested for distributional assumptions. Based on results of the Lilliefors test for

[1] Scott Petersen, personal communication.

normality (Conver 1980), it was concluded that the use of lognormal distributions is reasonable. A normal probability plot using specific conductance values (natural logarithmic unit) from well 299-E26-11 is shown in Figure 6.4. A good fit to a straight line verifies the goodness-of-fit test result.

Power curves were prepared by the Statistics Group of PNNL for various decision values (for the combined Shewhart-CUSUM control charts) and compared to EPA reference power curves. Results are presented in Appendix D. Based on the analysis and discussion presented in Appendix D, it is concluded that the combined Shewhart-CUSUM control chart approach with control limits set at 4 sigma units provides the greatest sensitivity for detecting a change with the optimum reduction in false positives, and while maintaining adequate power. Following the procedure outlined in Appendix D, Shewhart-CUSUM control limits were calculated and presented in Table 6.2. It should be noted that in this table (and Tables 6.3 and 6.4) the k and h values of CUSUM test change as the baseline sample size reaches 12 (see Appendix D, Section D.3).

The control limits (presented in Table 6.2) are not the "trigger values" that could elevate the regulated unit from detection to assessment or compliance monitoring status. They are presented as *early warning*

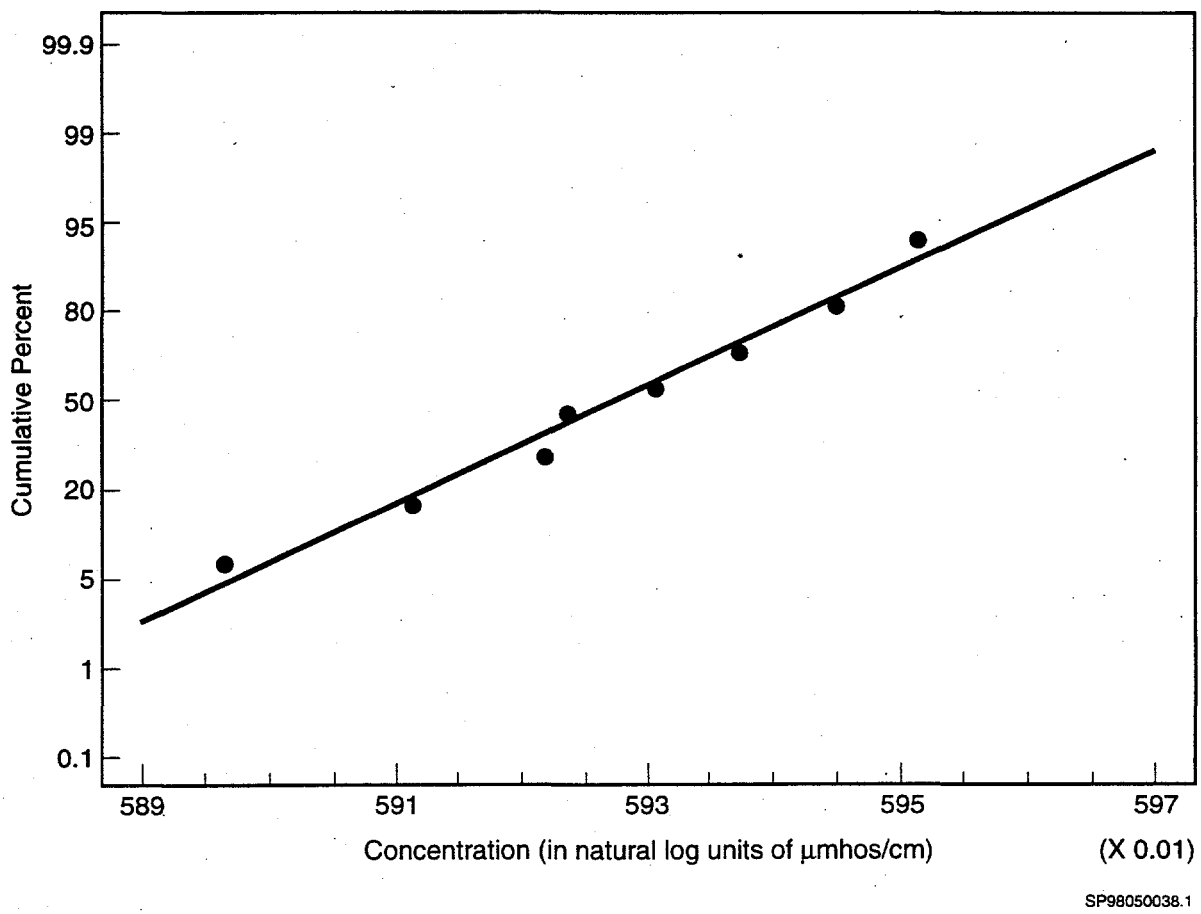

Figure 6.4. A Normal Probability Plot of Specific Conductance in Well 299-E26-11

values. If a future observation (specific conductance) in a B pond monitoring well exceeds its own Shewhart-CUSUM control limit, but is below the trigger value (i.e., the sitewide natural groundwater background of 513 μmho/cm or its most recently updated value), a statistically significant result will not be declared. However, a mini-assessment (ASTM 1996) will be initiated to identify the likely cause, as suggested below.

As noted earlier (see Section 6.9.1), exceedence could be due to upgradient sources. An updated specific conductance map could first be used to assess trends, and to determine whether the triggered well is part of a larger area trend or more localized. If it is not part of a general trend, then major anion and cation composition could be evaluated to see if it is abnormal (non-natural). Stiff diagrams or Piper diagrams could be used to compare natural composition pattern with the triggered well composition. If it has a natural groundwater background composition, then detection monitoring would be continued. If it has a different composition (i.e., sulfate-dominated, nitrate-dominated, etc.), then a local upgradient source could be indicated or the regulated unit might be causing it. The monitoring program would need to be adjusted to determine the cause of the elevated specific conductance and where it is coming from (e.g., local upgradient source or the facility).

Table 6.2. Summary Statistics and Calculated Specific Conductance CUSUM-Shewhart Control Limit for the B-Pond Network

Description	B Pond Monitoring Network							
	2-E26-11	6-40-36	6-41-42	6-42-37	6-43-43	6-43-45	6-44-39B	6-40-39
Baseline Period	01/17/94 – 01/07/97	01/05/94 – 07/16/96	01/14/94 – 04/14/97	01/07/94 – 07/16/96	01/04/94 – 04/08/97	01/11/95 – 04/08/97	01/17/94 – 04/10/97	01/14/93 – 04/12/95
Number of Samples	8	12	13[a]	11	11	10	14	10
Fitted Distribution	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal
Mean[b] (μmho/cm)	375	314	239	356	194	202	198	303
Standard Dev.[b] (μmho/cm)	6.7	9.2	8.8	14.9	15.2	6.6	17.6	13.4
CV (%)	1.8	2.9	3.7	4.2	7.8	3.3	8.9	4.4
Parameters:[c] SCL	4.5	4	4	4.5	4.5	4.5	4	4.5
h	4.5	4	4	4.5	4.5	4.5	4	4.5
k	1	0.75	0.75	1	1	1	0.75	1
$\bar{x}$ (ln μmho/cm)	5.9270	5.7485	5.4711	5.8752	5.2671	5.3090	5.2865	5.7117
s (ln μmho/cm)	0.0179	0.0293	0.0367	0.0417	0.0780	0.0324	0.0887	0.0442
Control Limit[b] μmho/cm)	407	353	277	430	275	234	282	369

(a) Outlier(s) removed.
(b) Based on lognormal distribution unless otherwise specified.
(c) See definitions provided in Appendix D, D.3.

6.9.4 Evaluation of Gross Alpha and Gross Beta Results

Gross alpha and gross beta results will be compared with Shewhart-CUSUM control limits as shown in Table 6.3 and 6.4, respectively. The control limits were derived based on the procedure described in Appendix D. A statistical goodness-of-fit test (i.e., Lilliefors test) was performed to evaluate the data distributions. In general, lognormal distributions were found to be reasonable approximations, except for gross alpha results obtained from well 699-43-43, for which a normal distribution was a better fit. Gross alpha and gross beta data from well 699-40-36 showed short-term spikes around April 1994, which are not representative of normal conditions. These spurious data were not included in the baseline data sets for calculation of control limits because their inclusion would result in artificially high control limits and a higher false negative rate of the statistical test (see ASTM 1996, pages 12-13). Future sampling data from each well will be compared with these limits on a semi-annual basis in accordance with decision rules presented in Appendix A (see A.7). Verification sampling will be conducted to confirm the initial exceedence (of these Shewhart-CUSUM control limits) before a statistically significant evidence of contamination is declared (see Section 6.9.5).

Table 6.3. Summary Statistics and Calculated Gross Alpha CUSUM-Shewhart Control Limit for the B-Pond Network

Description	B Pond Monitoring Network							
	2-E26-11	6-40-36	6-41-42	6-42-37	6-43-43	6-43-45	6-44-39B	6-40-39
Baseline Period	03/20/91 – 07/08/97	01/09/95 – 09/03/97	01/08/93 – 07/24/97	01/22/92 – 09/03/97	11/21/88 – 07/06/95	07/08/91 – 07/23/97	01/08/93 – 10/10/96	07/08/91 – 07/21/95
Number of Samples	13	10	17	19	17	25	14	13
Fitted Distribution	Lognormal	Lognormal	Lognormal	Lognormal	Normal	Lognormal	Lognormal	Lognormal
Mean[(b)] (pCi/L)	2.27	2.48	1.74	5.32	0.92	1.24	1.14	3.10
Standard Dev.[(b)] (pCi/L)	0.84	0.86	1.02	1.46	0.60	0.69	0.61	1.39
CV (%)	37.1	34.9	58.7	27.5	64.9	56.0	53.5	45.0
Parameters:[(c)] SCL	4	4.5	4	4	4	4	4	4
h	4	4.5	4	4	4	4	4	4
k	0.75	1	0.75	0.75	0.75	0.75	0.75	0.75
$\bar{x}$ (ln pCi/L)	0.7568	0.8510	0.4053	1.6353	NA	0.0783	0.0028	1.0378
s (ln pCi/L)	0.3591	0.3388	0.5443	0.2696	NA	0.5221	0.5016	0.4295
Control Limit[(b)] (pCi/L)	9.0	10.8	13.2	15.1	3.3[(d)]	8.7	7.5	15.7

(a) Outlier(s) removed.
(b) Based on lognormal distribution unless otherwise specified.
(c) See definitions presented in Appendix D, D.3.
(d) Based on normal distribution.

Table 6.4. Summary Statistics and Calculated Gross Beta CUSUM-Shewhart Control Limit for the B-Pond Network

Description	B Pond Monitoring Network							
	2-E26-11	6-40-36	6-41-42	6-42-37	6-43-43	6-43-45	6-44-39B	6-40-39
Baseline Period	03/20/91 – 07/08/97	01/09/95 – 09/03/97	01/08/93 – 07/24/97	01/22/92 – 09/03/97	11/21/88 – 07/06/95	12/06/89 – 07/23/97	01/08/93 – 07/22/97	12/05/89 – 07/21/95
Number of Samples	13	10	17	18	21	28	13[a]	16
Fitted Distribution	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal	Lognormal
Mean[b] (pCi/L)	5.94	6.39	7.41	5.69	5.75	4.76	4.68	5.94
Standard Dev.[b] (pCi/L)	1.85	3.18	3.38	2.63	2.08	1.71	2.63	2.10
CV (%)	31.2	49.7	45.7	46.3	36.3	35.9	56.3	35.3
Parameters:[c] SCL	4	4.5	4	4	4	4	4	4
h	4	4.5	4	4	4	4	4	4
k	0.75	1	0.75	0.75	0.75	0.75	0.75	0.75
$\bar{x}$ (ln pCi/L)	1.7353	1.7450	1.9082	1.6413	1.6873	1.4989	1.4056	1.7726
s (ln pCi/L)	0.3046	0.4696	0.4351	0.4404	0.3514	0.3477	0.5246	0.3428
Control Limit[b] (pCi/L)	19.2	47.4	38.4	30.1	22.0	18.0	33.2	22.1

(a) Outlier(s) removed.
(b) Based on lognormal distribution unless otherwise specified.
(c) See definitions presented in Appendix D, D.3.

6.9.5 Verification Sampling

In the case of an initial exceedence (exceeding the trigger value), verification sampling is needed to determine if the exceedence is an artifact caused by an error in sampling, analysis, or statistical evaluation or an actual variation in groundwater chemistry. Verification sampling is an integral part of the statistical methodology and is the best currently available approach to balance false-positive and false-negative decisions in groundwater monitoring applications (Gibbons 1994, page 15). Recent EPA guidance (EPA 1992) encourages the use of re-sampling as a means to reduce the facility-wide false-positive rate.

For the B Pond System, verification sampling will be conducted as follows. If the initial sample result exceeds the "trigger value" (i.e., for specific conductance, a revised site-wide background of 513 µmho/cm is used; for gross alpha and gross beta, Shewhart-CUSUM control limit is used), then a re-sample will be obtained and analyzed for the constituent in question. Adequate time *should* elapse to ensure statistical independence between the original triggering measurement and the re-sample measurement. If the verification result is less than the "trigger value," then detection monitoring will be continued. A statistically significant result will be declared only if the re-sample result is larger than the "trigger value," as described above. Split samples (duplicate samples sent to two different laboratories) will be used in the verification sampling as appropriate (e.g., the magnitude of exceedence is small).

6.9.6 Non-Detects

Non-detects are not expected to occur for the constituents of interest (i.e., specific conductance, gross alpha and gross beta) for the B Pond System. Should the need arise to address non-detects for future constituent(s) of interest, it will be handled using the recommendations stated in the EPA guidance documents (EPA 1989; EPA 1992).

6.9.7 Outliers

An *outlier* is an observation that does not conform to the pattern established by other observations in the data set. Possible reasons for its occurrence include contaminated sampling equipment, inconsistent sampling or analytical procedure, data transcription error, and true but extreme measurements. Statistical methods such as Grubbs' method (Grubbs 1969) for testing of outliers and/or the box-and-whisker plot (Ostle and Malone 1988) may be used.

A new analytical result could be an outlier, perhaps due to a transcription error, sampling error, or analytical error. In such a case, the Shewhart and CUSUM portions of the control chart are affected quite differently. The Shewhart portion of the control chart compares each *individual measurement* to the control limit (i.e., the Shewhart portion does not have memory of what has occurred in the past). In contrast, the CUSUM portion incorporates all previous values in the computation and the *cumulative sum* is compared to the control limit. The effect of an outlier (e.g., an initial value exceeding the control limit but not confirmed by verification sampling), if not corrected, will be included in the future cumulative sum and will invalidate the statistical test. Therefore, when a verification sample result indicates that the initial exceedance is caused by errors in sampling, field measurement, or laboratory analysis, the initial value will be replaced by the verification sampling result (see ASTM 1996, page 13; Gibbons 1994, pages 166-167).

6.10 Determining the Rate and Direction of Groundwater Flow

Depth to water will be measured in the eight B Pond System groundwater monitoring wells during sampling and as part of the sitewide water table elevation process. Maps produced from the sitewide evaluation process will be used to interpret the direction of groundwater flow and to derive the hydraulic gradient for the B Pond System. The gradient, in turn, will be used with estimated values of hydraulic conductivity and effective porosity to calculate flow rate using the Darcy equation.

7.0 Data Management and Reporting

This section describes data-management practices and reporting requirements for the regulated unit. A more exhaustive identification of procedures used can be found in the *QA Plan ETD-012, Rev. 0, The Hanford Ground-Water Monitoring Project Quality Assurance Project Plan.*

7.1 Data Storage and Retrieval

All contract analytical laboratory results are submitted by the laboratory in electronic form to be loaded into the Hanford Environmental Information System (HEIS) database. Hard copy data reports are also received and are considered the record copy of the data. Parameters measured in the field either are entered into HEIS manually or through electronic transfer. Data from the HEIS database may be downloaded to smaller databases, such as the Geosciences Data Analysis Toolkit (GeoDAT) for data validation, data reduction, and trend analysis. Copies of supporting analytical data are sent yearly to PNNL for storage. Field records are stored at PNNL.

7.2 Data Verification and Validation

Verification of analytical data provided by the subcontracted laboratory will be performed in accordance with an internal PNNL procedure, *Verification of Analytical Data (Hardcopy)*. This procedure includes checks for: 1) completeness of hardcopy deliverable; 2) condition of samples upon receipt by the laboratory; 3) problems that arose during the analysis of the samples; and 4) correct reporting of results. The procedure also describes the actions to be taken associated with incomplete or deficient data.

Verification and validation of groundwater chemistry data is performed according to the process as defined in an internal PNNL procedure, *RCRA Groundwater Data Validation and Verification Process.* Data are reviewed quarterly to ensure they are complete and representative. The review includes evaluation of quality control data (e.g., field blanks, duplicates, and laboratory blanks) and a technical review by a project scientist familiar with the hydrogeology of the site. The technical review may include comparison of recent data to historical trends, comparison of related constituents, etc. Suspect data are investigated through the data-review process in accordance with an internal PNNL procedure, a *Data Review Procedure*, and are flagged in the database.

7.3 Reporting

The results of the statistical evaluation will be submitted to Ecology in the form of RCRA quarterly reports and the groundwater monitoring annual report. The statistical results may include a list of groundwater parameters analyzed, detection and/or quantitation limits, and baseline values (e.g., sitewide natural background or Shewhart-CUSUM control limits). If statistically significant evidence of contamination is determined (after the confirmation re-sampling evaluation process) for one or more of the constituents of concern at any monitoring well at the compliance point, and if the owner or operator decides not to make

a false-positive claim, then the following steps will be taken if the B Pond System is brought into the Hanford Facility RCRA Permit (Ecology 1994) and is subject to final-status requirements.

- Notify Ecology in writing within 7 days of the finding indicating which chemical parameters or dangerous-waste constituents have shown statistically significant evidence of contamination.

- Determine whether dangerous constituents are present and, if so, in what concentration.

- The owner or operator may re-sample within one month and repeat the analysis for those compounds detected in the above (i.e., second bullet).

- The dangerous constituents detected, either in the initial analysis or in the second confirmation analysis, will form the basis for compliance monitoring.

- Submit an application for a permit modification to establish a compliance-monitoring program to Ecology in 90 days or within the time agreed to in writing by Ecology.

In case of a false-positive claim, the following procedures will apply:

- Notify Ecology in writing within 7 days of the finding (i.e., exceedence) and indicate that a false-positive claim will be made.

- Submit a report to Ecology within 90 days or within the time agreed to in writing by Ecology. This report should demonstrate that a source other than the regulated unit caused the contamination or that the contamination resulted from an error in sampling, analysis, evaluation, or natural variation in groundwater chemistry.

- Submit an application for a permit modification, if necessary, to make any appropriate changes to the detection-monitoring program within 90 days or within the time agreed to in writing by Ecology.

- Continue to monitor in accordance with the detection-monitoring program.

- Submit an application for a permit modification, if the detection monitoring program is determined to no longer satisfy the requirements [of WAC 173-303-645 (9)], to make any appropriate changes to the program within 90 days or within the time agreed to in writing by Ecology.

Subsequent to a confirmed statistically significant increase revealed by the detection monitoring, the following actions will be taken as long as the B Pond System remains as an interim-status facility.

- Notify Ecology in writing within 7 days of the date of such confirmation that the facility may be affecting groundwater quality.

- Develop and submit to Ecology a groundwater quality assessment plan within 15 days after the above notification, or within the time agreed to by Ecology in writing.

The owner/operator is allowed, in the assessment plan, to institute a short-term sampling and analysis program [referred to as the first determination in 40 CFR 265.93 (d)(5)] to demonstrate that contamination is falsely indicated (e.g., an upgradient source). Based on the results of the first determination, if the owner/operator determines that no hazardous waste or hazard waste constituents from the facility have entered the groundwater, then he may reinstate the detection-level program. If, however, the regulated unit is the source of groundwater contamination, the owner/operator must immediately develop and implement a groundwater quality assessment program.

8.0 Compliance-Monitoring Program

A compliance-monitoring program that satisfies requirements set forth in WAC 173-303-645 (10) will be established for the B Pond System: 1) if groundwater sampling during detection-level monitoring reveals statistically significant evidence of contamination over baseline concentrations for groundwater (see Section 6.8); and 2) if it is brought into the Hanford Facility RCRA Permit (Ecology 1994) and therefore is subject to final-status requirements. If compliance monitoring is required, then the DQO process will be used to guide the selection of constituents of concern, sampling and analysis, statistical methods, etc. If other groundwater constituents indicative of migrating waste products are identified, then the list of groundwater parameters will be revised to include such constituents. In the compliance-monitoring programs, the constituents of concern will be compared to concentration limits such as MCLs or alternate concentration limits. A revised groundwater monitoring plan will be prepared and submitted to Ecology for approval before compliance monitoring is effected.

9.0 Corrective-Action Program

If, at a point of compliance (a well), dangerous constituents of concern are measured in the groundwater at concentrations that exceed the applicable groundwater-concentration limit, Ecology must be notified in 7 days, and an application to modify the permit to include a corrective-action plan must be sent to Ecology within 90 days or within the time agreed to by Ecology. After concurrence is obtained from Ecology, a corrective-action level-monitoring program could be established. The development of a corrective-action level-monitoring program will be initiated by integration of RCRA/CERCLA programs, and will follow guidance in Ecology et al. (1994). A description of the groundwater monitoring plan that is appropriate for a corrective-action program will be prepared and submitted to Ecology when the need for corrective action is first identified.

10.0 References

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Code of Federal Regulations

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40 CFR 264, Code of Federal Regulations, Title 40, Part 264, Subpart F. *Standards for Owners of Hazardous Waste Treatment, Storage, and Disposal Facilities.*

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Appendix A

Application of the Data Quality Objectives Process

Appendix A

Application of the Data Quality Objectives Process

This appendix presents the results of the Data Quality Objectives (DQO) process as applied to development of a sampling and analysis plan (described in Section 6.0 of the main report) for the revised B Pond RCRA groundwater monitoring program. The following sections are based on the seven step process originally devised for use at remedial action sites (EPA 1994).

A.1 Step 1: State the Problem

The regulated unit received radioactive and dangerous waste constituents in the past. The unit is no longer in use (expansion ponds 3A, 3B, and 3C were clean closed) and has been partially stabilized (the main pond and the 216-B-3 Ditch). However, the possibility exists that residual waste may continue to drain from the vadose zone beneath the main pond and B-3-3 ditch into the unconfined aquifer. Thus a site-specific monitoring program is needed to assess post-operational impact of the facility on groundwater quality. The data acquired from the sampling and analysis program developed will be used to:

- provide input for regulatory compliance; and
- support decisions regarding the closure of the 216-B-3 Pond and the adjacent portions of the 216-B-3-3 ditch.

A.2 Step 2: Identify the Decisions

Based on discussions of issues raised during meetings of the DQO process scoping team (the project scientist, project management, groundwater monitoring strategy task lead, and project statistician), it was determined that the sampling and analysis plan for B-Pond will address the following two decisions.

- Are dangerous constituents (or surrogates) from the B Pond System *detected* at the compliance point?
- Are existing wells adequate for detection purposes?

Note that "detected" is defined [in WAC 173-303-645 (2)(I)] as statistically significant evidence of contamination as described in WAC 173-303-645 (9)(g).

A.3 Step-3: Identify Inputs to the Decisions

Decision 1: Are dangerous constituents (or surrogates) from the B Pond System *detected* at the compliance point?

The primary inputs to this decision are as follows.

a. What are the *constituents of interest* (including indicator parameters, where appropriate) based on the conceptual model?

b. For each constituent of interest identified in a), what is the *monitoring objective*?

c. Where is the *point of compliance*? Note that the point of compliance is a vertical surface located at the hydraulically downgradient limit of the waste management area that extends down into the uppermost aquifer underlying the regulated unit [WAC 173-303-645 (6)(a)].

d. What is the groundwater *flow direction*?

e. What is the *compliance period*?

f. What are the applicable *concentration limits*, if any, for constituents of interest identified in a) above?

Questions and inputs identified above are addressed in Sections 5.0 and 6.0 or by reference to supporting documents.

Decision 2: Are existing wells adequate for detection purposes?

This decision is related to the monitoring system as a whole. That is, whether the monitoring system is adequate to detect contamination when constituents of interest have migrated from the waste management area to the uppermost aquifer. The primary inputs to this decision are:

a. Does the monitoring network consist of a *sufficient number* of wells?

b. Are monitoring wells installed at appropriate *locations* and *depths* to yield groundwater samples from the uppermost aquifer to represent the *quality* of background groundwater that has not been affected by leakage from the regulated unit and to represent the quality of groundwater passing the point of compliance? Note that a determination of background quality may include sampling of wells that are not hydraulically upgradient of the waste management area [see WAC 173-303-645 (8)(a)].

c. Are monitoring wells *constructed* to meet the requirements in Parts 1 and 3 of WAC 173-160, *Minimum standards for construction and maintenance of wells*?

d. Are the following *procedures* and *techniques* in place?

- decontamination of drilling and sampling equipment;
- sample collection;
- sample preservation and shipment;
- analytical procedure and quality assurance; and
- chain of custody control.

The inputs identified above are listed to maintain consistency with the DQO process. Except for the item discussed in the following paragraph, input elements are described by documents referenced in the main body of the report.

Monitoring Well Depths and Locations: The locations of monitoring wells and the depths within the aquifer to which these are open requires special analysis. Concentrations of constituents are known to vary with depth in the aquifer. Hence, it is essential that the vertical position of sampling points be considered in a groundwater monitoring network. Key factors requiring evaluation are: 1) The stratigraphic/ geologic controls on groundwater movement in the vadose and saturated zones. Clay and silt-rich strata have been identified above and within the aquifer at the B Pond System. These horizons partially control infiltration and groundwater flow. 2) The location and magnitude of the hydraulic driving force(s) affecting the B Pond System; Groundwater flow is essentially radial, with the apex of the hydraulic potential field located somewhat east of the main pond. 3) Observed vertical differences in groundwater chemistry; systematic and nonsystematic differences are observed between wells pairs screened at different horizons within the aquifer. Some of the differences may be due to changes in discharge rates to the facility (and, thus, the driving forces). Other differences may involve transport characteristics of specific constituents in the waste stream.

These factors are acknowledged in the design of the B Pond System well network. The effects of the factors are addressed by the selection of both depth and areal coverage (horizontal location) of the wells.

A.4 Step 4: Define the Boundaries of the Decisions

The "spatial" boundary for this regulated unit is both *regional* (i.e., 200 East Area) as well as *site-specific* (i.e., pertains to boundary of the regulated unit) depending on the stated monitoring purpose and how this will be achieved in an efficient and cost-effective manner. Based on the conceptual model depicted for the B Pond System (see Section 5.0), specific conductance, gross alpha, and gross beta were selected as the constituents of interest for the B Pond System. These indicators will be statistically evaluated at each point of compliance, on a *site-specific* scale, to detect whether chemical/radioactive parameters or dangerous constituents from the regulated unit have impacted groundwater beneath the site. Nitrate, I-129, arsenic and tritium were identified as contaminants of concern existing in groundwater that could be associated with B Pond operations. Because these constituents are also associated with existing widespread sitewide plumes, they will be monitored, on a *regional* scale, to track to the movement of the

plumes through coordination with long-term, sitewide groundwater monitoring efforts. Statistical evaluations designed for detecting leakage from the facility will not be performed. The "temporal" boundary for purposes of this project is defined as the active life of the unit (including any waste-management activity before permitting and during the closure period). Typically, groundwater monitoring is required for a period of 30 years following completion of closure activities (if not clean closed), although this period may be shortened or extended by the regulatory authority.

A.5 Step 5: Develop Decision Rules

The following decision rules are formulated as if-then statements in accordance with the DQO process. A generic form is presented here. More specific decision rules are provided in the last step of the DQO process (i.e., optimization). Furthermore, it is assumed that the inputs related to the network and constituents of interest are adequately addressed in Sections 5.0 and 6.0 or by reference to supporting documents. Thus, only the primary decision (decision 1) concerning *detection* of dangerous waste constituents and or their surrogates (gross alpha, gross beta or specific conductance) is considered here. Specifically, these decision rules will be applicable to those constituents of interest to be monitored on a site-specific scale and which are subject to statistical evaluations (e.g., specific conductance, gross alpha, and gross beta).

Decision 1: Are dangerous waste constituents (or surrogates) from the B Pond System detected at the point of compliance?

If the computed groundwater statistic, which uses data for any point-of-compliance well for any chemical parameter or dangerous waste constituents, provides **statistically significant evidence** of contamination over background or baseline concentrations, *and* this result is confirmed by verification sampling (resample the triggering well), **then** determine if the regulated unit is the source of groundwater contamination; otherwise, continue detection monitoring. For example, it will first be determined if an upgradient or residual groundwater source from past operations could account for the detection. If an upgradient or residual source can account for the detection, then no further action is indicated. If the regulated unit is the source of groundwater contamination, then initiate compliance monitoring. Otherwise, continue detection monitoring.

Before a thorough assessment-level (or compliance-level) monitoring effort is initiated, the following actions are needed:

Actions: The initial response to investigating the nature and extent of apparent contamination from the regulated unit would be to determine the specific constituent(s) responsible for the increase (i.e., if gross beta, gross alpha, or specific conductance are exceeded). If Sr-90 (a major contaminant of concern from early B pond operations) accounts for anomalous gross beta, then breakthrough to groundwater and/or migration of contamination to the monitoring well may be indicated. If elevated gross alpha occurs, samples would be analyzed for uranium. If uranium accounts for the anomalous gross alpha, the unit is the assumed source. Likewise, if specific conductance exceeds "trigger" limits, an evaluation of the major cation/anion composition would be made. If subsequent analyses indicate that the increase is due to nitrate (or sulfate), the regulated unit could be the cause. A cation/anion composition similar to

natural groundwater would be indicative of a specific conductance increase due to the gradual replacement of pond water (Columbia River water) and groundwater mixtures with ambient upgradient groundwater.

If the above analyses indicate that the B Pond System may be the origin of elevated parameters, subsequent actions may include evaluation of possible driving forces (e.g., nearby leaking utility line, effects of 3C pond discharges, etc.) or similar events at a nearby unit.

If contamination is detected, and is clearly attributable to the B Pond System, then the clean closure option could be impacted, unless there is a clear cause and effect explanation for which corrective action can be taken (i.e., repair of a water line, surface runoff control, infiltration barrier, etc.). If no anomalies attributable to B pond are observed during the interim between the present and the scheduled closure date, then the monitoring data will support a decision to clean close the unit.

Also, a 30-year post-closure monitoring program may be required if clean closure is disallowed (i.e., because of continuing groundwater contamination attributable to this unit).

A.6 Step 6: Specify Acceptable Decision Errors (Uncertainty)

The goals of statistical evaluation methods proposed for the B Pond System are:

1. To keep the network-wide false-positive rate (across all constituents and wells being tested) at an acceptably low level; and

2. To have adequate statistical power (= 1 - the false negative rate) to detect real contamination when it occurs.

The desired sitewide false-positive rate (covering all wells and constituents) could be achieved by limiting the number of tested constituents to the most useful indicators and by performing verification sampling to confirm the initial exceedence(s). The power of a statistical test can be improved by a variety of methods, such as adequately characterizing the hydrogeology and the fate and transport characteristics of potential contaminants at the site, properly locating monitoring wells, increasing sample sizes, and reducing measurement variability by using proper analytical, quality control, and quality assurance procedures (see 53 FR 39720). Narratives in the main body of the report address these components.

Following EPA recommendation (EPA 1992, page 64), a goal of keeping sitewide *false positive rate* of approximately 5% for each monitoring period is judged to be adequate for the B Pond System. The other goal is to maintain adequate power for detecting contamination. For this evaluation, the EPA reference power curves (see EPA 1992, page B-6, reproduced here as Figure A-1) will be used. If the power of a proposed test strategy is comparable to the EPA reference power curves then it is judged to have adequate power.

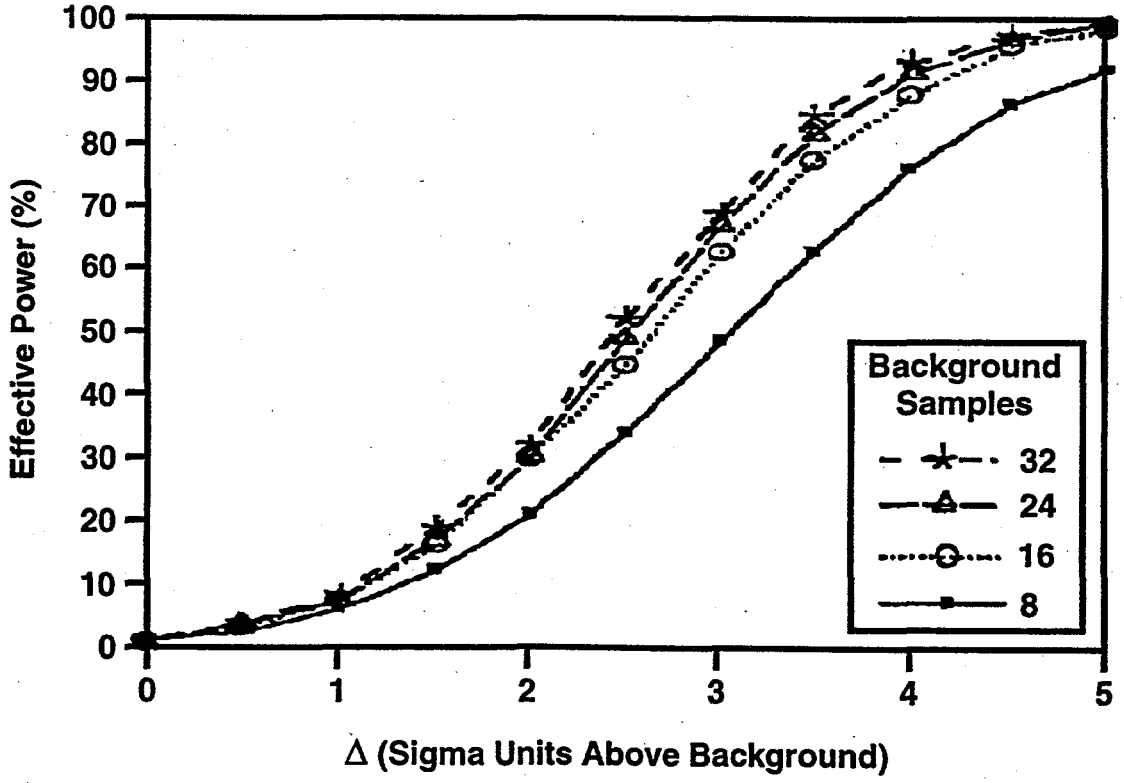


Figure A.1. EPA Reference Power Curves

The power of the proposed testing strategy for the B Pond System was evaluated using power curves generated by PNNL's Statistics Group. Results are presented in Appendix D. The most conservative case of a contamination scenario, which affects only a single constituent in a single well (i.e., like "finding a needle in a haystack"), was used for comparisons with EPA reference power curves.

A.7 Step 7: Optimization

The optimization of the monitoring plan is achieved primarily through:

a. Integrating groundwater monitoring activities with sitewide efforts for tracking movement of existing contaminant plumes, where appropriate (e.g., arsenic, tritium, nitrate, and I-129).

b. Limiting the number of tested constituents to the most useful and cost effective indicators (e.g., gross alpha, gross beta, and field specific conductance).

c. Performing verification sampling to confirm any initial exceedence(s) thus reducing false positive error rate.

d. Following guidance in ASTM (1996) and EPA (1992), seek alternative sampling and statistical methods that balance site-wide false positive and false negative error rates, thereby potentially achieving significant cost savings. For example, instead of using the default statistical method (analysis of variance method for detection purpose) which needs 4 independent samples per sampling event, an alternative method which needs only one sample per sampling event, is proposed [see item f below]. By this method, contamination from the regulated unit will be detected on a more timely basis because the test is applied to individual measurement which does not necessitate a waiting period to obtain four independent samples.

e. Evaluate power of various testing schemes and select the one that provides the greatest sensitivity for detecting a change with the optimum reduction in false positives and in the mean time maintains adequate power (see Appendix D).

f. Incorporating site-specific conditions into the decision rules (used for statistical evaluation) as described below.

Because of unique hydrologic conditions (radial flow) at B pond, statistical evaluations based on comparison between analytical results from downgradient wells and background levels established in an upgradient well(s) cannot be used. As solution to this problem, a hybrid approach using intra-well comparisons and Hanford Site background values will be employed, as follows:

- Specific conductance will be evaluated by comparison to the Hanford sitewide background (DOE 1997a). Intra-well control limits will be used to track the recovery of groundwater to natural conditions, and to ensure the goals of the monitoring plans are met

- Gross alpha and gross beta will be evaluated by intra-well comparison methods as described by ASTM (1996)

Specifically, the decision rules are:

1. If a future measurement of **specific conductance** at the point of compliance is greater than the upper 95% confidence limit on the 95th percentile calculated (based on a log-normal distribution) using the sitewide background data set (modified, or updated periodically as appropriate, to represent a 200 Areas background composition) and if this result is confirmed by verification sampling (i.e., re-sampling the triggering well[s]), then determine if the regulated unit is the source of the contamination and if so, initiate compliance monitoring. If an upgradient or residual source from past operations can account for the detection, then no further action is indicated and continue detection monitoring.

2. If a future measurement of **gross alpha or gross beta** at any point of compliance (well) is greater than the respective Shewhart-CUSUM control limit and if this result is confirmed by verification sampling (i.e., re-sampling the triggering well[s]), then determine if the regulated unit is the source of the contamination, and if so, initiate compliance monitoring. If an upgradient or residual source from

past operations can account for the detection, then no further action is indicated and continue detection monitoring.

In addition to comparing with sitewide natural background, conductivity results will be plotted and evaluated using the *combined Shewhart-CUSUM control chart*. If future observations for specific conductance in any of the B Pond System network wells exceeds its own Shewhart-CUSUM control limit but is below the trigger (i.e., the sitewide natural background), a statistically significant result will not be declared. However, a mini-assessment could be initiated to identify the likely cause (see Section 6.0).

Based on the foregoing considerations, an optimized sampling and analysis schedule that describes sample frequency, statistical evaluation methods, the number of samples needed, etc., is shown in Table A.1. The specific analytes listed are those identified in the main text. Integration of the site-specific monitoring program for the B Pond System with long-term sitewide monitoring is one aspect of the optimization. The proposed sampling and analysis is both cost effective and meets data quality objectives.

Table A.1. Summary of an Integrated Sampling and Analysis Plan Proposed for the B Pond Monitoring System

Responsible Program	Constituent of Interest	Monitoring Objective	Sample Frequency per Sampling Event	Number of Samples	Subject to Stat. Evaluation?	Trigger
B Pond System[a]	Specific Conductance	Detection[c]	Semi-annually	1	Yes	Sitewide Natural Background
	Gross Alpha	Detection[c]	Semi-annually	1	Yes	Control Limit[f]
	Gross Beta	Detection[c]	Semi-annually	1	Yes	Control Limit[f]
	Field pH	Supplemental[d]	Semi-annually	NA[e]	No	NA
	Temperature	Supplemental[d]	Semi-annually	NA[e]	No	NA
	Turbidity	Supplemental[d]	Semi-annually	NA[e]	No	NA
Sitewide Monitoring[b]	Nitrate	Plume Tracking	TBD	TBD	No	NA
	Tritium	Plume Tracking	TBD	TBD	No	NA
	Arsenic	Plume Tracking	TBD	TBD	No	NA
	Iodine-129	Plume Tracking	TBD	TBD	No	NA

(a) Applicable to all wells in the B pond network; constituents of interest may be expanded based on future needs.
(b) Monitoring wells, sample frequency, and number of samples per sampling event will be identified based on need.
(c) See definition in Appendix B (Step 2).
(d) Field parameters.
(e) Not applicable, continuous readings are recorded during purge and sampling cycle.
(f) Combined Shewhart-CUSUM control limits (for each well) are shown in Tables 6.8-2 and 6.8-3 for gross alpha and gross beta, respectively.
TBD = to be determined.
NA = not applicable.

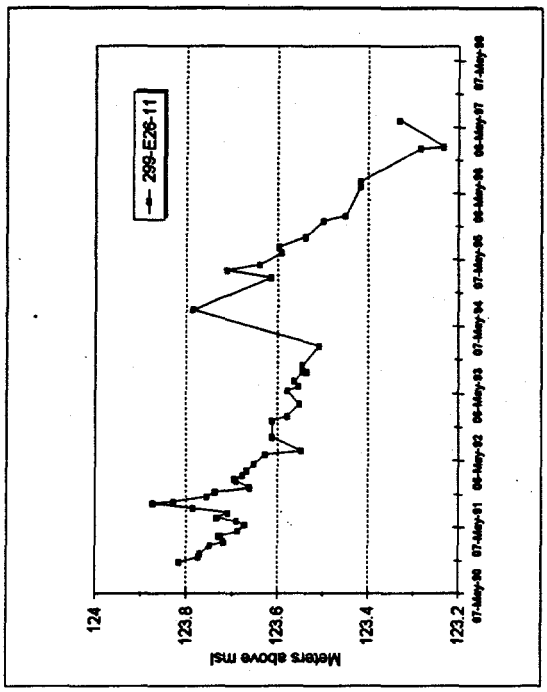
Appendix B

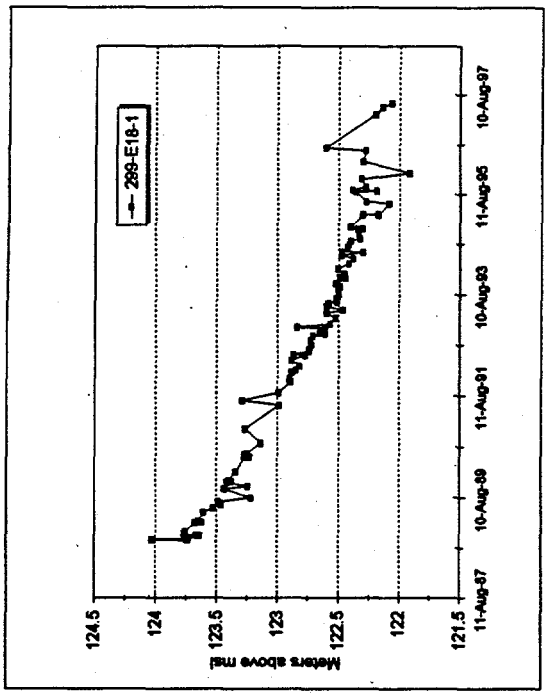
Hydrographs of Wells in the 216-B-3 Pond System Groundwater Monitoring Network

Appendix B

Hydrographs of Wells in the 216-B-3 Pond System Groundwater Monitoring Network

The hydrographs in this appendix incorporate all available data for the 25 wells in the original B Pond System network, and well 299-E26-11, which is included in the revised network. The most recent data are for June 1997, although measurements for some wells end in late 1996. Data points determined to be erroneous have been removed in some plots.


299-E26-11
Meters above msl
124
123.8
123.6
123.4
123.2
07-May-90
07-May-91
06-May-92
06-May-93
07-May-94
07-May-95
06-May-96
06-May-97
07-May-98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123.5
123
122.5
122
121.5
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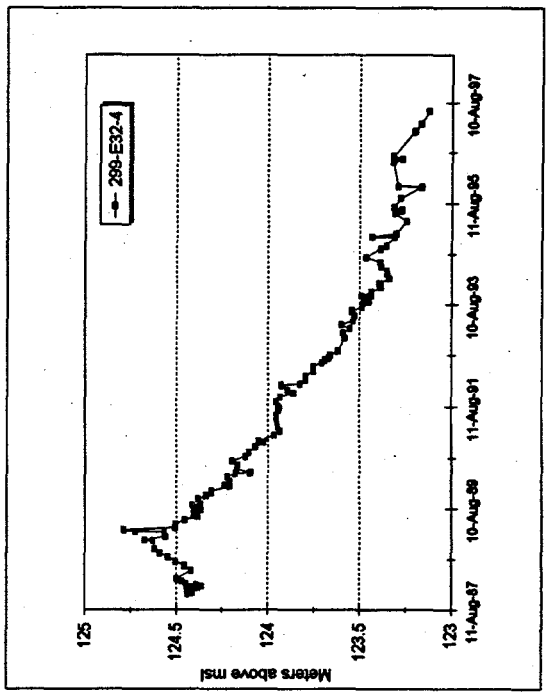
10-Aug-89
11-Aug-91
10-Aug-93
11-Aug-95
10-Aug-97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Meters above msl
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123.5
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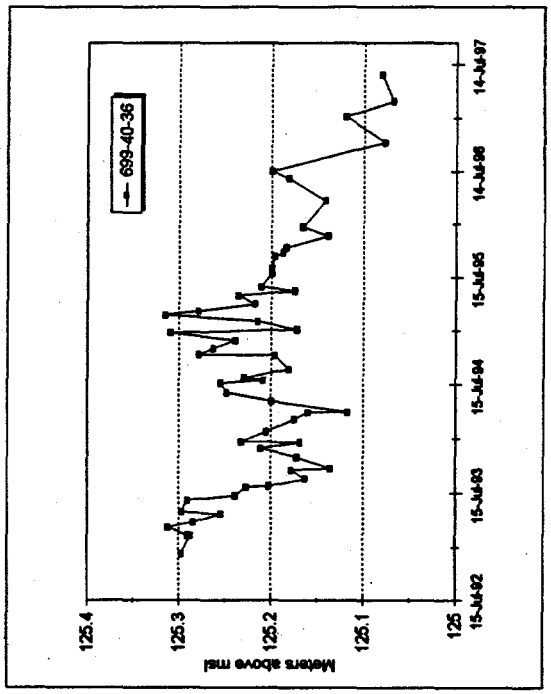
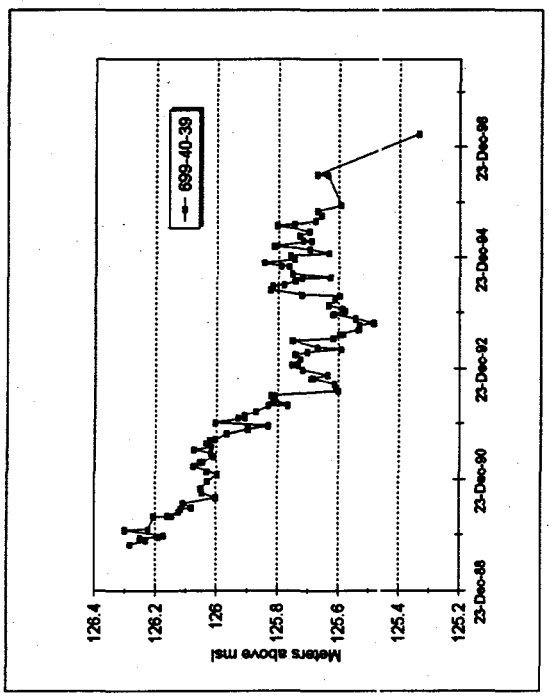
10-Aug-97


699-40-36
Meters above msl
125.4
125.3
125.2
125.1
125
15-Jul-92
15-Jul-93
15-Jul-94
15-Jul-95
14-Jul-96
14-Jul-97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Meters above msl
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126.2
126
125.8
125.6
125.4
125.2
23-Dec-88
23-Dec-90
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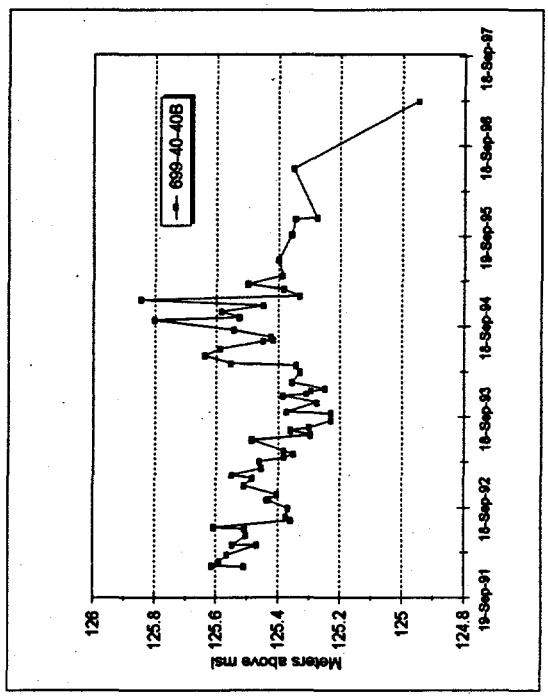
23-Dec-94
23-Dec-96


699-40-40B
Meters above msl
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125.6
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125.2
125
124.8
19-Sep-91
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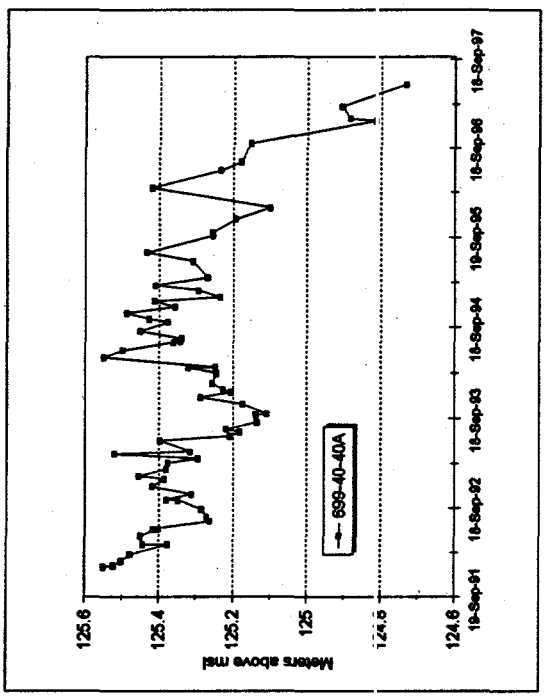
19-Sep-97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Meters above msl
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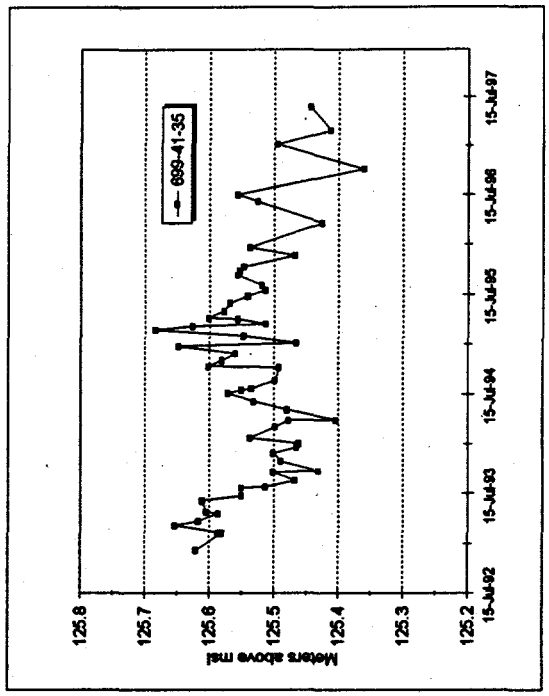
19-Sep-96
19-Sep-97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125.7
125.6
125.5
125.4
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125.2
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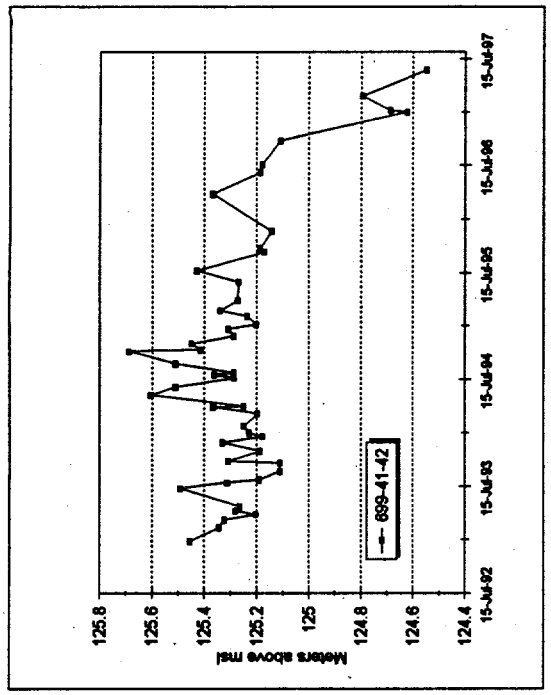
15-Jul-96
15-Jul-97


Meters above msl
125.8
125.6
125.4
125.2
125
124.8
124.6
124.4
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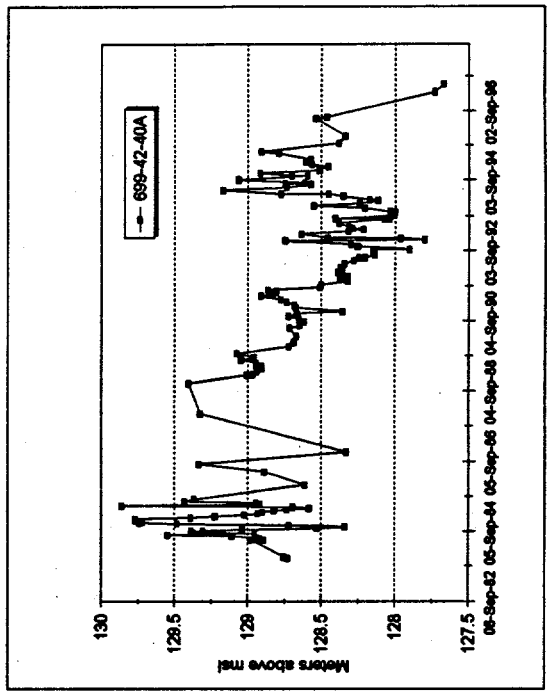
15-Jul-95
15-Jul-96
15-Jul-97
699-41-42


Meters above msl
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129.5
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128.5
128
127.5
06-Sep-82
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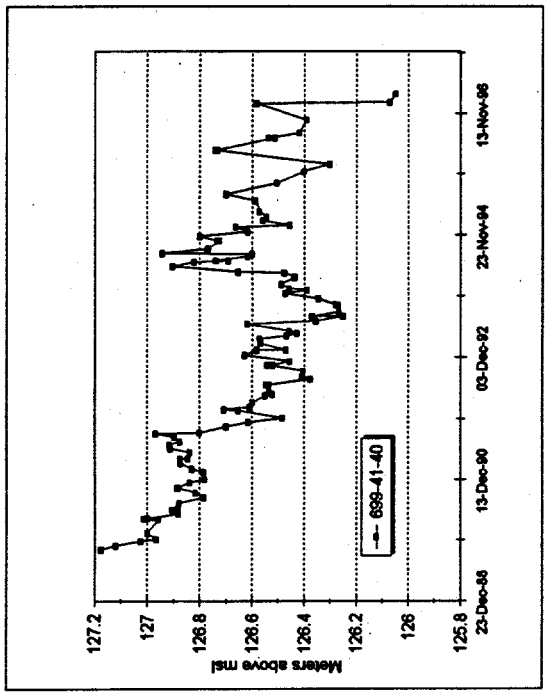
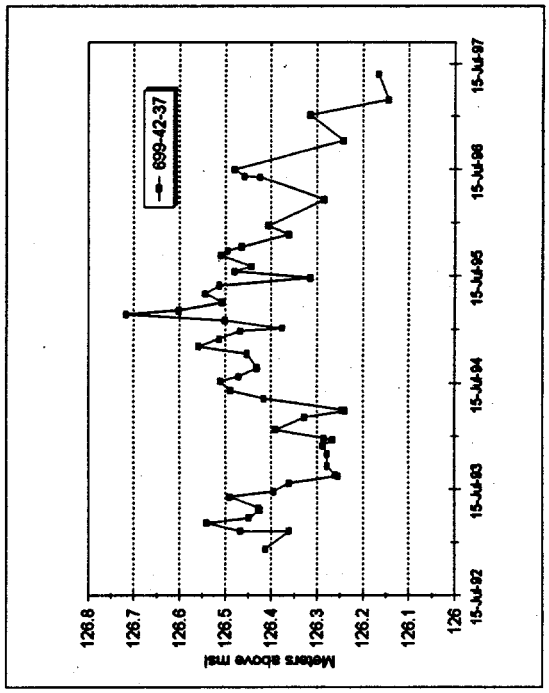
03-Sep-94
02-Sep-96
699-42-40A


Meters above msl
127.2
127
126.8
126.6
126.4
126.2
126
125.8
23-Dec-88
13-Dec-90
03-Dec-92
23-Nov-94
13-Nov-96
699-41-40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126.7
126.6
126.5
126.4
126.3
126.2
126.1
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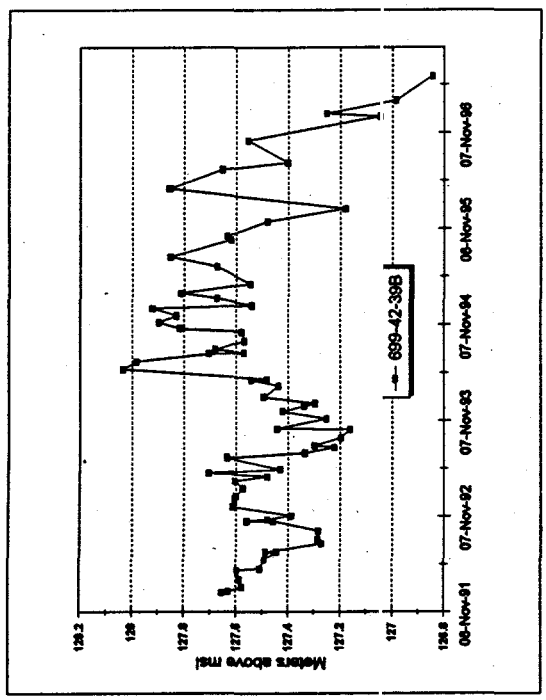
15-Jul-97
699-42-37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Meters above msl
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128
127.8
127.6
127.4
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127
126.8
06-Nov-91
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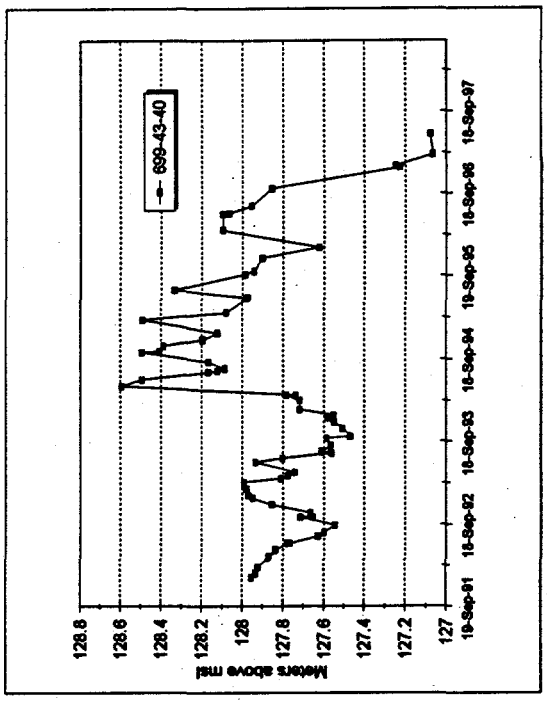
07-Nov-94
06-Nov-95
07-Nov-96


699-43-40
Meters above msl
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128.6
128.4
128.2
128
127.8
127.6
127.4
127.2
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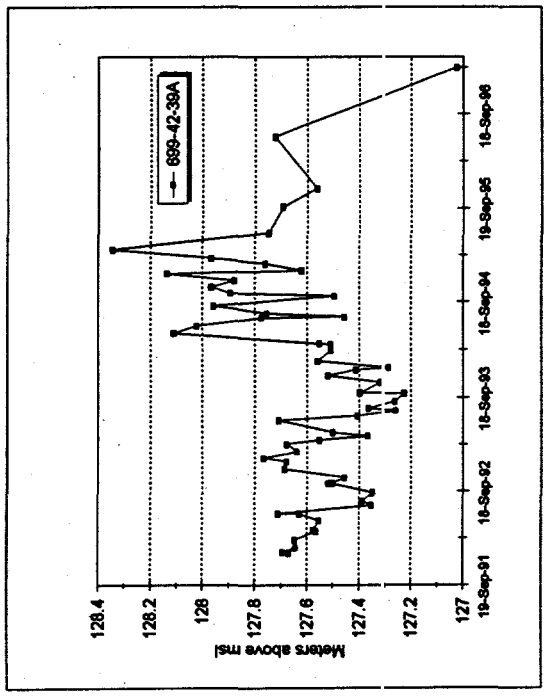
19-Sep-91
19-Sep-92
19-Sep-93
19-Sep-94
19-Sep-95
19-Sep-96
19-Sep-97


699-42-39A
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128.2
128
127.8
127.6
127.4
127.2
127
19-Sep-91
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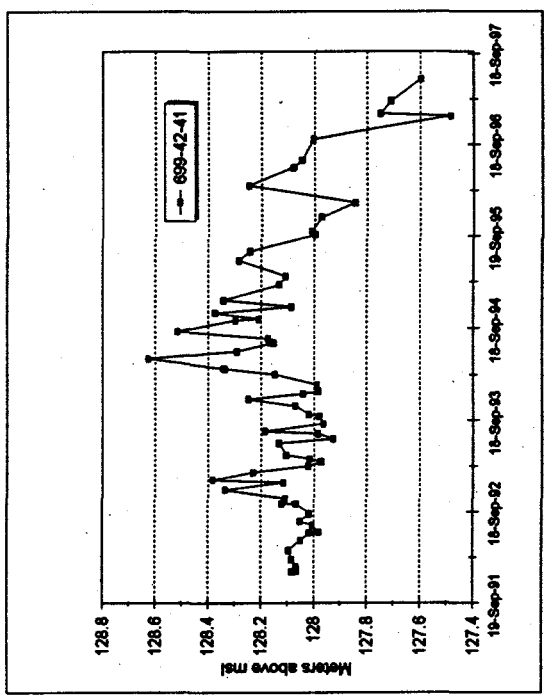
19-Sep-95
19-Sep-96


699-42-41
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128.4
128.2
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127.8
127.6
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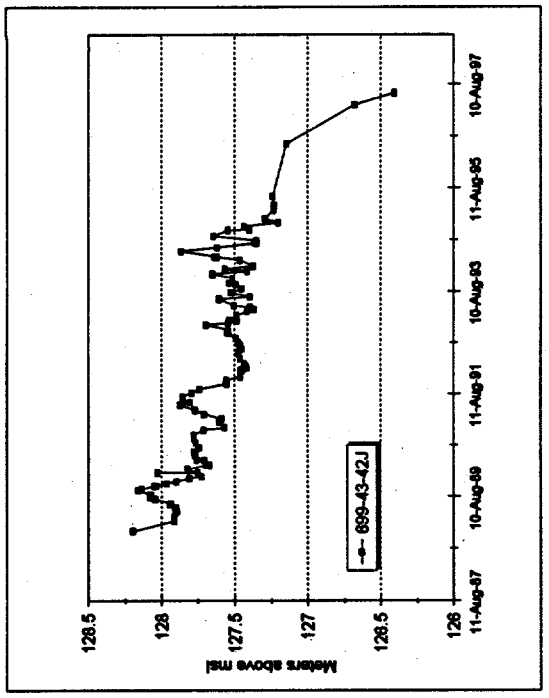
19-Sep-96
19-Sep-97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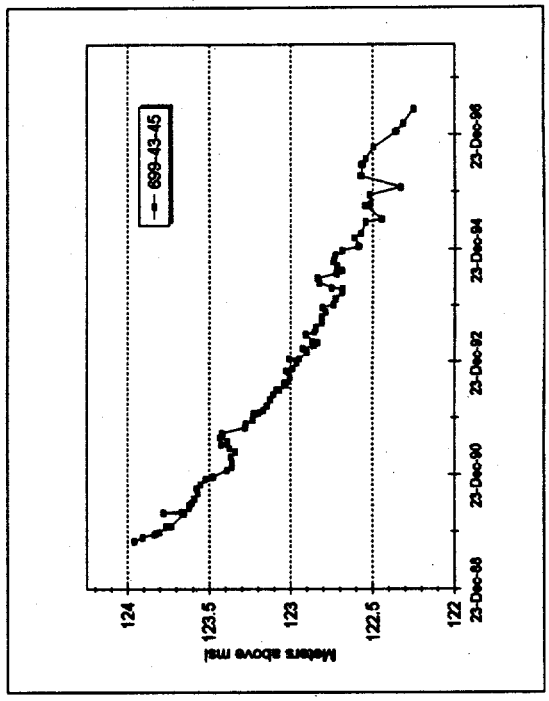
10-Aug-97
699-43-42J


Meters above msl
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122.5
122
23-Dec-88
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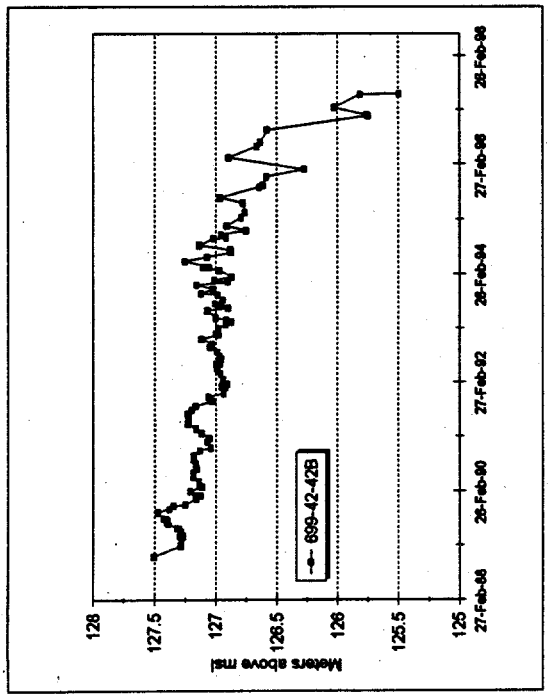
23-Dec-92
23-Dec-94
23-Dec-96
699-43-45


Meters above msl
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127
126.5
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125.5
125
27-Feb-88
26-Feb-90
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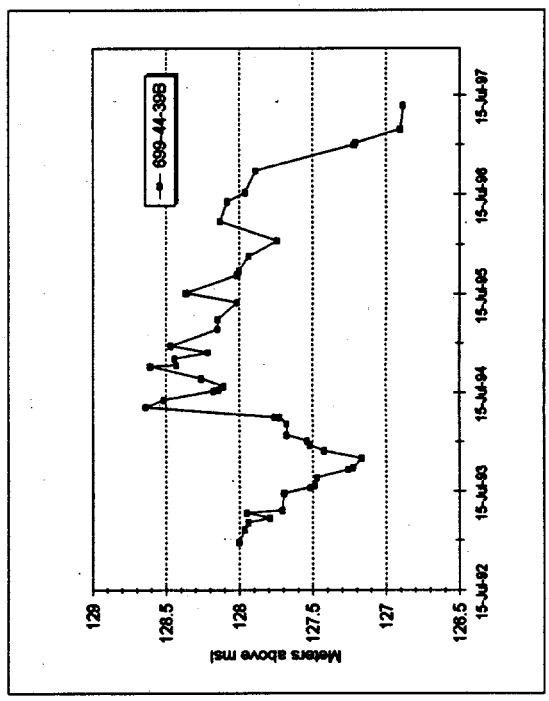
26-Feb-94
27-Feb-96
26-Feb-98
699-42-42B


Meters above msl
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127.5
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15-Jul-92
15-Jul-93
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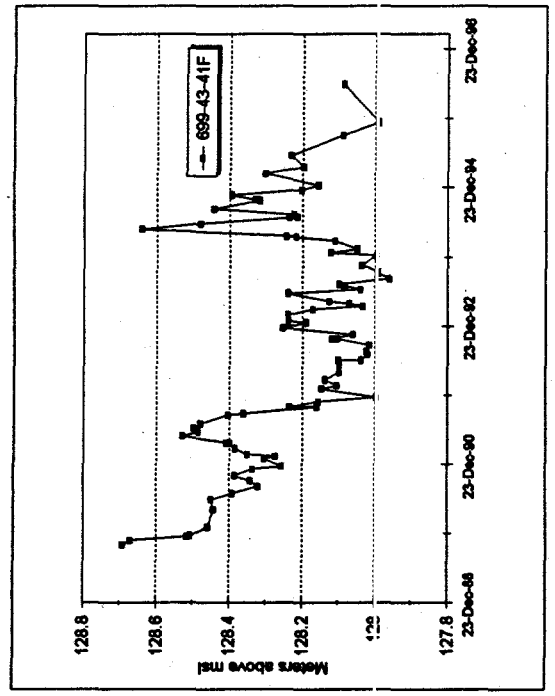
15-Jul-97
699-44-39B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Meters above msl
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127.8
23-Dec-88
23-Dec-90
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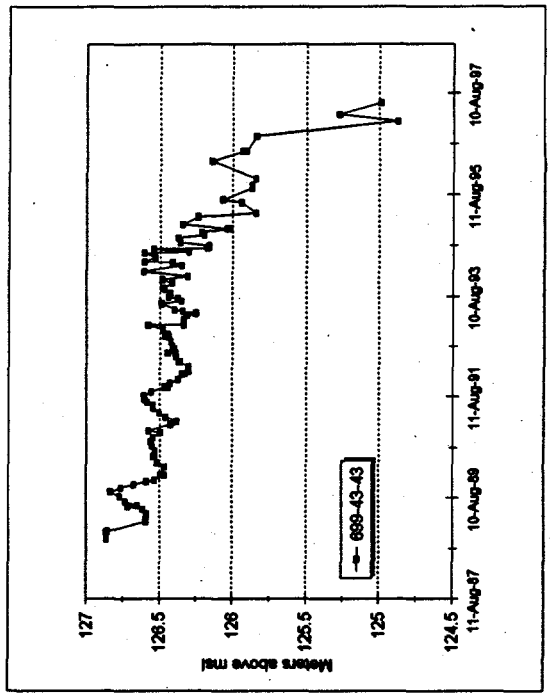
23-Dec-94
23-Dec-96


699-43-43
Meters above msl
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125.5
125
124.5
11-Aug-87
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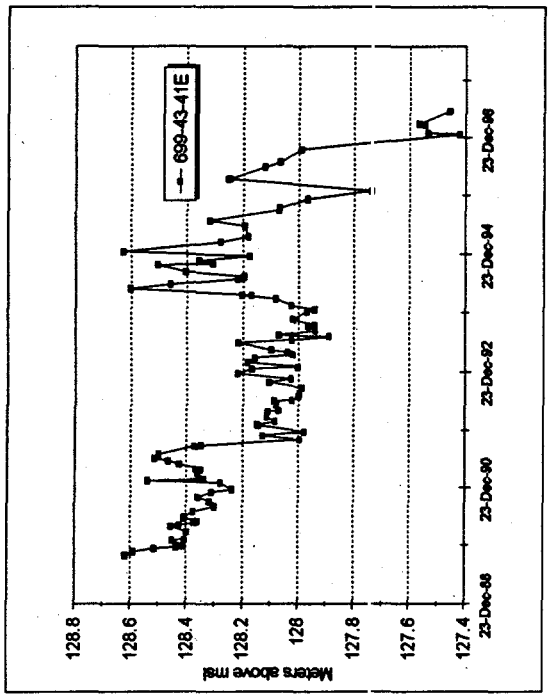
11-Aug-91
10-Aug-93
11-Aug-95
10-Aug-97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127.4
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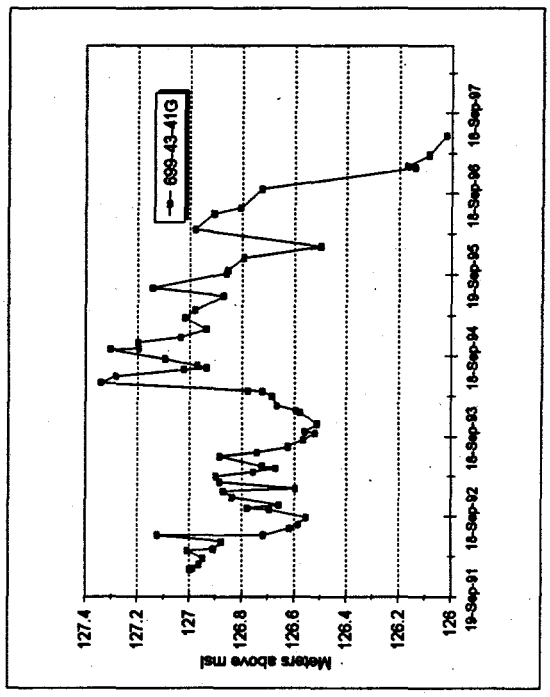
23-Dec-94
23-Dec-96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Meters above msl
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126.8
126.6
126.4
126.2
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19-Sep-91
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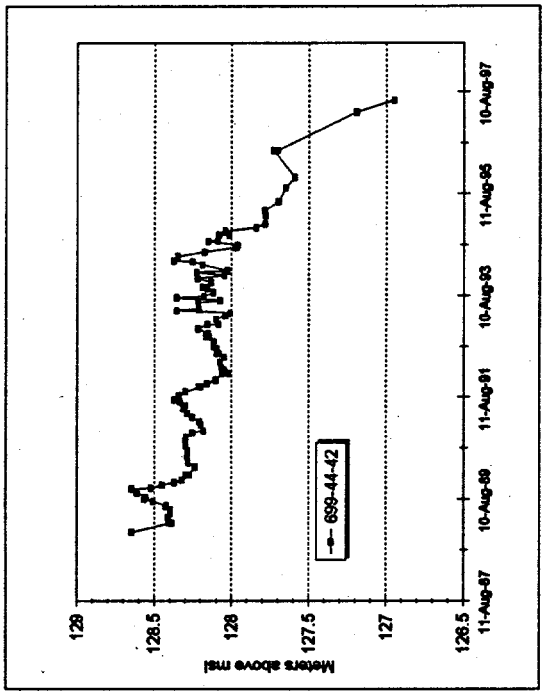
18-Sep-96
18-Sep-97


Meters above msl
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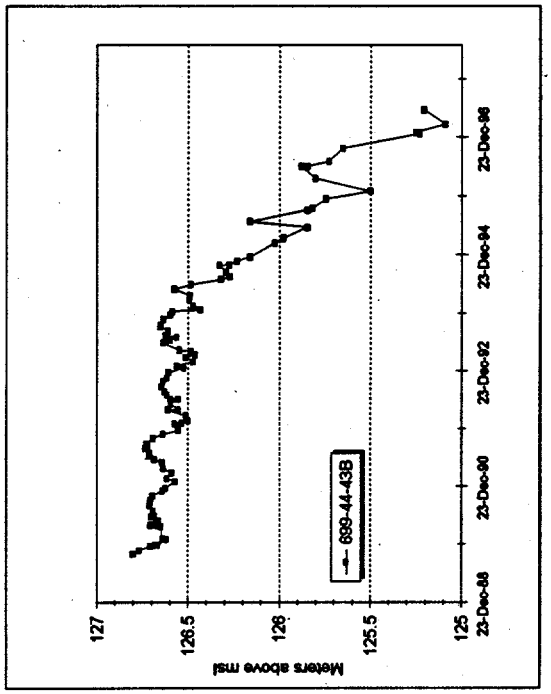
699-44-42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125.5
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23-Dec-88
23-Dec-90
23-Dec-92
23-Dec-94
23-Dec-96
699-44-43B

Appendix C

Construction Details and Lithologic Logs for B Pond Groundwater Monitoring Wells

Appendix C

Construction Details and Lithologic Logs for B Pond Groundwater Monitoring Wells

This appendix illustrates construction parameters, lithologic/stratigraphic information from well drilling and completion, and locations of the 8 groundwater monitoring wells selected for the new B Pond monitoring network. Vertical scales are indicated, but horizontal is not to scale on lithology and well construction columns.

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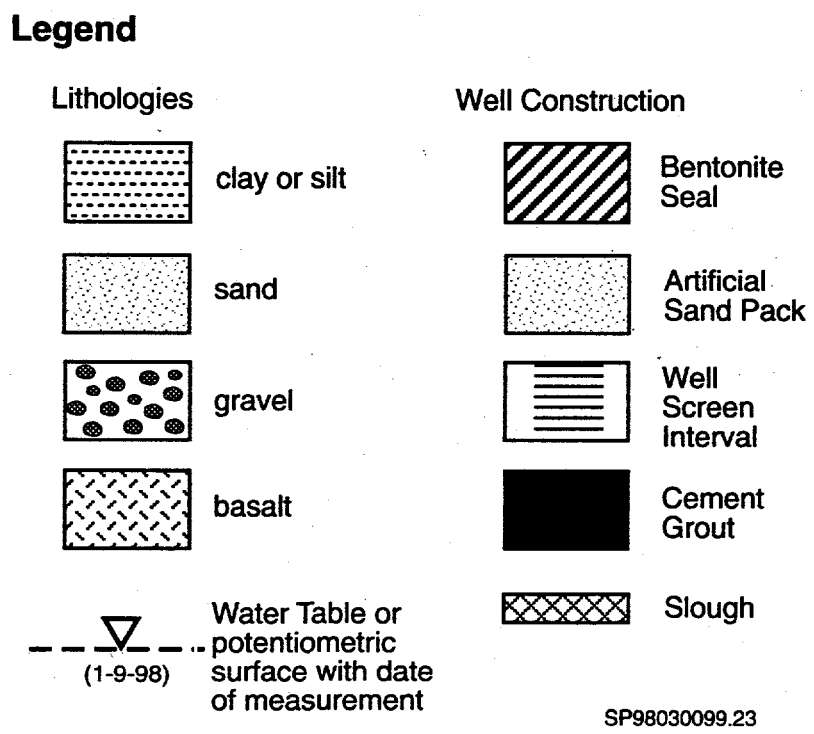

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Delaney, C.D. 1993. *Borehole Completion Data Package for the CY 1992 216-B-3 Pond Drilling Project*, WHC-SD-EN-DP-053, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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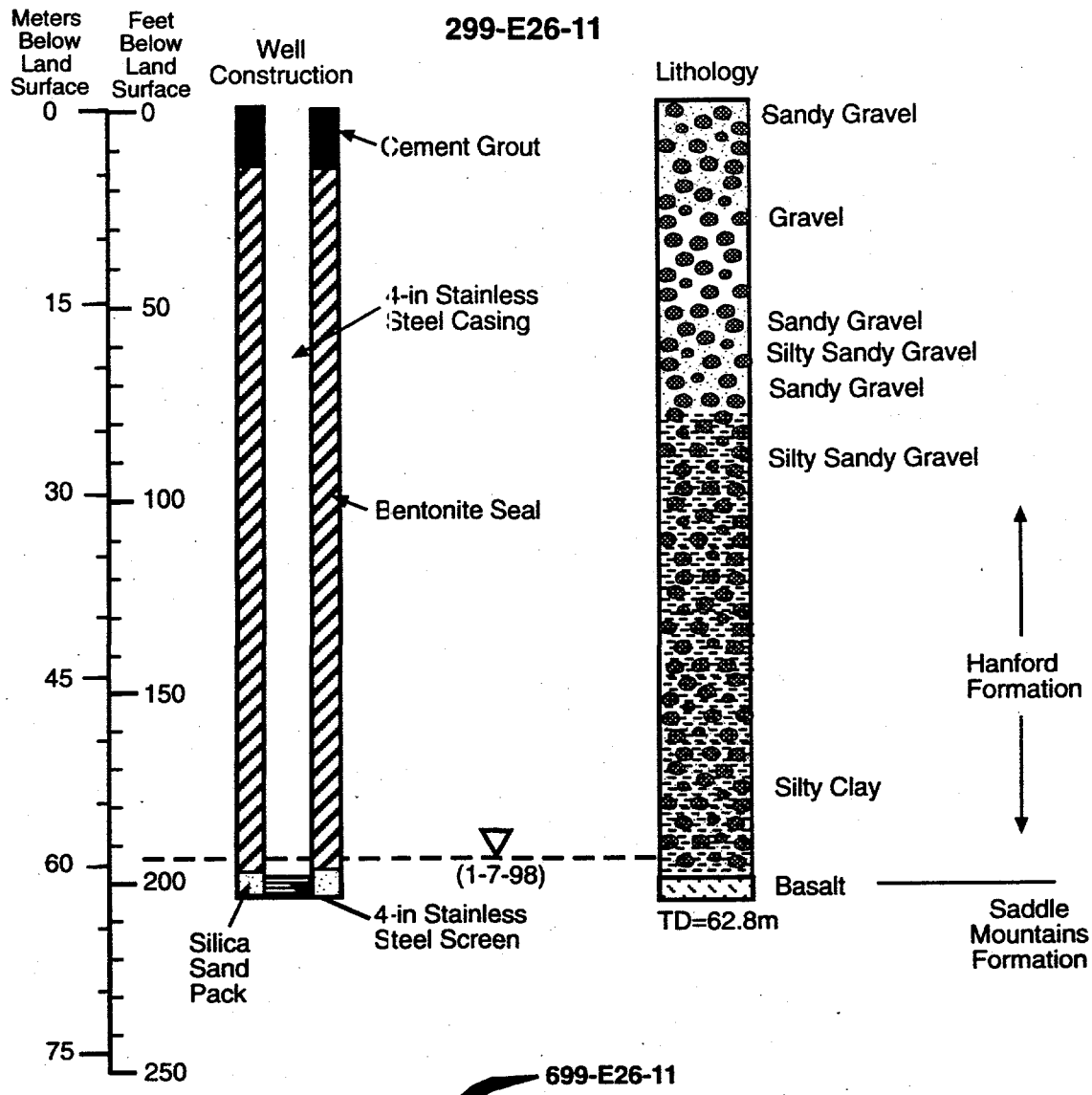

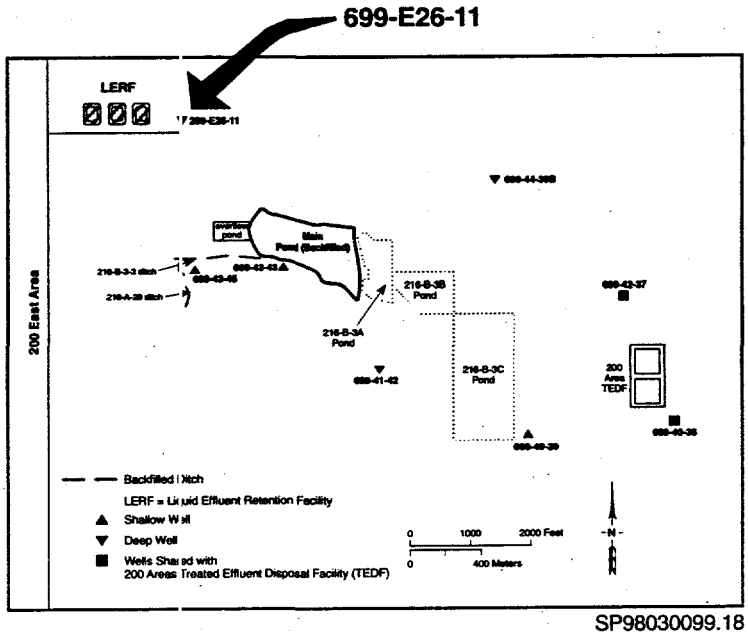

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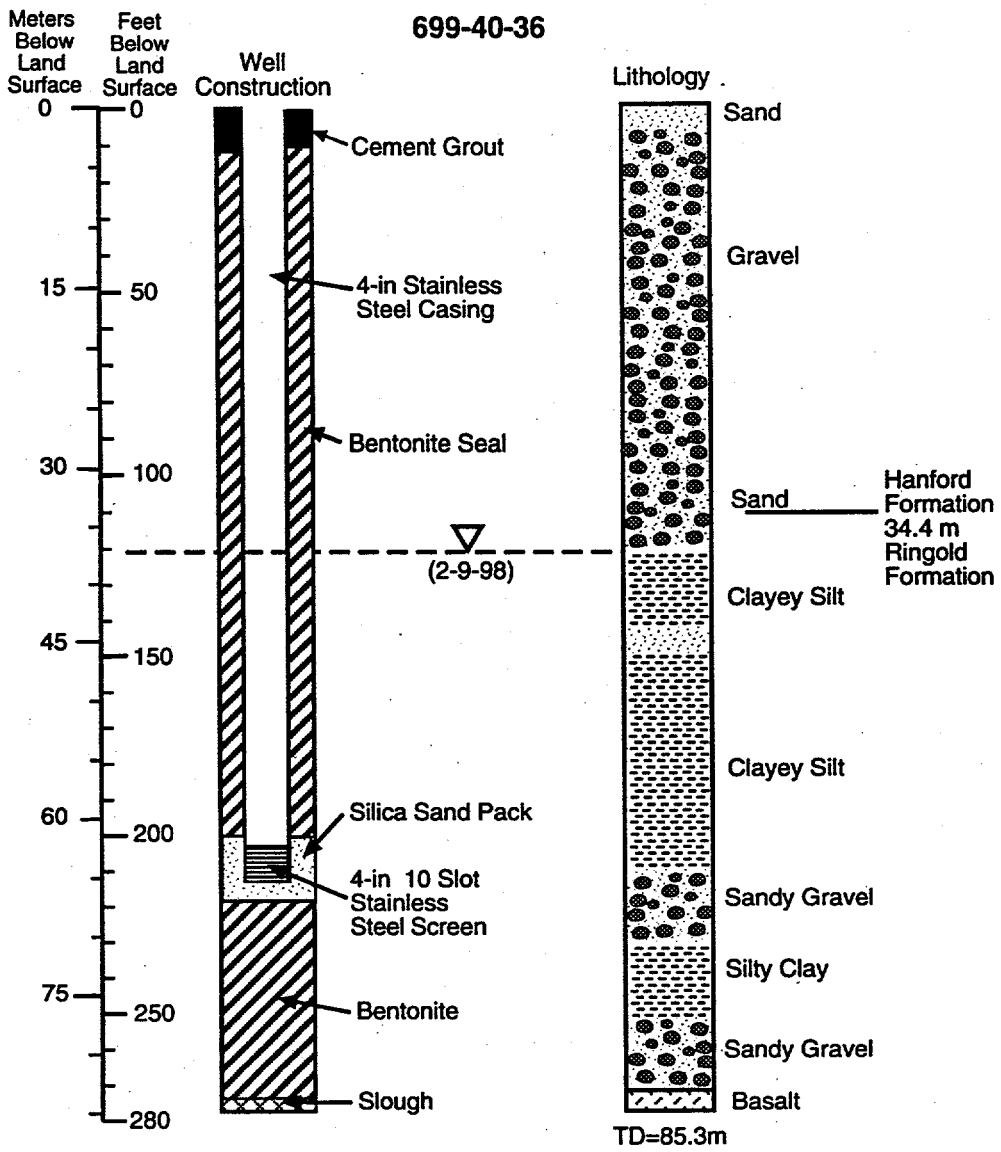

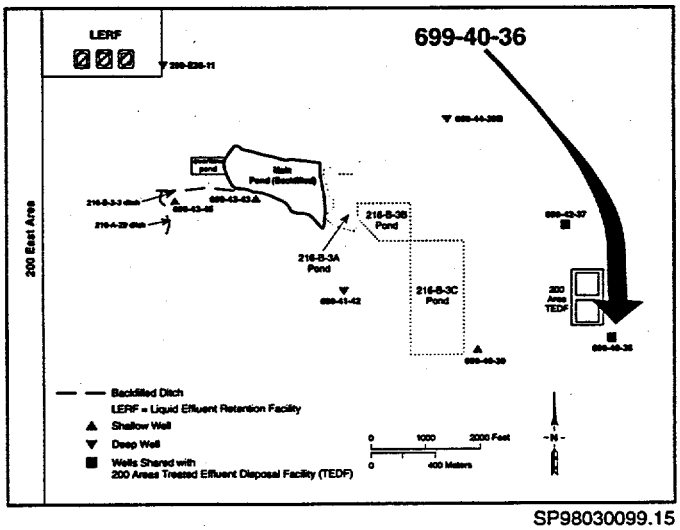

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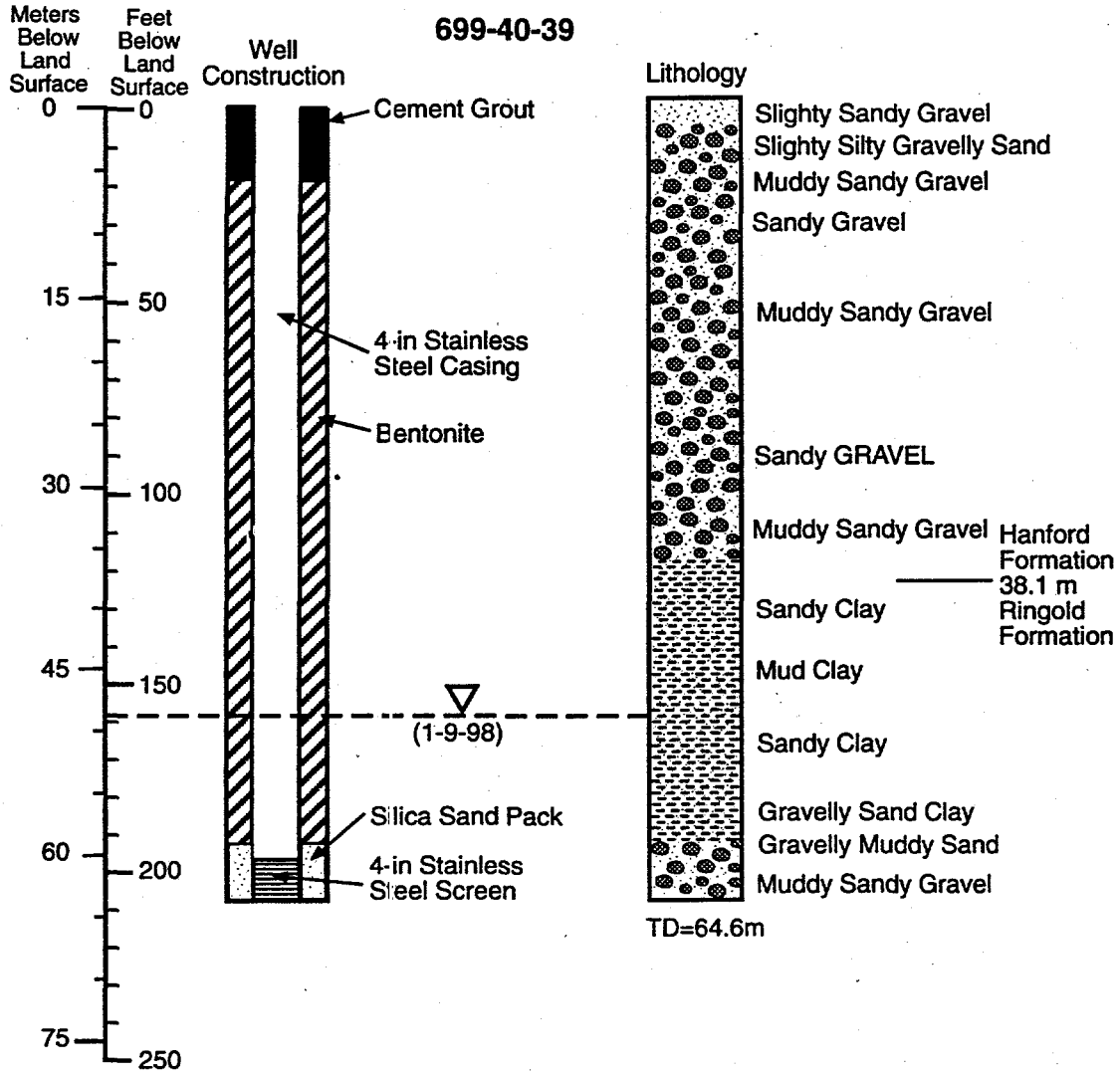

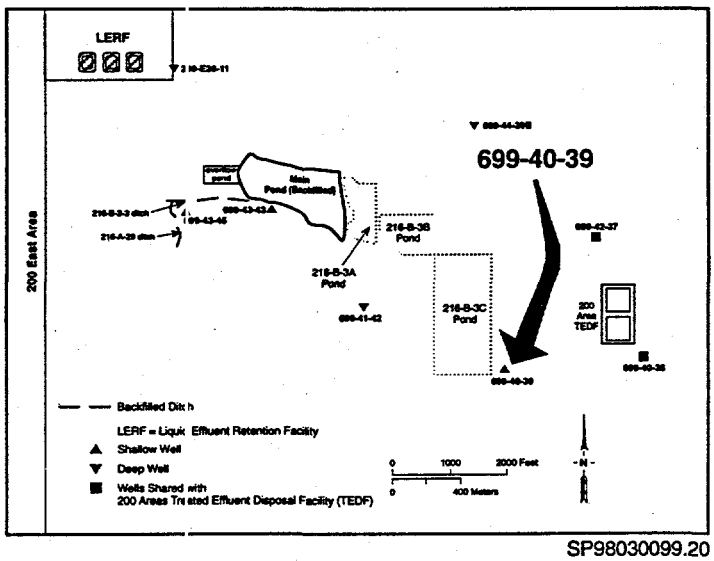

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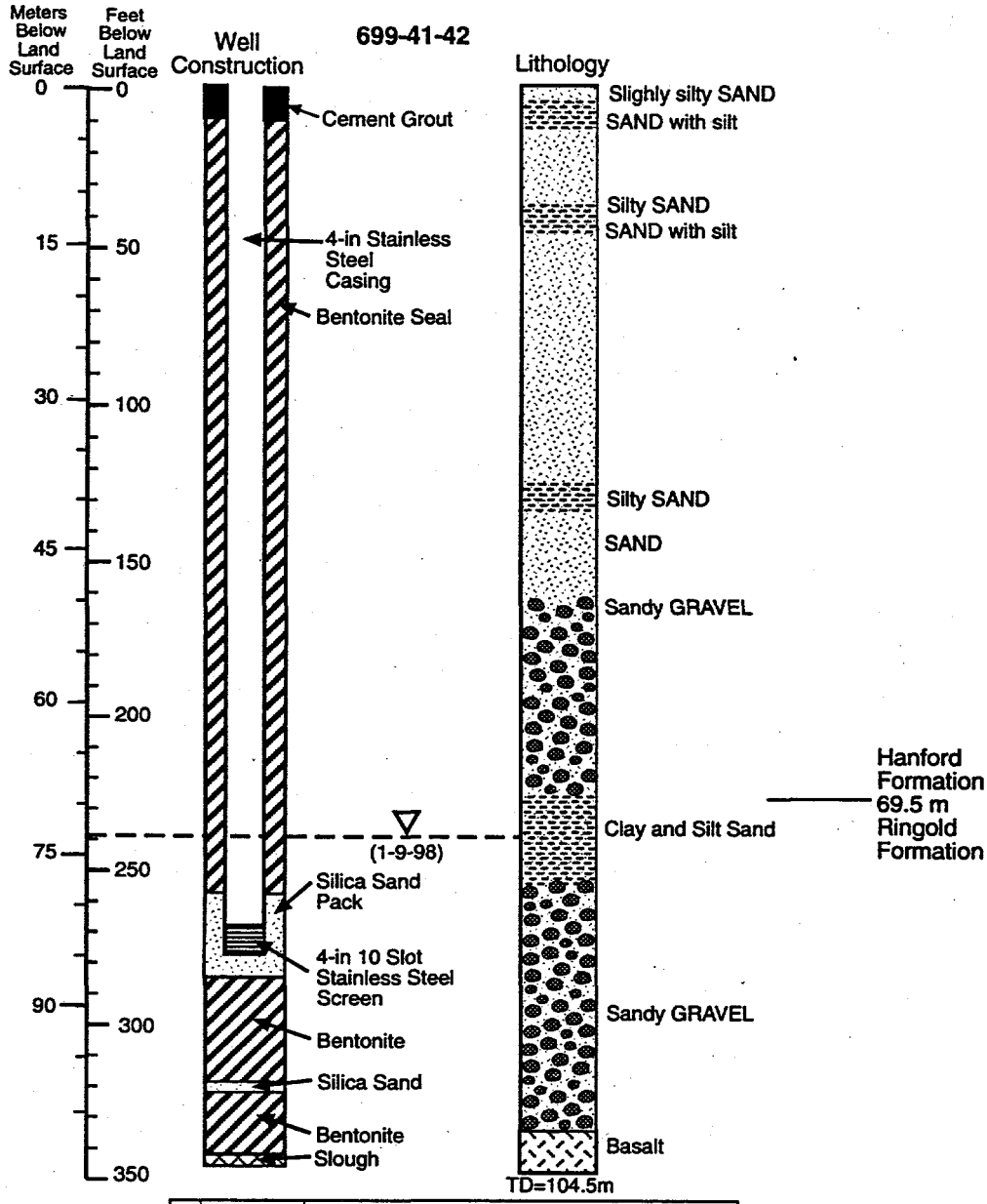

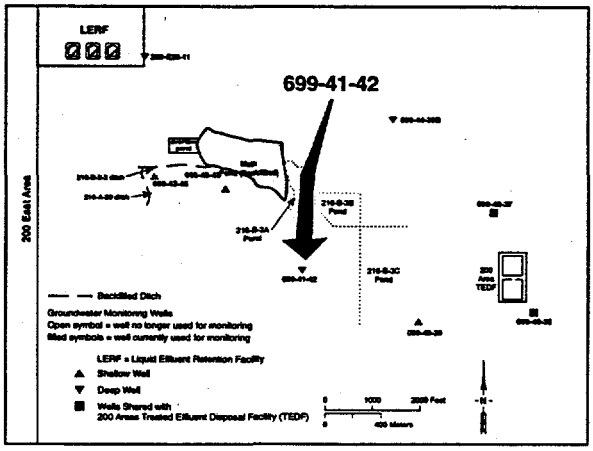

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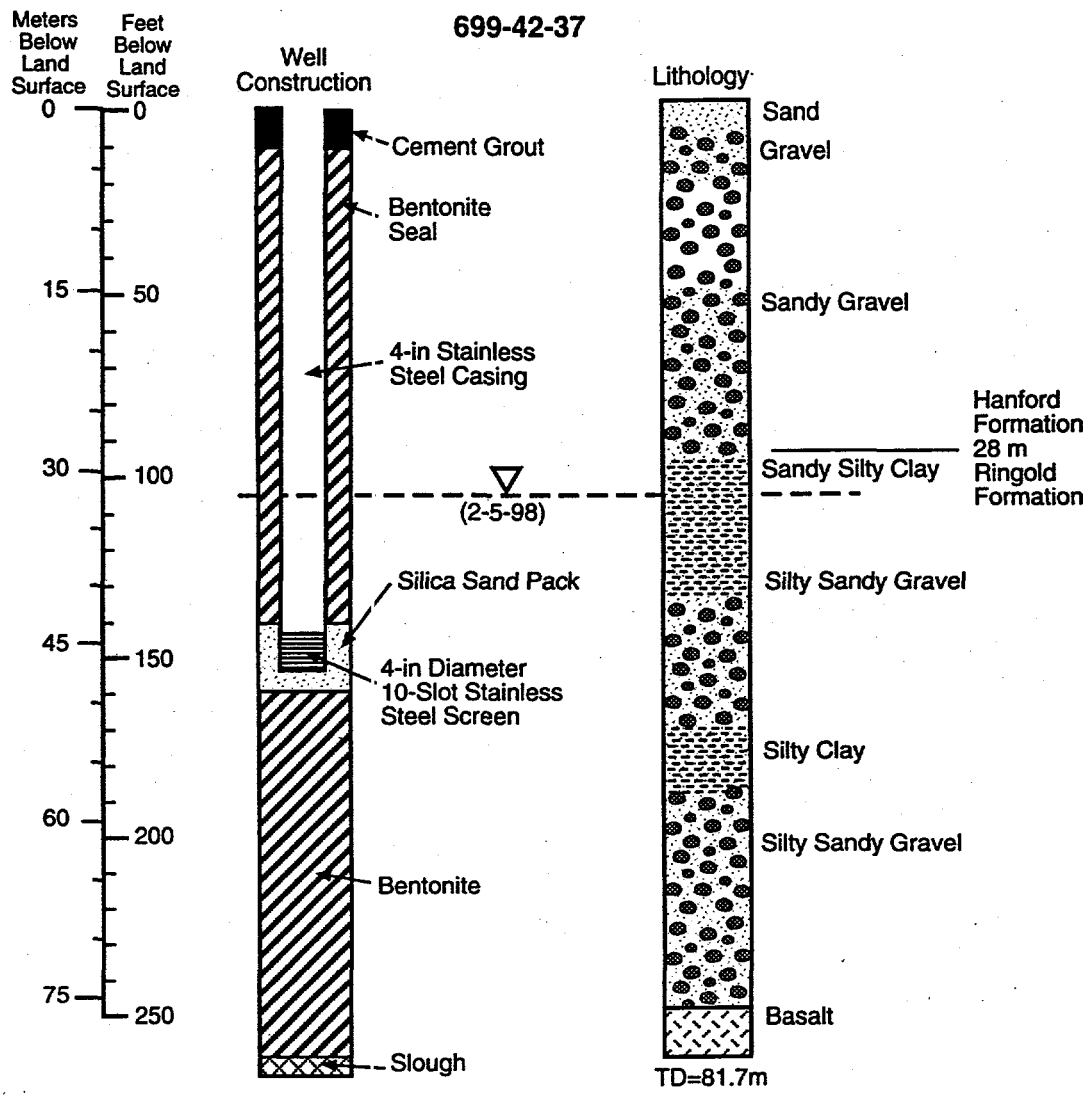

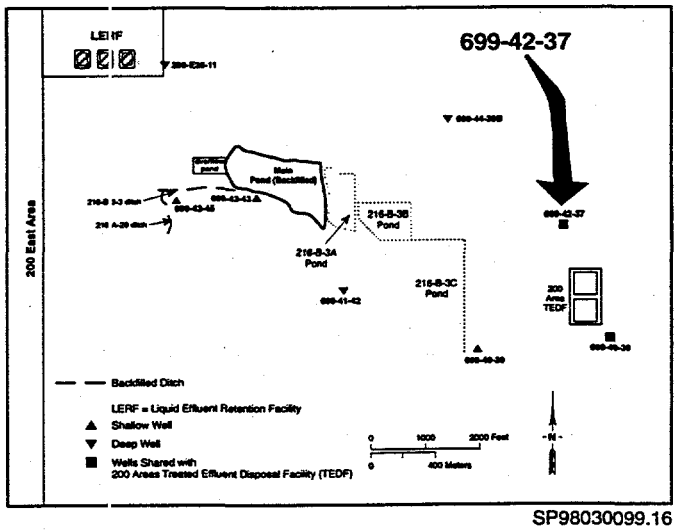

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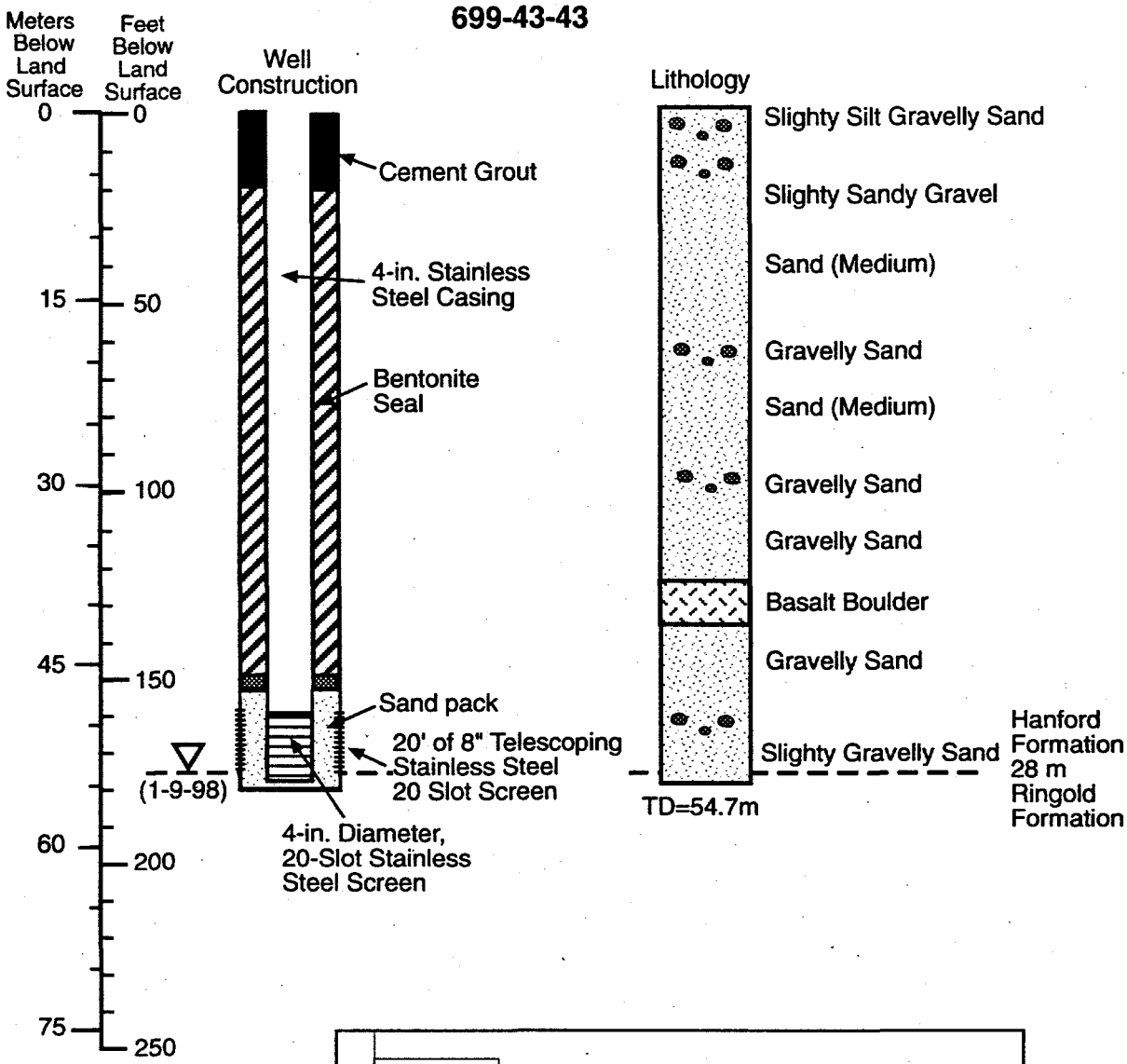

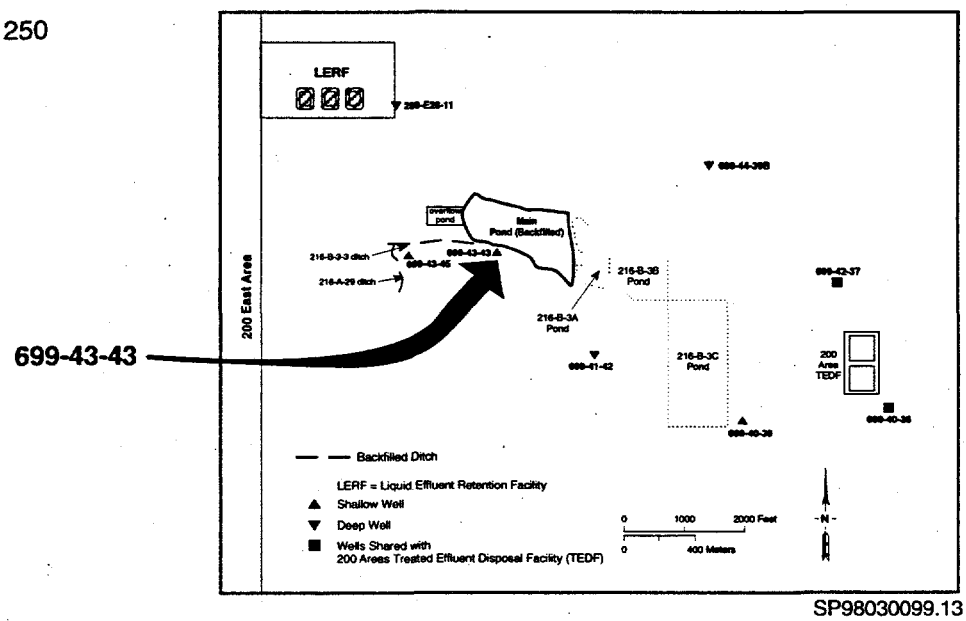

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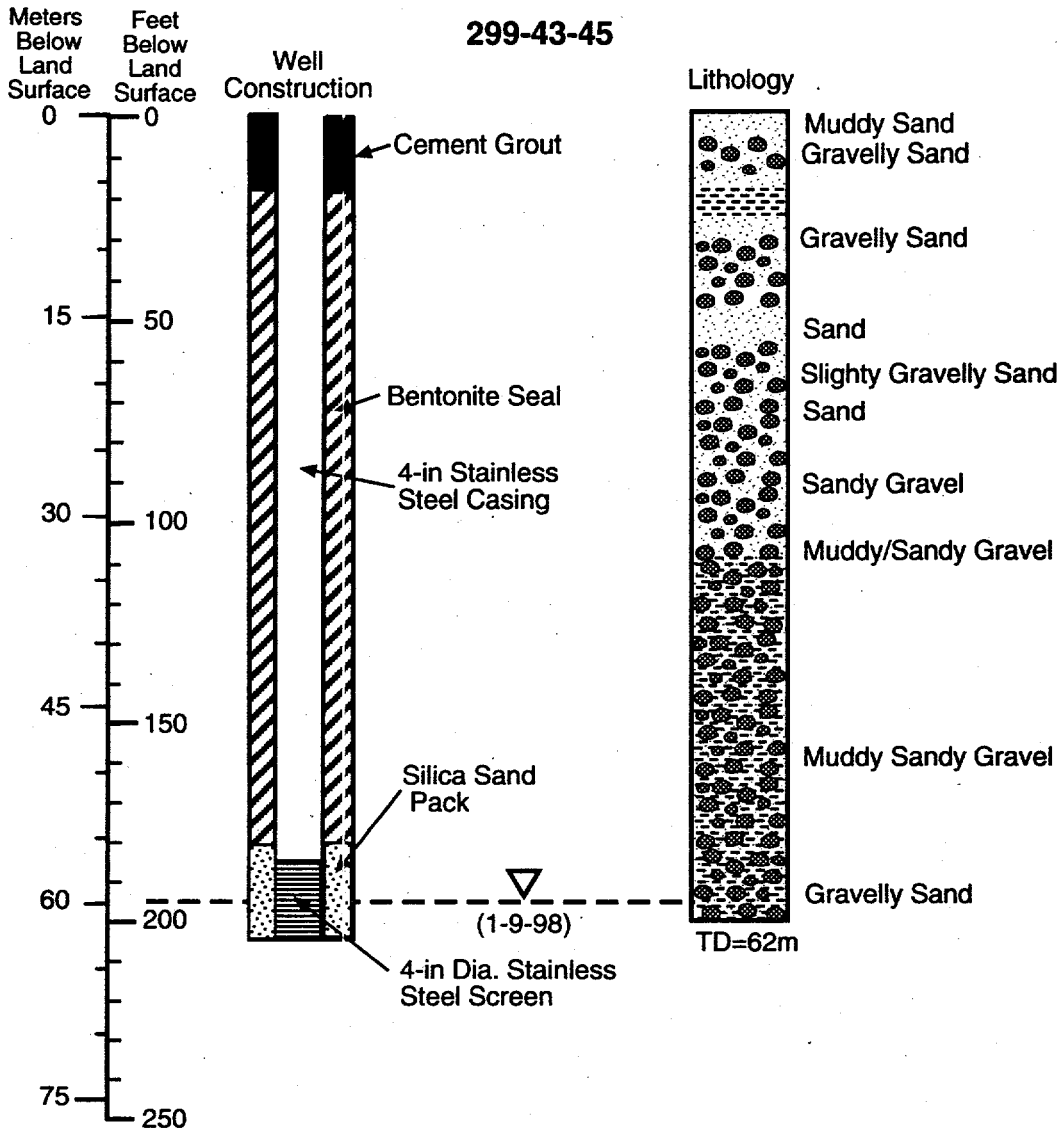

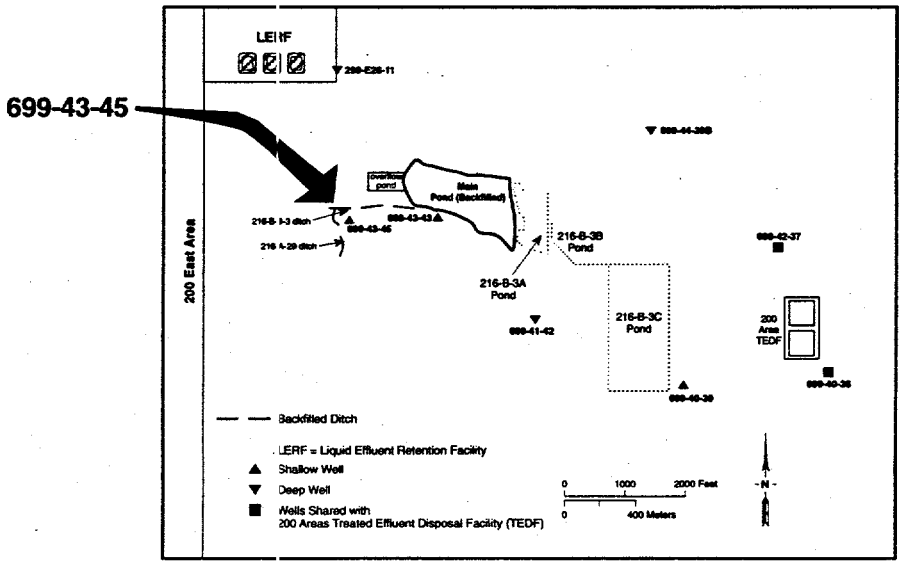

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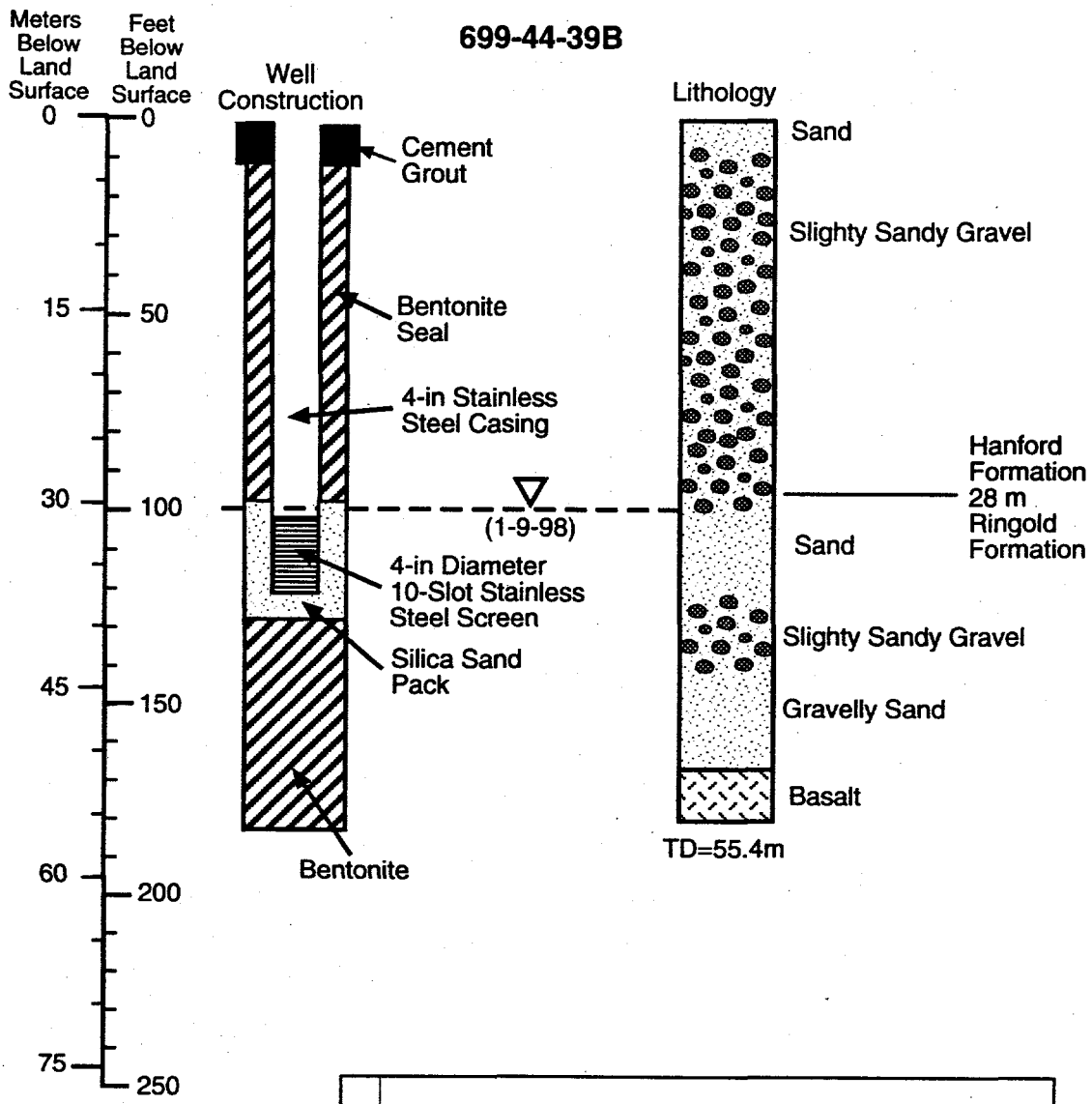
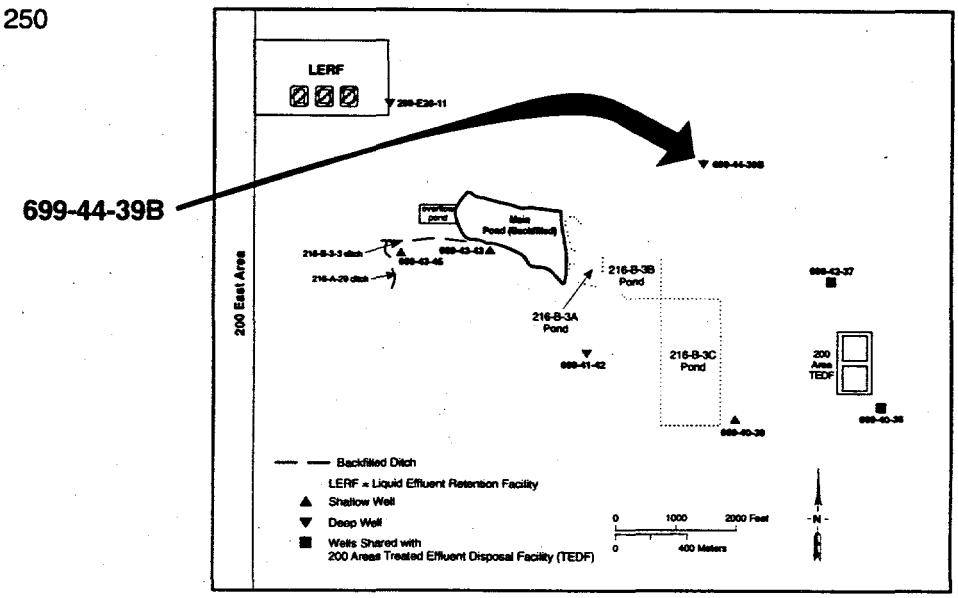




SP98030099.14

Appendix D

Evaluation of the Combined Shewhart-CUSUM Tests

Appendix D

Evaluation of the Combined Shewhart-CUSUM Tests

This appendix presents the rationale (Section D.1), assumptions (Section D.2), and step-by-step procedure (Section D.3) for the combined Shewhart-CUSUM control approach. Power curves of various testing strategies for the B Pond System (prepared by the Statistics Group of PNNL) are compared with the EPA reference power curves (Section D.4). Computation of the power curves for the B pond monitoring wells is presented in Section D.5. Based on comparisons with EPA reference power curves and other site-specific considerations (see discussion in Section D.6), trigger values for the combined Shewhart-CUSUM control chart approach are proposed for the B Pond System. This proposed sampling procedure and statistical approach should result in a more cost-effective monitoring system without sacrificing detection sensitivity.

D.1 Rationale

As discussed in Section 6.9.1, the narrowness of plumes in the aquifer makes the tests of means (i.e., the ANOVA method) inappropriate. Alternative sampling procedure and statistical method that meet the performance standards as specified in 40 CFR 264.97 (I) and WAC 173-303-645 (8)(ii) should be sought. An intra-well comparison approach (i.e., the combined Shewhart-CUSUM control chart) which is widely used in industrial quality control is proposed for the B Pond System for the following reasons:

- Groundwater flow direction is radial.
- For RCRA monitoring, a decision is made at the end of each sampling period as to whether additional regulatory action is needed. Hence during the operating life of a facility, one is dealing with a sequence of decisions (as in quality control applications) rather than just one decision.
- The Shewhart-CUSUM control chart combines the advantages of the Shewhart control chart (sensitive to large and abrupt shifts) with a cumulative sum (CUSUM) control chart (sensitive to small and gradual changes) and allows data from a well to be viewed graphically over time (i.e., to detect changes from baseline or background concentrations over time).
- This method is recommended by EPA (1989 and 1992), ASTM (1996), and statistical professionals (Gibbons 1994) for intra-well comparisons.

D.2 Assumptions

This method assumes the data are independent and normally distributed with a fixed mean μ and variance σ^2. The most important assumption is independence. To ensure independence of data, wells should not be sampled too frequently (e.g., more than quarterly). Non-normal data distributions can be handled by transformations (e.g., lognormal). In general, a representative baseline period that covers at least 8 independent samples is needed to provide reliable estimates of process mean and standard deviation.

D.3 Step-by-Step Procedure

The procedure for applying the Shewhart-CUSUM control chart method, for each constituent of interest, is as follows.

1. Identify a representative baseline period and obtain estimates of the process mean ($\bar{x}_b$) and the standard deviation (s_b) using baseline data in each well. At least 8 historical independent samples (n = 8) are needed to provide reliable estimates of the population mean μ and standard deviation σ.

2. Select the 3 Shewhart-CUSUM parameters, k, h, and SCL as defined below.

   k = a parameter selected to be about one-half of the shift in the mean we are interested in detecting in the CUSUM control chart scheme. (Note: when k = 1, a shift of 2 standard deviation units will be detected).

   h = the decision value (expressed in units of standard deviations) that is compared with the cumulative sum in the CUSUM control chart.

   SCL = the upper Shewhart control limit which is expressed in units of standard deviations.

   For a given h value, the k value that leads to minimum sample size is a value half way between the acceptable mean concentration and another level which is considered to be an indication of possible increased contamination. For ease of application, ASTM (1996, page 12) suggests using k = 1, h = SCL = 4.5 when n is less than 12. This will result in a single control limit with no compromise in leak detection capabilities (i.e., the test will be more sensible to detect a release because a lower decision rule is used for h).

3. Denote a new measurement at time t_i as x_i and compute the standardized value z_i:

$$z_i = (x_i - \bar{x}_b)/s_b$$

4. At each time period, t_i, compute the cumulative sum S_i, as:

$$S_i = \max\,[0, (z_i - k) + S_{i-1}],$$ where max [a, b] is the maximum of a and b, and $S_0 = 0$.

5. Plot the values of S_i and z_i on the y-axis versus t_i on the x-axis on a time chart. To take advantage of the good properties of both the Shewhart scheme and the CUSUM scheme, it is desirable to have an objective decision rule for signaling quickly when a change has taken place and when further action (e.g., more extensive assessment level monitoring effort) is necessary. This is accomplished by declaring the process out-of-control if any sample result is above a specified upper Shewhart control limit (SCL) or if the CUSUM statistic S_i (at time i) is above a specified limit h as discussed below. It should be noted that when the number of baseline data points is greater than or equal to 12 then use the values: $k = 0.75$, $h = 4$, and $SCL = 4$ (ASTM 1996, page 12).

6. Perform verification sampling if $S_i \geq h = 4.5$ or $z_i \geq SCL = 4.5$ (see Section 6.9.5). Otherwise, continue detection monitoring. It should be noted that when the number of baseline data points is greater than or equal to 12 then use the values: $k = 0.75$, $h = 4$, and $SCL = 4$ (ASTM 1996, page 12). Declare an "out-of-control" situation if verification sample confirms the initial exceedence. However, if verification sample indicates that the initial exceedence is caused by errors in sampling, field measurement, or laboratory analysis an "out-of-control" signal will not be declared. In this case, replace the initial value by the verification sampling result. (Note: If the initial suspected value is not corrected, it will be included in the future cumulative sum and will invalidate the statistical test.)

7. Baseline data should be updated periodically (every one to two years) and must be modified for non-detects or trend (see discussion in Section D.5). Any outlier(s) in the historical database, must be removed. Methods for handling non-detects, adjustment for trend, and detecting outliers are described in ASTM (1996, pages 12-13) and Gibbons (1994, pages 165-166).

D.4 Comparison with EPA Power Curves

EPA has reviewed the literature and conducted simulations (Lucas 1982; Starks 1989; and EPA 1989). EPA recognized that RCRA groundwater monitoring decisions are similar to a quality control scheme and should be interested in distributions of *run lengths* in both in-control and out-of control situations. An *in-control run length* is the number of sampling periods from start-up until a decision is made, on the basis of groundwater sample measurements, that additional regulatory action is required when, in fact, there is no leakage from the regulated unit. An *out-of-control run length* is the number of sampling periods from the time that a pollutant plume originating from the regulated unit intercepts a well site until a decision is made that additional regulatory action is needed. Naturally, one wants to use a quality control scheme that has, on average, long in-control run lengths and short out-of-control run lengths.

Starks (1989) conducted Monte Carlo simulations to estimate the distributions of run lengths under various conditions (i.e., varying k values and using different decision values for h and SCL). Based on EPA simulations and literature review results, it was recommended that $k = 1$, $h = 5$, and $SCL = 4.5$ are the most appropriate values for groundwater applications (Lucas 1982; Starks 1989; and EPA 1989). These parameter values give the desired properties for the average run length (the average run length is long when the process is in control and it is very short when the process is out of control). In addition, a baseline period with at least 8 samples was recommended (referred to as the eight period learning stage in

Starks [1989]). This would account for some of the characteristics that are unique to groundwater monitoring (sampling and measurement is expensive and the time between sampling event is long to ensure independence of data).

A comparison of the power curves for three control limit cases (case 1: SCL = 2 and h =2; case 2: SCL =3 and h =3; and case 3: SCL = 4 and h = 4) with the EPA reference power curves (EPA 1992, page B-6) is shown in Figures D.1 through D.3, respectively. It should be noted that in all three cases evaluated the k value is fixed at 0.75 sigma units because the number of samples in the baseline period is more than 12 in 7 out of 8 monitoring wells for the B Pond System. This would quickly detect a 1.5-sigma unit shift above the mean concentration. It also should be noted that in all three cases evaluated, 1 re-sample is considered for the verification sampling.

There are 5 curves in the upper portion of each figure which show the probability of detecting a shift of various sigma units above baseline in each of five consecutive sampling periods that are assumed to be no closer than three months apart to ensure independence of data (Gibbons 1994). The EPA reference power curves for n = 8, 16, 24, and 32 are shown at the bottom of each figure for comparison purposes. (Note: only the "16" background sample-size case from the EPA reference set is used because it is most comparable with the number of baseline samples from the B Pond System monitoring network.) The power curves in the figures show the probability of detecting a shift from 0 to 5 standard deviation units in mean concentration in a single constituent in a single downgradient well. If a constituent of interest from a particular well has a standard deviation of 2.5 pCi/L, then the standardized sigma units in Figures D.1 through D.3 would translate into a shift of 2.5 pCi/L at 1 sigma unit, 5.0 pCi/L at 2 sigma units, 7.5 pCi/L at 3 sigma units, 10 pCi/L at 4 sigma units, and 12.5 pCi/L at 5 sigma units.

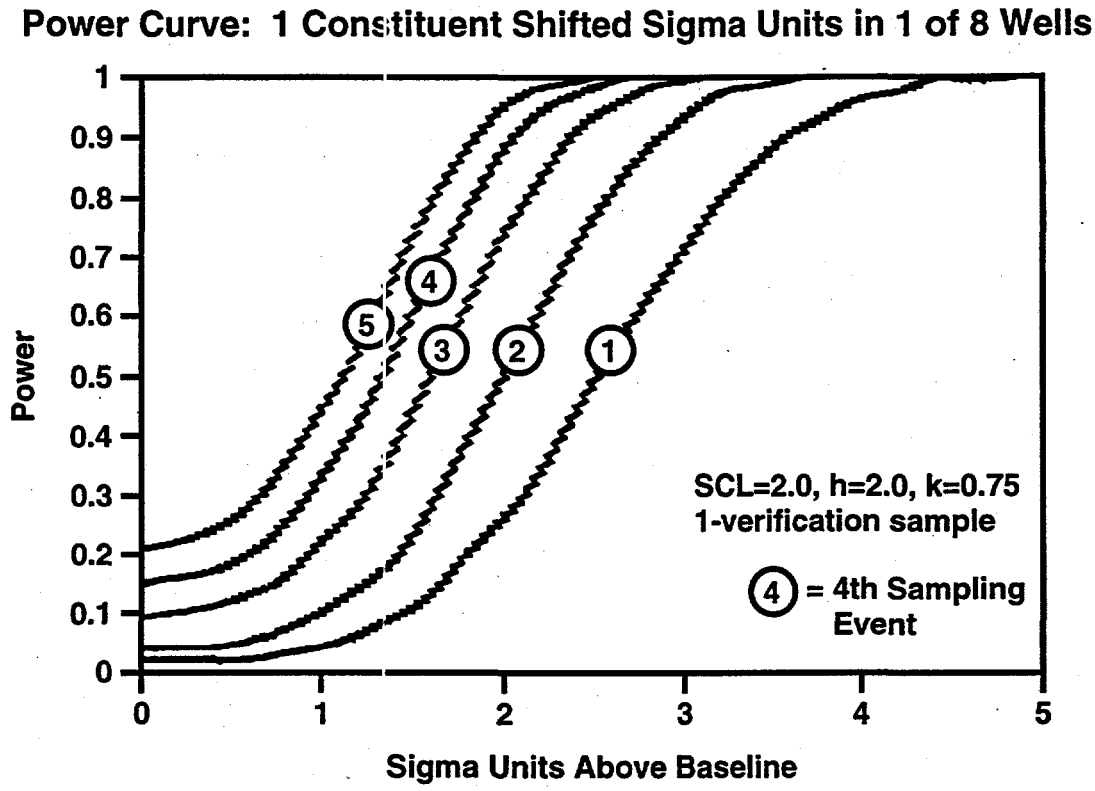
In evaluating any alternative testing strategy EPA recommended the following two criteria (EPA 1992, page 64):

1. The overall network-wide false positive rate (across all wells and constituents) should be kept to approximately 5%.

2. The statistical power should be comparable to those indicated by the EPA reference power curves.

The three cases are evaluated on the basis of these two criteria. The goal is to select a testing strategy that achieves the best balance between the false positive and false negative (= 1 - Power) rates. Results are discussed as follows.

One important feature in the EPA reference power curves is the low rate of false positives (i.e., the % power at near "0" sigma units). The nearest to this reference or desirable condition for the B pond power curve examples is in case 3 (Figure D.3) for which SCL = 4 and h = 4. The most striking feature of the comparison is the relatively high false positive rate for case 1 (where SCL = 2 and h = 2), as compared to case 2 (where SCL = 3 and h = 3) and case 3 (where SCL = 4 and h = 4). False positive rates for case 1 are much higher than those indicated in the EPA reference power curves. For example, at the 5th sampling event, a false positive rate of 20% is indicated (Figure D.1). This means that a site will be falsely



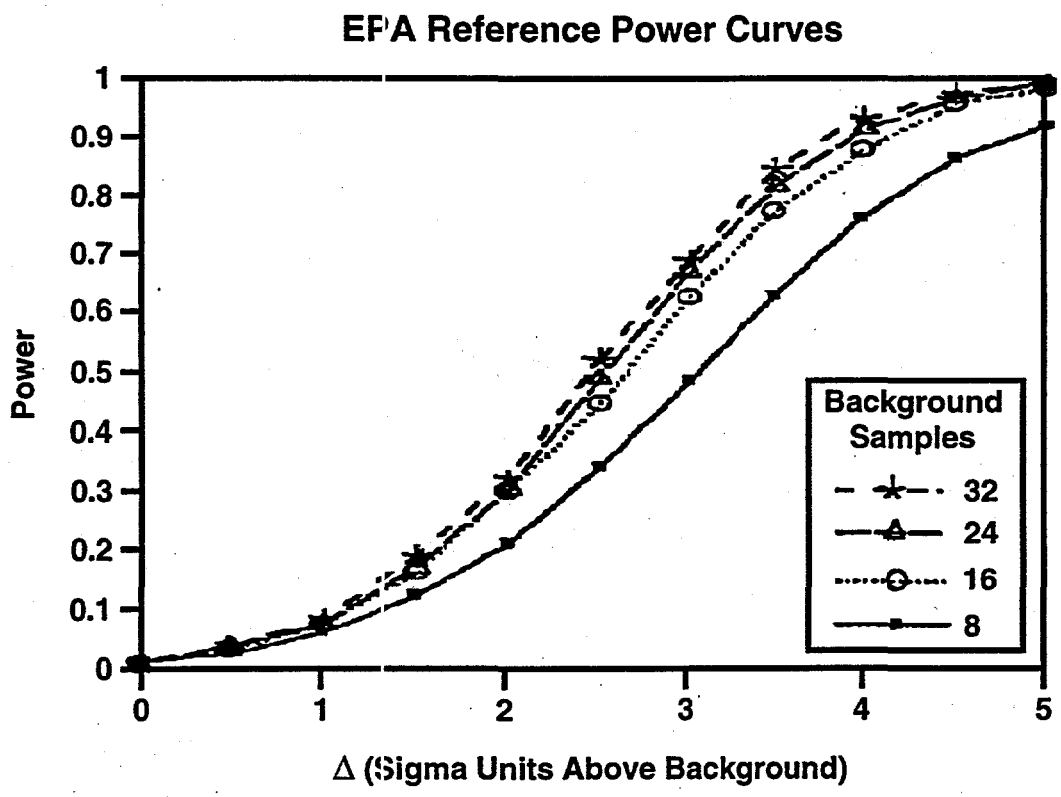
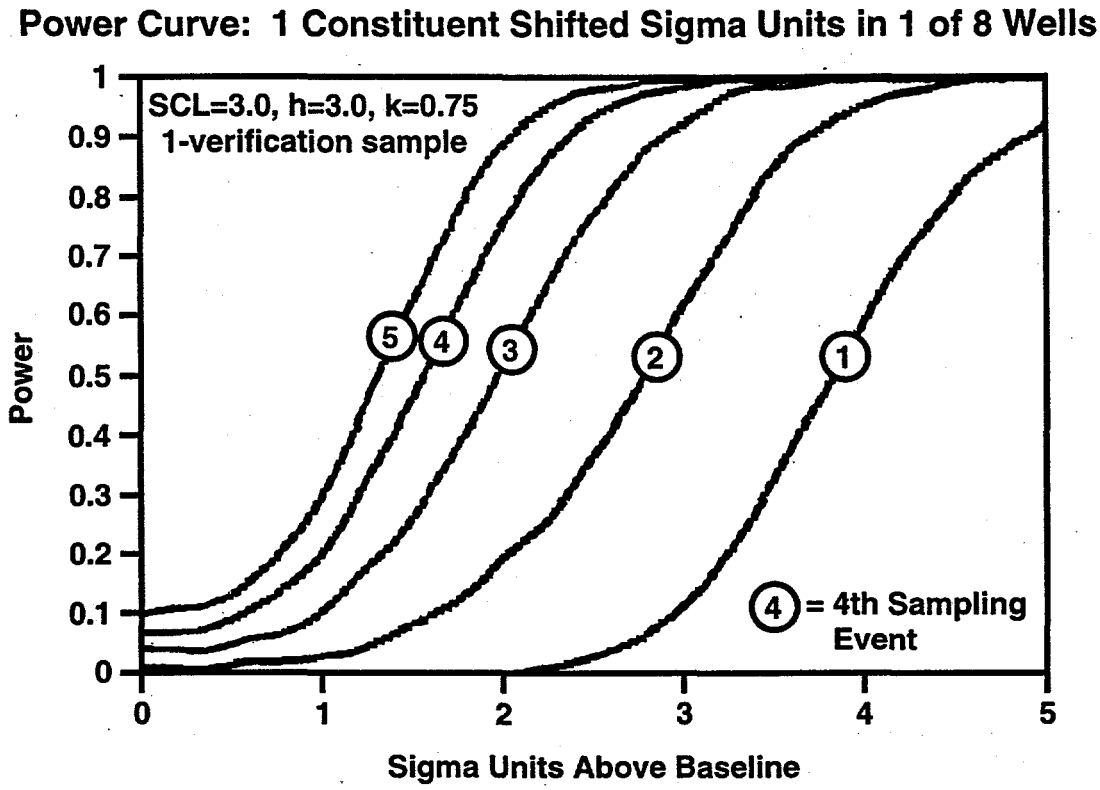


Figure D.1. Case 1



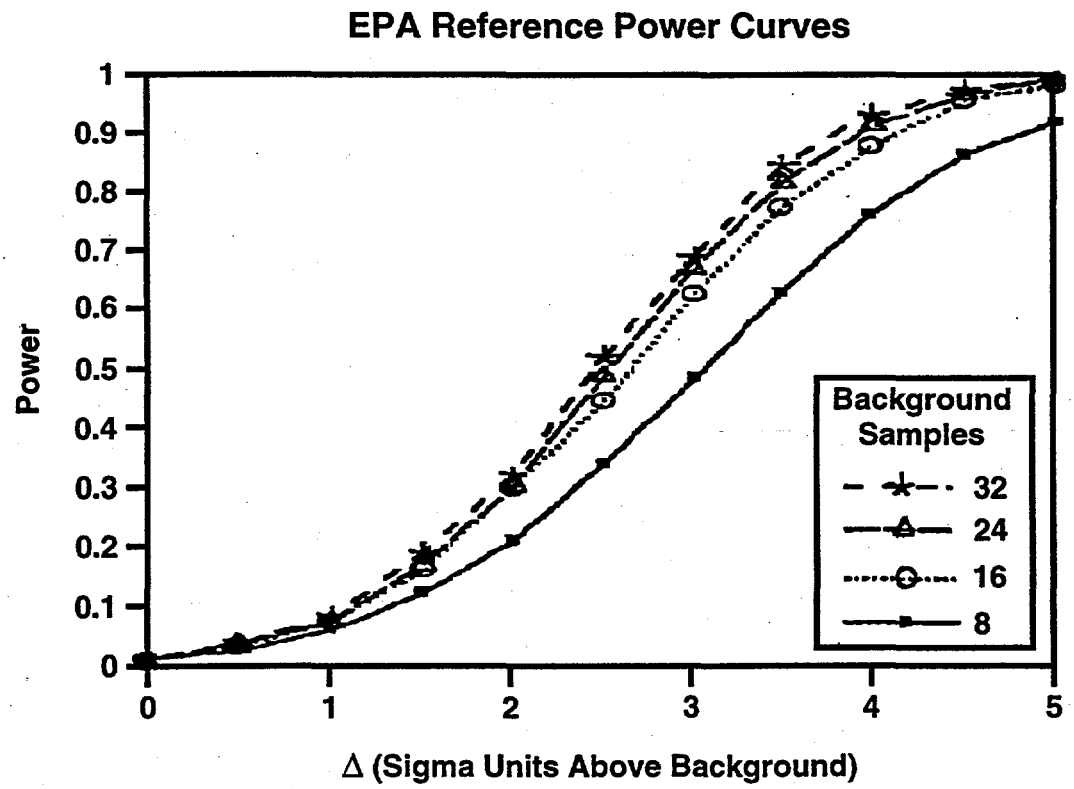
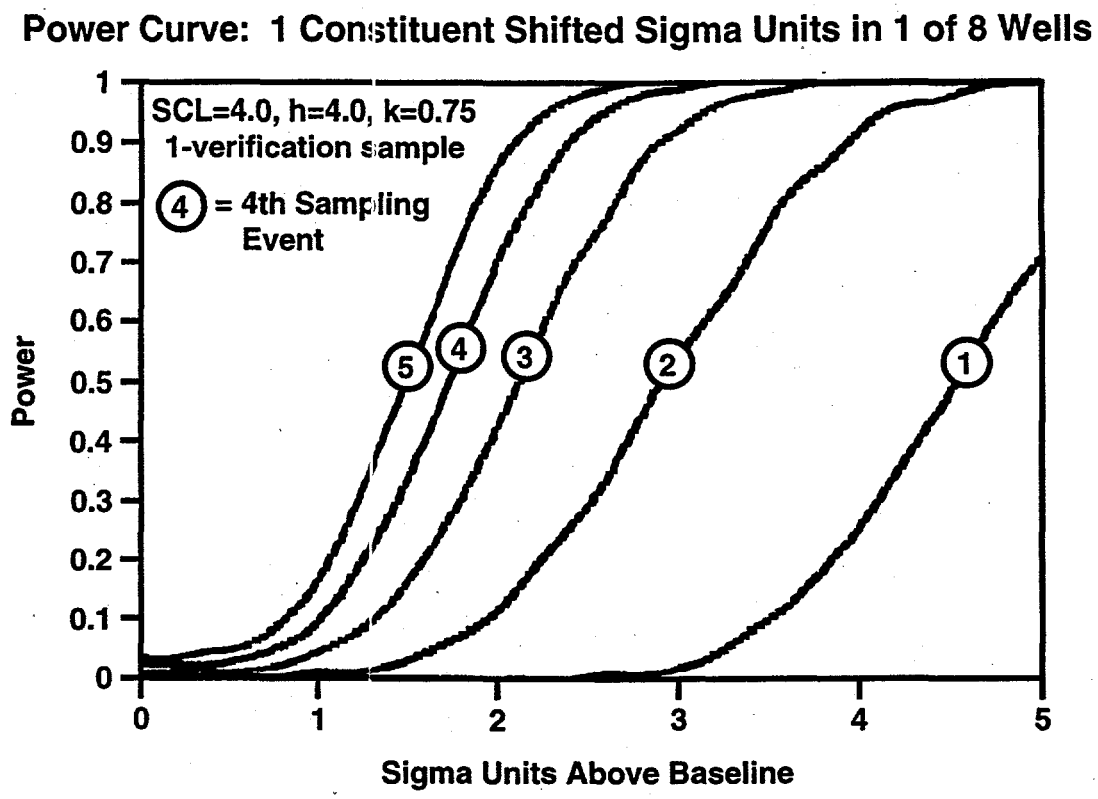


Figure D.2. Case 2



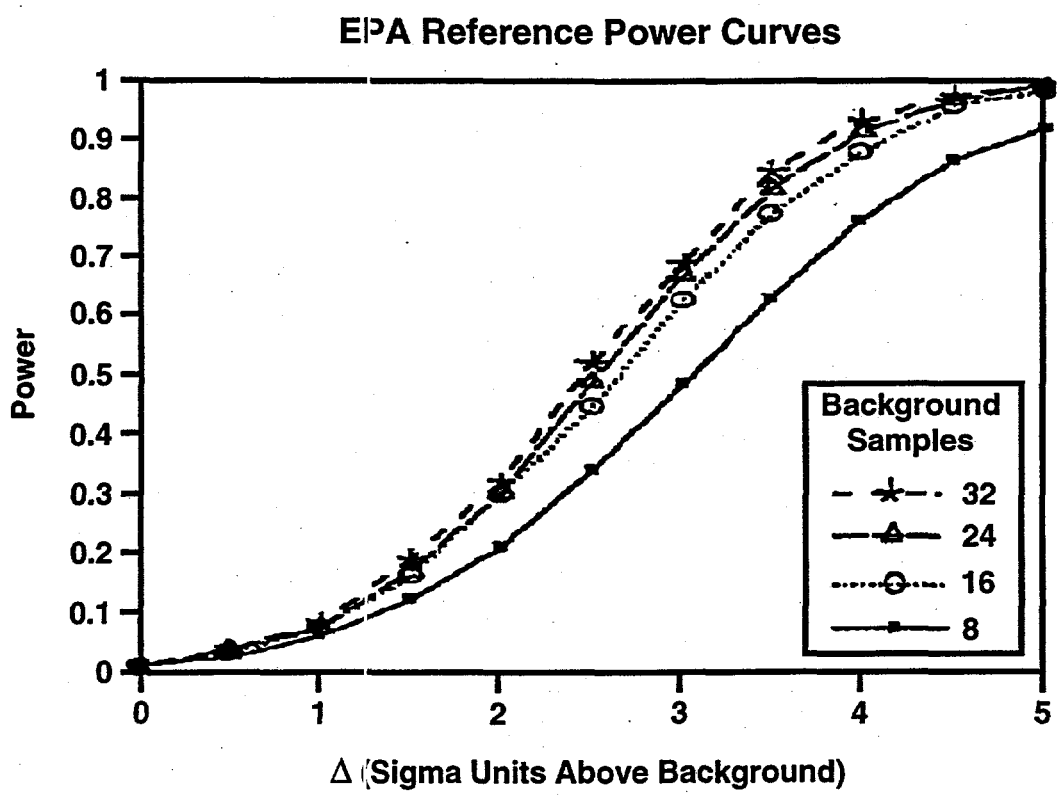


Figure D.3. Case 3

triggered into assessment, by chance alone, 1 out of 5 times under case 1 conditions. Even case 2 (Figure D.2) has relatively high false positive rate (i.e., 10%) as compared to case 3 (~3%, Figure D.3).

All 3 cases (Figures D.1, D.2, and D.3) illustrate an increase in power after the first sampling event. That is, the power of the combined Shewhart-CUSUM control chart increases with time. The greatest incremental improvement in power occurs with the second sampling event. Case 1 shows higher power during the second sampling events. But, in the third sampling event, the incremental power diminishes and all three cases have similar power for detecting a shift (in mean concentration) of 3-sigma unit or larger. It should also be noted that in case 3, the power in the second sampling event is similar to the referenced EPA curve for 16 background samples, but, the Shewhart-CUSUM curves are steeper (i.e., greater power) than the referenced EPA curves for later sampling times.

In light of these factors, case 3 (which has a 3% false positive rate) comes closest to meeting the EPA's goal of 5% false positive rate even after the 5th sequential sampling event and it has similar or better power after the first sampling event. In addition to statistical considerations as noted above, there are other factors for consideration in selecting a testing strategy to account for the unique conditions at the B pond area. The discussion is provided in Section D.6.

D.5 Computation of Power Curves

The power curves for the B-pond monitoring network were calculated by R. F. O'Brien and Guang Chen of PNNL Statistics Group using Monte Carlo simulations. These simulations were performed assuming that the data for all constituents of interest (i.e., specific conductance, gross alpha, and gross beta) can be transformed appropriately to a normal distribution with mean 0 and standard deviation 1. This assumption was tested by the Lilliefors test of normality and found to be valid (see Sections 6.9.3.2 and 6.9.4). Additionally it was also assumed that concentrations in each well are independent between time periods (temporal independence) and wells (spatial independence). These independence assumptions are judged to be valid for the B Pond System because sufficient time will be allowed between each sampling event and monitoring wells are not located in close proximity to each other.

The power curves in each figure were obtained by first computing the probability of 1 constituent of interest in 1 well of the network exceeding the Shewhart and CUSUM control limit by the nth sampling period (where n ranged from 1 to 5). These probabilities were computed in two steps.

Step 1. For each incremental shift in the mean concentration, probabilities were calculated by first finding the probability of 1 constituent in 1 well of the network exceeding the combined Shewhart-CUSUM control limit after either the 1st, 2nd, 3rd, 4th, or 5th sampling period. The SCL and h values were set at various levels of interest (i.e., case 1, 2, and 3) and for shifts in the mean concentrations from 0 to 5 standard deviations (sigma units) in increments of 0.2 sigma units. For each incremental shift in the mean concentrations, 10,000 simulations were performed to estimate the probability of an exceedence. In each simulation, a pseudo-random normal random deviate was generated from a normal distribution with a fixed incremental shift in the mean and a standard deviation of 1. The probability of an exceedence in the nth sampling period (n = 1 to 5), for a specific shift in the mean, was calculated as the proportion of the 10,000 pseudo-random numbers

that exceeded the control limit in the nth sampling period (i.e., the number of times an exceedence occurred in the nth sampling period divided by 10,000).

Step 2. In this step, for each incremental shift in the mean, the cumulative probability of 1 constituent of interest in 1 well exceeding the control limit by at least the nth sampling period was calculated by adding up the individual probabilities of an exceedence in each sampling period from n = 1 up to n = 5. These probabilities are those plotted in Figures D.1, D.2, and D.3.

D.6 Discussion

The three primary indicator constituents of interest, gross alpha, gross beta, and specific conductance, all have a natural background resulting from water-rock reactions during evolution of the ambient groundwater. This natural background forms a permanent baseline above which changes due to addition from the regulated unit will be detected. It should also be noted that gross alpha, gross beta, and specific conductance are about 3 to 4 times lower in river water (pond water) than natural groundwater composition upgradient from the B Pond area. Thus, the existing concentrations of all three of these indicators will tend to increase in time in response to decreased recharge of pond water. Thus, baseline indicator concentrations based on the past few years will tend to be lower than in the future as the amount of pond water that mixes with ambient groundwater diminishes. In the near term, this could result in a tendency toward increased false positive occurrences especially if the control limits are set low (e.g., SCL = 2 and h = 2). Accordingly, the baseline should be re-established every two years or so to adjust for this changing condition (e.g., one could consider keeping a moving window of the most recent 8 or 12 observations).

The approach used to evaluate power (requiring detection of only 1 out of three co-contaminants in one well) may underestimate the actual power of the test, at least in the case of gross alpha. For example, uranium, the constituent of concern for which gross alpha is used as the indicator, decays from U-238 by alpha emission to an intermediary daughter radionuclide (Pa-234) which beta decays to U-234, another alpha emitter. Thus, if an increase in uranium occurs due to leaching from the regulated unit, gross beta will increase (with gross alpha) as well. In this case, an increase in both should be required to record a positive occurrence. Even if this is not incorporated into the statistical decision, it should be used as a qualitative data evaluation in the event that gross alpha increases are observed.

D.7 Conclusions

Based on the analysis presented in this appendix and the foregoing discussion, it is concluded that the Shewhart-CUSUM control chart approach combined with control limits (SCL and h) set at 4 sigma units (Figure D.3) provides the greatest power to detect a change in the mean concentration above baseline while keeping the false positive rate at acceptably low levels. In addition, the power curve simulations were considered for the most conservative case of a release scenario that affects a single constituent in a single downgradient well. In reality, multiple constituents in multiple wells will likely be impacted. Therefore, the actual power may be considerably larger than estimates obtained by simulation. This proposed sampling procedure and statistical approach should result in a less costly monitoring system while still achieving the required power and the required false positive decision error rate.