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GROUND-WATER SAMPLE COLLECTION AND
ANALYSIS PLAN FOR THE GROUND-WATER
SURVEILLANCE PROJECT

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December 1991

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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SUMMARY

The Pacific Northwest Laboratory performs ground-water sampling activities at the U.S. Department of Energy's (DOE's) Hanford Site in support of DOE's environmental surveillance responsibilities. The purpose of this document is to translate DOE's General Environmental Protection Program (DOE Order 5400.1) into a comprehensive ground-water sample collection and analysis plan for the Hanford Site.

This sample collection and analysis plan sets forth the environmental surveillance objectives applicable to ground water, identifies the strategy for selecting sample collection locations, and lists the analyses to be performed to meet those objectives.

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1.0 INTRODUCTION

This sample collection and analysis plan sets forth the environmental surveillance objectives applicable to ground water, identifies the strategy for selecting sample collection locations, and lists the analyses to be performed to meet those objectives. The plan will be used by the Pacific Northwest Laboratory^(a) (PNL) to direct ground-water sampling activities and the subsequent analyses necessary to satisfy the environmental surveillance needs of the Office of Assistant Manager for Technical Support of the U.S. Department of Energy, Richland Field Office (RL), as stated in DOE Order 5400.1 (DOE 1988b).

Environmental surveillance of ground water is performed at the Hanford Site as an integral part of the Hanford Site Groundwater Protection Management Program (DOE 1989b). The program includes 1) ground-water monitoring at active waste disposal facilities to ensure compliance with the Resource Conservation and Recovery Act (RCRA), 2) characterization of inactive waste disposal sites to ensure compliance with requirements of the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA), 3) operational monitoring in and adjacent to reactor and chemical processing operations to monitor for compliance with DOE requirements, and 4) environmental surveillance to assess the impact of Hanford operations on ground water both on and off site independently of the operating contractor's programs. This plan also provides additional clarification to project participants on requirements in the Environmental Monitoring Plan for the Hanford Site (DOE 1991).

1.1 OBJECTIVES

The goal of the ground-water portion of the Environmental Surveillance Program is to monitor the ground water to determine the extent to which DOE activities at Hanford have affected on and off site ground-water quality.

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute.

This goal is in support of DOE Order 5400.1, which states that environmental surveillance shall be designed to satisfy one or more of the following objectives:

- verify compliance with applicable environmental laws and regulations
- verify compliance with environmental commitments made in Environmental Impact Statements, Environmental Assessments, Safety Analysis Reports, or other official DOE documents
- characterize and define trends in the physical, chemical, and biological condition of environmental media
- establish baselines of environmental quality
- provide a continuing assessment of pollution-abatement programs
- identify and quantify new or existing environmental-quality problems.

These objectives have been modified through discussions with RL to apply specifically to the Ground-Water Surveillance Project. Thus, ground-water sampling and analysis activities described in this document will be performed to meet the following objectives:

- identify and quantify existing, emerging, or potential ground-water quality problems
- review all ground-water quality data gathered on the Hanford Site to prepare an integrated assessment of the condition of ground water
- assess the potential for contaminants to migrate off the Hanford Site through the ground-water pathway
- characterize the ground-water flow system as needed to support other program objectives.

1.2 COORDINATION WITH OTHER HANFORD SITE MONITORING PROGRAMS

In addition to the monitoring activities performed specifically for environmental surveillance, other ground-water monitoring activities are being conducted at the Hanford Site to meet various requirements. Ground-water samples are collected to monitor the effects of operations in and around the 200 Areas for compliance with DOE orders (Serkowski and Jordan 1989) and for

facility-specific monitoring for compliance with RCRA (40 CFR 265) and Washington Administrative Code (WAC 173-303 and -304, WAC 1986a,b).

The facility-specific activities include sampling programs at facilities listed in Table 1.1. The compliance monitoring results (primarily for chemicals) contribute information useful in determining the total impact of Hanford operations on ground water and, therefore, are used in meeting DOE's environmental surveillance responsibilities. Characterization of ground-water contaminant plumes at waste sites that are no longer in use will be conducted in compliance with CERCLA. The Federal Facility Agreement and Consent Order (DOE 1989a) identifies these sites and the timetable for investigation and remediation. Drinking water supplies on site are sampled for the Hanford Environmental Health Foundation. Wells supplying water to the Fast Flux Test Facility (FFTF) water system are sampled by the Ground-Water Surveillance Project.

Sample collection and analysis for the Ground-Water Surveillance Project is coordinated with sampling performed for other ground-water monitoring programs. Once the wells to be sampled for ground-water surveillance are selected, the sampling schedules for other programs are reviewed. Wells to be sampled by more than one program are identified (e.g., CERCLA, RCRA, Operational and Ground-Water Surveillance). Well visits are coordinated so that samples for multiple programs are obtained during one well visit. Analyses that will be performed by one of the other programs are deleted from the list of analyses to be performed for the Ground-Water Surveillance Project. This process is used not only to eliminate redundancy, but also to minimize the amount of purge water generated at Hanford.

Analytical results from all ground-water sampling and analysis programs are stored in the Hanford Environmental Information System (HEIS). The use of this shared data management system allows each program to have access to all available data. This allows all ground-water quality data for the site to be used in the Ground-Water Surveillance Project's assessment of the impact of Hanford operations on ground-water quality.

TABLE 1.1. Waste Disposal Facilities with Ongoing RCRA Sampling Projects

100-D Pond
1301-N Crib
1324-N/NA Ponds
1325-N Crib
183-H Solar Evaporation Basins

216-A-10 Crib
216-A-29 Ditch
216-A-36B Crib
216-B-3 Pond
Grout Treatment Facility
Liquid Effluent Retention Facility (200 Area)

Solid Waste Landfill
Nonradioactive Dangerous Waste Landfill

216-B-63 Ditch
216-S-10 Pond
216-U-12 Crib
Single-Shell Tanks
200 Area Low-Level Burial Grounds
2101-M Pond

300 Area Process Trenches

2.0 HANFORD SITE GROUND-WATER MONITORING FACILITIES

This section provides background information on the number and types of wells constructed on the Hanford Site. Also included is a discussion of well design and construction.

2.1 AVAILABLE WELLS

Over 3500 wells have been installed on the Hanford Site (McGhan 1989). At the time construction of the Hanford Engineering Works (HEW) began in 1943 (HEW is a former designation for the Hanford Site), there were more than 200 farm, stock, and domestic wells on the site. These wells were generally hand-dug, less than 50 ft in depth and were used for domestic and irrigation water supply. Wells installed following occupation of the area by the U.S. government were constructed for a variety of purposes. Some were installed to provide sanitary water for U.S. Army and other facilities (Walters and Grolier 1960). Others were installed for use in ground-water monitoring programs to determine the effect of Hanford Site operations on ground water. Some were installed to obtain geologic information on the area to support DOE program needs or to assess the acceptability of the area for commercial nuclear power plant construction. Numerous vadose zone monitoring wells have been installed near waste storage tanks to detect tank leaks. In addition, deep wells were drilled for use in the Basalt Waste Isolation Project to assess the feasibility of using the deep basalt formations beneath the Hanford Site for permanent disposal of nuclear wastes (Fecht and Lillie 1982).

As of January 1989, approximately 2900 of the original 3500 wells installed still exist. Those that no longer exist have either caved in, or been lost or destroyed through a variety of processes. Very few of the wells have been abandoned in accordance with current Washington Administrative Code (WAC 173-160, WAC 1990) requirements for well abandonment. About 1990 of the remaining wells were drilled to depths below the water table, making them useable for ground-water sampling and monitoring. Of these, 1470 still allow access to ground water. The rest are dry because of sediment accumulation in the well or a drop in the water-table elevation (McGhan 1989). Approximately

600 of the 1470 wells are used for ground-water sampling, with additional wells being used to monitor water-table elevations.

2.2 WELL DESIGNS

Wells installed since 1985 have been constructed to meet WAC 173-160 requirements. These wells are generally completed with a 10-cm-(4-in.) diameter stainless steel casing and continuous slot well screen. The screen generally extends 3 m (10 ft) into the aquifer and approximately 1 m (several feet) above the water table to permit sampling of the upper portion of the aquifer and allow detection of any immiscible constituents that might be floating on the water table. A sand pack of appropriate size is placed outside the screen and extends 1 to 1.5 m (3 to 5 ft) above the screen. The annular space above the sand pack is filled with bentonite to approximately 6 m (20 ft) below land surface. A cement seal is placed from the top of the bentonite to land surface.

Most Hanford Site ground-water monitoring wells installed before 1985 are 15 or 20 cm (6 or 8 in.) in diameter, constructed of carbon steel casing. Confined aquifer monitoring wells have screens or perforated casing within the monitored aquifer. Monitoring wells for the unconfined aquifer are completed with well screens or perforated casing generally in the upper 3 to 6 m (10 to 20 ft) of the aquifer. Completion at the water table allows samples to be collected near the top of the aquifer where maximum concentrations for some radionuclides were measured at a few Hanford Site locations (Eddy et al. 1978). Several small-diameter (5-cm) wells are sampled for radionuclides only.

While the wells constructed before 1985 do not meet state regulations for monitoring well construction, many are being sampled for selected constituents. These wells are being used because they provide access to the aquifer in areas where more modern wells do not exist. The carbon steel casing is expected to have little effect on concentrations of non-reactive, highly soluble species such as nitrate, tritium and most volatile organics. More reactive species, such as Cr^{+6} (as Cr_2O_7^- or CrO_4^-), would be expected to react with the casing material and be removed from water standing in the well casing. Other constituents of concern (e.g., ^{137}Cs , ^{90}Sr , ^{99}Tc , Pu isotopes,

¹²⁹I) have reactivities somewhere between that of tritium and Cr⁺⁶. To enhance the representativeness of samples to be analyzed for constituents that may react with casing material, wells are purged for 20 min. (or three borehole volumes, whichever is less) before sample collection. Within this 20-minute period, 60% of the wells will have been purged of three borehole volumes, and approximately 30% of the wells will have been purged of between one and three borehole volumes. Several wells with very large water volumes will have been purged of less than one borehole volume.

3.0 MONITORING WELL SELECTION CRITERIA

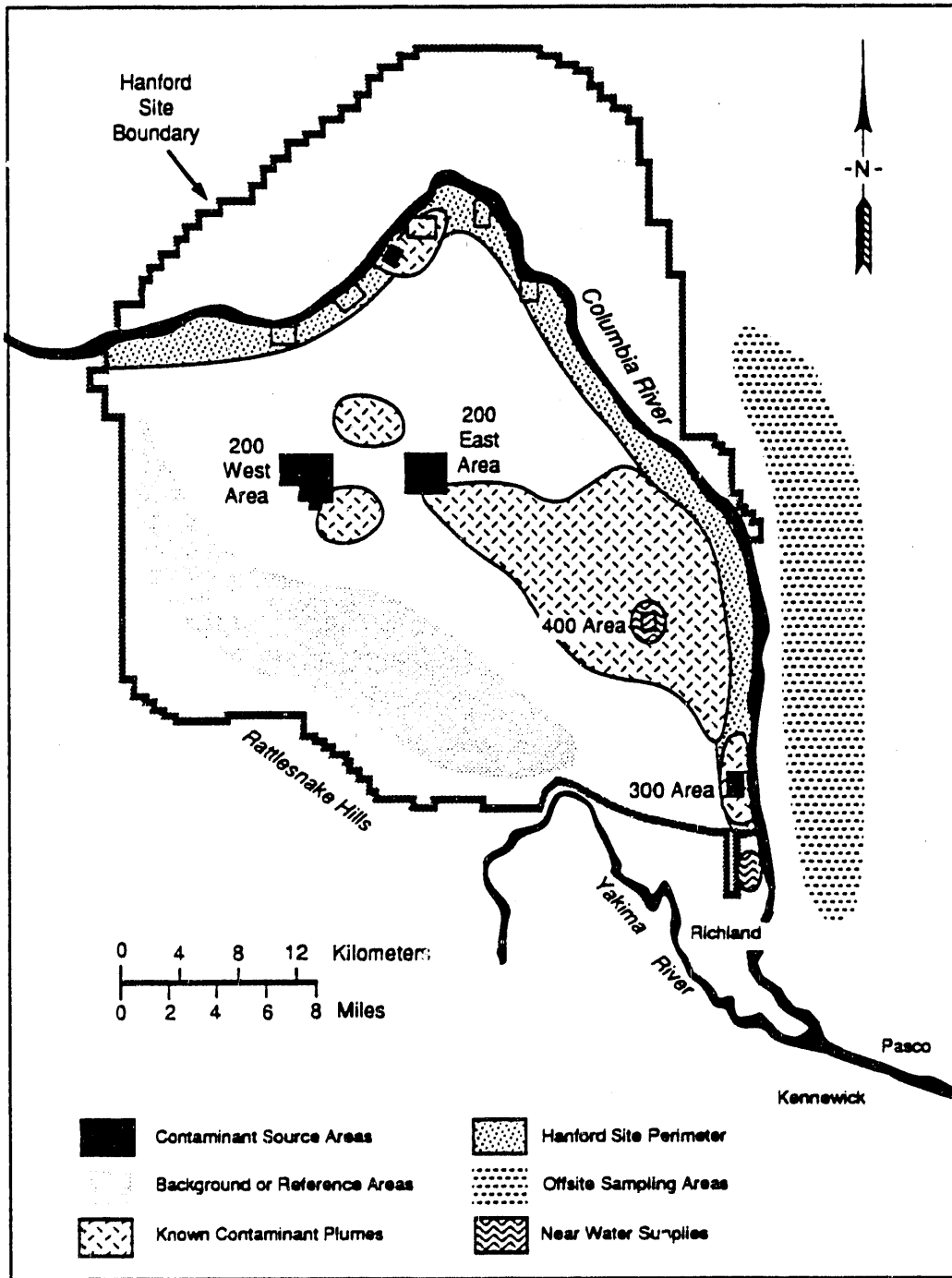
Nine groups of wells have been identified for monitoring to satisfy the project objectives stated in Section 1.1. Selection criteria include wells

- in contaminant source areas
- in and bordering known contaminant plumes
- sampled to screen for potential contaminants
- near water supplies
- at the Hanford Site perimeter
- open to the confined aquifer
- offsite
- in background or reference areas
- co-sampled with the Washington State Department of Health.

Figure 3.1 illustrates the generalized locations of the six discrete groups of wells. The three remaining groups are distributed across the Hanford Site. A brief rationale for each of the nine groups selected is presented in the following text. A more detailed discussion of contaminant source areas and known contaminant plumes can be found in Appendix A. Specific wells to be sampled and the rationale for their selection are presented in the Environmental Monitoring Master Sampling Schedule that is prepared annually (e.g., Bisping et al. 1991).

3.1 CONTAMINANT SOURCE AREAS

Known or potential contamination of the Hanford subsurface and associated aquifers is the result of diverse and specialized industrial operations required to perform the Hanford mission, which, since 1944, has included weapons grade plutonium production and purification, uranium recovery, TRU and fission product recovery, and waste management and disposal. Operations associated either directly or indirectly with plutonium production can be broadly divided into three areas of activity: fuel fabrications, reactor operations, and chemical separations. In addition, various research and development



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FIGURE 3.1. Generalized Locations of Wells for Monitoring Purposes

activities performed on or near the site have increased the potential for unusual contamination problems. These activities, combined with site and vehicle maintenance, may have contributed contaminants to ground water. The potential for offsite migration of Hanford related contaminants is clearly recognized in site ground-water monitoring strategies and the possibility of onsite migration of contaminants from neighboring industrial or agricultural sources must also be considered. These contaminant sources are discussed in detail in Appendix A.

Contaminant source areas are monitored to characterize and define trends in the chemical condition of the ground water and to identify and quantify existing, emerging, or potential ground-water quality problems. Source areas include regions with active waste disposal facilities or with facilities that have generated or received waste in the past. These include the 100, 200, and 300 Areas on the Hanford Site as well as the central landfill. Ground-water monitoring in these areas is performed primarily by the RCRA compliant or operational monitoring programs conducted by the operating contractor. Additional sampling has been initiated or is planned as part of CERCLA Remedial Investigation/Feasibility Study (RI/FS) activities on the Hanford Site. The Ground-Water Surveillance Project will supplement these monitoring activities as necessary to meet the needs of the Environmental Surveillance Program.

As actions are initiated to cleanup contaminant source areas on the Hanford Site, monitoring will expand to provide a continuing assessment of these pollution-abatement programs.

3.2 KNOWN CONTAMINANT PLUMES

Wells located within known contaminant plumes continue to be monitored to characterize and define trends in the concentrations of the associated radiological or chemical constituents. These wells are also monitored to meet the objective to quantify existing ground-water quality problems and to provide a baseline of environmental conditions against which future changes can be assessed. These wells will continue to be monitored as releases of waste to disposal facilities is halted and cleanup of the site begins to provide a continuing assessment of the effect of pollution abatement programs. Discrete ground-water contaminant plumes have been identified for numerous constituents

as described in Appendix A. A more complete description of known contaminant distributions is provided by Evans et al. (1990).

3.3 SCREENING FOR POTENTIAL CONTAMINANTS

During the process of planning the sampling schedule each year, particular wells may be selected for collection of screening samples. This may include wells that are not normally sampled being sampled for a comprehensive list of constituents, or selecting a large group of wells to sample for a constituent that has not been looked for widely on the Hanford Site. Examples of this include a screening for ^{129}I in 1989, screenings for plutonium and ^{99}Tc in 1990 and 1991, and screenings for semivolatile organics in 1987 and 1988. These screenings are performed to identify and quantify existing, emerging, or potential ground-water quality problems.

3.4 NEAR WATER SUPPLIES

Water supplies on and near the site potentially provide the most direct route for human exposure to contaminants in ground water. Three water supplies exist on site. One of these is for staff and visitors at the FFTF, one is for the Yakima Barricade guard house, and one is for the Hanford Patrol shooting range. Water supply wells for the City of Richland are adjacent to Hanford's southern boundary. Wells near these water systems, and in some cases the water supply wells themselves, are monitored to identify any potential water-quality problems before regulatory limits are reached.

3.5 HANFORD SITE PERIMETER

Wells along the Hanford Site perimeter will be monitored to assess the quality of ground water when it becomes accessible to the public (where access to the water can no longer be restricted by DOE). Wells in a region 2 km wide along the Hanford Site boundary have been identified for this group. Data gathered from wells in this region help address a number of the objectives of the program including the identification and quantification of existing, emerging, or potential ground-water quality problems, and the assessment of the potential for contaminants to migrate off the Hanford Site through the

ground-water pathway. Wells in this region to the west of the operating areas allow the chemistry of water moving onto the site to be characterized.

3.6 CONFINED AQUIFER

Surveillance and monitoring efforts in the past have focused on delineating the extent of ground-water contamination within the unconfined aquifer. The potential for transfer of contaminated ground water to the underlying upper-confined aquifer system(s) has been reported previously in a number of reports (e.g., Gephart et al. 1976; Spang et al. 1980; and Graham et al. 1981). No sitewide or offsite investigations, however, have been initiated to assess the extent of areal contamination within the upper-confined aquifer system(s). The few localized investigations that have been made (i.e., Strait and Moore 1982; Graham et al. 1984; and Early et al. 1988) are restricted to limited regions adjacent to the 200 Areas.

Of particular importance is the recognition that the upper-confined aquifer system is used for domestic water supply immediately outside the Hanford Site (e.g., east of the Columbia River). Because the Columbia River does not form a dominant line-sink (potential discharge) area along its entire course (DOE 1988a), the potential exists for ground-water withdrawals outside the Hanford Site to cause offsite migration of contaminated ground water within the upper-confined aquifer system(s). Information obtained from monitoring wells open to the confined aquifer will be used to assess the potential for contaminants to migrate off the Hanford Site through the ground-water pathway.

3.7 OFFSITE

Ground water is used for a domestic and agricultural water supply immediately outside the Hanford Site. While it is unlikely that contaminants have migrated offsite through the ground-water pathway, these water sources must be monitored to maintain a baseline of information on concentrations of contaminants that are potentially of Hanford origin.

It is unlikely that contaminants have migrated offsite to the north, west, or east through the ground-water pathway because water table elevations

in the unconfined aquifer and hydraulic head in the confined aquifers are higher in those regions than on the Hanford Site.

Hydraulic head gradients to the south of the site are influenced to a large degree by the operation of the Richland water supply system, irrigation of farmland, and the head relationship between the Yakima and Columbia rivers. Water levels and ground-water quality will be monitored in this area to assess the potential for contaminants to move offsite.

3.8 BACKGROUND OR REFERENCE AREAS

The goal of the Environmental Surveillance Program is to determine the impact of Hanford operations on the environment. To determine this impact, the quality of water on the Hanford Site prior to start up of operations must be known. Because this information does not exist, concentrations of naturally occurring chemical and radiological constituents in ground water sampled from wells located in areas unaffected by Hanford operations (e.g., upgradient of operating facilities) can be used to provide ground-water quality estimates for the period before Hanford operations began. In addition, the concentration of contaminants contributed by offsite operations upgradient of Hanford must also be determined to allow the contribution from Hanford and non-Hanford sources to be distinguished.

3.9 WASHINGTON STATE DEPARTMENT OF HEALTH

Each year approximately 20 wells on the Hanford Site are selected for joint sampling by the Washington State Department of Health and the Environmental Surveillance Program. This cooperative sampling provides a mechanism for the state to assess the quality of the DOE program and provides information for the Washington State Department of Health's assessment of radiological quality of ground water in the state.

4.0 ANALYSES TO BE PERFORMED

Table 4.1 lists chemicals and radionuclides analyzed for in samples collected for ground-water surveillance. These constituents have been selected either because they exist naturally in ground water and can be used to help understand the ground-water flow system or because they may have been disposed of at Hanford. Analyses for all constituents shown in the table are not performed on all samples. A sample may be analyzed for a constituent if

- the constituent has been observed in previous samples from that well
- the well is downgradient of a disposal site known to have received that constituent
- the constituent is of natural origin and is being used to help understand the ground-water flow system
- the well has been selected for inclusion in a sitewide screening for a constituent
- the well is being sampled to determine the concentration of chemicals or radionuclides of interest in areas unaffected by Hanford operations.

Additional analyses are performed to document the areal distribution of contaminants of concern, and to determine concentrations of regulated materials in areas of public access.

Analytical methods used for chemicals analyzed are based on EPA SW-846 (EPA 1982), ASTM (ASTM 1991), or other standard methods. No comparable standard methods are available for radiological analyses. Methods for analyzing radiological parameters are developed by the contract laboratory and approved by PNL. The methods are listed in Appendix B. The analyses to be performed on samples from each well are presented in the Environmental Monitoring Master Sampling Schedule (e.g., Bisping et al. 1991).

TABLE 4.1. Radionuclides and Chemicals Analyzed for the Hanford Ground-Water Surveillance Project

<u>Radiological Parameters</u>	<u>Chemical Parameters</u>
Gamma Scan	pH (field and laboratory)
(¹³⁷ Cs, ⁶⁰ Co observed)	Conductance (field)
²⁴¹ Am	Alkalinity
³ H	B, Be, Na, Mg, Al, K, Mo
⁹⁰ Sr	Ca, V, Cr, Mn, Fe, Ni, Co
⁹⁹ Tc	Cu, Zn, Sr, Ag, Cd, Sb, Ba
¹²⁹ I	F ⁻ , Cl ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻
Uranium Isotopes	As, Se, Pb, Bi
Uranium (total)	Hg
Plutonium 238, 239, 240	CN ⁻
Gross Alpha	NH ₃
Gross Beta	Volatile Organic Constituents (Specific VOCs listed in Appendix B)

5.0 SAMPLE COLLECTION

This section presents the rationale for three aspects of sample collection: the frequency of sample collection, the selection of sample containers and preservation techniques, and the sample collection methods.

5.1 SAMPLING FREQUENCY

Wells sampled for environmental surveillance have generally been sampled quarterly for 1 year or more. The data obtained from this initial sampling have been evaluated and a long-term monitoring frequency established. In general, wells near waste disposal sites where changes in contaminant concentrations may occur over short periods continue to be sampled quarterly. Wells sampled to track the migration of contaminants away from source areas are sampled semiannually. Wells in areas unaffected by Hanford operations and where changes in concentration have been observed to occur gradually are sampled annually. Other sampling frequencies may be established in response to special situations.

5.2 SAMPLE CONTAINERS AND PRESERVATION

Sample containers and preservation techniques used for each sample are selected to minimize the alteration of the analytes of interest prior to analysis. Bottle type and preservative for each parameter analyzed are shown in Appendix B, Table B.2.

Precleaned sample containers are used to collect ground-water samples that will be analyzed for hazardous chemical constituents. Containers used for the collection of ground water to be analyzed for radiochemical constituents do not have to be precleaned to EPA protocols by the manufacturer. Precleaning of bottles used for radionuclides is not required because it is unlikely that contamination of the bottles with radionuclides of interest would occur during manufacturing.

Many of the constituents measured in Hanford ground water require preservation to prevent degradation after collection. Commonly used chemical preservatives include HNO_3 , HCl , H_2SO_4 , and NaOH . Use of these preservatives

is documented in a log that identifies the preservative, manufacturer, lot or batch number (if available), and date bottle was opened. Samples are also cooled in some cases to preserve them.

Holding time requirements specified in EPA SW-846 are used by the Ground-Water Surveillance Project for chemical constituents measured in ground-water samples. Holding times for radiological species are similar to holding times for nonradioactive constituents. However, the half-life of a radioisotope must also be considered.

5.3 COLLECTION METHODS

Samples are collected following internally documented sampling procedures (PNL 1989) based on EPA guidelines (EPA 1986). Deviations from EPA (1986) are generally in response to site-specific considerations or available data indicating that the EPA recommended method is no longer the most appropriate. These deviations are discussed in the following sections.

5.3.1 Pumping Method

EPA recommends the use of a gas operated fluorocarbon or stainless steel squeeze pump (also known as a bladder pump) or a fluorocarbon or stainless steel bailer to collect samples. Bladder pumps are not used for ground-water surveillance because they have limited capability to lift water from the depths encountered in Hanford wells. In addition, reports by Liikala et al. (1988) and Evans et al. (1989) showed that there was no significant difference in the concentrations of volatile organic compounds in water samples collected by a bailer, bladder, or submersible pump. Thus, whenever possible, stainless steel submersible pumps have been installed in wells that are to be sampled. Wells that are too small in diameter or have an insufficient water column are sampled using a fluorocarbon bailer, as are those where the transmissivity of the aquifer is too low to allow pumping.

Wells used in monitoring networks established by the operating contractor around waste disposal facilities are often fitted with a stainless steel, positive displacement (Hydrostar) pump. Data from these wells are also used to meet the objectives of the Ground-Water Surveillance Project.

5.3.2 Purge Time and Treatment

Standing water in wells fitted with submersible pumps is removed before sample collection to ensure that the sample collected is representative of the water in the aquifer around the well. Because newly constructed wells are generally completed in the upper few meters of the aquifer, the water column is short, allowing three well volumes to be purged before sample collection. Older wells, which often have a longer standing water column, are purged for sufficient time to remove three times the volume of water standing in the well or for 20 min., whichever is less. The volume of water removed after a 20-min. purge generally ranges from 600 to 750 L (160 to 200 gal), depending on the depth of the well and standing water level. A 20-min. limit has been set because in most wells this is sufficient to remove three well volumes.

During purging, several chemical and physical parameters are monitored to ensure that water representative of aquifer conditions is collected for analysis. Temperature, pH, and electrical conductivity are measured three times on the water being discharged from the well. The sample is collected at the end of the purge time only if the last two measurements are within the specifications stated in the sampling procedure.

Ground-water samples continue to be collected with a bailer in a few wells where a submersible pump cannot be installed. It has generally been impractical to purge three borehole volumes from these wells. To minimize the problems created by not purging the well, tritium and nitrate are the only constituents analyzed for in samples collected with a bailer. These two constituents are very soluble in ground water and, in general, do not react with well construction material; therefore, the analytical results are considered indicative of concentrations in the aquifer even though the well has not been purged. All purge water is handled in accordance with the "Strategy for Handling and Disposing of Purgewater at the Hanford Site, Washington," which is included as an appendix to DOE (1989a).

5.3.3 Filtering

Ground-water samples collected for metals analysis are filtered in the field. A disposable, 0.45- μm pore-sized filter pack is connected to the sampling line. The filter is purged with 500 mL of well water, and then a sample is collected. Samples are filtered to eliminate contributions from geologic material and corrosion from carbon steel casing. This practice is justified because the objective of the program is to determine the impact of Hanford operations on ground-water quality, not to determine the concentration of a certain constituent that would be consumed if the well supplied drinking water.

Samples collected for radionuclide analysis are not filtered. This is because most of the radionuclides present in samples collected at Hanford are the result of Hanford activities and do not have a natural source. The results from analysis of unfiltered samples will include the soluble and particulate radionuclides. This is a conservative approach to determining the concentration of radionuclides in ground water.

5.3.4 Chain of Custody

All samples are tracked by chain-of-custody procedures from sampling through analysis and disposal. A chain-of-custody form is generated when sample containers are prepared. This form accompanies the sample from that point through disposal of the sample. Each time the sample changes hands both the person accepting the sample and the person relinquishing the sample sign the form to document the exchange.

6.0 QUALITY CONTROL

Quality control (QC) activities are performed to determine how well analytical results represent actual concentrations of chemicals and radionuclides in the aquifer. The analytical laboratory maintains a program to assess the quality of its work. This generally involves analyses of known standards and duplicates of samples. The program submitting samples to the laboratory often performs a variety of activities to independently assess the quality of the analytical results. These may include submitting duplicate samples to another laboratory, submitting samples to which known quantities of a constituent have been added, and submitting samples to determine if contaminants have been added to the sample by the container, the sample collection process, or the act of transporting the sample to the laboratory. The required QC program for the Ground-Water Surveillance Project is presented in the project QA plan. A summary of QC checks used by the project to assess the quality of sample collection and analysis is presented in Table 6.1. The primary analytical laboratory operates an internal laboratory QC program implemented through its analytical procedures.

6.1 INTERLABORATORY COMPARISONS

Interlaboratory comparisons between the quality control laboratory and the primary analytical laboratory will be approximately 1 per 20 field samples

TABLE 6.1. Summary of Quality Control Checks

<u>Data Characteristic Evaluated</u>	<u>Sample Type</u>	<u>Frequency</u>
Field/Transport Contamination	Field Blank	1 per 20 samples or per sample event
Field/Transfer Contamination	Field Blank	1 per 20 samples or per sample event
Laboratory Contamination	Blank	1 per batch or per sample event
Laboratory Accuracy	Blind Standards	See Table 6.2
Precision (field variability)	Field Duplicates	1 per 20 samples or per sample event
Precision (laboratory variability)	Laboratory Replicates	1 per batch
Container Contamination	Empty Container	1 per lot

TABLE 6.2. Blind Standards

<u>Analyses</u>	<u>Approximate Frequency</u>
Volatile Organic Constituents	Monthly
Metals	Quarterly
As, Se, Pb	Quarterly
Hg	Quarterly
Anions	Quarterly
Cyanide	Quarterly

(with duplicate). Interlaboratory blind standard comparisons will also be performed. These comparisons are discussed further in Section 6.2.

6.2 BLIND STANDARDS

The frequency at which blind standards are submitted to the primary analytical laboratory depends on 1) which constituents are detected at or above the drinking water standard (DWS) or screening levels, 2) which constituents are detected, but at levels below DWS or screening levels, and 3) specific constituents that may be present, based on disposal records, but have not been detected. The frequency of testing for the constituent and the complexity of the analysis method are also considered. Table 6.2 shows the types and frequency of blind standard analyses performed.

The acceptance limit for blind standards is ± 2 standard deviations (s.d.) from actual value. In interlaboratory comparisons using actual field samples, a difference between laboratory results of 2.8 s.d. is allowed. This criterion is based on the reproducibility limit, with 95% confidence that random error is not responsible for the difference.

When results of blind standards, or interlaboratory comparisons fall outside the acceptance limits specified above, the cause must be investigated. Normally this means additional samples will be submitted to the laboratory to determine the adequacy of corrective action.

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APPENDIX A

CONTAMINANT SOURCES AND PLUMES

APPENDIX A

CONTAMINANT SOURCES AND PLUMES

This appendix provides further details of known or potential contamination of the Hanford subsurface and associated aquifers. Contaminant sources are discussed followed by details of known contaminant plumes.

A.1 CONTAMINANT SOURCES

Contaminant sources discussed here include weapons grade plutonium production and purification, uranium recovery, transuranic (TRU) and fission product recovery, and waste management and disposal. Plutonium production operations can be broadly divided into three categories: fuel fabrication, reactor operation, and chemical separation. Research and development activities as well as site and vehicle maintenance activities may also have contributed contaminants to the subsurface.

A.1.1 Fuel Fabrication

Fuel fabrication operations have taken place in the 300 Area throughout most of Hanford's operational history starting in 1944 and terminating in 1987. The purpose of this activity was the fabrication of uranium-silicon metallic fuel elements used as both fuel and feedstock for the production reactors. Uranium-235 enrichments have ranged from 0.72% (natural abundance) to 1.3%. Fuel produced early in the process was enclosed in aluminum cladding. More recently zirconium cladding was used. In addition to uranium, other known large volume wastes associated with the process have included nitric acid, copper (extrusion waste), hexavalent chromium (decontamination agent), and trichloroethylene (cleaning solvent). Radiological wastes have included technetium-99 and uranium-236, both of which are associated with the recycling of processed and recovered uranium. It is important to note that while significant local disposal of fuel fabrication waste is known to have occurred in the 300 Area, some fuel fabrication wastes were transferred to other parts of the site. For example, the 183 H Solar Evaporation Basins

located in the 100-H Area received 300 Area fuel fabrication waste containing uranium, chromium, and technetium-99. Leakage of one of the basins has resulted in contamination of ground water with those species in the 100-H Area (Hall 1989). Ground-water contamination in the 300 Area is associated primarily with the past use of holding ponds (particularly the North and South Process Ponds) and several process trenches including the 300 Area Process Trench, which is still in operation.

A.1.2 Reactor Operations

Nine production reactors have operated in the Hanford 100 Areas throughout the history of the site. Eight of the reactors used single pass cooling. Cooling water was taken from the Columbia River and discharged back to the river after a single pass through the reactor. Those reactors are respectively B and C (100-B Area), KE and KW (100-K Area), D and DR (100-D Area), H (100-H Area) and F (100-F Area) Reactors. The eight reactors were operated in various combinations from 1944 to 1971. A ninth, dual-use (electrical generation and plutonium production) reactor, N Reactor, was built in 1964 and operated until 1987. The N Reactor used secondary cooling.

Reactor operations have resulted in the release of a number of different types of contaminants. Radiological contamination associated with cooling water discharge has resulted in some localized contamination throughout the 100 Areas. This contamination consists primarily of long-lived fission products from fuel element failure and activation products associated with translocated corrosion products and activation of cooling water impurities. In the case of the single pass reactors, most of the more mobile components have been flushed into the river by the very large volumes of cooling water used. Radiological contamination of the ground water from those reactors is thus relatively limited. The "feed and bleed" system employed at the N Reactor has discharged far more limited volumes of water and as a result mobile radiological contamination of ground water associated with N Reactor operation (primarily strontium-90) remains as a persistent contamination issue.

Reactor operations have also been the source of several kinds of chemical contamination. Cooling water was typically treated with sodium chromate

to inhibit corrosion of aluminum reactor components. This practice resulted in the discharge of hexavalent chromium, a highly mobile and toxic form of the element. While much of the chromium has clearly been flushed out by the high volumes of cooling water used, significant residual levels of chromium associated with fractured cooling water retention basins and discharge trenches continue to provide a source of chromium contamination to the ground water throughout the 100 Areas. Hexavalent chromium was also used for some decontamination activities and discharged to cribs. Other decontamination wastes included large quantities of nitric, oxalic, and sulfamic acid. Sulfuric acid used for treatment of radiological waste ion exchange media was discharged to a crib in the 100-N Area resulting in exceptionally high sulfate levels in the ground water near the crib.

A.1.3 Chemical Separations

Chemical separations activities performed in the 200-East and 200-West Areas represent the most complex collection of site activities that have produced a large volume of releases to the environment. Major processing campaigns have included bismuth phosphate process (200-East and 200-West, 1945-1952); uranium recovery process (200-West and 200-East, 1952-1958); REDOX (200-West, 1951-1967); PUREX (200-East, 1956-1972 and 1983 to 1989); waste fractionation process (200-East, 1968-1983); plutonium purification and reclamation (200-West, 1949-present); and uranium purification process (200-West, 1952-present). High-level waste streams associated with these activities have typically been stored in underground storage tanks, of either single-shell, or more recently, double-shell design.

Process condensates associated with fuel decladding, fuel dissolution, and other related activities have been disposed to numerous cribs throughout the 200 Areas as have a variety of decontamination wastes. Finally, large volume, and typically uncontaminated, cooling water has been discharged to surface impoundments such as U-Pond, Gable Mountain Pond, and most recently, B-Pond. In some cases single-shell tank waste was further processed to remove radiological contaminants prior to crib or trench discharge of the aqueous supernatant. Leakage of single-shell tanks has also resulted in release of aqueous waste streams to the soil column. A complete description of

activities associated with single-shell tank wastes is given in a recent report by the site operating contractor, Westinghouse Hanford Company (WHC) (Waite 1991).

Long-lived radiological wastes associated with crib or trench discharges that have affected the ground water include tritium, cobalt-60, strontium-90, technetium-99, iodine-129, and uranium. Plutonium and cesium-137 are in some cases associated with these wastes but have not typically affected the ground water because of strong binding to soil minerals. One significant exception is the 216-B-5 Reverse Injection Well, which was used for a limited time in the early days of the project (1945-1947) to inject the supernatant overflow from a B-Plant settling tank directly below the water table. Detectable levels of both plutonium and cesium-137 are still present in monitoring wells near that facility. Several cribs near the Z-Plant (Plutonium Finishing Plant) in the 200-West Area have also received relatively large burdens of transuranics (primarily plutonium and americium); however, it is generally believed that those wastes have not reached the ground water.

Chemical usage associated with the separations activities has also been diverse. Chemicals associated with separations activities which are known or suspected to have been released in significant quantities include nitrate, fluoride, ammonia, sulfate, bismuth phosphate, sodium bismuthate, sodium dichromate, lanthanum fluoride, sodium ferrocyanide, nickel, cadmium, aluminum, zirconium, carbon tetrachloride, methyl isobutyl ketone (hexone), tributyl phosphate, dibutyl phosphate, dibutylbutylphosphonate, and lard oil (Stenner et al. 1988; DOE 1991).

Some compounds may have been introduced as impurities or degradation products of other materials. For example, the sizable chloroform plume found in the 200-West Area is likely to have been either a degradation product or an impurity in the carbon tetrachloride used for plutonium purification chemistry at Z-Plant. Many of these chemical species are not expected to impact ground water because of their known chemical properties. Multivalent cationic species such as cadmium, nickel, and zirconium tend to be strongly sorbed on to soil minerals. Bismuth compounds generally tend to be insoluble. Many organic species such as the largely aliphatic or olefinic components of lard oil will exhibit a hydrophobic character severely restricting their subsurface

mobility. Some transformation or degradation in the environment is also possible. For example, ammonia will convert to nitrate on a relatively short time scale.

The presence of complexing agent has the potential to alter mobilities in unexpected ways. For example, ferrocyanide shows evidence of greatly enhancing the mobility of cobalt-60 probably as the result of the formation of a mobile anionic ligand complex. In addition to ferrocyanide and the organophosphates, a number of other complexing agents have been used in the 200 Areas including citric acid, EDTA, and NTA. Those materials were generally retained in underground tanks; however, some release may have occurred as a result of tank leaks. Some chemicals are quite mobile and do impact the ground water. Notable examples include anionic species (nitrate, sulfate, fluoride, chromate, and ferrocyanide) and sparingly soluble low molecular weight organics (carbon tetrachloride, chloroform, trichloroethylene, etc).

A.1.4 Research and Development

Numerous, diverse, research and development activities have been performed on the Hanford Site over its 40-year history. Activities have included experimentation associated with the plutonium production mission as well an extremely complex mix of other projects spanning virtually all scientific disciplines. Research activities performed in the 300 Area have been particularly diverse. It is thus virtually impossible to accurately forecast all possible chemical and even radiological contaminants that could potentially affect the ground water from research and development activities. Some degree of flexibility in the current monitoring and future characterization programs is thus needed.

A.1.5 Maintenance

The Hanford Project has been, and continues to be, a large and complex industrial operation involving such activities as facilities, vehicle, and grounds maintenance. Some of these activities have the potential for subsurface chemical impacts. For example, vehicle maintenance operations conducted in the 1100 Area have resulted in known releases of battery acid (lead and sulfate), degreaser solvents (TCE, PCE, and TCA), antifreeze (ethylene glycol) (Evans et al. 1989). Disposal of vehicle maintenance degreaser

solvents in sanitary trenches at the Hanford Central Landfill has resulted in some ground-water contamination requiring long-term monitoring (Evans et al. 1989).

Chemicals associated with grounds maintenance require some assessment also. Herbicides are used in some areas for control of unwanted vegetation such as tumbleweed. Pesticides may also be used for control of harmful insects. Those chemicals are not expected to represent serious threats to ground-water integrity and no point sources or significant transport mechanisms to the water table have been identified; however, since the potential exists, network analytical planning must include some provision for analysis of pesticides and herbicides.

A.1.6 Offsite Sources

The Hanford Site is to a large extent isolated from other sources of pollution; however, some inputs from other sources are inevitable. At a minimum, some global contributions are present. Global fallout from nuclear weapons testing contributes measurable levels of long-lived fission products and plutonium. These components have not typically had time to reach the ground water through natural recharge but do affect the Columbia River, which in turn provides a route to the ground water through the use of the Columbia River for cooling water. Similarly, cosmic-ray-produced sources provide some finite amount of radiological background for such species as tritium and carbon-14.

In addition to global sources there are some local sources of potential on-site transport. Agricultural operations in the area have the potential to contribute some nitrate input. Agricultural activities have been greatly expanded in the area just south of the Hanford Site. In addition to potential agricultural contaminants, that activity will greatly alter the water balance associated with artificial recharge and thus may significantly increase the rate of on-site transport. Industrial operations near the site margins include a food processing plant, a municipal landfill, a commercial nuclear fuel fabrications facility, and a commercial nuclear power reactor complex. Industrial activities in the area are continuing to expand. Their effects on the site will need to be continually reassessed.

A.2 KNOWN CONTAMINANT PLUMES

Discrete ground-water contaminant plumes have been identified for numerous constituents including radiological, hazardous chemical, and non-hazardous indicator species. These plumes and the constituents composing them are detailed in the following subsections.

A.2.1 Radiological Constituents

Tritium

Numerous tritium plumes exist on the site. The most extensive plume originates from the southeast corner of the 200-East Area near PUREX and extends eastward to the Columbia River. The plume extends southward almost to the 300 Area and northward along the river to the area of the old Hanford Town Site covering an area of approximately 300 km². In addition to the PUREX plume a sizable plume extends eastward from the cribs associated with REDOX. Other minor plumes are located in the 100-N, 100-D, 100-H, and 100-F Areas. High tritium levels have recently been observed adjacent to the 100-K Area fuel storage basin. Tritium plume maps are prepared annually and published in the Hanford Site Annual Environmental Monitoring Report. The most recent version can be found in Jaquish and Bryce (1990).

Cobalt-60

Cobalt-60 is typically strongly sorbed on soil (Routson et al. 1978) and does not show up in ground-water plumes (Evans et al. 1990). The one major exception on the site is found directly north of the 200-East Area. The plume is believed to be associated with fractionated single-shell tank wastes originating from U-Plant. Waste streams from the uranium recovery process temporarily stored in single-shell tanks were treated with sodium ferrocyanide and nickel to coprecipitate cesium-137 prior to soil column disposal in the BY Cribs and one of the BX Trenches during the period 1954 and 1955. That practice was changed after a relatively short time because of the discovery in 1956 that large amounts of cobalt-60 were being mobilized into the ground water. Most of the cobalt-60 from that era has decayed to relatively minor levels. The plume found north of the 200-East Area is the remnant of that earlier waste stream. For a more comprehensive discussion of this situation see Waite (1991), Section 3.2.

Strontium-90

Strontium-90 contamination is found in the ground water in several locations on the Hanford Site. Small but significant plumes are found in the 100-B, 100-D, 100-F, 100-H, and 100-K Areas associated with past reactor operations. A major strontium-90 plume is present in the 100-N Area downgradient of the 1301-N liquid waste disposal facility (LWDF). It has been somewhat difficult to accurately define the extent of that plume because of the scarcity of wells in the area of interest. New well construction in the 100-N Area for RCRA compliance has focused almost exclusively on the more recently utilized 1325-N LWDF. Most of those wells were installed in essentially uncontaminated areas although some strontium-90 contamination is evident near the head of the 1325 Trench. Strontium-90 originating at the 1301-N LWDF has been observed at levels up to nearly 3000 times the DWS near the head of the trench and at somewhat lower levels in a series of seepage wells on the shore of the Columbia River. Data from the seeps are presented by Dirkes (1990). A small plume is found in the southeastern part of 200-West Area near the former site of REDOX operations. Strontium-90 is also present in ground water in the central portion of the 200-East Area apparently originating from the 216-B-5 Reverse Injection Well. For more information see Evans et al. (1990).

Technetium-99

Technetium-99 plumes are found in many areas of the site; however, limited monitoring information has been available on this species in the past. A more complete picture of its distribution has only recently emerged. Some measurable technetium is found in 100-B Area ground water and a major technetium plume is present in the 100-H Area associated with the 183-H Solar Evaporation Basin leakage (Hall 1989). The extent of technetium-99 contamination at the 100-N Area is not well documented at present but does appear to be less pervasive than is the strontium-90 contamination. Technetium-99 plumes are present in both the 200-West and 200-East Areas. The plume in the 200-West Area resulted from disposal of uranium recovery waste to the 216-U-1 and 216-U-2 Cribs from 1951 to 1967. The plume has migrated somewhat to the west with ground-water flow and is now centered beneath U-Plant with some extension to the west. The dominant 200-East Area technetium-99 plume is actually located in a region just north of the 200-East Area in the 600 Area.

It is believed to be associated with BY Cribs waste streams. Low-level technetium-99 is also associated with the main PUREX tritium plume.

Iodine-129

Iodine-129 is of importance for several reasons. Iodine-129 has a very long half-life (16 million years) and is thus potentially persistent in the environment following release. Also, because ingestion of iodine results in selective accumulation in a very small organ (the thyroid), the hazard potential is considered to be abnormally high. Iodine-129 thus has the lowest regulatory limit for drinking water (1 pCi/L) of any of the long-lived radiological species under consideration at Hanford. In addition, iodine has high mobility in ground water and some degree of volatility rendering it prone to release with the larger volume process condensate liquids. There are thus large-area, low-level iodine-129 plumes associated with the main PUREX and REDOX process condensate plumes discussed above. As is the case with tritium from the same processes, locally elevated concentrations of iodine-129 are found near the source cribs at PUREX and REDOX. Iodine-129 levels drop to near the DWS throughout the remainder of the plumes. Incremental addition of iodine-129 from the PUREX process condensate plume is measurable in the Columbia River downstream of the site using special high-sensitivity methods; however, the incremental input represents a final concentration of less than 0.1% of the DWS.

Cesium-137

Cesium-137 tends to be strongly sorbed on soil and does not typically form extensive ground-water plumes. The only notable exception on the site is the area immediately adjacent to the 216-B-5 Reverse Injection Well in the 200-East Area. Cesium-137 has been detected in three monitoring wells near site of the reverse well.

Plutonium

Plutonium is also strongly sorbed on soil and is not typically found in ground water (Silva et al. 1978). Again, the exception is the site of the 216-B-5 Reverse Well, which shows significant levels of plutonium 238, 239, and 240.

Uranium

The highest uranium levels in Hanford ground water occur in the 200-West Area in wells adjacent to the inactive 216-U-1 and 216-U-2 Cribs (Baker et al. 1988). The plume is centered beneath U-Plant extending to the north. There is also a small uranium plume in the northwest corner of the 200-East Area downgradient of B-Plant. The source of the plume is believed to be the 216-B-12 Crib, which received an estimated 21 tons of uranium during its operation between 1957 and 1973 (Stenner et al. 1988).

A small uranium plume of unknown origin exists in the 100-F Area. A uranium plume also exists in the 100-H Area associated with the 183-H Solar Evaporation Basins. Other 100 Area sites do not show significant uranium contamination in the local ground water.

A sizable uranium plumes exists in the unconfined aquifer beneath much of the 300-Area in the portion of the area downgradient of a number of active and inactive LWDFs known to have received uranium containing fuel fabrications wastes.

A.2.2 Hazardous Chemical Constituents

Nitrate

Nitrate has been used in extremely large quantities throughout the history of the site for numerous applications. The use of nitric acid as a fuel dissolver reagent has resulted in large amounts of nitrate containing process condensate to be disposed to cribs and trenches. Extensive nitrate plumes thus originate from both the PUREX and REDOX LWDFs, forming plumes over the same areas as described above for tritium. There are also tritium plumes associated with each of the 100 Areas. There are at least two distinct nitrate plumes in and south of the 300 Area. Elevated nitrate concentrations are also found in the 3000 Area and points south, probably as a result of agricultural inputs unrelated to Hanford Site operations. In addition, at least two localized areas of elevated nitrate concentration within the bounds of the site at the western edge of the 600 Area are believed to be of agricultural origin. Nitrate plume maps are prepared annually and published in the Hanford Site Annual Environmental Monitoring Reports. The most recent version can be found in Jaquish and Bryce (1990).

Sulfate

While sulfate is not normally considered to be a hazardous chemical, there are secondary water-quality standards regulating the excessive buildup of sulfate in ground water. In addition, sulfate is a good indicator of site operational impacts on the ground water since it was used in large quantities for numerous purposes. A comprehensive assessment of sulfate plumes has not been rigorously conducted as yet, but several known sulfate plumes are worthy of mention.

Distinct sulfate plumes are found in the 100-D, 100-F, 100-H, and 100-N Areas. In the case of the 100-N Area plume, sulfate levels are quite high extending up to as much as four times the secondary water quality standard. Elevated sulfate levels are seen in numerous wells in both the 200-East and 200-West Areas. There is a small sulfate plume of unknown origin directly south of B-Pond. The most prominent sulfate plume in the 600 Area is located directly north of 200-East Area and is apparently coincident with other contaminant plumes at that location, which originated in the BY Cribs.

Fluoride

Fluoride has been used in very large quantities on the site, particularly as a fuel decladding agent. While much fluoride containing waste has been disposed to ground it typically does not appear at elevated levels in the ground water. It is conceivable that much of the fluoride has been immobilized through geochemical reactions in the soil column (i.e., formation of fluorite or fluorapatite, for example). The only known exception to this general rule is found in the 200-West Area near T-Plant. The source of the plume is believed to be LWDFs associated with Z-Plant that received several hundred tons of aluminum fluoride nitrate. It is possible that formation of the fluoroaluminate ion may have stabilized the fluoride sufficiently to allow penetration to the ground water. It is, however, noteworthy that there is no detectable aluminum associated with the plume at this time.

Ferrocyanide

Ferrocyanide (measured as total cyanide) is found in the ground water immediately north of the 200-East Area BY Cribs. Other contaminants and

indicator parameters associated with this plume include tritium, cobalt-60, technetium-99, nitrate, sulfate, calcium, and strontium.

A small cyanide plume is also present in the 200-West Area apparently associated with ferrocyanide containing T-Plant waste disposed to the 216-T-26 Crib.

The chemical form of the cyanide is believed to be ferrocyanide based on its known form of injection combined with some limited laboratory studies by a special ion chromatography method; however, the laboratory studies were somewhat inconclusive.

Chromium

Significant chromium plumes are found in the 100-B, 100-D, 100-H, and 100-K Areas. In parts of the 100 Area (particularly near the 100-D and 100-H Areas) the chromium plumes extend well beyond the reactor site boundaries,

Two separate but relatively minor chromium plumes have been observed in the 200-West Area. One plume is located near REDOX and the other is in the north end of the site just to the west of T-Plant. Neither plume has a well established origin but the plume associated with T-Plant is likely to have originated at the T-28 Crib, which received decontamination waste from T-Plant in the early 1960s. The REDOX plume is likely to have originated from one of the S Cribs. Hexavalent chromium was used as an oxidizing agent in the REDOX process.

Carbon Tetrachloride

A large ground-water plume of carbon tetrachloride spans most of the 200-West Area. The plume originates from three cribs (216-Z-9, 1955-1962; 216-Z1A, 1949-1959; and 216-Z18, 1969-1973) used for disposal of organic and other liquid waste from the plutonium purification process. The best inventory estimates (DOE 1991) show approximately $3.63E5$ to $5.8E5$ L of carbon tetrachloride disposed to those three cribs. The center of the plume is near Z-Plant. Carbon tetrachloride levels up to 1700 times the DWS have been observed. The plume has been under observation, at least to a limited extent, since early 1986. During that time the western edge of the plume has shown definite evidence of spread, whereas other margins of the plume appear to be

relatively stable. A limited scale remedial action was recently started on this plume using vacuum extraction techniques (DOE 1991). It will thus be extremely important to maintain a careful long-term monitoring record of carbon tetrachloride in all accessible wells in the 200-West Area and immediate environs. Significant levels of carbon tetrachloride are not present in ground water elsewhere on the site. The plume appears to have a sharp boundary when investigated by high sensitivity electron capture gas chromatography methods, which provide detection sensitivity to more than three orders of magnitude below the DWS.

Chloroform

In addition to the carbon tetrachloride plume, a sizable chloroform plume also exists in the 200-West Area near Z-Plant. The origin of the chloroform plume is unclear. It is likely to be associated in some way with the carbon tetrachloride disposal either as a degradation product or source impurity. The chloroform plume overlaps the carbon tetrachloride plume but is not exactly coincident with it. The chloroform plume appears to have two centers located very close to the 216-Z-9 and 216-Z-18 Cribs, whereas the carbon tetrachloride plume is centered approximately 300 m due north of the 216-Z-18 Crib.

Chloroform is found at a number of other locations on the site such as the 300-Area where chlorinated water is used for process applications. Chloroform is typically found in treated water including city supplied drinking water as the result of the reaction of chlorine with trace natural organic impurities in the water.

Trichloroethylene

Trichloroethylene (TCE) contamination is found at levels in excess of the DWS at several locations on the site including the west side of the 100-F Area, the 200-West Area, the Central Landfill, the north end of the 300 Area, and the Horn Rapids Disposal Site. In addition, measurable levels of TCE below the DWS have been found widely distributed in the 100 Areas.

The TCE plumes in the 200-West Area are in precisely the same locations as the chromium plumes, which is suggestive of a common origin. No other source information is currently available.

The chlorinated solvent contamination in the Central Landfill is known to have been caused by the disposal to sanitary trenches of degreaser wastes from the 1100 Area vehicle maintenance operation. The spatial distribution of TCE at the landfill is not well determined because wells could not be placed in the landfill itself; however, a soil gas survey conducted in the near surface (Evans et al. 1989) showed a wide distribution of chlorinated solvents throughout the Central Landfill. Other chlorinated solvents found in the ground water at the landfill include trichloroethane, perchloroethylene, dichloroethane, and traces of carbon tetrachloride.

TCE contamination in the 300 Area resulted largely from disposal of an estimated 100 tons of degreaser solvent to each of the North and South Process Ponds. Because of the relatively close proximity to the Columbia River, combined with the relatively high hydraulic conductivity in the 300 Area, very little of the original TCE remains and the levels in the ground water are relatively low. In addition to the TCE, some degradation products, primarily cis-dichloroethylene, are also present in the plume.

TCE was found during a preliminary soil gas survey of the Horn Rapids Disposal Site as part of the 1100-EM-1 CERCLA RI/FS investigation. The finding was subsequently confirmed by the installation of ground-water wells. Ground-water concentrations of up to approximately 18 times the DWS were observed. The origin of this plume is still under investigation.

A.2.3 Non-Hazardous Indicator Species

The chemical monitoring program includes major ion species used to determine water chemistry parameters and ion balances. Some of those species can also serve as indicators of site-related activities. For example, the waste streams disposed to the BY Cribs were treated with calcium and strontium nitrate to help promote the precipitation of strontium-90. The resulting radiological and chemical plumes now evident directly north of those cribs do indeed show evidence of calcium and strontium plumes in addition to the other parameters already discussed as regulated constituents. Analysis of plumes formed by indicator species can provide additional information on the behavior of the ground-water flow system.

Calcium may enter the ground-water system through direct injection as described above, through acid attack on soil minerals, or through ion exchange phenomena. In addition to the BY Cribs plume, calcium plumes have been observed at the Central Landfill, the 100-D, 100-F, 100-H, 100-N, 200-East, 200-West, and the 400 Areas. Other potentially useful indicator species for which site-related impacts have been observed include sodium and chloride. A complete analysis of all possible indicator plumes has not yet been completed.

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APPENDIX B

CONTAINERS, PRESERVATIVES, ANALYTICAL METHODS, AND DETECTION LIMITS FOR
CHEMICAL AND RADIOLOGICAL SPECIES IN GROUND WATER

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CONTAINERS, PRESERVATIVES, ANALYTICAL METHODS, AND DETECTION LIMITS FOR CHEMICAL AND RADIOLOGICAL SPECIES IN GROUND WATER

All ground-water monitoring samples are analyzed according to detailed, written analytical procedures. Minimum detectable concentrations for the various medium/analysis combinations and other analytical information are shown in Table B.1.

TABLE B.1. Minimum Detectable Concentrations for Medium/Analysis Combinations

<u>Constituent</u>	<u>Collection and Preservation^(a,b)</u>	<u>Analysis Methods^(c)</u>	<u>Detecting Limit,ppb^(d)</u>
Zinc	P, HNO ₃ to pH<2	SW-846, ^(e) #6010	20
Calcium			30
Barium			1
Cadmium			5
Chromium			10
Lead			50
Silver			10
Sodium			200
Nickel			20
Copper			2
Manganese			5
Potassium			1,500
Iron			10
Magnesium			80
Boron			10
Cobalt			20
Molybdenum	20		
Arsenic	P, HNO ₃ to pH<2	SW-846, #7060	5
Mercury	G, HNO ₃ to pH<2	SW-846, #7470	0.1
Selenium	P, HNO ₃ to pH<2	SW-846, #7740	5
Lead	P, HNO ₃ to pH<2	SW-846, #7421	5
<u>Anions by IC^(f)</u>			
Nitrate	P, None	EPA Method 300.0 ^(g)	500
Sulfate			500
Fluoride			500
Chloride			500
Phosphate			1,000
<u>Other Parameters</u>			
Total carbon	G, None	SW-846, #9060	2,000
Total organic carbon	G, H ₃ PO ₄ to pH<2	SW-846, #9060	1,000
Ammonium ion	G, H ₂ SO ₄ to pH<2	ASTM D1426-C or -D	100
Sulfide	NaOH/ZnAc to pH>10	SW-846, #9030	10,000
Cyanide	NaOH > pH 12	SW-846, #9010	20

CDM = Contractor Determined Methods

(a) P, plastic; G, glass

(b) All samples will be cooled to 4°C upon collection.

(c) Constituents grouped together are analyzed by the same method.

(d) Detection limit units except where indicated.

(e) Adapted from USEPA Method 6010 (EPA 1986).

(f) IC, ion chromatography.

TABLE B.1. (contd)

<u>Constituent</u>	<u>Collection and Preservation^(a,b)</u>	<u>Analysis Methods^(c)</u>	<u>Detecting Limit, ppb^(d)</u>		
<u>Volatile Organics (VOA) (Contractor Laboratory)</u>					
Carbon tetrachloride	G, HCL Zero Headspace	SW-846, #8240	5		
Benzene			5		
Methylethyl ketone			10		
Toluene			5		
1,1,1-trichloroethane			5		
1,1,2-trichloroethane			5		
Trichloroethylene			5		
Tetrachloroethylene			5		
Xylene (O, P)			5		
Chloroform			5		
1,1 dichloroethane			5		
1,2 dichloroethane			5		
Trans-1,2 dichloroethylene			5		
Methylene chloride			10		
Vinyl chloride			5		
Xylene (M)			5		
p-dichlorobenzene			10		
Methyl isobutyl ketone			10		
<u>Volatile Organics (PNL)</u>					
Carbon tetrachloride	G, HCL Zero Headspace	EPA Method 502.2	2		
Benzene			0.5		
Toluene			0.5		
1,1,1-trichloroethane			2		
1,1,2-trichloroethane			2		
Trichloroethylene			2		
Tetrachloroethylene			2		
Xylene (O, P)			0.5		
Chloroform			2		
1,1 dichloroethane			3		
1,2 dichloroethane			2		
Trans-1,2 dichloroethylene			3		
Methylene chloride			5		
Vinyl chloride					0.5
Xylene (M)					0.5
p-dichlorobenzene					

CDM = Contractor Determined Methods

(a) P, plastic; G, glass

(b) All samples will be cooled to 4°C upon collection.

(c) Constituents grouped together are analyzed by the same method.

(d) Detection limit units except where indicated.

(e) Adapted from USEPA Method 6010 (EPA 1986).

(f) IC, ion chromatography.

TABLE B.1. (contd)

<u>Constituent</u>	<u>Collection and Preservation^(a,b)</u>	<u>Analysis Methods^(c)</u>	<u>Detecting Limit,ppb^(d)</u>
<u>Radiological</u>			
Alpha	P, HNO ₃ to pH<2	SW-846, #9310	4 pCi/L
Beta (excluding H-3)	P, HNO ₃ to pH<2	SW-846, #9310	4 pCi/L
Tritium	P, None	ASTM, D2476-81	500 pCi/L
I-129	P, 4#C in Dark		1 pCi/L
I-129	P, 4#C in Dark		1E-5 pCi/L
Sr-90	P, HNO ₃ to pH<2	CDM	5 pCi/L
Gamma	P, HNO ₃ to pH<2	CDM	5 pCi/L
Co-60			20 pCi/L
Cs-137			20 pCi/L
Ru-106			20 pCi/L
Tc-99	P, HNO ₃ to pH<2	CDM	5 pCi/L
Natural Uranium	P, HNO ₃ to pH<2	CDM	0.5 pCi/L
Isotopic Uranium	P, HNO ₃ to pH<2	CDM	0.1 pCi/L
Isotopic Plutonium	P, HNO ₃ to pH<2	CDM	0.01 pCi/L

CDM = Contractor Determined Methods

(a) P, plastic; G, glass

(b) All samples will be cooled to 4°C upon collection.

(c) Constituents grouped together are analyzed by the same method.

(d) Detection limit units except where indicated.

(e) Adapted from USEPA Method 6010 (EPA 1986).

(f) IC, ion chromatography.

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