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October 1991

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

Pacific Northwest Laboratory
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CHARACTERISTICS OF THE VOLATILE ORGANIC COMPOUNDS-ARID INTEGRATED DEMONSTRATION SITE

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Richland, Washington 99352

SUMMARY

The Volatile Organic Compounds - Arid Integrated Demonstration Program (VOC-Arid ID) is targeted at demonstration and testing of technologies for the evaluation and clean up of volatile organic compounds and associated contaminants at arid DOE sites. The initial demonstration site is an area of carbon tetrachloride (CCl_4) contamination located near the center of the Hanford Site.

The Hanford Site is a DOE facility located in the semiarid region of southcentral Washington State, which has an annual precipitation of 16 cm/yr (6.3 in/yr). Contamination at the demonstration site originated from past disposal of liquid wastes generated at the Plutonium Finishing Plant (PFP). These liquid wastes contained an estimated 363 to 580 cubic meters (96,000 to 150,000 gallons) of CCl_4, as well as plutonium (Pu), americium (Am), chloroform, sodium nitrate, and other organics (e.g., tributylphosphate and lard oil). An estimated total of 13,200 cubic meters (3.5 million gallons) of liquid waste was discharged to three unlined subsurface liquid disposal facilities (cribs) between 1955 and 1973.

These cribs (similar to septic tank drain fields) were designed to permit infiltration of waste effluents directly into the underlying soil column. This soil column consists of heterogeneous clastic sediments (predominantly unconsolidated sands and gravels) with a wide range of textures and hydraulic properties. A highly calcareous (caliche) layer, the Plio-pleistocene unit, is located approximately 40 m (130 ft) below the cribs and 30 m (100 ft) above the water table. This low permeability layer slopes to the south, nearly opposite to the local direction of ground water flow.

The unconfined aquifer beneath these cribs lies approximately 73 m (240 ft) below land surface and consists predominantly of poor to well consolidated conglomerate (the middle Ringold unit). Hydraulic conductivities range from 0.3 to 1550 m/day (1 to 5,100 ft/day) with the higher conductivities generally located near the top of the aquifer. Ground water velocities are estimated to range up to 47 m/day (150 ft/day). A low permeability mud layer (consisting of the lower and fine-grained-basal Ringold units) lies

approximately 76 m (250 ft) below the top of the aquifer. A thick sequence of basalt flows (the Columbia River Basalt Group) forms the site bedrock, and the base of the unconfined aquifer. Both the lower/fined-grained-basal Ringold Unit and the basalt surface slope to the south, while the local groundwater flow direction is to the northwest. Regional groundwater flow is to the east, toward the Columbia River.

Past liquid waste disposal to the three CCl_4 cribs has resulted in both soil and groundwater contamination. The recognition of a substantial CCl_4 plume (up to 12.6 km^2 [4.9 mi^2]) in the unconfined aquifer has resulted in the initiation of an Expedited Response Action to reduce the amount of CCl_4 in the vadose zone. Groundwater concentrations of CCl_4 as high as 8,100 ppb (1,600 times the Maximum Concentration Limit) have been reported. However, the estimated mass of CCl_4 delineated by the groundwater plume accounts for less than 2% of the total estimated inventory released to the three cribs. Initial tests using vapor extraction equipment yielded an estimated 680 kg (308 lbs) of CCl_4 from the vadose zone beneath one of the cribs. Calculated air permeabilities were on the order of 10^{-8} cm^2 (10^{-11} ft^2) and air conductivities on the order of 10^{-4} cm/sec (10^{-7} ft/sec). To date, no separate organic phase liquid CCl_4 has been detected in either the vadose zone or groundwater.

The current subsurface distribution of CCl_4 is unknown; however, it is assumed that the majority of the CCl_4 remains in the subsurface. With the density of CCl_4 1.58 times that of water, the upward movement of CCl_4 vapors into the atmosphere (via atmospheric pumping and/or diffusion) is considered minimal compared to the effects of density-driven vapor flow. Density flow is a very plausible mechanism for the movement of CCl_4 vapors from the vadose zone into the groundwater. The movement of organic phase liquid CCl_4 through porous media would leave some residual liquid retained in the soil pores. The large volumes of aqueous wastes and organic phosphates discharged along with the CCl_4 would likely trap this residual organic phase liquid in the larger soil pores, while the aqueous wastes would occupy and move through the smaller connecting pores. Thus, it is improbable that liquid organic phase CCl_4 reached the groundwater driven under its own pressure gradient, unless it was localized in large open channels (such as those along the outside of unsealed well casings). However, once in the groundwater, the dense non-aqueous (organic) phase liquid (DNAPL) would likely sink through the aquifer and pool on low permeability layers. CCl_4 in the aqueous phase, or as an emulsion of very small CCl_4 globules in water, is another potential mechanism by which CCl_4 might have reached the groundwater.

The movement of CCl_4 and other volatile organic contaminants in the subsurface is very complex. The problem at the Hanford Site is further complicated by the concurrent discharge of other waste constituents including acids, lard oil, organic phosphates, and transuranic radionuclides. In addition, the subsurface environment is very complex, with large spatial variabilities in hydraulic properties. A thorough understanding of the problem is essential to the selection of appropriate containment, retrieval, and/or in situ remedial technologies. The effectiveness of remedial technologies depends on knowing where the contaminants are, how they are held up in a given physical and chemical subsurface environment; and knowing the physical, chemical, and microbiological changes that are induced by the various remedial technologies.

ACKNOWLEDGMENTS

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The authors thank Dr. Nancy R. Hinman and Dr. Ken M. Krupka for providing groundwater composition analyses and geochemical modeling results for the 200 West Area wells.

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INTRODUCTION

The Volatile Organic Compounds-Arid Integrated Demonstration Program (VOC-Arid ID) is a U.S. Department of Energy (DOE) program targeting the acquisition, demonstration, and deployment of technologies for evaluation and cleanup of volatile organic and associated contaminants in soils and groundwater at arid DOE sites. Many DOE laboratories, universities, and industries will participate in the program. Candidate technologies will be demonstrated in the areas of site characterization; performance prediction, monitoring, and evaluation; contaminant extraction and ex situ treatment; in situ remediation; and site closure and monitoring. The performance of these demonstrated technologies will be compared to baseline technologies and documented to promote the transfer of new technologies to industry for use at DOE facilities. The initial demonstration site for this program is an area of carbon tetrachloride contamination located on the DOE Hanford Site.

The purpose of this report is to inform principal investigators of candidate technologies, about the nature and extend of VOC contamination and the physical setting of the initial demonstration site. It provides background information on the source of the carbon tetrachloride contamination, the environmental characteristics of the site, the state of current knowledge regarding soil and groundwater contamination, and a discussion of conceptual models for the behavior of these contaminants. These descriptions are based on previous studies and information generated in support of the Expedited Response Action being taken by Westinghouse Hanford Company (Hagood and Rohay 1991; DOE 1991).

BACKGROUND

The Hanford Site has been a defense materials production complex since 1943. Liquid wastes (some containing carbon tetrachloride) generated during plutonium recovery processes operated at the Plutonium Finishing Plant (PFP) were discharged to nearby subsurface liquid disposal facilities (cribs). These discharges have resulted in the contamination of the underlying soils and groundwater by carbon tetrachloride, chloroform, and a variety of associated mixed hazardous and radioactive wastes. The following describes the location of the host site, the operational history of the PFP, the liquid waste disposal facilities (cribs) of interest, and the waste disposal history and inventory of these cribs.

Much of the information presented in the following sections has been summarized from DOE 1991. The reader is referred to this reference for more detailed information.

LOCATION

The Hanford Site is located in south central Washington State and is portioned into several operational areas. The 200 Areas (200 East and 200 West) are located near the center of the site and the PFP, formerly referred to as Z-Plant, is located in the west central portion of 200 West Area (Figure 1). Carbon tetrachloride contamination in the soil (vadose zone) is primarily located in the immediate vicinity of three cribs south of the PFP. The carbon tetrachloride plume in the unconfined aquifer extends beneath nearly all of the 200 West Area.

PLUTONIUM FINISHING PLANT OPERATIONS

The PFP is a complex of chemical processing facilities designed to process plutonium extracted from irradiated uranium fuel rods into its final product form (DOE 1991). The PFP received the plutonium extract as a plutonium nitrate solution and processed it into its final metallic forms. The process lines generated side streams that contained recoverable quantities of plutonium, including scrap from machining of the plutonium metal shapes.

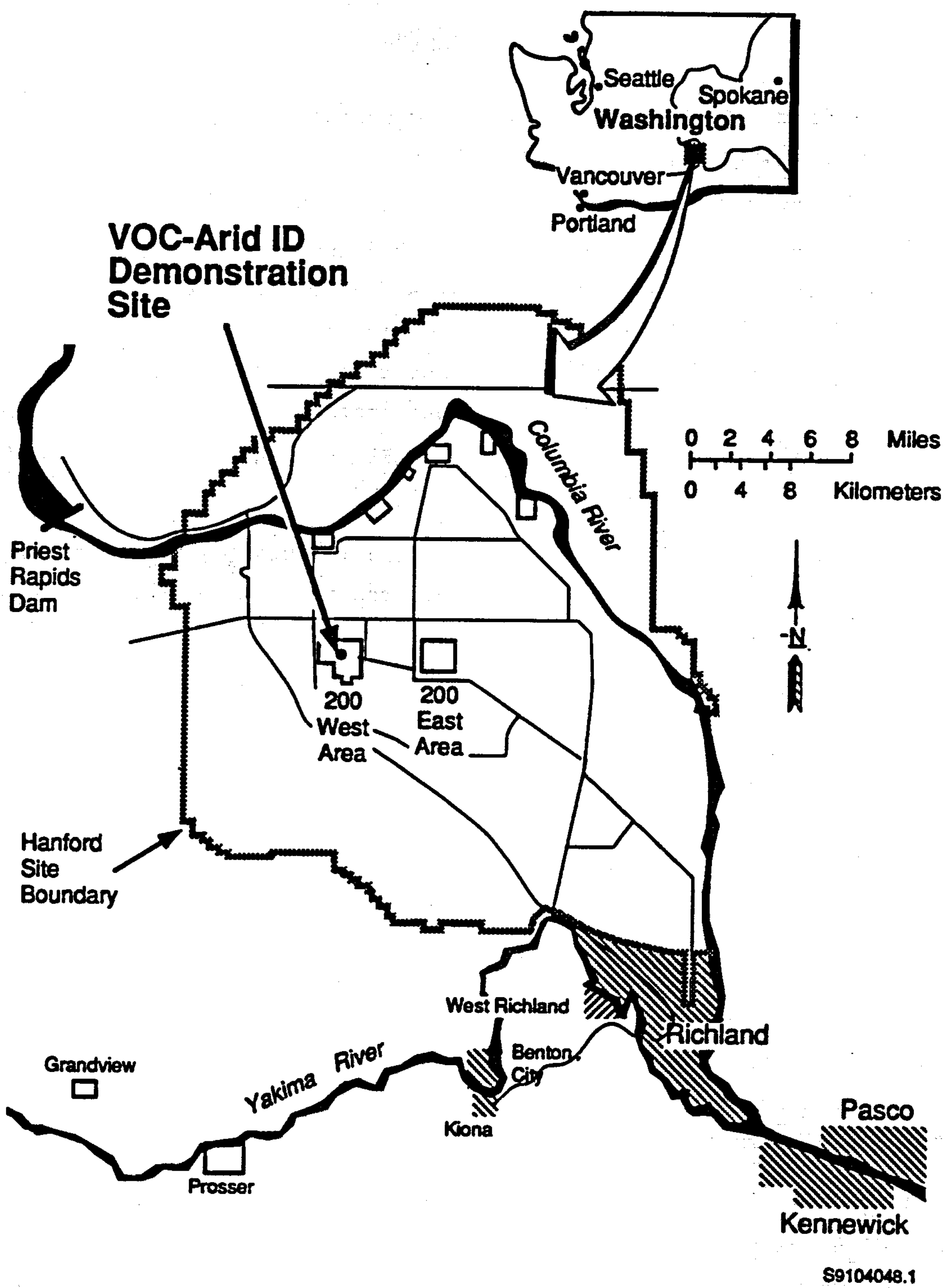

FIGURE 1. Location of the VOC-Arid ID Site (after Last and Rohay, 1991)

Plutonium from these side streams was recovered by the Recuplex Plutonium Scrap Recovery Facility (Recuplex) and the Plutonium Reclamation Facility (PRF). Recuplex, located in the 234-5Z building, operated from 1955 through 1962 (DOE 1991) and served as a multipurpose solvent extraction plant that recovered plutonium generated by various plutonium purification and fabrication production lines. The Plutonium Reclamation Facility (PRF) was housed in the 236-Z building and operated from 1964 to 1979, again from 1984 to 1987, and is scheduled to resume operation in late 1991 (DOE 1991). This facility had essentially the same mission as Recuplex but used superior solvent extraction column technology. The PRF also included the Waste Treatment and Americium Recovery Facility that was located in the 242-Z building and operated concurrently with the PRF (DOE 1991).

Historically, these facilities mixed large quantities of carbon tetrachloride (CCl_4) with other organics to recover plutonium from the side streams using column extraction processes (DOE 1991). These countercurrent column extraction processes forced up an aqueous feed stream containing impurities and plutonium from the bottom of the extraction column, while a dense organic stream (consisting primarily of CCl_4 and tributyl phosphate) moved downward through the column. The organic stream extracted plutonium from the aqueous stream and carried it out through the bottom of the column. Most of the impurities remained in the aqueous stream and exited through the top of the column. The plutonium-bearing organic stream then entered another extraction column where the plutonium was recovered by another aqueous stream.

The chemical processes used by Recuplex and PRF resulted in the production of actinide-bearing aqueous and organic waste liquids (DOE 1991). Descriptions of the three principal types of waste streams are presented below.

Organic Waste Streams

Two organic streams (solvents) were used in the Recuplex process: a tributyl phosphate (TBP) based solvent and a dibutyl butyl phosphate (DBBP) based solvent. Ionizing radiation and nitric acid would eventually degrade these solvents which were then discharged to the crib, in batches, and replaced with a fresh batch of solvent.

The TBP-based solvent consisted of CCl_4 and TBP primarily in a ratio of 85:15 of CCl_4 to TBP (DOE 1991). Tetrachloroethylene (also referred to as perchloroethylene) was also used at times in combination with the CCl_4 (DOE 1991). Each batch of TBP-based solvent consisted of approximately 200 L (53 gal) (DOE 1991).

The DBBP solvent stream, consisting of 50:50 CCl_4 to DBBP, was used for batch rework of aqueous liquid from the primary extraction column that exceeded plutonium concentration discharge specifications (DOE 1991). The DBBP-based solvent was stripped of plutonium prior to discharge to the cribs. Each batch of DBBP-based solvent was approximately 100 L (26 gal).

Similar organic streams were also used in the PRF processes. A TBP based solvent with a ratio of 80:20 CCl_4 to TBP was used in the plutonium recovery processes, and a DBBP based solvent with a ratio of 70:30 CCl_4 to DBBP was used in the americium recovery processes (DOE 1991).

Aqueous Waste Stream

The aqueous waste stream, characterized as a high-salt aqueous waste, was primarily a concentrated (5 to 6 $\underline{M}$) sodium nitrate ($NaNO_3$) solution with a pH of 1. Organic liquids consisting of CCl_4, TBP, and DBBP occurred in saturation amounts in the aqueous phase (DOE 1991). Kasper (1982) estimated that <5% of the high-salt aqueous waste consisted of the organic component. Large volumes of aqueous waste were discharged to the soil column through the same liquid waste disposal facilities (cribs) that received the organic wastes.

The Recuplex wastes consisted of aluminum, magnesium, sodium, calcium, and other metallic nitrate salt wastes. These aqueous wastes were accumulated in a large stainless steel tank and partially neutralized to a pH of 2.5 by the addition of sodium hydroxide (DOE 1991).

Lubrication Oil

A lubrication/cutting oil (also referred to as fabrication "fab" or lard oil) consisting in a ratio of a 75:25 CCl_4 to lard oil mixture was used as a lubricant on PFP plutonium cutting and milling tools. CCl_4 was also used to clean the cutting oil from the millings and work surfaces (DOE 1991). The used lubrication oil with a final ratio estimated at 50:50 CCl_4 to lard oil was discharged to the same cribs as the organic and aqueous wastes.

LIQUID WASTE DISPOSAL FACILITIES

Liquid wastes from the Recuplex and PRF plutonium recovery processes were discharged to the soil column via 3 different cribs from 1955 until 1973 when the discharge of organic solvents to these facilities was discontinued (DOE 1991). Recuplex wastes were discharged to the 216-Z-9 Trench and PRF wastes were discharged to the 216-Z-1A Tilefield and 216-Z-18 Crib (Figure 2) (DOE 1991). The physical design and disposal history of each of these cribs is described below.

216-Z-9 Trench

The 216-Z-9 trench is an enclosed underground trench (or chamber), covered by a concrete pad 0.23 m (9 in) thick (DOE 1991). The base of the unlined trench is 18.3 m (60 ft) long by 9.1 m (30 ft) wide and 6.1 m (20 ft) deep (DOE 1991). The 36.5-m (120 ft) by 27.4-m (90 ft) concrete trench cover is supported by six concrete columns 7 m (23 ft) high (DOE 1991). Waste was discharged to the trench via one of two 3.8 cm- (1.5 in) stainless steel pipelines that terminated approximately 5 m (16 ft) above the trench bottom. Figure 3 is a schematic map of this facility, illustrating the location of monitoring wells and boreholes.

The 216-Z-9 trench operated from 1955 through 1962 and received all the organic and aqueous waste discharged to the soil from the Recuplex facility. It received no other wastes. In 1973, nuclear and soil analyses of the trench indicated that the concentration of plutonium in the top 30 cm (1 ft) of soil posed a criticality risk. Thus, 1100 L (290 gal) of a 10 g/liter (1.4 oz/gal) cadmium nitrate solution was sprayed on the bottom of the trench (Smith 1973). Later, the top 30 cm (1 ft) of soil in the trench bottom was mined, removing an estimated 58 kg (128 lbs) of plutonium by 1978. Mining equipment used in this operation is still present at the site.

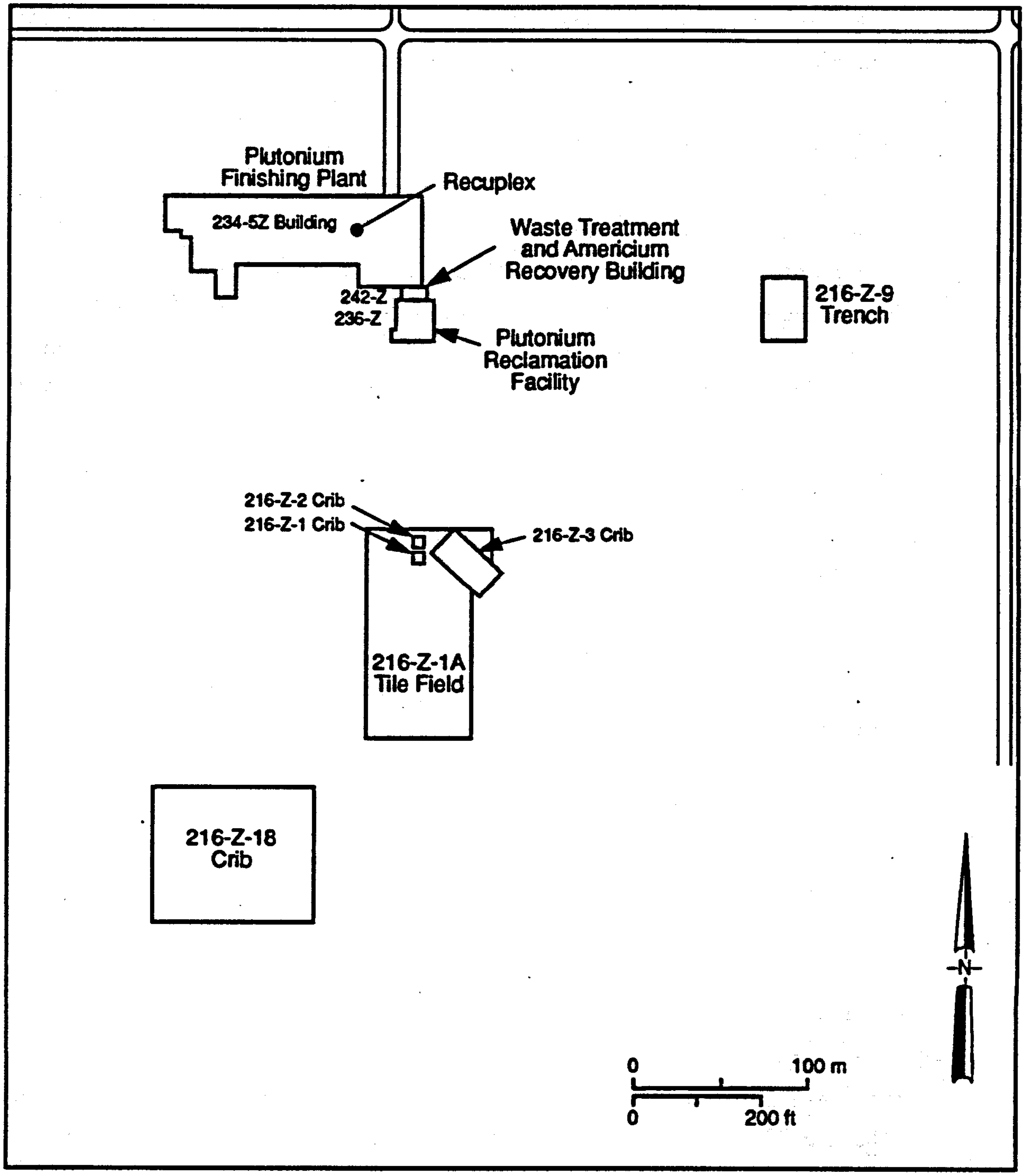

FIGURE 2. Site Map of Carbon Tetrachloride Disposal Sites in the Vicinity of Z Plant (DOE 1991)

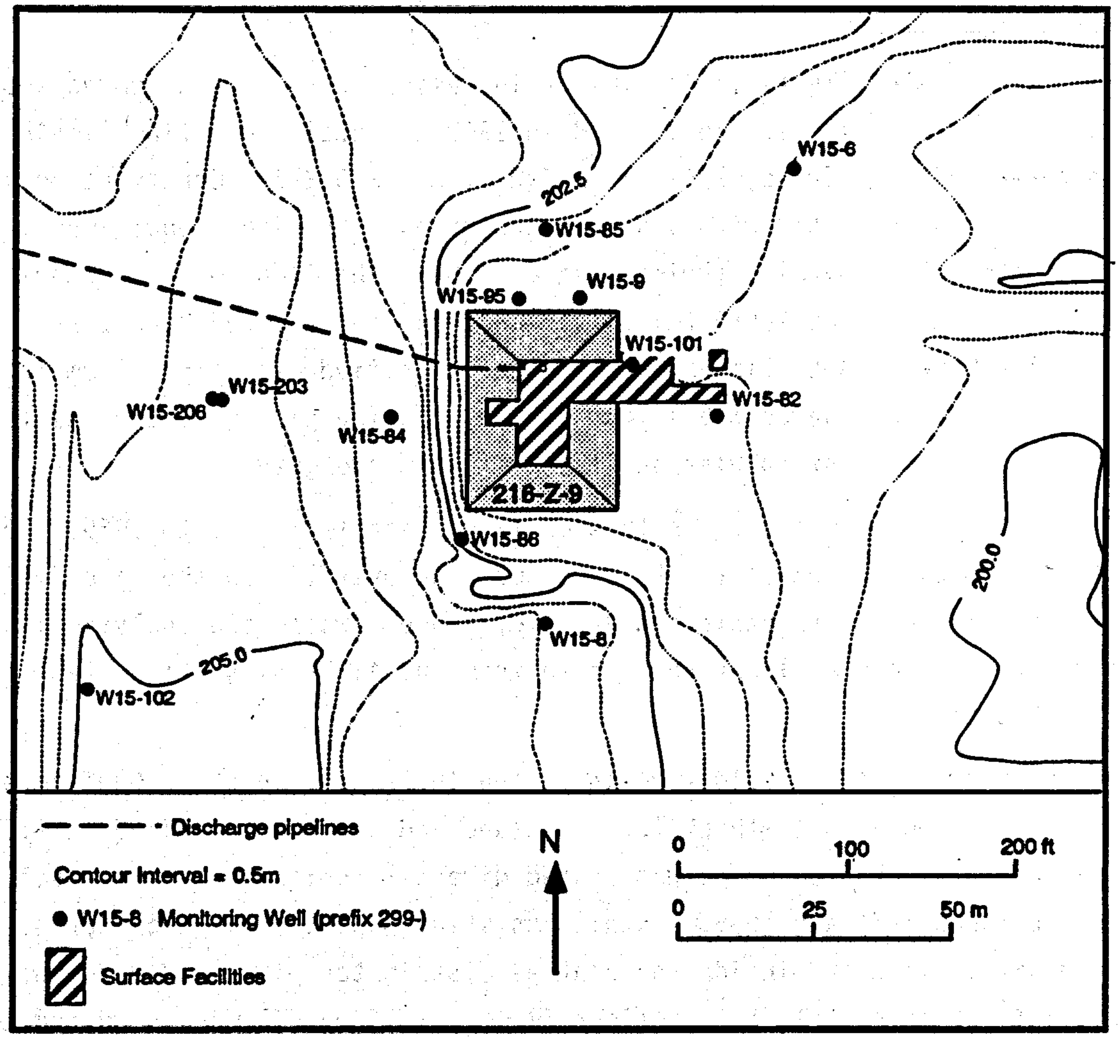

FIGURE 3. Topographic Map of the 216-Z-9 Trench

216-Z-1A Tile Field

The 216-Z-1A tile field is similar in design to that of a common septic tank drain field. It was constructed in 1949 to receive overflow liquid waste from three adjacent cribs, 216-Z-1, 216-Z-2, and 216-Z-3. Construction of the tile field was initiated with a 5.8 m-deep-excavation with floor dimensions of approximately 35 m by 84 m (Price et al. 1979). The floor of the excavation sloped slightly to the south (min. 1% slope) and was covered by a 1.2-m-thick layer of cobbles. A herringbone pattern of vitrified clay pipe 20 cm in diameter was placed on the cobble layer (Figure 4). The piping system was then overlain with 15 cm of cobbles and 1.5 m of sand and gravel.

The tile field was used in this configuration from 1949 to 1959. The waste stream discharged to the three cribs, and overflow to the tile field consisted of neutral to basic (pH 8 to 10) process waste and analytical laboratory and development laboratory waste from the 41-Z-361 settling tank of the PFP (Z-Plant).

Prior to the tile field's reactivation in 1964, a sheet of 0.05-cm-thick polyethylene and a 30-cm-thick layer of sand and gravel were added and the liquid waste discharge piping was routed directly to its central distributor pipe. Between 1964 and 1969, a stainless steel pipe 5 cm in diameter was progressively inserted inside the central distributor pipe to divide the tile field into three operational sections (Z-1AA, Z-1AB and Z-1AC). During this time the tile field received the aqueous and organic waste from the PRF. No other facility received PRF wastes during this time, except on two brief occasions while modifications were made to the piping system and waste was discharged to the adjacent 216-Z-1 and 216-Z-2 cribs.

216-Z-18 Crib

The 216-Z-18 crib operated as a replacement for the 216-Z-1A tile field, receiving aqueous and organic wastes from the PRF between 1969 and 1973. This drain-field-type crib consists of five parallel trenches, each 63 m long by 3 m wide, and ranging from 4.5 m to 5.5 m deep. The floor of each trench was covered with approximately 0.3 m of gravel. Two parallel fiberglass-reinforced, epoxy distributor pipes 7.6 cm in diameter were placed on the

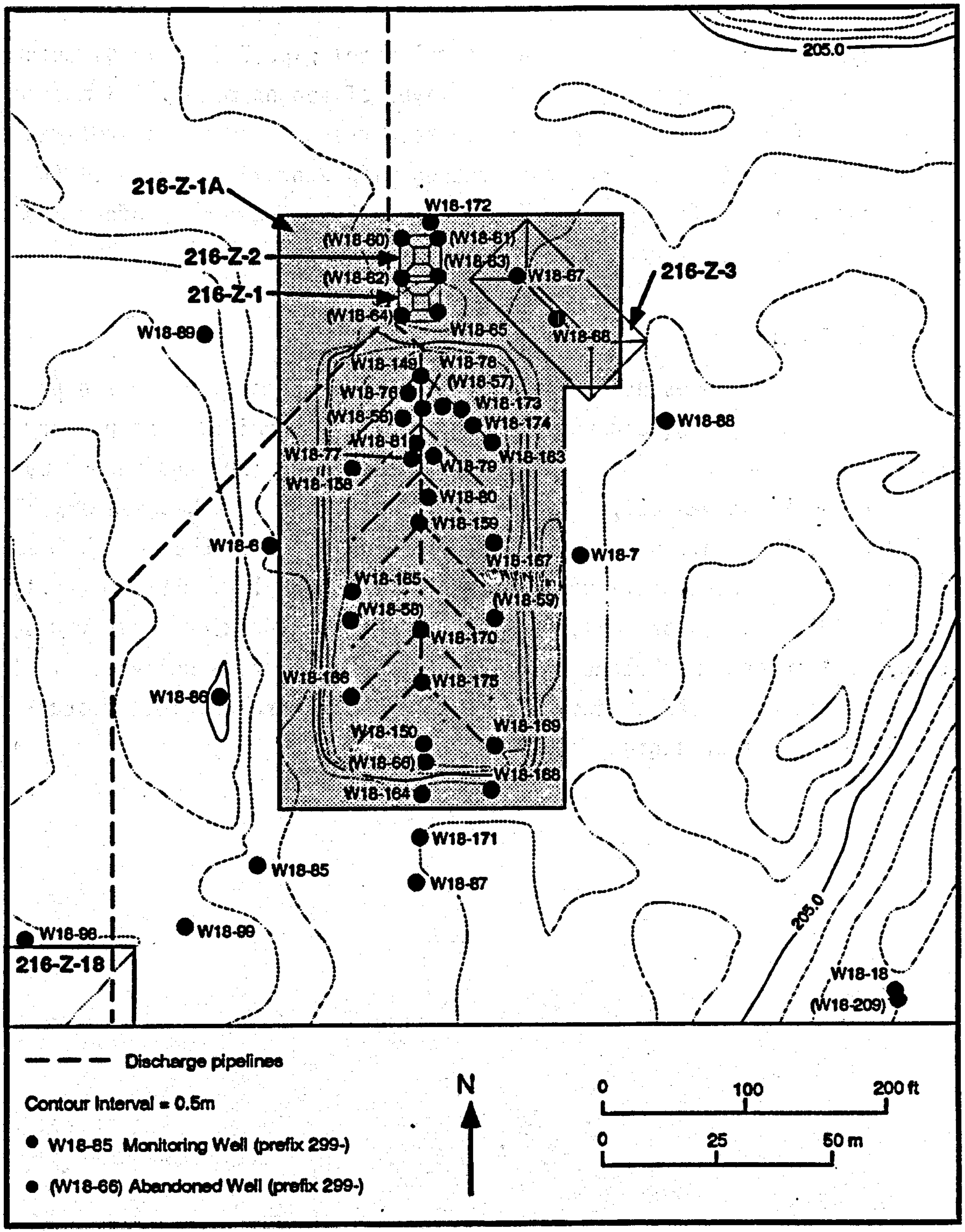

FIGURE 4. Map of the 216-Z-1A Title Field

gravel layer within each trench. A central steel pipe 7.6 cm in diameter connected each trench (Figure 5). Another layer of approximately 0.3 m of gravel was placed over the distributor pipes in each trench, and the gravel was covered by a membrane barrier that was covered with approximately 15 cm (6 in.) of sand and then backfilled to grade. In 1991, Westinghouse Hanford indicated that the western-most trench never received any waste.

WASTE INVENTORIES

The chemical processes used by recuplex and PRF resulted in the production of actinide-bearing aqueous and organic waste liquids. The primary radionuclide component of these liquids was plutonium (Pu) and the primary organic constituent was CCl_4. In 1991, DOE estimated that between 363,000 and 580,000 L (95,900-153,000 gals) of CCl_4 was discharged to the soil between 1955 and 1973. Other constituents present included: TBP, DBBP, monobutyl phosphate (MBP), DBP, lard oil, cadmium, nitrates, hydroxides, fluorides, sulfate, chloroform, methylene chloride, and various radionuclides. Table 1 summarizes the estimated inventory of each crib; a more complete discussion of the inventories is presented in DOE 1991.

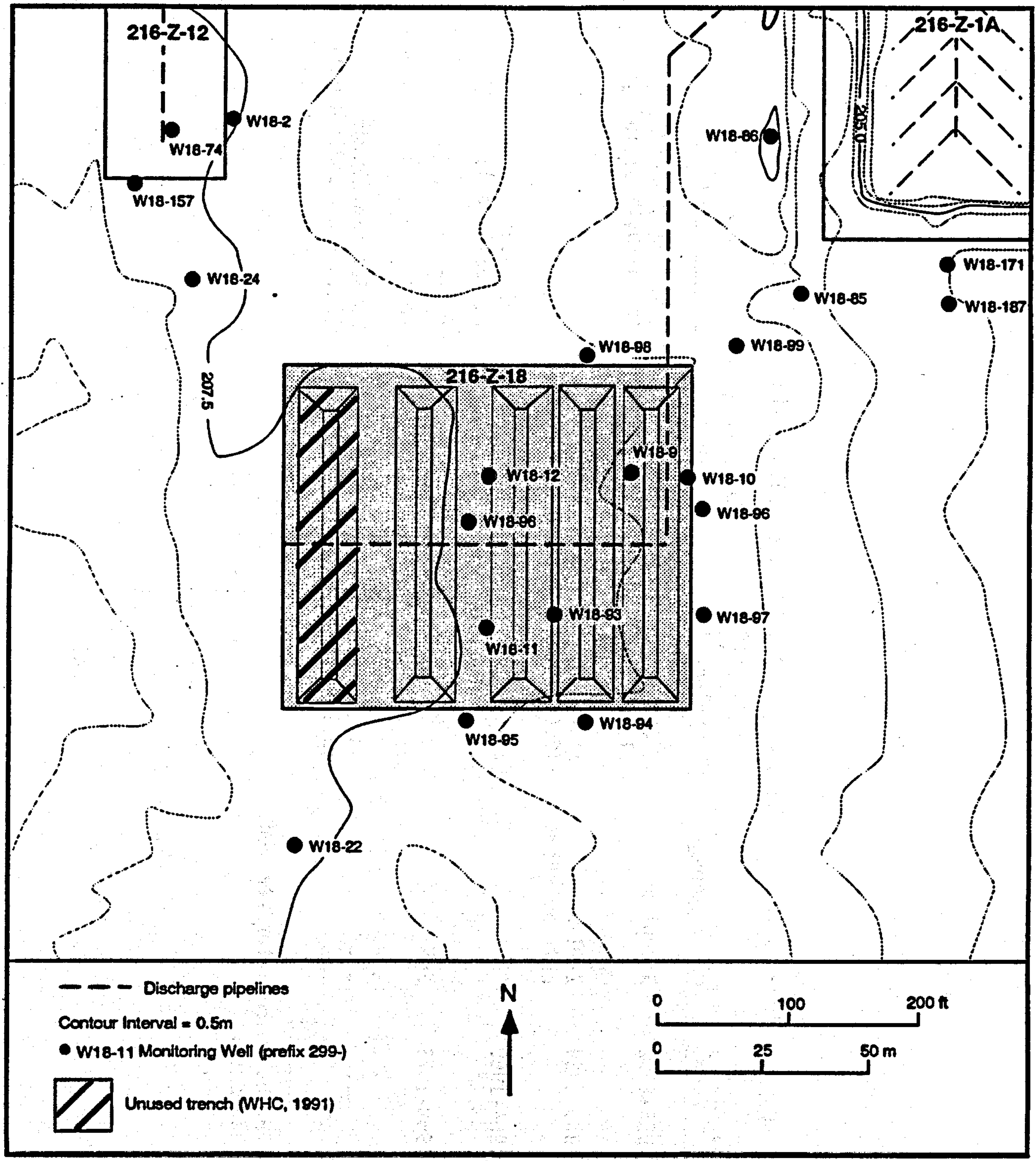

FIGURE 5. Topographic Map of the 216-Z-18 Crib

TABLE 1. Inventories for the Carbon Tetrachloride Cribs (after DOE 1991)

Crib	Operating Dates	Waste Source	Total Volume (L)	Plutonium (kg)	Carbon Tet. (L)
216-Z-9	1955-1962	Recuplex	4.09E+06 (1.29E+0.6 gal)	106[a] (234 lbs)	8.30E+04-3.00E+05 (2.19E+04-7.93E+04 gal)
216-Z-1A	1949-1959	Z-Plant crib overflow	1.00E+06 (2.64E+05 gal)	---	---
	1964-1969	PRF	5.20E+06 (1.37E+06 gal)	57 (126 lbs)	1.70E+05[b] (3.96E+04 gal)
216-Z-18	1969-1973	PRF	3.86E+06 (1.02E+06 gal)	23 (51 lbs)	1.10E+05 (2.91E+04 gal)
TOTAL	---	---	14.15E+06 (3.74E+06 gal)	186 (410 lbs)	3.63E+05-5.80E+05 (95,900 gal-153,000 gal)

(a) 58 kg (128 lbs) were later removed.
(b) Includes lard oil.

ENVIRONMENTAL SETTING

This section describes the environmental setting of the VOC-Arid ID demonstration site, including its climate, geology, and hydrogeology.

CLIMATE

The Hanford Site is located in a semiarid region east of the Cascade Mountains of Washington State. The Cascade Mountains greatly influence the climate of the Hanford Site by causing a rain shadow effect and also serving as a source of cold air drainage. Climatological data have been collected at the Hanford Meteorological Station (HMS) located just east of the 200 West Area. A summary of these data through 1980 has been published by Stone et al. (1983).

Prevailing winds on the 200-Area plateau are from the northwest, with monthly average wind speeds ranging from 10 to 11 km/h (6 to 7 mi/h) during the winter months and 14 to 16 km/h (9 to 10 mi/hr) during the summer months. Strong southwesterly winds are frequent during the spring and fall.

The average monthly temperatures range from a low of -1.5°C (29.3°F) in January to a high of 24.7°C (76.5°F) in July. The annual average relative humidity at the Hanford Meteorological Station is 54%. Humidity is highest during the winter months, averaging about 75%, and lowest during the summer, averaging about 35%.

Average annual precipitation at the HMS is 16 cm (6.3 in). Most of the precipitation occurs during the winter with nearly half of the annual amount occurring from November through February. Winter monthly average snowfall ranges from 0.8 cm (0.3 in) in March to 13.5 cm (5.3 in) in January. Snowfall accounts for about 38% of all precipitation from December through February.

GEOLOGY

The subsurface geology of the demonstration site consists of a thick accumulation [>150 m (500 ft)] of clastic sedimentary deposits overlying basalt bedrock (Figure 6). These sedimentary deposits include several lithologic units (basal, lower, middle, and upper) of the Mio-Pliocene age Ringold Formation, the Plio-Pleistocene unit, the Early "Palouse" soil, and the glaciofluvial Hanford formation. A thin veneer of Holocene sand locally covers the ground surface.

The stratigraphic relationships between these units have been interpreted from numerous boreholes located in the vicinity of the PFP (Figure 7). These relationships are illustrated via geologic cross sections presented in Figures 8-10. These interpretations were based on evaluation of the following types of data: 1) geologist's logs, 2) gross gamma logs, 3) driller's logs, 4) granulometric analyses, and 5) calcium carbonate analyses. These data were evaluated in accordance with characteristics identified by Bjornstad (1985) and DOE (1988) to distinguish between primary geologic units. A discussion of the principal geologic units (based on previous reports on the 200 West Area (Tallman et al. 1979, 1981; DOE 1988; Last et al. 1989; Last and Bjornstad 1989; Bjornstad 1990) is presented below. Lithologic and well construction diagrams for the boreholes/wells located in the immediate vicinity of the PFP can be found in DOE 1991.

Saddle Mountains Basalt Formation (Bedrock)

The Saddle Mountains Basalt is the uppermost formation of the Columbia River Basalt Group (Swanson et al. 1979). The Elephant Mountain basalt dated at 10.5 million years (McKee et al. 1977) is the uppermost member of the Saddle Mountains Formation underlying the PFP. The Elephant Mountain basalt forms the base of the suprabasalt aquifer system. The PFP is located along the north flank of the Cold Creek Syncline, thus, the basalt surface in this area dips gently to the southwest (Figure 11).

Ringold Formation

The Ringold Formation consists of fluvial-lacustrine deposits from the ancestral Columbia and Salmon-Clearwater rivers (Tallman et al. 1979, 1981; Fecht et al. 1985). Locally, the Ringold Formation has been broken into four units: the basal, lower, middle, and upper units.

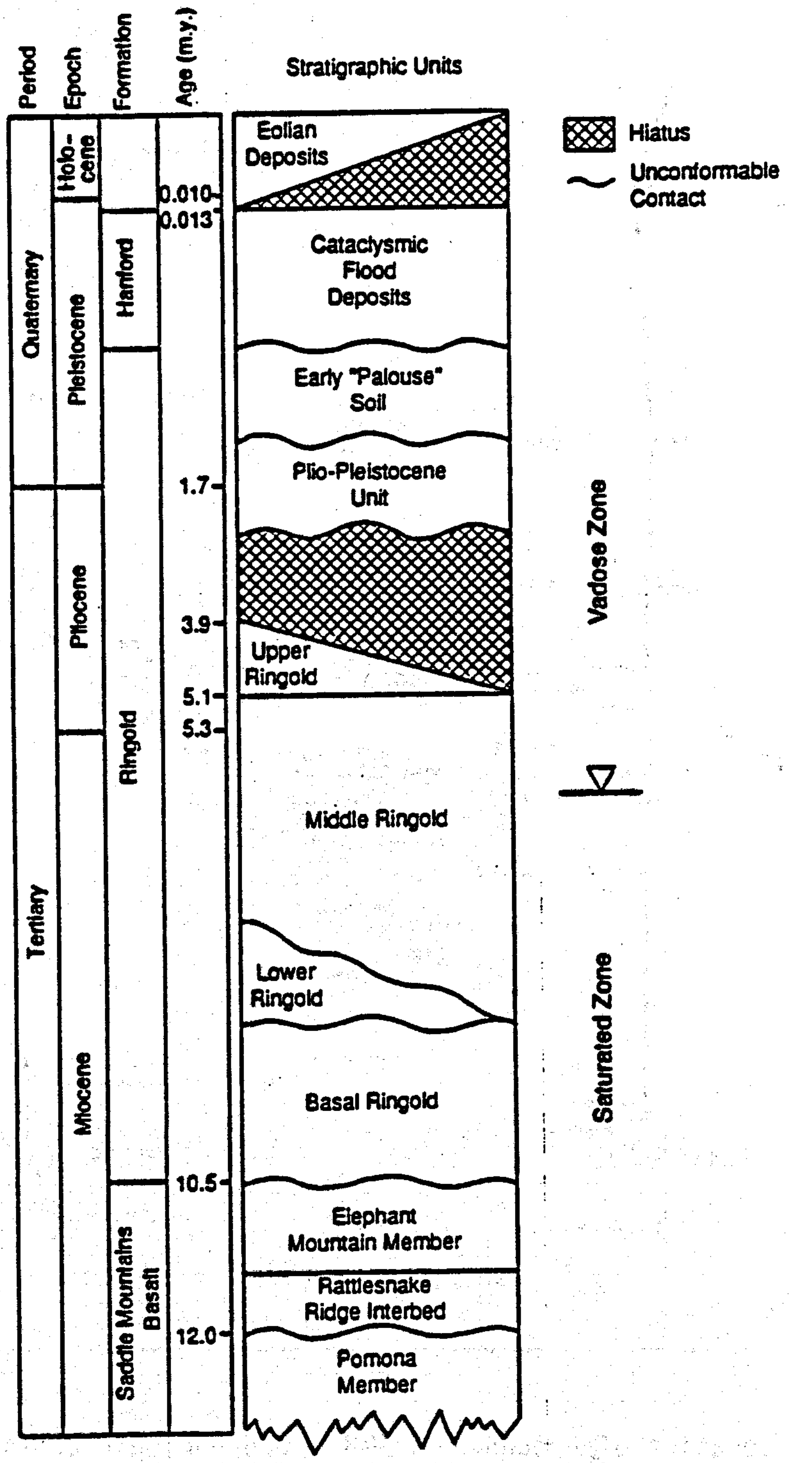

FIGURE 6. Stratigraphic Column for the 200 West Area (after Last et al. 1989)

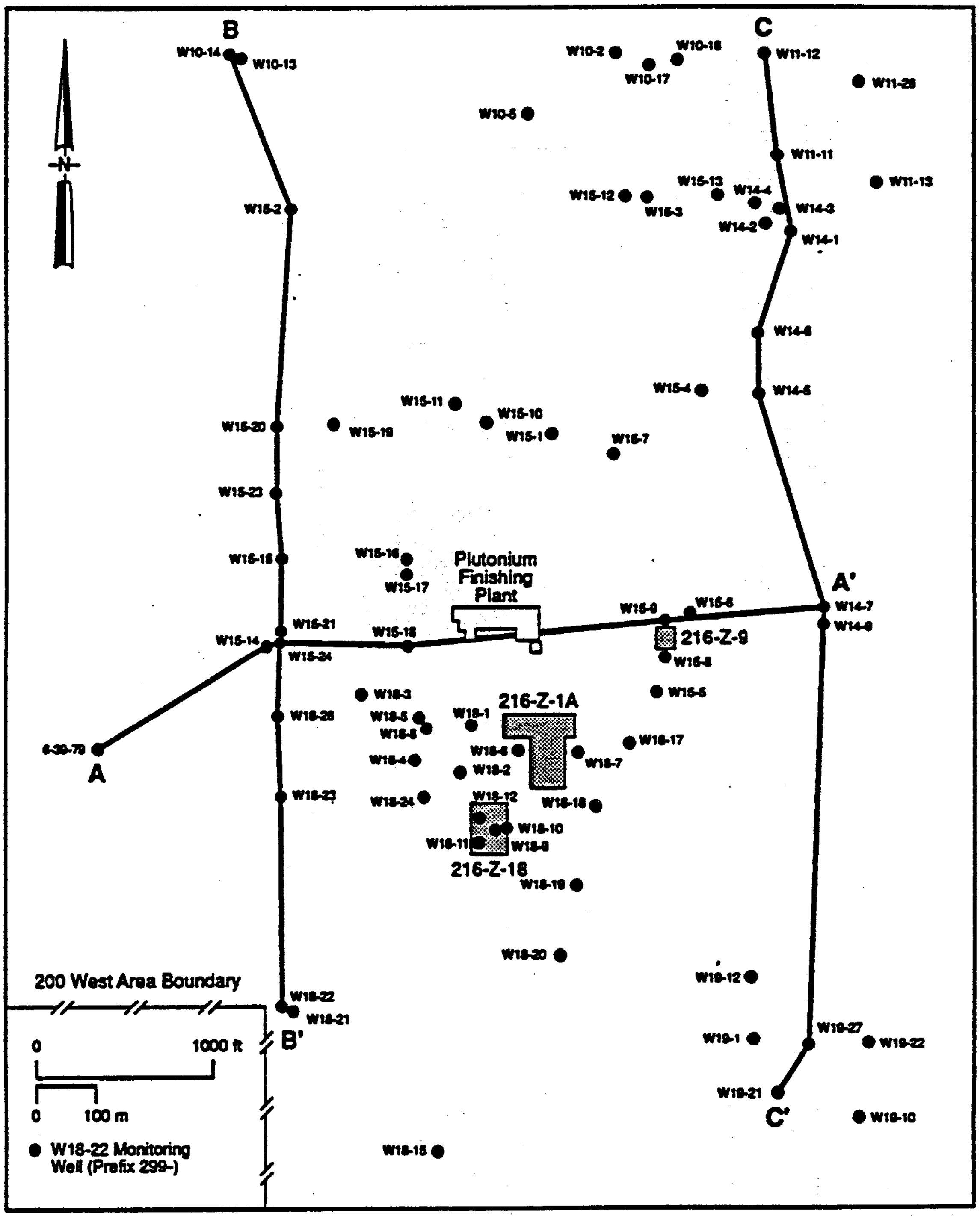

FIGURE 7. Location of Groundwater Wells and Geologic Cross Sections

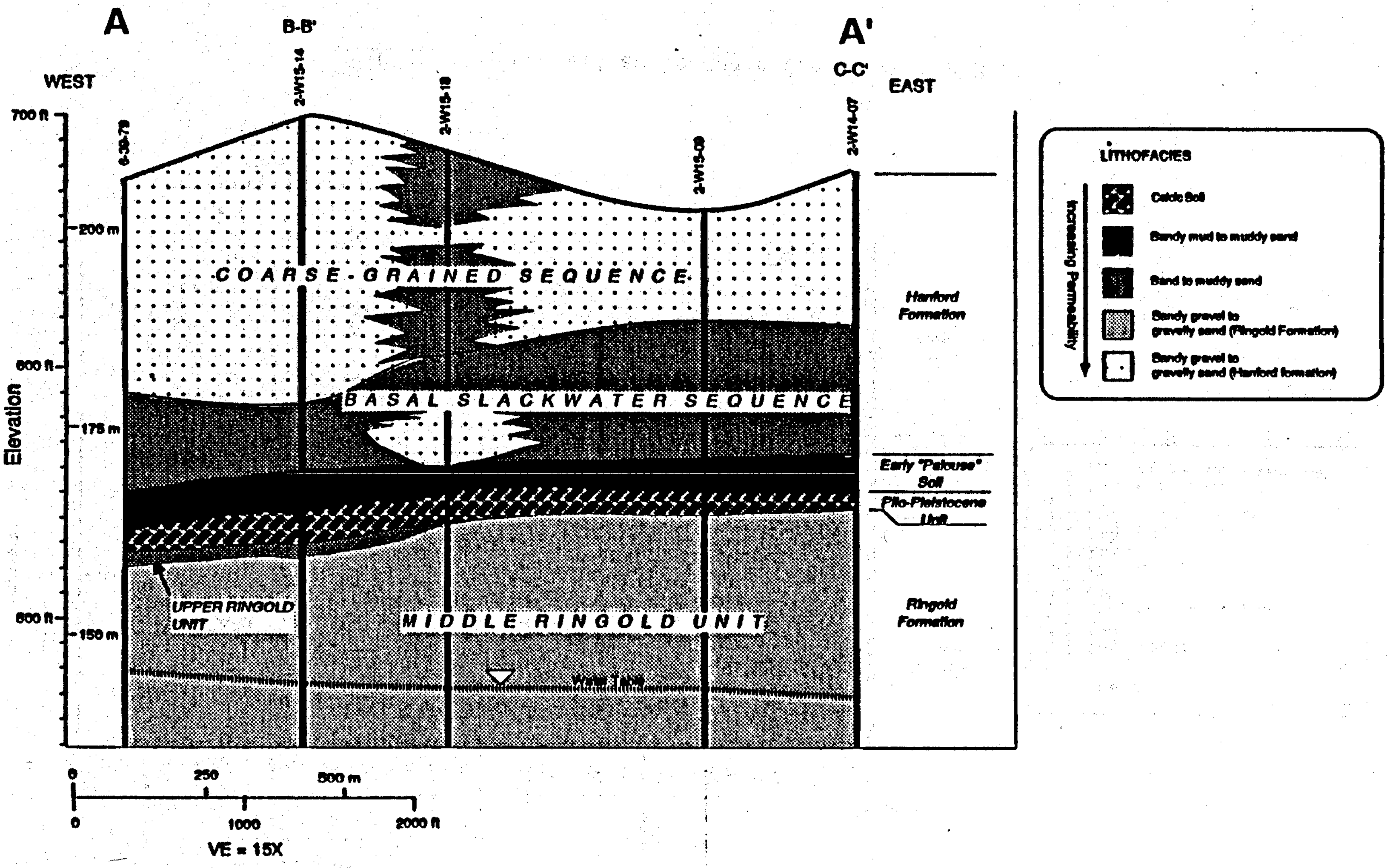

FIGURE 8. Generalized Geologic Cross Section A-A'

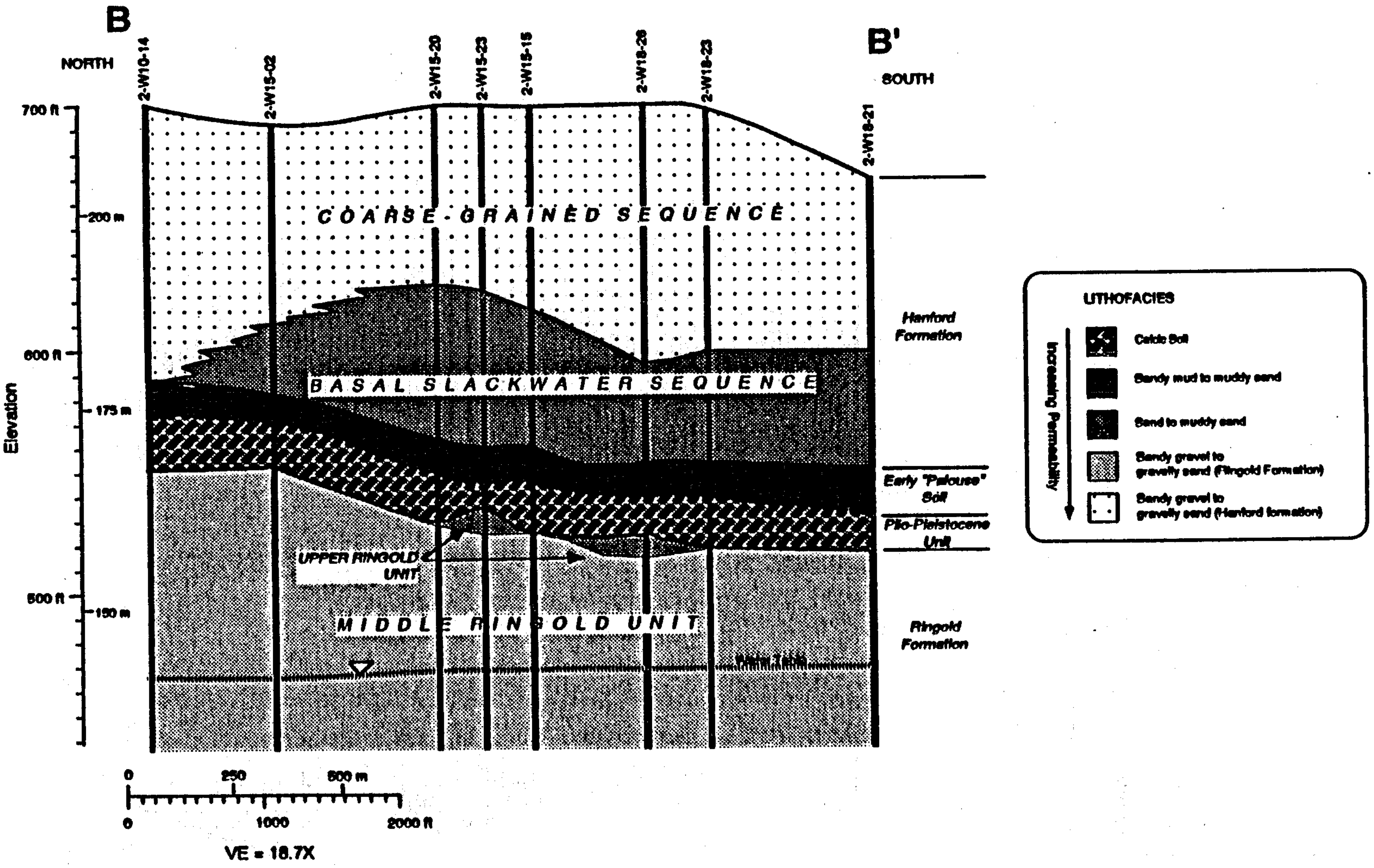

FIGURE 9. Generalized Geologic Cross Section B-B'

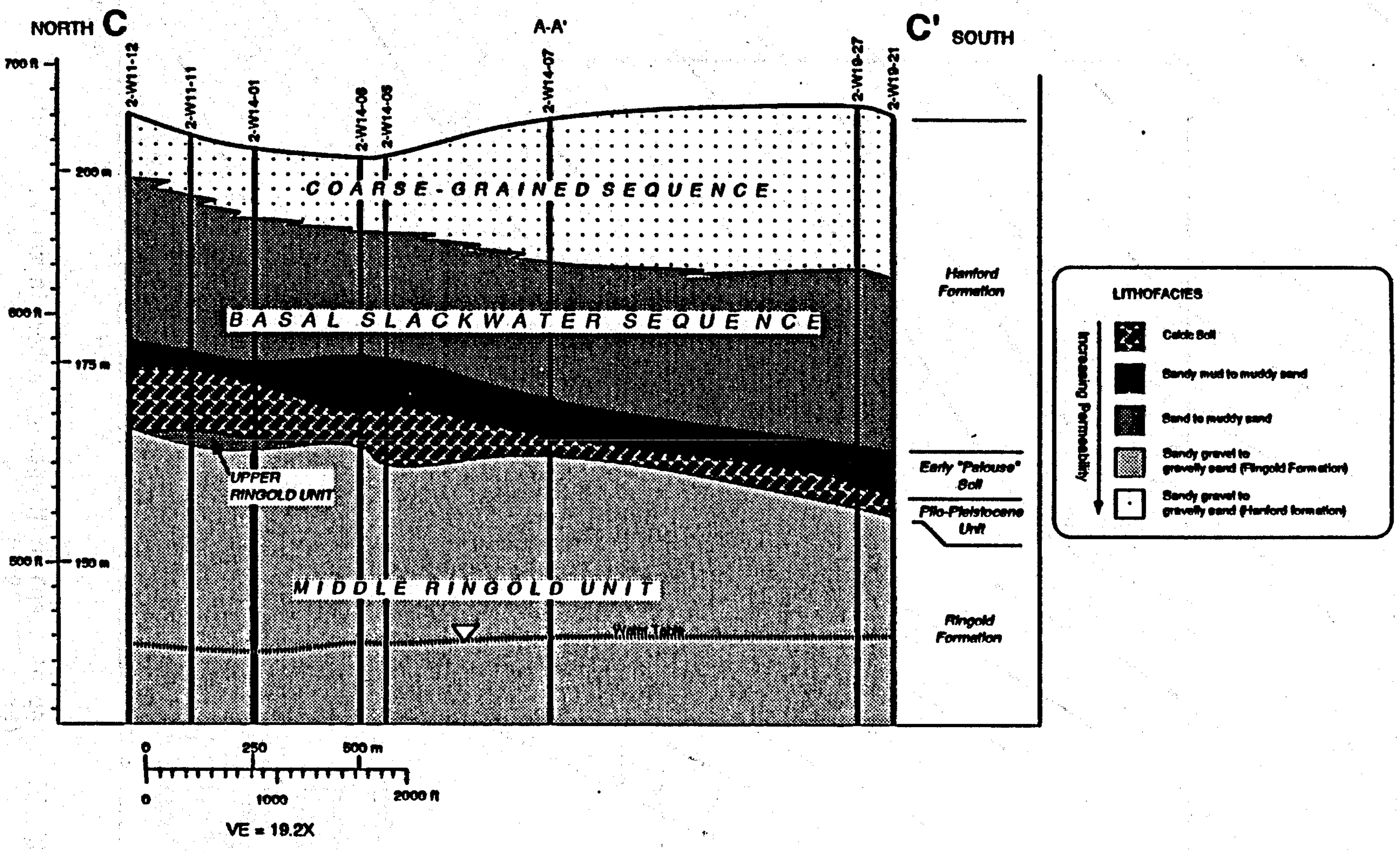

FIGURE 10. Generalized Geologic Cross Section C-C′

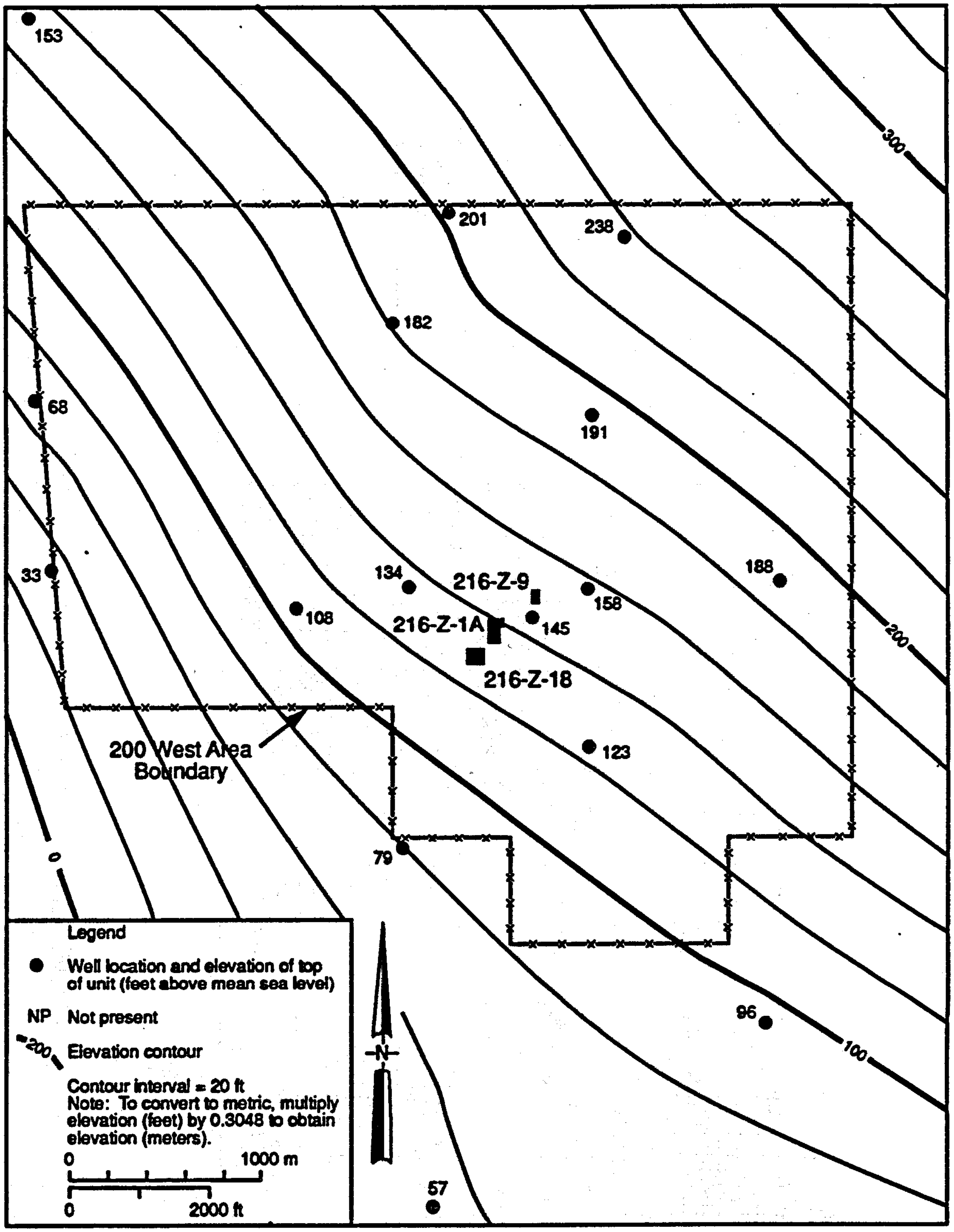

FIGURE 11. Top of Elephant Mountain Member in the 200 West Area (From DOE 1991)

The basal Ringold unit is subdivided into coarse-grained and fine-grained subunits. The coarse-grained subunit lies above the Elephant Mountain Member and consists of clast-supported sandy gravel to gravelly sand. This is overlain by increasingly finer sand and mud which forms the fine-grained subunit. The latter subunit pinches out or was eroded in the eastern portion of the 200 West Area (Last et al. 1989). A Paleosol sequence is often present at the top of the basal Ringold unit. This unit is equivalent to fluvial sequence A (FSA) identified in DOE 1991. Thickness of the basal Ringold unit ranges from 0 to 27 m (0-90 ft).

Overlying the fine-grained basal Ringold unit is a laminated mud sequence of the lower Ringold Unit. Like the fine-grained basal Ringold, the lower Ringold unit pinches out in the northeastern portion of 200 West Area (Last et al. 1989). Where present, the fine-grained basal/lower Ringold units create a layer confining water movement and form the bottom of the unconfined aquifer in the western portion of the 200 West Area. The thickness of the fine-grained basal/lower Ringold ranges from 0 to 12 m (0-90 ft). The lower Ringold unit and fine-grained basal Ringold Unit together is equivalent to the Ringold lower mud (LM) unit described by DOE (1991). The top of the lower Ringold unit dips toward the southwest (Figure 12).

The middle Ringold unit, which is up to 91 m (300 ft) thick and present everywhere within the 200 West Area, consists primarily of coarse-grained sandy gravel and muddy sandy gravel. The uniform clast-supported texture of the middle Ringold unit is sometimes interrupted by thin zones of sand and/or mud. The middle Ringold unit is equivalent to fluvial sequence E (FSE) identified in DOE 1991.

The upper Ringold unit is discontinuous beneath the 200 West Area and consists of finer-grained deposits, mostly muddy sand to gravelly sand. The contact with the underlying middle Ringold unit is gradational and is generally defined as where the amount of light-colored arkosic sand exceeds the amount of gravel. This unit is found almost exclusively in the west-central portion of the 200 West Area, with the southern extent lying beneath the PFP where it is up to about 6.1 m (20 ft) thick (Figure 13). The present

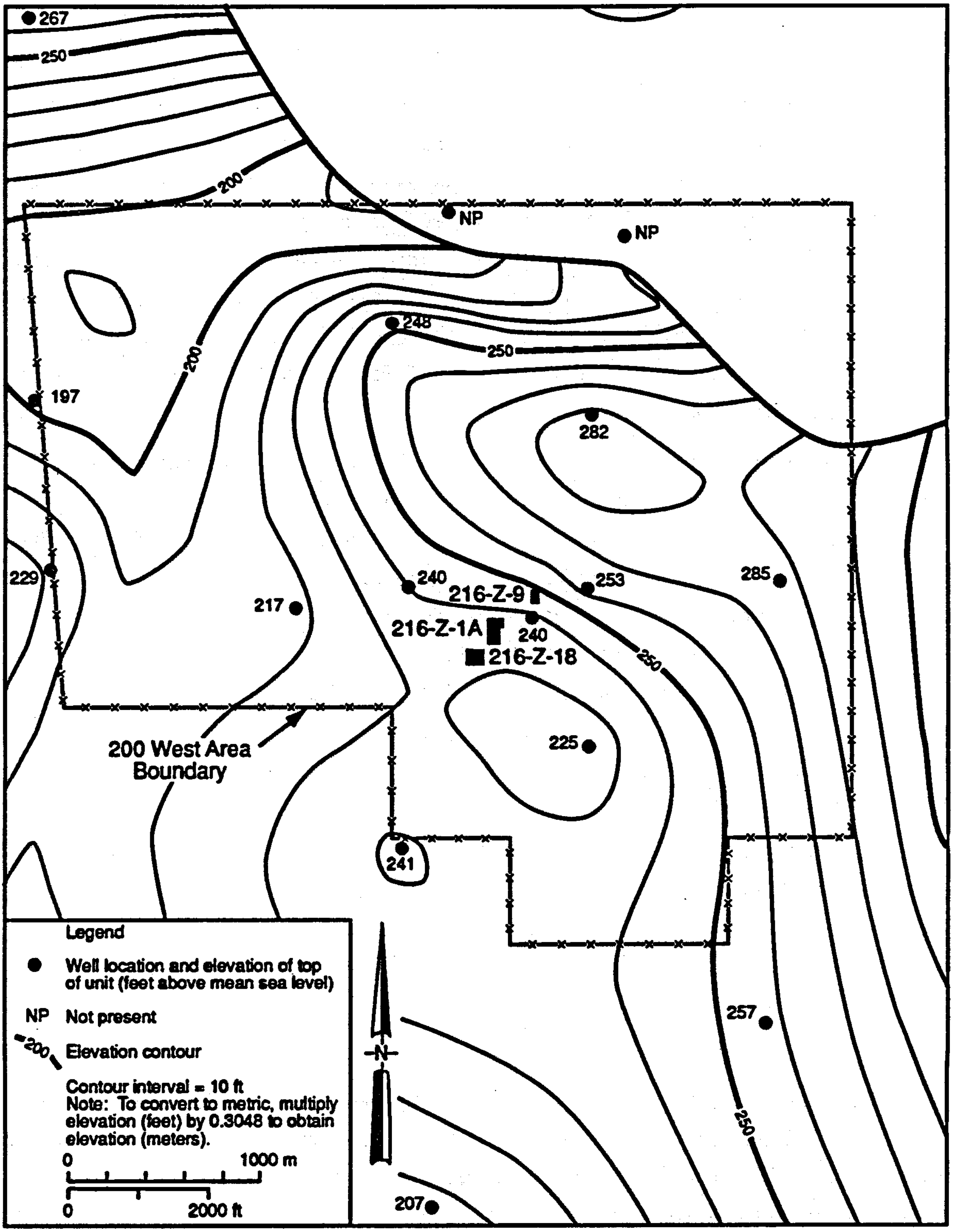

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FIGURE 12. Top of the Lower Ringold Unit in the 200 West Area (from DOE 1991)

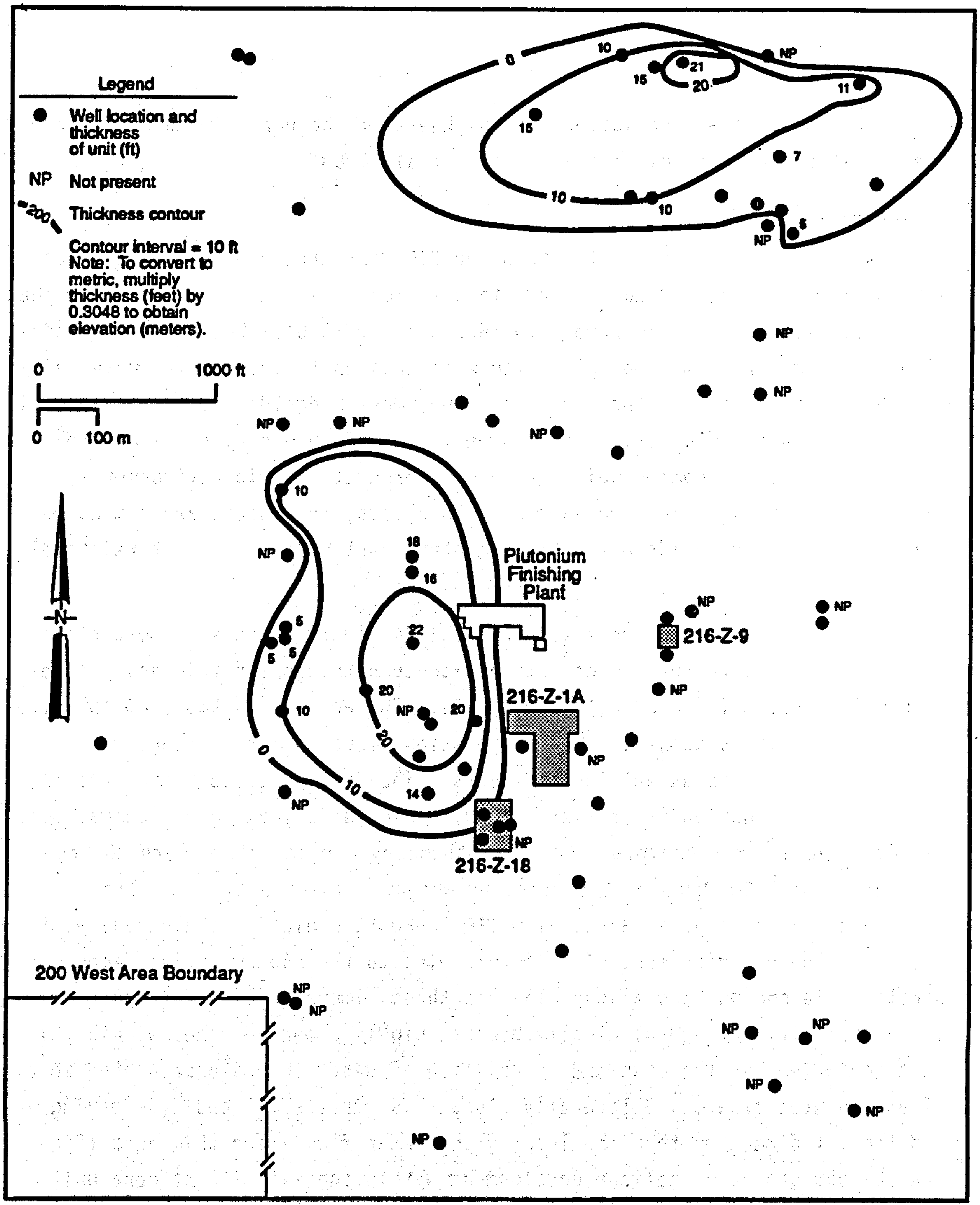

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FIGURE 13. Isopach Map of the Upper Ringold Unit

distribution and large variations in thickness of the upper Ringold unit are the result of post-Ringold erosion (Last et al. 1989).

Plio-Pleistocene Unit

The Plio-Pleistocene unit within the 200 West Area consists of a calcareous mixture of sand and mud representing a highly weathered paleosurface that developed atop the Ringold Formation (Brown 1959, 1960). While some aggradation of new material may be associated with this unit, much of the material is the result of in situ weathering of the uppermost Ringold Formation (i.e., middle or upper Ringold units). The concentration of secondary calcium carbonate cement (caliche), a common soil-development product in arid environments, exceeds 30% by weight in some samples. In places, this secondary cement may completely fill the voids between sedimentary particles, making it relatively impermeable.

The Plio-Pleistocene unit (Bjornstad 1984, 1985) appears to be a continuous stratum beneath the demonstration site even though its thickness varies from 0.5 to 9.1 m (2 to 30 ft) (Figure 14). The actual thickness of the Plio-Pleistocene unit is subject to interpretation since the lower boundary is gradational with the underlying sediments. The interpretation used here is based on a combination of driller's logs, geologist's logs, gross gamma logs, and $CaCO_3$ data. For example, the lower boundary was selected where the concentration of $CaCO_3$ became <5 percent by weight. In general, the Plio-Pleistocene unit is about 3 to 6.1 m (10 to 20 ft) thick in the vicinity of the PFP. The upper surface of this unit dips to the southwest, as demonstrated by a contour map (Figure 15) and three-dimensional view (Figure 16). This is significant hydrologically because highly-cemented zones within this unit could inhibit the downward percolation of water in the unsaturated zone. If unsaturated flow moved laterally along this surface, it could be moving in a different direction than the local groundwater flow. The thickness (Figure 14) and degree of caliche development within the Plio-Pleistocene unit vary considerably from one location to another. The Plio-Pleistocene unit is generally thinner to the south and east of the PFP but is also thin (1.5 m) (5 ft) just southwest of the PFP (Figure 14). Considerable relief with

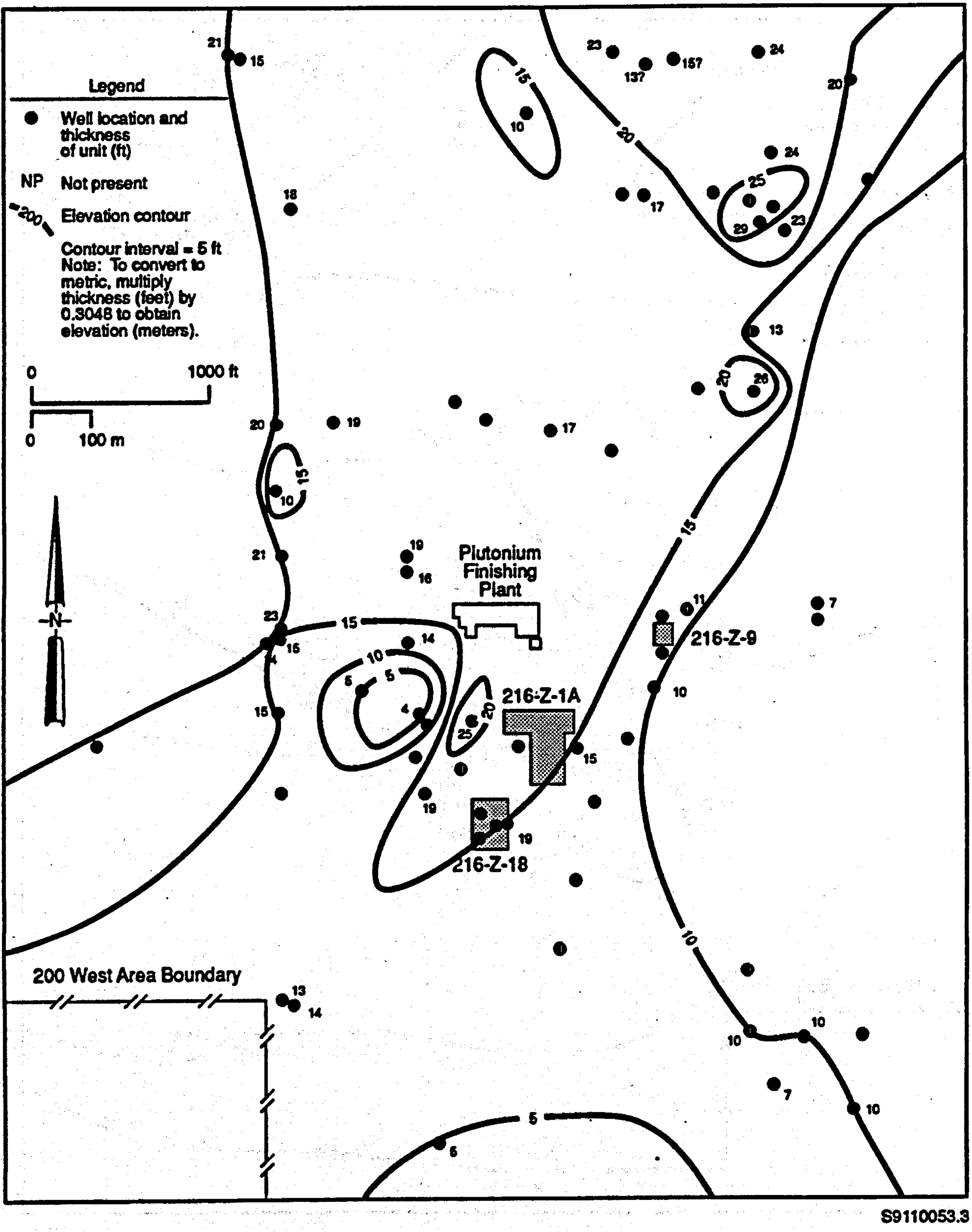

FIGURE 14. Isopach Map of the Plio-Pleistocene Unit

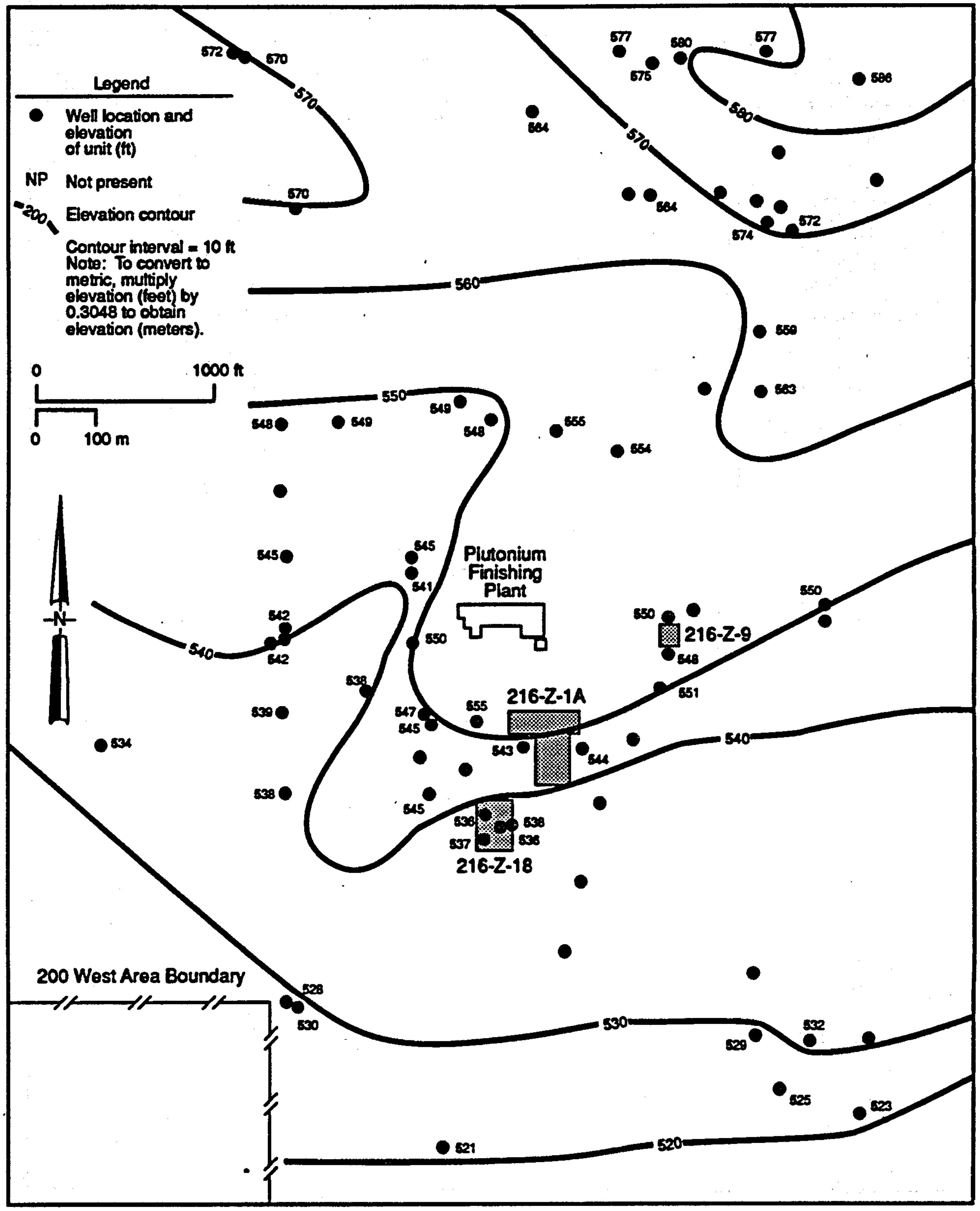

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FIGURE 15. Contour Map of the Top of the Plio-Pleistocene Unit

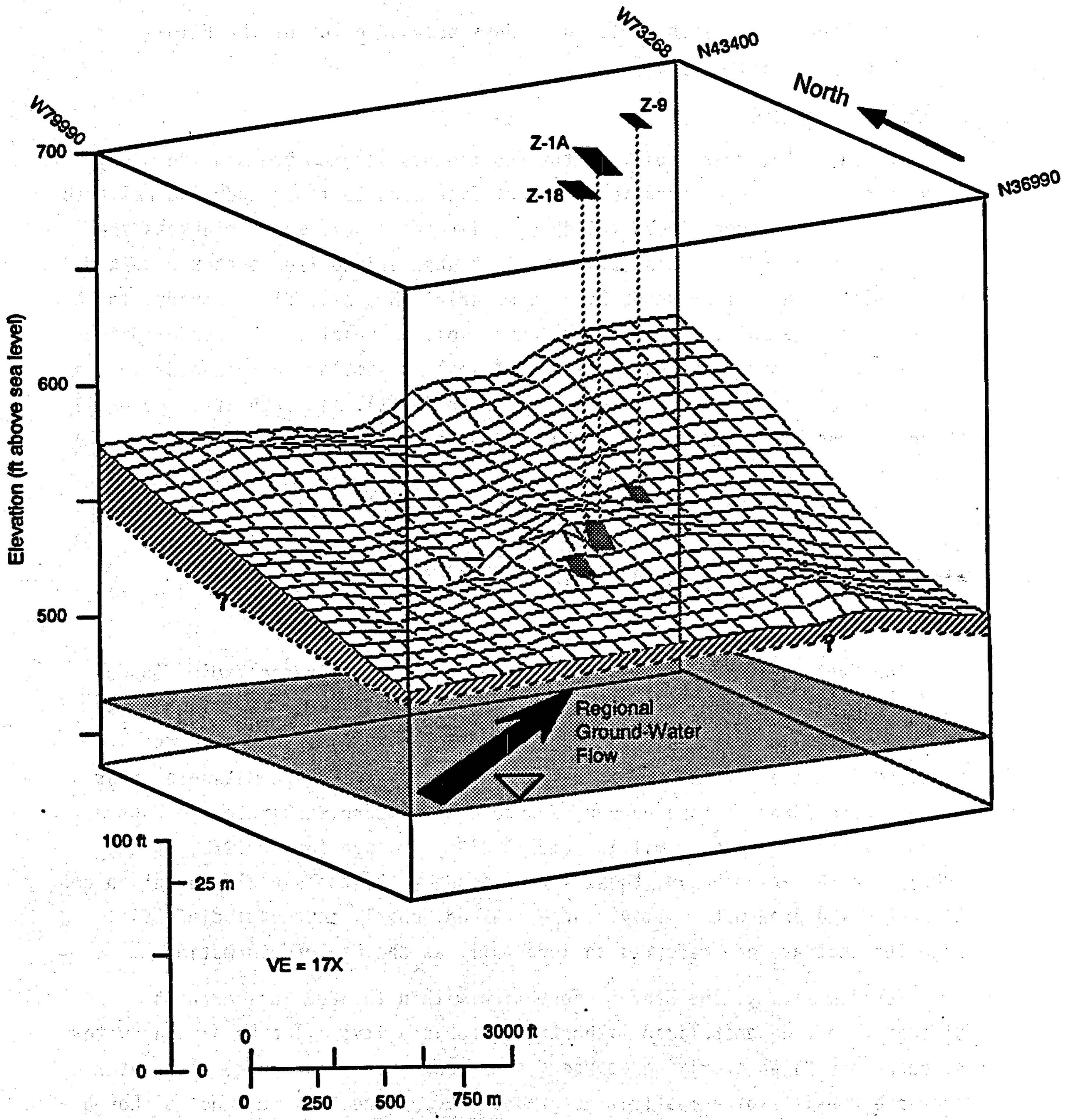

FIGURE 16. Three-Dimensional View of the Plio-Pleistocene Unit

northeast trending paleochannels and ridges occurs on top of the Plio-Pleistocene unit (Figure 15).

Early "Palouse" Soil

The Early "Palouse" soil, another continuous stratum beneath the study area, consists of an unconsolidated muddy fine sand to fine sandy mud believed to be early Pleistocone loess (windblown silt and sand), which blankets the Plio-Pleistocene unit. This eolian deposit was derived from either reworked Plio-Pleistocene unit or upper Ringold material (Brown 1960). Compared to the Plio-Pleistocene unit, the Early "Palouse" soil is relatively unconsolidated and less calcareous. The Early "Palouse" soil is similar in thickness to the Plio-Pleistocene unit about 3 to 6.1 m (10 to 20 ft), although it is generally thinner directly beneath the PFP than in surrounding areas (Figure 17). Like the Plio-Pleistocene unit, this unit is much finer grained and less permeable than the overlying Hanford formation. The top of the Early "Palouse" soil generally is similar to the top of the Plio-Pleistocene unit (Figure 15), and dips nearly opposite to the direction of groundwater flow.

Hanford Formation

The Hanford formation was deposited by Pleistocene cataclysmic floods (Myers and Price et al. 1979), which first inundated eastern Washington as early as 1 million years ago (Bjornstad and Fecht 1989). These floods resulted from the sudden release of glacial waters from Lake Missoula, near the northern Idaho/Montana border, and covered eastern Washington perhaps dozens of times between 1 million and 13,000 years ago (Baker 1973, Waitt 1980). In the Pasco Basin, these floods eroded into the Ringold Formation and blanketed the area with mostly coarse-grained, poorly sorted glaciofluvial deposits that are now referred to informally as the Hanford formation.

For simplicity, the Hanford formation within the 200 West Area is divided into two generalized lithostratigraphic units: 1) a basal slackwater sequence and 2) an overlying coarse-grained sequence. The basal slackwater sequence consists of a mostly fine-grained muddy sand to sandy mud, although coarser-grained facies may also be present. The overlying coarse-grained sequence, which consists of mostly gravel and sand, is probably associated

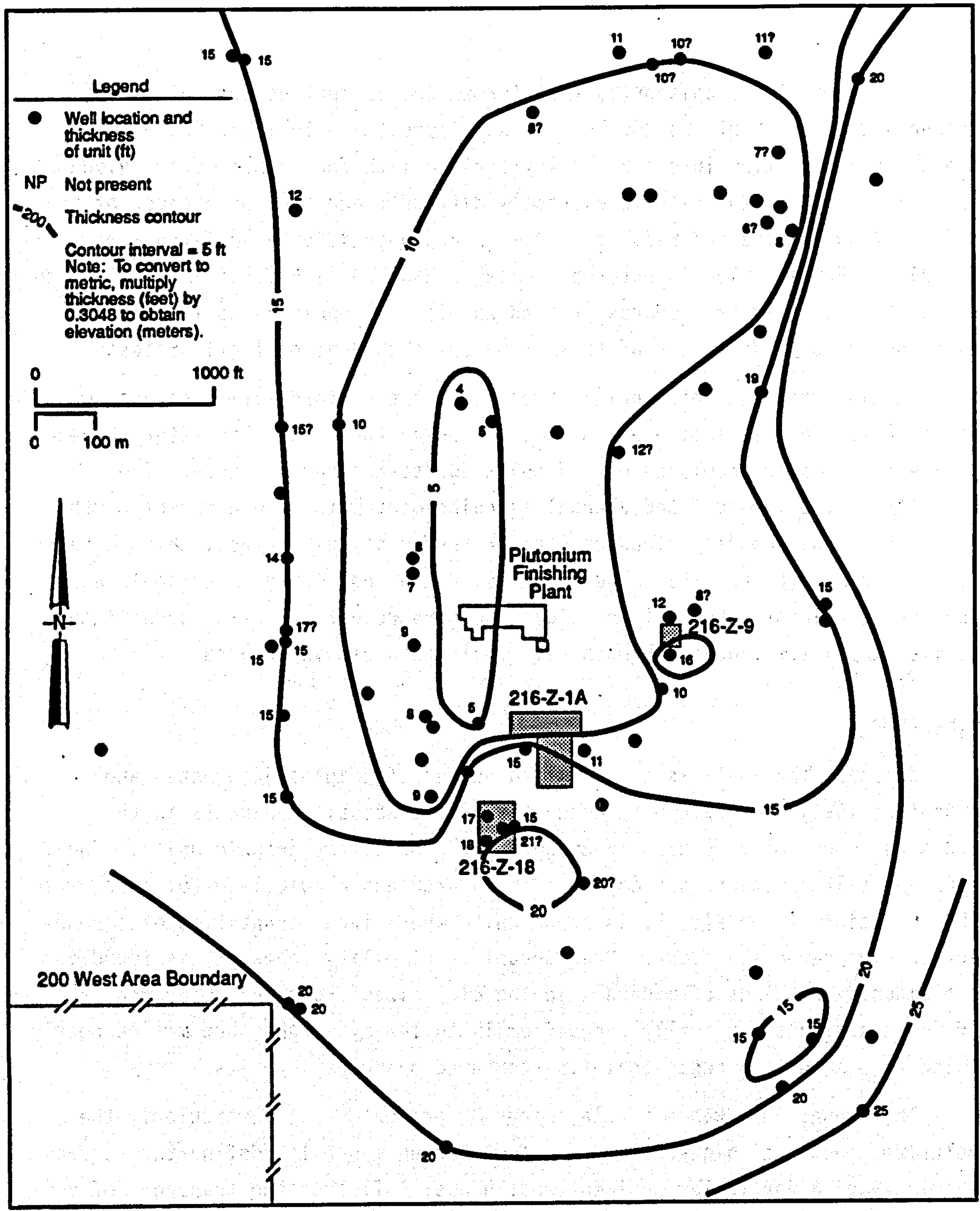

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FIGURE 17. Isopach Map of the Early "Palouse" Soil

with the latest flood episode(s) that formed the present network of flood channels just north of the 200 West Area (Figure 18). In 1991, DOE divided the Hanford formation into six locally defined lithofacies but more regional correlation of the subunits is extremely difficult and tenuous because of the dynamic flow systems and resultant erosion and deposition associated with flooding. For example, in outcrop exposures Hanford lithofacies may alternate and grade laterally from coarse-grained cobbles and boulders to fine-grained sand and mud over distances of tons of meters (hundreds of feet) or less.

An old buried paleochannel is present in the Hanford formation just west of the PFP. This is indicated in Figure 8 where the basal slackwater sequence has been eroded and replaced with a thick coarse-grained sequence. The position of the buried flood channel is coincident with a more recent north-south trending secondary flood channel preserved at the surface, which bisects Cold Creek bar (Figure 19). The thickness of the coarser-grained sediments and the coincident nature of the older and more recent channels suggests that earlier and later floods may both have followed a similar course.

MINERALOGY

Based on the analysis of a limited number of samples (Bjornstad and Amonette, 1991), the bulk mineralogy of the suprabasalt sediments in the 200 Areas does not vary greatly among the various stratigraphic units. The sand and silt fractions are dominated by quartz and plagioclase feldspar, with the exception of the Plio-Pleistocene unit, where large quantities of secondary calcium carbonate occur. Considerable variability, however, is found in the amounts and kinds of minerals in the clay-sized fraction. Clay contents of these sediments typically range from 1% to 14% by weight, but may be nearly twice this amount in occasional fine-textured overbank deposits.

The amounts and kinds of clay minerals present, and, particularly the relative amounts of high-charged and low-charged minerals, define the surface chemistry of a particular sediment and, hence, influence the transport of contaminants through that sediment. Smectites, which are moderately charged 2:1 layer-silicates, dominate the clay mineral suite for the specimens analyzed (Figure 20). The proportion of smectite in the clay fraction ranges from 95%

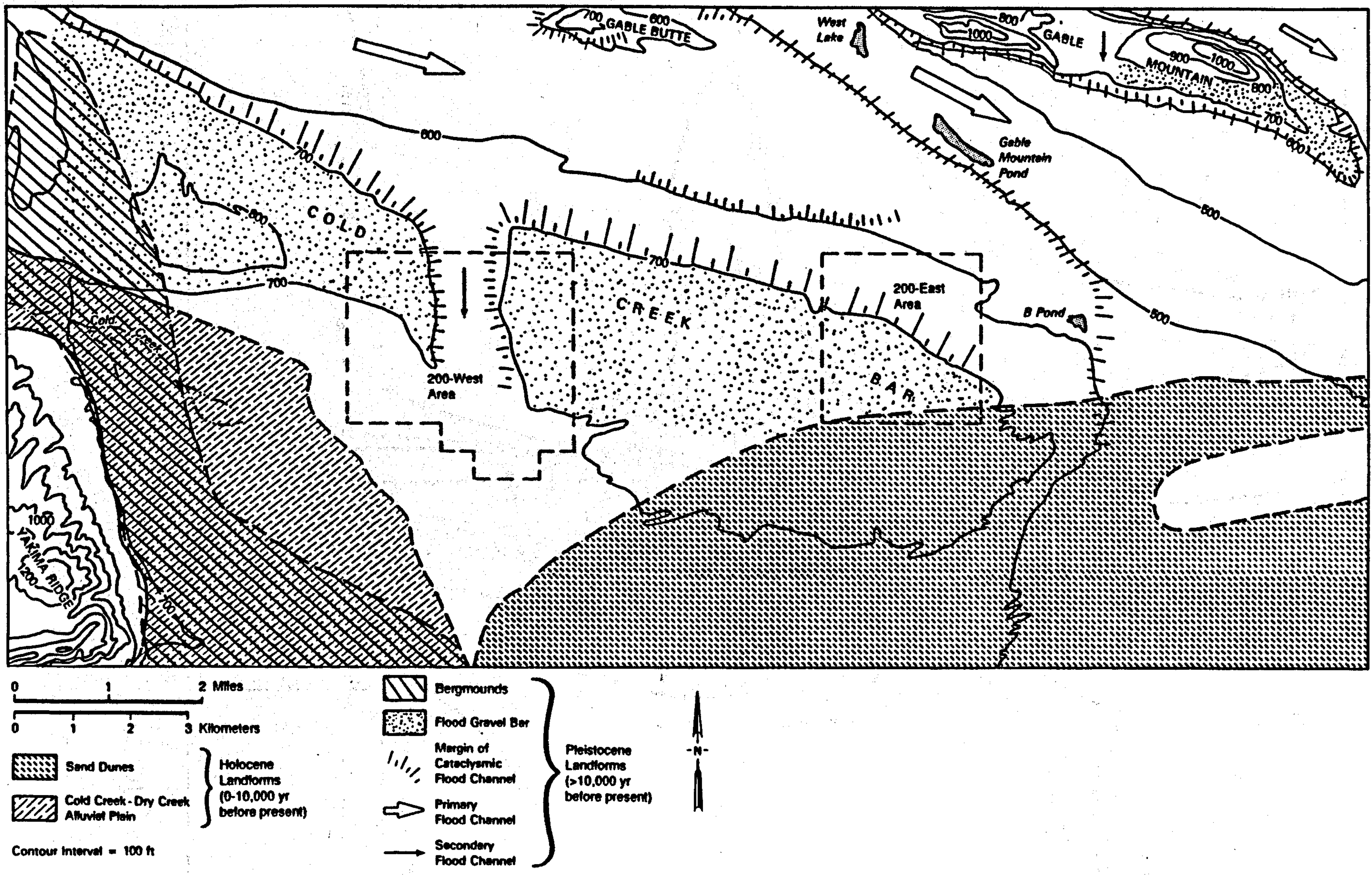

FIGURE 18. Paleochannels and Other Features Associated with Cataclysmic Flooding (from Last et al. 1989)

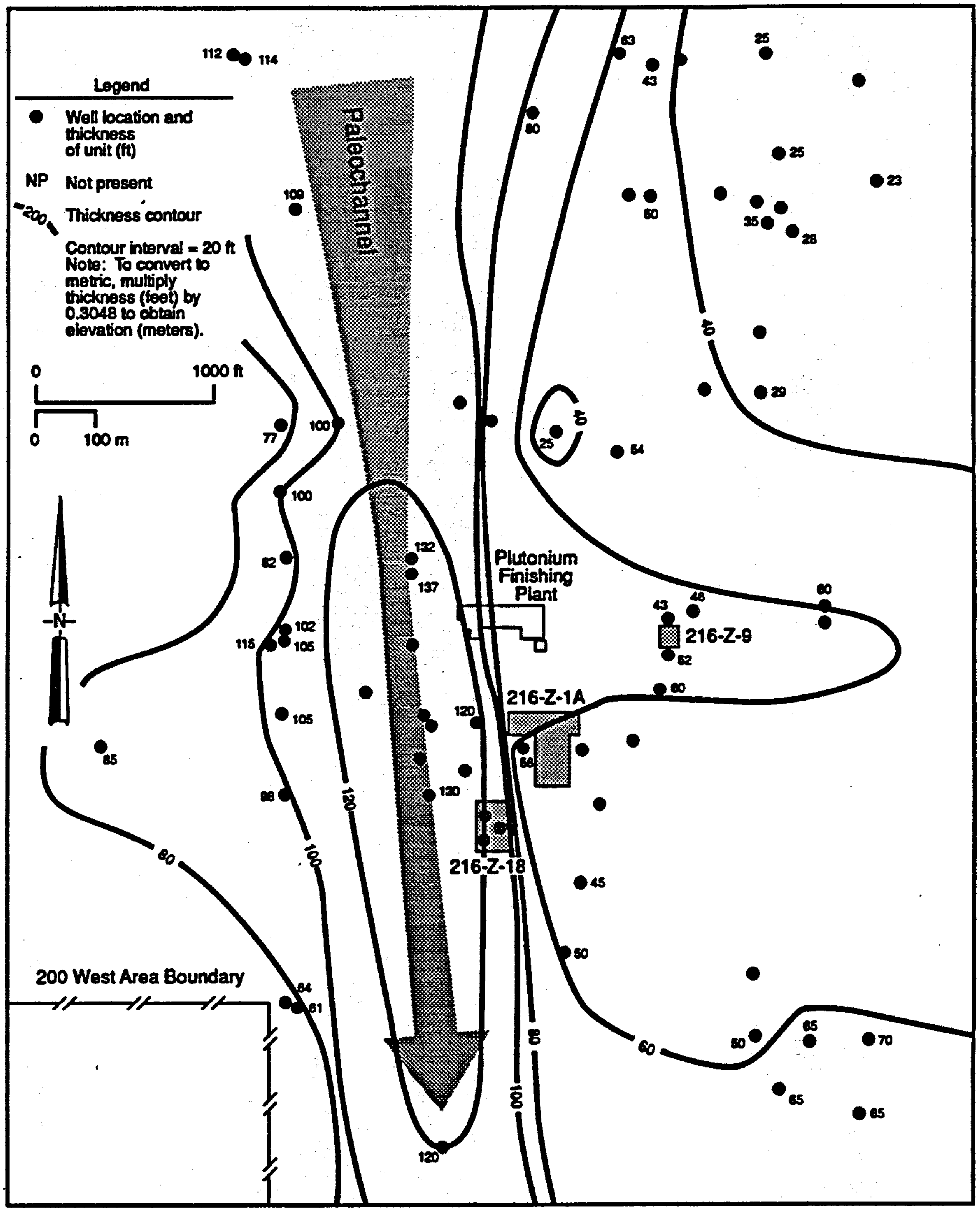

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FIGURE 19. Isopach Map of the Basal Slackwater Sequence of the Hanford Formation

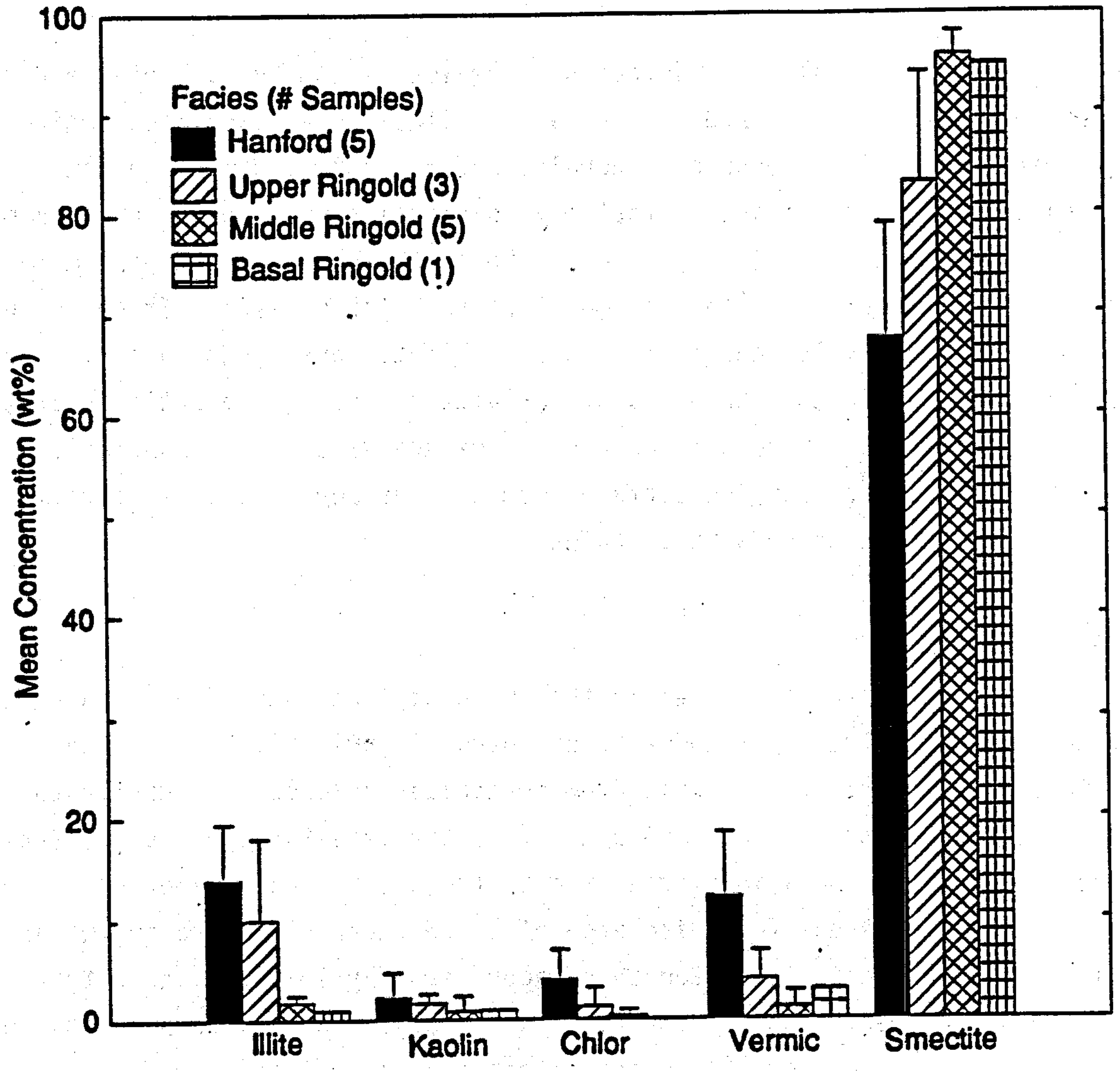

FIGURE 20. Clay Minerals in the Suprabasalt Sediments of the 200 Areas, Near the VOC-Arid ID Site (Bjornstad and Amonette 1991)

in the Middle and Basal Ringold facies to as low as 55% in some of the Hanford facies specimens from the 200 East Area. Illites and vermiculites, which are high-charged smectite precursor minerals, and chlorites, which are non-expanding 2:1:1 layer silicates that may be smectite precursors, make up most of the remainder of the clay fraction. The amounts of each of these minerals are inversely proportional to the amount of smectite present. Trace amounts of kaolinite, a very-low-charge 1:1 layer-silicate, are found in clay fractions from all sediments, but show no correlation with the quantities of the 2:1 layer silicates. More samples need to be analyzed before conclusions about the clay mineralogy and surface chemistry of any particular stratigraphic unit can be drawn with certainty.

HYDROGEOLOGY

Recharge to the groundwater in the 200 West Area comes from both natural and artificial sources. Groundwater discharge is primarily east to the Columbia River. Natural recharge from precipitation occurs primarily to the west of the 200 West Area on and adjacent to the basalt ridges (e.g., Yakima Ridge, Figure 18). Artificial recharge to the unconfined aquifer occurs primarily in the 200 Areas from discharge of waste streams and cooling water. Artificial recharge is estimated to be approximately 10 times the natural recharge at the Hanford Site (Graham et al. 1981). Natural recharge on the Cold Creek Bar (Figure 18) has been estimated at near 0 to 10 cm/yr (0-4 in/yr) (Gee 1987), which is almost negligible compared to artificial recharge as a means of carrying contaminants from the vadose zone to the water table.

The vadose zone is relatively thick in the 200 West Area, ranging from 62-84 m (203-276 ft). Within most of the 200 West Area the water table lies within the middle Ringold unit. As previously discussed, the geologic units found in the 200 West Area have a wide range of textures and hydraulic properties. These properties have been calculated using a variety of techniques including laboratory measurements, percolation tests, and aquifer tests.

Considerable data exists for the Hanford and Ringold formation, while relatively little hydrologic information is available for the Early "Palouse" soil and Plio-Pleistocene unit.

Bjornstad (1990) reported data for water content, water retention, and saturated hydraulic conductivity determined from core samples and aquifer tests of wells near the Low Level Burial Grounds in the 200 West Area. More recent data have been collected by Westinghouse Hanford from core samples obtained from wells north of the PFP. The Westinghouse Hanford data include primary drainage (drying) and imbibition (wetting) characteristics and saturated hydraulic conductivities. The ranges of hydraulic properties reported for the principal geologic units within the 200 West Area are presented in Table 2, demonstrating the considerable variation that occurs between and within these units because of their heterogenous nature.

In general, hydraulic conductivities are greatest for the Hanford formation, while a one-to-three order of magnitude difference exists between the Hanford formation and the Middle Ringold unit (DOE 1988). However, large differences in the range of hydraulic conductivities exist within these units. For example, the upper portion of the middle Ringold units generally has higher hydraulic conductivity values (0.02 to 61 m/d) (0.07 to 200 ft/d) compared to the lower portion of the middle Ringold unit (0.5 to 1.2 m/d) (1.6 to 3.9 ft/d). This may be due to a higher degree of compaction and/or alteration in the older Ringold sediments. Seismic refraction surveys (DOE 1988) indicate that the lower portion of the middle Ringold unit has a higher seismic velocity that probably coincides with a lower hydraulic conductivity. The Early "Palouse" soil, Plio-Pleistocene unit, lower Ringold unit, and upper basal Ringold subunit have relatively low permeability because of their fine-grained texture.

In addition to aquifer testing and laboratory determination of saturated hydraulic conductivity, field percolation tests were conducted in the early 1980s in the immediate vicinity of the 216-Z-20 crib. Based on the ponded infiltration rates during these tests, and assuming a unit hydraulic gradient, hydraulic conductivities were calculated that range from 3.0 to 17.2 m/d, over a volumetric water content range from 0.23 to 0.35.

TABLE 2. Reported Hydraulic Properties for the 200 West Area

Stratigraphic Unit	Saturated Hydraulic Conductivity (m/d)	Effective Porosity	Storativity	Gravimetric Moisture Content (%) (Range/Average)[a]
Hanford formation	600 to 3,000[b] (2,000 to 10,000 ft/d)	~0.3[b]	0.07[b]	0.3-33.2/5.3
Early "Palouse" Soil	0.12			2.7-29.5/13.9
Plio-Pleistocene Unit	0.10			1.8-5.8/3.8
Upper Ringold Unit	0.03 to 61[c] (0.10 to 200 ft/d)			1.9-11.4/6.6
Middle Ringold Unit	0.3 to 1550[a] (1.0 to 5100 ft/d)	0.1[d]-0.2[b]	0.05-0.2[c]	0.9-6.6/2.4
Lower Ringold Unit	1.0 to 3.6[b] (3.3 to 11.8 ft/d)	0.1[b]	0.002[b]	N/A
	1.6×10^{-5}[d] (5.3×10^{-5} ft/d)			
Basal Ringold Unit	0.001 to 0.61[c] (0.003 to 2 ft/d)			N/A

(a) From DOE (1991).
(b) From Graham et al. (1981).
(c) From Last et al. (1989).

Effective porosity ranges from about 0.3 for the Hanford formation to 0.1-0.2 for the Ringold Formation (Table 2). No effective porosity or storativity data are available for the Early "Palouse" soil and Plio-Pleistocene unit. On the average, moisture contents in the vadose zone are greatest for the Early "Palouse" soil and least for the middle Ringold unit (DOE 1991). Subsurface moisture content appears to be influenced by sediment texture and proximity to zones of artificial recharge. Soil air permeabilities obtained from the vadose zone (Hanford formation) during vapor extraction testing at the 216-Z-1A tile field ranged from 2×10^{-8} to 5.6×10^{-8} cm^2 (2×10^{-11} to 6×10^{-11} ft^2) with air hydrologic conductivity of 1.3×10^{-4} to 3.7×10^{-4} cm/sec (4.3×10^{-6} to 1.2×10^{-5} ft/s) at the 17-23 m (56-75 ft) depth in well 299-W18-171 (DOE 1991).

Regional groundwater flow is generally from west to east (Newcomer et al. 1991). The present direction of groundwater flow in the vicinity of the 200 West Area is largely influenced by a groundwater mound created by past artificial recharge at the 216-U-10 pond (U pond) and current discharges to the 216-U-14 ditch northeast of U pond (Figure 21). Since 1984 when U pond was deactivated, the groundwater mound has diminished, causing the water table to drop as much as 4 m (13 ft). The water level in the vicinity of PFP has also dropped by approximately 2 m (6.6 ft) since 1984. The water table in the vicinity of PFP (Figure 22) ranges from approximately 62-84 m (200 to 275 ft) below ground surface and from 142 to 144 m (467 to 472 ft) above sea level. The mound is expected to continue influencing groundwater flow for a number of years. Groundwater velocities in the vicinity of the PFP have been estimated at 0.01 to 1 m/d (0.03 to 3 ft/d) (Last et al. 1989).

GROUNDWATER CHEMISTRY

In discussing the composition of groundwater in the unconfined acquifer beneath the 200 West Area, distinctions must be made between background concentrations and concentrations that have anthropogenic origins. An estimate of the average background composition of Hanford groundwater from the unconfined acquifer was made by Evans et al. (1988) and compares well with values reported by Gephart et al. (1979) from site-wide monitoring studies in

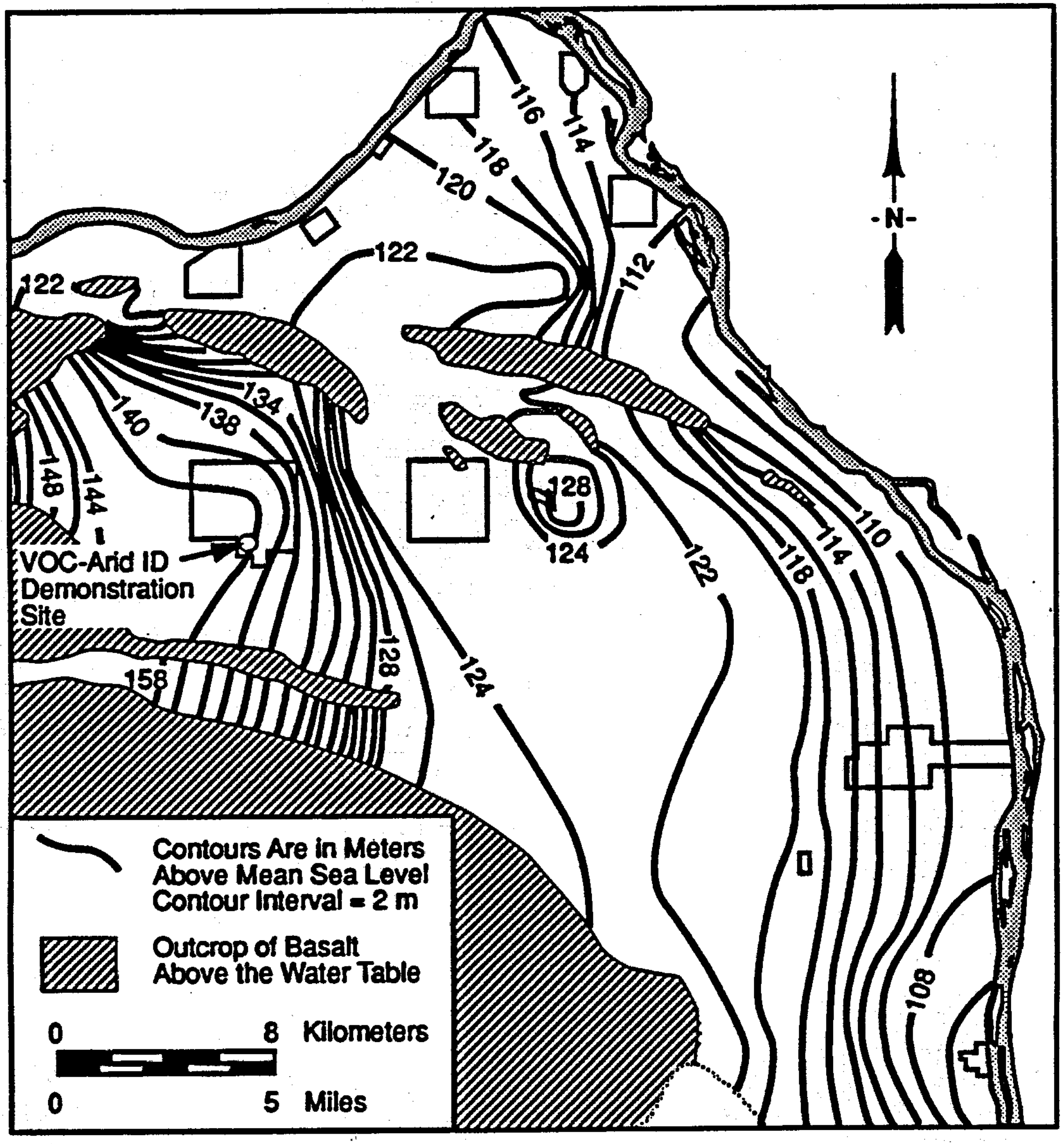

FIGURE 21. Water Table Elevation for the Hanford Site Measured in June 1989 (Jaquish and Bryce 1990)

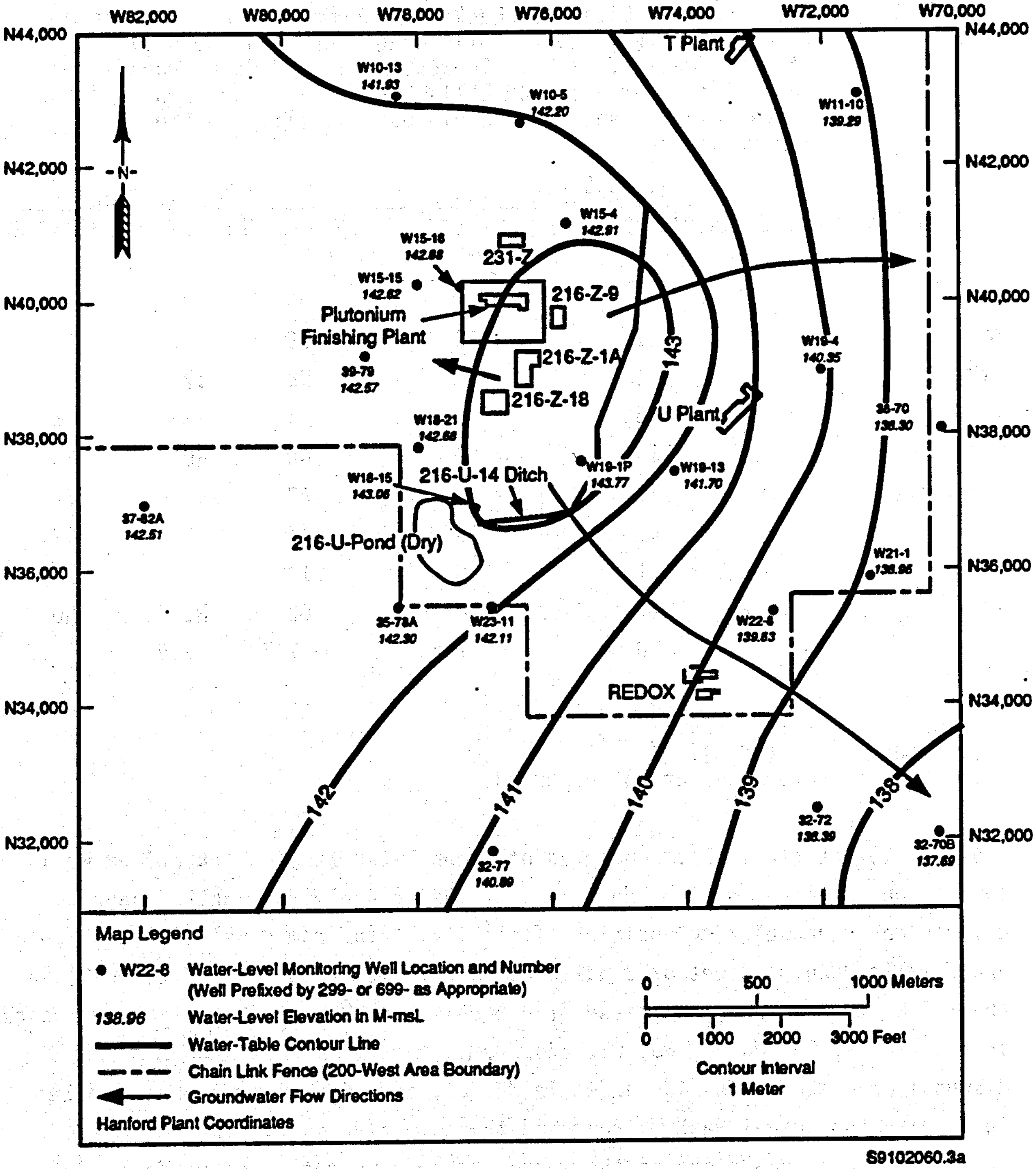

FIGURE 22. Groundwater Map (modified from Newcomer et al. 1991)

TABLE 3. Reported Mean Site-Wide Background Compositions of Hanford Groundwater from the Unconfined Aquifer, Mean Composition of Groundwater from the 200 West Area, and Mean Groundwater Composition for Selected Wells Up-Gradient and Down-Gradient of the 216-U-1 and 216-U-2 Disposal Facility in the 200 West Area

Constituent	Hanford Site-Wide		200 West Area		
	Background[a]	Background[b]	Mean mgL^{-1}	Up-Grad	Down-Grad
Na^{+}	23	21	52	22	41
Mg^{+2}	11	12	19	6	17
Ca^{+2}	41	43	58	17	59
K^{+}	6	6	5	3	6
SiO_2	35	ND[c]	ND	ND	ND
Alkalinity (as CO^{-2}_{3})	75	123	127	103	152
SO^{-2}_{4}	43	40	44	17	47
Cl^{-}	11	9	17	4	22
NO^{-3}_{1}	27	ND	162	ND	ND
pH	ND	7.64	7.73	7.9	7.7

(a) Gephart et al. (1979).
(b) Evans et al. (1988).
(c) ND = Not Determined or Not Reported.

the late 1970's (Table 3). Analyses of groundwater samples taken from wells in the 200 West Area during the spring of 1987 clearly show anthropogenic effects on groundwater composition (Table 3). Data from 4 wells up-gradient and 9 wells down-gradient of 2 waste disposal cribs (216-U-1 and 216-U-2) in the 200 West Area show a decrease of 0.2 units in pH and substantial increases in alkalinity, Ca, Mg, K, Na, Cl, and SO_4^{-2}, presumably as a result of the disposal practices. The increases in Na, Cl, and SO_4^{-2} concentration can be related to the actual waste stream and those in alkalinity, Ca, Mg, and K concentration to reactions of the waste stream with soil constituents. Results of geochemical modeling calculations performed with the MINTEQ code (Felmy et al., 1984) show that both up-gradient and down-gradient groundwater samples are near equilibrium with calcite. The results for the up-gradient wells suggest that the true background concentrations for the 200 West Area groundwater may be lower, and the background pH higher, than the site-wide values recommended by Evans et al. (1988).

WASTE SITE CONTAMINATION

This section presents current information regarding the extent of vadose zone and groundwater contamination beneath the three carbon tetrachloride (CCl_4) receiving cribs: 216-Z-9, 216-Z-1A, and 216-Z-18. This information is based primarily on the results of previous investigations (e.g., Price et al. 1979) and the ongoing ERA (DOE 1991).

VADOSE ZONE CONTAMINATION

Well and borehole drilling operations in the vicinity of cribs 216-Z-9, 216-Z-1A, and 216-Z-18 have historically detected CCl_4 odors in the vadose zone. Since 1987, well-drilling operations using portable photoionization detectors (PIDs) have also detected CCl_4 vapors away from the cribs throughout most of the 200 West Area. Figure 23 illustrates the location of wells where CCl_4 vapor has been detected during recent well-drilling operations. Most of these detections have been below the Plio-Pleistocene unit that occurs approximately 40 m (130 ft) beneath the surface.

Soil samples collected while drilling several boreholes were analyzed for volatile organic contaminants using standard laboratory procedures (Airhart 1990, Barton 1990, Goodwin 1990, and Goodwin and Bjornstad 1990). Eleven of the sixteen boreholes yielded CCl_4 concentrations above the detection limits. Although CCl_4 was detected both above and below the caliche layer, the highest concentrations were generally found below the caliche and just above the water table (DOE 1991). Other substances were also identified in these soil samples. A complete list of detected constituents is provided in Table 4.

To support the ERA, Westinghouse Hanford performed several site-specific investigations, including soil gas surveys, well head gas sampling, and vapor extraction testing. A soil gas survey was performed near the 216-Z-1A and 216-Z-18 cribs (Figure 24). Results indicate that CCl_4 is present beneath this entire area. Soil gas values ranged from 1.49 to 14.95 ppm of chlorinated hydrocarbons (DOE 1991).

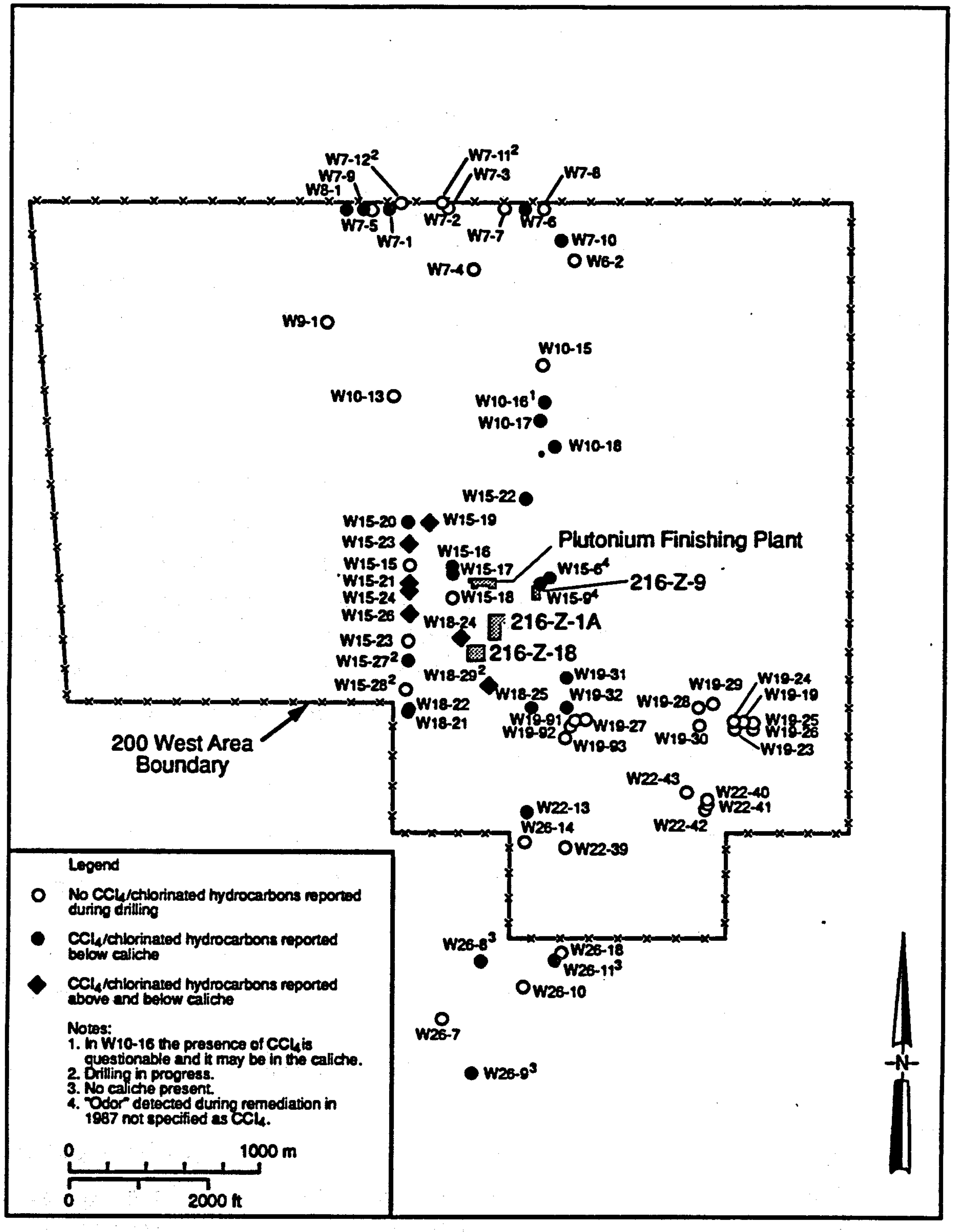

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FIGURE 23. Wells with CCl_4 in the Vadose Zone, 1987-1991 (DOE 1991)

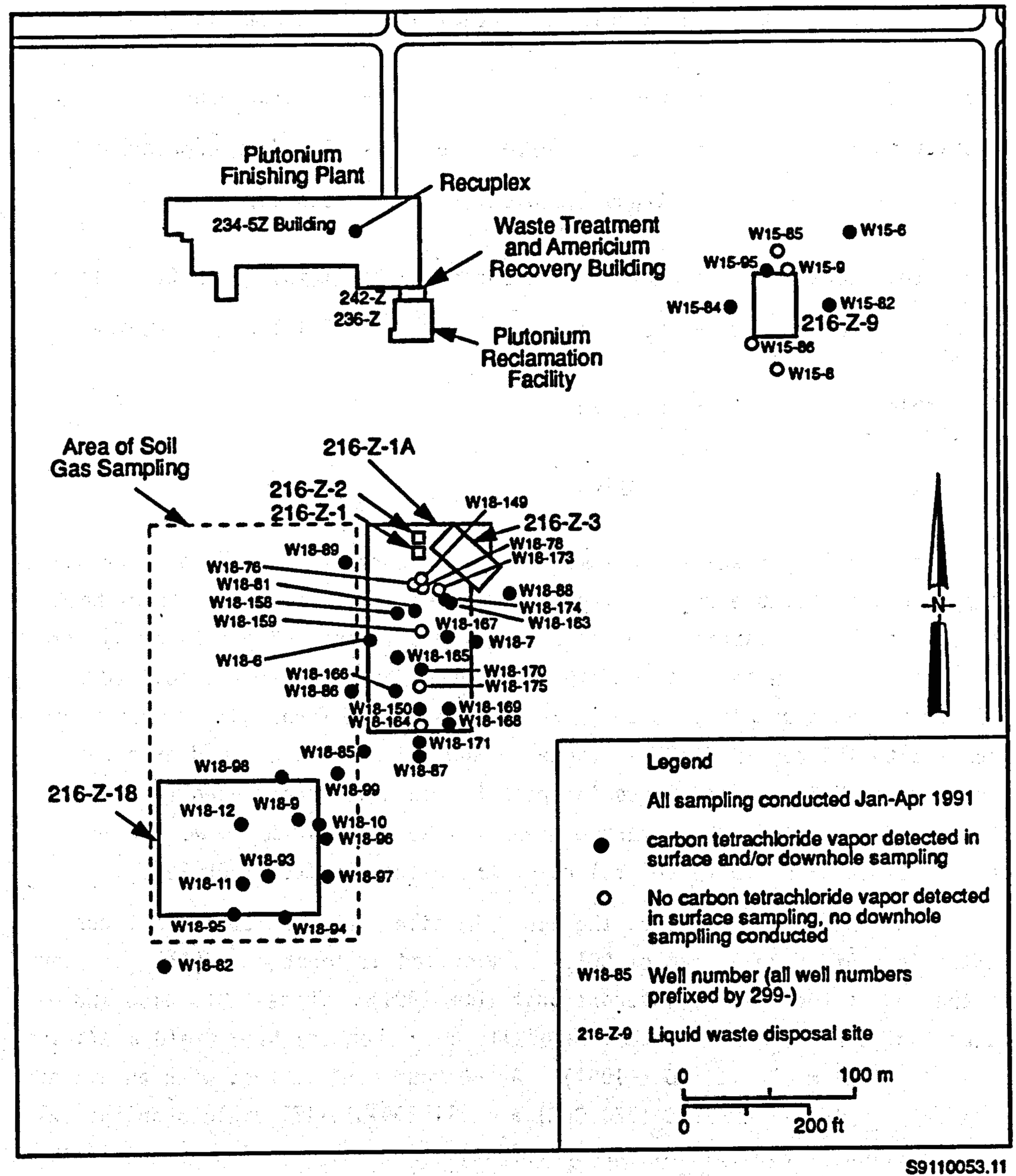

FIGURE 24. Wells in Which CCl_4 Vapor was Detected Near the Plutonium Finishing Plant, 1991 (DOE 1991)

TABLE 4. Chemical Species Detected in Borehole Samples from the 200 West Area (from DOE 1991)

- acetone
- benzene
- chlorobenzene
- chloroform
- 1,2-dichloroethane
- 1,1-dichloroethylene
- cis-1,2-dichloroethylene
- trans-1,2-dichloroethylene
- ethyl benzene
- fluoromethane
- methylene chloride
- methyl isobutyl ketone
- tetrachloroethylene
- toluene
- 1,1,1-trichloroethane
- trichloroethylene
- p-xylene
- m-xylene
- o-xylene

Well head sampling results are summarized in Figure 24. Nearly all the wells sampled had detectable organic vapors (with CCl_4 confirmed). Wells without detectable organic vapors were either sampled only on high pressure days or had cement plugs in the bottom with no apparent openings to the soil (DOE 1991). Downhole sampling in the 216-Z-9 trench area found CCl_4 values ranging from 2.3 to 106 ppm (DOE 1991); those in the 216-Z-1A tile field area ranged from 1.7 to 16.2 ppm; and those in the 216-Z-18 crib area ranged from <1 to 140 ppm (DOE 1991). The primary concentrations of CCl_4 vapors were found between 24 to 63 m (79 to 207 ft) below the ground surface (DOE 1991).

Vapor extraction tests at the 216-Z-1A tile field indicated that concentrations of up to 89 ppm of CCl_4 had migrated at least 40 m (130 ft) deep to the top of the Plio-Pleistocene unit (DOE 1991). These tests also indicated that the CCl_4 had migrated laterally away from the tile field a distance of at least 24 m (80 ft) (DOE 1991). An 80-hour venting test with an average flow rate of 151 liters/sec (320 CFM) at well 299-W18-171 yielded an initial concentration of 200 ppm vol, which gradually increased to 600-700 ppm after 30 hours and peaked at 915 ppm at 67 hours (DOE 1991). An estimated 136 kg (300 lbs) of CCl_4 were removed during this test. A 24-hour vent test with an average flow rate of 26 liters/sec (55 CFM) at well 299-W18-167 yielded relatively constant CCl_4 values ranging from 180 to 200 ppm (DOE 1991). An estimated 3.6 kg (8 lbs) of CCl_4 were removed during this 24 hr period. Carbon tetrachloride was the only volatile organic compound identified in the gas samples (DOE 1991).

Radiological contamination at these cribs has been the subject of several studies. Smith (1973) investigated the distribution of Pu in the top 3 m (10 ft) below the 216-Z-9 trench. He estimated that the top 30 cm (1 ft) of soil beneath the trench contained 40 kg of Pu. Price and Ames (1975) examined the actinide (Pu, Am) contamination at the 216-Z-9 and 216-Z-1A cribs. They confirmed that the highest concentrations of Pu and Am were located just below the bottoms of the facilities, and that concentrations decreased at least three orders of magnitude within the first 2 or 3 m (6 to 10 ft). Price and Ames (1975) also found that two types of Pu occurrence were responsible for this distribution, "particulate" and "nonparticulate." The "particulate" Pu was described as discrete Pu particles 2 to 5 μm (2000 to 5000 Angstroms) in diameter, consisting primarily of PuO_2, which were filtered out of the waste solution. The "nonparticulate" form of Pu was believed to have originated as Pu(IV) in solution, which was partially removed in conjunction with silicate hydrolysis reactions between the acidic waste solutions and the sand to silt sized rock fragments (especially the glassy portions of the basalt fragments).

The presence and extent of Pu and Am beneath the 216-Z-1A tile field were investigated in detail in 1979 (Price et al. 1979). This study found that the distributions of Pu and Am were similar, with the highest concentration of Pu at about 4 x 10^4 nCi/g and of Am at 2.5 x 10^3 nCi/g, located immediately beneath the tilefield's central distributor pipe. The concentrations of Pu and Am generally decreased with depth except at silt-enriched horizons and boundary areas between major sedimentary units where they increase. The maximum vertical penetration of actinide contamination was located approximately 30 m (100 ft) below the bottom of the crib (Price et al. 1979). The lateral extent of contamination was estimated to be located within a 10 m (33 ft) wide zone encompassing the perimeter of the crib. Figure 25 is a graphical representation of the waste plume beneath the 216-Z-1A tile field

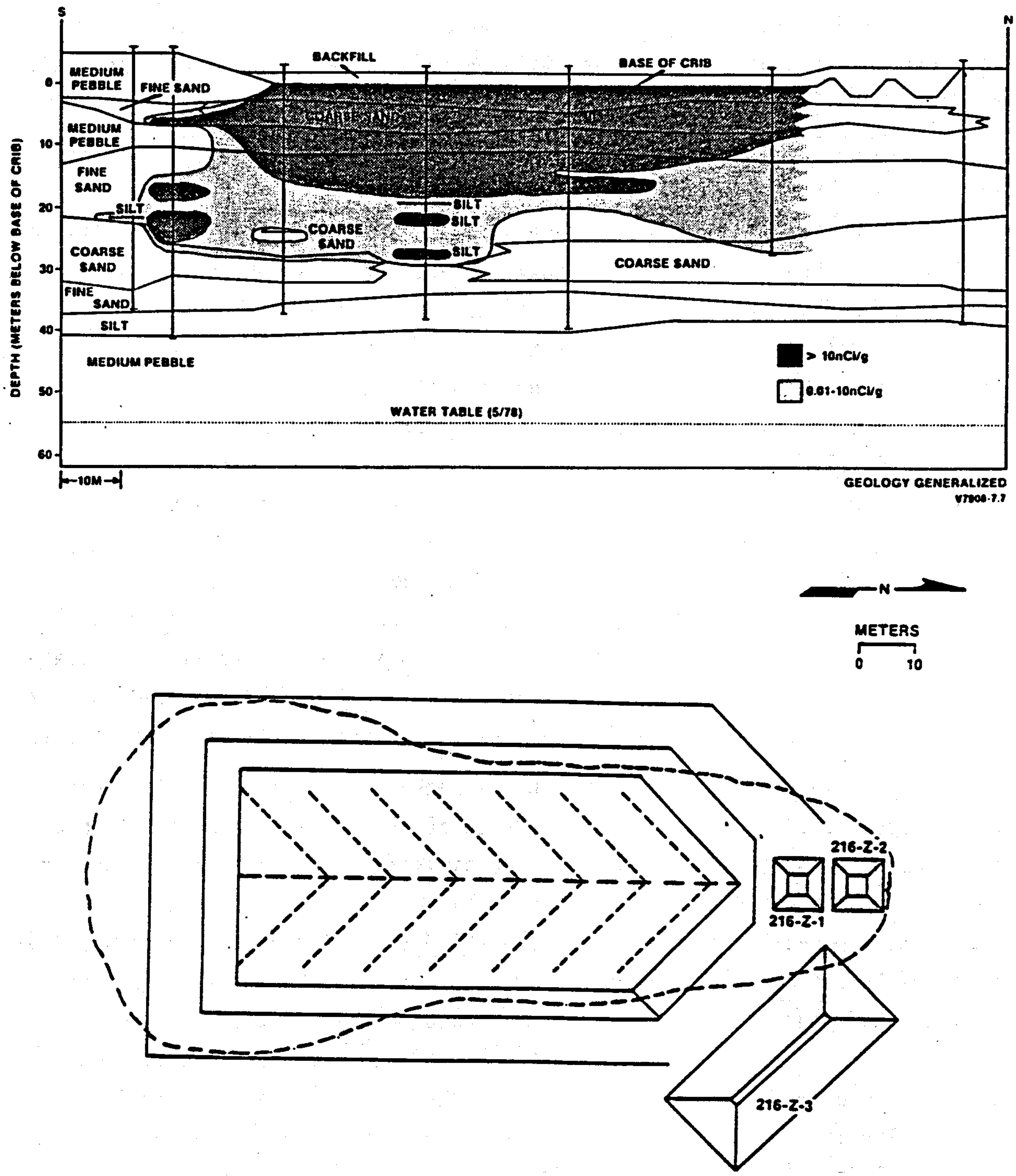

FIGURE 25. Total Transuranic Activity Distribution Beneath the 216-Z-1A Tile Field (after Kasper et al. 1979)

(from Kasper et al. 1979). Fecht, Last, and Price (1977) identified the presence of radioactive contaminants at the 7.6 to 18.3 m (25-60 ft) depth below the 216-Z-18 crib.

GROUNDWATER CONTAMINATION

The aquifer directly beneath the PFP has become contaminated as a result of past waste disposal practices from the PFP and other chemical processing and waste management facilities in 200 West Area. The principal aquifer contaminants beneath the PFP area are: CCl_4, chloroform, nitrate, ferrocyanide, plutonium, and uranium. A discussion of the contaminant distribution of these constituents follows. The zones of contamination are defined by that area that exceeds the appropriate Maximum Concentration Limit (MCL) described by EPA (1976), or the Derived Concentration Guide (DCG) set by DOE (1981). Existing groundwater quality data originates predominantly from wells completed at the top of the unconfined aquifer. Limited data are available to assess the vertical distribution of contaminants. Thus, the following discussion focuses on the horizontal contaminant distribution at the top of the unconfined aquifer.

Other contaminants found in the groundwaters beneath the 200 West Area are discussed by Evans et al. 1990.

Carbon Tetrachloride

A plume of carbon tetrachloride-contaminated groundwater spans most of the 200 West Area. The center of the plume is located near the PFP. The size of the plume is estimated at between 7 km^2 (2.7 mi^2) (Figure 26) and 12.6 km^2 (4.9 mi^2) (DOE 1991). DOE (1991) concluded that approximately 2% of the estimated CCl_4 inventory could be accounted for in the groundwater, but noted considerable uncertainty in the vertical profile of the contamination. Carbon tetrachloride levels up to 8100 ppb (Evans et al. 1990) [1600 times the MCL (5 ppb)] have been observed in well 299-W15-16, yet a companion well, 299-W15-17, completed at the bottom of the aquifer, has yielded no detectable CCl_4. No separate organic phase liquid CCl_4 has been detected.

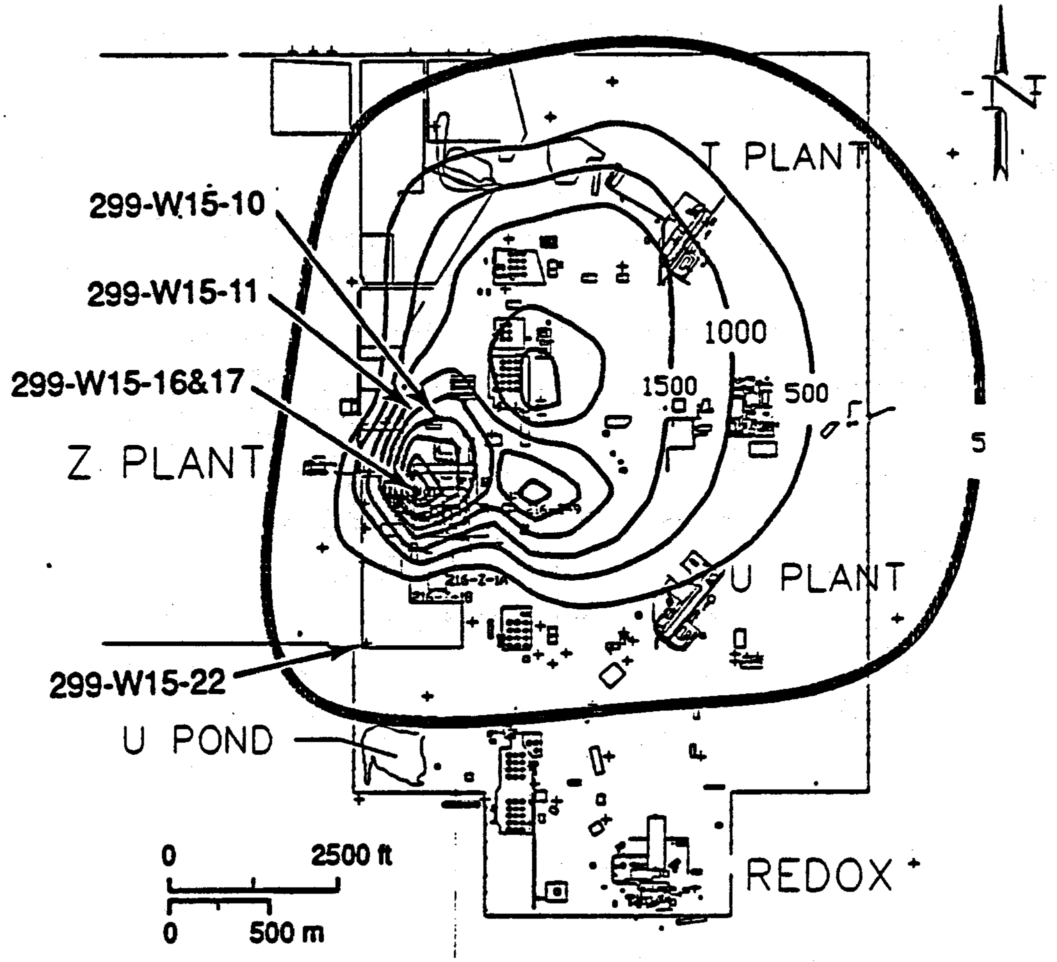

FIGURE 26. CCl_4 Groundwater Plume in the 200 West Area (contour interval is 500 ppb)

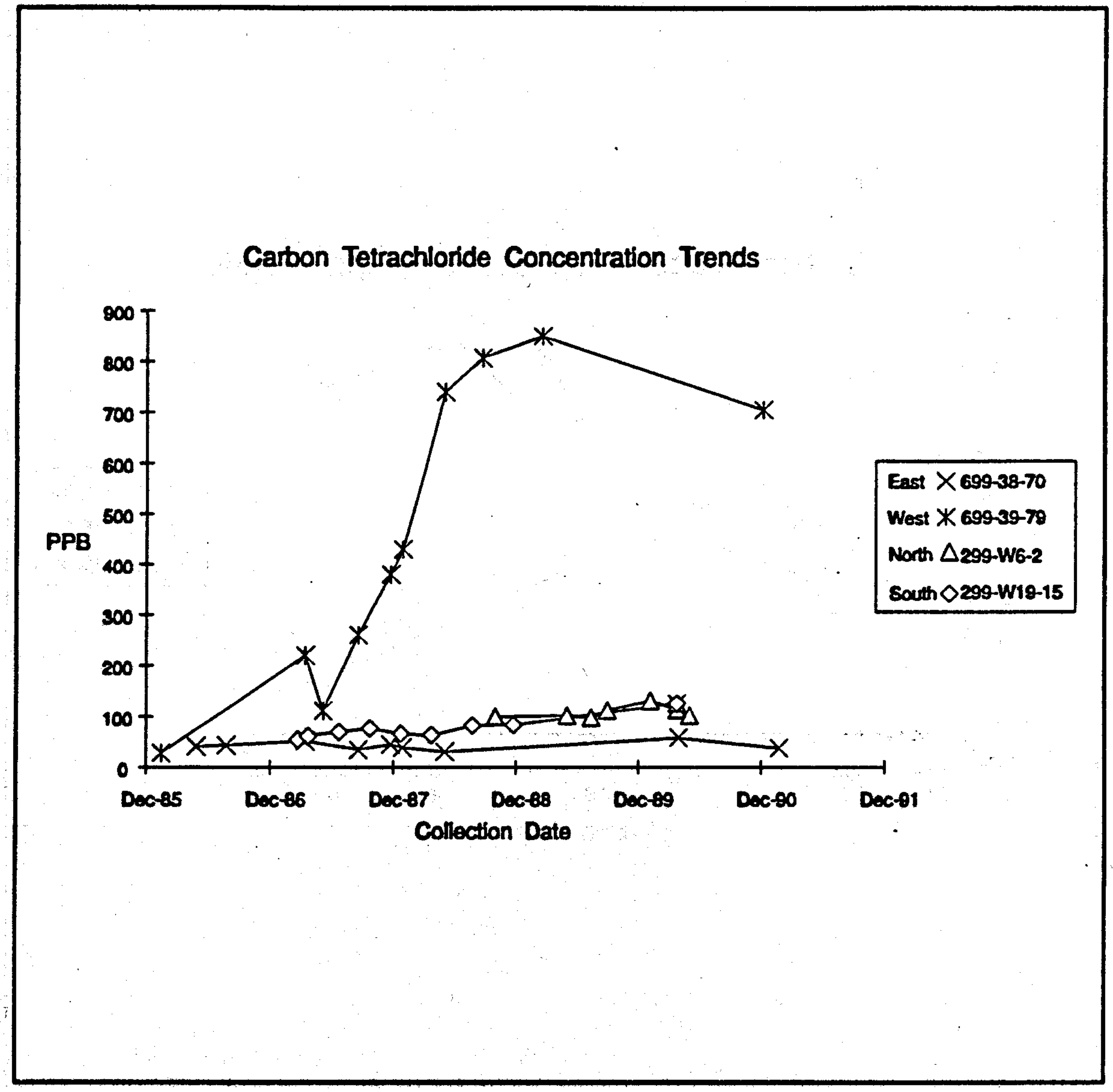

FIGURE 27. CCl_4 Concentration Trends in Monitoring Wells Located Near the Margins of the CCl_4 Plume

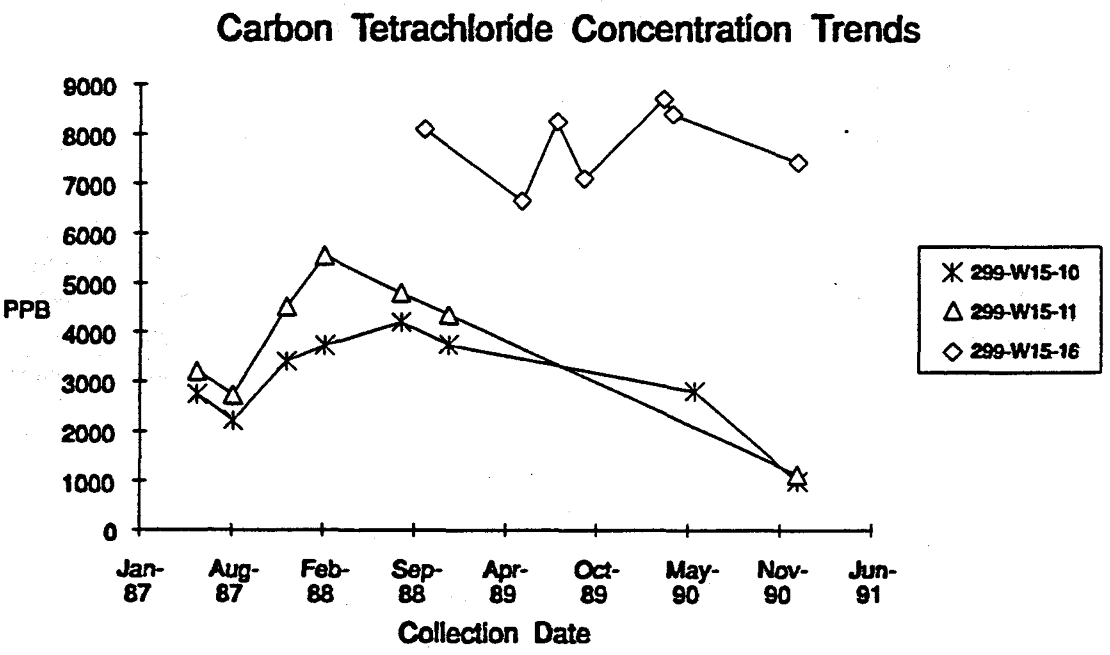

FIGURE 28. CCl_4 Concentration Trends in Monitoring Wells Located Near the Center of the CCl_4 Plume

The extent of contamination vertically within the unconfined aquifer is uncertain. Contamination appears to extend down at least 50 m within the aquifer in well 299-W15-6, yet no contamination is detected at the base of the aquifer in wells 299-W15-17 and 299-W15-22 (DOE 1991). The plume has been under limited observation since early 1986. During that time the western edge of the plume has spread, whereas other margins of the plume appear to be relatively stable. Figure 27 shows the time trend concentrations of CCl_4 in key wells monitoring the west, north, south, and east margins of the plume, and indicates that concentrations have increased along the western margin of the plume in well 699-39-79. Some drop off is evident in wells 299-W15-10 and 11, whereas the highest measurements observed (299-W15-16) have remained relatively constant at least over the 2-year monitoring period since that well was installed (Figure 28).

The plume appears to have a sharp boundary. Samples from just outside the plume show no contamination, even when analyzed by high sensitivity electron capture gas chromatography methods that provide detection sensitivity to more than three orders of magnitude below the MCL.

It will be extremely important to maintain long-term monitoring of CCl_4 in all accessible wells in the 200 West Area and immediate environs.

Chloroform

A sizable chloroform plume also exists in the 200 West Area near the PFP (Figure 29). Compared to the CCl_4 plume (Figure 24), a relatively small area is affected at concentration levels exceeding the 100 ppb MCL. The source of the chloroform is unclear. It is likely to be associated with CCl_4 disposal, either as a degradation product or source impurity (perhaps from the use of chlorinated water). The chloroform plume overlaps the carbon tetrachloride plume but is not exactly coincident with it. The chloroform plume appears to have two centers located close to the 216-Z-9 and 216-Z-18 cribs, whereas the CCl_4 plume is centered approximately 300 m due north of the 216-Z-18 crib.

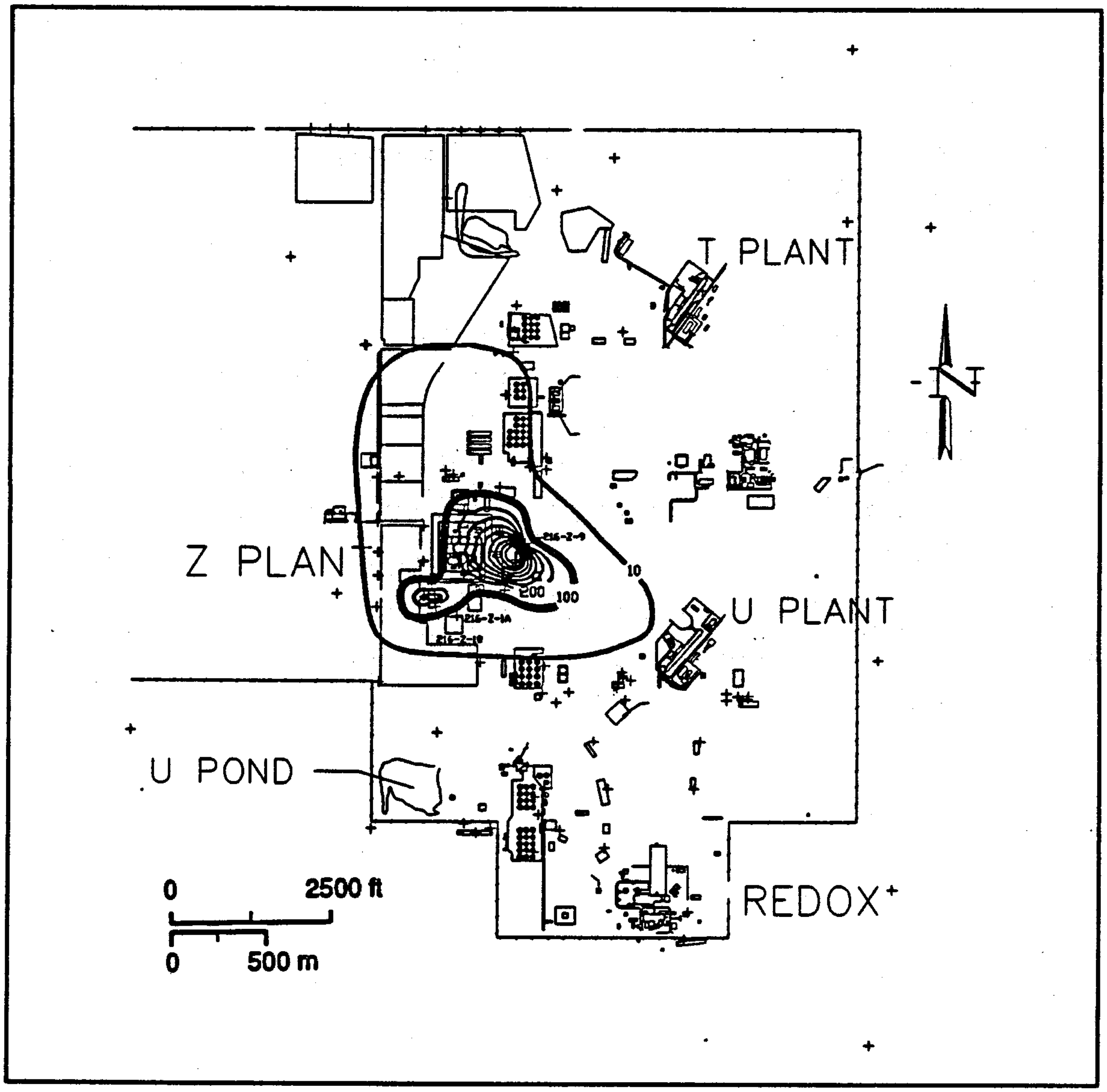

FIGURE 29. Chloroform Groundwater Plume in the 200 West Area (contour interval is 100 ppb)

Nitrate

Nitrate has been used historically at the Hanford Site in extremely large quantities for numerous applications. The use of nitric acid as a fuel dissolver reagent has resulted in disposal of large amounts of nitrate-containing process condensate to cribs and trenches. An extensive nitrate plume exceeding the MCL (45 ppm) extends beneath most of the 200 West Area (Figure 30). The large nitrate plume near U Plant is centered around the 216-U-1 and 216-U-2 cribs. Those cribs received in excess of 1000 tons of nitrate between 1951 and 1967. There is also a large nitrate plume covering most of the north end of the 200 West Area, probably resulting from T Plant operations. The small nitrate plumes located near Z Plant probably originate from the 216-Z-1A or 216-Z-18 cribs. In general, the nitrate plume overlaps the CCl_4 plume (Figure 24).

Ferrocyanide

A small ferrocyanide plume (measured as total cyanide) is present beneath the 200 West Area, apparently associated with T Plant waste containing ferrocyanide disposed to the T-26 crib and possibly to the 216-Z-9 crib (Figure 31). The maximum cyanide level observed was 115 ppb in well 299-W14-2.

The chemical form of the cyanide is believed to be ferrocyanide. That conclusion is based on its known form of injection and limited laboratory studies using a special ion chromatography method; however, the laboratory studies were somewhat inconclusive. An improved standard analytical method for ferrocyanide monitoring is still needed.

Technetium-99

A sizable technetium-99 plume is present in the 200 West Area (Figure 32). This plume originated from disposal of uranium recovery waste to the 216-U-1 and 216-U-2 cribs from 1951 to 1967. The plume has since migrated eastward and is now centered beneath U Plant, with some extension to the east. Peak concentrations of technetium-99 have ranged up to 41,000 pCi/L in 1989. The western edge of the plume overlaps with the CCl_4 and chloroform plumes.

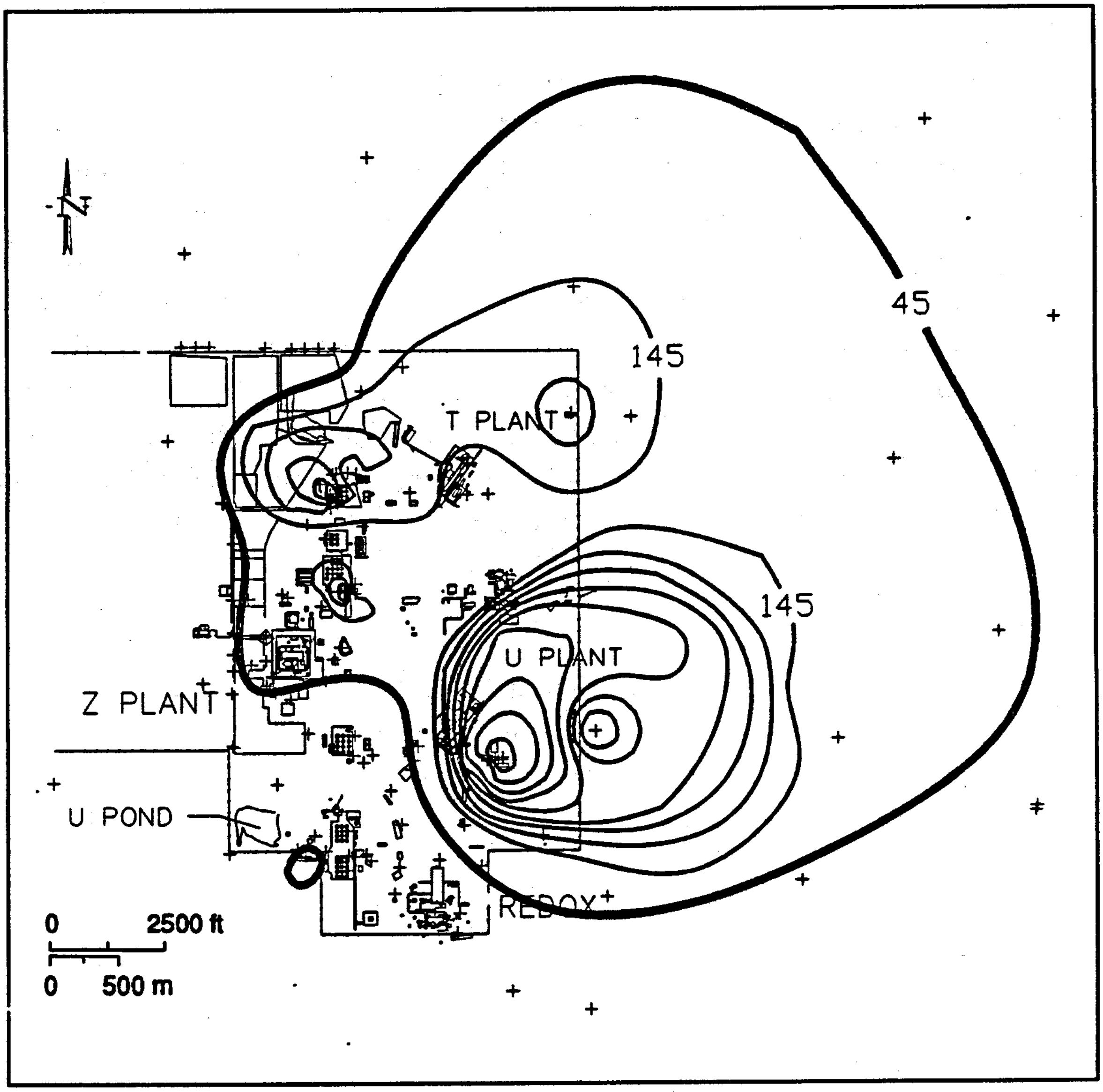

FIGURE 30. Nitrate Groundwater Plume in the 200 West Area (contour interval is 100 ppm)

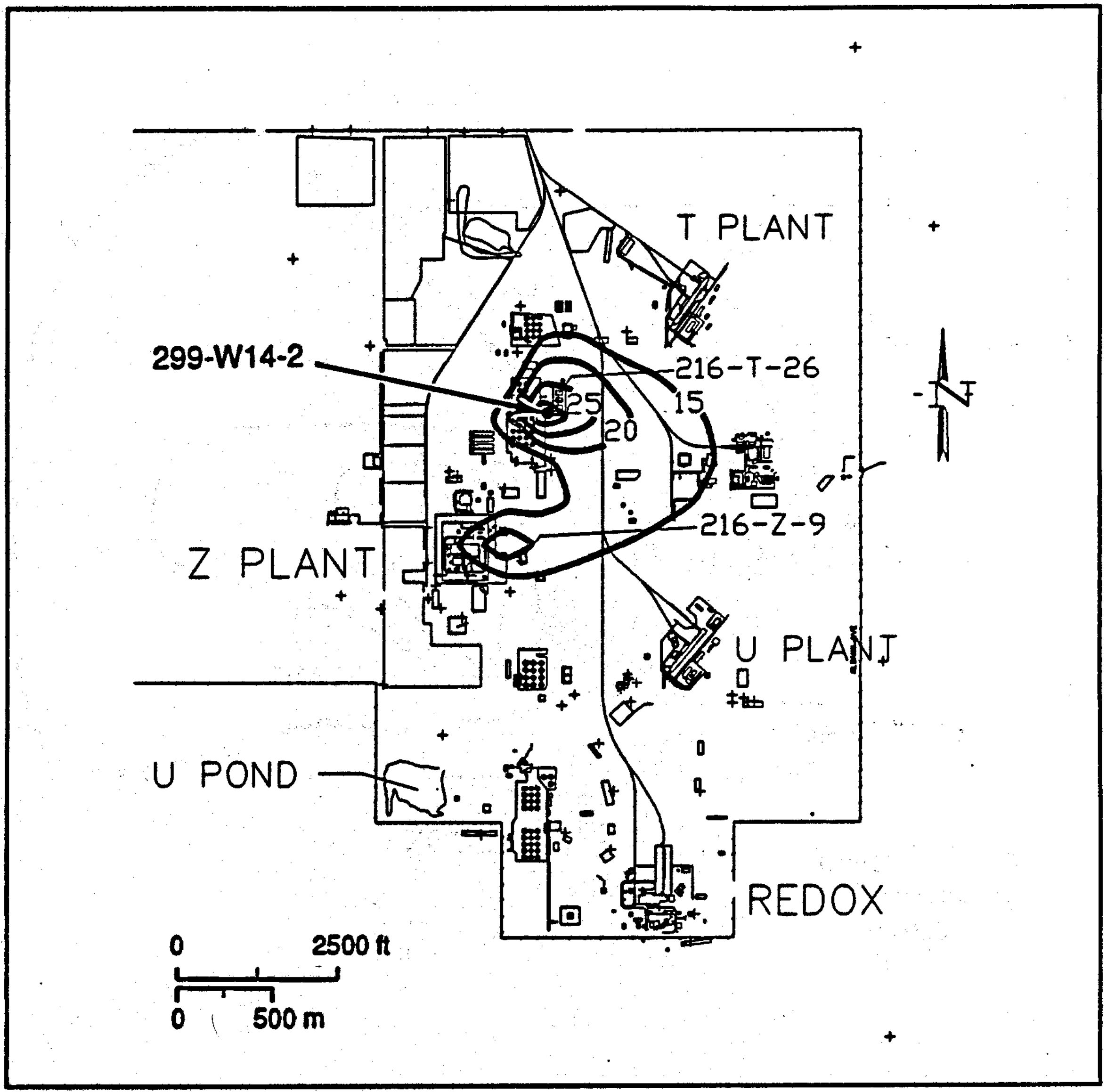

FIGURE 31. Cyanide Groundwater Plume in the 200 West Area (contour interval is 5 ppb)

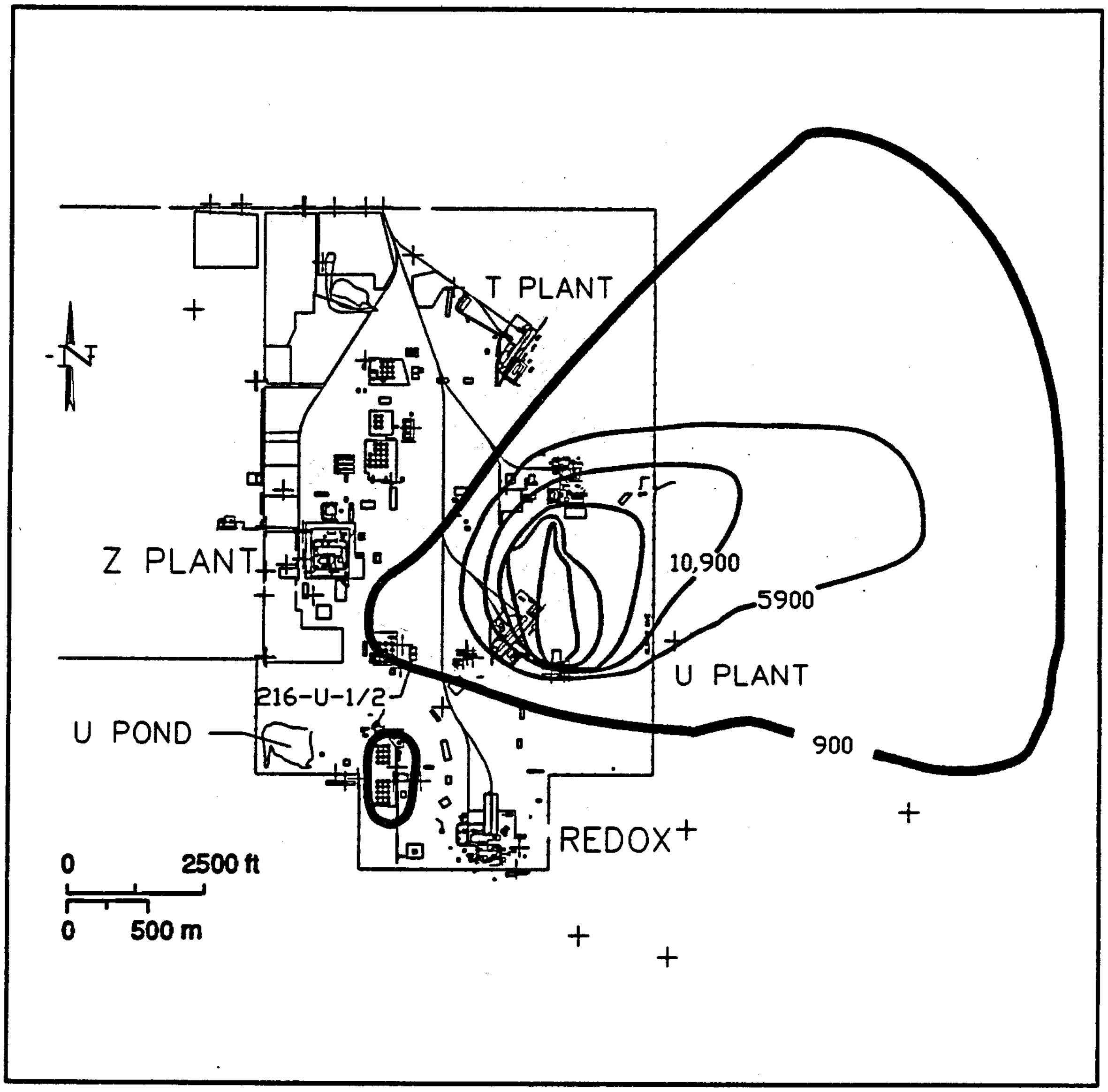

FIGURE 32. Technetium-99 Groundwater Plume in the 200 West Area (contour interval is 5000 pCi/L)

Iodine-129

There is a large, low-level iodine-129 plume associated with the main REDOX process condensate plume (Figure 33). As with tritium, also associated with the same process, locally elevated concentrations of iodine-129 are found near the source cribs at REDOX. There also appears to be a more diffuse plume centered under U Plant, extending to the west near the PFP.

Plutonium

One groundwater sample collected in May 1990 from well 299-W15-8 (Figure 24) showed measurable plutonium (8.4 pCi/L). This observation has not yet been confirmed because of the temporary shutdown of the monitoring program; however, the well in question is located on one corner of the 216-Z-9 crib that received a large inventory of plutonium during its operation (Table 1). More extensive plutonium monitoring in the 200 West Area is clearly needed.

Uranium

The highest uranium levels in Hanford Site groundwater 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 north to T Plant and west to the PFP, overlapping with the CCl_4 and chloroform plumes (Figure 34). Uranium levels in the groundwater near U Plant range from 2000 to 3000 pCi/L and have been considerably higher over the past 5 years.

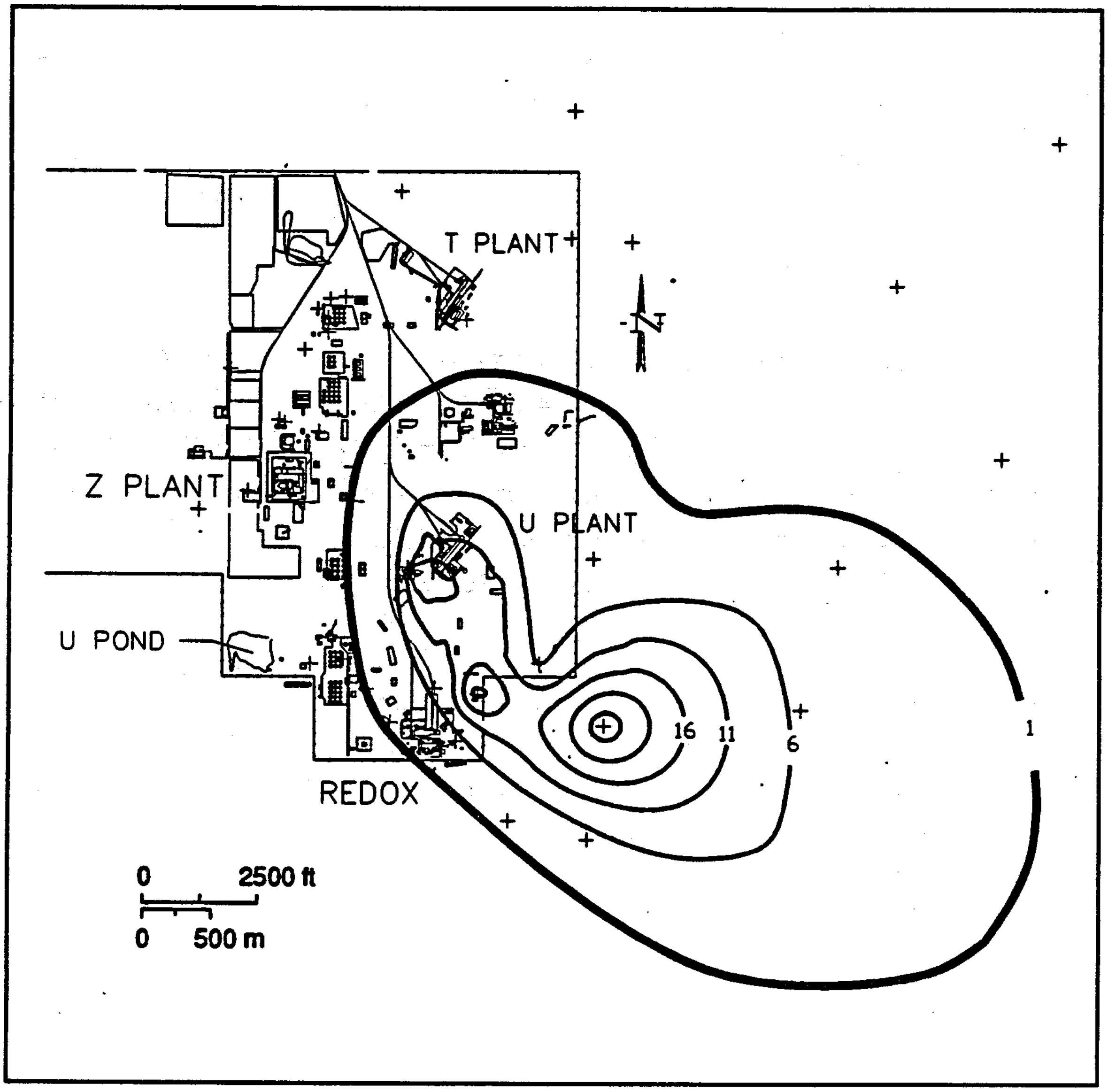

FIGURE 33. Iodine-129 Groundwater Plume in the 200 West Area (contour interval is 5 pCi/L)

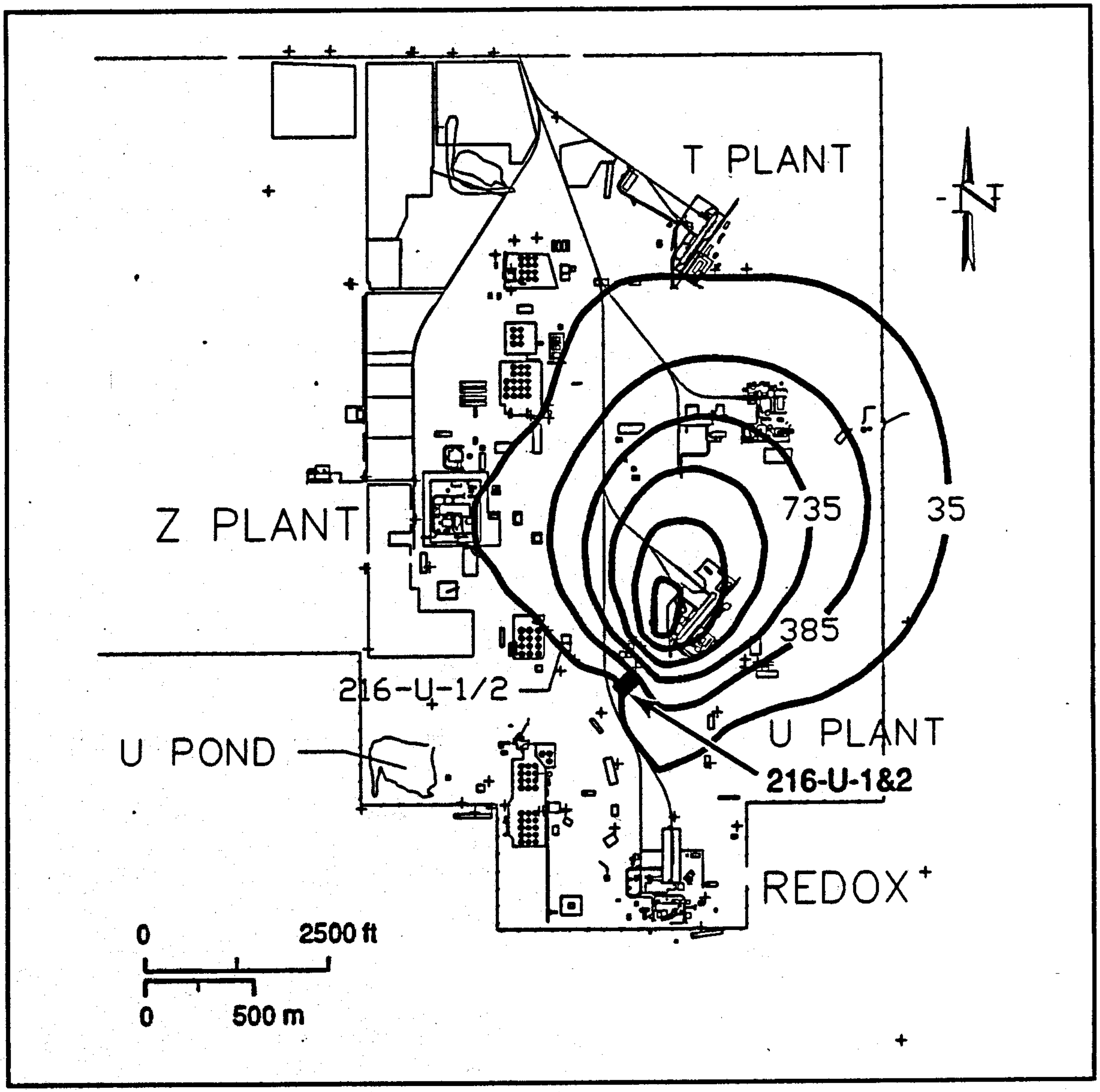

FIGURE 34. Uranium Groundwater Plume in the 200 West Area (contour interval is 5 pCi/L)

DISTRIBUTION AND DEGRADATION MECHANISMS

An estimated total of 360 to 580 m^3 (96,000 to 150,000 gal) of CCl_4 were discharged to the 216-Z-9, 216-Z-1A, and 216-Z-18 cribs, however, only about 2% of this volume has been accounted for in the underlying aquifer. Three scenarios have been suggested to describe the fate of the CCl_4. The first scenario assumes that CCl_4 has entered the vapor phase and has left the system via the atmosphere. The second assumes that CCl_4 remains in the vadose zone in either vapor, aqueous, and/or non-aqueous phases. The third assumes that CCl_4 resides in the unconfined aquifer in aqueous phase and/or in dense non-aqueous phase bubbles. Figure 35 illustrates the conceptualized CCl_4 distribution based on a combination of these scenarios.

The following sections discuss the primary factors controlling the distribution and transport of CCl_4 in the vadose zone and groundwater, including the physical processes of downward and upward CCl_4 migration. Sediment interactions and microbiological degradation mechanisms are also discussed.

CCl_4 BEHAVIOR IN THE VADOSE ZONE

CCl_4 was discharged to the cribs as a mixed organic liquid phase and as a dissolved component in the aqueous waste stream. In an organic liquid phase, CCl_4 will move primarily in response to the organic liquid pressure gradient. As a dissolved component in water, CCl_4 will move in response to the water pressure gradient and by diffusion in water. To predict CCl_4 migration in the subsurface, pore-size distributions of the geologic media must be characterized. Of particular importance is the frequency and distribution of larger flow channels (i.e., large pore sizes, fractures, or manmade voids) in the underlying strata. Organic liquids, less easily adsorbed than water, will preferentially move in the larger flow channels. This may cause irregular and discontinuous flow patterns.

As liquid CCl_4 is discharged to the subsurface, it begins moving into the subsurface air and water. Because of its high vapor pressure, CCl_4 will move

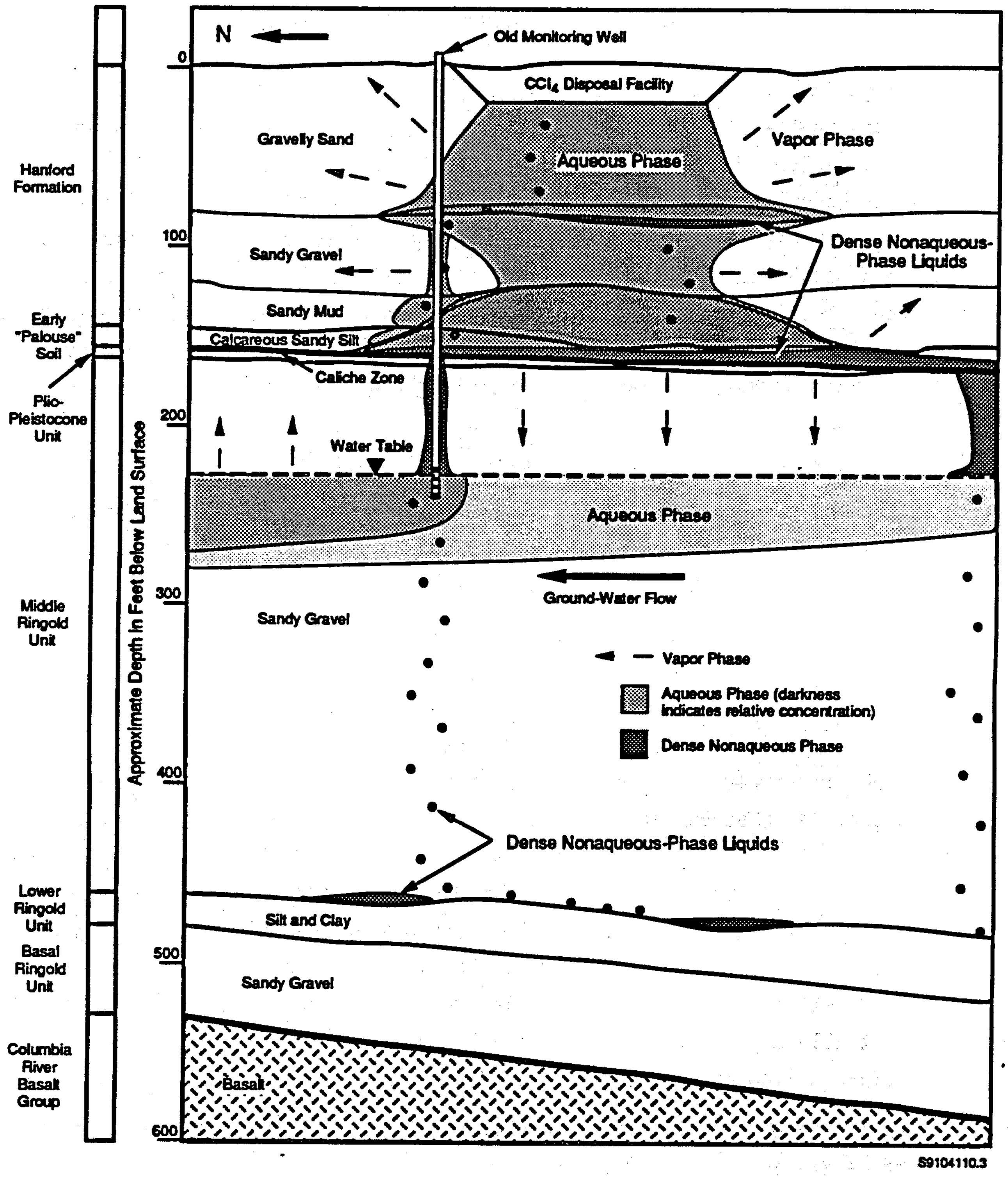

FIGURE 35. Conceptualized CCl_4 Distribution

into the gas phase more readily than other contaminants. The CCl_4 will move from a liquid state, (either a pure liquid or a dissolved component in water), to a gaseous state until the gas phase CCl_4 concentration reaches thermodynamic equilibrium with the liquid phase at the prevailing temperature and pressure. The CCl_4 will also move from an organic liquid phase to water and from the gas phase to water.

As much as 0.95 kg (2.09 LBS) of CCl_4 is estimated to be contained in a cubic meter (35.31 cu ft) of gas at 25°C (77°F) (Falta et al. 1989). At 20°C (68°F) the vapor concentration of CCl_4 is estimated to be 0.80 kg/m^3 (0.05 lbs/ft^3). The solubility limit of CCl_4 in water at 20-30°C (68-86°F) is reported to be 0.757 kg/m^3 (0.047 lbs/ft^3) (Mercer and Cohen 1990). Note that the gas phase may contain as much or more CCl_4 than the aqueous phase per unit of fluid volume. These amounts are expected maximum values. Typically, lesser amounts are reported in subsurface sampling investigations, suggesting some rate-limiting mass movement. Nevertheless, the amount of CCl_4 in the gas phase will be at least as much as is in the aqueous phase according to Henry's Law constant for CCl_4 (Falta et al. 1989).

Sediment Interaction

In addition to depending on intrinsic physical and aqueous properties, the behavior of CCl_4 in the vadose zone will depend on the nature of its interactions with the solid surfaces encountered. The solids supporting the greatest amounts of surface area are expected to be the layer silicate clay minerals, particularly smectite. On average, lesser amounts of calcium carbonate and iron oxide phases are expected to be present, but in certain stratigraphic units (e.g., the Plio-Pleistocene caliche layer) these surfaces may predominate. Other surfaces may also be present as a result of the adsorption or precipitation of the alkyl phosphate complexing agents (TBP and DBBP) disposed along with the CCl_4, and the possible precipitation of nitrate salts from the concentrated aqueous waste stream. The relative proportions of these various surfaces in the 200 West Area vadose zone are unknown and will require careful and thorough characterization if CCl_4 behavior in the vadose zone is to be adequately understood.

Because CCl_4 has no formal dipole moment and does not carry a charge, the interaction of CCl_4 with surfaces is expected to depend on London-van der Waals bonding. The forces involved are relatively weak compared to the Coulombic forces that operate on ions and molecules such as H_2O that have substantial dipole moments. Consequently, the extent of adsorption of CCl_4 by hydrophilic surfaces (i.e., charged surfaces and surfaces that have high dielectric constants and are consequently easily wetted by polar solvents) will be minimal when more competitive polar species, such as H_2O, are present. Uncharged surfaces and surfaces with minimal dielectric constants, however, are less attractive to H_2O, do not wet, and consequently are termed hydrophobic surfaces. It is to these surfaces that CCl_4 may adsorb, however weakly, because no attractive force besides the London-van der Waals force exists to make other species more competitive. The adsorption affinities of hydrophilic and hydrophobic surfaces for CCl_4 are weak and esssentially identical; ions and polar molecules, however, have much stronger affinities for hydrophilic surfaces than CCl_4 and, consequently, adsorption of CCl_4 to these surfaces is diminished by competition with ions and polar molecules when they are present.

Both hydrophilic and hydrophobic surfaces may be present in the vadose zone sediments and, in the absence of water or other polar compounds, would be expected to adsorb CCl_4 equally well. However, water vapor will be present in these sediments, especially near the water table, and thus some competition for sorption of CCl_4 on the hydrophilic surfaces will occur. Because most of the surfaces encountered in the sediments are expected to be hydrophilic, characterization of this competitive reaction in terms of solid surface hydrophilicity and the relative vapor pressures of water, other polar species, and CCl_4 is needed.

One measure of the hydrophilicity of the solid surfaces is given by the ion exchange capacity. The layer silicate clay minerals exhibit cation exchange capacities (CECs) ranging from essentially nil to about 200 cmol kg^{-1} arising from isomorphous substitution of ions in their structures. The CEC for a typical smectite, the dominant clay mineral in these sediments, would be in the 40- to 80- cmol kg^{-1} range and changes little with pH. Cation and anion exchange capacities for the calcium carbonate and iron oxide phases, however, are pH dependent and generally much lower. At the pH levels expected in these sediments (pH 7.5 - 8.5), very low anion exchange capacities would occur. Thus, the layer silicate clay minerals would be expected to offer the most hydrophilic surfaces, followed by the carbonate and oxide minerals.

Hydrophobic surfaces would include those created by adsorption or precipitation of the alkyl phosphate compounds. These compounds actually are surface-active agents, in that one portion of the compound (associated with the P-O bonds) is hydrophilic and the other portion (associated with the butyl groups) is hydrophobic. The hydrophilic portion would be expected to coordinate with structural ions exposed at mineral surfaces (e.g., Ca in carbonates, Fe and Al in layer silicates and oxides). The orientation of the molecule would be such that a "new" hydrophobic surface would be formed by the butyl groups. Given the large quantities of these compounds disposed along with the CCl_4, it seems likely that significant hydrophobic surface area may have formed in the vadose zone sediments with consequent effects on retention and transport of CCl_4. However, in the absence of characterization data, this conclusion remains hypothetical.

Downward Migration

The existence of CCl_4 vapors in the vadose zone has been recently confirmed by Westinghouse Hanford. An estimated 680 kg (308 lbs) of CCl_4 vapors were extracted from the vadose zone during some vapor extraction tests (DOE 1991). The CCl_4 has also been measured in the underlying aquifer as a dissolved component of groundwater (Evans et al. 1990, DOE 1991). To date, no liquid (organic phase) CCl_4 has been detected in the subsurface from any investigation. While it is currently unknown how CCl_4 traveled through the vadose zone and contaminated the groundwater, three possible pathways are: 1) organic liquid phase CCl_4 could have moved through a network of larger flow channels (i.e., preferred pathways) to the water table; 2) dissolved CCl_4 in the aqueous waste stream could have migrated to the aquifer; and/or 3) CCl_4 in the gas phase could have moved downward to the groundwater.

Before any conclusions can be made about current CCl_4 distributions, the distribution of flow channels (i.e., soil pores) in the vadose zone and underlying aquifer beneath the disposal sites must be known. It is reasonable to assume that CCl_4 in the vadose zone exists in subsurface gas and liquid phases and may be adsorbed to some extent on solid surfaces.

The most probable scenario for CCl_4 reaching the water table as a continuous organic liquid phase is that it traveled downward through larger flow channels or preferred natural or artificial pathways. If CCl_4 moved downward through the subsurface in natural porous geologic material, it would have to pass through the Plio-Pleistocene unit (caliche layer) that is cemented by $CaCO_3$ and assumed to act as an barrier to downward fluid movement. Hence, fluids will pass through the caliche layer only via fractures, weakly cemented regions, and/or deteriorated areas. Areas in the caliche may have deteriorated because the aqueous waste stream was very acidic (reported pH = 2.5) and could have dissolved the caliche cementing agent.

The CCl_4 could also reach the groundwater through artificial pathways (i.e., unsealed boreholes) that penetrate the caliche layer. If CCl_4 encountered voids outside the casing of these unsealed boreholes it could move unimpeded to the underlying aquifer. Many such boreholes were adjacent to the 216-Z-9 crib. Three vadose zone boreholes were constructed in 1954, wells 299-W15-82, 299-W15-84, and 299-W15-85 (Figure 3). The boreholes were drilled down to the caliche layer and were located within 15 m (50 ft) of the 216-Z-9 crib. More importantly, in 1957, during the time CCl_4 was being discharged to the 216-Z-9 crib, a borehole penetrated the caliche layer. Well 299-W15-86, located less than 6 m (20 ft) from the 216-Z-9 crib, was drilled to a depth of 43.5 m (143 ft) below ground surface, which is below the caliche layer but above the water table. Liquid CCl_4 discharged to the crib could have traveled down voids outside the casing of this borehole, passed through the caliche layer, may have reached the aquifer. Two other boreholes were drilled, well 299-W15-5 in 1957 and well 299-W15-6 in 1959, that penetrated the caliche layer and the aquifer. Wells 299-W15-5 and 299-W15-6 were located approximately 80 m (260 ft) and 34 m (112 ft) from the 216-Z-9 crib; it is possible that liquid CCl_4 traveled down the outside of the boreholes' casings and contaminated the aquifer since these wells were not sealed while CCl_4 was being discharged. Once in the aquifer, liquid CCl_4 would begin to dissolve into the groundwater. The relatively high concentrations of CCl_4 (i.e., significantly greater than background levels) found deep in the aquifer when sampling well 299-W15-6 (DOE 1991) could be the result of liquid CCl_4 having moved down this borehole.

Because liquid CCl_4 is significantly more dense than water (i.e., fluid density of 1.58 g/cm^3 (13.19 lbs/gal) for CCl_4 versus 1.0 g/cm^3 (8.35 lbs/gal) for water), CCl_4 will tend to move downward more vertically and less horizontally than water. However, when CCl_4 encounters confining geologic layers or preferred flow paths, movement is primarily horizontal. Because of the tendency of CCl_4 to move downward, the amount of liquid CCl_4 discharged to the cribs may be compared to the volume of pore space directly below the cribs to evaluate if CCl_4 could have possibly reached the aquifer as an organic liquid phase. If the discharged liquid CCl_4 volume is a significant fraction of the pore space volume beneath the cribs, then CCl_4 may have reached the aquifer as a liquid. Such calculations do not consider the forces generating fluid movement and are therefore a crude estimate.

Assuming a subsurface porosity of 0.3, the volume of pore space directly between the 216-Z-9, 216-Z-1A, and 216-Z-18 cribs and the aquifer are approximately 2950 m^3 (1 x 10^5 ft^3), 53,000 m^3 (2 x 10^6 ft^3), and 57,000 m^3 (2 x 10^6 ft^3), respectively (see Table 4). Comparing these figures to the estimated discharges of 83-300 m^3 (3000-10,600 ft^3), 170 m^3 (6000 ft^3), and 110 m^3 (3880 ft^3) of liquid CCl_4 and assuming that the CCl_4 evenly distributes itself throughout the pore space, the subsurface CCl_4 contents under the 219-Z-9, 216-Z-1A and 216-Z-18 cribs are 0.10, 0.003 and 0.002, respectively. Note that only under 216-Z-9 crib is the estimated liquid CCl_4 content higher than a negligible value. Note also that these calculations use the upper estimate of CCl_4 discharges to the 216-Z-9 crib and assume that CCl_4 could pass through the caliche layer.

As an organic liquid such as CCl_4 moves through porous media, some of it stays behind as most of the fluid continues to move on. It is assumed that the portion left behind is discontinuous and immobile (i.e., held strongly by capillary forces). This amount is frequently referred to as a residual saturation. Typical reported values for residual saturations range from 0.1 to

TABLE 4. Crib Pore Volume and Estimated CCl_4 Contents

Crib	Width (m)	Length (m)	Crib Area (m^2)	Depth to GW (m)	Pore Volume (m^3)[a]	CCl_4 Volume Discharged (m^3)	Depth to Caliche (m)	CCl_4 Content if Evenly Distributed (b)
216-Z-9	9.1 (30 ft)	18.3 (60 ft)	166 (1,786 ft^2)	59 (194 ft)	2,947 1.04 x 10^5 ft^3)	83-300 (3,000-10,600 ft^3)	22 (72 ft)	0.10
216-Z-1A	35 (115 ft)	84 (275 ft)	2940 (31,600 ft^2)	60 (197 ft)	52,900 (1.87 x 10^6 ft^3)	170 (6,000 ft^3)	21 (69 ft)	0.003
216-Z-18	4 @ 3 (4 @ 10 ft)	4 @ 63 (4 @ 207 ft)	3024 (32,500 ft^2)	63 (207 ft)	57,150 (2.02 x 10^6 ft^3)	110 (3,880 ft^3)	18 (59 ft)	0.002

(a) Assuming porosity of 0.3.
(b) Using upper estimate of 300 m^3 (10,600 ft^3) discharged.

over 0.4 (Mercer and Cohen 1990). Using 0.1 as a residual saturation estimate, and assuming the highest estimate for 216-Z-9 Crib CCl_4 discharge, indicates that only 216-Z-9 crib received enough liquid CCl_4 discharge to result in organic liquid, phase CCl_4 being present at the residual saturation down to the aquifer. These calculations show it is improbable that CCl_4 reached the aquifer as an organic liquid phase driven under its own pressure gradient. However, these calculations do not account for any CCl_4 that may have concentrated in a small area (i.e., preferred flow paths) and could have passed through the caliche layer, (e.g., travel down the outside of unsealed boreholes).

Another possible mechanism for organic liquid CCl_4 reaching the water table is by movement as an emulsion. During some discharges, a mixture of waste water and CCl_4 were disposed to the cribs and an emulsion of CCl_4 and water may have formed. The CCl_4 globules may have been small enough to be transported with the waste water as it migrated through the subsurface. The volume of aqueous discharges were such that small organic phase CCl_4 globules could have reached the water table, provided there were passages through the caliche layer. Most of the liquid waste was aqueous. However, the CCl_4 globules in the waste emulsion may have coalesced in the subsurface and resisted further downward movement. The movement of oil-water emulsions in porous media is not well-understood and difficult to predict.

Aqueous discharges that followed liquid CCl_4 discharges did not necessarily move liquid CCl_4 toward the aquifer. It may be conjectured that water moving downward through the subsurface will also push organic liquid downward. However, the movement of organic liquid by water depends on many factors, especially the extent of interfacial tensions and the state of the organic liquid within the soil pores. Little is known of these factors during the time of the discharges. Unless the interfacial tension between liquid CCl_4 and water was reduced significantly in the aqueous discharges, the movement of CCl_4 would be minor. No laboratory investigations have been conducted to address this phenomenon. Typically, as water displaces organic liquid from soil pores, some organic liquid moves in response to the water movement and some becomes trapped by water. The amount of organic liquid that becomes trapped by water and consequently becomes immobile can range from 0.15 to 0.50 (Wilson et al. 1990). Since the majority of the liquid CCl_4 was discharged in small batches that were preceded by, and followed by, continued aqueous discharges, it is unlikely that liquid CCl_4 was displaced to any significant extent by the aqueous discharges.

Dissolved CCl_4 in water may have also reached the water table. CCl_4 dissolved in water moves in the subsurface in response to water pressure gradients and by molecular diffusion. Because of the tortuous nature of the soil pores and the low water content of the vadose zone at Hanford, molecular diffusion would contribute negligibly to the net downward movement of CCl_4. An upper estimate of the natural downward water and dissolved CCl_4 flux can be determined by assuming that the recharge rate to the aquifer is equivalent to the precipitation rate of 0.16 m/yr (6 in./yr). At this downward rate, assuming an average water content in the vadose zone of 0.10, the travel time would be approximately 35 years. This calculated travel time assumes that the cemented caliche layer would not impede the downward movement of CCl_4. However, the large aqueous discharges to the cribs would increase water pressure gradients and the amount of subsurface water beneath the cribs. The larger pressure gradient would provide a greater force to drive the water downward faster, and the higher water content would distribute the water in larger flow channels. Preliminary simulations of water infiltration from a hypothetical percolation pond in an area similar to the disposal cribs suggest that, under saturated or near saturated conditions, water could travel from the surface to the water table in a period of months, not years. The simulated conditions were similar to conditions that would be associated with large aqueous discharges to the cribs. It is difficult to predict the downward CCl_4 flux rate as an organic liquid and as dissolved in the aqueous phase without numerical models that consider all of the relevant transport processes, and detailed records of subsurface conditions at the time of the discharges. The numerical models are still in an early stage of development and detailed records of the subsurface conditions are sparse. It is important to note that the large aqueous discharges would accelerate the downward movement of dissolved CCl_4, but not necessarily the downward movement of organic phase liquid CCl_4.

CCl_4 can also be transported by the gas phase. Because of its high vapor pressure, CCl_4 molecules will move from an organic liquid phase and from a dissolved state in the aqueous phase to the gaseous phase. Once in the gaseous phase, CCl_4 molecules can move in response to several different mechanisms; by advective gas phase movement, by diffusional processes, and by gas phase density differences. Advective gas flow is caused by gas phase pressure gradients and diffusion occurs because of chemical concentration differences. Advective and diffusive movement can be upward or downward; the gravity-driven flow of vapors more dense than ambient vapors will be primarily downward. Density-driven gas flow occurs because of differences in vapor densities. The density of vapors containing CCl_4 molecules could be as high as 1.65 times that of natural subsurface vapor (Falta et al. 1989); CCl_4 vapors could have moved downward by density-driven gas flow in the larger flow channels where this phenomenon is significant. Once at the water table these vapors would diffuse into the groundwater, there by contaminating it.

Upward Migration

The natural processes by which CCl_4 vapors can escape the subsurface are fluctuations in atmospheric pressures (i.e., atmospheric pumping) and diffusion. The existence of wells in the area is assumed to contribute negligibly to the movement of CCl_4 vapors to the atmosphere because 1) wells typically have temporary or permanent caps and 2) the surface area of the boreholes in contact with the subsurface geologic material containing vapors (i.e., unsealed or perforated well pipe sections) is minuscule compared to the area of subsurface contamination. To estimate the potential movement of CCl_4 vapors out of the subsurface to the atmosphere, gas pressure variations at the soil surface and in boreholes must be known.

Falta et al. (1989) conducted simulations of CCl_4 movement in the gas phase. The results of their computer simulations show that as the permeability of the subsurface increases, density-driven vapor flow becomes more dominant. Density-driven gas flow can mute the effects of diffusion to the point that there will be only minor upward movement of CCl_4 vapors. Under these conditions, it is expected that the loss of CCl_4 vapors to the atmosphere will be negligible. Because of the low liquid content near the ground surface and the sandy nature of the geologic strata at Hanford, permeabilities adjacent to the cribs are assumed to be large enough so that density-driven vapor flow will dominate, suggesting that only a negligible amount of CCl_4 discharged to the cribs would be lost to the atmosphere by natural processes. Furthermore, the movement of vapors out of the subsurface by atmospheric pumping will likely only affect the upper regions of the subsurface. Considering the volume and pattern of the aqueous discharges to the cribs, it is reasonable to assume that the bulk of the CCl_4 would be located deeper where atmospheric pumping would have a negligible effect.

Degradation

Microorganisms in the subsurface can degrade or alter the mobility of contaminants. To predict degradation by microorganisms, information about the types of organisms present in the subsurface and their in situ metabolic activity must be known. At the Hanford Site, several recent investigations were conducted to obtain basic information regarding the distributions, functions and types of microorganisms in the uncontaminated subsurface. This work was sponsored by the Subsurface Science Program of the U.S. Department of Energy.

During 1990 and 1991, samples were obtained from two vadose zone locations on the Hanford Site. An objective of the sampling investigations was to evaluate indigenous organisms of undisturbed sites. Investigations of the samples indicated that culturable microorganisms are present in the subsurface. Their populations, however, were relatively small and appeared to be in a dormant state.

The metabolic activity of the microorganisms was evaluated by adding glucose to the cultures and observing the rate at which carbon mineralized. The results revealed low mineralization rates, implying that the organisms were in a dormant state. This is not surprising considering the lack of moisture at the Hanford Site. Amendments were added to some of the cultures to stimulate microbial activity. Analyses of these data suggest that microbial metabolic activity in the vadose zone sediments could be enhanced for the purpose of bioremediation by adding exogenous nutrients.

There is limited current information on the microbiology at the Hanford Site. The capacity of the indigenous microorganisms to degrade specific organic contaminants or transform metals and radionuclides is unknown. In an earlier study, denitrifying bacteria from a groundwater sample was isolated and shown to be capable of degrading CCl_4 under denitrifying conditions when supplied with an exogenous electron donor such as acetate. CCl_4 is believed to be degraded by microorganisms anaerobically. There does not appear to be any aerobic degradation of CCl_4. Because the vadose zone is largely aerobic, it is questionable whether CCl_4 will be degraded naturally in the vadose zone. More investigations are needed to develop estimates of CCl_4 degradation rates in the subsurface. It may be possible that under appropriate conditions, CCl_4 may be anaerobically degraded in the vadose zone.

CCl_4 BEHAVIOR IN GROUNDWATER

In the 200 West Area, the plume of groundwater CCl_4 contamination with concentrations greater than 5 ppb covers a surface area of approximately 7 km^2 (2.7 mi^2), as shown in Figure 26. These contaminant concentration profiles are developed by interpolating among groundwater well measurements. DOE (1991) estimated a larger contaminated area of approximately 12.6 km^2 (4.9 mi^2). Assuming that the contamination extends to 10 m (30 ft) below the groundwater surface, DOE (1991) estimated between 5,250 (11,600 lbs) to 15,740 kg (34,700 lbs) of CCl_4 to be in the aquifer beneath the 200 West Area. Surprisingly, this amount is less than 2 percent of the 2.7 to 4.4 million kg (1.2 to 2 million lbs) of CCl_4 estimated to have been discharged to the disposal cribs. These figures support the concept that the majority of the discharged CCl_4 wastes are still entrained within the vadose zone as previously suggested. Exceptions could be if 1) liquid CCl_4 moved downward to the base of the aquifer where it has not yet been detected, or 2) monitoring and site characterization activities have yet to locate other areas of high CCl_4 contamination. However, the upper part of the aquifer has been relatively well-characterized by measurements in existing wells scattered throughout the 200 West Area.

The CCl_4 can move in the aquifer by several mechanisms. If a pool of organic liquid CCl_4 exists, it can move in response to its own pressure gradient. It may also move downward through the aquifer because its liquid density is approximately 1.58 times that of water. In either case, the liquid CCl_4 must first displace water from the flow channels in order to move spatially as an organic liquid. This requires that a threshold pressure difference between liquid CCl_4 and water is surpassed. The magnitude of the pressure difference across phase boundaries (capillary pressure) is governed by the flow channel size distribution of the geologic strata containing liquid CCl_4 and water. The smaller the flow channels, the larger the required threshold capillary pressure will be. In large flow channels, such as those outside the unsealed casings of some boreholes, liquid CCl_4 may sink to the bottom without having to overcome a threshold pressure difference.

If liquid CCl_4 in the aquifer is not in a pool but exists as small dispersed globules, its mobility is severely restricted. The liquid CCl_4 phase is no longer continuous and does not possess a pressure gradient to move it. Typically, the small dispersed globules are relatively immobile in porous media when they are larger than the small passageways connecting larger pore bodies (such as those found in geologic materials with spherical grains). Globule immobility in aquifers is well-documented in petroleum literature (Willhite 1986). Dispersed liquid CCl_4 globules can develop after the passage of a continuous pool of liquid CCl_4, or as water displaces liquid CCl_4 from flow channels as would occur if the water table rose or the subsurface water content increased. Globules can also form in the vadose zone; because they are relatively immobile, it is difficult to cleanup such subsurface contamination without injecting chemical agents to dissolve them. This contamination has the long-term potential for hazardous chemicals to dissolve into the groundwater. Further study of the behavior of CCl_4 globules in porous media is needed to better understand the mechanisms that can be used to reduce the long-term hazard.

As a dissolved component in water, CCl_4 molecules can move with the groundwater flow pattern, in contrast to organic phase CCl_4 movement, caused by a pressure gradient. When dissolved CCl_4 moves with the groundwater flow, it spreads throughout the subsurface by advective water movement, by molecular diffusion, and by hydrodynamic dispersion (Hillel 1980). Spatial differences in water pressures cause advective water movement, random thermal motion contributes to molecular diffusion, and the microscopic variability of flow velocities in flow channels cause hydrodynamic dispersion. All three of these processes contribute to the spreading of CCl_4 contamination in the aquifer.

Factors that affect the shape of the contaminant plume are subsurface hydrologic conditions (e.g., hydraulic properties of the aquifer, flow velocities), geochemical processes (e.g., chemical interactions, fluid/solid reactions), and biological phenomena. Several important hydraulic properties also must be known to accurately predict contaminant migration. These include anisotropy (i.e., changes in directional properties) and variability in hydraulic conductivity, dispersion, and effective porosity. These hydraulic properties have not been well-characterized for the various hydrogeologic strata composing the unconfined aquifer. Most existing data are limited to single-well lateral hydraulic conductivities (i.e., averaged values), and to a small number of laboratory core analyses for vertical conductivity and total porosity. More characterization of the spatial variability of hydraulic properties is needed.

While subsurface hydrologic conditions largely control the physical movement of the contaminant plume, chemical processes can exert a significant influence in the attenuation of contaminant concentrations. Such important chemical/geochemical phenomena include the adsorption of chemical complexes on solid surfaces; chemical complexation with other discharged wastes that affect their mobility; chemical degradation; interphase transfer of contaminants from a pure-phase to water and air, and vice versa. Chemical process rate coefficients must be measured to predict these phenomena, which may be a function of pH, redox potential, contaminant concentration, cosolvents, and other factors. Currently, the effect of these factors on CCl_4 behavior in the subsurface is unknown; controlled field and laboratory tests must be conducted to assess them.

PREDICTIVE MODELING

The primary purpose of predictive modeling is to bring together results from theory, characterization, experiments, pilot tests, and field history, and to project them into the future. It is called "predictive" to imply an exploration of possible effects and alternatives in process design. Predictive modeling seeks to provide answers such as where to drill a well next, which remediation process is better than another, or which parameter is critical and which is minor.

Modeling is used to establish baseline performance evaluations and safety analyses for field projects. Safety is a special concern for the VOC Arid ID since the cribs which received CCl_4 waste also received radioactive waste. This raises a concern for the fate of fluids introduced during any remediation process. Also, because of VOC phase behavior, vapors not adequately contained by well pattern and vapor extraction process design could continue to contaminate the groundwater. Understanding the current vapor extraction remediation process being used in the ERA (DOE 1991) enables a comparison of cost, efficiency, and effectiveness of alternative technologies.

Predictive tools are used as part of characterization to identify principal or controlling factors. Analyses can then concentrate on these important aspects to make the best use of resources. Modeling and simulation can also be used to extract information from system performance, adding to characterization work already completed. The evolving conceptual model will be used to design future well placement, sampling and testing.

Current modeling or simulation efforts are concentrated on in situ bioremediation processes and chemical manipulation in the subsurface environment. A simulator has been developed and is being applied on several projects to reliably predict flow and transport for non-isothermal systems where VOC phase behavior (e.g., volatility of CCl_4) is present. The Predictive Tools for Subsurface Systems project will support further development and integration of these tools to provide a simulator with multiprocess support. The project will also apply these tools to performance evaluation, monitoring, safety analyses, and characterization for the VOC Arid Site Integrated Demonstration.

Critical data for predictive modeling include capillary pressure, porosity, permeability, relative permeability, and phase behavior. Capillary pressure, relative permeability and phase behavior usually must be measured for the specific site (although they are often estimated from experiments in the literature). Porosity, permeability and other parameters are needed for every point in space for the region of interest. For example, permeability is directional, and three values are needed for every point (non-isotropic). Only a few holes are drilled, so a conceptual model must be built from geological information, field tests and simulations to provide realistic values for these points. These will not be exact; a system is needed that is complete enough to exhibit field scale phenomena, to make projections and differentiate between competing alternatives and processes. As more data are acquired, the conceptual model is updated. Modeling and simulation are not delayed when new data are lacking; valuable work can still be done toward future data acquisition.

REMEDIAL ACTION ALTERNATIVES

The successful remediation of this site is dependent on a thorough understanding of the complex physical, chemical and microbiological mechanisms controlling the movement and degradation of CCl_4 and its accompanying contaminants. DOE (1991) has selected vapor extraction as the proposed remedial alterative for an Expedited Response Action to reduce the CCl_4 contamination in the vadose zone. This selection was based on the conceptual model that most of the CCl_4 remained in the vadose zone and was in the vapor phase. Besides vapor extraction DOE (1991) also looked at no action and institutional control alternatives, various alternatives for containment (ground freezing, slurry trench/wall), and other alternatives for collection (excavation, soil flushing, liquid product extraction), and treatment (biological, physical). Potential remedial alternatives that are being considered for demonstration as part of the VOC-Arid ID program include in situ heating and corona destruction, and heat-induced passive VOC retrieval.

The selection of appropriate remedial processes (containment, extraction, and/or insite treatment) requires a knowledge of the distribution, physical and chemical behavior of the contaminants, and a thorough understanding of the site characteristics. The most important site characteristic that affects the performance of remediation technologies is the orientation and distribution of subsurface pore spaces. It is through these pore spaces that contaminants and nutrients to enhance biodegradation move. The total volume of these pore spaces determines the mass density or porosity of the subsurface. Furthermore, the amount of water and/or contaminants retained in a porous medium is strongly affected by the pore structure. Several soil and hydraulic properties are correlated to the size distribution of pore spaces.

Variability in pore structures often determines whether water and/or contaminant/migration will be smooth and predictable or uncertain. An example of the affect of pore structure on remediation activities is soil vapor extraction. Because vapor in the subsurface will be primarily contained in the larger flow channels, the efficiency of a soil vapor remediation system may be significantly reduced if a few of these larger flow channels (e.g., old root channels, animal burrows, unsealed boreholes, clastic dikes) connect the subsurface to the surface. Under this scenario, the majority of the vapor flow would occur through these larger flow channels, bypassing the contaminated area of concern. Identifying areas where larger flow channels are likely to exist will be important in developing a remediation strategy.

Other site characteristics that affect the efficiency and performance of remediation technologies include particle-size distributions, water content distributions, mineralogy, organic content of the soils, thickness of the unsaturated zone, and aquifer thickness. Heat conduction through a porous medium will largely depend on the amount of mineral grain contact, which is a function of particle-size and pore space distributions, and the water content. The subsurface is less efficient in conducting heat when it is dry; the drier it is, the greater the energy required to heat a unit volume of the subsurface. The success of remedial heating may depend on knowing the water content of the subsurface.

CONCLUSIONS

Volatile organic chemical contamination at the Hanford Site has resulted in a multiphase, multicomponent system that presents significant challenges in remediation, modeling, and simulation. Besides the already formidable problem of spatial variability in hydraulic properties, CCl_4 was disposed with acids, oils, fats, etc. The flow, transport, and phase behavior characteristics for these unique chemical combinations must be ascertained specifically for the geologic materials at the demonstration site.

The current subsurface distribution of CCl_4 at the demonstration site is unknown; however, it is assumed that the majority of the CCl_4 discharged to the disposal cribs is still in the subsurface, even after 30 years. Because of density-driven vapor flow effects and the assumption that CCl_4 has not been degraded significantly by subsurface microorganisms, there do not appear to be any major mechanisms by which CCl_4 could have escaped the subsurface. The mechanisms by which CCl_4 contaminated the groundwater are not very clear. CCl_4 could have been transported to the water table in the gas phase via density driven vapor flow, in water as a dissolved component, and as an organic liquid phase if emulsified flow and/or natural or artificial preferred flow paths occurred.

The movement of CCl_4 and other volatile organic contaminants in the subsurface is very complex. A thorough understanding of this problem is essential to the selection of appropriate remedial technologies. The effectiveness of these technologies depends on knowing where the contaminants are, how they are held up in a given physical and chemical subsurface environment; and the physical, chemical, and microbiological changes induced by the various remedial technologies.

Among the questions still unanswered at the demonstration site are 1) how has the complex chemical makeup of the waste affected the behavior of CCl_4, 2) what is the form of the CCl_4 in the vadose zone and ground water, 3) did the CCl_4, lard oil, and other organics form an emulsion which was carried along with the water, 4) what is the significance of CCl_4 vapor phase movement in contaminating the groundwater, 5) how do dispersed globules of organic liquid CCl_4 behave in the vadose zone and groundwater, 6) what are the flow channel size distributions of the subsurface geologic strata, and 7) are large preferred pathways present which would permit organic liquid phase flow to occur? Future site characterization efforts should address these concerns.

REFERENCES

Airhart, S. P. 1990. Borehole Completion Data Package for the 216-S-10 Ditch and Pond. WHC-MR-0206, prepared by Pacific Northwest Laboratory for Westinghouse Hanford Company, Richland, Washington.

Barton, K. R. O. 1990. Borehole completion Data package for Low-Level Burial Grounds - 1990. WHC-MR-0205, prepared by Pacific Northwest Laboratory for Westinghouse Hanford Company, Richland, Washington.

Baker, V. R. 1973. "Paleohydrology and Sedimentology of Lake Missoula Flooding in Eastern Washington." Special Paper 144, Geological Society of America, Boulder, Colorado.

Baker, S. M., J. L Devary, R. P. Elmore, R. F. Lorang, A. J. Rossi, and M. D. Freshley. 1988. U1/U2 Uranium Plume Characterization, Remedial Action Review and Recommendation for Future Action. WHC-EP-0133, Westinghouse Hanford Company, Richland, Washington.

Bierschenk, W. H. 1959. Aquifer Characteristics and Groundwater Movement at Hanford. HW-60601, General Electric Company, Richland, Washington.

Bjornstad, B. N. 1984. Suprabasalt Stratigraphy Within and Adjacent to the Reference Repository Location. SD-BWI-DP-039, Rockwell Hanford Operations, Richland, Washington.

Bjornstad, B. N. 1985. "Late-Cenozoic Stratigraphy and Tectonic Evolution Within a Subsiding Basin, South-Central Washington." In Geological Society of America Abstracts with Programs, Vol. 17, No. 7, p. 524.

Bjornstad, B. N., and J. E. Amonette. 1991. "Some Mineralogical and Geochemical Characteristics of the Suprabasalt Sediments, Hanford Site, South-Central Washington." EOS 72.

Bjornstad, B. N. and K. R. Fecht. 1989. Pre-Wisconsin Glacial-Outburst Floods: Pedogenic and Paleomagnetic Evidence from the Pasco Basin and Adjacent Channeled Scabland." In Geological Society of America Abstracts with Programs, Vol. 21, No. 5, p. 58.

Bjornstad, B. N. 1990. Geohydrology of the 216W-5 Burial Ground, 200 West Area, Hanford Site. PNL-7336, Pacific Northwest Laboratory, Richland, Washington.

Brown, D. J. 1959. Subsurface Geology of Hanford Separation Areas. HW-61780, General Electric Company, Richland, Washington.

Brown, D. J. 1960. An Eolian Deposit Beneath 200-West Area. HW-67549, General Electric Company, Richland, Washington.

DOE (U.S. Department of Energy). 1981. "Environmental Protection, Safety, and Health Protection Program for DOE Operations." DOE Order 5480.1A, Washington, D.C.

DOE (U.S. Department of Energy). 1988. Consultation Draft, Site Characterization Plan, Reference Repository Location, Hanford Site, Washington, Vol. 1. DOE/RW-0164, U.S. Department of Energy, Washington, D.C.

DOE. 1991. Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume, DOE/RL-91-32, Draft A.

EPA. 1976. National Interim Primary Drinking Water Regulations. EPA-570/9-76-003, Office of Water Supply, Washington, D.C.

Evans, J. C., P. J. Mitchell, and D. I. Dennison. 1988. Hanford Site Ground-Water Monitoring for April Through June 1987. PNL-6315-1, Pacific Northwest Laboratory, Richland, Washington.

Evans, J. C., R. W. Bryce, D. J. Bates, and M. L. Kemner. 1990. Hanford Site Ground-Water Surveillance for 1989. PNL-7396, Pacific Northwest Laboratory, Richand, Washington.

Falta, R. W., I. Javandel, K. Pruess, and P. A. Witherspoon. 1989. "Density-Driven Flow of Gas in the Unsaturated Zone due to the Evaporation of Volatile Organic Compounds." Water Resources Research. 25:2159-2169.

Fecht, K. R., G. V. Last, and K. R. Price. 1979. Evaluation of Scintillation Probe Profiles From 200 Area Crib Monitoring Wells. ARH-ST-156, Atlantic Richfield Hanford Company, Richland, Washington.

Fecht, K. R., S. P. Reidel and A. M. Tallman. 1985. Paleodrainage of the Columbia River System on the Columbia Plateau on Washington State: A Summary. RHO-BWI-SA-318 P, Rockwell Hanford Operations, Richland, Washington.

Felmy, A. R., D. C. Girvin, and E. A. Jenne. 1984. MINTEQ: A Computer Program for Calculating Aqueous Geochemical Equilibria. (NTIS PB84-157148) EPA-600/3-84-032, National Technical Information Service, Springfield, Virginia.

Gee, G. W. 1987. Recharge at the Hanford Site: Status Report. PNL-6403, Pacific Northwest Laboratory, Richland, Washington.

Gephart, R. E., R. C. Arnett, R. G. Baca, L. S. Leonhart, and F. A. Spane, Jr. 1979. Hydrologic Studies Within the Columbia Plateau, Washington: An Integration of Current Knowledge. Rockwell International, Richland, Washington. RHO-BWI-ST-5.

Goodwin, S. M. 1990. Borehole Completion Data Package for the 216-U-12 Crib. WHC-MR-0208, prepared by Pacific Northwest Laboratory for Westinghouse Hanford Company, Richland, Washington.

Goodwin, S. M, and B. N. Bjornstad. 1990. 200-East and 200-West Areas Low-Level Burial Grounds Borehole Summary Report. WHC-MR-0204, prepared by Pacific Northwest Laboratory for Westinghouse Hanford Company, Richland, Washington.

Graham, M. J., M. D. Hall, S. R. Strait and W. R. Brown. 1981. Hydrology of the Separations Area. RHO-ST-42, Rockwell Hanford Operations, Richland, Washington.

Hagood, M. C., and V. J. Rohay. 1991. 200 West Area Carbon Tetrachloride Expedited Response Action Project Plan. WHC-EP-EN-AP-046, Rev. 0. Westinghouse Hanford Company, Richland, Washington.

Hillel, D. 1980. "Fundamentals of Soil Physics." Academic Press. New York. 413 pp.

Jaquish, R. E., and R. W. Bryce, (eds). 1990. Hanford Site Environmental Report for Calendar Year 1989. PNL-7346, Pacific Northwest Laboratory, Richland, Washington.

Kasper, R. B. 1982. 216-Z-12 Transuranium Crib Characterization: Operational History and Distribution of Plutonium and Americium. RHO-ST-44, Rockwell Hanford Operations, Richland, Washington.

Last, G. V. and B. N. Bjornstad. 1989. Revised Ground-Water Monitoring Plan for the 200 Areas Low-Level Burial Grounds. WHC-SD-EN-AP-015, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Last, G. V. and V. J. Rohay. 1991. Carbon Tetrachloride Contamination, 200 West Area, Hanford Site. PNL-SA-19564, Pacific Northwest Laboratory, Richland, Washington

Last, G. V., B. N. Bjornstad, M. P. Bergeron, D. W. Wallace, D. R. Newcomer, J. A. Schramke, M. A. Chamness, C. S. Cline, S. P. Airhart, and J. S. Wilbur. 1989. Hydrogeology of the 200 Areas Low-Level Burial Grounds - An Interim Report. PNL-6820 Vol. 1 and 2, Pacific Northwest Laboratory, Richland, Washington.

McKee, E. H., D. A. Swanson and T. L. Wright. 1977. "Duration and Volume of Columbia River Basalt Volcanism; Washington, Oregon and Idaho." Geological Society of America, Abstracts with Programs 9(4):463-364.

Mercer, J. W., and R. M. Cohen. 1990. "A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization and Remediation." J. Contaminant Hydrology 6:107-163.

Myers, C. W., and S. M. Price (eds.). 1981. Subsurface Geology of the Cold Creek Syncline. RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Myers, C. W., and S. M. Price, et al. 1979. Geologic Studies of the Columbia Plateau: A Status Report. RHO-BWI-ST-4, Rockwell Hanford Operations, Richland, Washington.

Newcomer, D. R., K. D. Pohlod, and J. P. McDonald. 1991. Water-Table Elevations on the Hanford Site, 1990. PNL-7693, Pacific Northwest Laboratory, Richland, Washington.

Price, S. M., R. B. Kasper, M. K. Addition, R. M. Smith, and G. V. Last. 1979. Distribution of Plutonium and Americium Beneath the 216-Z-1A Crib: A Status Report. RHO-ST-17, Rockwell Hanford Operations, Richland, Washington.

Smith, A. E. 1973. Nuclear Reactivity Evaluation of 216-Z-9 Enclosed Trench. ARH-2915 Atlantic Richfield Hanford Company, Richland, Washington.

Stone, W. A., J. M. Thorp, O. P. Gifford and D. J. Hoitink. 1983. Climatological Summary for the Hanford Area. PNL-4622, Pacific Northwest Laboratory, Richland, Washington.

Swanson, D. A., T. L. Wright, P. R. Hooper and R. D. Bentley. 1979. Revisions in Stratigraphic Nomenclature of the Columbia River Basalt Group. Bulletin 1457-G, U.S. Geological Survey, Washington, D.C.

Tallman, A. M., J. T. Lillie and K. R. Fecht. 1981. "Suprabasalt Sediments of the Cold Creek Syncline Area." In Subsurface Geology of the Cold Creek Syncline, eds. C. W. Myers and S. M. Price, pp. 2-1 to 2-28. RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Tallman, A. M., K. R. Fecht, M. C. Marratt and G. V. Last. 1979. Geology of the Separation Areas, Hanford Site, South-Central Washington. RHO-ST-23, Rockwell Hanford Operations, Richland, Washington.

Waitt, R. B. 1980. "About Forty Last-Glacial Lake Missoula Jokulhlaups Through Southern Washington," Journal of Geology 88.

WHC (Westinghouse Hanford Company). 1991. WIDS Database Field Descriptions and Data. WHC-MR-0056, Rev.1, Westinghouse Hanford Company, Richland, Washington.

Willhite, G. P. 1986. "Waterflooding." Society of Petroleum Engineers. Richardson, TX. 326 pp.

Wilson, J. L., S. H. Conrad, W. R. Mason, W. Peplinski, and E. Hagan. 1990. "Laboratory Investigation of Residual Liquid Organics." Robert S. Kerr Environmental Research Laboratory, Office of research and Development, U.S. Environmental Protection Agency, Ada., OK. EPA/600/6-90/004. 267 pp.

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