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Carbon Tetrachloride Contamination, 200 West Area, Hanford Site

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Arid Site Integrated Demonstration for Remediation of Volatile Organic Compounds

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Introduction

The Arid Site Integrated Demonstration is a U.S. Department of Energy (DOE) program targeted at the acquisition, development, demonstration, and deployment of technologies for evaluation and cleanup of volatile organic and associated contaminants in soils and ground waters. Several DOE laboratories, universities, and industry 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 host site is the Hanford Site's 200 West Area (Figure 1). The Hanford Site has been a defense materials production complex since 1943 and encompasses approximately 560 mi^2 of semiarid terrain located in southcentral Washington state. The location of the demonstration contains primarily carbon tetrachloride (CCl_4), chloroform, and a variety of associated mixed waste contaminants.

Chemical processes used to recover and purify plutonium at Hanford's plutonium finishing plant (Z Plant) resulted in the production of actinide-bearing waste liquid. Both aqueous and organic liquid wastes were generated, and were routinely discharged to subsurface disposal facilities. The primary radionuclide in the waste streams was plutonium, and the primary organic was CCl_4.

This paper contains brief descriptions of the principal CCl_4 waste disposal facilities in Hanford's 200 West Area, associated hydrogeology, existing information on the extent of soil and ground-water contamination, and a conceptual outline of suspected subsurface CCl_4 distributions. These descriptions are preliminary and are based on information gathered in support of the Expedited Response Action being taken by Westinghouse Hanford Company (Hagood and Rohay 1991).

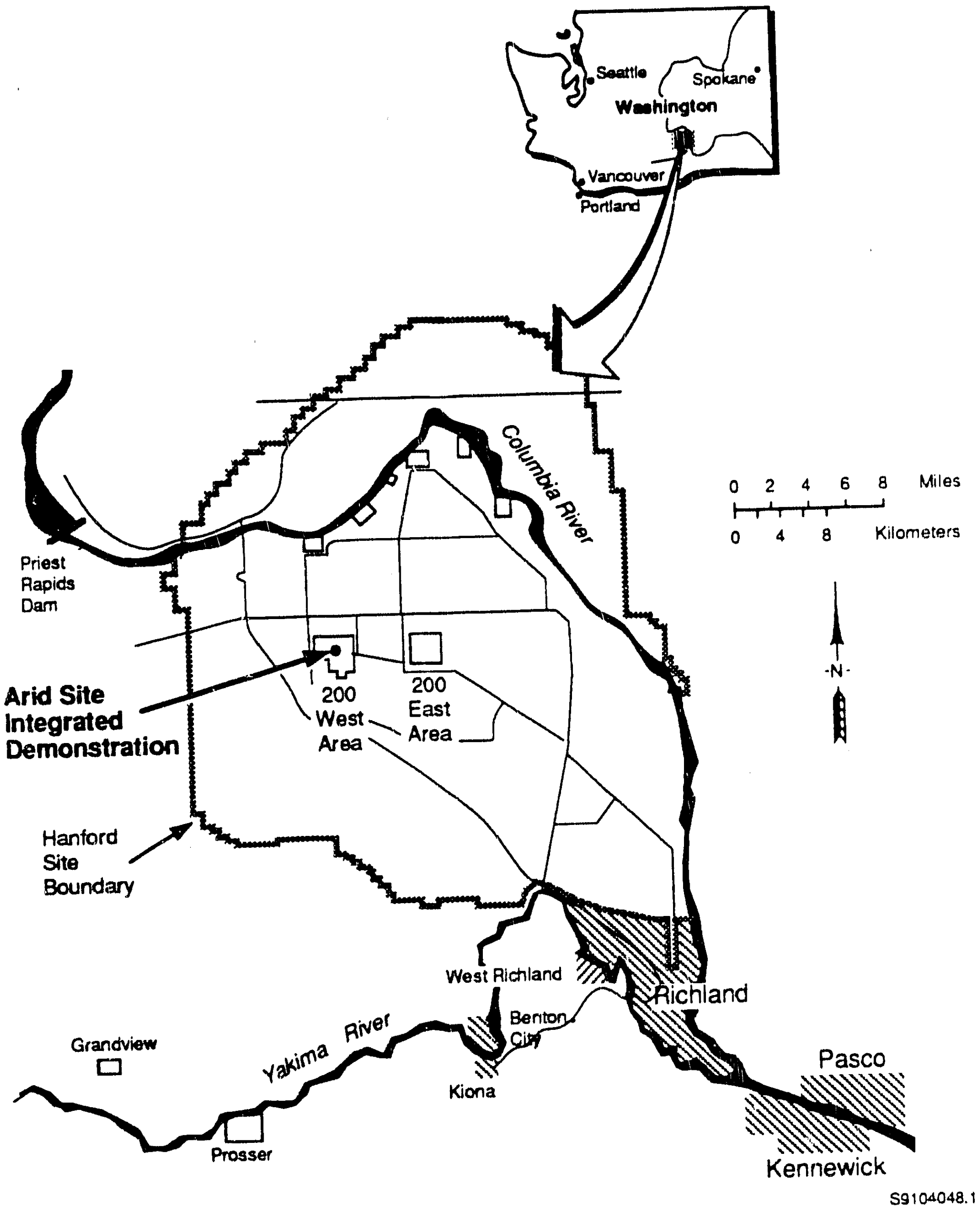

Figure 1. Location of the Arid Site Integrated Demonstration on the Hanford Site

Waste Disposal History

Aqueous and organic wastes containing CCl_4 from plutonium recovery processes at Hanford's Z Plant were discharged primarily to three liquid waste disposal facilities: the 216-Z-9 trench, the 216-Z-1A tile field, and the 216-Z-18 crib. Each of these disposal facilities has a slightly different design; however, they each consist of a 6-m-deep excavation, an effluent distribution system, and a cover. The cover consists of either polyethylene sheeting and earthen backfill or a concrete slab (Figure 2). The purpose of these disposal facilities was to promote infiltration of waste liquids into the underlying, relatively dry soil column.

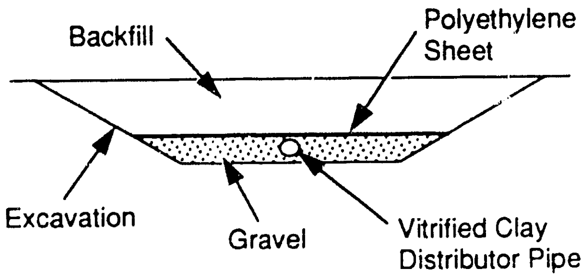

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Figure 2. Typical Construction of a Liquid Waste Disposal Facility

The majority of liquid wastes discharged to the three disposal facilities occurred between 1955 and 1973. The composition of the waste varied throughout the years as production practices and technologies changed. However, the aqueous waste streams can be characterized as a concentrated, acidic, sodium nitrate solution containing organic chemicals at less than 5% by volume (Kasper 1982). Organic liquid wastes primarily consisted of CCl_4, tributyl phosphate (TBP), and dibutyl butyl phosphonate (DBBP). Lesser amounts of dibutyl phosphate (DBP) and monobutyl phosphate (MBP) were also discharged. In addition, a lard oil, used as a cutting oil mixture to machine plutonium, was disposed in the organic waste stream.

Table 1 contains the estimated inventory data for each liquid disposal facility. A minimum of 637 t of CCl_4 was disposed to the subsurface. Recent estimates by personnel familiar with historic Z Plant operations suggest that up to 1,200 t of CCl_4 may have been discharged over the years. Co-contaminants and/or degradation products include TBP, DBBP, MBP, DBP, lard oil, cadmium, nitrates, hydroxides, fluorides, sulfates, chloroform, and various radionuclides, including plutonium and americium.

Table 1. Estimated Contaminant Inventory in Liquid Waste Disposal Facilities

	216-Z-9 Trench	216-Z-1A Tile Field	216-Z-18 Crib
CCl_4 (t)	114	263	260
Pu (kg)	150[a]	57	23
Total liquid volume (L)	4.09×10^6	6.2×10^6	3.86×10^6
Period of use	1955 to 1962	1964 to 1969	1969 to 1973

(a) 58 kg were later removed.

Hydrogeologic Setting

The geology beneath Hanford's Z Plant liquid disposal facilities is dominated by 170 m of sedimentary materials overlying basalt bedrock. The unsaturated zone above the water table ranges in thickness, from approximately 58 to 65 m, and consists of five hydrostratigraphic units. The uppermost unit consists of a coarse-grained sand/gravel sequence underlain by a fine-grained sand/mud sequence (the Hanford formation). Underlying these sands and gravels is an unconsolidated, calcareous, fine sandy silt (early "Palouse" soil) 1.5 to 3 m thick. The Plio-Pleistocene paleosurface (i.e., caliche zone) underlying the silt is characterized by relatively high concentrations of calcium carbonate cement and ranges from a gravelly sand to a sandy mud. The high cementation and laterally continuous nature of this unit may create a layer with relatively low permeability throughout Hanford's 200 West Area, and its lateral continuity is unknown. The fluvial-lacustrine Ringold Formation underlies the Plio-Pleistocene unit and overlies the Miocene Columbia River Basalt Group. The silty to gravelly sand of the upper Ringold unit is discontinuous across the 200 West Area. The middle Ringold unit is a sandy gravel with occasional discontinuous thin zones of laminated sand.

The water table lies within the upper portion of the middle Ringold unit. The low-permeability silts and clays of the lower Ringold unit act locally as the confining sediments that separate the aquifer of the middle Ringold unit from the sands and gravels of the basal Ringold unit. The saturated thickness of the unconfined aquifer underlying Hanford's Z Plant liquid disposal facilities is approximately 70 m. In the eastern portion of Hanford's 200 West Area, the lower Ringold unit is not present, and the base of the unconfined aquifer is the top of the Columbia River Basalt Group. Ground-water flow directions in the unconfined aquifer generally radiate outward from the southwestern portion of Hanford's 200 West Area primarily because of the residual influence of the ground-water mound associated with the decommissioned 216-U-10 Pond.

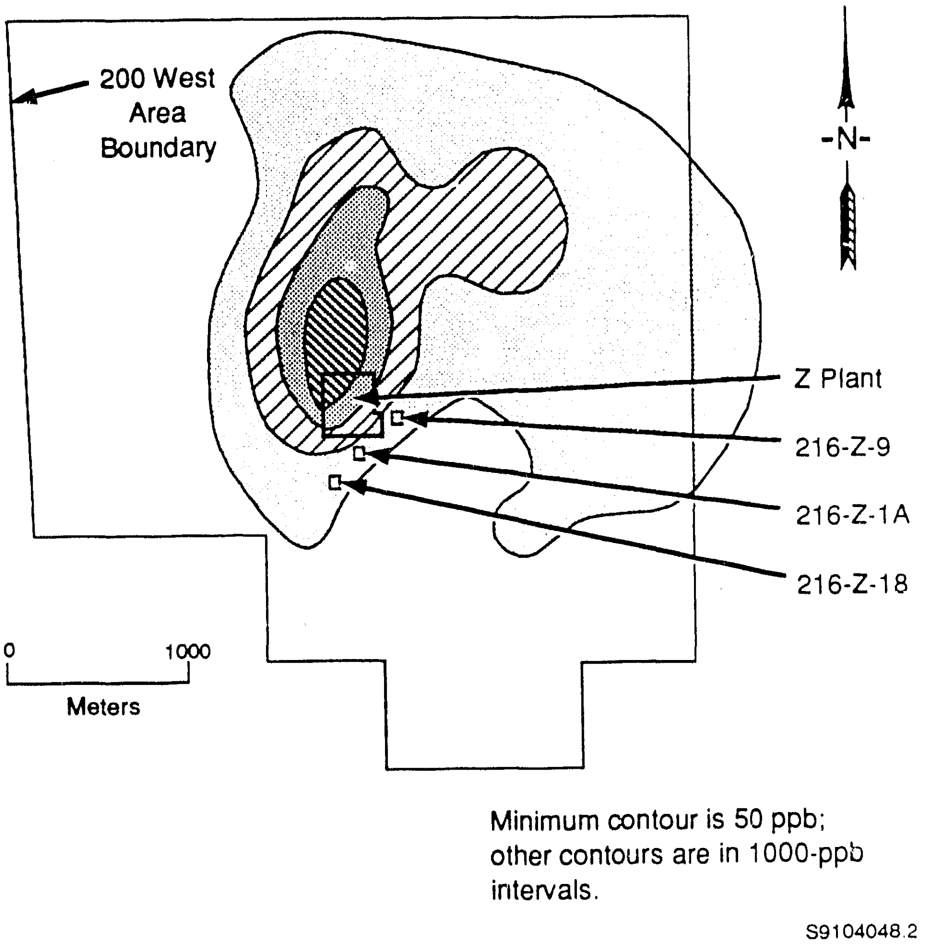
Resulting Soil Contamination

During well drilling operations at numerous sites in Hanford's 200 West Area, CCl_4 vapors have been detected. These vapors have been encountered above the caliche layer near these liquid disposal facilities. However, they have been encountered only below the caliche layer away from these disposal sites. The current horizontal and vertical distributions of CCl_4 in the vadose zone are unknown.

In 1979, an investigation at the 216-Z-1A tile field revealed that the highest measured concentrations of actinides (plutonium and americium) occurred immediately beneath the tile field. The concentrations of actinides in the sediments were shown to generally decrease with depth beneath the tile field, with the exception of silt-enriched horizons and boundary areas between major sedimentary units. The maximum vertical penetration of actinide contamination was found to be located approximately 30 m below the bottom of the tile field (Price et al. 1979). Lateral migration of actinides is estimated to encompass a 30-m-wide zone around the tile field. Based on the above data, it is assumed that the actinide concentrations at the other sites follow a similar pattern.

Resulting Ground-Water Contamination

The CCl_4 ground-water contaminant plume shown in Evans et al. (1990), covers at least 5 km^2 [virtually all of Hanford's 200 West Area north and east of the CCl_4 discharge area (Figure 3)]. This contaminated area possesses CCl_4 concentrations at least 10 times greater than the U.S. Environmental Protection Agency's (EPA) maximum contaminant level of 5 ppb. The highest concentrations measured in the upper part of the aquifer (8,700 ppb in 1990) were found approximately 450 m downgradient from the three liquid disposal facilities. Previous and ongoing ground-water monitoring activities have only been able to account for less than 1% of the CCl_4 discharged to the subsurface. It is being assumed that the majority of the inventory still resides in the overlying unsaturated zone or has been lost to the atmosphere.



Minimum contour is 50 ppb; other contours are in 1000-ppb intervals.

Figure 3. CCl_4 Contaminant Plume in Hanford's 200 West Area

In addition to CCl_4, a smaller chloroform plume appears centered between Hanford's Z Plant and the 216-Z-9 trench. The maximum observed concentration in this plume exceeds 1,000 ppb. The EPA's maximum contaminant level for chloroform is 100 ppb. Evans et al. (1990) suggest that chloroform is probably a degradation product of the CCl_4. Degradation is suspected to occur through radiolytic processes prior to disposal and/or through natural transformation processes in the subsurface. Other ground-water contaminants found by Evans et al. (1990), which currently intersect the CCl_4 plume, include cyanide, fluoride, hexavalent chromium, trichloroethylene, nitrate, ^3H, ^{90}Sr, ^{99}Tc, ^{129}I, and uranium.

Hypothesized Distributions

Three CCl_4 distribution scenarios have been suggested to account for the estimated 637 to 1,200 t of CCl_4 discharged to the subsurface. The first scenario assumes that the majority of the disposed CCl_4 has volatilized and migrated to the atmosphere via diffusion and/or atmospheric pumping. The second scenario assumes that the majority of the CCl_4 remains in the unsaturated zone in either vapor, aqueous, and/or nonaqueous forms; that is, the majority of the CCl_4 has not permeated the cemented caliche layer and thus has not yet contacted the unconfined aquifer. The third scenario assumes that the majority of the CCl_4 has passed through the caliche layer and now resides in the unconfined aquifer in dense nonaqueous-phase bubbles, and has thus gone undetected. Figure 4 illustrates these possible scenarios for CCl_4 distribution. In reality, the CCl_4 subsurface distribution is probably some combination of all three scenarios. CCl_4 most likely exists in vapor, aqueous, and nonaqueous phases and is probably present in both the unsaturated zone and the unconfined aquifer.

Westinghouse Hanford Company is currently pursuing an Expedited Response Action that is based on the assumption that most of the CCl_4 is in the unsaturated zone in the vapor phase. Under this assumed distribution, CCl_4 vapor can move downward and laterally away from the disposal facilities by density-driven vapor flow. By this mechanism, the CCl_4 vapors can be a continuous source of contamination to ground water. Furthermore, if the rate of lateral CCl_4 vapor transport is faster than the rate of ground-water transport, the vapors can potentially contaminate offsite ground water sooner than would be predicted, based on ground-water flow velocities. Because the direction of vapor transport can be independent of the direction of ground-water transport, both upgradient and downgradient ground water could become contaminated.

The complex hydrogeologic system at Hanford further complicates using simple conceptual models to predict contaminant migration. Stratification of the unsaturated zone sediments acts to impede vertical movement and to promote horizontal movement. The caliche layer may act as a partial barrier to vertical liquid migration, and its sloping nature may cause CCl_4 liquid to move in a direction opposite to ambient ground-water flow. The uneven surface of the caliche layer may also result in isolated pockets of liquid CCl_4, and its variable cementation may provide permeable pathways for CCl_4 to reach the aquifer. Any fractures in the caliche layer would provide preferential pathways to the aquifer. Old, poorly sealed wells may also provide a conduit for CCl_4 to penetrate deeper in the unsaturated zone and uppermost aquifer. The low-permeability silts and clays of the lower Ringold unit form the base of the unconfined aquifer. Its sloping nature may affect nonaqueous-phase CCl_4 movement in the same manner as that described for the caliche layer.

The influence of geochemical and microbiological processes on the fate of CCl_4 in this environment further complicates the conceptual understanding of this complex problem

Conclusion

The large inventory of CCl_4 disposed to underground tile fields near Hanford's Z Plant has resulted in approximately 70 vertical meters of contaminated unsaturated sediments and a 5-km^2 plume of contaminated ground water. The limited available field data, complex hydrogeologic environment, and the presence of several contaminants have resulted in multiple conceptualizations concerning the distribution, physical state, and ultimate fate of these contaminants. This CCl_4-contaminated area provides an excellent test site for performance comparisons of different technologies needed to characterize, analyze, and remediate arid and semiarid sites containing volatile organic contaminants.

Acknowledgment

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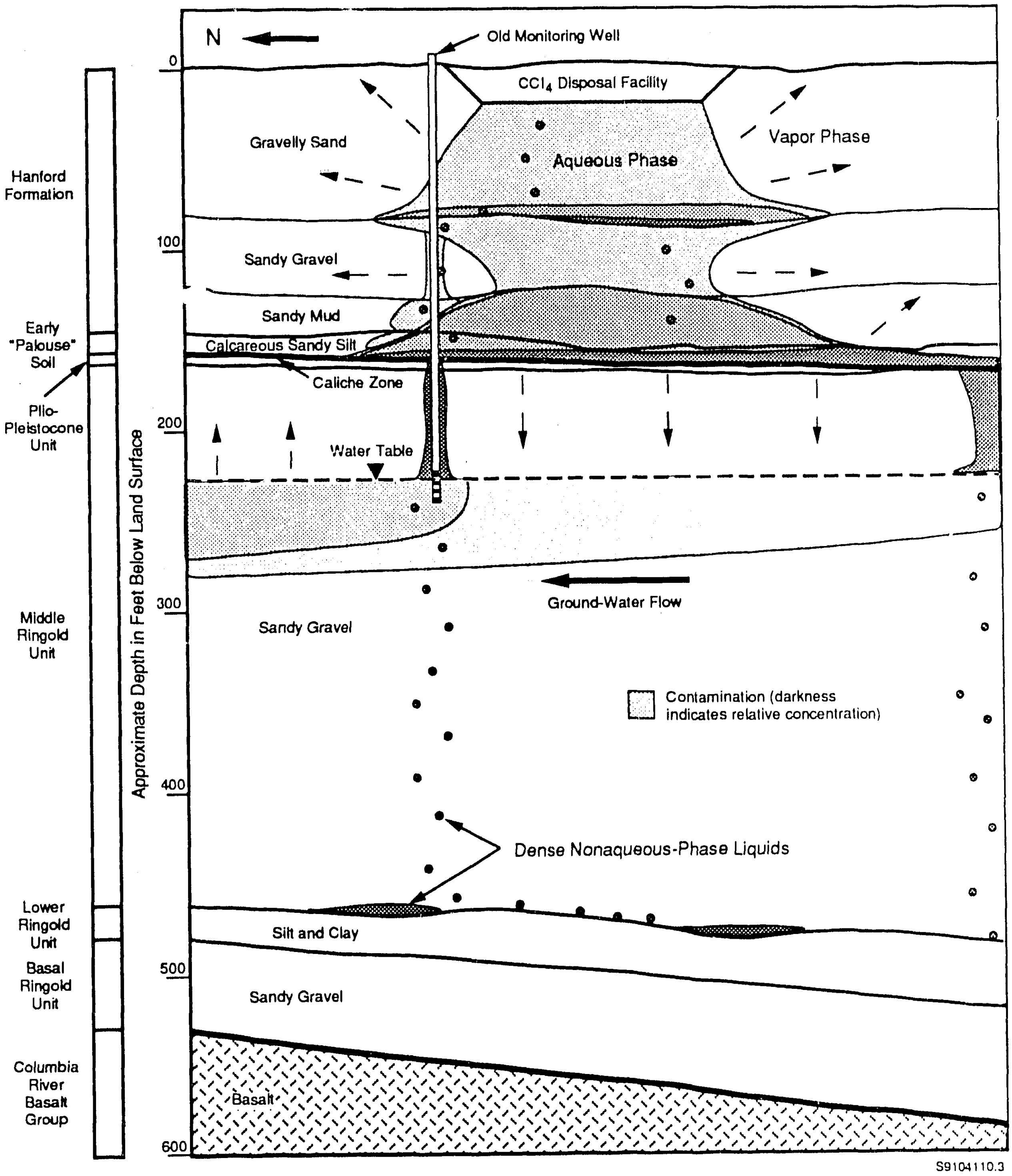

Figure 4. Three Conceptual Phases for CCl_4 Inventory in Hanford's Z Plant Liquid Waste Disposal Facilities

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