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A Research Report for
Westinghouse Hanford Company

The Predicted Impacts to the Groundwater and Columbia River from Ammoniated Water Discharges to the 216-A-36B Crib

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March 1988

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

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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A RESEARCH REPORT FOR
WESTINGHOUSE HANFORD COMPANY

THE PREDICTED IMPACTS TO THE GROUNDWATER AND COLUMBIA RIVER FROM AMMONIATED WATER DISCHARGES TO THE 216-A-36B CRIB

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Richland, Washington 99352

SUMMARY

The objective of this study by Pacific Northwest Laboratory was to assess the impact that past and potential future discharges of ammoniated water to the 216-A-36B crib have on groundwater and river concentrations of hazardous chemical constituents. Until August 1987, the 216-A-36B crib, located in the 200-East Area of the Hanford Site, accepted ammoniated water discharges. Although this study addresses known hazardous chemical constituents associated with such discharges, the primary concern is the discharge of NH_4OH because of its microbiological conversion to NO_2^- and NO_3^-. As a result of fuel decladding operations, material balance calculations indicate that NH_4OH has been discharged to the 216-A-36B crib in amounts that exceed reportable quantities under the Comprehensive Environmental Response, Compensation and Liability Act of 1980. Although flow to the crib is relatively constant, the estimated NH_4OH discharge varies from negligible to a maximum of 10,000 g-moles/h. Because these discharges are intermittent, the concentration delivered to the groundwater is a function of soil sorption, microbiological conversion rates of NH_4^+ to NO_2^- and NO_3^-, and groundwater dispersion.

This report provides results based on the assumptions of maximum, nominal, and discontinued NH_4OH discharges to the crib. Consequently, the results show maximum and realistic estimates of NH_4^+, NO_2^- and NO_3^- concentrations in the groundwater.

Because this study shows NH_4^+ conversions to NO_2^- and NO_3^- to be rapid and complete, predicted concentrations of NO_3^- in the groundwater caused by NH_4^+ discharges to the crib are noticeable. The calculated groundwater concentrations beneath the crib would be 430 mg/L NO_3^- under maximum yearly average operations and 320 mg/L under conditions representing past operations during fiscal years 1984 through 1987. (For comparison purposes, drinking water standards, although they do not apply because there are no community water systems on the Hanford Site, are 45 mg/L.) These predicted concentrations compare favorably with measured groundwater NO_3^- concentrations in the vicinity of the crib. Therefore, we conclude that ammoniated water discharges to the 216-A-36B crib have a significant effect on observed NO_3^- concentrations in the

groundwater by micro-biological conversion of NH_4^+ to NO_3^-. However, under maximum discharge and complete microbiological conversion assumptions, predicted concentrations of NO_3^- in the river are extremely low ($3x10^{-4}$ mg/L). By comparison, this amount is more than 5 orders of magnitude below drinking water standards.

The effect of leaching the soil column with clean water delivered at the same discharge rate to the crib was also modeled after equilibrium concentrations in the soil column were reached. NO_3^- concentrations in the aquifer at the crib boundary begin to drop within approximately 75 days. Concentrations at the future control zone boundary [the zone defined in Appendix B of the Final Environmental Impact Statement: Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes (DOE/EIS-0113)] start to drop within approximately 650 days. After approximately 730 days, the NO_3^- concentrations become negligible (near zero). The concentrations remain high for nearly two years because an estimated 31,000 kg (68,000 lb) of NO_3^- from converted NH_4^+ is held in the soil column prior to the water leach.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to all contributors of this report. Westinghouse Hanford Company provided much of the technical information on decladding and crib operations. Significant contributors from Pacific Northwest Laboratory included Frank Hara and Kris McFadden - analytical support; Kathy Cramer - review of regulations; Barb Denovan - NH_4OH conversion studies; Wayne Martin, Clark Lindenmeier, and Stephanie McLaurine - adsorption/desorption laboratory work; Virgina LeGore - radionuclide counting; and Paula Heller - sediment physical property measurements.

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1.0 INTRODUCTION

It was reported in August 1987 that ammonium hydroxide (NH_4OH) was being discharged to the 216-A-36B crib at the Hanford Site in amounts that exceeded reportable quantities as defined by CERCLA[a]. This discharge had been a result of PUREX (plutonium and uranium extraction) operations. Westinghouse Hanford Company (WHC) requested that the Pacific Northwest Laboratory (PNL) evaluate the effects of past and future discharges of ammoniated water to this crib on groundwater and river concentrations of hazardous chemical constituents.

1.1 APPROACH

The following approach was taken to address the effects on groundwater:

- Applicable environmental regulations were reviewed with appropriate WHC and PNL experts, and the chemistry of the waste was compared to applicable regulations to identify specific chemicals for the evaluation (Section 3.0).
- Because of the potential for conversion of ammonium ion (NH_4^+) to nitrite/nitrate (NO_2^-/NO_3^-), several studies were conducted to estimate the effect on groundwater by these species (Sections 4.0 and 5.0):
    - Adsorption/desorption studies were conducted to determine NH_4OH sorption coefficients (K_ds) and capacities using a soil that is representative of that found at the crib site (Section 4.0).
    - A literature search was conducted to gain an improved perspective of the biological processes that convert NH_4OH to NO_2^-/NO_3^- (Section 5.0).
    - A test was conducted to qualitatively measure the NH_4OH conversion rate to NO_2^-/NO_3^- (Section 5.0).

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[a] Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA 1980).

  - Groundwater samples were analyzed to determine the presence of nitrifying bacteria, which are necessary for the conversion process, as well as denitrifying bacteria (Section 5.0).

- Calculations were made to estimate the volatilization of NH_3 from the crib, as required to determine the amount of NH_4^+ or NO_3^- that migrates into the groundwater (Section 6.0 and Appendix B).
- An assessment was made of NH_4OH and NO_3^- transport in the vadose zone and groundwater. Contaminant concentrations were predicted at various control points. This assessment was corroborated with existing field data to the extent possible (Section 7.0).
- An assessment of contaminant concentrations in the groundwater and the river focused on the fate of NH_4OH in the waste water of both past and future discharges (Section 8.0). The assessment was based on the information gained through the preceding efforts. A number of cases were evaluated for migration to the crib boundary, the 6.4 km by 12.8 km (4.0 mi by 8.0 mi) future control zone of the 200-East and 200-West Areas (described in Appendix B of DOE 1987), and the Columbia River.

1.2 PROCESS BACKGROUND

To understand the significance of the discharges to the 216-A-36B crib, which have been curtailed since August 1987, it is important to understand the processes leading to these discharges. A description of the crib is given in Appendix C.

Ammonium discharges to the crib have resulted primarily from the decladding operations of spent fuel at the head end of the PUREX process. The PUREX process separates plutonium from uranium and fission products in irradiated fuel. During the decladding operation, spent fuel is boiled in a solution of NH_4F/NH_4NO_3 to remove the zirconium cladding. This leads to the following reaction:

$$6NH_4F + Zr(s) \rightleftarrows ZrF_6^{-2} + 2NH_4^+ + 4NH_3 + 2H_2(g) \qquad (1.1)$$

The hydrogen reacts with NO_3^- to form more NH3 as follows:

$$4H_2 + NH_4NO_3 \rightleftarrows 2NH_3 + 3H_2O \qquad (1.2)$$

Ammonium gas is discharged from the dissolver, reaching a peak concentration within 2 h of each decladding operation. The theoretical peak number of moles discharged in any one hour is approximately 10,000 g-moles. If discharged to the crib in this concentration and amount, NH_4OH discharges would exceed the State of Washington's Department of Ecology (WDOE) 1-wt% criterion for class C toxic substances (WAC 173-303). These amounts fall off rapidly after the 7-h decladding operation. Following decladding, the decladding solution is transferred to a coating receiver tank, and a metathesis solution is introduced to the dissolver for fuel dissolution. During metathesis, significantly smaller amounts of NH3 (theoretically, 3% of previous amount) are discharged, so that the total discharge per decladding operation is 49,000 g-moles. Although the decladding operation from one dissolver may overlap the metathesis of another, the theoretical time period for each decladding operation is 29 h. Therefore, under these theoretical amounts, each decladding operation would exceed the 24-h CERCLA reportable quantity of 454 kg (1000 lb) of NH_4OH discharge per 24-h operation. Historically, however, the PUREX plant has not operated at 100% efficiency. During fiscal years (FY) 1984 through 1987, an average of 87 decladding operations per year were conducted.

Ammonia is scrubbed from the overheads of the dissolver with water to form NH_4OH. The scrub solution is concentrated, and until August 1987, the overheads from the concentrator had been discharged to the 216-A-36B crib. The rate of discharge had been maintained at a near constant level of 13,100 L/h (57.7 gal/min) during decladding and was reduced to approximately 7500 L/h (33 gal/min) between declads. The NH_4OH discharge concentrations were, however, directly proportional to the rate at which NH3 was exhausted from the dissolvers.

2.0 CONCLUSIONS

This report predicts groundwater and river concentrations from the maximum potential future discharges to the crib, as well as those from past discharges. The study also estimates the impacts from suspending future NH_4OH discharges and flushing the crib with water. Predictions of contaminant concentrations in the groundwater from these operations require that NH_4^+ desorption data be compiled and assimilated into hydrologic and geochemical models.

Evaluation of the chemistry of discharges based on analytical data supplied by WHC of one ammonia scrubber discharge sample from August 23, 1985, shows that the only component of environmental concern is NH_4^+ because of its biological conversion to NO_2^- and NO_3^-. The data support estimated theoretical quantities of NH_4OH in the discharge upon which this study is based. All other potential contaminants to the groundwater beneath the crib were low. By comparison, the discharge concentrations of other potential contaminants are below drinking water standards, CERCLA reportable quantities, and WDOE limits for dangerous waste classifications. As noted earlier, however, the theoretical amounts of NH_4OH would exceed CERCLA discharge reportable quantities.

Since this study's objective addresses potential hazardous chemical components, the effect of basic discharges on groundwater was evaluated. The discharges have negligible impact to the groundwater from the standpoint of basic solutions, since their maximum pH is 11.5 and dangerous waste classifications (WAC 173-303) are pH 12.5. The alkaline NH_4OH discharges react with the soil beneath the crib and further reduce the pH before the discharges reach the groundwater. Aluminasilicates in the soil beneath the crib react with OH^-, consuming the hydroxyl ion. The capacity of the soil to partially neutralize the basic discharges is at least 250 times that of all past discharges, assuming conservatively that only one hydroxyl ion is consumed for every aluminasilicate molecule. Consequently, the aspect of basic discharges was not addressed further in this study.

Ammonium ion discharges, however, are estimated to create contaminant concentrations in the groundwater that (for comparison sake only) exceed primary drinking water standards. Drinking water standards do not apply because there are no community water systems on the Hanford Site; they are discussed in this report for comparison only. This estimate is based on modeling results that consider vertical downward transport with no lateral dispersion, a conservative assumption. Microbiological conversion data presented in Section 5.0 indicate that NH_4^+ is rapidly converted in the vadose zone and groundwater to NO_2^- and NO_3^-, such that concentrations of NO_3^- up to 430 mg/L may occur in the groundwater as a result of past and potential future discharges. The results of this study suggest that NH_4^+ may be converted to NO_2^- in the vadose zone with subsequent conversion to NO_3^- in the groundwater. Because this study has found the conversions to be rapid, the estimated groundwater concentrations in this report are given in milligrams per liter NO_3^-. The evaluation in Section 6.0 of this report shows that volatilization of NH_3 from the crib produces atmospheric discharges that are far below CERCLA reportable quantities and that volatilization does not significantly reduce the amount of NH_4^+ and its conversion products ($NO_2^=$ and $NO_3^=$) being transported to the groundwater.

Groundwater concentrations were estimated for two cases: 1) a maximum yearly average of 122 declads per year was assumed for normal operation to provide a reasonable maximum discharge for potential future operations, and 2) the actual yearly average of 87 declads per year from FY 1984 through 1987 was assumed for considering the impacts of past operations. The transport and conversion of NH_4^+ in the vadose zone create predicted NO_3^- concentrations in the groundwater of 430 mg/L for normal operations and 320 mg/L for past operations.

The NO_3^- concentrations predicted in the groundwater are higher than concentrations observed in wells monitoring the crib (Law and Schatz 1986). The observed concentrations of NO_3^- range from 92 to 140 mg/L. The discrepancy may be due to the time lag for the nitrates to reach the monitoring wells. Groundwater samples collected in September 1987 show 240 mg/L NO_3^-, much closer to the predicted 320 mg/L. The remaining discrepancy may be explained by the fact that the number of decladding operations at the time of this latter sample was fewer than the annual average (18 as opposed to 87).

An additional case was run where NH_4^+ discharges from past operations were followed by a clean water discharge to the crib. Modeling results indicate that NO_3^- levels in the groundwater at the crib boundary begin to drop after 75 days, and that they approach zero, due to clean water leaching, after 105 days. Seventy-five days are required before groundwater concentrations begin to drop because of the accumulated nitrate inventory in the vadose zone. Based on 4-year average discharge quantities, the number of moles of leachable NO_3^- remaining in the soil column would be 3% of the estimated moles of NH_4^+ discharged to the crib from FY 1984 through 1987.

In conclusion, it appears that the NH_4^+ discharges to the 216-A-36B crib are likely to be the main cause for existing measured NO_3^- concentrations in the groundwater around the crib. However, the maximum predicted concentration in the Columbia River is more than five orders of magnitude below drinking water standards (3×10^{-4} mg/L).

3.0 APPLICABLE REGULATIONS

This section provides a brief description of the regulations (federal and state) that are applicable to the disposal of waste into the crib studied in this analysis.

3.1 RESOURCE CONSERVATION AND RECOVERY ACT

The Resource Conservation and Recovery Act (RCRA) of 1976, as amended, provides for protection of public health and the environment from activities associated with the management and disposal of solid and hazardous wastes. Criteria were developed under RCRA for identifying hazardous wastes, which are thus subject to regulations governing hazardous materials. Characteristics of hazardous waste include toxicity, persistence and degradation in nature, and other related factors such as ignitability, corrosiveness, and reactivity. The RCRA established performance standards that apply to operators who transport, produce, store, treat, and dispose of hazardous waste.

The U.S. Environmental Protection Agency (EPA) promulgated Title 40, Code of Federal Regulations (CFR), Parts 260 through 265 and 270 (EPA 1986c) to implement RCRA. The EPA has authorized Washington State to conduct hazardous waste programs for hazardous wastes, and Washington has promulgated hazardous waste regulations in WAC 173-303.

The regulations in WAC 173-303 list guidelines for classifying a waste as "extremely hazardous," "dangerous," or "undesignated" (i.e., unregulated under WAC 173-303). When these guidelines are applied to the ammonia scrubber discharge stream (at a 3-day average concentration of approximately 1800 mg/L, 0.2 wt% NH_4OH), the waste stream is classified as an undesignated waste. However, if theoretical peak concentrations described in Section 1.0 were encountered during the 7-h decladding cycle, the equivalent concentration and minimum quantity limits identified in WAC 173-303 would be exceeded (>1 wt% NH_4OH), classifying the discharge as a dangerous waste.

3.2 SAFE DRINKING WATER ACT

The Safe Drinking Water Act (SDWA) of 1974 was enacted to set drinking water standards for owners/operators of public water systems and to protect underground injection that can contaminate drinking water sources. Under SDWA authority, the EPA issued national interim primary drinking water regulations in 40 CFR 141 (EPA 1986a) and national secondary drinking water regulations in 40 CFR 143 (EPA 1986b) that apply to public water systems. The 40 CFR 141 regulations set forth both radiological and nonradiological standards, while 40 CFR 143 established "reasonable goals" for maintaining aesthetic drinking water quality. Washington State has adopted both sets of EPA standards as drinking water limits (WAC 248-54). While these standards only directly apply to water delivered to the consumer by a public water system, they are commonly used for comparison of contaminants found in groundwater. They are presented in this report strictly for providing that comparison.

There are no primary or secondary drinking water standards for NH_4^+, but the NO_3^- that results from the nitrification has a primary standard of 45 mg/L. A standard of 1 mg/L has been proposed for NO_2^-, but is not currently in effect (EPA 1985). Several other constituents (chromium, uranium, zinc, fluoride, chloride, and cadmium) have been detected in the discharges to the 216-A-36B crib that have either primary or secondary standards, but are present in low enough concentrations so as not to approach maximum concentration levels in the aquifer.

3.3 COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY ACT

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 created the first comprehensive federal law to respond to releases of hazardous substances to the environment. The CERCLA scheme applies to contaminants released to air, water, or land. In accordance with Section 9602 thereof, a reportable quantity for hazardous and radioactive materials was established. These quantities were established to protect human health and the environment. If the reportable quantity for a material is exceeded during a 24-h period, the release must be reported to the National Response Center.

The primary reportable quantities of interest to this analysis are those for NH_4OH and NH_3, which are 454 and 45.4 kg (1000 and 100 lb) per 24-h period, respectively.

4.0 SOIL ADSORPTION-DESORPTION STUDIES

In order to determine the impact that NH_4OH discharges have on groundwater and river concentrations, it is important to understand the mobility of NH_4^+ in the soil beneath the crib. Because NH_4^+ is generally sorbed and desorbed from sediments in the vadose zone at rates dependent on NH_4^+ concentration, competing ion concentrations, and sediment properties, studies of soil adsorption-desorption were conducted. The data reported in this chapter were then used, along with microbiological conversion data and ammonia volatilization data in Sections 5.0 and 6.0, respectively, to model the effects on groundwater concentrations.

Several laboratory tests were performed using actual and diluted waste solutions in contact with a sediment sample collected from the Hanford Grout Technology Program's test grout facility. The sediment used in all tests was obtained from the test grout facility, which is northeast of the 216-A-36B crib. Its particle-size distribution, identity, and suitability for determining behavior under the 216-A-36B crib are described in Appendix A. Appendix A also describes the analyses of the waste solutions (labeled A through D) as well as groundwater and sediment samples used in the adsorption and microbiology tests. Further, desorption or leaching studies were performed on selected sediment samples that had been previously loaded with NH_4^+. This data helps quantify NH_4^+ behavior when exposed to a clean water flush. Distilled water or 0.5N KCl solution was used to leach the sediment.

The results of chemical analyses performed on samples of the waste solution used and of 1:10 and 1:100 dilutions are shown in Appendix A (Tables A.1 and A.2, respectively). The dilutions were used to evaluate the linearity of adsorption and to ascertain whether the sediment sorption capacity for NH_4^+ remained constant regardless of the solution concentration. As described in the introduction of this report, the NH_4^+ concentration of solutions discharged to the 216-A-36B crib was quite variable over time, depending on which part of the PUREX cycle was operating.

For this study it was assumed that the highest concentration of NH_4^+ discharged during a 3-day time-averaged PUREX cycle was 942 mg/L. During the initial zirconium cladding dissolution, much higher NH_4^+ concentrations (as high as 12,000 mg/L) were likely discharged to the crib for several minutes to a few hours, but the performance assessment tools available necessitate that the PUREX cycle be time averaged. Past operating history suggests that at maximum annual operation, a cycle is completed approximately every 72 h; thus, the 3-day time-averge scenario is developed.

The wide range in NH_4^+ concentrations observed or predicted to be discharged to the crib over a typical year (4 to 12,000 mg/L) could cause variable sorption reactions, complicating the determination of NH_4^+ sorption on the sediments. The other dissolved constituents in the condensates do not appear to vary as much as the NH_4^+ cation. NH_4^+ sorption is complicated because the upper range of the NH_4^+ concentrations could rapidly saturate available cation exchange sites of the crib sediments such that further NH_4^+ retention would be minimal. During discharge periods when the NH_4^+ levels are low, desorption of NH_4^+-saturated sediments might occur, although the condensates do not contain significant concentrations of competing cations.

To alleviate the concern of nonlinear sorption behavior due to large variations in NH_4^+ concentrations, we performed standard batch and column adsorption tests on concensates with a range of NH_4^+ concentrations. The retardation parameters, K_d (distribution coefficient) and R (retardation factor), were measured for NH_4^+ concentrations between 30 and 3400 mg/L. Estimates of the total sediment NH_4^+ exchange capacity were also calculated to allow simple ion exchange calculations to be performed. Finally, the desorption, or leaching tendency, of NH_4^+ adsorbed on the sediment was investigated as a function of the original concentration used to load the sediments.

4.1 BRIEF DESCRIPTION OF TESTS

The standard batch K_d method described in Relyea, Serne, and Rai (1980) was used. Either 1 or 5 g of sediment were contacted with 30 mL of NH_4^+-laden solution for 7 days. The tests were run in triplicate, and blank tubes (solution but no sediment) were processed identically. After 7 days, the tubes were centrifuged, and supernatant solution was filtered through 0.4-μm membrane filters. The concentration of NH_4^+ from the blank tubes was compared to the effluents from the sediment-charged tubes. The difference was attributed to sediment adsorption. The batch K_d tests were run using sample A and 1:10 and 1:100 dilutions of sample D. Desorption tests were run on NH_4^+-laden sediments (wet weight 50 g) using 100 mL of 0.5N KCl in a batch mode. The desorption contact time was between 1 and 5 days, depending on the test.

Two types of column tests were performed: standard single-pass flow-through column tests (Relyea, Serne, and Rai 1980) and vacuum extractor column tests (Serne, Peterson, and Gee 1983). The NH_4^+ solution was passed through sediment packed in cylindrical columns. Effluent solution was collected and measured for pH and NH_4^+ concentrations. The results of numerous aliquots were plotted as the ratio of effluent/influent NH_4^+ concentration versus cumulative pore volumes. The retardation factor and total adsorption capacity were determined when 50% breakthrough and 100% breakthrough occurred, respectively. For one adsorption column, a complete chemical analysis of the effluent solutions was performed.

Because of time constraints, the flow rates of the various column tests had to be varied. The flow rates also differed from the vacuum extractor tests. Results from tests with different flow rates may be affected by kinetic effects. Several of the adsorption tests were leached with deionized water after the loading period.

Pertinent details on the various column and vacuum extractor adsorption tests are shown in Table 4.1. Similar details on the desorption tests are shown in Table 4.2.

4.2 BATCH ADSORPTION RESULTS

The results of the three sets of batch adsorption tests are shown in Table 4.3. The first set includes six individual tests, each representing 7 days of contact. Three tests involved 1 g of sediment, and three involved 5 g. The former tests yield K_d results that are quite variable because the high NH_4^+ concentrations rapidly saturated the sediment, and effluent concentrations in two of the tests remained approximately the same as the influent.

TABLE 4.1. Experimental Details for Column and Vacuum Extractor Adsorption Tests

Test	Influent Solution	NH_4^+, mg/L	pH	Column Diameter, cm	Length, cm	Weight of Soil, g	Porosity, %	Flow Rate Volume, mL/h	Pore, cm/hr	Residence Time, h/pore volume
1	Sample C	1620	10.8	6.3	7	418.3	33.2	2.83	0.27	25.5
2	Sample A/B	2310 to 3400	10.7 to 10.9	13.3	10.8	519.4	39.7	6.5	0.57	18.8
3	Effluent Test 2	4 to 3350	8 to 11.2	10.6	410.8	415.5	39.75	0.2	0.57	18.8
4	Effluent Test 3	1.5 to 2610	7.5 to 11.0	7.9	810.8	311.6	39.73	0.9	0.57	18.8
5	Effluent Test 4	0.9 to 2020	7.8 to 10.5	5.32	10.8	207.8	39.7	2.6	0.57	18.8
6	Effluent Test 5	1.1 to 1.4	7.7 to 8.1	2.66	10.8	103.9	39.7	1.3	0.57	18.8
7	1:10 Dilution Sample D	250	10.1	7.98	5.4	155.8	39.7	7.5	1.13	4.8
8	Effluent Test 7	0.7 to 224	8.0 to 10.2	5.32	5.4	103.9	39.7	5.0	1.13	4.8
9	1:100 Dilution Sample C	25.8	9.4	1.7	13	51.9	38.7	15.1	17.2	0.76

TABLE 4.2. Experimental Details for Desorption Tests

			Column				Flow Rate		
Test	Sediment from Adsorption Test	Estimated NH_4^+ Loading, mg/g	Diameter, cm	Length, cm	Weight of soil, g	Porosity %	Volume, mL/h	Pore, cm/h	Residence Time, h/pore volume
10	2	1.8	7.98	10.8	155.8	39.7	7.5	1.1	9.85
11	4	1.2	5.32	10.8	103.9	39.7	5.0	1.1	9.85
12	7	0.9	2.66	5.4	51.9	39.7	2.5	1.1	4.8
13	8	0.9	2.66	5.4	51.9	39.7	2.5	1.1	4.8
14	9	0.5	1.7	13	51.9	38.7	15.1	17.2	0.76

TABLE 4.3. Batch K_d Results

Solution	NH_4^+ mg/L	Test	Weight of Soil, g	K_d mL/g	Average K_d, mL/g
Sample C	3440 ± 50	1	1	4.9	
		2	1	0.2	
		3	1	-1.1	n=5 1.3 ± 5.2
		4	5	Spilled	
		5	5	1.9	n=2 1.3 ± 0.8
		6	5	0.7	
Diluted 1:10	252 ± 25	7	5	5.5	
Sample D		8	5	5.2	n=3 5.5 ± 0.4
		9	5	5.9	
Diluted 1:100	25.8 ± 4.6	10	1 g	16.3	
Sample D		11	1 g	14.4	n=3 14.8 ± 1.9
		12	1 g	13.7	

The precision of K_d tests is best when approximately 50% of the mass of adsorbate added is removed from solution. In the first three thests (1 g), less than 1% of the mass was adsorbed for sample 2 and 3.

The average K_d for the first set of tests is 1.3 mL/g whether all data points are used or just the 5-g samples. The latter samples yielded a smaller standard deviation.

The batch K_d results for diluted NH_4^+ process condensate increase as the NH_4^+ concentration decreases. The K_d increases from a value of 1.3 to 14.8 mL/g as the concentration of NH_4^+ drops from 3440 to 21 mg/L. This suggests that we have not reached the region where NH_4^+ can be treated as a trace constituent within the system. Trace constituents generally show a constant K_d when the solution concentration is varied.

The three data sets were used to develop a Freundlich isotherm for NH_4^+ adsorption. The Freundlich isotherm is an empirical relationship that relates the mass of a species that adsorbs (per gram of sediment) to the equilibrium concentration of the species in solution. The isotherm has two fitting parameters, K and N. The relationship is

$$X = KC^N \tag{4.1}$$

where X is the amount of solute adsorbed per unit of weight of solid, C is the equilibrium solute solution concentration, and K and N are the constants.

The Freundlich isotherm can be transformed to a linear form by taking logarithms of both sides of the equation. Table 4.4 shows the logarithmic transformed data for the average of the three K_d data sets shown in Table 4.3.

TABLE 4.4. Freundlich Isotherm Data

Initial Concentration, mg/L	Equilibrium NH_4^+ Concentration, mg/L (C)	Log C	Kd, mL/g	Adsorbed NH_4^+, mg/g (X)	Log X
3440	2827	3.45	1.3	3.68	0.566
252	131.5	2.12	5.5	0.79	-0.102
20.7	13.9	1.14	14.8	0.205	-0.688

y-intercept = -1.28 = log K

Slope = 0.540 = N

K = 0.05

C = Equilibrium solute solution concentration.

X = Amount of solute adsorbed per unit of weight of solid.

K, N = Constants.

The value of N is 0.54. If the adsorption isotherm were linear, N would equal 1.0. It is quite common for the value of N to be less than 1 for trace constituent adsorption (Langmuir 1981). As the solution concentration drops, the amount adsorbed drops less for an adsorbate with N value less than 1 than for an adsorbate with an N value of 1 or greater. That is, as the solution concentration drops, the sediment becomes relatively more selective toward adsorption of the adsorbate. The NH_4^+ isotherm suggests that the sediment adsorption is almost a function of the square root of the NH_4^+ concentration in solution.

From the Freundlich isotherm we can calculate the expected K_d for a solution with 942 mg/L NH_4^+ (the value for the 3-day time-averaged scenario). The value would be 2.25 mL/g. At the discharge point during the NH_4OH pulse, a K_d value of 1.3 mL/g is reasonable. As other waste dilutes the NH_4^+ concentration, a K_d as high as 15 mL/g could be found in sediments on the perimeter of the wetting front and deep underground.

4.3 RESULTS OF COLUMN TESTS

Three NH_4^+ solutions (high, medium, and low) were loaded onto separate columns to measure the retardation factor and total sorption capacity. After NH_4^+ was loaded, several of the columns were leached with deionized water.

The retardation factor can be related to the K_d under the following conditions. If the sediment were a porous medium, if essentially all the porosity were available for flow (or one can determine the effective porosity), and if the adsorption were reversible and were to follow linear adsorption isotherms, then the following relationship holds for initially dry columns:

$$R = (\rho/\theta)\ K_d \qquad (4.2)$$

where R = retardation factor (unitless)
ρ = bulk density (g/cm^3)
θ = porosity (unitless)
K_d = distribution coefficient (cm^3/g).

For column experiments that receive a constant pulse of adsorbate, the ideal breakthrough curve is an S-shaped curve that yields the value of R at the pore volume where C/C_o (the ratio of the effluent/influent concentration) equals 0.5. The data for tests 1 through 13 (see Tables 4.1 and 4.2) used a constant input during the loading phase, and breakthrough curves can thus be plotted from the results in Tables 4.5 through 4.8. The complete adsorption-desorption effluent curves are shown in Figures 4.1 through 4.7. The bulk density and porosity values in Table 4.1 and the estimated value of R (at $C/C_o = 0.5$) were used to calculate an equivalent K_d.

TABLE 4.5. Column Adsorption Experiment (Test 1)

Time, days	Pore Volume	pH	Initial NH_4^+, mg/L	Average NH_4^+, mg/L
0.5	0.69	7.52	0.82	0.8
1.0	1.13	7.54	0.75	0.8
1.5	1.82	9.2	33	32
2.0	2.24	10.19	625	598
2.5	2.87	10.27	940	883
3.0	3.37	10.46	1580	950
3.5	3.59	9.79	605	545
4.0	4.03	9.85	651	655
4.5	4.39	10.10	801	731
5.0	4.74	10.24	985	864
5.5	5.08	10.45	1130	1039
6.0	5.54	10.15	935	810
6.5	6.12	10.41	1060	1072

The K_d values estimated from the 0.5 value for breakthrough are compared with the batch K_d values in Table 4.9. In most cases the K_d calculated from column tests is slightly lower than the batch K_d value or is within the estimated uncertainty. For this NH_4^+ study, several observations were made during the testing. First it was found that the waste solutions and soil effluents were unstable with respect to NH_4^+. The high pH values (9.5 to 11) allow a significant fraction of the total nitrogen to be present as dissolved NH_3 gas. This species can volatilize and be lost from the sample solution when opened to the atmosphere. Table 4.5 shows NH_4^+ measurements of column effluents as first measured (typically within 1 day of sampling) and as an average of 5 to 10 repeat analyses performed over a week. In almost all cases where the pH is above 10, the average concentration is lower than in the first analyses. We suspect that NH_3 volatilization is removing mass from the sample solution. A similar trend is reported in Appendix A for dilutions of sample D stored in polyethylene containers for several days. The single-pass column effluent (Test 1 and Figure 4.1) was collected in open beakers, and the error bars on the data points include results of both the average concentration and first

TABLE 4.6. Vacuum Extractor Adsorption/Leach Test (Tests 2 through 6 on Table 4.1 and Tests 10 and 11 on Table 4.2)

	Extractor Column 1				Extractor Column 2				Extractor Column 3				Extractor Column 4				Extractor Column 5			
Effluent Number	Time, days	Pore Unit	pH	NH_4^+, mg/L	Time, days	Pore Unit	pH	NH_4^+, mg/L	Time, days	Pore Unit	pH	NH_4^+, mg/L	Time, days	Pore Unit	pH	NH_4^+, mg/L	Time, days	Pore Unit	pH	NH_4^+, mg/L
	(Test 2)				(Test 3)				(Test 4)				(Test 5)				(Test 6)			
1	1	0.5	8.17	4	4	0.6	7.49	1.5	1	0.17	7.88	2.0	2	0.12	7.87	1.38	4	0.1	7.80	1.13
2	2	1.8	10.70	790	5	1.2	7.47	2.4	2	0.60	8.00	1.2	3	0.5	8.08	1.21	6	0.4	8.01	1.41
3	5	3.0	10.77	3270	6	1.8	10.65	831	3	1.0	8.18	0.9	6	0.8	7.94	1.13				
4	6	4.3	11.23	3350	7	2.5	11.00	2610	4	1.4	7.79	2.0	7	1.1	7.71	1.41				
5	7	5.6	11.13	2800	8	3.1	10.93	2510	7	1.9	10.50	768								
6	8	6.8	10.94	2280	11	3.8	10.56	2170	8	2.3	9.82	2020								
7	9	8.1	10.91	2120	12	4.4	10.65	1950												
8	12	9.4	10.20	2390																
9	13	10.7	11.03	2100																
	(Test 10)								(Test 11)											
10	15	13.2	10.70	1310					10	3.1	10.74	1270								
11	16	15.7	9.97	217					11	4.0	10.09	190								
12	19	18.2	-	158					14	4.8	-	160								
13	20	20.7	9.65	138					15	5.6	9.81	82								
14	21	23.2	9.38	227					16	6.5	9.56	64								
15	22	25.7	9.20	111					17	7.3	9.23	51								
16	23	28.2	9.14	85					18	8.1	9.26	41								
17	26	30.7	9.37	83					21	9.0	8.97	40								

TABLE 4.7. Vacuum Extractor Adsorption/Leach Test (Tests 7 and 8 on Table 4.1 and Tests 12 and 13 on Table 4.2)

	Extractor Column 1				Extractor Column 2			
Effluent	Contact Time, days	Pore Volume	pH	NH_4^+, mg/L	Contact Time, days	Pore Volume	pH	NH_4^+, mg/L
	(Test 7)				(Test 8)			
1	1	4.20	8.02	0.79	1	1.56	7.91	0.67
2	2	9.24	9.48	20.5	4	4.08	7.85	0.67
3	5	14.29	10.07	124	5	6.60	8.45	1.16
4	6	19.32	10.21	129	6	9.12	8.92	8.61
5	7	24.37	10.11	224	7	11.64	9.72	45.0
6	8	29.31	9.90	209	8	14.16	9.82	109
7	9	34.45	9.89	219	11	16.68	9.59	157
8	12	39.50	9.12	211				
	(Test 12)				(Test 13)			
9	13	44.54	9.99	170	12	19.20	10.00	176
10	14	49.58	9.60	84	13	21.7	9.57	63
11	15	54.62	9.17	52	14	24.24	9.32	40
12	16	59.66	9.17	44	15	26.76	9.17	40

value measured. The vacuum extractor results in Figures 4.2 through 4.7 show more well-behaved effluent curves, perhaps because the effluent was collected in a sealed syringe that minimized volatilization.

In the batch K_d analyses, any sample volatility losses would bias the K_d to higher values. Further, the 7-day contact time for the batch tests is considerably longer than the residence times of solution in the column tests. If the NH_4^+ adsorption is slow to reach equilibrium, the column results can also be lower than batch results. This is especially true for Test 9, where 1:100 diluted sample D is forced through the column with a residence time of only 0.76 h. Regardless of the true causes for the differences in sorption values (K_d values), the column results can be used in performance assessment calculations to yield conservative predictions.

TABLE 4.8. Column Adsorption/Leach Experiment (Tests 9 and 14)

Time, days	Pore Volume	pH	NH_4^+, mg/L
	(Test 9)		
1	32.8	9.01	4.38
4	116.8	9.41	19.10
5	151.8	9.68	26.3
6	183.3	9.37	21.7
7	216.5	9.49	21.7
8	243.7	9.45	20.4
11	339.8	8.96	24.6
	(Test 14)		
12	367.0	9.43	17.7
13	398.5	8.88	13.0
14	435.7	8.79	5.5
15	459.3	8.50	2.3

4.4 RESULTS OF DESORPTION TESTS

The solutions that are discharged when NH_4^+ is not present are condensates of very low ionic strength. To evaluate the potential for low ionic-strength solutions to displace adsorbed NH_4^+, deionized water was used as a leachant. The results of leaching tests described in Table 4.2 were shown in Figures 4.2 through 4.7. The details were presented in Tables 4.6 through 4.8. The figures show that the NH_4^+ concentrations rapidly drop to low values (in relationship to C_0) and continue to decrease slowly. An estimate of the amount of NH_4^+ leached from the sediment sorption site can be calculated from the assumption that the first desorption aliquot contains one pore volume of original solution that had an NH_4^+ concentration equal to the lost effluent collected during loading. This mass of NH_4^+ (concentration times one pore volume) should be subtracted from the total mass leached. To estimate a K_d value for NH_4^+ desorption, one can determine how many pore volumes are needed to leach 50% of the mass originally loaded on the sediment column. An estimate of the NH_4^+ loading on each column was made under the assumption that the loading portions

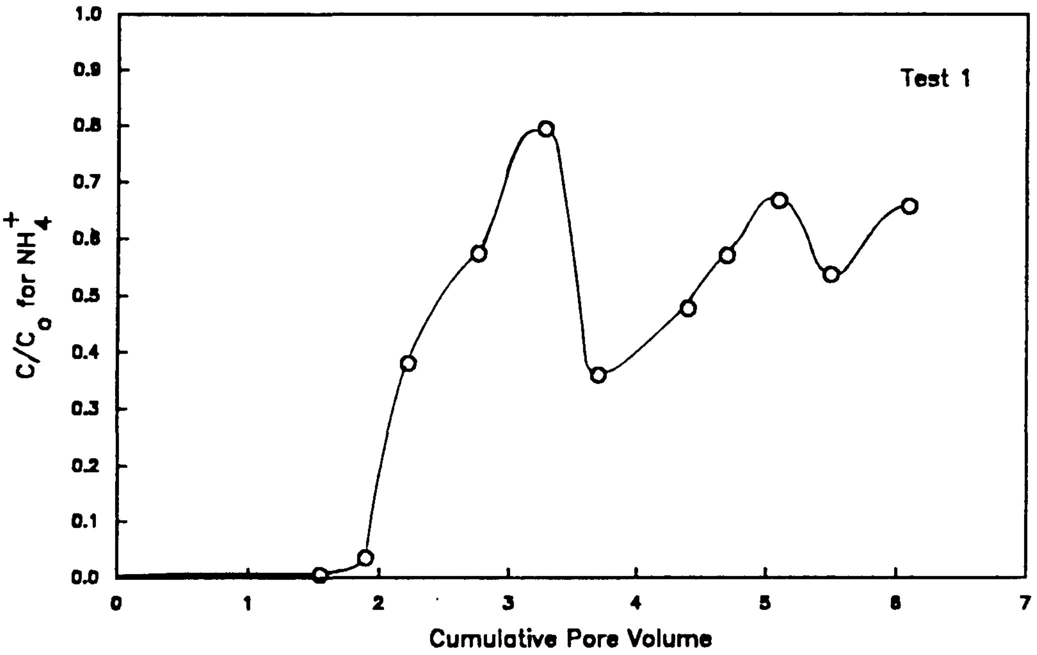

FIGURE 4.1. Column Results for Solution with Highest NH_4^+ Concentration (C = effluent concentration; C_o = influent concentration)

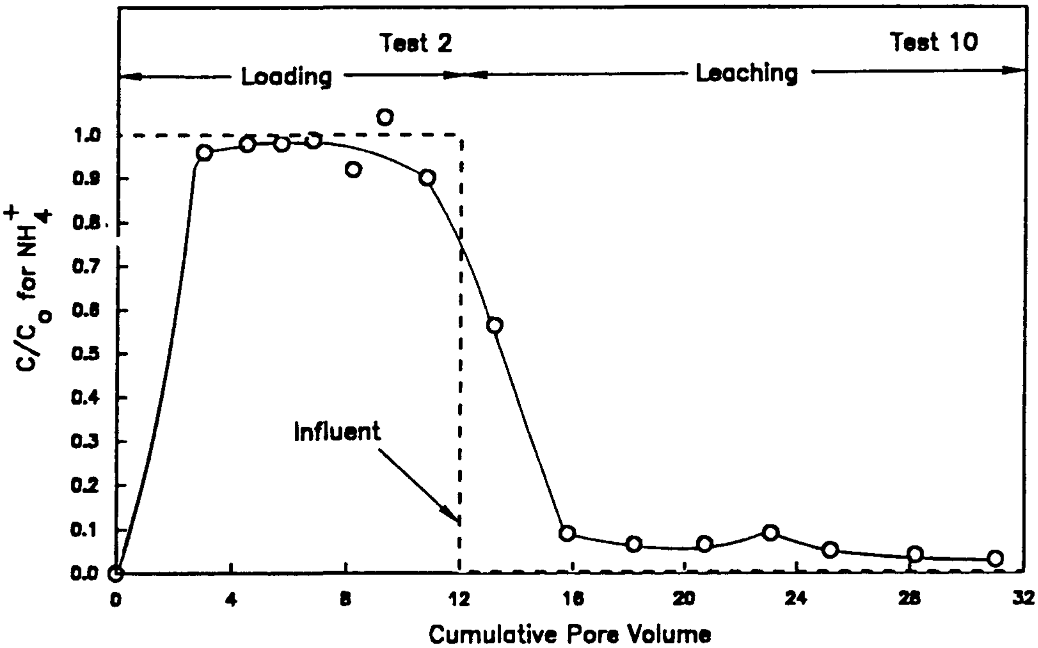

FIGURE 4.2. Effluent Curve for Adsorption and Leaching Tests 2 and 10 (C = effluent concentration; C_o = influent concentration)

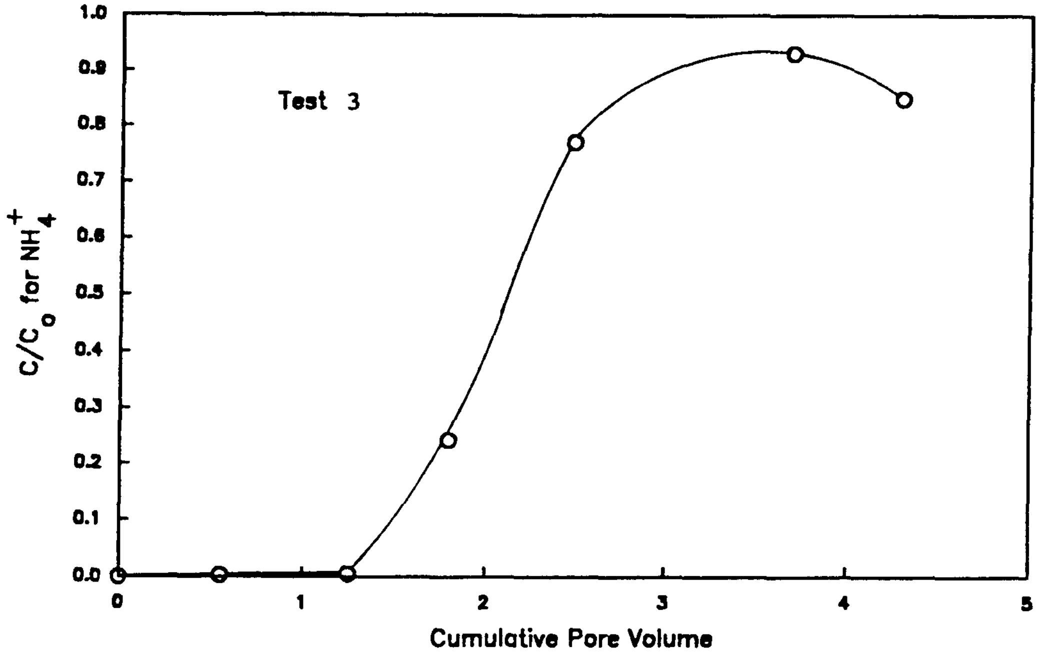

FIGURE 4.3. Breakthrough Curve for High-Concentration NH_4^+ Study (C = effluent concentration; C_o = influent concentration)

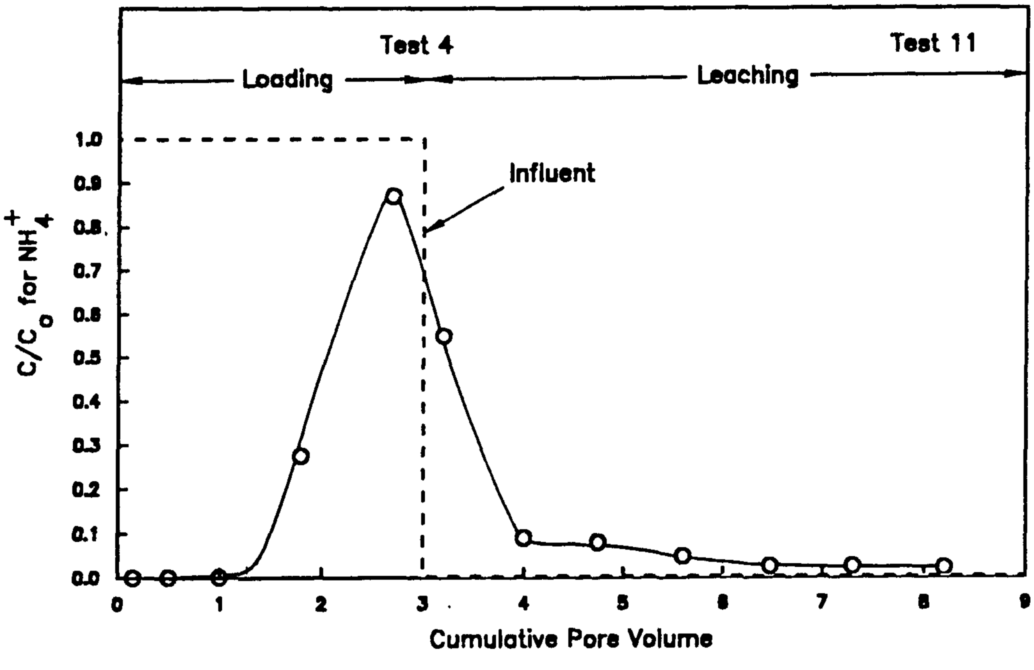

FIGURE 4.4. Effluent Curve for Adsorption and Leaching Tests 4 and 11 (C = effluent concentration; C_o = influent concentration)

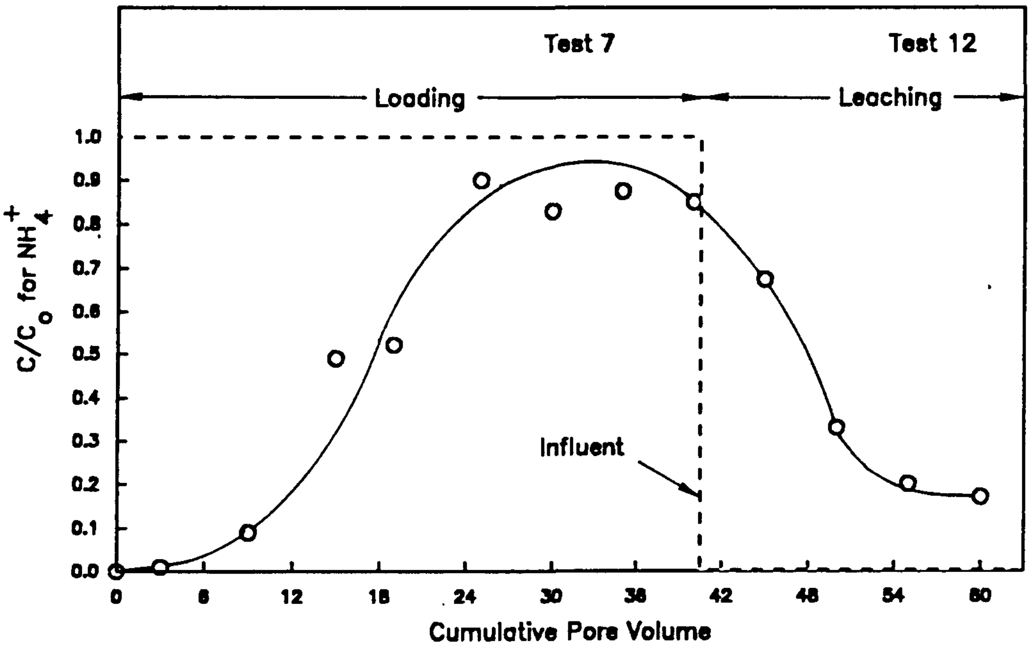

FIGURE 4.5. Effluent Curve for Adsorption and Leaching Tests 7 and 12 (C = effluent concentration; C_0 = influent concentration)

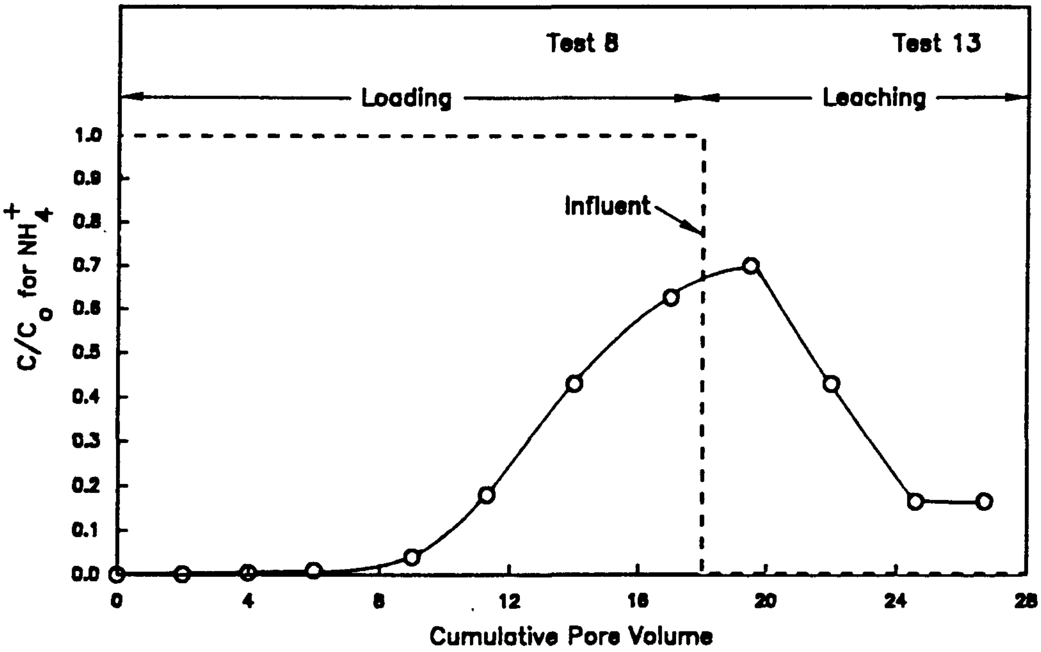

FIGURE 4.6. Effluent Curve for Adsorption and Leaching Tests 8 and 13 (C = effluent concentration; C_0 = influent concentration)

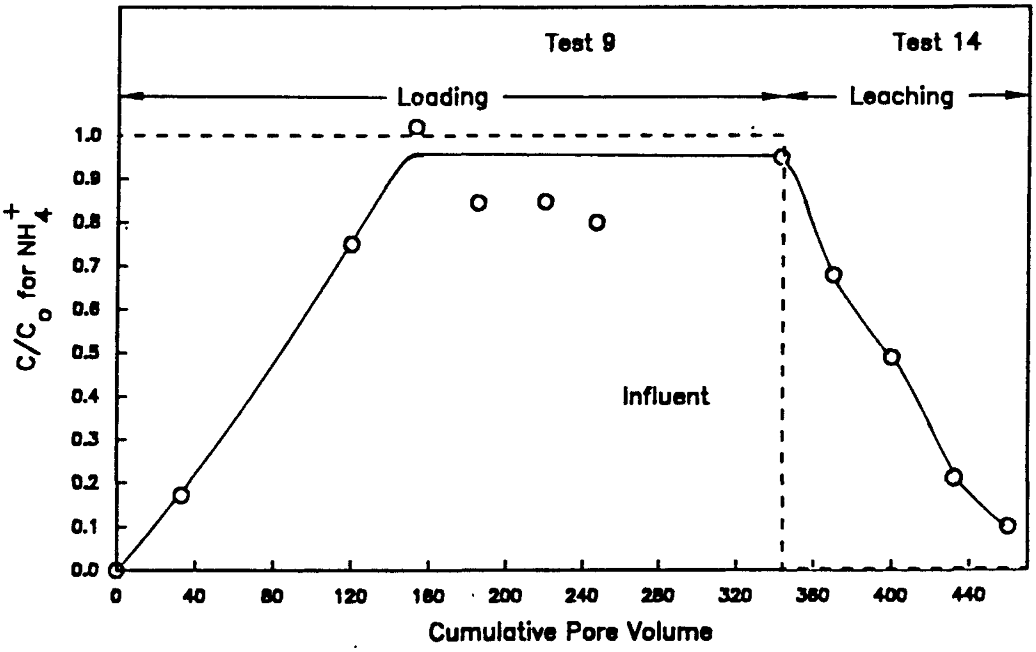

FIGURE 4.7. Effluent Curve for Adsorption and Leaching Tests 9 and 14 (C = effluent concentration; C_o = influent concentration)

TABLE 4.9. Comparison of K_d Values from Adsorption Tests

Test	Influent Level NH_4^+, mg/L	Observed R, unitless	K_d Value, mL/g Measured	K_d Value, mL/g Calculated
Batch K_d	3400	-	1.3 ± 0.8	-
Test 1	1620	2.5		0.43
Test 2	3440	2.3		0.53
Test 3	3440	2.1		0.48
Test 4	3440	2.0		0.46
Batch K_d	250	-	5.5 ± 0.1	-
Test 7	250	16.5		3.8
Test 8	250	15.0		3.4
Batch K_d	20.7	-	14.8 ± 1.9	-
Test 9	25.8	87		19.1

of the breakthrough curves were ideal S-shaped curves. Then, the adsorption capacity is determined from the following equation

$$L = \frac{(C_o)\ (PV=0.5)\ (V)}{(W)} \tag{4.3}$$

where L = loading capacity (mg NH_4^+ adsorbed/g of soil)
C_o = influent concentration (mg NH_4^+/L)
PV = 0.5 = the pore volume to reach 50% breakthrough (unitless)
V = volume of pore volume (L/pore volume)
W = dry weight of soil (g).

Table 4.10 gives the values of L for each adsorption test for which breakthrough occurred. The calculations neglect irregularities in the breakthrough curves. In general, the larger the initial NH_4^+ concentration,

TABLE 4.10. Capacity Based on Breakthrough Data for Loading Portions of the Test

Test	PV = 0.5	W, g	C_o, mg/L	V, L	$L^{(a)}$, mg/g
1	R = 2.5	418.3	1620	0.07246	0.70
2	R = 2.3	519.4	3400	0.120	1.81
3	R = 2.1	415.5	3400	0.096	1.65
4	R = 2.0	311.6	2670	0.072	1.23
5	R = No breakthrough				
6	R = No breakthrough				
7	R = 16.5	155.8	250	0.0357	0.94
8	R = 15	103.9	250	0.0238	0.86
9	R = 87	51.9	25.8	0.01143	0.49

(a) Value is likely low because of volatilization.
PV = Pore volume (unitless).
W = Dry weight of soil (g).
C_o = Influent concentration (mg/L of NH_4^+).
V = Volume of pore volume (L/pore volume).
L = Loading capacity (mg NH_4^+ adsorbed/g of soil).
R = Retardation factor (unitless).

the greater the loading of the soil prior to breakthrough. The experiments do not suggest that a fixed capacity for NH_4^+ adsorption is occurring. In terms of milliequivalents (meq)/100 g (the conventional exchange capacity units), the NH_4^+ loading ranges from 2.7 to 10.1 meq/100 g. These values are inclusive of the total cation exchange capacity of soils on the Hanford Site. A value approximating 2 to 5 meq/100 g is typical for coarse sands, and 5 to 20 meq/100 g is typical for fine sediments.

Table 4.11 lists the NH_4^+ leached from each desorption test, the total NH_4^+ originally loaded on the column, and an estimate of the number of pore volumes required to leach 50% (the equivalent R value for desorption). From knowledge of the bulk density and porosity of the sediment in each test, a K_d (desorption) value can be calculated. This value is also listed in Table 4.11. For comparison purposes, the K_d data from all experiments are summarized in Table 4.12; the desorption K_d values are larger than the adsorption values as commonly found (Barney 1984; Serne and Relyea 1983). This difference would result in slightly lower release and transport of NH_4^+ to the water table in cases where breakthrough occurred because of leaching as opposed to continual loading of NH_4^+. The latter condition may occur at the 216-A-36B crib. The values used in performance assessment calculations ranged from 0 to 7.0. The equivalent R values were 1 to 31.

TABLE 4.11. Percentage NH_4^+ Leached and K_d Desorption

Test	Mass NH_4^+ Leached, mg	Total Mass Adsorbed, mg	% Leached	Estimated Pore Volumes to Leach 50%	Calculated K_d (desorption), mL/g
10	446.7	940.1	47.5	21.5	4.9
11	196.1	383.3	51.2	17	3.9
12	55.7	146.4	38	31.5	7.2
13	34.8	89.4	39	29.2	6.7
14	12.9	25.4	50.6	118.4	26

TABLE 4.12. Summary of NH_4^+ K_ds

Initial NH_4^+ Concentration, mg/L	K_d, mL/g	
	Adsorption	Desorption
3400	0.4 to 1.3	3.9 to 4.9
942	2.2	-
250	3.4 to 5.5	6.7 to 7.2
25	14.8 to 19.1	26

4.5 ADSORPTION CAPACITY RESULTS

A second method of determining the amount of NH_4^+ adsorbed (capacity) to the sediment was to strip adsorbed NH_4^+ with a strong KCl solution (0.5N) in a batch contact. Vacuum extractor tubes from tests 2, 4, 7, and 8 that had been contacted with the sample A solutions and a 1:10 dilution of sample D, respectively, were used. Potassium is well known to compete actively with NH_4^+ for exchange sites. For sediments from tests 2 and 4, 50 g wet weight (~41.5 g dry) were contacted with 100 mL of 0.5N KCl for 5 days. The NH_4^+ released to solution was measured. For sediments from tests 7 and 8, the procedure was repeated three times (three KCl treatments) with 1-day contact between solution removal. Raw data are shown in Table 4.13. The wet sediment was originally saturated with the NH_4^+-laden solution from the adsorption tests; thus, the mass of residual NH_4^+ in the pores was subtracted from the total NH_4^+ leached to calculate the mass of NH_4^+ actually released from the sediment. This value was then divided by the dry weight to estimate the loading. The comparison between loading calculations based on KCl extraction and the original adsorption breakthrough curves is shown in Table 4.14. Except for sediment from test 2, the two independent measurements of the amount of NH_4^+ adsorbed on the sediment agree. This correlation suggests that NH_4^+ adsorption capacity varies with the NH_4^+ concentration of the loading solutions. For the high-NH_4^+ solution, an average value of approximately 1.8 mg NH_4^+/g of soil was obtained. If this value represents the maximum, the total exchange capacity of the soil

TABLE 4.13. KCl Extraction Data for Sediments From Selected Tests

Test	Wet Weight, g	Dry Weight, g	Residual Solution, g	NH_4^+, mg/L	NH_4^+ Mass Exchanged, mg	L, mg/g
2	50.01	41.51	8.50	1420	123.9	2.98
4	50.09	41.57	8.52	735	56.3	1.35
7	50.14	41.53	8.51	306	28.5	
			5.50	150	13.3	
			4.50	26	1.9	
					43.7	1.05
8	50.01	41.51	8.50	277	25.9	
			5.50	160	14.6	
			8.68	23	0.9	
					41.4	1.00

TABLE 4.14. Comparison of Sediment Loading Capacity for NH_4^+ (mg NH_4^+/g of soil)

Test	Based on Breakthrough	Based on KCl
1	0.70	-
2	1.81	2.98(a)
3	1.65	-
4	1.23	1.35(a)
7	0.94	1.05
8	0.86	1.00
9	0.49	-

(a) Only one extraction used; other data suggest that at least two extractions are needed to remove total exchangeable NH_4^+. True value is thus larger.

is approximately 10 meq/100 g. Because the loading values are less than 1.8 mg NH_4^+/g of soil, it also appears that dilutions of the waste solution did not fully saturate the exchange sites.

4.6 CHEMICAL COMPOSITION OF COLUMN LEACHATE

A complete chemical analysis of the effluent from test 1 was performed to aid in data interpretation. Table 4.15 gives the results for each aliquot collected. The effluents show that significant NH_4^+ concentrations and high pH occur after 2.2 pore volumes. The earlier aliquots show elevated calcium, magnesium, strontium, and sodium concentrations, which likely represent flushing of dissolved salts and cations displaced as NH_4^+ adsorbs onto exchange sites. Calcium concentrations reach steady state at 5 to 6 mg/L, which is slightly higher than the 1.2 mg/L present in sample C. Sodium concentrations reach steady state at a value of 30 mg/L, significantly above the influent. The magnesium effluent concentration drops to values below detection limits similar to the waste solution influent. Potassium concentrations remain in a narrow band between 7 and 10 mg/L. There is no potassium peak as for calcium, magnesium, and sodium, possibly because potassium competes favorably with NH_4^+ for exchange sites and is only slowly flushed from the column.

As the pH rises to 10 and higher, the effluent silicon concentration increases to a value around 55 mg/L from a value of 18 mg/L in the sample C influent. The increase probably represents soil dissolution. (The sediment will slowly dissolve and create lower pH values from the extremes found in the NH_4OH distillates.)

4.7 SUMMARY OF FINDINGS

Adsorption of $NH_42NH_4^+$ adsorption onto the Hanford-type soil sediments does not follow a linear adsorption isotherm. The K_d increases as the NH_4^+ concen-tration in solution drops. Between solution concentrations of approximately 15 and 3000 mg/L NH_4^+, the K_d increases from 0.5 to 15 mL/g. Once adsorbed, NH_4^+ will desorb with a small hysteresis (increase in effective K_d). For performance assessment calculations, however, a linear desorption K_d can be used, which is approximately twice as large as the calculated linear adsorption K_d.

TABLE 4.15. Chemistry of Adsorption Column Effluent (Test 1)

		Sample(a)												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Constituent	Sample C	0.5(b)	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5
Al	1.97	<0.03	0.32	0.60	0.73	0.74	0.68	0.76	0.71	0.75	0.74	0.83	0.80	0.92
B	<0.01	0.091	0.069	0.073	0.079	0.072	0.054	0.030	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	<0.01	0.031	0.047	0.051	0.030	0.024	0.015	0.027	0.027	0.027	0.024	0.024	0.024	0.017
Ca	1.2	43.2	19.1	13.2	8.1	6.6	6.4	5.9	6.1	6.4	6.6	6.6	6.6	4.8
Cu	0.190	0.267	0.368	0.533	0.373	0.215	0.038	0.153	0.138	0.123	0.114	0.114	0.099	0.106
Fe	<0.005	<0.005	0.037	0.103	0.127	0.095	0.055	0.039	0.036	0.045	0.030	0.048	0.027	0.047
K	1.1	10.7	8.4	7.0	8.3	9.3	8.8	10.6	10.7	8.1	8.1	8.6	7.0	9.3
Mg	<0.06	8.90	3.90	2.50	0.54	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Mn	<0.005	0.041	0.022	0.014	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Na	1	60	39	33	28	29	28	31	30	30	31	31	32	33
P	0.30	0.20	0.29	0.44	0.40	0.38	0.31	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.19
as PO_4	0.90	0.60	0.87	1.32	1.20	1.14	0.93	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.57
Si	18.6	18.1	17.1	21.2	33.1	44.3	46.5	55.8	54.0	53.7	54.6	55.2	55.2	55.6
Sr	<0.002	0.179	0.085	0.061	0.036	0.030	0.028	0.027	0.027	0.027	0.027	0.027	0.027	0.016
Zr	0.2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
F^-	<0.05	2.0	2.1	3.4	2.5	1.4	1.4	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
Cl^-	<0.5	7	1	1	1	1	1	1	2	0	0	1	1	1
NO_2^-	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
NO_3^-	<0.03	<0.03	<0.03	<0.03	0.3	0.2	0.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SO_4^{--}	2	129	33	11	7	7	7	5	5	6	5	6	6	6
as H_3BO_3	-(c)	0.52	0.39	0.42	0.45	0.41	0.30	0.17	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
pH	-	7.52	7.54	9.21	10.19	10.27	10.46	9.79	9.85	10.10	10.24	10.45	10.15	10.41
Eh	-	398	415	402	355	343	350	329	265	274	324	301	259	207
TOT. ALK(d)	-	75	61	110	304	1325	1849	938	1076	1256	1380	1725	1325	1697
NH_4	1620	0.82	0.75	33	625	940	1580	605	651	801	985	1130	935	1060
Pore Volume		0.65	1.1	1.7	2.2	2.7	3.2	3.5	3.8	4.2	4.5	4.8	5.2	5.8

(a) All values in mg/L with the exception of Eh, which is in mV.
(b) Time in days.
(c) - denotes data not available.
(d) Total Alkalinity as CO_3^{--}.

A Freundlich isotherm was developed to estimate a K_d adsorption for any concentration of NH_4^+ between 20 and 3500 mg/L. The total sediment capacity for adsorption of NH_4^+ appears to be in the vicinity of 1.0 to 1.8 mg/g or between 6 and 10 meq/100 g. This value decreases as the NH_4^+ solution concentration drops below 250 mg/L. In other words, dilute solutions of NH_4^+ appear incapable of completely saturating sediment exchange sites with NH_4^+. For calculations of specific retention capacity, if we assume that no microbial nitrification takes place, the above capacity could be used. Using the crib geometric configuration in Table 4.16 and a bulk density of 1.5 g/cm^3, the soil column below the crib could retain the mass of NH_4^+ shown in Table 4.16. The sediments below the 216-A-36B crib, assuming no nitrification, would become saturated with NH_4^+ in between 0.5 and 1.0 year under the assumed scenario of one declad every 3 days.

TABLE 4.16. NH_4^+ Saturation(a) of Sediments Below the 216-A-36B Crib

Cross Section	500.9 m (5392 ft^2)
Depth to Water Table	86.8 m (285 ft)
Soil Volume	4.35×10^{10} cm^3 (1.537×10^6 ft^3)
Soil Weight, 1.5 g/cm^3 Assumed Density	6.53×10^{10}
NH_4^+ Crib Capacity, 1 mg/g	6.53×10^{10} mg NH_4^+
NH_4^+ Discharge/year Normal Case	1.021×10^{11} mg

(a) Crib saturated with NH_4^+ in ~0.5 year.

5.0 BIOLOGICAL CONVERSION OF AMMONIUM

5.1 BACKGROUND AND OBJECTIVE OF TASK

The rates of conversion of NH_4^+ to NO_2^- and NO_3^- following the release of ammoniated waters to the cribs during PUREX operations is important because of the higher mobility of NO_2^- and NO_3^-, compared to that of NH_4^+. The process whereby NH_4^+ is oxidized to NO_2^- and NO_3^- is referred to as nitrification. Nitrification takes place in virtually all soils and aquatic environments where NH_4^+ is present and environmental conditions are favorable. Adequate moisture and oxygen concentrations are keys to favorable environmental conditions for nitrification. The overall process of nitrification is shown in Equations (5.1) and (5.2).

$$NH_4^+ + 3/2\ O_2 \xrightarrow{6e} NO_2^- + H_2O + 2H^+ \qquad (5.1)$$

$$NO_2^- + 1/2\ O_2 \xrightarrow{2e} NO_3^- \qquad (5.2)$$

Nitrification is mainly, if not exclusively, a biological process carried out by bacteria comprising the family Nitrobacteriaceae. The genera within this family are divided into two groups, depending on whether they oxidize NH_4^+ to NO_2^- or oxidize NO_2^- to NO_3^-. Although the family is comprised of eight genera, most studies have been limited to two: Nitrosomonas that carry out Equation (5.1), and Nitrobacter that carry out Equation (5.2). Nitrifying bacteria are chemoautotrophs; that is, they oxidize NH_4^+ or NO_2^- to derive energy for metabolic functions and synthesize all of their cell constituents from CO_2.

The main environmental factors limiting nitrification in soils and aquatic environments are NH_4^+ concentrations, O_2, CO_2, pH, and temperature. Maximum nitrification in the northwestern United States occurs at temperatures between 20° and 25°C (Mahendrappa, Smith, and Christianson 1966). The pH range for nitrification appears to be between 4.0 and 8.0; however, some nitrification may occur at higher pHs (Schmidt 1982). There is no evidence that assimilable carbon is ever limiting to nitrifiers (Schmidt 1982). On the other hand, O_2 depletion in soil or groundwaters will likely cause nitrification to cease. Another environmental factor relevant to nitrification in Hanford sediments between the ground surface and the unconfined aquifer is moisture levels. Desiccation reduces nitrifying populations and, therefore, nitrification rates are generally not expected to be high in the dry vadose zone at the Hanford Site. However, the continual discharge of liquids to the cribs raises the moisture content in the vadose zone below the cribs to optimum values.

Because nitrification is carried out by a limited number of bacteria, the process is particularly sensitive to environmental perturbations. Nitrifying bacteria are considered to be the most sensitive of the physiological groups of bacteria to exotic chemicals that reach their environment (Schmidt 1982). A number of inorganic and organic substances have been shown to inhibit nitrification, including numerous aromatic and aliphatic organic compounds, carbon disulfide, nickel, cadmium, zinc, copper, lead, mercury, chromium, and vanadium (Babich and Stotzky 1985; Schmidt 1982).

Because of the potential importance of biological nitrification in governing the fate of NH_4^+ released into Hanford soils and groundwater, we decided that nitrifying bacteria indigenous to Hanford soils and groundwater would be studied to determine their role in converting NH_4^+ to NO_2^- and/or NO_3^-. The objective of this task was to quantify the population densities of nitrifying bacteria indigenous to Hanford soils and groundwater and to determine the rate constant for conversion reactions. An additional experiment was run to identify the population densities of denitrifying bacteria in Hanford soils and groundwater. Denitrifying bacteria convert NO_3^- to N_2O and/or N_2 and represent a means by which NO_3^- in the Hanford unconfined aquifer may be removed.

5.2 DESCRIPTION OF METHODS

Population densities for nitrifiers (both NH_4^+ and NO_2^- oxidizers) were determined by the most probable number (MPN) method of Schmidt and

Belser (1982). Denitrifiers were determined by the MPN method of Tiedje (1982). A theoretical account of the MPN method is given by Alexander (1982). The methods involve incubating soil or groundwater samples in a medium that selects for the development of the organism(s) of interest. A quantitative assessment of population densities is based on readily recognizable transformations occurring in the medium following incubation; i.e., the formation of NO_2^- or NO_3^- for nitrifying bacteria and the disappearance of NO_3^- for denitrifying bacteria. On the basis of probability theory, it is possible to calculate, from the number of positive and negative tubes receiving a certain quantity of inoculum, the MPN of bacteria (nitrifiers or denitrifiers) in the inoculum. Multiplying the results by the appropriate dilution factor gives the MPN value for the sample.

Nitrification potential in Hanford soil and groundwater samples was determined by the method of Schmidt and Belser (1982). Groundwater samples (500 mL) and Hanford soil (50 g of soil in 500 mL of dH_2O) were incubated in 1000-mL flasks. Each flask was amended to 106 mg/L NH_4^+ as $(NH_4)_2SO_4$ and was incubated under aerobic conditions in a New Brunswick Controlled Environment Incubator Shaker(a) at 25°C for 35 days. Aerobic conditions were maintained by rotary shaking at 150 rpm. Two controls were used for each groundwater and soil sample. One control, treated as described except without NH_4^+ amendment, was used to monitor background nitrification rates. The other control was heat sterilized, amended with NH_4^+, and used to monitor abiotic NH_4^+ conversions.

Periodically, aliquots from each sample and corresponding controls were analyzed for NH_4^+, NO_2^-, and NO_3^-. NH_4^+ was analyzed using an Orion(b) (Model 951201) gas-sensing specific-ion electrode; NO_2^- was measured of calorimetrically after treatment with N-(1-naphthyl)ethylene diamine dihydrochloride; and NO_3^- was measured by ion chromatography. Except for the soil sample, background levels of NO_3^- and NH_4^+ interfered with measurements of their production or loss; therefore, NO_2^- accumulation was used to determine nitrification rates.

(a) Controlled Environment Incubator Shaker is a registered trademark of New Brunswick Scientific, Edison, New Jersey.

(b) Orion Research, Cambridge, Massachusetts.

First-order rate constants were obtained from regression analysis of the log plot of NO_2^- accumulation versus time. Second-order rate constants were obtained by dividing the first-order rate constant by the nitrifying bacteria concentration.

5.3 RESULTS AND DISCUSSION

Bacterial population densities for Hanford groundwaters and the selected Hanford sediment are shown in Figure 5.1. These data represent the first known analysis of Hanford groundwaters for microbial populations and are, therefore, difficult to interpret. However, based on previous analysis of groundwaters in other locations in the United States, the population densities are not unreasonable (Bitton and Gerba 1984). Population densities for total heterotrophs and nitrifying bacteria were positively correlated with NH_4^+ levels in the groundwaters (Figure 5.2). These data suggest an increase in bacterial population with increasing chemical contamination of the groundwaters.

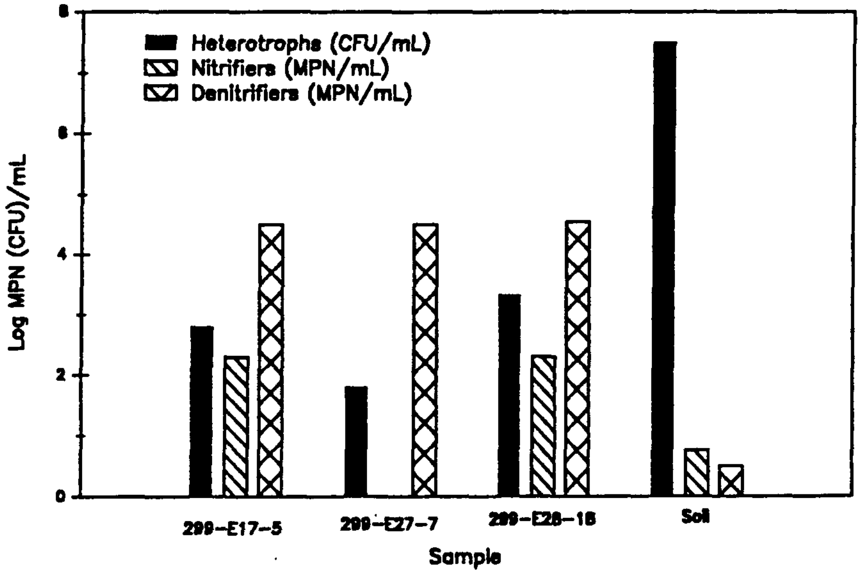

FIGURE 5.1. Bacterial Population Densities Observed in Selected Hanford Groundwaters and One Soil Sample (CFU = colony farming unit; MPN = most probable number)

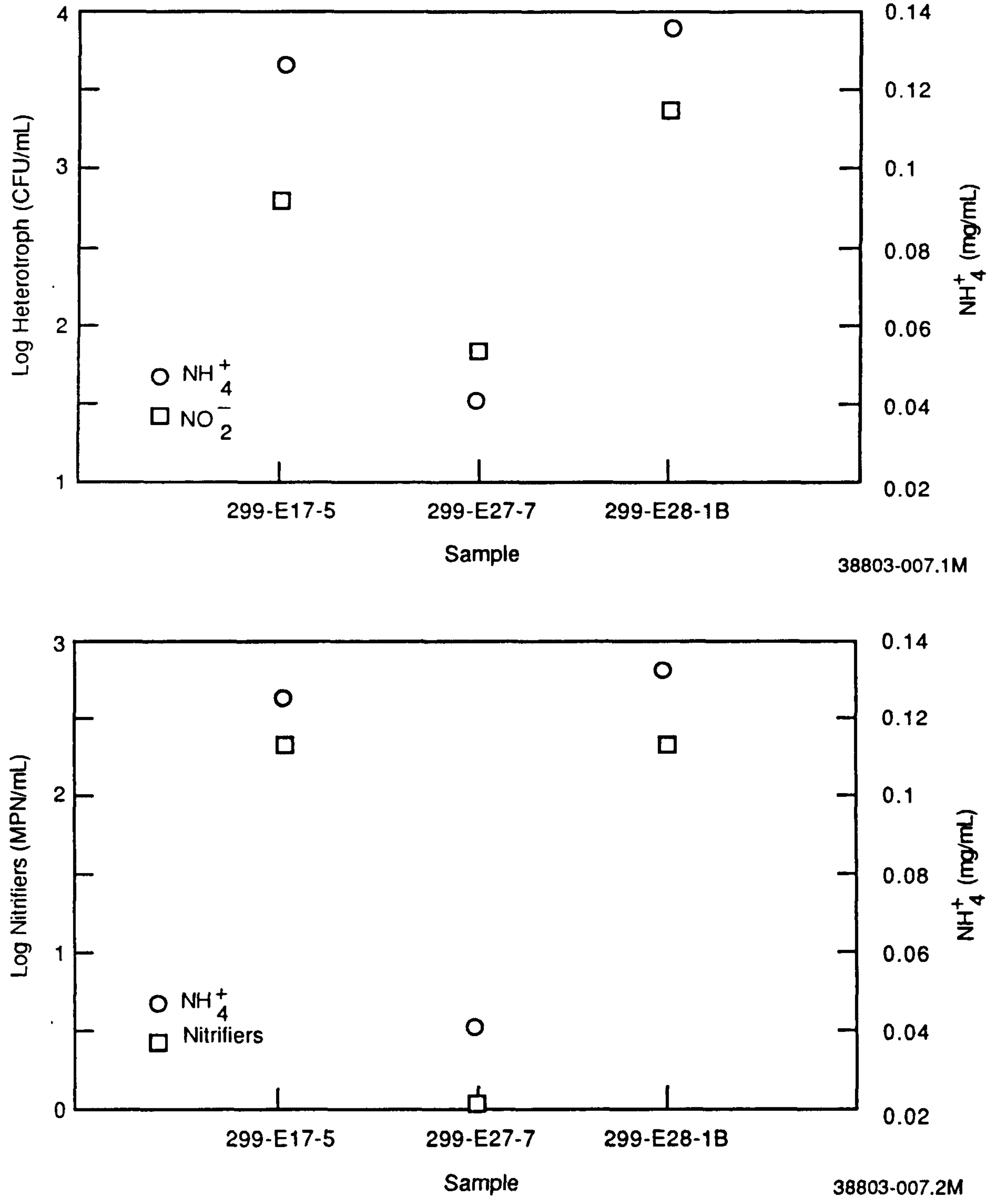

FIGURE 5.2. Population Densities for Heterotrophs and (a) Nitrifiers (b) and NH$_4^+$ Concentrations in Selected Hanford Groundwaters (CFU = colony farming unit; MPN = most probable number)

Population densities of denitrifiers were very high (3.13×10^4 MPN/mL) in the groundwaters. These organisms only denitrify under anaerobic conditions and may not be active under in situ conditions; however, the population levels observed indicate that under appropriate conditions (i.e., reduced oxygen levels) denitrification may rapidly occur in Hanford groundwaters. Determination of oxygen beds and denitrification rates were, unfortunately, beyond the scope of this study.

Nitrification rates for Hanford groundwaters and soil are given in Table 5.1. Two of the groundwaters and the soil sample showed significant nitrification during the 35-day incubation period; however, in each sample, nitrification did not begin until approximately the 20th day of incubation (as shown in Figure 5.3 for the Hanford soil). This observation is not unusual for microbial processes, and probably reflects the adaptation and enrichment period required by the nitrifying bacteria to the experimental conditions.

First-order rate constants in groundwater samples 299-E-17-5 and 299-E-28-18 were similar and reflect the high numbers of nitrifying bacteria observed in these samples. Groundwater sample 299-E-27-7 did not exhibit any significant nitrification within the 35-day incubation period; however, data collected on days 31 and 35 suggest that some conversion of NH_4^+ may be occurring (data not shown). Groundwater sample 299-E-27-7 was collected from a well northeast of the 241-C tank farm and did not show any elevated

TABLE 5.1. Bacterial Concentrations, Pseudo-First-Order, and Second-Order Rate Constants for Groundwaters and Soil Used in NH_4^+ Conversion Studies

Sample	First-Order Rate Constant, day^{-1}	Bacterial Concentrations, organisms/L	Second-Order Rate Constant, $liters \bullet organisms^{-1} \bullet day^{-1}$
299-E-17-5	0.3718	1.93×10^5	19.26
299-E-27-7	NUD[(a)]	0.00	NUD
299-E-28-18	0.3162	2.00×10^5	15.81
Hanford Soil	0.577	2.50×10^2	231.0

(a) NUD - nitrification undetected.

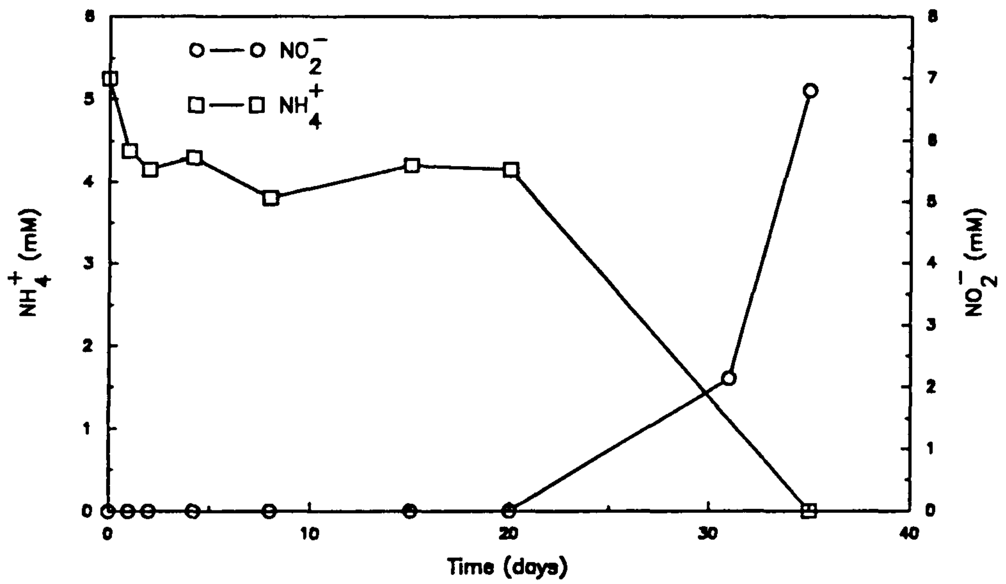

FIGURE 5.3. Conversion of NH_4^+ to NO_2^- in Hanford Soil

concentrations of constituents indicative of waste disposal (Appendix A). This sample was assumed to represent Hanford groundwater unimpacted by disposal activities. The low population densities and absence of significant nitrification in groundwater sample 299-E-27-7 support this assumption. However, the indication that NH_4^+ conversion is beginning to occur in 299-E-27-7, coupled with the high nitrification rates in 299-E-17-5 and 299-E-28-18, suggests that microorganisms in Hanford groundwaters can proliferate and become metabolically active under favorable environmental conditions (i.e., adequate nutrients, pH, temperature, etc.).

The Hanford soil used in this experiment showed complete conversion of NH_4^+ to NO_2^- (see Figure 5.3); however, NO_3^- did not accumulate during the incubation period and remained below 1 mg/L. This observation contradicts what is commonly seen in most agricultural soil (e.g., the rapid conversion of NO_2^- to NO_3^-; Schmidt 1982). The reason for this anomaly is unknown at this time. Two possible explanations are 1) not enough time has elapsed for the NO_3^- to be converted to NO_3^-, or 2) the organisms responsible for converting NO_2^- to NO_3^- are being inhibited in the Hanford soil.

The results of this work indicate that Hanford groundwaters are inhabited by bacterial populations with the ability to convert NH_4^+ entering their environment. Furthermore, it is believed that the total bacterial population of Hanford groundwaters increases with increasing chemical contamination. This pattern may reflect an increase in nutrients for indigenous microbial populations. Conversion rates have been determined to support the modeling effort in Section 7.0 so that the effects on groundwater concentrations can be estimated. In addition, the high levels of denitrifiers, as well as the observed nitrification rates, suggest that possible in situ biological amelioration techniques may be feasible for remediating NO_3^--contaminated Hanford groundwaters.

6.0 VOLATILIZATION OF AMMONIA

An important aspect of the problem is to estimate NH_3 releases to the air to determine if volatilization diverts significant amounts of NH_3 from the soil column and whether these NH_3 emissions violate the CERCLA regulatory limitation of 45.4 kg (100 lb) of NH_3 during a single day. The waste stream is discharged to a crib, which consists of gravel fill laid at the bottom of a trench with a perforated pipe extending along the top of the gravel (see Appendix C). The gravel is covered with a plastic vapor barrier, and the crib is then backfilled to the original grade. The crib includes a vertical pipe that penetrates the earthen fill and gravel to the bottom of the trench and is used to monitor the level of liquid in the gravel. The perforated pipe laid on top of the gravel conducts waste to the crib and ends with a vertical riser that serves as a vent.

Potential paths for the release of NH_3 from the crib to the air are

- upward by diffusion through the earthen fill
- upward by diffusion through the monitor or vent pipes
- upward through the vent pipe by displacement of air in the pipe leading to the crib.

The peak concentration of NH_3 discharged to the 216-A-36B crib has been estimated to be 12,000 mg/L as NH_4^+, which is 0.7 mole NH_3 in water. As discussed below, this concentration is pertinent to bounding calculations of the release of NH_3 through vent pipes.

The wastes are moderately dilute aqueous NH_3 solutions that are extremely dilute in anions other than hydroxide. Except when extremely dilute or in the presence of appreciable acid, the partial pressure of NH_3 over ammoniated water is approximately proportional to the molality of the NH_3 in the water. The constant of proportionality is readily available in the literature (Perry 1963), and is approximately 0.05 atm/mole at 50°C, the temperature at which the waste enters the crib. Hence, the equilibrium partial pressure of NH_3 is 0.035 atm over a 0.7-mole solution at 50°C. The corresponding mole fraction of NH_3 in air would also be 0.035 atm at a total pressure of 1 atm, and can be converted using the ideal gas law to a concentration of NH_3 in 20°C air to give 1.5 x 10^{-6} g-mole/cm3.

Diffusion of NH_3 in air at 1 atm and 20°C occurs with a binary diffusion coefficient of approximately 0.2 cm^2/s (Welty, Wicks, and Wilson 1976). Assuming a typical void fraction of 35%, the effective diffusivity is approximately 0.08 cm2/s. The flux of NH_3 in a pipe is given by Fick's first law of diffusion for dilute systems (Bird, Stewart, and Lightfoot 1960):

$$N = A\ D\ \delta C/\delta L \tag{6.1}$$

where N = rate of mass transfer (g-mole/s)
A = area across which the diffusion occurs (cm^2)
D = diffusivity (cm^2/s)
δC = change in concentration of NH_3 in air (g-mole/cm^3)
δL = change in distance over which the change in concentration occurs (cm).

The largest diameter of the pipes venting the cribs is 25 cm (10 in.), with a cross-sectional area of 506.7 cm^2 (78.5 in.^{2}). The shortest length is approximately 213 cm (7 ft). Therefore, the loss of NH_3 by steady-state diffusion in a pipe would be limited to (506.7)(0.2)(1.5 x 10^{-6})/(213) = 7 x 10^{-7} g-mole/s, or 2 x 10^{-3} lb/d of NH_3. Hence, the release of NH_3 by this means cannot approach the 45.4-kg (100-lb/d) limit, and will have no significant effect on the source to the groundwater.

The maximum concentration of NH_3 in air in the pipe leading to the crib would be 1.5 x 10^{-6} g-mole/cm^3, or 2.6 x 10^{-5} kg/L. The pipe leading to the crib is up to 25 cm (10 in.) in diameter; the volume per length is then 51 L/m (0.55 ft^3/ft). The length of pipe leading to the crib is on the order of 1600 m (5250 ft). Hence, the amount of NH_3 that could reside in such a pipe and be expelled to the air when waste flows down the pipe is on the order of (1600)(51)(2.6 x 10^{-5}) = 2.1 kg (4.6 lb). Since, at most, only a few such operations occur per day, the amount of NH_3 expelled to the air by this means could not approach the 45.4-kg/d (100 lb/d) limit, and would not significantly affect the source term to the groundwater.

The principal path for release of NH_3 to the air appears to be by steady-state diffusion through the soil overlying the area of a crib. Even using the maximum hourly discharge rate to the crib, which is intermittent, the maximum amount of NH_3 sent to this crib would be at a rate on the order of 4100 kg/d (9000 lb/d). Hence, the estimated amount of volatilization per day can be compared with 4100 kg (9000 lb) to determine whether the source of NH_3 to the groundwater is significantly affected.

To calculate an upper bound for this release, we disregard the plastic sheet laid on top of the gravel in the crib (i.e., assume that it has deteriorated and no longer is a barrier) and assume that NH_3 at some constant mole fraction is present in the air in the interstices in the soil at the top of the gravel. The diffusion process, then, is through a porous medium between the top of the gravel, held at a particular mole fraction, and the top of the soil, held at zero-mole fraction. The rate of diffusion can be calculated from the mole fraction profile in the air in the soil, where the mole fraction profile satisfies Laplace's equation in accordance with Fick's second law of diffusion at steady state.

To solve Laplace's equation for this case, we can approximate the diffusion process as though it were from a fictitious line source of mass, located somewhere below the crib, to the plane representing the top of the soil. The surfaces of constant diffusion potential (i.e., constant mole fraction of NH_3) are curved for this approximation. The location of the fictitious line source can be set so that a particular surface of constant potential falls approximately at the top of the gravel in the crib. The strength of the line source can then be chosen so that the value of the potential that is constant over this surface is equal to the mole fraction assumed to exist at the top of the gravel. Finally, existing theory on the solution to Laplace's equation for this case (Lamb 1932) can be used to estimate the diffusive flow of mass from the line source to the surface (itself a surface of constant potential), which is also the flow of mass from any particular surface of constant potential, including the surface representing the top of the gravel. Hence, the flow from the fictitious line source is the estimated rate of NH_3 release from the top of the gravel to the air. This calculation is discussed in Appendix B.

The depth to the top of the gravel is 6.4 m (21 ft); the bottom of the crib is 0.91 m (3 ft) below the top of the gravel. The bottom of the crib is 3.35 m (11 ft) wide, and the side slope of the excavation is 1:1.5.

An equation describing the release from the top of the crib to the top of the soil based on the line source approximation described above is

$$N = 2 \pi L D \frac{C_o}{1.422} \tag{6.2}$$

where N = rate of release of NH_3 (g-mole/s)

L = length of the crib (cm)

D = effective diffusivity of NH_3 in the soil (cm^2/s)

C_o = concentration of NH_3 in air at the top of the gravel ($g\text{-mole}/cm^3$).

The development of Equation (6.2) and the determination of the 1.422 factor are discussed in Appendix B.

The characteristic time for relaxation of a non-steady-state diffusion profile in this case is on the order of 5 days. Hence, it is the NH_3 concentration averaged over a few days that is the driving force for steady-state diffusion across the soil. An estimate of this average would be that in equilibrium with the concentration of NH_3 in the waste stream averaged over the stream's 20-day flow cycle. As discussed above, the average molality is 0.7, and the equilibrium NH_3 concentration in air would be 1.5×10^{-6} $g\text{-mole}/cm^3$ (1.62×10^{-3} lb/ft^3).

Using $L = 152$ m (500 ft), $D \approx 0.08$ cm^2/s, and $C_o \approx 1.5 \times 10^{-6}$ $g\text{-mole}/cm^3$, the rate of release of NH_3 is 8.1×10^{-3} g-mole/s (26 lb/d). The calculation is conservative, in that a maximum discharge rate of 4100 kg/d (9000 lb/d) was assumed, the effect of the vapor barrier was neglected, and the model corresponds to release of NH_3 from a region much larger than the gravel portion of the crib. Even so, we estimate that the 45.4-kg/d (100-lb/d) CERCLA limit will not be exceeded, and that the maximum amount of NH_3 volatilizing from the crib is on the order of 11.8 kg (26 lb) or 0.3% of the maximum estimated amount discharged to either crib. Because this amount has a negligible impact on concentrations to the groundwater, NH_3 volatilization has not been included in the transport modeling analysis.

7.0 HYDROGEOLOGY AND CONTAMINANT MOVEMENT TO VARIOUS CONTROL POINTS

This section describes the predictions of NO_3^- concentration in the unconfined aquifer and the Columbia River.

7.1 HYDROGEOLOGY OF THE SOUTHEASTERN PORTION OF THE 200-EAST AREA

The 216-A-36B crib is located in the southeast corner of the 200-East Area of the Hanford Site and penetrates 7.32 m (24 ft) below land surface. Liquid effluents discharged to the crib infiltrate through the vadose zone to the water table. The effluents then migrate in the unconfined aquifer toward the Columbia River.

7.1.1 Vadose Zone

The vadose zone consists predominantly of alluvial sediments informally known as the Hanford Formation. Silty sands of the upper 4.6 m (15 ft) are underlain by alternating layers of gravelly sand and medium sand that grade into predominantly gravelly sand below approximately 46 m (150 ft) in depth (Appendix A, Figure A.1).

The vadose zone beneath the 216-A-36B crib extends from the bottom of the crib 7.3 m (24 ft) below land surface to the water table at an elevation of 124 m (406 ft) (Table 7.1). The soil profile is 86.9 m (285 ft) in length.

TABLE 7.1. Characteristics of the 216-A-36B Crib

Bottom Area	501 m^2 (5,392 ft^2)
Land Surface Elevation	218 m (715 ft)
Water Table Elevation	123 m (406 ft)
Crib Depth	7.3 m (24 ft)
Unsaturated Soil Column	86.9 m (285 ft)

Six soil samples were collected from an excavation for the 241-AP tank farm in the 200-East Area near the 216-A-36B crib (Sewart et al. 1987). The soil type numbers in Appendix A, Figure A.1 identify the stratigraphic layers below the cribs as described by field geologists and matched with the six samples. Moisture-retention characteristics were measured for the samples, and the corresponding unsaturated hydraulic conductivity relationships were calculated. The specific discharges from the cribs were used to fix the unsaturated hydraulic conductivity and moisture content by assuming unit gradient conditions in the soil profile. The unsaturated hydraulic conductivities and moisture contents were used in the estimations of travel times through the vadose zone.

The specific discharge (q) was calculated as follows

$$q = Q/A \tag{7.1}$$

where A is the bottom area of the crib (see Table 7.1) and Q is the average discharge to the crib. The volume of the soil column beneath the crib is approximately 43,520 m^3 (1,536,720 ft^3). The 1985-1986 average discharge to the crib was 65,990 m^3/yr (2,330,000 ft^3/yr). The specific discharge equals 0.360 m/d (1.18 ft/d) for the 216-A-36B crib. This results in 15 pore volumes for an assumed 10% effective porosity and 3.8 pore volumes for an assumed 40% effective porosity. The affected volume beneath the crib is assumed to be vertically beneath the area of the crib bottom with no lateral seepage. The unsaturated hydraulic conductivities and resulting moisture contents for the six samples are listed in Table 7.2. Comparison of the specific discharges with hydraulic conductivities indicates that saturated conditions exist in samples 5 and 6. However, these soil types are located near the surface and are assumed to not occur below the trench bottom.

Groundwater travel time through the vadose zone beneath the crib was estimated with the equation

$$T = L \cdot \theta / q \tag{7.2}$$

TABLE 7.2. Sample Characteristics for the 216-A-36B Crib

Sample	K_s, cm/d	$K(\theta)$, cm/d	θ
1	220	36.0	0.286
2	52	36.0	0.496
3	160	36.0	0.403
4	200	36.0	.340
5	2.7	2.7	0.428
6	1.2	1.2	0.417

K_s = saturated hydraulic conductivity.
$K(\theta)$ = unsaturated hydraulic conductivity.
θ = moisture content (vol%).

where T = time
L = vertical length of soil column
θ = volumetric moisture content
q = specific discharge.

The total travel time through the soil profile was determined by summing the calculation for each layer as shown in Appendix A, Figure A.1. For calculational purposes, the top of the soil column was assumed to begin at the base of the second layer (silty sand), and the length of the bottom layer was adjusted to match the soil profile length to the water table. The travel time for the soil profile characteristics is 0.208 yr. Travel time is given for the effective porosity equal to the calculated moisture contents.

7.1.2 Saturated Zone

The unconfined aquifer at the Hanford Site occurs in the fluvial sediments of the Ringold Formation and the glaciofluvial Hanford Formation sediments (Graham et al. 1981). The lower portion of the Ringold Formation consists of relatively impermeable, fine-grained sediments that form the lower boundary of the aquifer where they occur. In other portions of the site, the basalt bedrock forms the base of the aquifer. The principal water-bearing layer consists of silty sands and gravels of the Middle Ringold Formation. The sands and gravels of the Middle Ringold Formation and the Hanford

Formation sediments constitute a highly permeable aquifer system. Hydraulic conductivities may exceed several thousand meters per day with transmissivities of hundreds to thousands of meters squared per day. Hydraulic conductivities may exceed several thousand meters per day with transmissivities of hundreds to thousands of meters squared per day.

Groundwater travel times through the unconfined aquifer were determined with a model of the aquifer based on the variable thickness transient code (Cearlock, Kipp, and Friedrichs 1975; Kipp et al. 1976; Reisenauer 1979a, 1979b, 1979c). Groundwater streamlines and the resulting travel times from the crib to a 30.5-m (100-ft) site boundary, to the future control zone [2 km (1.24 mi) downstream], and to the Columbia River were determined to be 0.023, 1.7, and 48 years, respectively. All travel times are based on an effective porosity of 10%. The travel time to the 30.5-m (100-ft) site boundary was determined by an inspection of travel times scaled from longer path lengths. The 2-km (1.24-mi) values are based on an inspection of travel times for streamlines intersecting the future control zone at approximately 2 km (1.24 mi). The travel times to the Columbia River are based on an average of 10 streamlines. Streamlines from the southeast corner of the 200-East Area to the Columbia River are shown in Figure 7.1.

7.2 MODELING ANALYSIS OF THE AMMONIA DISCHARGES

The rates of NH_3 discharge to the 216-A-36B crib were discussed previously. This section of the report describes NH_4^+ movement through the subsurface. The process is characterized by NH_4^+ adsorption to the soil material and by nitrification reactions that result in the conversion of NH_4^+ to NO_2^- and NO_3^-.

In the transport model based on the TRANSS code (Simmons, Kincaid, and Reisenauer 1986), the NH_4^+ was treated as a known quantity or inventory. This quantity was transported through the soil profile and into the groundwater regardless of whether it was NH_4^+, NO_2^-, or NO_3^-. The transformation of NH to NO_4^- was assumed to not affect the properties of the quantity being transported.

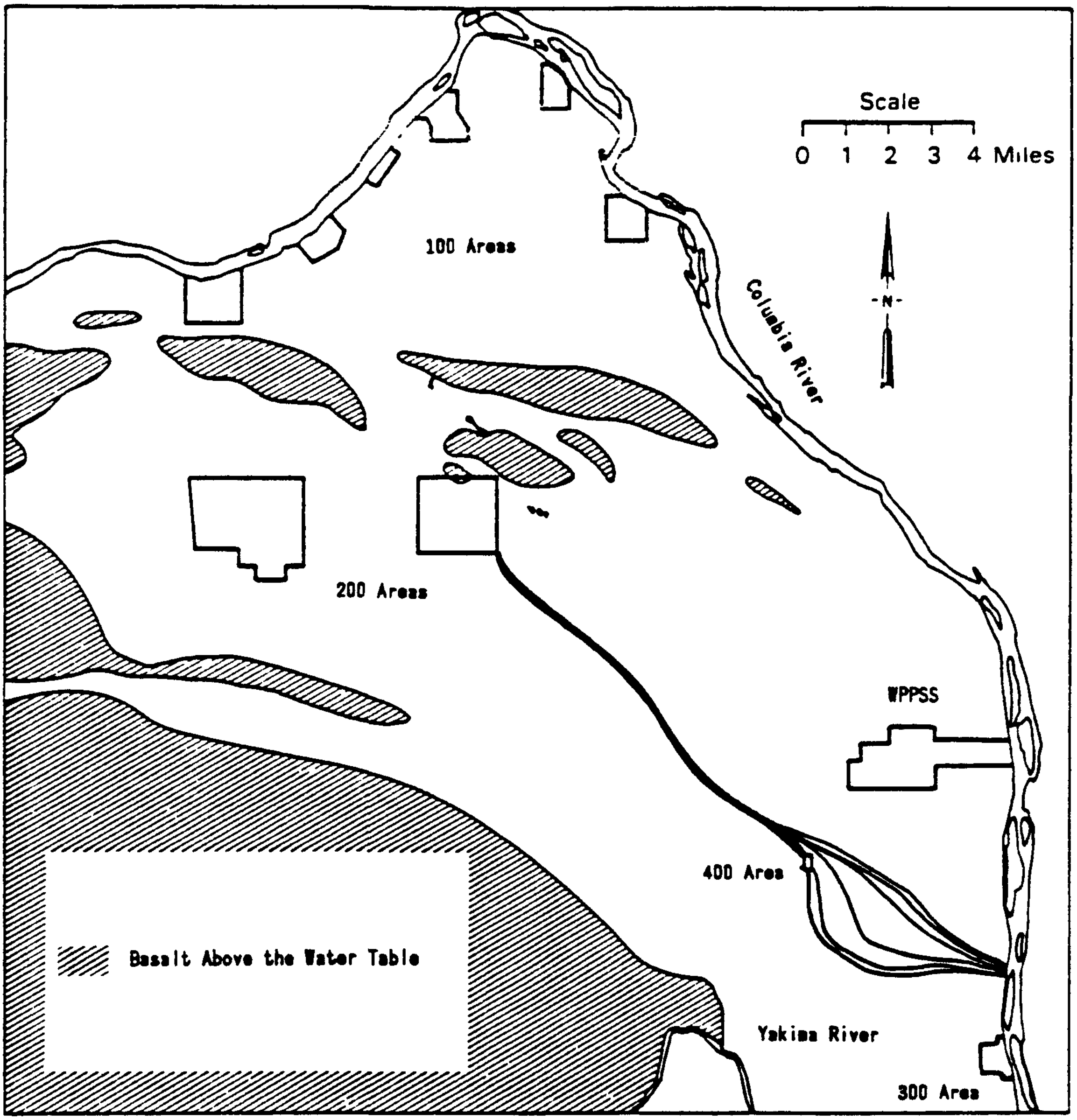

FIGURE 7.1. Streamlines from the Southeast Corner of the 200-East Area to the Columbia River

7.2.1 Ammonia Transformation

Simultaneous movement of interacting nitrogen species from the 216-A-36B crib to the water table and from the entry point into the saturated groundwater zone to a 2-km (1.24-mi) distance was investigated with a numerical model. The CHAIN code (Van Genuchten 1985) was used to simulate the movement of interacting nitrogen species through a semi-infinite soil column. The CHAIN code solves the set of coupled differential equations that describe the one-dimensional convective-dispersive transport of four chain members. Major assumptions and limitations of the CHAIN code are steady-state flow conditions, a homogeneous soil, and systems that are initially free of solutes. This prevents using the CHAIN code for combined unsaturated and saturated flow. Therefore, these regions must be modeled separately.

The CHAIN code can simulate the three-species nitrification chain

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \qquad (7.3)$$

and requires as input the first-order rate constants for decay from NH_4^+ to NO_2^- (k_1) and from NO_2^- to NO_3^- (k_2), and the retardation factor of each species.

7.2.1.1 Rate Constants for Decay

First-order nitrification rate constants (k_1) for Hanford groundwaters and soil were listed in Table 5.1. In this analysis the lower value of k_1 (0.316 day^{-1}) for Hanford groundwaters and the reported value of k_1 (0.577 day^{-1}) for Hanford sediments were used.

The determination of nitrification rate constants described in Section 5.0 did not provide rate constants for the conversion of NO_2^- to NO_3^- (k_2). In the soil, the fate of the NH_4^+ is not yet clear. In this analysis, only the conversion of NH_4^+ to NO_2^- in the soil is estimated. It is assumed that this NO_2^- is rapidly converted to NO_3^- in the groundwater. In the groundwater, it is clear that NO_2^- is converted to NO_3^-, although k_2 has not been determined. Three species-decay values for Columbia silt loam were reported by Misra, Nielson, and Biggar (1974). They reported a k_1 value of 0.24 day^{-1} (very close to the values determined for Hanford groundwaters) and a k_2 value of 0.024 day^{-1} for conversion of NO_2^- to NO_3^-. The value of k_2 reported by Misra, Nielson, and Biggar (1974) was used in the groundwater analysis.

7.2.1.2 Contaminant Movement Through the Vadose Zone Beneath the 216-A-36B Crib

The base of the 216-A-36B crib is 868.7 m (285 ft) above the water table. The crib receives a 6-h pulse of NH_4^+ every 3 days, and receives slightly contaminated waste water between pulses. A unit hydraulic study of the soil profile beneath the crib indicates that the specific flux of water is approximately 2.7 cm/h. The same calculations indicate that the volumetric water fraction is approximately 0.33. A dispersion coefficient of 54.1 cm^2/h was used.

The crib receives NH_4^+ at 3-day intervals. Three days is small compared to the time scale (years) of the discharge, so it was assumed that the soil profile received a constant input of NH_4^+. Because the profile receives a nearly constant supply of NH_4^+, it was assumed that no more NH_4^+ could be adsorbed and the NH_4^+ was not retarded in the model. The NO_2^- also was not retarded. The constant rate k_2 was given a value of 0.577 day^{-1}.

Steady-state simulations were made of the NH_3 movement through the soil column. The input concentration of NH_4^+ was 1.0. The NH_4^+ had been totally converted to NO_2^- by a depth of 40 m (131 ft). The concentration of NO_2^- arriving at the water table was 1.0.

7.2.1.3 Contaminant Movement Through the Saturated Zone

All of the NH_4^+ had been converted to NO_3^- at the 2-km (1.24-mi) boundary. This analysis indicates that if the rate constants for decay are appropriate for the saturated zone, then no matter how much NH_4^+ reaches the water table, all of it will be converted to NO_3^- by a distance of 2 km (1.24 mi).

We wanted to know what species arrived at a 2-km (1.24-mi) distance from the crib for the various cases. A 2-km (1.24-mi) pathline with a pore water velocity of 14 cm/h and a porosity of 0.33 was modeled. A steady influx of NH_4^+ with a unit concentration was introduced into the groundwater system. No retardation was applied. A dispersion coefficient of 54.0 cm^2/h was used. The k_1 and k_2 values described previously for the groundwater as in the other cases were used.

In the unsaturated and saturated zones, the CHAIN code tells us that the conversion process is rapid and that retardation in the unsaturated zone has little effort. Also, because no NH_4^+ reaches the groundwater, no retardation should be assumed in the groundwater. Consequently, the most meaningful modeling runs with combined saturated and unsaturated flow will be with a retardation of 1.

7.2.2 Estimation of Contaminant Concentrations in the Groundwater

Four cases of NH_4^+ transport were investigated for the 216-A-36B crib. For each case, concentrations were predicted at the same three points downgradient from the cribs in the unconfined aquifer as were discussed previously. These points are 1) the site boundary assumed to be 30.5 m (100 ft) downgradient, 2) a future control zone assumed to be 2 km (1.24 mi) downgradient, and 3) discharge at the Columbia River.

The investigation was conducted with the TRANSS code, which incorporates a simplified one-dimensional approach to contaminant transport and may be used for radioactive or nonradioactive species. Simmons, Kincaid, and Reisenauer (1986) describe the information required by the model. The primary input includes the groundwater travel times through the unsaturated and saturated zones, the flux and concentration of contaminated water discharged to the crib, and the coefficients that describe the interaction between the dissolved contaminant and the particular soil column and aquifer materials. The latter elements include coefficients of retardation and dispersion. The K_d of NH_4^+/NO_3^- from which retardation is calculated was reported in Section 4.0 for a typical soil type underneath the crib as part of this investigation.

7.2.3 Results of Modeled Scenarios

The predicted concentrations of reportable quantities in the groundwater and the Columbia River resulting from the different cases are summarized in Table 7.3. These concentrations represent the total NO_3^- in the groundwater because analysis of the NH_3 transformation indicated rapid conversion to NO_3^-.

The NO_3^- concentrations predicted in the aquifer (see Table 7.3) are higher than concentrations observed in wells monitoring the crib during 1985, which range from 92 to 140 mg/L (Law and Schatz 1986). The observed concentrations range from 92 to 140 mg/L. This discrepancy may be caused by the fact that equilibrium has not yet been attained in the soil column and groundwater beneath the crib. More recent groundwater samples collected in September 1987 show 240 mg/L NO_3^-, much closer to the predicted 320 mg/L. The

TABLE 7.3. Predicted NO_3^- Concentrations in the Groundwater Resulting from Discharge of NH_4^+ to the 216-A-36B Crib

	Location	Normal Operations, mg/L	Past Operations(a), mg/L
R=1	Facility Boundary	430	320
	2 kilometers	430	320
	Columbia River(b)	3×10^{-4}	1.7×10^{-4}
R=31	Facility Boundary	430	320
	2 kilometers	430	320
	Columbia River	3×10^{-4}	1.7×10^{-4}

(a) Average from 1984 through 1987.
(b) Concentration in the Columbia River.
R = retardation factor.

remaining discrepancy may be explained by the fact that there were only 18 discharges containing NH_4^+ in FY 1987 versus the yearly average of 87 decladding operations.

The concentrations reported in the Columbia River are far below those of the groundwater at the discharge point, because of dilution with the river. The estimated concentrations are assumed to be uniformly mixed in the river.

The effect of leaching with clean water at the same discharge rate to the crib after equilibrium concentrations are obtained was also modeled. Figures 7.2 and 7.3 show groundwater concentrations at the crib boundary and the future control zone, respectively. They are plotted with time from the period at which the leach water was initiated. Results show that NO_3^- concentrations begin to drop at the crib boundary within 75 days. The NO_3^- concentration does not decrease sooner because of the retention of an estimated 31,000 kg (68,000 lb) of converted NO_3^- in the soil column. The NO_3^- concentrations begin to fall at the future control zone within 2 years of initiating the leach water.

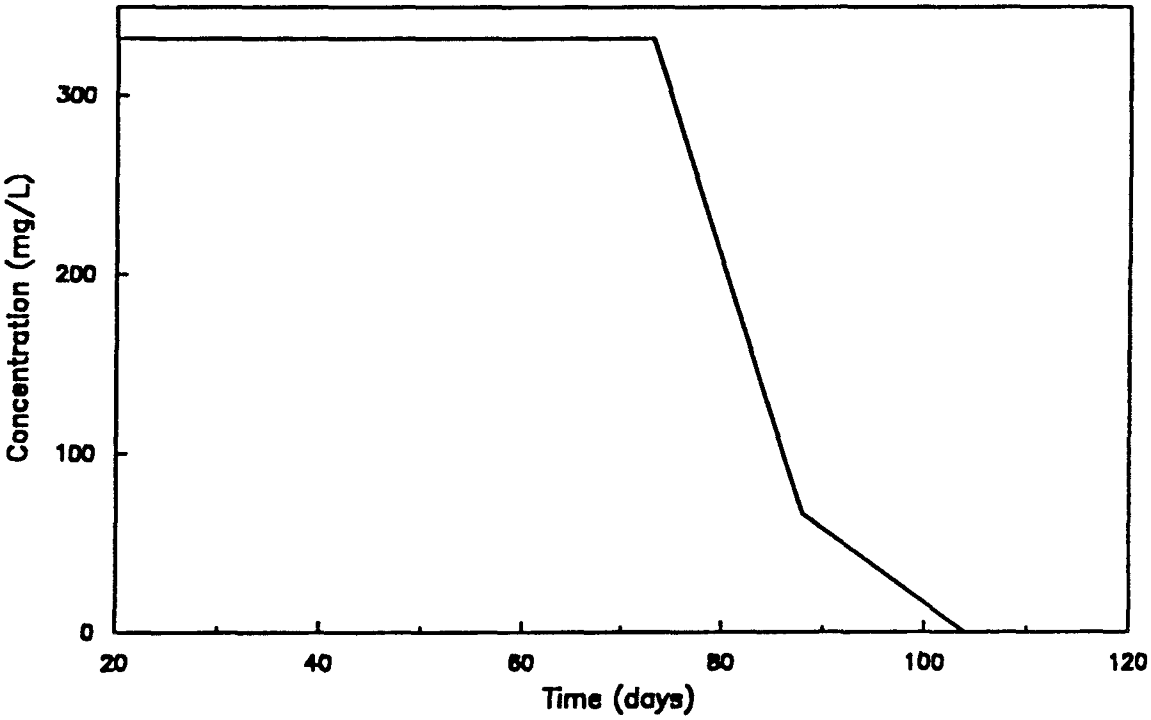

FIGURE 7.2. NO_3^- Concentrations in the Groundwater, at the Crib Boundary, Caused by Water Leaching

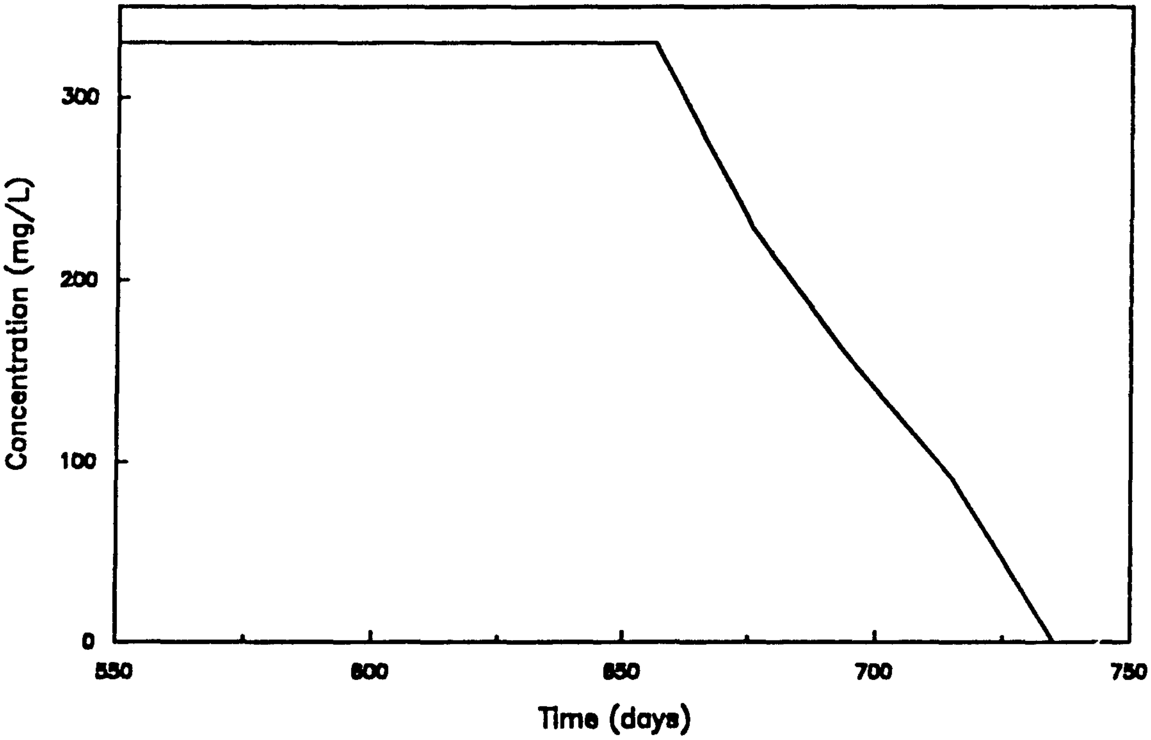

FIGURE 7.3. NO_3^- Concentrations in the Groundwater, at the Future Control Zone, Caused by Water Leaching

8.0 PERFORMANCE ASSESSMENT RESULTS

The potential impacts on groundwater and river concentrations of hazardous chemical constituents resulting from discharges to the 216-A-36B crib are discussed in this section. The impacts are determined at two locations: 1) at the boundary of the future control zone and 2) at the Columbia River.

The future control zone is an area 64 km (40 mi) wide (north to south) by 13 km (8 mi) long (east to west) that will encompass the 200-East and 200-West Areas of the Hanford Site. If institutional control is absent at the Hanford Site, markers placed along the boundary of the control zone will serve as an early warning of radioactive disposal sites within the zone. A distance of 2 km (1.24 mi) downgradient to the boundary of the control zone was used for the analysis of the impacts.

The predicted concentrations of contaminants in the groundwater and the river are compared to CERCLA reportable quantities, toxicological thresholds, and drinking water standards.

8.1 IMPACTS AT THE FUTURE CONTROL ZONE

The impacts of hazardous chemical concentrations from disposal of the ammonia scrubber discharge stream in the 216-A-36B crib were predicted for two cases: 1) normal operations at PUREX (122 declads per year) and 2) past operations (87 declads per year).

During normal and past operations, approximately 1724 kg (3800 lb) of NH_4OH are discharged to the crib during each 22-h decladding operation. This study estimates that a maximum of 11.34 kg (25 lb) of NH_3 gas from this 1724 kg (3800 lb) vaporizes and is released to the atmosphere. The discharge of NH_4OH substantially exceeds the CERCLA reportable quantity of 454 kg/d (1000 lb/d), but the release of NH_3 from the crib to the air is under the reportable quantity of 45.4 kg/d (100 lb/d). The peak concentrations of NH_4OH disposed in the crib exceed the 1-wt% limit set for class C toxic substances (WAC 173-303). Although drinking water standards do not apply, they are compared to estimated groundwater concentrations as a frame of reference. The 430 mg/L of NO_3^- in the aquifer predicted for the case of normal operations at

PUREX exceeds the drinking water limit by approximately one order of magnitude. For past operations, the predicted concentration of NO_3^- in the aquifer is approximately seven times higher (320 mg/L) than the drinking water standard. Only the concentration of NO_3^- (from NH_4^+ conversion) in the aquifer was determined because the previously described analysis indicated that all of the NH_4^+ was eventually converted to NO_3^-.

The aquifer concentrations, below the crib, of other waste stream constituents can be conservatively predicted by assuming that the constituents move at the rate of the infiltrating water (i.e., have K_d values of zero) and calculating the ratio of their input concentrations to those of the NH_4^+. The dilution factor between the concentration observed in the waste stream and that predicted in the aquifer is approximately 7 (i.e., the predicted aquifer concentration is approximately one-seventh the waste stream concentration).

The other waste species of interest, their concentrations in the ammonia scrubber discharge stream, and predicted aquifer concentrations can be found in Table 8.1. These concentrations (except for fluoride) are based on the analysis of one ammonia scrubber discharge sample taken on August 23, 1985. The fluoride concentration was based on hourly analyses of the stream over the first 10 h of a decladding operation. The value in Table 8.1 is the average of these 10 analyses diluted into the ammonia scrubber discharge volume over a 3-day period, the normal time between decladding operations.

TABLE 8.1 Species of Interest in the Ammonia Scrubber Discharge Stream

Waste Species	Concentration, µg/L	Aquifer Concentration, µg/L beneath the crib
Chromium	13	2
Benzyl Alcohol	12	2
Zinc	53	7
Chloride	390	50
Fluoride--normal operation	1200	160

The peak concentration observed for fluoride was approximately 32 mg/L (32,000 µg/L in the discharge stream).

By comparison, the drinking water level for fluoride at 14.7 to 17.6°C is 2000 µg/L; therefore, the predicted fluoride concentration is well below the drinking water level for the worst scenario (cell ring declad). Even though fluoride concentrations periodically exceed drinking water limits during a decladding operation, the limit is never approached in the groundwater. The drinking water levels for chromium, zinc (secondary limit), and chloride (secondary limit) are 50, 5000, and 250,000 µg/L, respectively. Therefore, these constituents are at least two orders of magnitude below their respective levels.

Only chromium has a reportable quantity identified under CERCLA, 0.454 kg/d (1 lb/d). At the listed concentration, approximately 1.81×10^{-4} kg (4×10^{-4} lb) would be released in a 24-h period, well below the reportable quantity.

If the chromium and the fluoride exist in the waste stream as $(NH_4)_2CrO_4$ (a class C toxic) and NH_4F (a class B toxic), their peak concentrations would be 46 and 62,000 µg/L, respectively. These concentrations are below the WAC 173-303 limits for a class C toxin and a class B toxin of 1 and 0.1 wt%, respectively.

Based on this analysis, the only constituents of concern in the waste stream from a regulatory standpoint are the NH_4OH CERCLA reportable quantity and WAC 173-303 1 wt% limit for Class C toxic substances.

8.2 CONCENTRATIONS IN THE COLUMBIA RIVER

Maximum predicted NO_3^- concentrations in the Columbia River resulting from discharges to the 216-A-36B crib are 3×10^{-4} mg/L, more than five orders of magnitude below drinking water limits.

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APPENDIX A

MATERIALS OBTAINED AND USED IN VARIOUS TESTS

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MATERIALS OBTAINED AND USED IN VARIOUS TESTS

This appendix describes the analyses performed on the NH_4^+-laden waste liquid, groundwaters, and sediment samples obtained and used in the adsorption experiments and microbiology tests.

LIQUID WASTE COMPOSITION

Four polyethylene 1-L bottles of process condensate from the 242-A evaporator were obtained from Westinghouse Hanford Company (WHC). This waste solution was used for tests because no actual NH_3 scrubber distillate samples were available at the time the studies were initiated. The process condensate used resulted from the concentration of decladding solution from the head end of the PUREX (plutonium and uranium extraction) process. The wastes were taken on August 31, 1987, stored in sealed containers and were analyzed by Pacific Northwest Laboratory (PNL) on September 30, 1987. The four samples represented replicates taken from a catch basin that holds solution prior to discharge. The bottles were labeled A, B, C, and D.

Chemical and radionuclide analyses were performed on the samples labeled A and B. Cations and selected trace metals were determined by inductively coupled plasma emission spectroscopy. Anions were determined by ion chromatography. Alkalinity was determined by titration with 0.02N hydrochloric acid. The pH and Eh values were determined with standard glass and platinum electrodes, respectively. The samples were radiocounted on a germanium (lithium) [Ge(Li)] detector and liquid scintillation detector to search for gamma and alpha-beta-emitting isotopes.

The results are shown in Table A.1. In general, the waste is an NH_4OH solution with trace amounts of aluminum, silicon, zirconium, sodium, and tritium. The NH_4^+ concentration shows more variation than one would expect for replicate samples, but is consistent with the range of theoretical concentrations of ammonium (4 to 12,000 μg/L). We suspect that some NH_3 gas volatilization during storage or sample collection might be causing the variability.

TABLE A.1. Chemical Analysis of Liquid Waste Sampled on August 31, 1987

Constituent[a]	Sample A	Sample B	Sample C
Al	1.0	2.1	2.0
Ca	0.8	1.1	1.2
Cu	<0.3	0.2	0.2
K	<0.3	0.9	1.1
Na	0.6	0.9	1.0
P	0.3	0.3	0.3
Si	10.6	19.6	18.6
Sr	0.002	0.004	<0.002
Zn	0.2	0.04	<0.02
Zr	0.42	1.4	0.2
NH_4^+	3400	2310	1620
Cl^-	<1	<1	0.5
NO_3^-	<1	<1	<0.03
SO_4	<4	<4	2
F	<1	<1	<1
Alkalinity (as CO_3^{2-})	1242	4140	-
pH	10.92	10.67	-
Eh (mV)	305	322	-
^3H (μCi/L)	2.52	2.65	-

(a) Units are given in milligrams per liter unless shown otherwise.

Sample D was used to dilute waste at 1:10 and 1:100 with distilled water. The resultant NH_4^+ concentrations and pH are found in Table A.2.

TABLE A.2. Analysis of Solution from Sample D

Dilution	Date	NH_4^+ mg/L	pH
1:10	10-14-87	277	10.07 ± 0.17
	10-16-87	227	
1:100	10-14-87	29	9.40 ± 0.03
	10-16-87	22.5	

Again, NH_3 volatilization is suspected as the cause of the difference observed over the 2 days between measurements.

MONITORING WELL ANALYSIS

On September 25, 1987, PNL and WHC collected water samples from the unconfined aquifer. The wells were pumped for approximately 20 min to clean the borehole and stabilize the chemical nature of the samples. Field pH, temperature, and conductivity measurements were recorded throughout the discharge period. Unfiltered and unpreserved samples were analyzed on September 30, 1987, using the same procedures as those discussed for the waste solutions.

The analytical results and well numbers are shown in Table A.3. Wells 299-E-17-5 and 299-E-28-18 show low (~0.1 mg/L) NH_4^+ concentrations NO_3^- concentrations up to 240 mg/L. Well 299-E-17-5 is just east of the 216-A-36B crib, while well 299-E-28-18 is just southeast of the 216-B-62 crib. Both cribs are known to receive NH_4^+-laden wastes. Well 299-E-27-7 is northeast of the 241-C tank farm, and does not show any elevated concentrations of constituents indicative of waste disposal.

The well water samples were used in tests to determine bacteria populations and conversion rates of NH_4^+ to NO_2^-/NO_3^-. The samples also indicate the concentration of NH_4^+ and NO_3^- (as well as other constituents) for the day of sampling. The data indicate low NH_4^+ levels, such that currently large masses of NH_4^+ may not be entering the groundwater from the crib under study.

TABLE A.3. Chemical Analysis of Groundwater Samples Collected on September 25, 1987

Constituent[a]	299-E-17-5	299-E-27-7	299-E-28-18
Al	<0.03	<0.03	<0.03
B	0.017	<0.01	<0.01
Ba	0.035	0.005	0.012
Ca	81.4	25.2	70.4
Fe	0.02	0.02	0.01
K	9.7	5.3	5.0
Li	0.01	<0.01	0.01
Mg	24.3	7.2	16.2
Mn	0.003	0.002	0.007
Na	32.7	10.3	27.6
Si	21.2	17.8	19.4
Sr	0.41	0.11	0.24
NH_4^+	0.123	<0.04	0.134
Cl^-	5.8	4.6	11
NO_3^-	240	1.9	48
SO_4^{2-}	40	16	120
Alkalinity (as CO_3^{2-})	60.72	57.9	66.2
Conductivity (field) (μS/cm)	776	233	580
pH--Laboratory	7.80	8.05	7.91
pH--Field	7.7	7.90	7.35
Eh (mV)	397	391	394
Temperature (°C) Field	20.5	20.5	20.8
^3H (μCi/L)	1.8	<0.02	<0.02
Cations (meq/L)	7.74	2.44	6.18
Anions (meq/L)	6.89	2.42	5.79

(a) Units are given in milligrams per liter unless shown otherwise.

DESCRIPTION OF SEDIMENT USED IN TESTS

The sediment sample used in this work was obtained from borehole 299-E 25-243 from the 3.35- to 3.81-m (11- to 12.5-ft) depth. The sample is from the grout vault site east of the 200-East Area close to the 216-A-37-1 crib. It was selected because of its immediate availability (necessary to support this study) and its expected similarity to soils beneath the 216-A-36B crib. The core, besides the above markings, contained the following markings: N40547.2 W45618.5 Grout PA-1. The core was obtained from PNL personnel who received it from WHC staff involved on the grout project.

The textural class based on two 50-g samples is 2.6% gravel, 63.5% sand, 23.3% silt, and 10.6% clay, which classifies the sediment as a sandy loam. The particle density of the sediment sample is 2.87 g/cm^3, which is heavier than quartz sand (2.65 g/cm^3). The sample appears to be of a finer particle size than the bulk of the sediments described by Smith and Kasper (1983) and Fecht, Last, and Marrat (1979) as being below the 216-A-36B crib. Compared to other sediments obtained from the 241-AP tank farm cut, which reaches to 15.24 m (50 ft), this sample also appears to be skewed toward finer particle sizes. Reisenauer (in Sewart et al. 1987) reports particle-size analyses on six sediments from the 241-AP tank farm excavation and presents a conceptual model that uses the six sediments to represent the vadose zone sediments below the grout site. The conceptual model is presented in Figure A.1, and the particle-size data are presented in Table A.4. The conceptual model is assumed to be representative of the sediment under the 216-A-36B crib. Figure A.1 suggests that 65% of the sediment profile could be represented by sediment type 1 or 4, which is quite coarse compared to the sample used in this study. The sediment used in this study is similar to soil 6 in Table A.4.

The finer particle size could give the sediment a larger adsorption capacity for NH_4^+ than the more representative coarser sediments. But given other uncertainties and simplifications necessary to perform this assessment, the amount of larger adsorption capacity is likely not significant. In fact, as pointed out in Section 7.0, higher retardation factors due to large adsorption capacity have no effect on groundwater concentrations because of the rapid microbiological conversion rate of NH_4^+ to mobile NO_2^- and NO_3^-.

The sediment sample obtained from the grout vault site was used in the NH_4^+ adsorption and capacity studies and bacteria enumeration studies presented in this report.

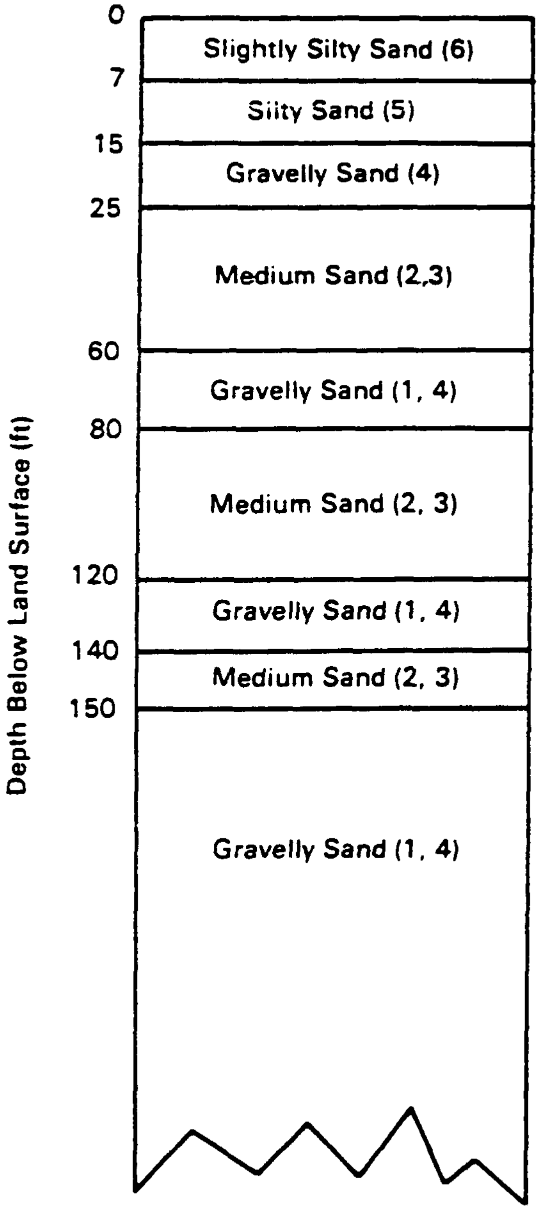

FIGURE A.1. Stratigraphy in the Vicinity of 216-A-36B Crib (after Sewart et al. 1987) (Numbers in parenthesis refer to soil type in Table A.4).

TABLE A.4. Particle Sizes for Six 241-AP Tank Farm Samples

Sediment	Soil Type, % 1	2	3	4	5	6
Gravel	37.63	0.01	0.68	32.08	0.08	1.38
Sand	61.12	90.99	96.34	66.56	26.98	65.09
Silt	1.25	6.00	1.99	1.36	63.95	26.63
Clay	0.00	3.00	0.99	0.00	8.99	6.90

REFERENCES

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APPENDIX B

APPLICATION OF SOLUTION TO LAPLACE'S EQUATION FOR AMMONIA VOLATILIZATION

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APPLICATION OF SOLUTION TO LAPLACE'S EQUATION FOR AMMONIA VOLATILIZATION

Steady-state diffusion is described mathematically by Laplace's equation, where the concentration (C) of NH_3 is the dependent variable. When this equation is solved for diffusion from a line source to a parallel flat surface, the solution is of the form (Lamb 1932)

$$C = - \mu \ln(r_1/r_2) \qquad (B.1)$$

where μ is a constant, r_1 is the distance from the line source to the point at which the concentration is computed, and r_2 is the distance from this point to a line source located above the parallel flat surface as a mirror image of the lower line source, where the flat surface is the "mirror." The solution corresponds to diffusion from one line source to the other, with the flat surface forming a plane of symmetry at which the concentration is computed to be zero. This satisfies a zero-concentration boundary condition at the surface.

The constant μ is chosen to match the concentration boundary condition at the location of the crib, once the distance of the line source below the surface is chosen. The sides of the 216-A-36B crib were excavated at a 1:1.5 slope. The bottom of the crib is 3.35 m (11 ft) wide; an extension of the sides downward forms a vertex 1.13 m (3.7 ft) below the bottom of the crib. We chose this to be the location of the line source. Because the gravel in the crib follows the sloped sides, it fills a trough of trapezoidal cross section. The farthest distance from the line source in the gravel fill is at the top edge of the fill. Since the side slopes at 56° and the depth of the gravel is 0.91 m (3 ft), this distance is $(0.91 + 1.13 \text{ m})/\cos(56°) = 3.66$ m (12 ft).

The depth of soil above the gravel is 6.4 m (21 ft), so that the line source is 0.91 + 1.13 + 6.4 = 8.44 m (27.7 ft) below the surface, and the distance between the line source and its mirror image is, hence, 16.9 m (55.4 ft). This pattern creates a geometric system with the radii r_1 and r_2 originating at points separated by distance 2L, where L is 8.44 m (27.7 ft), and where the angle between the vertical and r_1 is θ and the angle between the vertical and r_2 is ϕ. From trigonometry we find that $r_1 = 2L/(\cos\theta + \sin\theta \operatorname{ctn}\phi)$.

At the top outside edge of the gravel, we have $r_1 = 3.66$ m (12 ft) and $\theta = 56°$; thence, the value of ϕ can be found for that location. For this system, $r_1/r_2 = \sin\phi/\sin\theta$. Given the value for ϕ and knowing θ, we can compute the value of r_1/r_2 at this location. The value of the concentration at this location is $C = -\mu \ln(r_1/r_2)$. Knowing the value of C (the concentration of NH_3 assumed at the top of the crib) and given a value of r_1/r_2, we can compute the value of μ, which is found to be

$$\mu = -C_o/\ln(r_1/r_2) + -C_o/\ln(0.242) = C_o/1.422 \qquad \text{(B.2)}$$

With this value of μ inserted into the solution for Laplace's equation, the concentration C_o will exist everywhere that $r_1/r_2 = 0.242$, which defines a curved surface surrounding the line source (and the crib). Therefore, the solution corresponds to diffusion from this submerged curved surface to the surface of the soil as though the concentration C_o existed out to this surface. The solution, therefore, provides a conservative estimate of the rate of diffusion from the crib, which lies within the surface. The rate of diffusion is obtained by integrating Fick's first law around the line source itself, since at steady state the rate of diffusion across surfaces enclosing the line source is the rate of diffusion from the line source. This rate is

$$N = 2\pi LDC_o/(1.422) \qquad \text{(B.3)}$$

where L is the length of the line source (the length of the crib), and D is the effective diffusivity in the soil.

REFERENCE

Lamb, H. 1932. Hydrodynamics, p. 70. Cambridge University Press, Cambridge, England.

APPENDIX C

SITE DESCRIPTION

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SITE DESCRIPTION

The 216-A-36B crib is 162 m (532 ft) long by 13 m (43 ft) wide, and 7.3 m (24 ft) deep with a sideslope of 1:1.5. The crib contains an m-8 perforated pipe, 15 cm (6 in.) dia., placed horizontally 7 m (23 ft) below grade. The excavation has bottom dimensions of 152 m (500 ft) by 3.35 m (11 ft), contains 0.91 m (3 ft) of gravel fill, and is backfilled with native soil.

From 1966 to 1972, the site received the ammonia scrubber discharge (ASD) from fuel element decladding operations in the 202-A building. In 1972 the crib was deactivated when PUREX (plutonium and uranium extraction) operations ceased. When PUREX resumed operation in 1983, the crib was reactivated to receive the ASD stream from decladding operations.

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