PNNL-29999

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Prepared for the U.S. Department of Energy
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PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

Based on published data, this report identifies potential fate and transport mechanisms for the ammonium hydroxide condensate that was discharged to 216-A-37-1 Crib from Hanford fuel rod decladding before PUREX dissolution and separation operations. Crib 216-A-37-1 received 377 million liters of alkaline condensate discharged from March 1977 through April 1989. The following major processes were identified as controlling the ammonia (NH_3) fate and transport:

1. Liquid migration rates through the vadose zone
2. NH_3 microbial oxidation to nitrite and nitrate
3. Ammonia species [NH_4^+, NH_3(aq)] sorption to sediments
4. NH_3 precipitation reactions after pH buffering occurs in sediments

The travel time through the vadose zone was estimated to be 2.5 to 9 months during periods of high subsurface discharge rates. These travel times are based on tritium migration through the vadose zone, a co-contaminant also discharged to the 216-A-37-1 crib.

Nitrate groundwater concentration trends demonstrated that at least some of the ammonia discharged was rapidly oxidized to nitrate, which then migrated nearly un-retarded to groundwater. This implies that the microbial oxidation of ammonia to nitrate occurred within a few months.

The nitrate dilution from crib discharge to groundwater indicates that up to 80% of N-species mass is not present in groundwater but is retained in the vadose zone as adsorbed or precipitated ammonia. If the highly adsorbed ammonia was not oxidized to nitrate, it is unlikely to migrate given that it has been several decades since discharges to the crib occurred.

Additional characterization of sediments under the crib to quantify aqueous, adsorbed, and solid phase ammonia can confirm the spatial distribution of nitrogen species with depth and show whether N-species mass will continue to remain in the vadose zone or slowly migrate downward. In addition to measuring water content and water extractable concentrations of key species, recommended analyses also include performing sequential acid extractions to dissolve ammonia precipitates and solid phase mineral characterization to evaluate changes in aluminosilicate minerals beneath the crib.

Acknowledgments

Funding for this work was provided by the U.S. Department of Energy Richland Operations Office under the Deep Vadose Zone – Applied Field Research Initiative. Special thanks go to Sarah D. Springer (CHPRC) for supplying characterization data from the C4106 borehole. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the Department of Energy under Contract DE-AC05-76RL01830.

Acronyms and Abbreviations

ERDF	Environmental Remediation and Disposal Facility
HEIS	Hanford Environmental Information System
NQAP	Nuclear Quality Assurance Program
RCRA	Resource Conservation and Recovery Act of 1976

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1.0 Introduction

The purpose of this study is to evaluate the fate of ammonia produced at the Hanford Site PUREX facility that was discharged to the 216-A-37-1 crib (Figure 1) by quantifying the processes that control ammonia (aqueous and gas), nitrite, and nitrate mass reaching groundwater. The fate of ammonia and nitrogen species in the vadose zone under this crib has not previously been studied but was studied under crib 216-A-36B (Buelt et al. 1988), which also received ammonia condensate discharge.

In this study, crib ammonia concentration and discharge volume are described, as well as nitrogen species in wells in groundwater under the crib (Section 2). Processes that control the fate of ammonia in the vadose zone are identified in Section 3, and calculations are made in Section 4 to estimate the significance of different processes. A comparison of crib discharge concentrations to well concentrations of nitrogen species and an un-retarded co-contaminant (tritium) is also presented, as it shows the significance of some processes that occurred in the vadose zone.

Based on these analyses, Section 4 provides recommendations on sampling that can be used to confirm ammonia fate and transport estimates presented in this report.

2.0 Data Associated with Discharges to Crib 216-A-37-1

2.1 Fuel Rod Decladding and Ammonia Condensate

One of the initial operations at the PUREX facility in the 200 East Area of the Hanford Central Plateau is decladding zirconium from irradiated fuel rods. For this zirflex decladding process, fuel rods are boiled in an ammonium fluoride/ammonium nitrate solution for 7 hours, with an average of 87 declads per year (and maximum of 122 declads per year, Buelt et al. 1988). The reaction is summarized as (Goode et al. 1963)

$$6NH_4F + Zr(s) \Leftrightarrow ZrF_6^{\ 2-} + 2NH_4{+} + 2H_2(g) \tag{1}$$

followed by hydrogen reacting with nitrate to form more NH_3

$$4H_2 + NH_4NO_3 \Leftrightarrow 2NH_3 + 3H_2O \tag{2}$$

for 7 hours, with an average of 87 declads per year (and maximum of 122 declads per year, Buelt et al. 1988). Ammonia gas was discharged from the dissolver and condensed back into liquid from the 242A evaporator process condensate, via the 207-A South Retention Basin before disposal in cribs. Because the decladding was sporadic, discharge to the cribs varied over time in terms of ammonia concentration and volume. Ammonia gas is discharged from the dissolver, reaching a peak concentration within 2 h of each decladding operation. The solution was discharged to cribs at a rate of 13,100 liters/hour during decladding and 7500 liters/hour between declads.

2.2 Crib History

The PUREX facility operated from 1956 to 1972 and 1984 to 1989 (Agnew et al. 1997). The three cribs that accepted this alkaline waste were 216-A-10, 216-A-36B, and 216-A-37-1. The 216-A-37-1 crib was designed to receive 327,000 liters/day and received a total of 377 million liters of this alkaline condensate (Klem 1990) discharged from March 1977 through April 1989, with possibly some additional liquid discharged to the crib through 1994 (DOE 2011). Crib 216-A-37-2 (next to A-37-1 crib) received PUREX steam condensate.

The 216-A-37-1 crib is 213 m (700 ft) long, 3 m (10 ft) wide, and 2.4 to 4.3 m (8 to 14 ft) deep, with a 1-ft diameter corrugated perforated distribution pipe placed on 1 meter of gravel that was located 2 m (7 ft) below grade, then covered with gravel, plastic, then backfill (Figure 1b). There are two liquid level risers, a vent riser (sealed in 2000), and a diversion box. The inlet to the crib was at the southeast end so infiltration was favored at this end of the crib (DOE 2011). There were four groundwater wells installed in 1976 prior to crib use (299-E25-17, -18, -19, and -20) on the northern and southern sides of the crib (see Appendix A, Figure A.1 for a map). These wells were first sampled in 1980. One additional well (299-E25-95) was installed in the southeast edge of the crib in 2017.

Under the Resource Conservation and Recovery Act of 1976 (RCRA), cribs 216-A-10 and 216-A-36B had separate, interim-status groundwater monitoring programs, and groundwater under crib 216-A-37-1 was not monitored as the waste did not exceed dangerous waste concentrations (Washington Closure, 2020). However, in 1997, a single combined RCRA groundwater monitoring program was implemented by combining the three cribs based on similar waste history and hydrogeologic regime (Lindberg 1997). The groundwater monitoring plan was revised in 2005 to include additional upgradient and downgradient wells (Lindberg and Elmore 2005). The groundwater monitoring program was revised again in 2010 to remove the 216-A-10 crib, and separate monitoring well networks were proposed for the A-36B and A-

37-1 cribs (DOE 2011). In that plan, well 299-E25-31, which was previously used as an upgradient well, was replaced with well 299-E25-47. In 2017, well 299-E25-95 was added at the southeast end of the crib (DOE 2017).

Groundwater flow in this area is currently to the southeast, although historically groundwater mounding occurred in the 200 Area due to these cribs and B-Pond discharge. Groundwater levels increased as much as 5.5 m above pre-Hanford operational levels, causing groundwater flow directions to shift to the northeast.

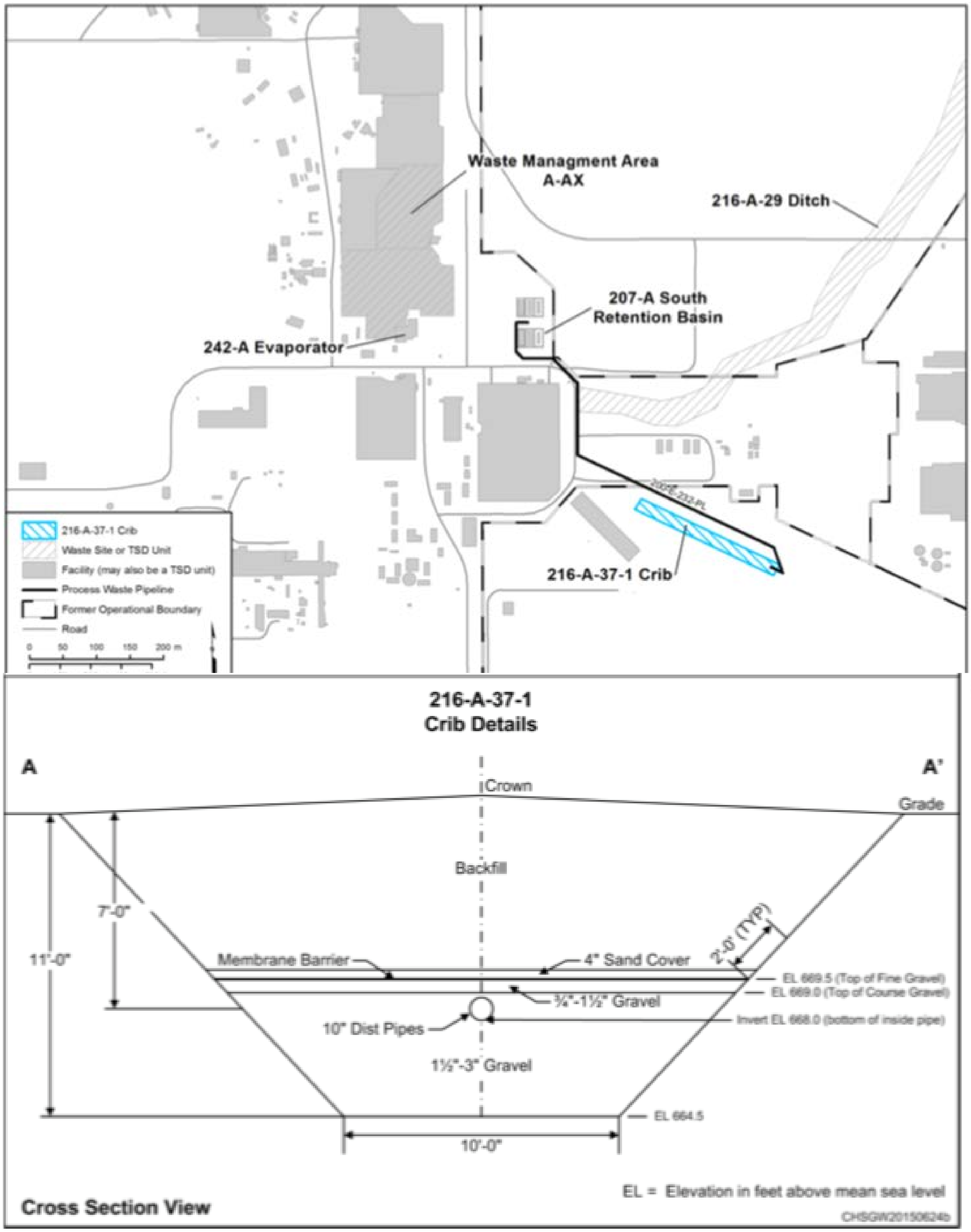

Figure 1. Location of the 216-A-37-1 crib (a) and construction diagram (b) (from DOE 2017).

2.3 Ammonia Condensate Discharge Chemistry and Volume

As described in Section 2.1, decladding operations were sporadic, so the ammonia discharge concentration and volume varied considerably over time. The average ammonia concentration for the 216-A-36B crib was 942 mg/L at a pH of 11.0 and ranged from 4.0 mg/L (pH 9.7) to 12,000 mg/L (pH 11.55, Buelt et al. 1988). For the 216-A-37-1 crib, the average ammonia concentration was 641 mg/L (WHC 1990) with a discharge rate of 49,120 kg/year (Lindberg 1997) and release volume of 1.34 x 10^7 liters (Brown et al. 1990). At these pH values, ammonia mass was primarily present as NH_3 (aq), and not NH_4^+ (Figure 2). The pH of the discharge water was dependent on the ammonia concentration and also other constituents (such as carbonates) that could buffer the pH. Because this crib waste stream was condensate, most ions were present at low concentration, with the exception of carbonate (1242 to 4140 mg/L, WHC 1990), likely present from partitioning of atmospheric carbon dioxide.

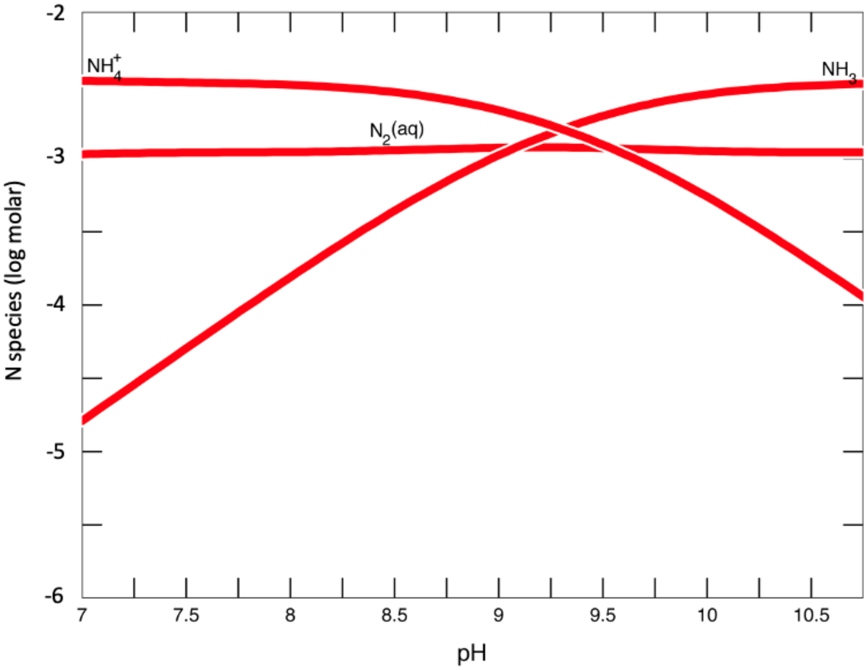

Figure 2. Aqueous speciation of ammonia at different pH (Szecsody et al. 2012).

Co-contaminants present in the crib discharge included radionuclides, metals, and some organic solvents. Radionuclides were also discharged in this alkaline waste, and included tritium, uranium, strontium-90, cesium-137, cobalt-60, ruthenium-106, and promethium-147 (Smith and Kasper 1983). Metals and organic solvents present in the ammonia discharge solution are shown in Appendix C. Because radionuclides and metals were present, ammonia may also have been present as complexes because many metals present as cations bind to ammonia [such as $Co(NH_3)_6^{3+}$, $Ru(NH_3)_5^{2+}$, and $Cr(NH_3)_6^{3+}$]. However, ammonia was present at a very high concentration relative to the metal concentrations, so most ammonia mass was NH_3 (aq).

2.4 Tritium Concentration and Transport in the Vadose Zone

The timing of tritium discharged to the 216-A-37-1 crib reaching groundwater can be used to estimate the travel time through the vadose zone. PUREX decladding discharge to the 216-A-37-1 crib was initiated in 1984 and terminated in 1989. The last discharge to the 216-A-37-1 crib was in 1989 (with 1.34 x 10^7 liters discharged, Brown et al. 1990).

Groundwater sampling was initiated in 1980 at four wells beneath the crib (wells 299-E25-17, 18, 19, and 20; see Appendix A, Figure A.2). Tritium concentrations in all four wells show peaks in 1986, 1988, and late 1989, with an additional peak in well 299-E25-20 in 1983. The last tritium peak in the four wells in 1989 indicated that the travel time was initially less than a year, and the slowly decreasing tritium over the next 5 to 7 years indicated slower water transport through the vadose zone after the crib discharge ceased.

The concentration of tritium discharged to the 216-A-37-1 crib compared to the tritium concentration in groundwater under the crib is useful for estimating the dilution in groundwater. Although the average tritium discharge concentration was not previously calculated, it can be estimated from the total tritium inventory in the crib and discharge volume. The total mass of tritium inventory discharged to the 216-A-37-1 crib is 861 Ci (decayed to the year 2000; Bergeron et al. 2001; Kincaid et al. 2006). The total water volume discharged to the crib is 377 million liters. Assuming the water was evenly discharged between March 1977 and April 1989 (Klem 1990), the calculated initial tritium discharge mass was 4410 Ci, so average discharge concentration was 1.17 x10^7 pCi/L. For comparison, the 216-AA-10 crib has a reported discharge tritium concentration of 2.50 x 10^5 pCi/L.

3.0 Processes that Control Ammonia, Nitrite, and Nitrate Transport in the Vadose Zone

3.1 Overview of Processes

The fate of the 3.77 x 10^8 liters of ammonia waste (average 641 mg/L, pH 11) discharged to the crib over 12 years is controlled by several factors (Figure 3):

- Rate of pore water migration through the ~296 ft of vadose zone from the variable source
- Ammonia gas/liquid partitioning (i.e., volatilization)
- Ammonia gas advection and diffusion
- Ammonia liquid/solid partitioning (i.e., ammonia adsorption and ammonia incorporation into precipitates)
- Ammonia nitrification to nitrite then nitrate

As described in the following sections, the effects of processes range from small (i.e., volatilization) to highly significant (i.e., nitrification).

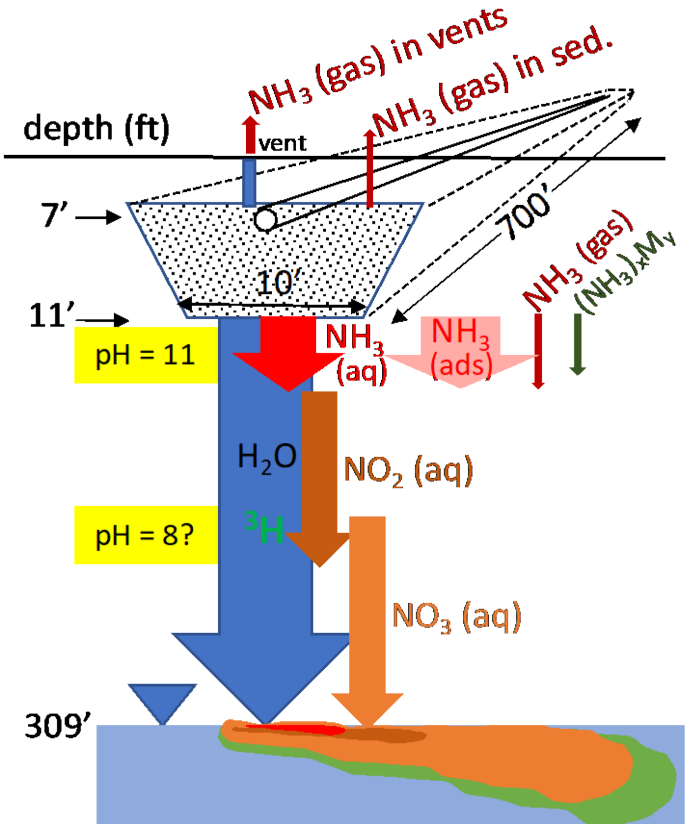

Figure 3. Conceptual description of 216-A-37-1 crib with ammonia transport in the subsurface as a liquid and gas, microbial nitrification to nitrite then nitrate, and ammonia adsorption in the vadose zone. Co-contaminant tritium shown in green.

3.2 Physical Processes

3.2.1 Crib Solution Migration Time through the Vadose Zone

During periods of decladding with high water discharge to cribs, the travel time from PUREX cribs through the vadose zone to groundwater has been previously estimated at 2 to 3 months (Buelt et al. 1988) and 8 to 9 months (Lindberg 1997) based on simulations assuming no low-K zones, which is consistent with tritium transport through the vadose zone to groundwater (see Section 2.4). Water infiltrating through the vadose zone is not saturated, even during periods of high discharge (Buelt et al. 1988). Assuming the infiltrating water under the crib spreads to four times the area of the bottom of the crib and is at 50% water saturation (5% g/g water content), the 377 million liters of water discharged is equivalent to approximately 16 pore volumes of water in the vadose zone.

3.2.2 Ammonia Liquid-Gas Partitioning

Because there are air-filled pore spaces and ammonia is volatile, some mass will partition into the gas phase. Given the dimensionless Henry's law constant of 6.58×10^{-4} (Szecsody et al., 2012), field bulk density (2.05 g/cm^3), and porosity (0.20), the equilibrium gas/liquid ammonia partitioning was calculated at different water contents (Table 1). The different water contents define the gas and liquid volumes. During periods of high discharge to the crib, the water content was likely 5% or higher and the liquid/gas partitioning was 1000 or higher. Between the top of the crib and the land surface, the water content was likely 1% to 4%. At these water content levels, there was still significant ammonia gas partitioning to pore water (Table 1), so any volatilization and upward ammonia gas diffusion and advection (described below) would be significantly retarded due to ammonia partitioning into the pore water.

Table 1. Ammonia equilibrium partitioning between gas and pore water in unsaturated sediments.

Water Content (g H_2O/g total)	H_2O Sat. (%)	NH_3 Partition Ratio (liquid/gas)
0.005	5.1	82
0.01	10.2	173
0.02	20.5	392
0.04	41	1056
0.08	82	6900
0.0975 (sat.)	100	--

3.2.3 Ammonia Gas Diffusion Upward to the Surface

Ammonia gas diffusion was previously estimated for conditions of crib 216-A-36B, which is at a 23-ft top depth compared to 10 ft for 216-A-37-1 (Buelt et al. 1988). In that study, diffusion in a 10-in.-diameter vent pipe (void of sediment, i.e., only diffusion in an air column) was estimated at 9.1×10^{-5} kg/day. The diffusion rate through the sediment was calculated assuming a) no plastic membrane on top of the crib gravel, and b) ammonia was only in gas phase and there was no retardation due to the liquid-gas partitioning. With these assumptions, the diffusion rate was estimated at 12 kg/day. Assuming 2% water content, this ammonia loss to volatilization would be 0.068 kg/day (25 kg/year).

3.2.4 Ammonia Gas Advection Upward to the Surface

Ammonia gas has a lower density (0.7264 kg/m^3 at 16°C) relative to air (1.221 kg/m^3 at 16°C), so unreacted ammonia partitioning into the gas phase would migrate upward by advection using Darcy's law more rapidly than diffusion (Altevogt et al. 2003, Wooding 2007):

$$q_{NH3} = k/\mu\ [dP/dz + (\rho_2 - \rho_1)g] \tag{3}$$

where k (m^2) is the sand or gravely sand permeability (10^{-9} to 10^{-10} m^2), μ is the viscosity (NH_3 viscosity at 16^{o}C is 9.77 x 10^{-6} Pa s; air viscosity at 16^{o}C is 1.8 × 10^{-5} Pa s), dP (Pa or kg m^{-1} s^{-2}) is the pressure difference (zero in this case), z is the distance (m), ρ (kg/m^3) is the gas phase density (listed above), and g (9.81 m/s^2) is the gravitational acceleration.

3.3 Geochemical Processes

3.3.1 pH Neutralization

The pH of the infiltrating water will control ammonia transport to some extent due to two processes: (1) changes in ammonia speciation (Figure 2) and (2) increasing ammonia (as a cation, NH_4^+) adsorption with increasing pH as surfaces become more negative. However, at a pH > 9.4, aqueous NH_3 is the major species and would likely show minimal sorption. Reaction of OH^- ions in the alkaline water with minerals will buffer the pH. The OH^- consumption capacity of Hanford, Ringold, and Cold Creek sediments has been measured as 0.33 to 0.44 mmol/g (Szecsody et al. 2013). In that study, infiltration of pH 13 water (0.1 M NaOH, 1 M $NaNO_3$) for 7 pore volumes into a 3-m-high infiltration column filled with Hanford formation sediment showed that the OH^- front migration was 40 times slower compared to the bromide tracer. Given that an estimated 16 pore volumes of water infiltrated through the 296 ft of vadose zone (see Section 3.2), a OH^- front that is retarded by a factor of 40 (i.e., pH 13 water) would reach approximately 120-ft depth. With the average pH of 11 for the 216-A-37-1 discharge, the pH is likely neutralized within tens of feet of the bottom of the crib. As described below, after the pH is neutralized, ammonia is present primarily as NH_4^+ (pH < 9.4) and exhibits greater cationic adsorption or cation exchange to sediments. During pH neutralization, aqueous Si, Al, K, and carbonate concentrations increased over hundreds of hours, so changes in these aqueous species are indirect indicators of past alkaline solution reactivity (Szecsody et al. 2013).

3.3.2 Ammonia Adsorption

As the aqueous ammonia infiltrates and reacts with sediment minerals, aluminosilicates dissolve, and as the pH neutralizes, other aluminosilicates precipitate and some incorporate ammonia (Szecsody et al. 2012). In addition, the adsorption of ammonia (if present as NH_4^+ at a pH < 9.4) to sediments delays downward migration. The adsorption of ammonia at different concentration to a surface Hanford formation sediment was previously measured as nonlinear (Figure 4, data from Buelt et al. 1988). In these experiments, ammonia was initially present as NH_3 (aq) for the two higher concentrations and NH_4^+ at low concentration. While the vials were sealed, there was atmospheric CO_2 in the headspace. Adsorption was measured after 7 days, and the final pH was not measured. Therefore, the adsorption isotherm represents a combination of NH_3(aq)/NH_4^+ adsorption at varying pH. Based on the Freundlich isotherm fit to the adsorption data and the average high and low ammonia concentrations in the waste, the NH_3 adsorption distribution coefficient (K_d) and retardation factor (R_f) were calculated for water saturated sediments, 50% water saturation, and 30% water saturation (Table 2). The retardation of ammonia at the average concentration in water saturated sediment was moderate ($R_f = 27$), but the retardation factor increases to 107% at 50% water content and to 177% at 30% water saturation. Infiltrating water from the crib is likely moving under unsaturated conditions (Buelt et al. 1988), so ammonia sorption is high. Sorption decreased at higher ammonia concentration, but the retardation factors at low water saturation still remain high. Sorption estimates are similar to those estimated in different soils (Coffee and Bartholomew 1964). Ammonia retardation from adsorption at the high concentration (0.7 mol/L) was low (8.4). Therefore, the most conservative transport scenario is that ammonia migrated approximately 50 times slower than tritium because ammonia was present as NH_3(aq) and the pH was greater than 9.4 under an assumption of constant flow conditions. As the pH is buffered by dissolution of sediment minerals and additional pore gas CO_2 partitioning into the pore water, the pH decreased below 9.4, and ammonia was present as NH_4^+ and exhibited higher cationic adsorption.

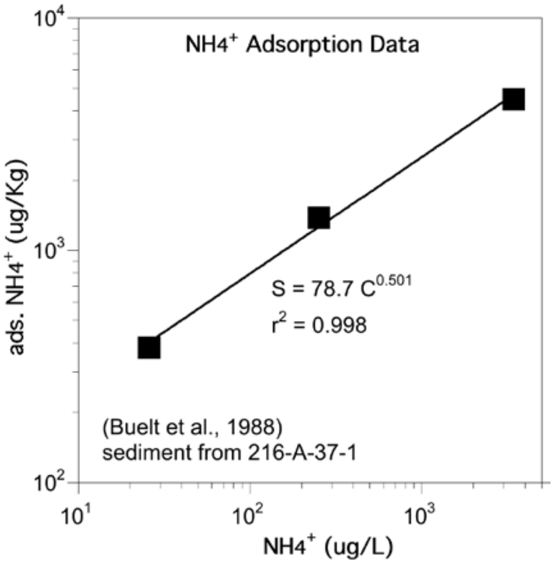

Figure 4. Measured ammonia adsorption to Hanford fm. sediment.

Table 2. Calculated ammonia retardation from adsorption to sediment at different concentrations.

NH_3 (aq) (mg/L)	NH_3 (aq) (mol/L)	NH_3 (gas) (%)	K_d (cm^3/g)	Rf 10% WC(a)	Rf 5% WC(a)	Rf 3% WC(a)
4.0 (low)	2.20×10^{-4}	3.51×10^{-4}	39.4	405	1616	2693
942 (mean)	0.055	0.085%	2.58	27.4	107	177
12,000 (high)	0.706	1.13%	0.725	8.43	30.7	50.5

(a) WC = water content, 10% WC is 100% water sat., 5% WC is 50% sat., 3% WC is 31% sat.

3.4 Microbial Nitrification of Ammonia

3.4.1 Laboratory Nitrification Studies

The oxidation of ammonia in shallow soil (i.e., within the root zone) is widely reported (Yang et al. 2010; Velthof et al. 2012; Bouwman et al. 2002) and the rate of oxidation upon application of ammonium nitrate and volatilization is well described (Cooter et al. 2012; Rochette et al. 2001; Fenn and Escarzaga 1976; Klausner and Guest 1977). In addition, sewage treatment plants use oxic biofilm trickling filters to oxidize ammonia (Xu et al. 2011). Unfortunately, both of these bodies of systems have significantly greater microbial populations than sediments in the deep subsurface, where infiltration of ammonia from 11-ft depth at the bottom of the 216-A-37-1 trench to the water table at 309-ft depth. For example, the total microbial population at a 3- to 6-ft depth in sediments from two boreholes in the 100N Area were 1 x

10^7 to 3×10^8 cells/g, whereas biomass at a 20 ft depth was 1×10^5 to 6×10^5 cells/g (i.e., 500 to 1000 times less at depth, Figure 5).

Ammonia nitrification is typically by a portion of the microbial biomass (N oxidizers, family Nitrobacteriaceae), where Nitrosomonas sp. oxidizes ammonia to nitrite:

$$NH_4^+ + 2H_2O \Rightarrow NO_2^- + 8H^+ + 6e^- \qquad (4)$$

and Nitrobacter produces nitrate:

$$NO_2^- + H_2O \Rightarrow NO_3^- + 2H^+ + 2e^- \qquad (5)$$

These reactions require oxygen, moisture, and organic matter. In one study, nitrification rates were calculated from 35-day-long laboratory experiments in a Hanford surface soil and in water from three 200 Area wells (Buelt et al. 1988). The shallow sediment had a first-order nitrification rate of 0.58/day Table 3, half-life 1.2 days), with fairly high microbial biomass and likely moderate natural organic matter in the shallow sediment. Assuming the biomass at a 20-ft depth was 500 to 1000 times lower (Figure 5), nitrification half-life is 1.6 to 3.3 years (Table 3). For the groundwater samples, one sample did not show any nitrification over the 35-day experiment, and the two others had a first-order nitrification rate of 0.32 to 0.37/day.

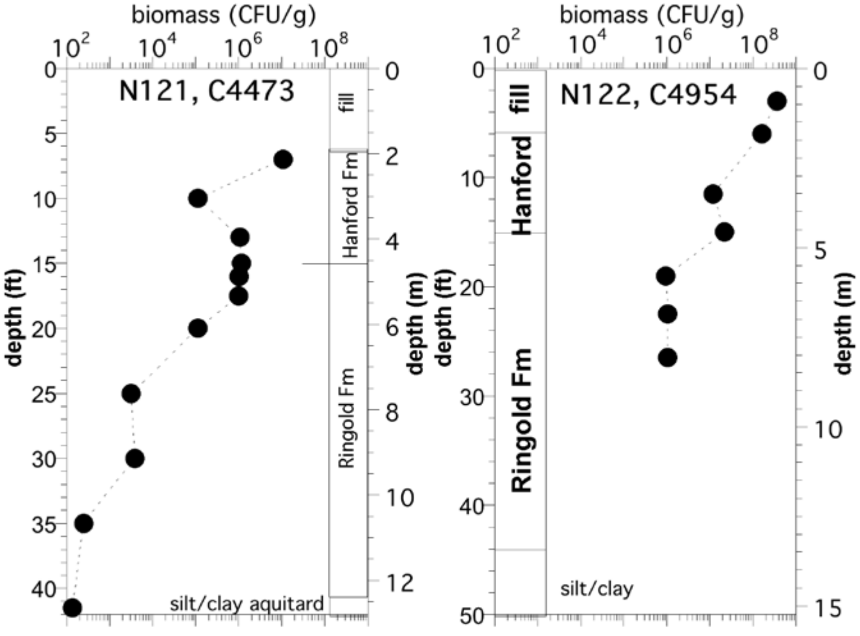

Figure 5. Total microbial biomass with depth in the Hanford 100N Area (from Szecsody et al. 2009).

Sediment from the Hanford Environmental Remediation and Disposal Facility (ERDF) pit at 20-ft depth was used at 4% water content (41% saturation) at different aqueous ammonia concentrations (18, 185, and 1846 mg/L), and in the presence and absence of oxygen (Table 3), to determine the rate of nitrification in a different study (Szecsody et al., 2015). Data from these experiments were fit with first-order reactions [Eqs. (4) and (5)] in series, as shown in Appendix B. Over 105 days, all six experiments showed less than 1% of the ammonia was oxidized to nitrite or nitrate. At the 4% water saturation in these experiments, sorption accounted for most of the ammonia mass not in aqueous solution (Table 2), although reactions with sediments may also incorporate ammonia into aluminosilicate precipitates

(Szecsody et al. 2015). Implications to field-scale discharge of ammonia are that most of the ammonia mass should be highly sorbed in shallow sediments under the crib. Adsorbed ammonia should still available for microbial nitrification to nitrite and nitrate.

Nitrification rates varied slightly (19- to 58-day half-life) and did not show the expected faster rate for experiments with oxygen and lower ammonia concentration. In addition, measurements of the microbial biomass showed a significant decrease over time, with higher ammonia concentrations resulting in greater microbial death (Table 3, from Szecsody et al. 2015).

Table 3. Ammonia nitrification rates observed in soils, sediments, and groundwater.

Sediment or Water	Total Biomass (CFU/mL)	Description of Experimental Conditions	NH_3 (aq) (mg/L)	NH_3->NO_2 Rate (1/day)	NO_2->NO_3 Rate (1/day)	Source
Hanford soil	7.5 x 10^7	50 g/500 mL	106	0.577(a)		Buelt et al. 1988
Groundwater 299-E17-5	9.0 x 10^2	water only	106	0.372		Buelt et al. 1988
Groundwater 299-E27-7	1.0 x 10^2	water only	106	none		Buelt et al. 1988
Groundwater 299-E28-18	6.0 x 10^3	water only	106	0.316		Buelt et al. 1988
Columbia silt loam				0.24	0.024	Misra et al. 1974
Hanford fm, ERDF pit, 20'	0(b)	4% H2O in sed., anoxic	1846	0.026 (c)	0.036	Szecsody et al. 2015
Hanford fm, ERDF pit, 20'	0(b)	4% H2O in sed., in air	1846	0.036(c)	0.036	Szecsody et al. 2015
Hanford fm, ERDF pit, 20'	6.2 x 10^1(b)	4% H2O in sed., anoxic	185	0.024(c)	0.036	Szecsody et al. 2015
Hanford fm, ERDF pit, 20'	4.6 x 10^1(b)	4% H2O in sed., in air	185	0.05(c)	0.036	Szecsody et al. 2015
Hanford fm, ERDF pit, 20'	1.4 x 10^2(b)	4% H2O in sed., anoxic	18.5	0.023(c)	0.012	Szecsody et al. 2015
Hanford fm, ERDF pit, 20'	1.4 x 10^2(b)	4% H2O in sed., in air	18.5	0.024(c)	0.036	Szecsody et al. 2015
				mg/kg/day		
Wastewater				0.5-30 x 10^2		Sundberg et al. 2007
				mmol/kg/day		
Calcareous soil				4.8		Ouyang et al. 2017
Composts				0.7		Ouyang et al. 2017
Soils				0.5		Ouyang et al. 2017

(a) In shallow soil. Assuming 24-ft-deep sediment has 500 to 1000 times lower microbial population, rate is 1.2E-3 to 5.8E-4/day.

(b) Initial biomass in ERDF pit was 3.6×107 CFU/mL, biomass reported in column is after 105 days.

(c) Assumes only 1% of the initial NH_3 mass was nitrified, with 99% loss to adsorption and precipitation to sediment.

3.4.2 Estimates of Ammonia Nitrification Rate Based on Well Data

Field-scale nitrification of high ammonia concentrations in vadose zone sediments at 10- to 300-ft depth could occur in spite of the low microbial populations. The infiltrating plume likely did not cause full water saturation within the sediments (Lindberg 1997), and with an average moisture content estimated at 5% (equivalent to 50% water saturation), oxygen present in the air-filled pore space to promote nitrification. Given that organic solvents co-contaminants were also present in the crib discharge (Appendix C), these provided the organic matter needed for nitrification to proceed. In addition, a characterization borehole drilled in 2003 showed that petroleum hydrocarbons were found at all depths in the vadose beneath the crib (Appendix D, Figure D.2b), providing further evidence of organic matter needed for microbially-facilitated nitrification.

Based on arrival of nitrate in wells under the crib relative to tritium, it is estimated that most of the ammonia mass was microbially oxidized to nitrate, with lesser amounts to nitrite. Both nitrate and nitrite do not adsorb and, therefore, generally travel at the same rate as tritium. A comparison of tritium and nitrate in well 299-E25-19 shows excellent correlation of peaks in 1984, 1985, 1987, 1990, and 1996 (Figure 6) as previously noted in Lindberg (1997), which implies both rapid nitrification of ammonia to nitrate and similar un-retarded migration of tritium and nitrate. Given the estimated 2.5- to 9-month travel times in the vadose zone (Buelt et al. 1988; Lindberg 1997), the rate of ammonia nitrification would need to oxidize at least a large fraction of the ammonia within a few months. If the ammonia nitrification rate was slower (i.e., years or longer), nitrate peaks would arrive in groundwater later than tritium, because of the high adsorption of ammonia ($R_f = 107$ at average NH_3 concentration and 50% water saturation). However, the timing of tritium and nitrate peaks in wells does not provide sufficient evidence to conclude whether all or only part of the ammonia mass reached groundwater as nitrate (see Section 4.1.1).

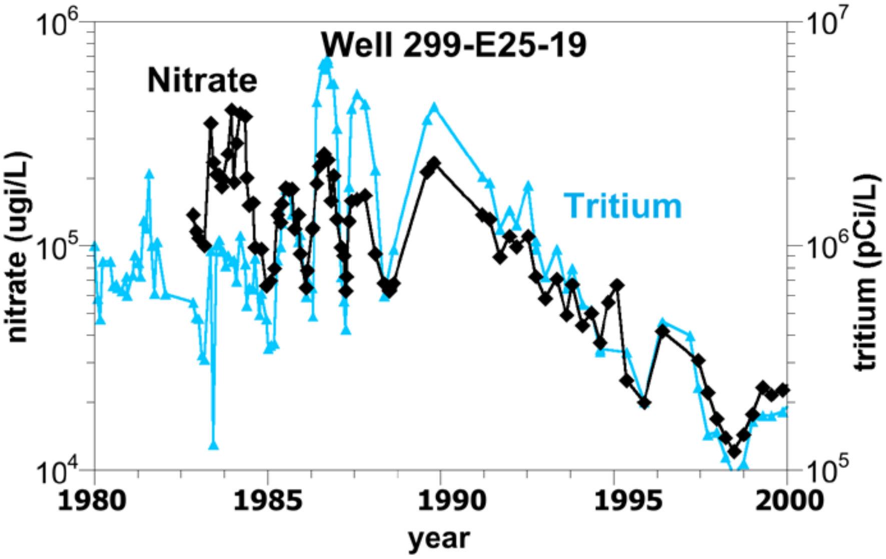

Figure 6. Comparison of the timing of peaks of the tritium and nitrate concentrations for 299-E25-19 for the years 1980 to 2000 (data from HEIS; https://ehs.hanford.gov/eda/ constituent: nitrate and tritium, well 299-E25-19).

Low concentrations of ammonia were present in two wells (299-E25-17, 19; see Appendix A, Figure A.4) under crib 216-A-37-1 in 1994 to 2004, indicating that it might be traveling more slowly than tritium (with peak arrivals 1986 to 1992). However, there is insufficient ammonia data to draw any conclusions. Most of the ammonia data are listed as non-detects and only the red circled points in Figure A.4 are identified as detectable ammonia concentrations.

4.0 Estimation of the Ammonia Fate Discharged in the Crib

Ammonia condensate discharged to the 216-A-37-1 crib migrated downward through and reacted with the vadose zone sediments. The main processes controlling ammonia fate have been identified as:

- Liquid migration rate through the vadose zone from the sporadic discharges
- NH_3 nitrification to nitrite and nitrate
- Changing ammonia sorption due changing pH and speciation
- Ammonia reactions with sediment buffering the pH and precipitating some NH_3 mass (see Figure 7 and Section 3.3).

Other processes likely occurred in the vadose zone but with minimal effect; these include volatilization and complexation with metals. Laboratory experiments have previously been used to quantify the rate of some of these processes (i.e., ammonia nitrification, ammonia adsorption to sediment, volatilization) (Buelt et al. 1988; Szecsody et al. 2015). Monitoring of N-species in wells under the crib provides compelling evidence of the significance of nitrification and ammonia adsorption (next section), although at field scale it is difficult to quantify the ammonia mass balance.

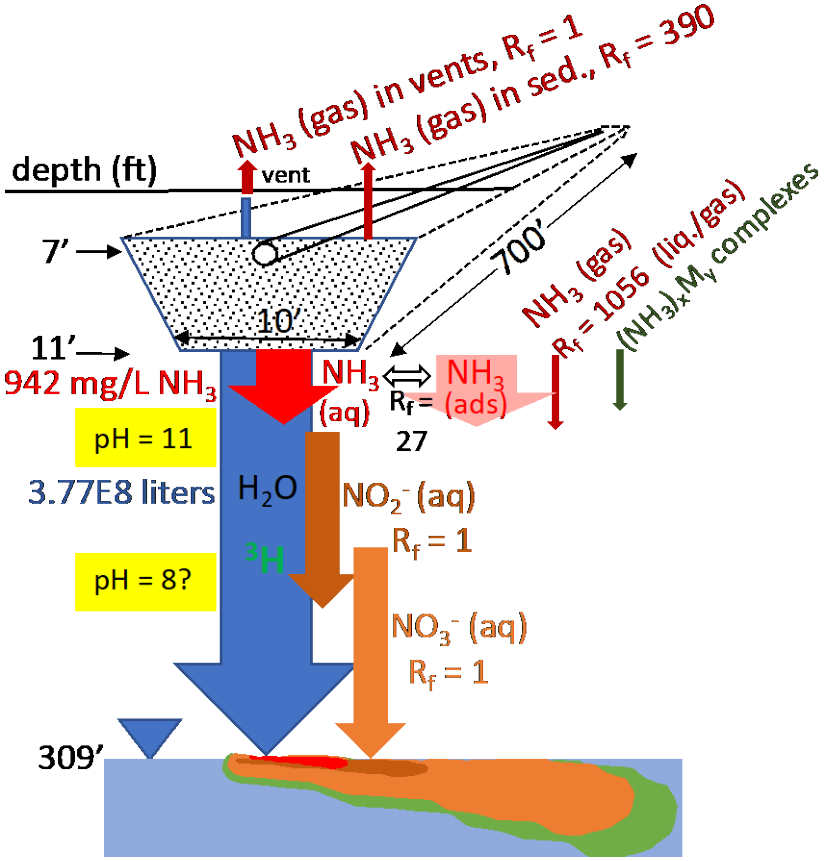

Figure 7. Conceptual diagram of processes that influence N-species transport in the vadose zone from 216-A-37-1 crib ammonia discharge. Co-contaminant tritium shown in green.

4.1.1 Ammonia Nitrification Mass from Crib and Well N-Species Concentrations

The similar timing of tritium and nitrate peaks in wells 299-E25-17, 18, 19, and 20 in 1984 to 1991, implies that some to all ammonia was rapidly oxidized to nitrate in the shallow vadose zone, then tritium and nitrate infiltrated to groundwater at the same rate (3.4.2 and Figure A.2 and Figure A.3). Although laboratory experiments at low (4%) water content do show relatively rapid nitrification half-life (14 to 30 days, Table 3) consistent with the hypothesized field rate, the experiments also showed that only 1% of the ammonia mass was oxidized and 99% of the mass partitioned to the sediment by adsorption and/or incorporation into aluminosilicate precipitates (data in Appendix B). The implication to field scale is that there could be considerable ammonia mass in the shallow vadose zone.

To estimate the mass balance of nitrogen species (and tritium) at field scale, where there is mass loss to the vadose zone as well as dilution as the water enters groundwater, crib and well concentrations were compared. The average calculated tritium concentration for the 216-A-37-1 crib was 1.17 x 10^7 pCi/L (see Section 2.4). For tritium, mean and peak tritium concentrations in wells 299-E25-17, 18, 19, and 20 (Appendix A, Figure A.2) are listed in Table 4. Wells 19 and 20 are on the southeast end of the crib, where the discharge pipe enters the crib (Figure 1), so they had the greatest infiltration volume. A comparison of the peak tritium concentration in wells to the average tritium discharge concentration to the crib indicates that the groundwater peak tritium concentrations were 61% (well E25-19), 19% (E25-20), 9.4% (E25-18), and 5.0% (E25-17) of the average tritium discharge concentration (Table 4, fourth column). These values imply that the dilution in groundwater may have ranged from 2 to 20 times. These tritium peak concentration ratios show a relative dilution that is expected for nitrate, assuming all of the ammonia was oxidized to nitrate and migrated through the vadose zone with tritium.

Table 4. Measured tritium and nitrate in wells under the 216-A-37-1 crib.

Well	Mean ^3H[(a)] (pCi/L)	Peak ^3H (pCi/L)	^3H Peak Well/Crib[(b)]	Mean NO_3[(a)] (mg/L)	Peak NO_3 (mg/L)	NO_3 Peak Well/Crib[(c)]	NO_3 Mass Loss $NO_3/^3H$[(d)]
299-E25-17	2.80×10^5	5.80×10^5	0.050	18	47	0.014 - 0.020	0.59 - 0.72
299-E25-18	2.90×10^5	1.10×10^6	0.094	25	89	0.026 - 0.038	0.59 - 0.72
299-E25-19	1.80×10^6	7.10×10^6	0.61	140	410	0.12 - 0.18	0.71 - 0.80
299-E25-20	9.60×10^5	2.20×10^6	0.19	230	460	0.13 - 0.20	0.00 - 0.28

(a) From 1984 to 1991.
(b) Assumes tritium discharge was 1.17E7 pCi/L.
(c) Assumes ammonia discharge was 942 (Buelt et al. 1988) or 641 mg/L (WHC 1990).
(d) 1 - [NO_3 peak well/crib divided by ^3H peak well/crib]

If all of the ammonia (average concentration 641 or 942 mg/L) was oxidized to nitrate, the corresponding average nitrate concentrations would be 2334 to 3430 mg/L, given the difference in molecular weight of ammonia and nitrate. The nitrate concentrations in wells varied from 18 to 460 mg/L (Table 4), so the molar ratio of nitrate in the wells to the initial ammonia in the crib was 12% to 20% for wells 299-E25-19 and 20, and 1.4% to 2.6% for wells 299-E25-17 and 18.

Comparing the tritium dilution that occurred between the average tritium crib discharge concentration to peak well concentration (2x to 20x) to nitrate, there was 0% to 80% N-species mass loss (Table 4, last column), which varied by well. Well E-25-20 had the least N-species mass loss with 0% to 28%, whereas wells E-25-17, 18, and 19 had 59% to 80% N-species mass loss. Although the N-species mass loss in the laboratory-scale study was attributed mainly to ammonia adsorption, at field scale over years to decades, the adsorbed ammonia should be bioavailable for nitrification to ammonia. Therefore, it is likely that there is considerable nitrate remaining in the vadose zone due to (a) lack of additional water discharge to the crib (i.e., considerably slower water flux through the vadose zone), (b) adsorption of ammonia in the unsaturated sediments, and (c) slow nitrification of the adsorbed ammonia. It also appears that if the ammonia in shallow sediment is primarily adsorbed and not precipitated, then adsorbed ammonia may not be bioavailable for oxidation to nitrate.

Although tritium and nitrate were measured in the four wells starting in 1981, ammonia and nitrite were measured starting in 1990 (Appendix A, Figure A.4). The possibility that ammonia reached groundwater prior to 1990 is unlikely due to high sorption of ammonia (retardation factor of 107 at the average ammonia concentration and 50% water saturation, Table 2).

It should be noted that nitrate concentrations in two wells (299-E25-17, 18) under the western (upgradient) half of the crib have steadily increased since the year 2000 due to nitrate migrating in groundwater from other upgradient sources (DOE 2011). Nitrate has also increased, but to a lesser extent, in the two wells in the southeast half of the crib (299-E25-19 and 20) that are further from the upgradient source.

4.1.2 Remaining N-Species Mass in the Vadose Zone from Borehole Data

A characterization borehole (C4106) drilled in 2003 near the southeast end of crib 216-A-37-1 provided characterization of tritium and nitrogen species in the sediment profile. Elevated tritium levels for the first 100 ft indicate that there is residual water in this upper vadose zone but it decreases with depth (Figure 8a). Nitrate was moderately elevated at 30 to 100 ft (20 to 100 mg/L), but with significantly higher concentration (1700 mg/L) at the shallowest depth (15 and 22 ft) (Figure 8b). The moderate levels of nitrate from 30 to 100 ft are at the same depth as elevated tritium, so it may be just residual pore water from the crib. However, the elevated nitrate at the shallowest depths (< 30 ft) may be indicative of a different source for nitrate, possibly adsorbed ammonia that has been slowly oxidized to nitrate. The 1700 mg/L nitrate at 15-ft depth is about half the concentration of the average ammonia discharge concentration (942 mg/L NH_3 if oxidized is 3410 mg/L nitrate), and thus represents a significant N-species concentration. Two metal co-contaminants (Ba and Cr) also showed elevated concentrations in the shallowest depth (Appendix D, Figure D.1), possibly due to precipitation.

The pH profile with depth was relatively constant at ~8.5 except for depths of less than 30 ft, which were slightly less alkaline (pH 7.5 to 8.2, Appendix D, Figure D.2a). Although the alkaline pH of the crib discharge solution was high (pH 10.5 to 11), as previously discussed (Section 3.3.1), it was likely neutralized within tens of feet of the surface within months. A previous laboratory study of Hanford and Ringold formation sediment dissolution in alkaline solutions resulted in increase of aqueous Si, Al, K, and CO_3 (Szecsody et al. 2013). Therefore, changes in these aqueous species can be used as indirect indicators of the depth of the reactivity of the ammonia discharge solution with sediments.

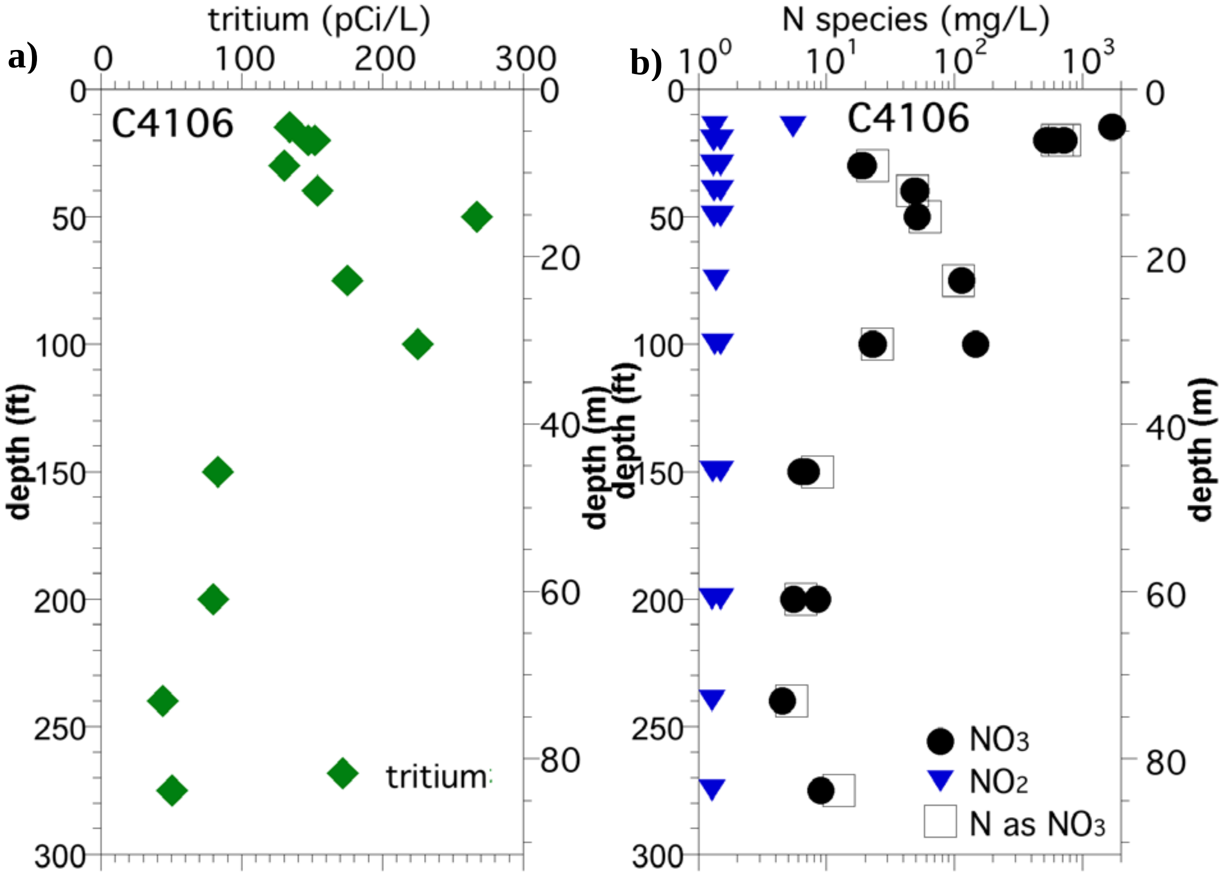

Figure 8. Analysis from characterization borehole C4106 at SE end of A216-A-37-1 crib: a) pH, and b) petroleum hydrocarbons, diesel range.

4.1.3 Ammonia Diffusion and Advection Upward from Crib 216-A-37-1

Ammonia mass loss due to gas diffusion and gas density-driven advection were evaluated for conditions of this crib. The estimated time for ammonia to reach the surface based only on ammonia gas diffusion was calculated in this study for the shallower 7-ft depth for the top of crib 216-A-37-1, in contrast to the 23-ft depth for crib 216-A-36B (Buelt et al. 1988). In this diffusion calculation, the gas to pore water ammonia partitioning was included at 1%, 2%, or 4% water content. Other assumptions included (a) constant ammonia mass at 7-ft depth, and (b) no membrane cover above the crib. Under these conditions, it would take 9 months to reach 10% of gas concentration at the surface, 5 years for 50% concentration, and 135 years to reach 90% of the equilibrium concentration (Figure 9). Given that (a) a membrane is in place (Figure 1a), (b) aqueous ammonia would migrate slowly downward and not be present at a constant concentration in the shallow sediment, and (c) microbial nitrification appears to have oxidized some to all ammonia to nitrite and nitrate within months to years, there would be insufficient aqueous ammonia remaining in the water in the crib after a few years for gas phase ammonia to diffuse upward to the land surface (i.e., ammonia could diffuse to the land surface mainly in the first few years of discharge).

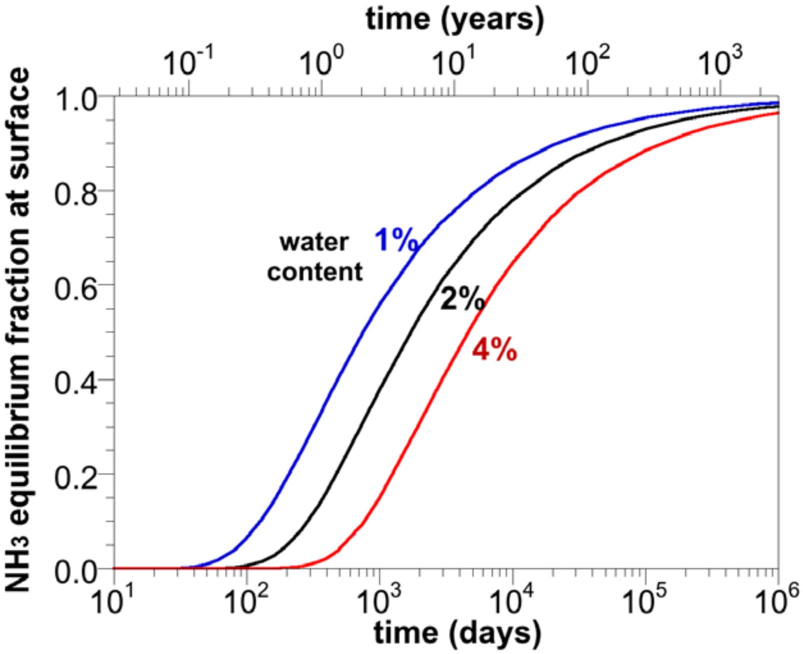

Figure 9. Time for diffusion of ammonia from a 7-ft depth to reach the sediment surface.

Because ammonia gas has a lower density relative to air, density-driven advection will cause some ammonia mass to migrate to the land surface, as described in Section 3.2.4. Equation (3) is used with the following parameters: (a) gas densities at 16°C (ammonia 0.7264 kg/m^3; air 1.221 kg/m^3), (b) ammonia viscosity at 16°C of 9.77 x 10^{-6} Pa s, (c) permeability for sand or gravely sand (10^{-9} to 10^{-10} m^2), (d) cross sectional area of the top of the crib (assuming no membrane in place, 700 ft x 10 ft or 650.3 m^2), (e) porosity of 0.20, and (f) 2% water content. With these parameters, it is estimated that 1.6 to 16 kg/year of ammonia gas would advect upward to the surface from the crib due to the density difference relative to air. In addition, the ammonia gas advection would be retarded for 36 days due to partitioning to pore water, after which ammonia gas advection would move upward un-retarded. Given the low ammonia mass present in gas phase, the ammonia gas flux by advection accounts for an insignificant portion of the ammonia mass discharge to the crib.

4.1.4 Recommendations for Additional Sediment Characterization

A characterization borehole drilled near the southeast end of 216-A-37-1 would provide evidence of whether there is additional nitrogen species mass (different species) remaining in the vadose zone as well as showing whether nitrate has migrated deeper, by comparing the nitrate profile to the C4106 borehole data (from 2003). The sediment profile in C4106 showed highly elevated nitrate at 15- and 22-ft depths, and somewhat elevated nitrate from 30 to 100 ft. Ammonia was not measured in sediment samples from the C4106 borehole. It is hypothesized that a fraction of the ammonia was initially oxidized to nitrate in the early 1980s, and a fraction of the ammonia remained in the shallow vadose zone under the crib due mainly to adsorption and possibly ammonia precipitation in aluminosilicates. Over time, the adsorbed ammonia was slowly oxidized to nitrate, which slowly migrates downward in the vadose zone. In addition, a previous laboratory study of Hanford and Ringold formation sediment dissolution in alkaline solutions resulted in increase of aqueous Si, Al, K, and carbonate (Szecsody et al. 2013), so these aqueous species can be used as an indirect indicator of ammonia discharge solution reactivity with sediments (and depth at which ammonia might be incorporated into precipitates), as the pH has been neutralized within months of discharge.

To address the current state of the ammonia and other nitrogen-containing aqueous, adsorbed, and (possibly) solid phases, the following characterization is proposed:

- Sediment sample depths: 11 ft (or as close to the bottom of the crib as possible), 13 ft, 15 ft, 20 ft, 25 ft, 30 ft, 40 ft, 60 ft, 80 ft, 100 ft, 120 ft, 140 ft, 190 ft, 240 ft, 300 ft
- Moisture content (critical)
- Fraction sediment size less than 2 mm (or some measure of the grain size distribution)
- Water extractable tritium
- Water extractable nitrate, nitrite, ammonia
- Water extractable potassium, aluminum, silica, and carbonate
- Ion exchange solution extractable (i.e., adsorbed) ammonia
- Acid extractable ammonia (i.e., dissolution of ammonia precipitates)
- Sediment total inorganic carbon (i.e., solid phase carbonates)
- Sediment total organic carbon
- Sediment solid phase mineral characterization to evaluate changes in aluminosilicate minerals for selected shallow sediments

The results of the N-species distribution in the vadose zone from this characterization borehole will indicate which of the following hypothesis can explain why N-species mass has remained in the shallow vadose zone and whether the N-species mass will remain or slowly move. These hypotheses are:

> Hypothesis 1. The shallow N-species mass is mainly adsorbed ammonia. These results are consistent with the predicted high ammonia sorption in unsaturated conditions (i.e., retardation factor 107), but would also imply that adsorbed ammonia is not available for microbial oxidation to nitrate.
>
> Hypothesis 2. The shallow N-species mass is mainly precipitated ammonia. These results imply that the precipitated ammonia is not available for microbial oxidation, but also implies that the precipitate(s) are slowly dissolving and being oxidized to nitrate.

5.0 Conclusions

Based on published data, this report identifies potential fate and transport mechanisms for the ammonium hydroxide condensate that was discharged to 216-A-37-1 crib from Hanford fuel rod decladding before PUREX dissolution and separation operations. Crib 216-A-37-1 received 377 million liters of alkaline condensate discharged from March 1977 through April 1989. The major processes identified as controlling the ammonia (NH_3) fate and transport included the following:

- Liquid migration rates through the vadose zone
- NH_3 microbial oxidation to nitrite and nitrate
- Ammonia species [NH_4^+, NH_3(aq)] sorption to sediments
- NH_3 precipitation reactions after pH buffering occurs in sediments

The range of average ammonia discharge concentrations is estimated to be between 641 and 942 mg/L. At this concentration range, the migration of ammonia is likely significantly retarded due to sorption to vadose zone sediments (with a retardation factor of 107). The discharge pH of 10.5 to 11 was likely neutralized within tens of feet beneath the crib due to reactions with clay minerals, and ammonia will be present as NH_4^+ after pH neutralization. Any oxidation of ammonia to nitrite and nitrate, however, likely migrated un-retarded through the vadose zone. Other processes that probably occurred in the vadose zone with minimal impact included (a) ammonia volatilization, (b) ammonia gas advection and diffusion, and (c) ammonia complexation with metals.

The travel time through the vadose zone was estimated to be 2.5 to 9 months during periods of high subsurface discharge rates. These travel times are based on tritium migration through the vadose zone, a co-contaminant also discharged to the 216-A-37-1 crib. Tritium concentration peaks in four wells (299-E25-17, -18, -19, and -20) beneath the crib occur between 1984 and 1991. Tritium concentrations in groundwater from 1984 to 1991 are 2 to 20 times more dilute than their discharge concentrations to the crib.

Nitrate groundwater concentration trends (i.e., peaks over time) show similar trends to tritium. Like tritium, nitrate concentration peaks occur between 1984 and 1991. This suggests that at least some of the ammonia discharged was rapidly oxidized to nitrate then migrated nearly un-retarded with tritium to groundwater. Un-retarded nitrate transport in the vadose zone implies that the microbial oxidation of ammonia to nitrate occurs within a few months. However, the nitrate dilution from crib discharge to groundwater indicates that up to 80% of N-species mass is not present in groundwater but rather is retained in the vadose zone as adsorbed or precipitated ammonia. If the highly adsorbed ammonia was not oxidized to nitrate, it is unlikely to migrate given that it has been several decades since discharges to the crib occurred.

Because the infiltrating water did not fully saturate vadose zone sediments, a small amount of ammonia mass could also partition into air-filled pores and advect and diffuse upward as NH_3 gas has a lower density than air. Previous calculations of NH_3 mass loss to diffusion through the sediment above the crib and through vent pipes indicated the mass is small. Calculations in this report additionally indicate that the density-driven NH_3 gas advection is also small.

Therefore, the preliminary conclusion is that ammonia discharged to the 216-A-37-1 crib initially adsorbed to sediments with some mass oxidized to nitrate and migrated through the vadose zone to groundwater at nearly the same rate as tritium. Therefore, a large fraction of the ammonia mass may still be in the ~290 ft of vadose zone under the crib, which is supported by a characterization borehole showing significant nitrate mass in the shallowest 100 ft of the vadose zone. Additional characterization of sediments under the crib to quantify aqueous, adsorbed, and solid phase ammonia would provide evidence of the spatial distribution of nitrogen species with depth. This characterization would also show whether N-species mass will continue to remain in the vadose zone or slowly migrate downward.

6.0 Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory Nuclear Quality Assurance Program (NQAP). The NQAP complies with DOE Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application* as its consensus standard and NQA-1-2012 Subpart 4.2.1 as the basis for its graded approach to quality. Reviews of calculations in this paper study were conducted for this work in accordance with the NQAP.

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Appendix A – Tritium and N-Species Concentrations in Wells Beneath Crib 216-A-37-1

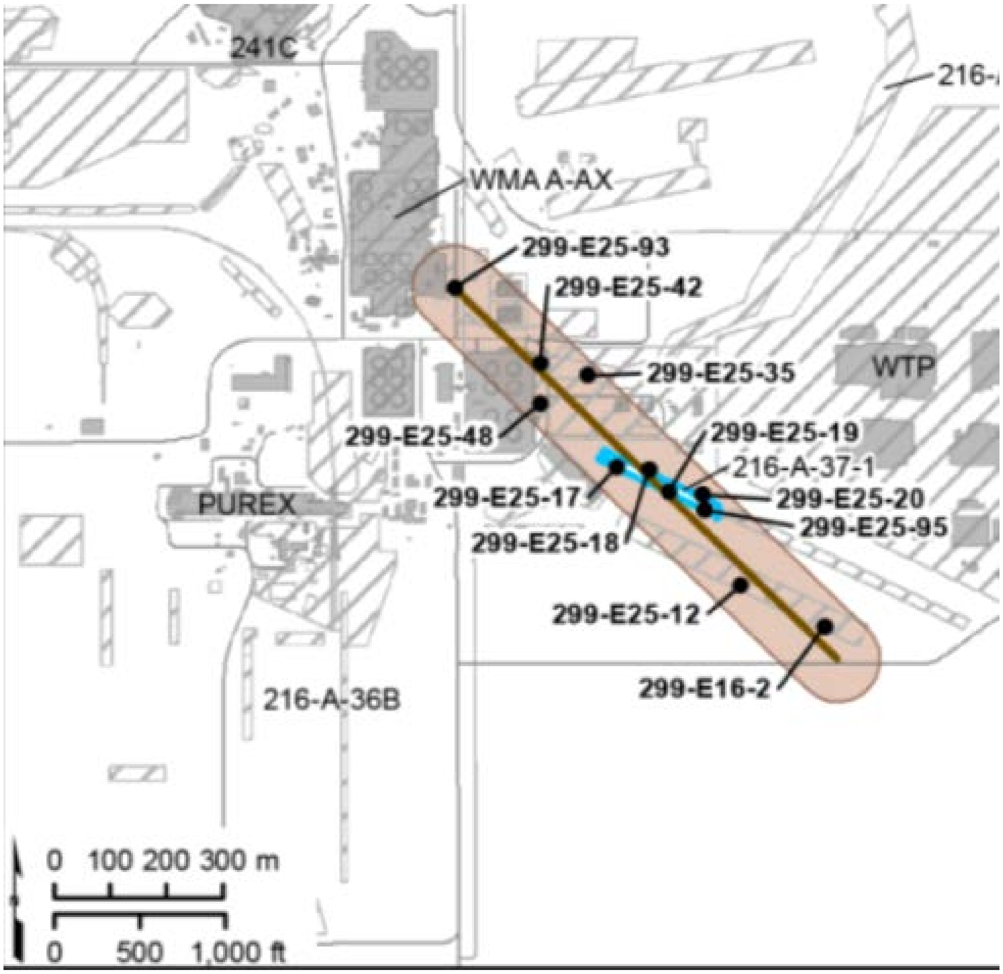


Figure A.1. Map of crib wells 299-E25-17, 18, 19, 20, 95 (from DOE 2011).

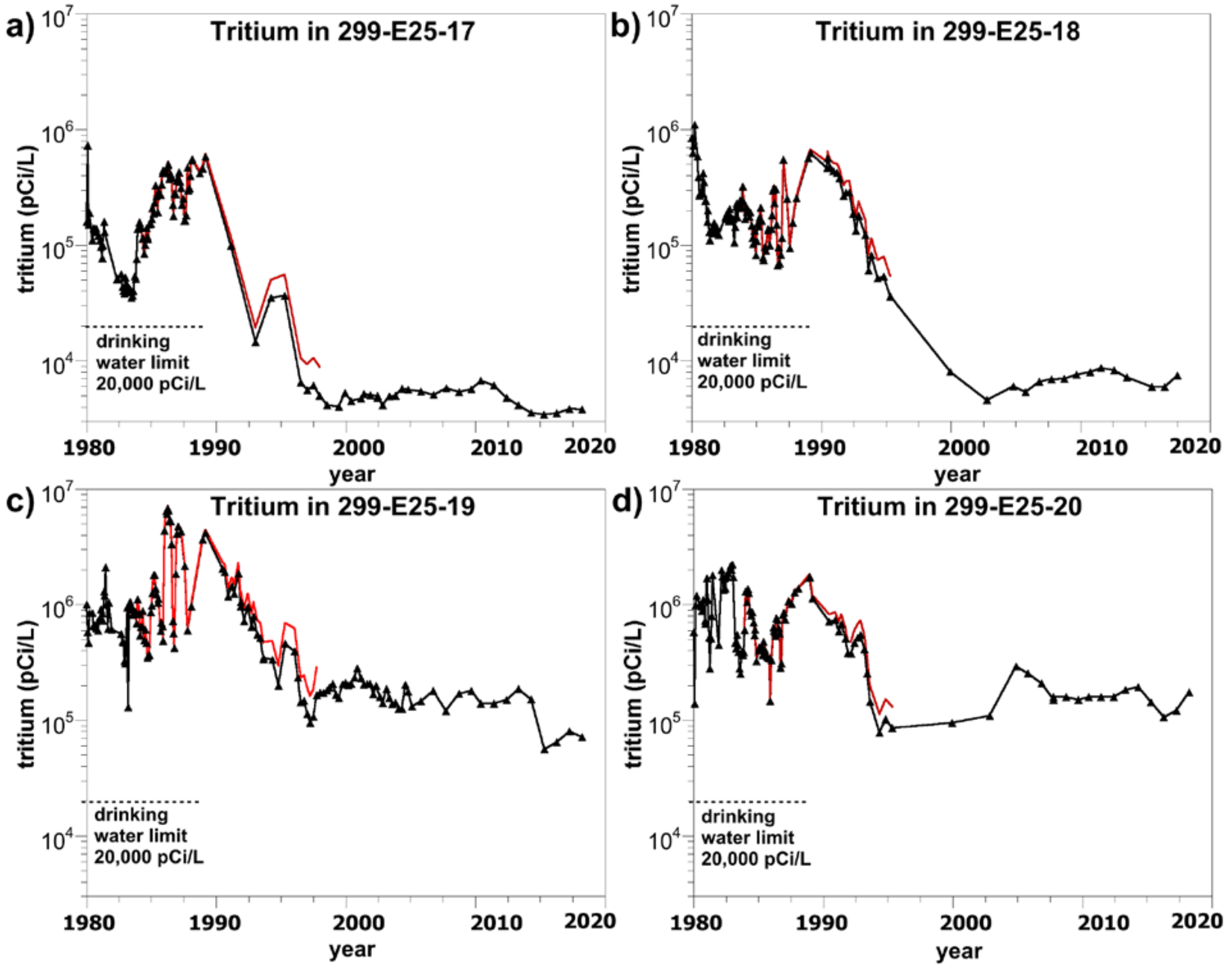


Figure A.2. Tritium in wells: a) 299-E25-17, b) 299-E25-18, c) 299-E25-19, and d) 299-E25-20 (data from HEIS; https://ehs.hanford.gov/eda/ constituent: tritium, wells 299-E25-17, -18, -19, and -20). Tritium in well 299-E-25-95 was not measured. Red line is the undecayed tritium concentrations estimated released in 1984 to 1988.

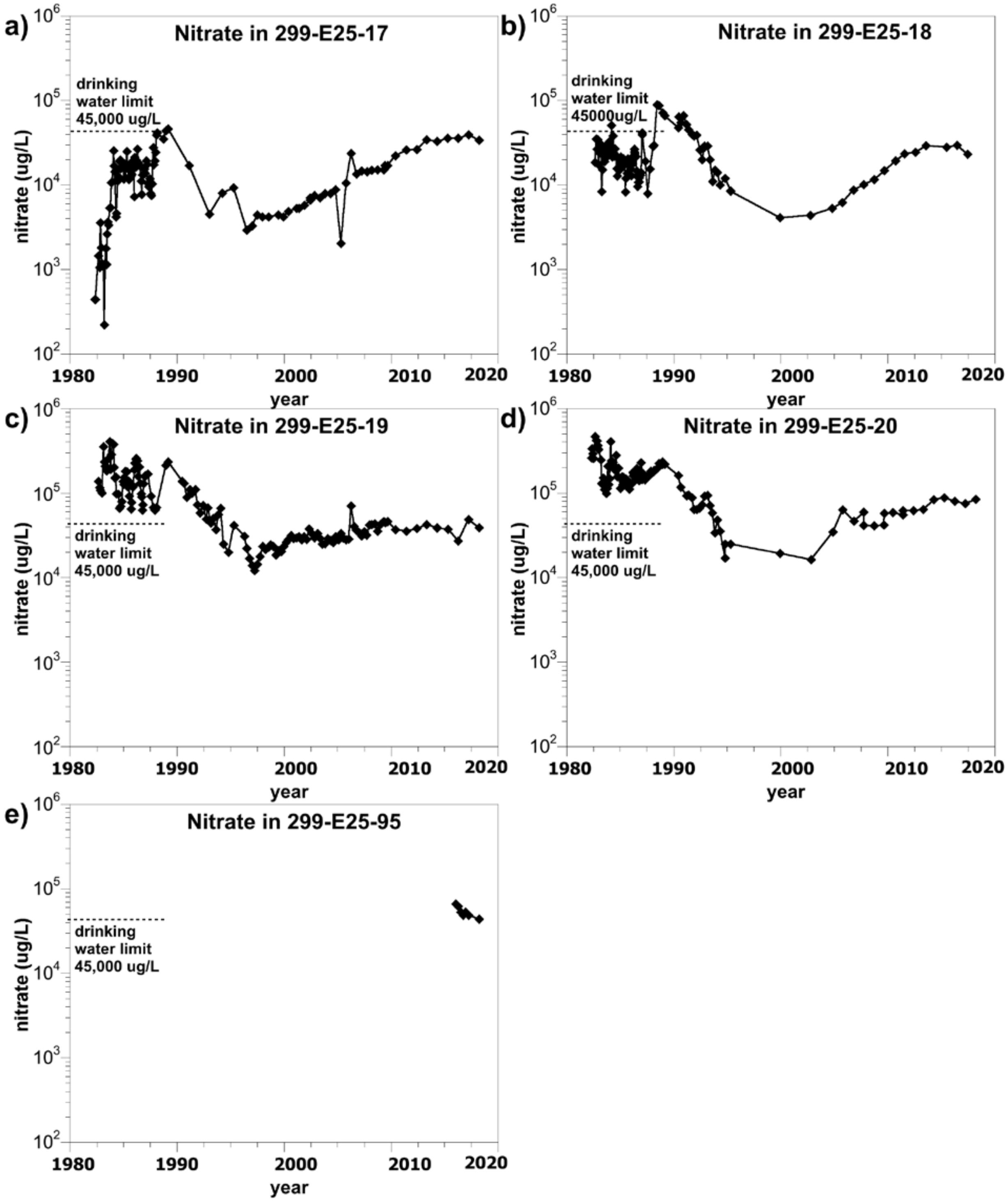


Figure A.3. Nitrate in wells: a) 299-E25-17, b) 299-E25-18, c) 299-E25-19, d) 299-E25-20, and e) 299-E-25-95 (data from HEIS; https://ehs.hanford.gov/eda/ constituent: nitrate, wells 299-E25-17, -18, -19, -20, and -95).

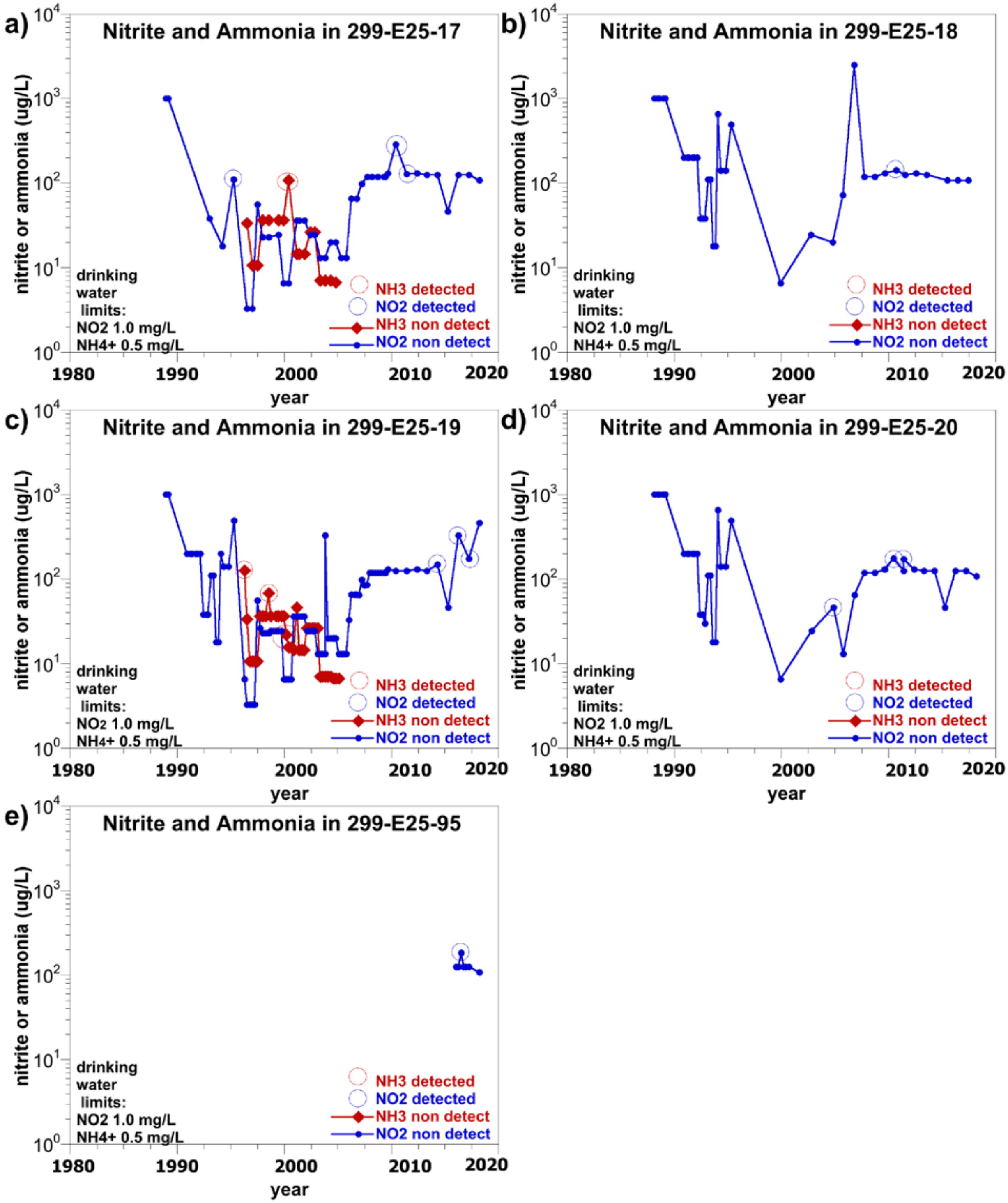


Figure A.4. Nitrite and ammonia in wells: a) 299-E25-17, b) 299-E25-18, c) 299-E25-19, d) 299-E25-20, and e) 299-E-25-95 (data from HEIS; https://ehs.hanford.gov/eda/ constituent: nitrite and ammonia, wells 299-E25-17, -18, -19, -20, and -95).

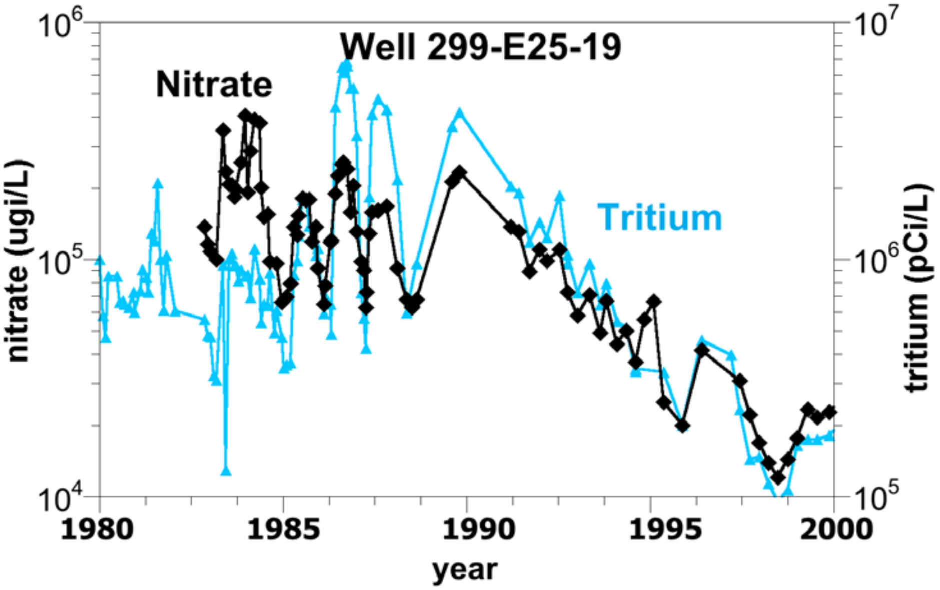


Figure A.5. Comparison of the timing of peaks of the tritium and nitrate concentrations for 299-E25-19 for the years 1980 to 2000 (data from HEIS; https://ehs.hanford.gov/eda/ constituent: nitrate and tritium, well 299-E25-19).

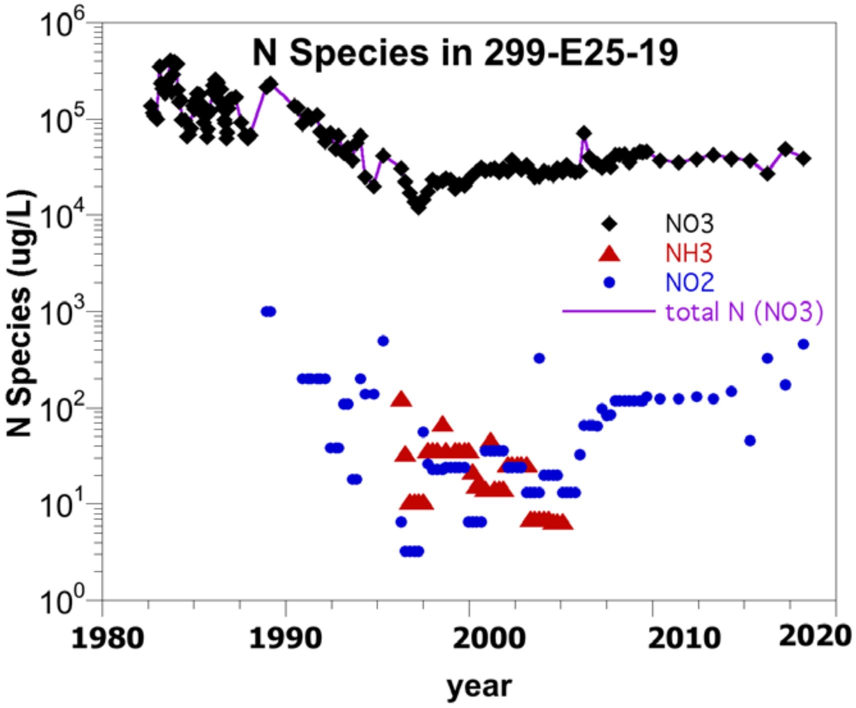


Figure A.6. Comparison of the concentrations of nitrate, nitrite, and ammonia for 299-E-25-19 (data from HEIS; https://ehs.hanford.gov/eda/ constituent: nitrate, nitrite, and ammonia, well 299-E25-19). The sum of the total N mass (purple line) was done in molar concentration, then plotted as nitrate (ug/L).

Appendix B – Ammonia Nitrification in Unsaturated Hanford Sediments

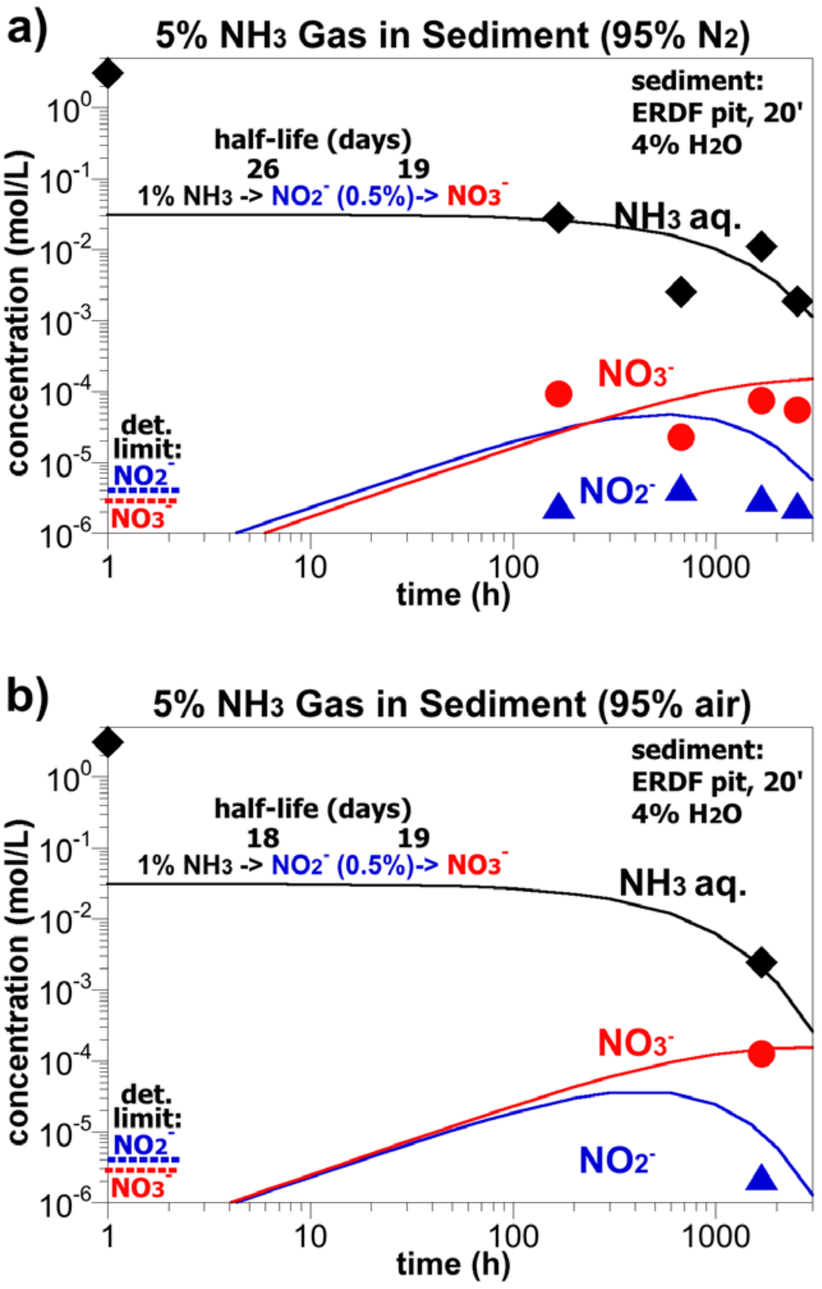


Figure B.1. 5% ammonia gas in Hanford formation sediments with mass loss and nitrification for a) 95% nitrogen (i.e., no oxygen in the gas phase), and b) 95% air. The 5% NH_3 in gas phase is equivalent to 1846 mg/L aqueous ammonia (3.1 mol/L). 99% of the NH_3 gas was lost to precipitation and adsorption to sediments. The best simulation fit to the data indicated 1% of the NH_3 gas was nitrified into nitrite then nitrate.

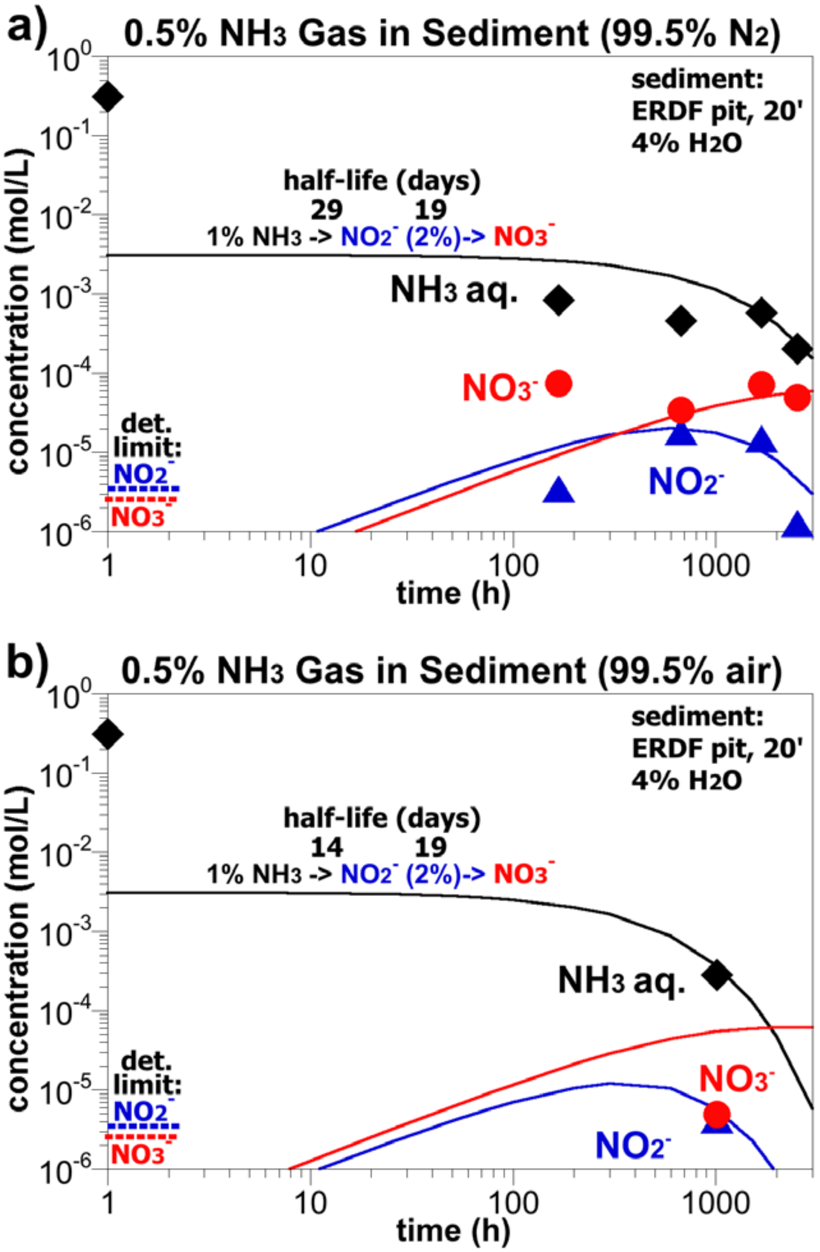


Figure B.2. 0.5% ammonia gas in Hanford formation sediments with mass loss and nitrification for a) 99.5% nitrogen (i.e., no oxygen in the gas phase), and b) 99.5% air. The 0.55% NH_3 in gas phase is equivalent to 185 mg/L aqueous ammonia (0.31 mol/L). 99% of the NH_3 gas was lost to precipitation and adsorption to sediments. The best simulation fit to the data indicated 1% of the NH_3 gas was nitrified into nitrite then nitrate.

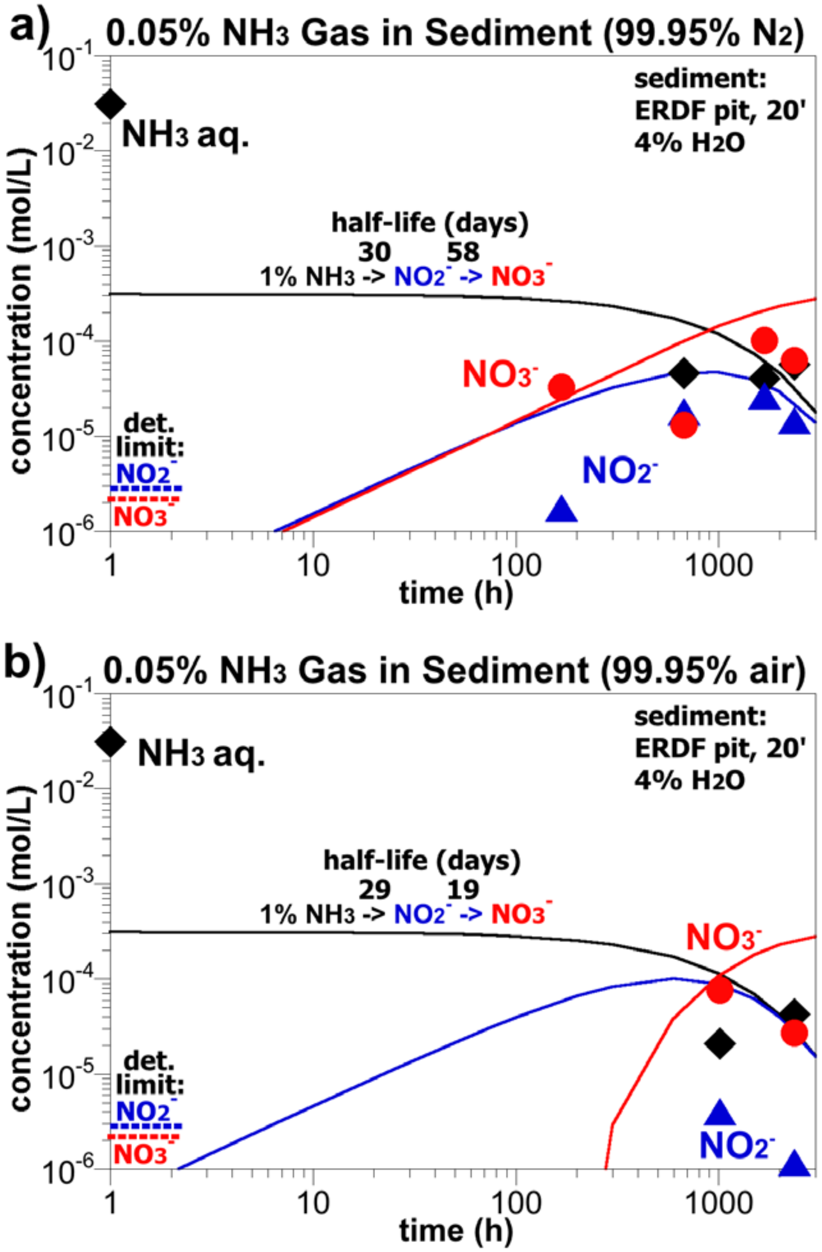
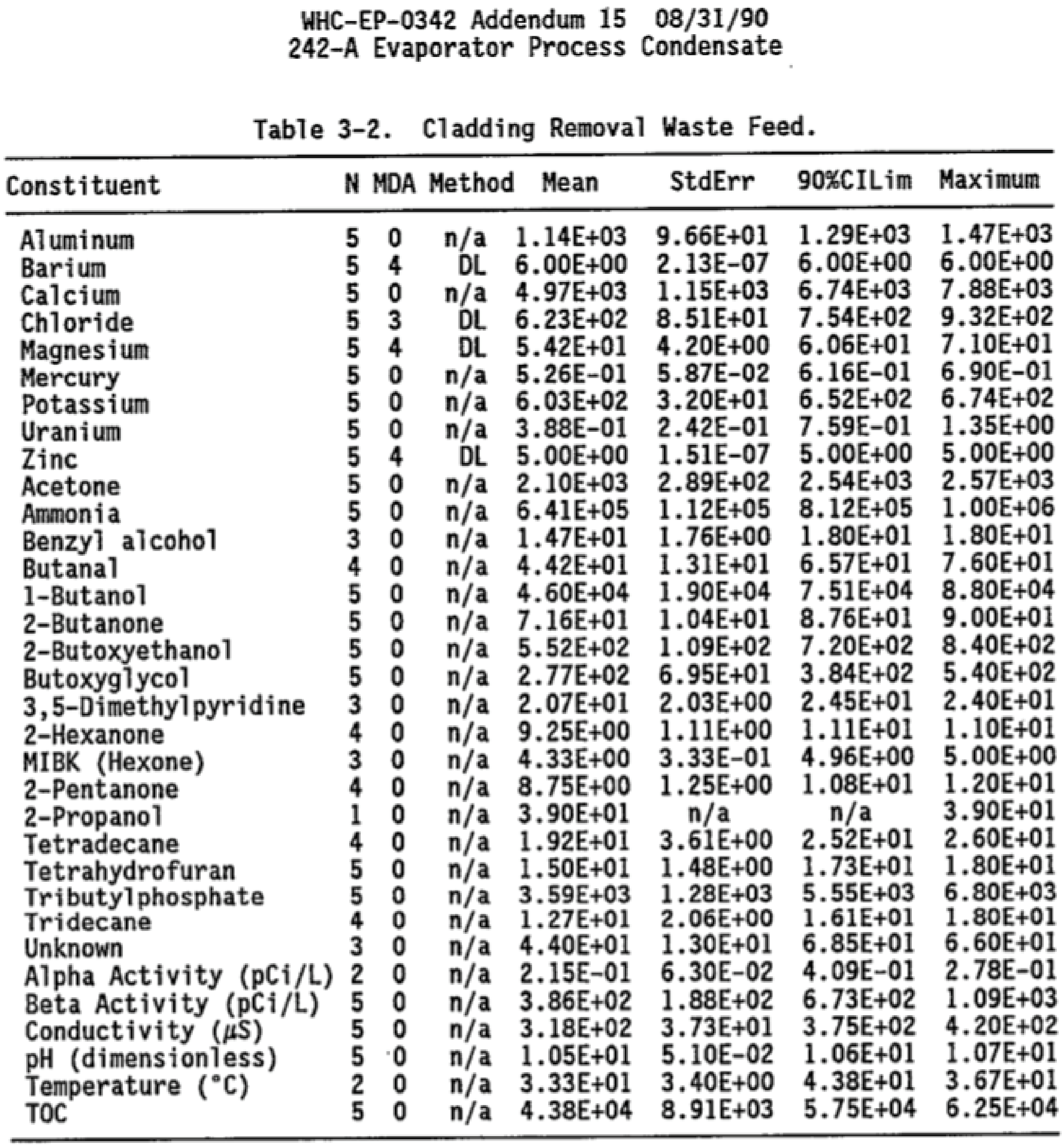


Figure A.3. 0.05% ammonia gas in Hanford formation sediments with mass loss and nitrification for a) 99.95% nitrogen (i.e., no oxygen in the gas phase), and b) 99.95% air. The 0.05% NH_3 in gas phase is equivalent to 18.5 mg/L aqueous ammonia (0.031 mol/L). 99% of the NH_3 gas was lost to precipitation and adsorption to sediments. The best simulation fit to the data indicated 1% of the NH_3 gas was nitrified into nitrite then nitrate.

Appendix C – Waste Feed from the PUREX Decladding Evaporator 242-A (from WHC 1990)



WHC-EP-0342 Addendum 15 08/31/90
242-A Evaporator Process Condensate

Table 3-2. Cladding Removal Waste Feed.

Constituent	N	MDA	Method	Mean	StdErr	90%CILim	Maximum
Aluminum	5	0	n/a	1.14E+03	9.66E+01	1.29E+03	1.47E+03
Barium	5	4	DL	6.00E+00	2.13E-07	6.00E+00	6.00E+00
Calcium	5	0	n/a	4.97E+03	1.15E+03	6.74E+03	7.88E+03
Chloride	5	3	DL	6.23E+02	8.51E+01	7.54E+02	9.32E+02
Magnesium	5	4	DL	5.42E+01	4.20E+00	6.06E+01	7.10E+01
Mercury	5	0	n/a	5.26E-01	5.87E-02	6.16E-01	6.90E-01
Potassium	5	0	n/a	6.03E+02	3.20E+01	6.52E+02	6.74E+02
Uranium	5	0	n/a	3.88E-01	2.42E-01	7.59E-01	1.35E+00
Zinc	5	4	DL	5.00E+00	1.51E-07	5.00E+00	5.00E+00
Acetone	5	0	n/a	2.10E+03	2.89E+02	2.54E+03	2.57E+03
Ammonia	5	0	n/a	6.41E+05	1.12E+05	8.12E+05	1.00E+06
Benzyl alcohol	3	0	n/a	1.47E+01	1.76E+00	1.80E+01	1.80E+01
Butanal	4	0	n/a	4.42E+01	1.31E+01	6.57E+01	7.60E+01
1-Butanol	5	0	n/a	4.60E+04	1.90E+04	7.51E+04	8.80E+04
2-Butanone	5	0	n/a	7.16E+01	1.04E+01	8.76E+01	9.00E+01
2-Butoxyethanol	5	0	n/a	5.52E+02	1.09E+02	7.20E+02	8.40E+02
Butoxyglycol	5	0	n/a	2.77E+02	6.95E+01	3.84E+02	5.40E+02
3,5-Dimethylpyridine	3	0	n/a	2.07E+01	2.03E+00	2.45E+01	2.40E+01
2-Hexanone	4	0	n/a	9.25E+00	1.11E+00	1.11E+01	1.10E+01
MIBK (Hexone)	3	0	n/a	4.33E+00	3.33E-01	4.96E+00	5.00E+00
2-Pentanone	4	0	n/a	8.75E+00	1.25E+00	1.08E+01	1.20E+01
2-Propanol	1	0	n/a	3.90E+01	n/a	n/a	3.90E+01
Tetradecane	4	0	n/a	1.92E+01	3.61E+00	2.52E+01	2.60E+01
Tetrahydrofuran	5	0	n/a	1.50E+01	1.48E+00	1.73E+01	1.80E+01
Tributylphosphate	5	0	n/a	3.59E+03	1.28E+03	5.55E+03	6.80E+03
Tridecane	4	0	n/a	1.27E+01	2.06E+00	1.61E+01	1.80E+01
Unknown	3	0	n/a	4.40E+01	1.30E+01	6.85E+01	6.60E+01
Alpha Activity (pCi/L)	2	0	n/a	2.15E-01	6.30E-02	4.09E-01	2.78E-01
Beta Activity (pCi/L)	5	0	n/a	3.86E+02	1.88E+02	6.73E+02	1.09E+03
Conductivity (µS)	5	0	n/a	3.18E+02	3.73E+01	3.75E+02	4.20E+02
pH (dimensionless)	5	0	n/a	1.05E+01	5.10E-02	1.06E+01	1.07E+01
Temperature (°C)	2	0	n/a	3.33E+01	3.40E+00	4.38E+01	3.67E+01
TOC	5	0	n/a	4.38E+04	8.91E+03	5.75E+04	6.25E+04

Appendix D – Selected Analyzed Species in Characterization Borehole C4106

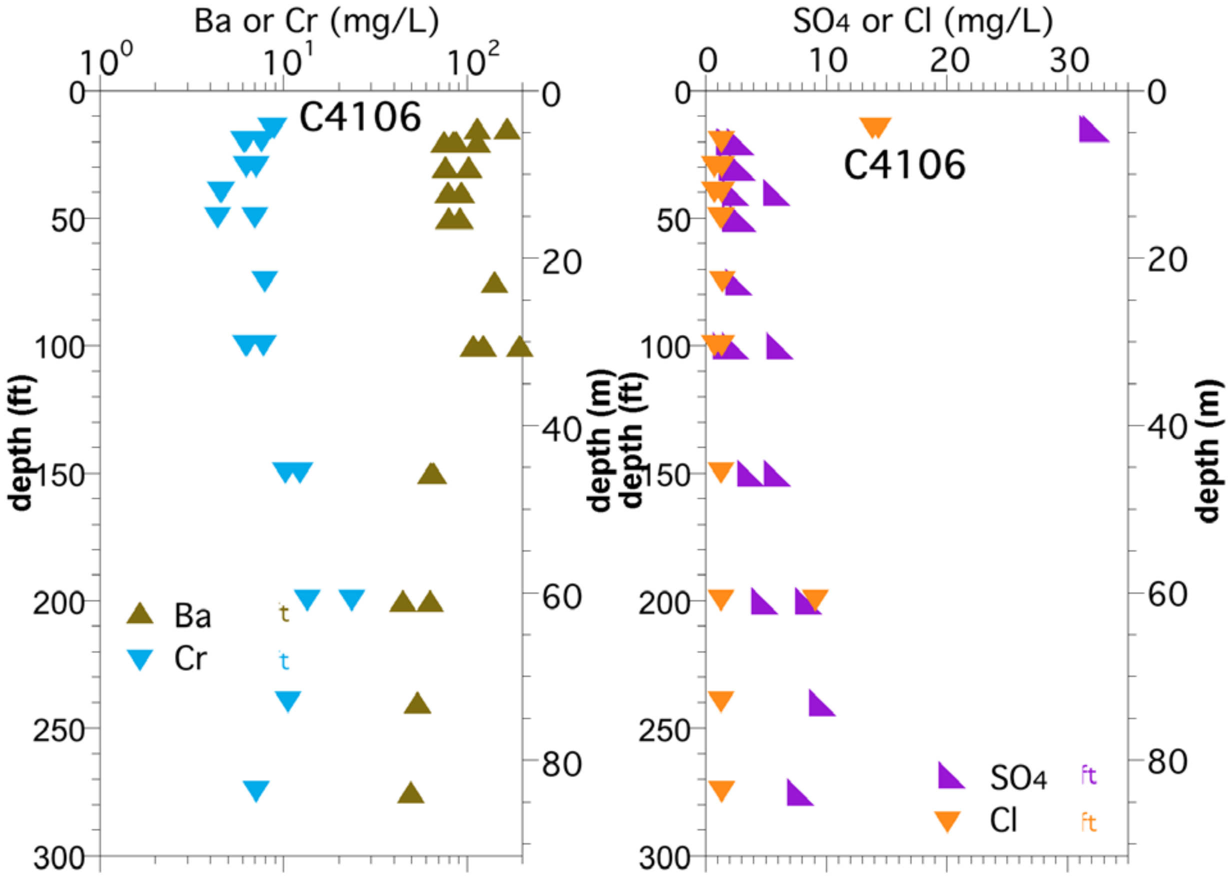


Figure D.1. Analysis from characterization borehole C4106 at SE end of A216-A-37-1 crib: a) Ba and Cr, and b) sulfate and chloride.

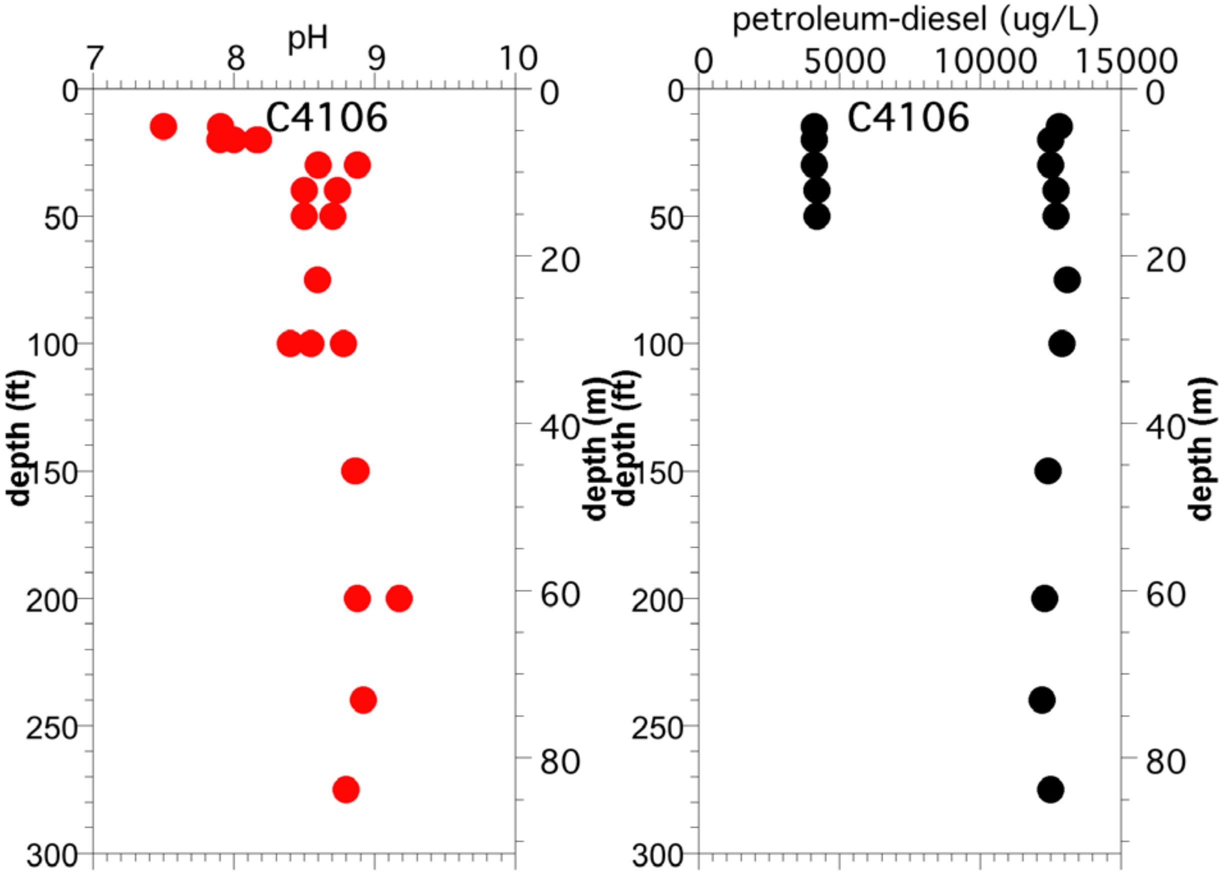


Figure D.2. Analysis from characterization borehole C4106 at SE end of A216-A-37-1 crib: a) pH, and b) petroleum hydrocarbons, diesel range.

PNNL-29999

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