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Characterization of Nitrate, Nitrite, Ammonia, and Tritium in D0220 Cores

September 2024

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Prepared for
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Abstract

This report describes characterization of nitrogen species (nitrate, nitrite, ammonia) in aqueous and solid phases in cores taken in borehole D0220 (well 299-E25-245) under crib 216-A-37-1 at the Hanford Site in 2022 to evaluate (a) the types of nitrogen species currently in the vadose zone and (b) the migration of nitrogen species in the vadose zone. Ammonia and tritium from PUREX decladding condensate were sporadically discharged to the crib from 1977 to 1989. During discharge operations, the estimated travel time through the vadose zone to groundwater was 2.5 to 9 months. After discharges ceased, vadose zone migration slowly returned to natural rates. By 2003, a characterization borehole (C4106) showed residual pore water with elevated tritium and nitrate in the first 100 ft of the vadose zone, which is likely from the crib. However, there was significantly more nitrate present at the shallowest depth (15 to 22 ft), which may indicate a different source for nitrate, such as adsorbed ammonia slowly being oxidized or nitrogen species precipitates slowly dissolving. Ammonia and nitrogen-containing precipitates were not measured in C4106 cores.

In this study, more extensive nitrogen species characterization was done on D0220 cores (drilled in 2022) at 40- and 262-ft depths, which included (a) aqueous nitrate, nitrite, and tritium; (b) adsorbed ammonia; (c) nitrogen in carbonates (or other minerals dissolved in acidic acid); (d) nitrogen in iron oxides (or other minerals dissolved in oxalic acid); and (e) nitrogen in hard-to-extract minerals (minerals dissolved in nitric acid). High pore water nitrate (226 to 331 mg/L) at 40-ft depth measured in D0220 (2022) compared to 60 mg/L at 40-ft depth in C4106 (2003) may indicate nitrate is migrating deeper. Tritium concentrations (pore water 132,000 to 148,000 pCi/L) measured in D0220 at 40-ft depth in 2022 were considerably higher than in C4106 at 40-ft depth (160 pCi/L). Additional nitrogen species mass was present in adsorbed and precipitated phases in D0220 cores. Low adsorbed ammonia was measured at 40.1- and 261.7-ft depths. Low concentrations of carbonate-associated nitrogen and iron oxide-associated nitrogen were present at 40.1- and 40.6-ft depths. Nitrogen species in solid phase extractions indicate nitrogen precipitates or aqueous nitrate or ammonia trapped in sediment microfractures that are coated by precipitates.

Overall, the nitrogen species and tritium characterization at two depths in D0220 showed that additional nitrogen species were present in the vadose zone. In addition, elevated pore water nitrate in D0220 at 40-ft depth from 2022 may indicate vertical migration compared to C4106 nitrate profile from 2003. Analysis of additional depths in D0220 and spatial variability of the nitrate plume along the length of the crib (from surface electrical resistivity) would be extremely useful for this comparison.

Acknowledgments

Funding for this work was provided by Central Plateau Cleanup Company. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the Department of Energy under Contract DE-AC05-76RL01830.

Acronyms and Abbreviations

NDIR	nondispersive infrared detector
NQAP	Nuclear Quality Assurance Program
pCi/L	picocuries per liter, units of radioactivity measurement for tritium
PNNL	Pacific Northwest National Laboratory
PTFE	polytetrafluoroethylene
PUREX	plutonium and uranium reduction and extraction process
RCRA	Resource Conservation and Recovery Act of 1976

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1.0 Introduction

This report describes characterization of nitrogen species (nitrate, nitrite, ammonia) in aqueous and solid phases in cores taken in borehole D0220 under crib 216-A-37-1 at the Hanford Site in 2022 to evaluate (a) types of nitrogen species currently in the vadose zone and (b) migration of nitrogen species in the vadose zone.

Crib 216-A-37-1 received 377 million liters of alkaline condensate discharged from March 1977 through April 1989. During discharge operations, the estimated travel time through the vadose zone to groundwater was 2.5 to 9 months based on the timing of tritium (a co-contaminant present) releases and monitoring in groundwater. Nitrate releases and 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. The nitrate dilution from crib discharge to groundwater indicates that up to 80% of N-species mass is not present in groundwater and thus may be retained in the vadose zone as aqueous, adsorbed, or precipitated nitrogen species (Szecsody et al. 2020). A borehole (C4106) drilled in 2003 near the southeast end of crib 216-A-37-1, located about 150 m to the northeast of D0220 (Figure 1), provided characterization of tritium and nitrogen species in the sediment profile at that time.

This study compares nitrogen species and tritium from cores of both boreholes to evaluate the movement of nitrogen species in the vadose zone. More specifically, cores from two depths in borehole D0220 as four samples (40.1', 40.6', 261.7', and 262.2') were analyzed for (a) pore water tritium, nitrate, and nitrite; (b) adsorbed ammonia; and (c) precipitate total nitrogen (i.e., ammonia or nitrate precipitates). These results are used to evaluate (a) the types of nitrogen species currently in the vadose zone and (b) the migration of nitrogen species in the vadose zone by comparison to a previous nitrogen species profile in the vadose zone (C4106).

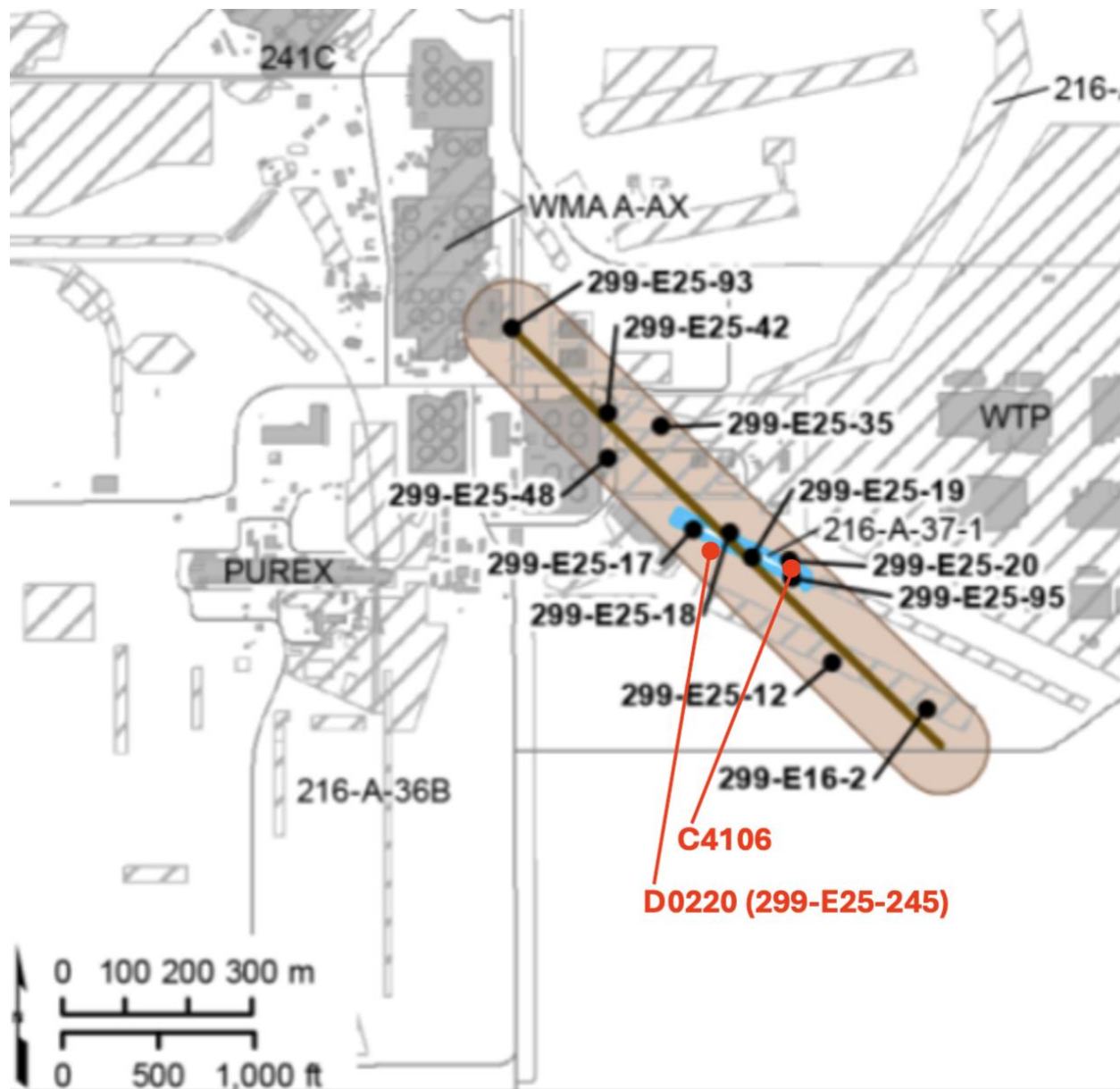


Figure 1. Map of PUREX crib 216-A-37-1 (blue), crib 216-A-37-2 (southeast of #1 crib), and surrounding wells and boreholes. Borehole C4106 (drilled 4/2003) was for cores only and was not completed as a well. Borehole D0220 (drilled 6/2022) was completed as well 299-E25-245 (source: DOE 2011). Brown line depicts wells in a northwest to southeast profile.

2.0 Background

The PUREX facility operated from 1956 to 1972 and 1984 to 1989 in the 200 East Area of the Hanford Site's Central Plateau (Agnew et al. 1997). One of the initial operations at the PUREX facility was decladding zirconium from irradiated fuel rods. 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.

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, 2017).

Because decladding operations were sporadic, 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) (Buel 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 a release volume of 1.34×10^7 liters (Brown et al. 1990).

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 1.34×10^7 liters discharged; Brown et al. 1990). 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 (Szecsody et al. 2020). 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.

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, as previously noted in Lindberg (1997), which implies both rapid nitrification of ammonia to nitrate and similar un-retarded migration of tritium and nitrate. 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, Szecsody et al. 2020), 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.

Borehole C4106, drilled in 2003, showed elevated tritium levels for the first 100 ft, indicating that there is residual discharge water in the upper vadose zone. Nitrate was moderately elevated at 30 to 100 ft, but with significantly higher concentration at the shallowest depth (15 and 22 ft). 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, because nitrate is not retarded in sediments, the elevated nitrate at the shallowest depths (<30 ft) may indicate a different source for nitrate, possibly adsorbed ammonia that has been slowly oxidized to nitrate or nitrogen species precipitates that are slowly dissolving.

3.0 Experimental

This section describes subsampling of sediment cores, sequential liquid extractions conducted on sediment samples, and nitrogen species and tritium analysis of extraction fluids.

3.1 Sediments

Two cores from borehole D0220 (well 299-E25-245) were obtained from Central Plateau Cleanup Company and subsampled at four depths (Table 1). Duplicate samples were used in analysis for the 40.1-ft depth. At the 262.2-ft depth, one sample used was the medium sand and the second sample used was from a silt/clay lens, as shown in Figure 2d, left center. The clay was analyzed separately, as it may retain higher contaminant concentrations due to higher water content. The water content of each core sample was measured (ASTM D2216-98 1998).

Table 1. Sediments from 100-KR-4 used for Cr analysis.

Borehole	Depth (ft, bgs)	HEIS #	Description	Moisture Fraction
D0220	40.1	B45899	Medium to fine sand	0.0496
D0220	40.1 dup	B45899	Medium to fine sand	0.0499
D0220	40.6	B45899	Medium to fine sand	0.0488
D0220	261.7	B458C3	Medium sand with some gravel	0.0645
D0220	262.2	B458C3	Medium fine sand with some clay	0.0587
D0220	262.2	B458C3	Medium sand (clay subsample)	0.0446

bgs = below ground surface; HEIS = Hanford Environmental Information System

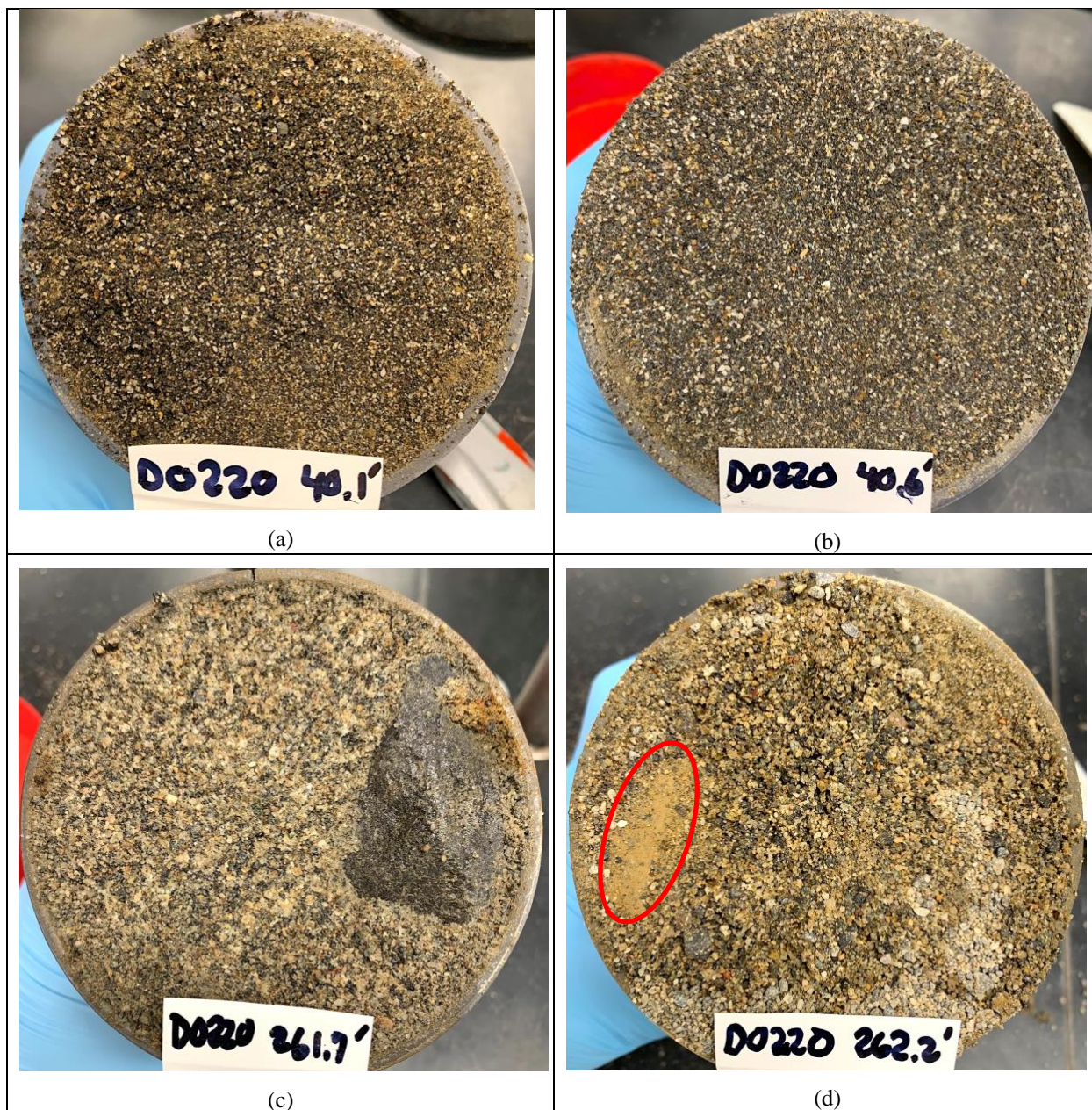


Figure 2. Borehole D0220 sediment samples at (a) 40.1-ft depth, (b) 40.6-ft depth, (c) 261.7-ft depth, and (d) 262.2-ft depth. Clay lens highlighted red in (d).

3.2 Sequential Liquid Extractions for Nitrogen Species

- For unsaturated sediment experiments, this study used a series of extractions to evaluate the different forms of nitrogen in the sediment, including (a) aqueous, (b) adsorbed, (c) precipitated in carbonates (Kohler et al. 2004), (d) precipitated in iron oxides (Chao and Zhou 1983; Hall et al. 1996), and (e) precipitated into hard-to-extract phases (i.e., aluminosilicates; EPA 1996). It should be noted that extractions 3 to 5 are operationally defined as the phase the extraction liquid is intended to extract (i.e., carbonates, iron oxides, aluminosilicates). In many sediments, multiple minerals dissolve in the different acidic solutions. Sequential liquid extractions have been used to characterize a wide variety of metals present in sediments in multiple surface phases (Becket 1989; Mossop et al. 2003; Gleyzes et al.

2002; Larner et al. 2006). Note that extraction solutions used in this study (described below) were modified to not contain nitrate, nitrite, or ammonia, in contrast to previous studies where the acetic acid solution contained calcium nitrate, the oxalic acid solution contained ammonium oxalate, and the hard-to-extract solution is typically 8 mol/L nitric acid. The sediment to solution ratio for all extractions is 1g to 3 mL. Extractions 1 through 4 are conducted at room temperature (20°C to 25°C).

- **Extraction 1.** For this aqueous extraction, 15 mL of deionized water was mixed with 5.0 (\pm 0.5) g of sediment. The exact weight of sediment added (to 1 mg accuracy) is recorded in a compatible container for 50 minutes by placing the tube on a slow ($<$ 30 rpm) mixer. The tube was then centrifuged at 3,000 rpm for 10 minutes, then liquid is drawn off the top of the sediment and filtered [0.45- μ m polytetrafluoroethylene (PTFE) filter] for analysis. The extraction 1 solution was used to measure (a) tritium by liquid scintillation counting (described in Section 3.3), (b) nitrite and nitrate by ion chromatography (Section 3.3), and (c) ammonia by Hach colorimetric analysis (Section 3.3).
- **Extraction 2.** For this extraction, 15 mL of the CaCl₂ ion exchange solution (reagent 2) was added to the tube containing sediment after the previous extraction solution is removed in an anaerobic chamber, mixed for 50 minutes at $<$ 30 rpm, centrifuged (3,000 rpm, 10 minutes), and liquid filtered using a 0.45- μ m PTFE filter. This ion exchange extraction solution was analyzed for ammonia by Hach colorimetric analysis.
- **Extraction 3.** For this extraction, 15 mL of the acetic acid solution (reagent 3) was added to the tube containing sediment after the previous extraction solution is removed, mixed for 5 days at $<$ 30 rpm, centrifuged (3,000 rpm, 10 minutes), and liquid filtered using a 0.45- μ m PTFE filter. This acetic acid extraction solution was analyzed for total aqueous nitrogen using the Shimadzu C/N analyzer (Section 3.3).
- **Extraction 4.** For this extraction, 15 mL of the pH 2.3 oxalic acid solution (reagent 4) was added to the tube containing sediment after the previous extraction solution is removed, mixed for 2 hours at $<$ 30 rpm, centrifuged (3,000 rpm, 10 minutes), and liquid filtered using a 0.45- μ m PTFE filter. This oxalic acid extraction solution was analyzed for total aqueous nitrogen using the Shimadzu C/N analyzer.
- **Extraction 5.** 15 mL of 8 mol/L sulfuric acid (reagent 5) was added to the tube containing sediment after the previous extraction solution is removed, mixed for 3 hours at 95°C with slow (6 rpm) rotary mixing, then centrifuged (3,000 rpm, 10 minutes), and liquid filtered (0.45- μ m PTFE). For this extraction, nitrile gloves are worn and filtering is conducted in a fume hood. This sulfuric acid extraction solution was analyzed for total aqueous nitrogen using the Shimadzu C/N analyzer.

3.3 Nitrogen Species and Tritium Analysis

Aqueous nitrite and nitrate were analyzed on a Dionex ICS-2000 ion chromatograph using a Pacific Northwest National Laboratory (PNNL) procedure (Operating Procedure OP-DVZ-CHPRC-0012, Rev. 0). All other anions were also analyzed (Br⁻, Cl⁻, F⁻, PO₄⁻³, SO₄⁻²) to ensure there was no overlap with known or unknown anions. Detection limits were 0.5 mg/L for nitrate and 0.25 mg/L for nitrite. Adsorbed ammonia was measured colorimetrically using a Hach 10031 kit. The detection limit was 0.1 mg/L.

Total extracted nitrogen from the sediment (extractions 3, 4, and 5) were measured using a carbon/nitrogen analyzer (Shimadzu model TOC-L CSH/CSN E100V) using a PNNL procedure (Operating Procedure OP-DVZ-CHPRC-0006, Rev. 0). For nitrogen analysis, the liquid sample is combusted by heating it to 680°C in a furnace to form nitrogen dioxide (NO₂) gas, which is analyzed in a nondispersive infrared detector (NDIR). The analog signal of the NDIR forms a peak, and the area is measured by the data processor. Each sample was analyzed four times. The detection limit of total N was 0.4 μ g/g. Extraction blanks were prepared for each extraction and subtracted from the total N for each

sediment extraction so that the reported total N was from the sediment and not (for example) from dissolved nitrogen in the extraction water.

Tritium was quantified in the deionized water extraction utilizing a liquid scintillation counter (Perkin Elmer 3100TR) using a PNNL procedure (Operating Procedure OP-DVZ-AFRI-001, Rev. 0). A series of three internal standards were used daily to verify the instrument was performing correctly. Quench standards were also used for tritium to account for count efficiency changes as the energy spectra changed, which may occur if different co-contaminants are present in different samples. The quench curve is used to accurately convert the energy-specific light emission spectra into isotope concentrations. The detection limit for tritium was 5 pCi/g.

4.0 Results

This section describes the results of the chemical extraction of nitrogen species and tritium from D0220 cores (Section 4.1) then compares the vadose zone depth profiles from D0220 to the profiles from C4106 for these nitrogen species and tritium (Section 4.2).

4.1 Nitrogen Species and Tritium Present in Borehole D0220

Pore water analysis showed that D0220 had elevated tritium (132,000 to 148,000 pCi/L) at the 40.1- and 40.6-ft depths and somewhat elevated nitrate (226 to 331 mg/L) at the 40.1-ft depth (Table 2). Greater depths (261.7, 262.2 ft) had low tritium (11,000 to 35,000 pCi/L) and low nitrate (73 to 85 mg/L) concentrations. No nitrite was detected at any depth. The 262.2-ft depth clay sample had slightly higher tritium and nitrate compared with the sand sample at the same depth.

The second extraction solution designed to exchange adsorbed ammonia did show measurable ammonia at the 40.1- and 261.7-ft depths that was significantly greater than the detection limit (0.1 mg/L).

Extractions 3, 4, and 5 were weaker to stronger acids designed to dissolve different mineral phases: (a) carbonates (extraction 3, acetic acid solution), (b) Fe-oxides (extraction 4, oxalic acid solution), and (c) aluminosilicates and other hard-to-extract phases (extraction 5, 8 mol/L sulfuric acid), although each of these extractions may, in fact, dissolve multiple mineral phases (see Section 3.2). With a detection limit of 0.5 µg/g, only the 40.1- and 40.6-ft depths showed significant carbonate-associated N (1.4 to 9 µg/g) and slightly elevated Fe oxide-associated N (1.2 to 2.4 µg/g).

These results imply that either (a) nitrogen is trapped in a precipitate dissolved by acetic acid or oxalic acid (b) or aqueous/adsorbed nitrate or ammonia is trapped in sediment microfractures that are coated by calcite or iron oxides. The final hot 8-mol/L sulfuric acid extraction dissolves multiple sediment minerals and mainly showed a relatively uniform 3.9 to 5.4 µg/g extractable N at 40.1-, 40.6-, 261.7- and 262.2-ft depths. The exception was the clay sample at 262.2-ft depth, which had 55 µg/g extractable N. This clay sample also had slightly elevated pore water nitrate (85 mg/L), so the sulfuric acid extractable N may represent some N species contamination or natural organic matter associated with the clay. Since the acetic acid and oxalic acid extractable N in the clay was low, it seems unlikely that there is N species contamination in this clay.

Table 2. Extraction results for borehole D0220 cores.

D0220 Depth (ft)	Pore Water Tritium (pCi/L)	Pore Water NO ₃ (mg/L)	Pore Water NO ₂ (mg/L)	ads. NH ₄ ⁺ (mg/L)	ppt N Carb.* (mg/L)	ppt N Fe Ox.* (mg/L)	ppt N Al,Si-ppt* (mg/L)	ppt N Carb.* (µg/g)	ppt N Fe Ox.* (µg/g)	ppt N Al,Si-ppt* (µg/g)
40.1	132,000	330.6	<0.25	1.51	51.5	13.6	30.8	8.96	2.36	5.36
40.1 dup	142,000	225.6	<0.25	BDL	11.0	9.8	30.9	1.45	1.29	4.07
40.6	148,000	96.6	<0.25	0.35	12.8	9.7	34.5	1.55	1.17	4.17
261.7	18,800	72.8	<0.25	2.32	9.3	7.1	41.2	1.08	0.83	4.80
262.2	11,400	26.3	<0.25	0.84	7.8	5.9	40.5	0.74	0.57	3.89
262.2 clay	34,800	84.8	<0.25	BDL	12.7	10.2	510	1.37	1.10	55.0

BDL = below detection limit

* extractions are operationally defined (see Section 3.2)

4.2 Comparison of Nitrogen and Tritium in Boreholes D0220 and C4106 and Implications for Migration

Previous analysis of pore water in borehole C4106 (from 2003) showed 500 to 1400 mg/L nitrate at 15- to 22-ft depth then 20 to 100 mg/L nitrate at 30- to 100-ft depth. In addition, tritium was 120 to 270 pCi/L at the 20- to 100-ft depth. As described earlier, the interpretation was that the lower nitrate concentrations at 30- to 100-ft depth may be residual pore water (i.e., depths that also contained some tritium), but the highly elevated nitrate concentrations at 20- to 30-ft depth may indicate a continuing source (i.e., recent infiltration event) or dissolution of a N-containing precipitate or oxidation of adsorbed ammonia. Ammonia was not analyzed in the C4106 pore water.

With essentially only two depths for borehole D0220, little can be said about the vertical nitrate profile in 2022 compared with the 2003 profile (C4106), except that the 40.1-ft depth contained 226 to 331 mg/L (D0220, 2022), which is much greater than 60 mg/L (C4106, 2003, Figure 3). Note that C4106 and D0220 are 160 m apart (Figure 4), so may have different contaminant depth profiles. C4106 is located at the southeast end of A216-A-37-1, where the input pipe is, so a greater volume of water may have infiltrated to depth, in contrast to D0220, which is located 2/3 of the crib length to the northwest (Figure 1), where less volume of water may have infiltrated into the vadose zone, so nitrate and tritium depth profiles may be shallower. Therefore, the higher nitrate at 40-ft depth in D0220 loosely implies that nitrate may be migrating deeper. Surface electrical resistivity arrays along the length of the crib would be highly useful for identifying the spatial variability of the shallow high-concentration nitrate.

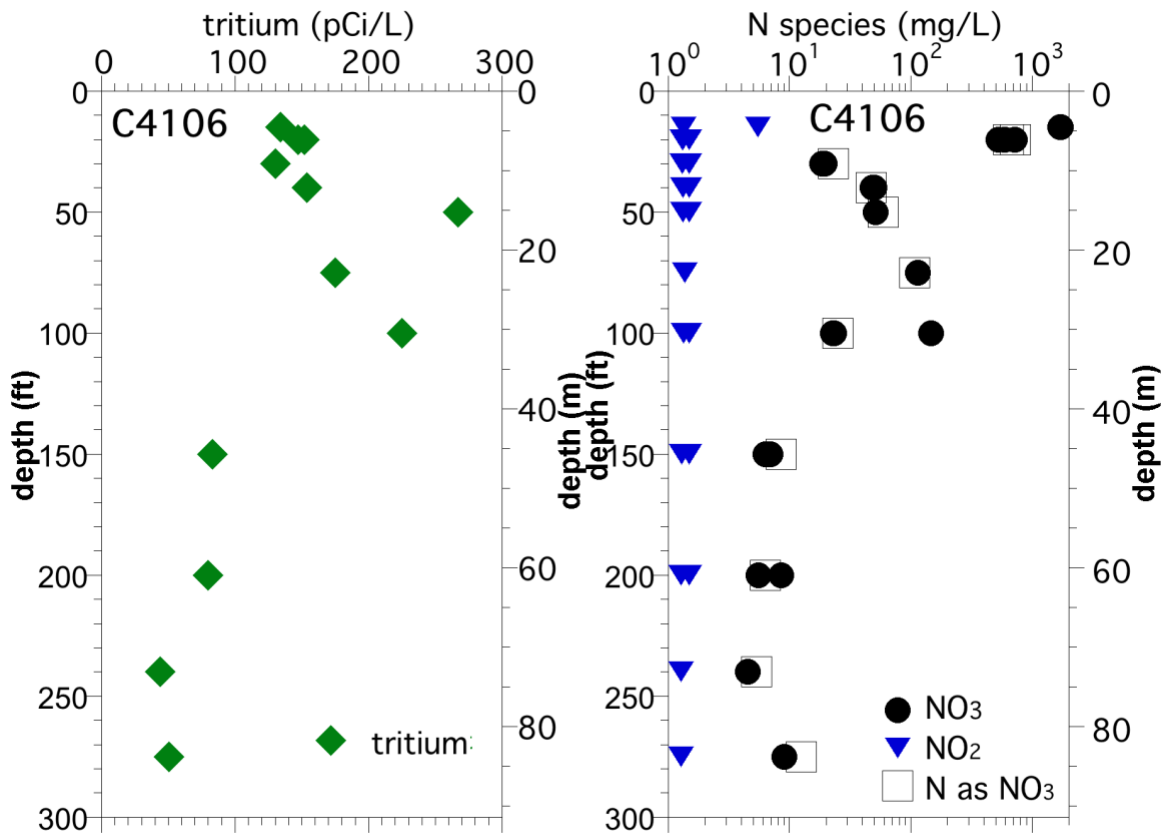


Figure 3. Analysis from characterization borehole C4106 (drilled in 2003) at SE end of A216-A-37-1 crib: (a) tritium and (b) nitrogen species (Szecsody et al. 2020).

Tritium concentrations (132,000 to 148,000 pCi/L) measured in D0220 at 40-ft depth in 2022 were considerably higher than in C4106 at 40-ft depth (160 pCi/L), although it is unclear if the C4106 reported values were in a 1:1 water extract of the sediment or in the pore water. Tritium concentrations in D0220 at 40-ft depth reported in the extract water (6,500 to 7,200 pCi/L) are still considerably greater than reported in C4106.



Figure 4. Wells and infrastructure surrounding borehole C4106 and D0220 (299-E25-245; both in yellow).

5.0 Conclusions

This report describes characterization of nitrogen species (nitrate, nitrite, ammonia) in aqueous and solid phases in cores taken in borehole D0220 under crib 216-A-37-1 at Hanford in 2022 to evaluate (a) types of nitrogen species currently in the vadose zone and (b) migration of nitrogen species in the vadose zone. The sporadic ammonia and tritium discharges from the crib from 1977 to 1989 initially reached groundwater at nearly the same time, implying both rapid nitrification of ammonia to nitrate and unretarded migration of tritium and nitrate through the vadose zone. By 2003, characterization of borehole C4106 showed elevated tritium and nitrate in the first 100 ft of the vadose zone, which is likely residual pore water from the crib. However, there was significantly higher nitrate present at the shallowest depth (15 to 22 ft), which may indicate a different source for nitrate, such as adsorbed ammonia slowly being oxidized or nitrogen species precipitates slowly dissolving.

In this study, more extensive nitrogen species characterization was done in D0220 cores (drilled in 2022) in comparison to cores from borehole C4106 (drilled in 2003), which included (a) aqueous nitrate, nitrite, and tritium; (b) adsorbed ammonia; (c) nitrogen in carbonates; (d) nitrogen in iron oxides; and (e) nitrogen in hard-to-extract minerals. High pore water nitrate (226 to 331 mg/L) at 40-ft depth in D0220 (2022) compared to 60 mg/L at 40-ft depth in C4106 (2003) may indicate nitrate is migrating deeper, as C4106 had higher nitrate (500 to 1400 mg/L) at shallower depths (15 to 22 ft). However, there may be spatial variability in the vadose zone nitrogen profile because infiltration from the crib likely varies along its length and the boreholes are in different locations. Tritium concentrations (132,000 to 148,000 pCi/L) measured in D0220 at 40-ft depth in 2022 were considerably higher than in C4106 at 40-ft depth (160 pCi/L), although it is unclear if the values reported for C4106 were based on a 1:1 water extract of the sediment or the pore water.

There was additional nitrogen species mass present in adsorbed and precipitated phases in D0220 cores. Low adsorbed ammonia was measured at 40.1- and 261.7-ft depths. Three solid phase extractions were conducted to determine if any nitrogen species were present in different mineral phases. Some carbonate-associated nitrogen (1.4 to 9 $\mu\text{g/g}$) was present at 40.1- and 40.6-ft depths. Slightly elevated iron oxide-associated nitrogen (1.2 to 2.4 $\mu\text{g/g}$) was also present at this depth (detection limit 0.5 $\mu\text{g/g}$). Finally, the sulfuric acid extraction dissolving multiple sediment minerals showed a uniform (4 to 5 $\mu\text{g/g}$) extractable N at all depths, except for a clay sample at 262.2-ft depth with elevated 55 $\mu\text{g/g}$. It is likely that this elevated nitrogen in the clay sample is natural organic matter. Nitrogen species in solid phase extractions indicate nitrogen precipitates or nitrate or ammonia trapped in sediment microfractures that are coated by precipitates.

Overall, the nitrogen species and tritium characterization at two depths in D0220 did show indications of additional nitrogen species (adsorbed ammonia and solid phase N) than just pore water nitrate. In addition, elevated pore water nitrate in D0220 at 40-ft depth from 2022 may indicate vertical migration compared to C4106 nitrate profile from 2003. Analysis of additional depths in D0220 would be extremely useful for this comparison. Spatial variability in infiltration between these two boreholes might also account for some of the difference in the nitrate vadose zone profiles. A surface electrical resistivity survey along the length of the crib would help characterize the spatial variability of the shallow nitrate profile.

6.0 Quality Assurance

This work was performed in accordance with the PNNL 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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