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Nitrate and Nitrite at Hanford – From Tanks to Natural Attenuation

February 2024

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

Washington River Protection *Solutions*, LLC (WRPS) contracted Pacific Northwest National Laboratory (PNNL) in support of their maturation testing and analysis to develop and deploy an ambient temperature solidification/stabilization process for low-activity waste (LAW) (referred to as "grout" in this report). The intent of this effort is to support a sample-and-send regulatory and processing strategy in the Hanford 200 West Area, specifically considering grout waste forms disposal at Hanford in the Integrated Disposal Facility (IDF). Currently the disposal of grouted LAW is not an option because the IDF is not permitted to receive this waste form. The material presented in this report is intended to help inform the U.S. Department of Energy (DOE), the site operating contractors, regulatory agencies, and stakeholders of the future implications of IDF disposal of a grouted LAW waste form, specifically for the behavior of nitrate (NO_3^-) and nitrite (NO_2^-) at the Hanford. The only calculation of nitrate release from a hypothetical grouted LAW inventory in the IDF showed that the overall release was slightly above the compliance limit of 45 mg/L nitrate and 3.32 mg/L nitrate after 1000 years (Asmussen et al. 2019). As such, uncertainty around the impact of nitrate and nitrite release from the IDF was identified in the recent National Academies of Sciences study of Hanford supplemental LAW by both the national laboratory team and Hanford stakeholders (Bates et al. 2023). However, these calculations (and others for the IDF involving secondary waste grout) may be conservative as no nitrate and nitrite retention in the grout waste form was assumed, nor any attenuation in the subsurface. There is evidence from the literature of processes that can attenuate nitrate migration both in the waste form and in the Hanford subsurface. If found to be technically defensible and likely to occur in the IDF and associated subsurface, then these processes should be included in modeling of the IDF to represent the behavior of nitrate and nitrite more accurately. Doing so would remove unnecessary conservatism in the modeling projections and reduce the uncertainty in assessments of facility compliance of a grouted LAW waste form in the IDF.

This report provides an overview of the contemporary knowledge of nitrate and nitrite at Hanford throughout the waste processing flowsheet and subsurface, including identifying the biogeochemical processes that occur both within the grout waste form matrix and in the subsurface environment. The information in this report can be used to guide future efforts of how the IDF performance assessment (PA) modeling tools represent grout waste forms by:

- Developing and documenting a conceptual model of the processes that impact the transport properties of nitrate and nitrite from grout waste forms made from LAW,
- Identifying how each underlying process could be numerically represented in reactive transport models,
- Identifying testing procedures to measure the impacts of the individual processes and to parameterize the numerical representations, and
- Prioritizing which processes are likely to have the greatest impact for nitrate and nitrite and initiating testing to parameterize the representations for highest priority items.

Based on the proposed conceptual model in this report a list of current uncertainties and gaps for the migration of nitrate and nitrite relevant to the IDF are presented. Closure of these gaps will provide further insight into nitrate and nitrite behavior that can support the full programmatic effort. From the evaluation of the relevant nitrate and nitrite information there are opportunities to better understand and predict the natural attenuation of nitrate in the subsurface below the IDF and accurately represent these processes in modeling projections. The highest priority items identified, which focus on assessing the technical defensibility of the likelihood of natural attenuation of nitrate and nitrite in or below the IDF, were:

Technical Gap	Proposed Approach	Impact
Are there stoichiometric correlations between the carbon inventory (both organic and inorganic) released from a grout waste form and the subsequent potential for biotic nitrate and nitrite removal? This also applies to other nutrients and electron donors released from the waste form (e.g., Fe (II), hydrogen, phosphate).	Organic and inorganic carbon release from grout waste forms is rarely tracked, yet, in the view of a natural attenuation mechanism for nitrate and nitrite, the availability of carbon (and other energy sources) would play a significant role in biotic activity. A study should be performed to document releases of carbon in relation to nitrate release from the same waste forms. This would be followed by comparing transport of these compounds in relevant IDF subsurface conditions and compared with naturally available carbon sources in the Hanford subsurface. Data from the lysimeter can also inform the laboratory test results.	Demonstrating that there is an adequate carbon source (or other energy sources) which travels simultaneously with nitrate released from a grout waste form to sustain biotic denitrification would build the technical defensibility of including subsurface biotic degradation of nitrate and nitrite in PA modeling.
What are the rates of nitrate and nitrite conversion in different aqueous environments in the Hanford subsurface? Specifically, information on nitrite can inform if complete conversion is possible.	There have been cursory studies of microbial conversion of nitrate and nitrite in Hanford environments; however, none in relevant conditions to the IDF subsurface or conditions relevant to grout leachates in the IDF. This study would give a sense of possible nitrate or nitrite conversion rates to be compared with migration and flow rates to assess the likelihood of conversion over time. End-products of the conversions would also be evaluated.	This study would give a sense of possible nitrate or nitrite conversion rates that can be coupled with COC migration and flow rates to assess the likelihood of conversion over time in or below the IDF. This assessment will inform the technical defensibility of nitrate and nitrite natural attenuation to be included in IDF PA modeling.
Are there mineral precipitation reactions that occur in the IDF and subsurface sediments involving nitrate or nitrite when contacted with an alkaline leachate from a grout waste form, similar to those that occurred in crib discharges?	Prior evidence has shown the formation of a nitrate-cancrinite mineral phase when alkaline waste discharges to Hanford sand occurred. Grout leachate is also highly alkaline and concentrated in salts. A laboratory effort should be performed to observe transformations of Hanford sediments when contacting grout leachates. The experiments would be supported with prior data comparing mineral changes	This effort would provide crucial information to support the technical defensibility of mineral incorporation of nitrate and nitrite in the IDF. Doing so would inform decisions of including mineral incorporation of nitrate and nitrite in PA modeling.

	from tank leaks and intentional discharges. This effort would provide information if mineral incorporation of nitrate and nitrite is likely in the IDF.	
How do nitrate to nitrite ratios from tanks and crib discharges correlate to existing and prior subsurface data?	Tracking previous conversions of nitrate and nitrite in the subsurface is challenging mainly due to a lack of initial data for the starting inventories of each. The ratios of nitrate and nitrite can be correlated to measured values in tanks and discharged wastes to see if any loss was observed. For example, an increase in the nitrate to nitrite ratio could indicate a loss of nitrite in the subsurface. This approach could also employ isotope ratios to determine nitrate sources (natural vs. from tanks).	This effort would fill a crucial information gap around the conversion of nitrate and nitrite in the Hanford subsurface by utilizing source term ratios from prior discharges. Specifically for nitrite, the available data on nitrite is limited as it was not a target of historical analyses, and many existing measurements are below detection limits. If existing data shows nitrite is lost in the subsurface (based on relative ratios to source term, or in experimental testing) it would build the technical defensibility for nitrite attenuation below the IDF.
Can grout performance be shown to consistently lower nitrate and nitrite release using alternate formulations or other methods?	Continue testing of alternate grout formulations to assess improved nitrate and nitrite release.	Success in this development can show that the waste form alone can be suitable for mitigation of nitrate and nitrite release from the IDF

Acknowledgments

The authors would like to thank Rodney Skeen, Ridha Mabrouki and David Swanberg at Washington River Protection Solutions, LLC for programmatic support. The authors also thank Jim Neeway, Hilary Emerson, and David Peeler (PNNL) and Rodney Skeen, David Swanberg and Jacob Reynolds (WRPS) for their technical reviews. The authors acknowledge Kearn (Pat) Lee for figure assistance.

Acronyms and Abbreviations

Acronym	Definition
CCU	Cold Creek unit
CCUc	Cold Creek unit – caliche
CCUg	Cold Creek unit – gravel dominated
CCUz	Cold Creek unit silt-dominated
CF	chloroform
COC	constituent of concern
CT	carbon tetrachloride
DCM	dichloromethane
DOE	U.S. Department of Energy
DRNA	dissimilatory nitrate reduction to ammonia
EPA	U.S. Environmental Protection Agency
EQL	estimated quantitation limits
ERT	electrical resistivity tomography
ETF	Effluent Treatment Facility
FBR	fluidized bed reactor
FS	feasibility study
FY	fiscal year
GFC	glass-forming chemicals
H1	Hanford formation unit 1
H2	Hanford formation unit 2
IDF	Integrated Disposal Facility Hanford
LAW	low-activity waste
LERF	Liquid Effluent Retention Facility
LFCM	liquid-fed ceramic melter
LSW	liquid secondary waste,
MIBK	methyl isobutyl ketone
MNA	monitored natural attenuation
OU	operable unit
P&T	pump and treat
PA	performance assessment
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
RI	Record index
ROD	record of decision
Rwie	Ringold formation member of Wooded Island unit E
VSL	Vitreous State Laboratory
WMA	Waste Management Area
WRPS	Washington River Protection *Solutions*, LLC
WTP	Hanford Waste Treatment and Immobilization Plant

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1.0 Introduction

Washington River Protection *Solutions*, LLC (WRPS) contracted Pacific Northwest National Laboratory (PNNL) in support of their technology maturation testing and analysis to develop and deploy an ambient temperature solidification/stabilization process for low-activity waste (LAW) (referred to as "grout" from this point onwards). The intent of this effort is to support a sample-and-send regulatory and processing strategy in the Hanford 200 West Area, where decisions could be made on waste composition to dispose of on-site or at an off-site disposal facility. This report specifically considers waste form disposal at the Hanford Site (referred to as "Hanford" in this report) in the Integrated Disposal Facility (IDF). Currently the disposal of grouted LAW waste forms in the IDF is not an option because the facility is not permitted to receive this waste form. The information presented in this report is intended to help inform the U.S. Department of Energy (DOE), the site operating contractors, regulatory agencies, and stakeholders of the future implications of on-site disposal of this waste form, specifically for nitrate (NO_3^-) and nitrite (NO_2^-). For IDF disposal, the waste form needs to sufficiently retain constituents of concern (COC), including nitrate and nitrite that both have large inventories in the Hanford tanks. "Sufficient retention" is defined as modeled compliance with the drinking water standard in groundwater at a monitoring point 100-m downgradient from the IDF. Because this definition of "sufficient retention" depends on several factors including the predictions of waste form aging, on the fate of the COCs upon environmental release and any attenuation processes experienced, these processes should be captured in long-term modeling projections. The only calculation of nitrate or nitrite release from a hypothetical grouted LAW inventory in the IDF showed that the overall release was slightly above the compliance limit after 1000 years without treatment and decreasing release by $< 2 \times$ would be compliant (Asmussen et al. 2019). As such, uncertainty around the impact of nitrate and nitrite release from the IDF was identified in the recent National Academies of Sciences review of Hanford supplemental LAW alternatives by both the national laboratory team and Hanford stakeholders (Bates et al. 2023). "Supplemental" LAW refers to the additional treatment capacity presumed to be required at Hanford to immobilize all the LAW. However, the IDF calculations (and others for the IDF involving secondary waste grout) may be conservative as the calculations assumed no retention of nitrate in the grout waste form, nor any attenuation in the subsurface. There is evidence of processes that can control nitrate or nitrite migration both from the waste form and in the Hanford subsurface. If technically defensible, these processes should be included in modeling of the IDF to improve the accuracy of the predicted behavior of nitrate and nitrite and remove unnecessary conservatism in the modeling projections.

This report provides an overview of the contemporary knowledge of nitrate and nitrite at Hanford, including identifying the biogeochemical processes that occur both within the immobilization waste form matrix and in the soil environment once COCs are released from the waste form. The intent of this effort is to develop a comprehensive upgrade on how the IDF performance assessment (PA) modeling tools represent grout waste forms by:

- Developing and documenting a conceptual model of the processes that will impact the transport properties of nitrate and nitrite from grout waste forms made from high salt containing liquids,
- Identifying how each underlying process could be numerically represented in reactive transport models,
- Identifying testing procedures to measure the impacts of the individual processes and to parameterize the numerical representations, and
- Prioritizing which processes are likely to have the greatest impact for nitrate and nitrite and initiating testing procedures to parameterize the numerical representations.

1.1 Integrated Disposal Facility (IDF)

The IDF is located in the 200 East Area of the Central Plateau at Hanford, southwest of the Hanford Waste Treatment and Immobilization Plant (WTP) (Krupka et al., 2004; USDOE, 2018). The IDF is a near-surface burial facility excavated about 13 m (42 ft) below the ground surface into the vadose zone which includes upper Hanford formation sediments. The current design of the IDF includes two cells (300,000-m^3 capacity) that were constructed in 2006, Figure 1 (Bates et al., 2019). The bottom of the facility includes primary and secondary geomembrane liners with a leak detection system installed between them. A low-permeability bentonite admix layer is installed beneath the secondary liner. A gravel drainage layer is installed above the primary liner and an operations layer consisting of compacted sands excavated during facility construction is installed above the drainage layer. Waste packages will be placed on the operations layers, the space between packages will be backfilled with lightly compacted Hanford formation sands excavated from the site, and an additional operations layer will be completed to serve as the base for the next lift of waste packages. Four lifts are planned for most waste packages. The liners and drainage layers are sloped to collect leachate from each cell and direct it to a sump where it is pumped to storage tanks prior to being treated for disposal. The IDF is currently planned to be covered with a Resource Conservation and Recovery Act (RCRA) Subtitle C barrier to limit intrusion of water and prevent inadvertent intrusion from plant and animal life. The cover will consist of silt loam and topsoil layers for water retention, sand, and gravel layers for drainage off the facility, and low permeability asphaltic layers. The long-term average water flux through the cover and into the underlying facility was assumed to be 3.5 mm/yr (0.14 in/yr) for the IDF PA based on current estimates for typical soils and vegetation in the 200 East Area. The center of the IDF is elevated to provide a slope to prevent mixing of leachates from the individual cells of the facility and will direct the liquids to the individual sumps of each cell. Contaminant releases from the IDF are anticipated to be primarily from the leachate collection system sumps located at the bottom corners of the facility (Figure 2).

Figure 1 – Photograph of the Hanford IDF facing south.

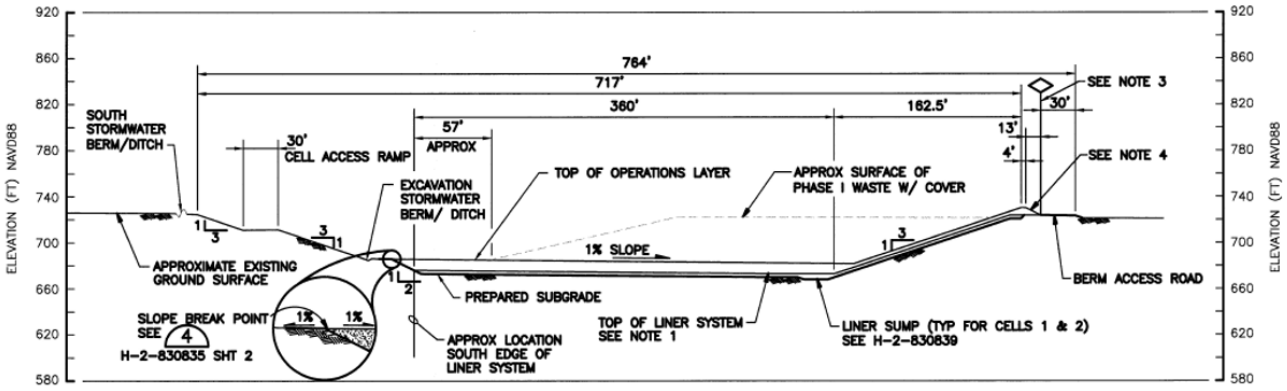

Figure 2 - North-south cross-section of the IDF showing the location of the liner sump from Figure 2-8 of (USDOE, 2018).

1.2 Geology Below the IDF

The generalized stratigraphy at the IDF site, shown in Figure 3, consists primarily of Hanford formation sands and gravels, Ringold formation units, and the underlying Columbia River basalts (Reidel and Fecht, 2005). The basalts occur across 200 East and the surrounding area and form the base of the unconfined aquifer. Total thickness of the unconsolidated Hanford and Ringold sediments ranges from more than 150 m (500 ft) at the southern end of the site to about 140 m (450 ft) at the north. Ringold Unit A is a sandy gravel with some interbedded sand and silt and is approximately 30 m (100 ft) thick to the west of the site. The Lower Mud is a sandy to silty mud grading downward to silty mud with organic-rich zones, with a maximum thickness at the site of about 18 m (60 ft). Unit E is a sandy gravel to gravelly sand with large pebbles and cobbles and is as much as 15 m (50 ft) thick at the site. A northwest-southeast trending erosional channel is present at the IDF site, centered along the northeast corner. The Ringold units pinch out to the northeast of the site as represented in the 2018 IDF PA (USDOE, 2018).

The Hanford formation at the IDF site consists of gravel- and sand-dominated facies. The lower gravel-dominated facies consist of cobbles and pebbles with minor amounts of sand and no cementation. The gravel is over 30 m (100 ft) thick in the northeast of the site and thins to the southwest. The sand-dominated facies consist of more than 82 m (270 ft) of fine- to coarse-grained sand with minor amounts of silt and clay. Some gravelly sands are present. The presence of silt and clay generally decreases to the northeast and east across the site. Three paleosols (buried horizons exhibiting some soil development) were identified in the Hanford formation sediments; typically, 10 to 15 cm (4 to 6 inches) thick, the paleosols had slightly higher moisture contents than surrounding sediments. A 3D recreation of the IDF subsurface is shown in Figure 4, which includes the Cold Creek formation that is present in the Hanford 200-E area. Clay lenses may also be present that can impede migration (Fendorf and Jardine, 2006).

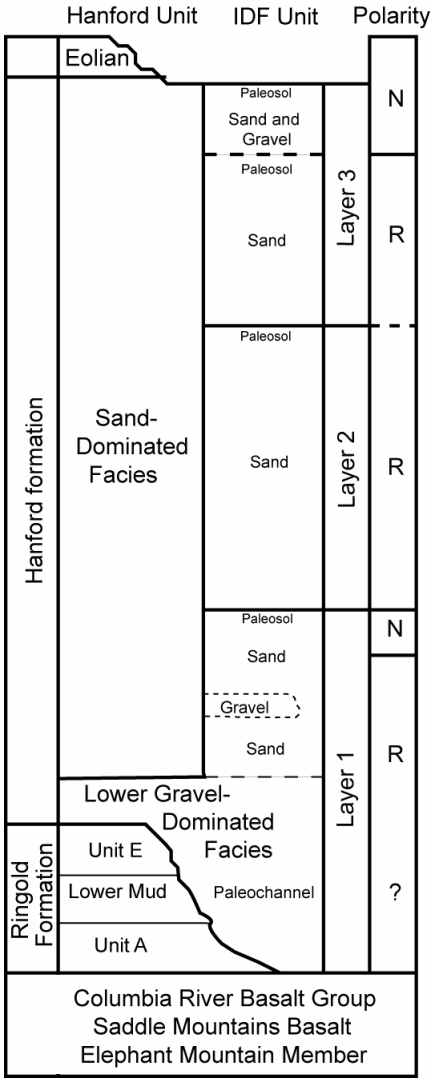

Figure 3 - IDF Site Stratigraphy
(Reidel and Fecht, 2005)

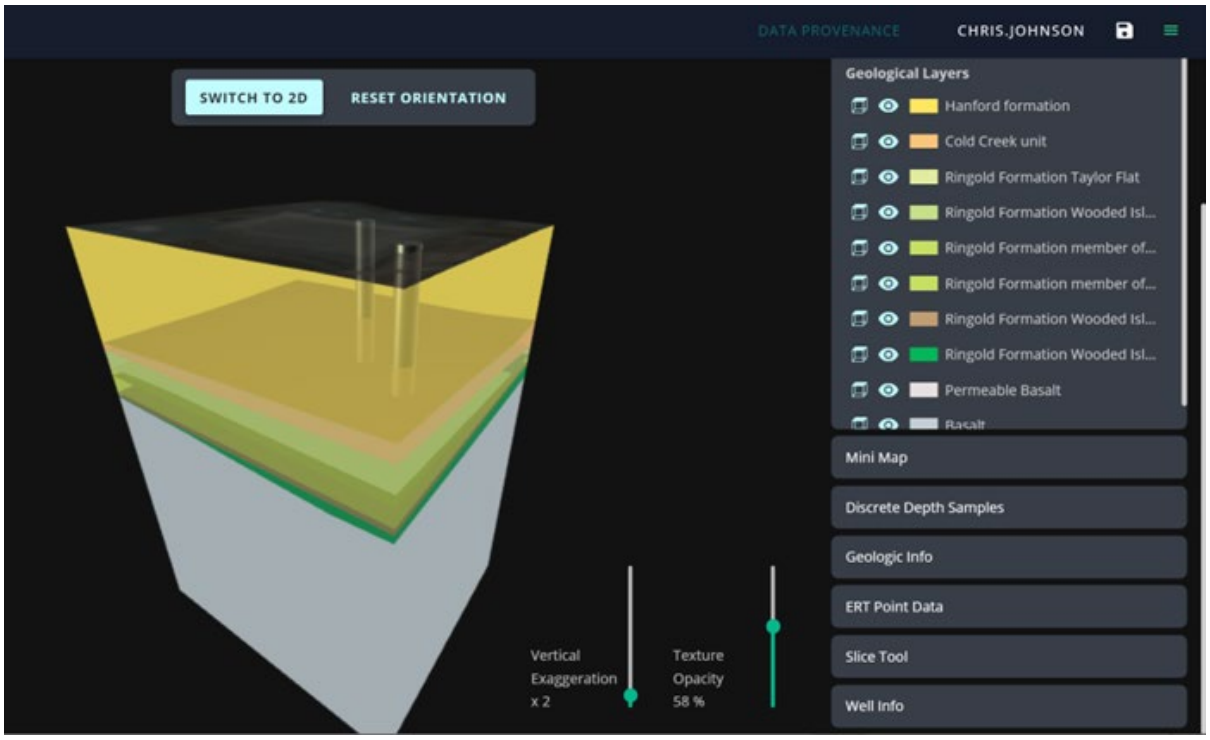

Figure 4 – View from ORIGEN (https://socrates.pnnl.gov) looking to the northwest showing the Hanford South geoframework model (CP-67635, Rev. 0) underneath the IDF. The tubes represent wells.

The water table occurs in Ringold Unit E to the south of the IDF site and in the lower gravel unit of the Hanford formation where the Ringold units have been eroded. Groundwater flow is generally to the east and southeast across the IDF site, ultimately discharging to the Columbia River.

Following release from the waste forms, the migrating species were modeled to be released from the IDF via the sump in the liner located at the bottom of the IDF. The release from the IDF to the vadose zone is assumed to occur at the sump location. Released contaminants are then transported through the vadose zone to the water table and migrate with the groundwater. A visual of the sump locations above the subsurface layers below the IDF is shown in Figure 5 and a conceptual view of COC release from the IDF is shown in Figure 6.

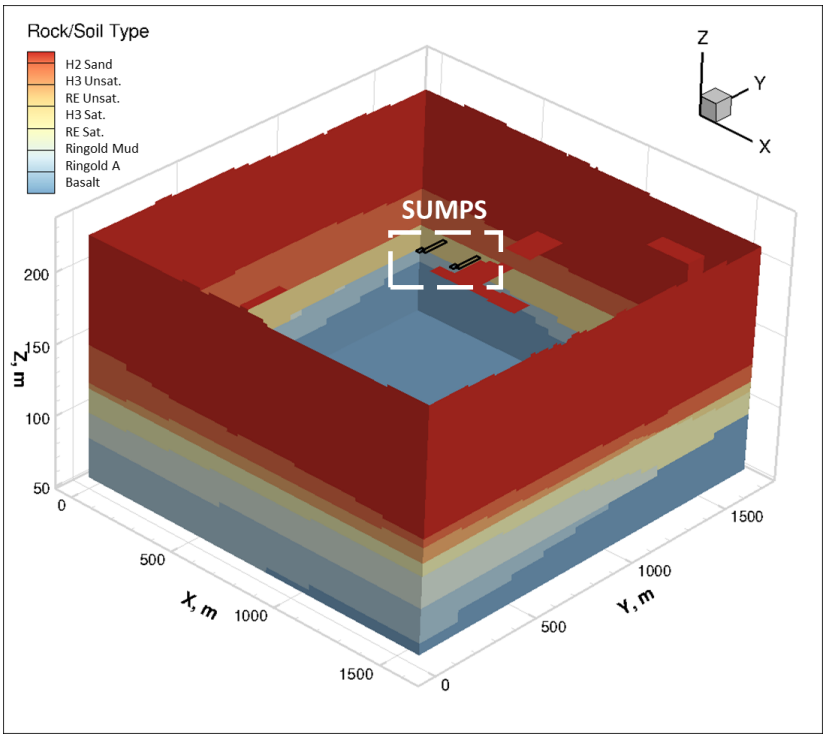

Figure 5 - Visualization of the simulated subsurface below the IDF and the location of the sumps where release of contaminants from the IDF occurred in the simulations (Asmussen et al., 2019).

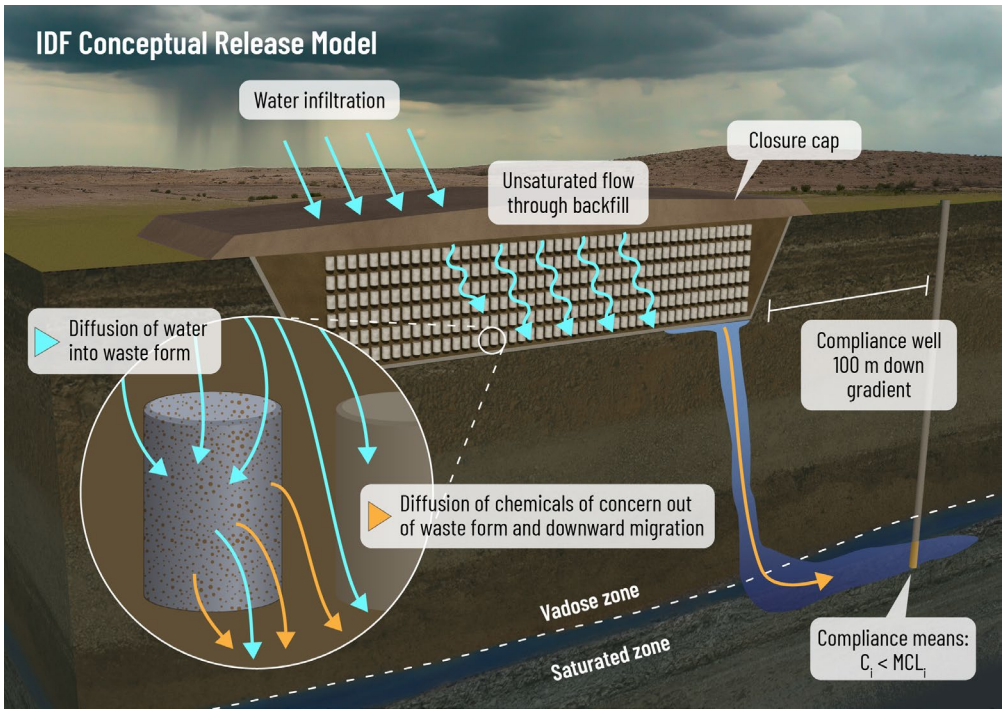

Figure 6 – Illustration (not to scale) of the release of COCs from grout waste forms in the IDF following facility failure.

1.3 Report Organization

Section 1.0 provides the report introduction. Section 2.0 covers the regulatory considerations of nitrate and nitrite. Section 3.0 presents information on the sources of nitrate and nitrite at Hanford, their inventories, and historical events. Section 4.0 presents the current information around nitrate and nitrite behavior in waste processing at Hanford in both the baseline vitrification flowsheet and a hypothetical grouted LAW flowsheet. Section 5.0 presents the current understanding of nitrate behavior in the Hanford subsurface with discussions around the behavior of nitrate and nitrite in the various zones at Hanford (perched water, vadose zone, and saturated zone), along with a review of nitrate removal at Hanford through active remediation, mineral precipitation and biotic degradation. A summary conceptual model with targeted research and development efforts is presented in Section 6.0. A short review summary of other Hanford-specific nitrate or nitrite studies, not directly relevant to the IDF or this report, is given in Appendix A.

1.4 Quality Assurance

This work was conducted with funding from WRPS under contract 82556: FY24 GLAW Development to Support Sample-and-Send). This work was performed in accordance with the Pacific Northwest National Laboratory (PNNL) Nuclear Quality Assurance Program (NQAP). The NQAP complies with the United States Department of Energy Order 414.1D, Quality Assurance, and 10 CFR 830, Subpart A, Quality Assurance Requirements. The NQAP uses NQA-1-2012, Quality Assurance Requirements for Nuclear Facility Applications, as its consensus standard and NQA-1-2012, Subpart 4.2.1, as the basis for its graded approach to quality. The information associated with this report should not be used as design input or operating parameters without additional qualification.

2.0 Regulatory Considerations

This section will provide an overview of the regulatory landscape related to Hanford waste and specifically nitrate and nitrite. The tank waste stored in Double Shell Tanks (DST) and Single Shell Tanks (SST) at the Hanford are regulated under RCRA[1]. Permitting documentation has designated the waste with characteristic, listed, and state-only waste codes. LAW and associated secondary waste will also be managed under RCRA, and may be disposed of in the IDF, located on the Hanford Central Plateau.

Nitrate (CAS 14797-65-0) and nitrite (CAS 14797-55-8) are not regulated as hazardous waste under RCRA, thus do not have an associated waste code in 40 CFR 261, "Identification and Listing of Hazardous Waste," or WAC 173-303, "Dangerous Waste Regulations." Nitrate and nitrite are also not considered as underlying hazardous constituents and are not regulated under the Land Disposal Restrictions (WAC 173-303-140). Hazardous waste[2] containing high levels of nitrate or nitrite can be designated as a "characteristic waste" under the oxidizer classification; however, treated LAW and associated secondary waste is not projected to have nitrate or nitrite concentrations at levels that would warrant designation as an oxidizer[3] (Westsik et al., 2013).

> Washington State state-only waste codes (WAC 173-303-100, "Dangerous waste criteria") provide additional criteria for designating a solid waste as dangerous (i.e., persistent, toxic, extremely hazardous). State-only waste codes are identified in the DST/SST Part A documents (Ecology 2009, Ecology 2011), in addition to listed and characteristic waste codes, and include the added designation of extremely hazardous waste. A revision was made to the "Dangerous Waste Regulations" in 1996 (Washington State Legislature, n.d.) that no longer requires designation of state-only waste codes for waste that has already been designated as hazardous waste in accordance with WAC 173-303-081, "Discarded chemical products," 173-303-082, "Dangerous waste sources," and/or 173-303-090, "Dangerous waste characteristics."

The U.S. Environmental Protection Agency (EPA) does recognize that consumption of high levels of nitrate and nitrite in drinking water can result in human health concerns. Infants that consume water containing elevated levels of nitrate or nitrite are at risk of developing a life-threatening illness (e.g., methemoglobinemia). Under the authority of the Safe Drinking Water Act[4], the EPA established maximum contaminant limits in 1991 to avoid methemoglobinemia (blue baby syndrome) (Knobeloch et al., 2000). Limits for nitrate and nitrite are 10 mg N/L and 1 mg N/L, respectively, and are enforceable for public water systems (EPA 2020, EPA 2023a, EPA 2023b, EPA 2023c). These values correspond to 45 mg/L nitrate and 3.32 mg/L nitrite. There are currently no regulatory actions to change these concentration limits. In Washington State, the Washington State Department of Ecology is responsible for determining compliance with these limits (WAC 246-290-310, WAC 173-200-040). The Hanford site monitors nitrate and nitrite in the groundwater and results are reported in the annual Hanford Groundwater Monitoring Report (USDOE, 2022).

In 1999, DOE issued the "Final Hanford Comprehensive Land-Use Plan Environmental Impact Statement," (USDOE, 1999) which provided an environmental review under the *National Environmental*

[1] https://www.epa.gov/fedfacts/resource-conservation-and-recovery-act-rcra
[2] Washington State regulations use the term "dangerous" waste, which is equivalent waste to the Federal term "hazardous" waste.
[3] In comments in a recent National Academies of Sciences Engineering and Medicine (NAS) public meeting (January 31, 2023) nitrate and nitrite were referred to as "extremely hazardous waste"; which was an incorrect application of this terminology (NAS, 2023).
[4] https://www.epa.gov/sdwa

Policy Act of 1969 on future land uses at Hanford. A subsequent record of decision was published on November 12, 1999 (64 FR 61615) that announced the DOE decision to adopt a Comprehensive Land Use Plan[1] based on the Preferred Alternative to best balance DOE's mission needs. For the Central Plateau, which includes the central waste management areas, the Preferred Alternative designated that future land use would be Industrial-Exclusive, which is defined as areas suitable for treatment, storage, and disposal of waste. An Industrial-Exclusive designation preserves DOE's remediation activities and use and allows for continued waste management operations on the Central Plateau. Groundwater use on the Hanford site is restricted except for research, monitoring, and treatment purposes (USDOE, 2009), and these restrictions are expected to continue in the future for the Central Plateau under the Industrial-Exclusive designation.

The Washington State Department of Ecology is the issuing agency for the IDF RCRA Permit. For dangerous waste disposed in the IDF, compliance with RCRA permit conditions provides protection of human health and the environment. Although the Comprehensive Land-Use Plan reflects no future use of groundwater in the vicinity of IDF, IDF Permit Condition III.11.I.5.a.ii requires mitigation measures if modeling indicates that future groundwater concentrations exceed 75% of the maximum contaminant limit (WA7890008967). There is no definition of what these mitigation methods could be, and so do not limit mitigation measures being applied to any component of the disposal system.

[1] https://www.energy.gov/nepa/eis-0222-hanford-comprehensive-land-use-plan

3.0 Nitrate and Nitrite at Hanford

This section will cover a discussion around the sources of nitrate and nitrite in the Hanford tanks, projected inventory of each, and historic discharges to the subsurface from the tanks.

3.1 Nitrate and Nitrite in Hanford Tank Waste

The Hanford tank wastes are comprised of a mixture of liquid supernate, a precipitated salt cake and a sludge component (Colburn and Peterson, 2021). Nitrate is ubiquitous throughout these phases due to the historical activities which generated the waste. The supernate is an alkaline solution made up of sodium salts, including $NaNO_3$ and $NaNO_2$ (Reynolds et al., 2013). The saltcake layer is primarily precipitated $NaNO_3$. Whereas the sludge contains some nitrate compounds, including nitrate-cancrinite ($Na_8[(NO_3)_2|Al_6Si_6O_{24}]\cdot 4H_2O$).

Multiple sources of nitrate and nitrite were introduced to the tanks during operations at Hanford. In the reprocessing of fuel at Hanford, the first steps involved dissolution of the Al-cladding using a mixture of NaOH and $NaNO_3$, then the de-cladded fuel was dissolved in hot HNO_3 (Colburn and Peterson, 2021). Nitrate is also found in the subsequent processing streams. For example, the REDOX process used a low-concentration HNO_3 solution with added $Al(NO_3)_3$ to drive extractants to an organic phase during separation, followed by HNO_3 to strip U. The PUREX process used hydroxylamine nitrate (NH_3OHNO_3), dissolved zircalloy in $NH_4(NO_3)$ and a neutralization step that precipitated nitrate. Other processes, such as Cs/Sr extraction and U recovery, also utilized nitrates. Some nitrite was generated from reduction of nitrate and the use of nitrite bearing chemicals. While attempts were made to recycle the HNO_3 in these processes (via chemical stripping to purify the HNO_3), a portion of the nitrate- and nitrite-containing wastes were transferred to the tanks as it could not be purified while the rest was recycled using the sugar de-nitration process (Peterson et al. 2018). As a result, there are large amounts of both nitrate and nitrite in the Hanford tanks, Table 1 (Adapted from Volume II Appendix E of (Bates, 2022)). These concentrations of nitrate and nitrite can dictate varying speciation changes of key components in the Hanford wastes (Delegard et al., 2018). When grouped by farm, the highest amount of nitrate is present in TX farm (22% of the total nitrate inventory), while the largest amount of nitrite is in the AN farm (20% of the total nitrite inventory).

Table 1 – Summary of the inventory splits of nitrate and nitrite across the Hanford tank farms, adapted from Table E-12 of Volume II and derived from the Hanford Best Basis Inventory in 2021 (Bates, 2022).

Tank Farm	Nitrate (kg)	% Total	Nitrite (kg)	% Total	200 East or 200 West
A	5.74×10^{5}	1%	3.69×10^{5}	3%	E
AN	4.44×10^{6}	9%	2.39×10^{6}	20%	E
AP	4.47×10^{6}	9%	2.00×10^{6}	17%	E
AW	3.18×10^{6}	6%	1.51×10^{6}	13%	E
AX	3.21×10^{5}	1%	1.74×10^{5}	1%	E
AY	4.28×10^{5}	1%	2.05×10^{5}	2%	E
AZ	5.52×10^{5}	1%	5.35×10^{5}	4%	E
B	1.69×10^{6}	3%	1.32×10^{5}	1%	E
BX	1.34×10^{6}	3%	1.36×10^{5}	1%	E
BY	5.19×10^{6}	10%	6.07×10^{5}	5%	E
C	1.66×10^{3}	0%	1.07×10^{4}	0%	E
S	7.08×10^{6}	14%	6.78×10^{5}	6%	W
SX	4.72×10^{6}	9%	8.79×10^{5}	7%	W
SY	9.83×10^{5}	2%	5.33×10^{5}	4%	W
T	5.79×10^{5}	1%	8.66×10^{4}	1%	W
TX	1.11×10^{7}	22%	8.49×10^{5}	7%	W
TY	5.66×10^{5}	1%	4.71×10^{5}	0%	W
U	3.72×10^{6}	7%	7.48×10^{5}	6%	W
Total	5.09×10^{7}	100%	1.19×10^{7}	100%	-

However, the nitrate and nitrite inventory in the tanks are varied over time because their ratio and ratio relative to hydroxide were used as a means of corrosion control by adjusting their individual concentrations. Stress corrosion cracking of the carbon steel tank liner can be driven by high nitrate concentrations, low or no nitrite, a low nitrite to nitrate ratio, low pH, and high hydroxide concentration (Brossia et al., 2008). Table 2 provides specific conditions that are used for corrosion control within an individual tank based on its nitrate concentration. Nitrate and nitrite are key species for corrosion as they can drive or stifle corrosion processes (Beavers et al., 2014). As such, the concentrations in the tanks are adjusted to maintain the required ratios through chemical additions of sodium hydroxide or sodium nitrate/nitrite.

With these ratios changing over time, there should be projections of evolving nitrate and nitrite inventories in future feed vector projections. These changing ratios may also impact waste processing as there could be stabilization or speciation changes generated within the tank waste (Delegard et al., 2018). To date, there is limited knowledge on such a process.

Table 2 – Example waste chemistry limits for the double shell tanks at Hanford as of 2014, adapted from Table 1 of Beavers et al. (2014). Note these values can change with updates to the corrosion control program.

$[NO_3^-]$ (mol/L)	Variable	Temp <75 °C (mol/L)	Temp 75 °C – 100 °C (mol/L)	Temp >100 °C (mol/L)
<1.0	$[OH^-]$	0.010 – 8.0	0.010 – 5.0	0.010 – 4.0
	$[NO_2^-]$	0.011 – 5.5	0.011 – 5.5	0.011 – 5.5
	$[NO_3^-]/([OH^-]+[NO_2^-])$	≤ 2.5	≤ 2.5	≤ 2.5
>1.0, <3.0	$[OH^-]$^	$0.1([NO_3^-]) - 10$	$0.1([NO_3^-]) - 10$	$0.1([NO_3^-]) - 10$
	$[OH^-] + [NO_2^-]$^	$\geq 0.4([NO_3^-])$	$\geq 0.4([NO_3^-])$	$\geq 0.4([NO_3^-])$
>3.0	$[OH^-]$	0.3 - 10	0.3 - 10	0.1 – 4.0
	$[OH^-] + [NO_2^-]$	≥ 1.2	≥ 1.2	≥ 1.2
	$[NO_3^-]$	≤ 5.5	≤ 5.5	≤ 5.5
^these minimum values are adjusted based on the product of the value and the actual nitrate concentration				

3.2 Historic Nitrate Releases from Hanford Operations

Intentional discharges of waste to trenches and cribs occurred historically at Hanford. These discharges have contributed to contamination in the Hanford subsurface. An example of the discharges of nitrate to the subsurface in the Hanford 200-W Area is given in Table 3.

Table 3 - Estimate of nitrate discarded to plutonium waste sites in the 200 West Area (Delegard et al., 2020).

Waste Site	Metal Nitrate Inventory		
	Metric Tons	Moles	Average Concentration (mol/L)
RECUPLEX inputs to the Z-9 Crib	1361	2.2×10^7	5.51
Plutonium Reclamation Facility aqueous inputs to the 216-Z-1A crib	1134	1.9×10^7	3.6
Process Chemical Discharge as Low-Salt Waste to 241-Z-361 in 1969	19.9	3.2×10^2	3.6×10^{-2}

There were other discharges of supernatant and evaporator bottoms resulting from evaporating supernatant. For example, in 1954 4,807,000 gallons of first cycle supernatant and 1,938,000 gallons of evaporator bottoms were discharged to the subsurface in the 200-W area at T plant (Anderson 1990). During operations of T lant 3,144,000 gal of supernatant were discharged to caverns. Discharges from the U recovery plant released ~40,000,000 gallons of in-plant scavenged waste which contained nitrate. Tank leaks have also led to releases of nitrate to the subsurface. Other discharges of ammonium hydroxide (NH_4OH) to cribs occurred at Hanford that contributed to the nitrate and nitrite plumes in the Hanford subsurface (Szecsody et al. 2020). Upon migration in the subsurface, the ammonium can be oxidized to nitrate. A schematic of these discharge patterns is given in Figure 7 where NH_4^+ can convert to either NH_3 or nitrate via chemical reactions or the more prominent microbial mediated conversion (in the microbial route nitrite is likely first produced and a second bacteria strain would convert to nitrate, while some bacteria have enzymes for the full conversion). An estimate of discharge to a single crib suggests that 1×10^6 kg of nitrate entered the subsurface after conversion from ammonium with discharges to the 216-A-37-1 crib based on ~4×10^8 L of waste released (Szecsody et al., 2020). These discharges provide intriguing test cases for nitrate and nitrite behavior in the subsurface when compared with other tracers.

For example, tritium was also discharged with the NH_4OH. Analysis of the well 299-E25-19 below the crib, shows that tritium and nitrate traveled ~300 ft (100 m) in 5 months and migrated at the same rate (Figure 8); it should be noted that only nitrate was analyzed and no measurement of nitrite or ammonium. However, with the concentrations discharged initially, it is estimated that 20 – 80% of the nitrate remained in the vadose zone after its conversion from ammonium. The slowed migration of nitrate below the crib may be due to retained water, sorption of NH_4 species that slowly convert to nitrate, or some natural attenuation of nitrate. Updated borehole sampling data can be used to make comparisons to tritium migration behavior and better inform on the behavior of nitrate (and nitrite) in the subsurface. These concepts are discussed further in Section 5.0.

Analysis of previous crib discharges through their associated sediments and borehole sampling will be highly informative in further piecing together the behavior of nitrate and nitrite in the subsurface.

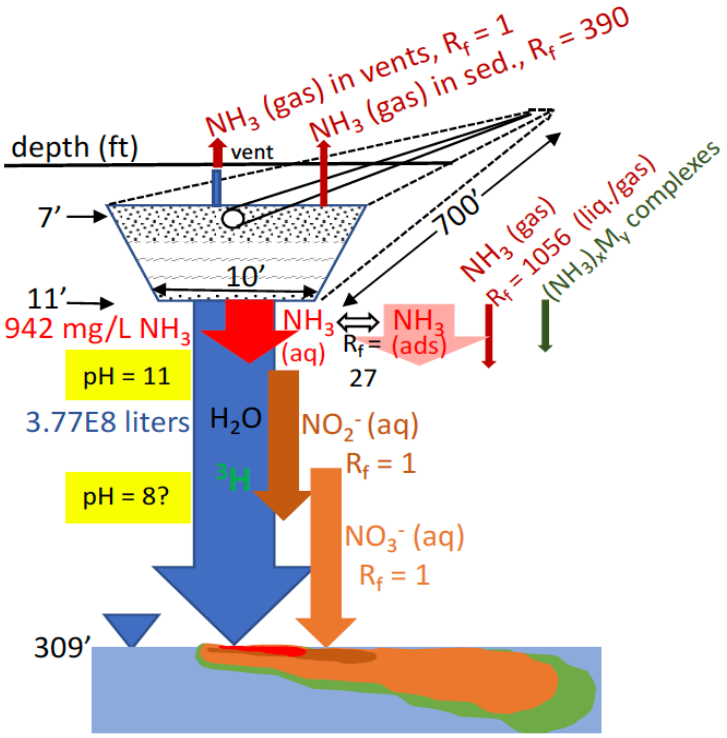

Figure 7 – Conceptual behavior of NH_4OH discharges to cribs at Hanford, adapted from Figure 3 (Szecsody et al., 2020).

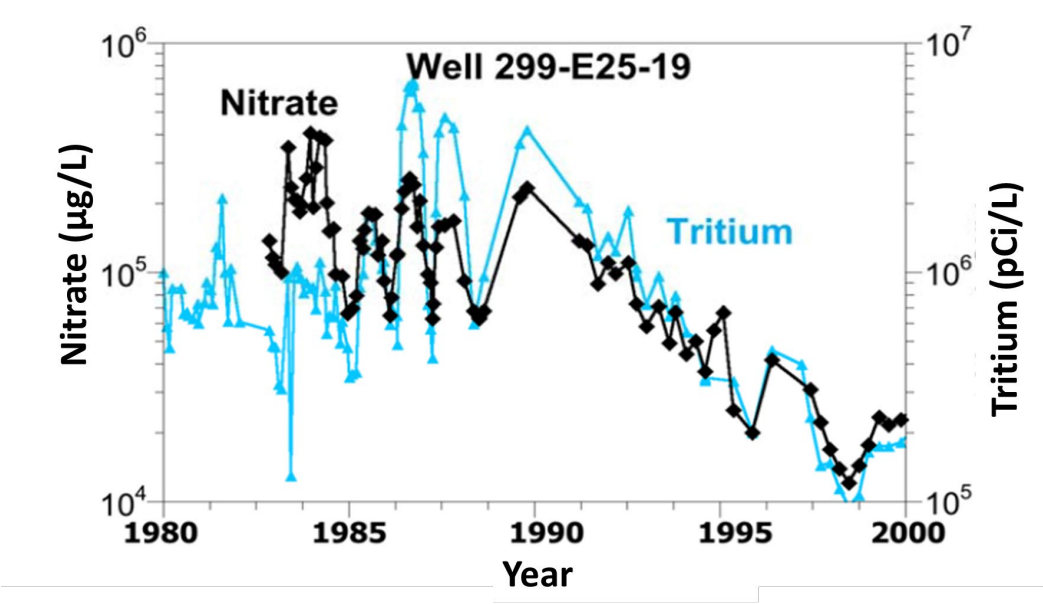

Figure 8 – Well monitoring data for nitrate and tritium from well 299-E25-19 below crib, adapted from Figure 6 of (Szecsody et al., 2020). The tritium results are decay corrected.

3.3 Hanford Groundwater Plumes

From the prior activities described in Section 3.2, there are significant plumes of nitrate and nitrite in the Hanford subsurface. Nitrate plume maps for 2021 across the Hanford (USDOE, 2022b) are shown in Figure 9. It should be noted that the plume at the southernmost point is from offsite agricultural activities. Agricultural activity is just one example of a nitrate and nitrite source at Hanford that is unrelated to the historic and current Hanford mission (Singleton et al., 2005).

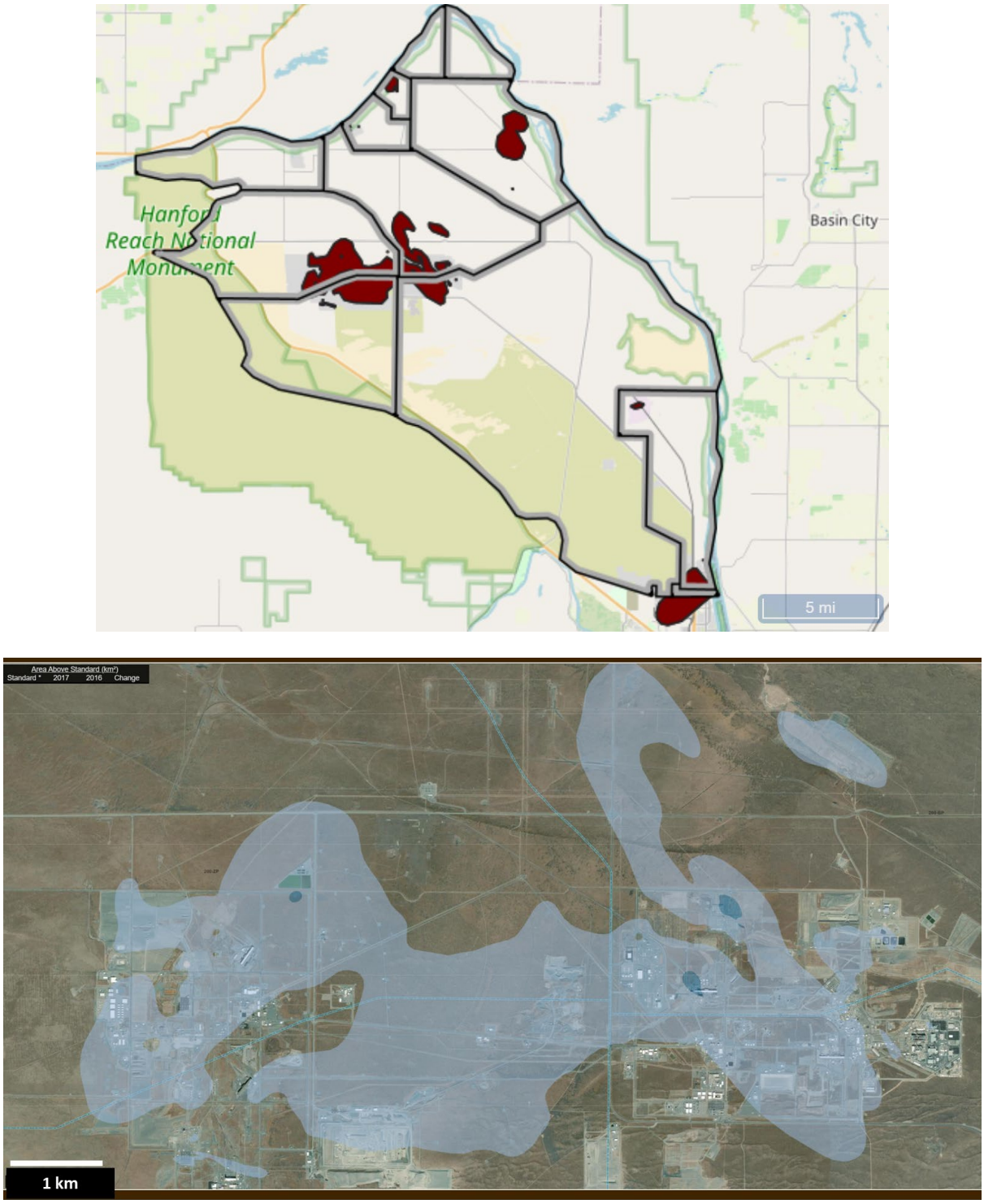

Figure 9 – (top) 2021 Nitrate contours (outer contour is 45 mg/L as nitrate [nominally equivalent to the EPA MCL of 10 mg/L as nitrogen]); southernmost plume is from offsite agricultural activities and is not a Hanford responsibility. (bottom) 2021 nitrate plume in the 200 Area of Hanford where dark blue is concentrations > 450,000 µg/L and light blue is > 45,000 µg/L

These plume maps were developed based on groundwater monitoring activities on the site, which are reported annually[1]. A map showing the average nitrate concentrations across the Hanford Central Plateau is presented in Figure 10. Zooming in on the 200-E area the evolution of the well concentrations for nitrate and nitrite shows a range of concentrations, Figure 11. The maximum concentrations observed in 2022 are given in Table 5.

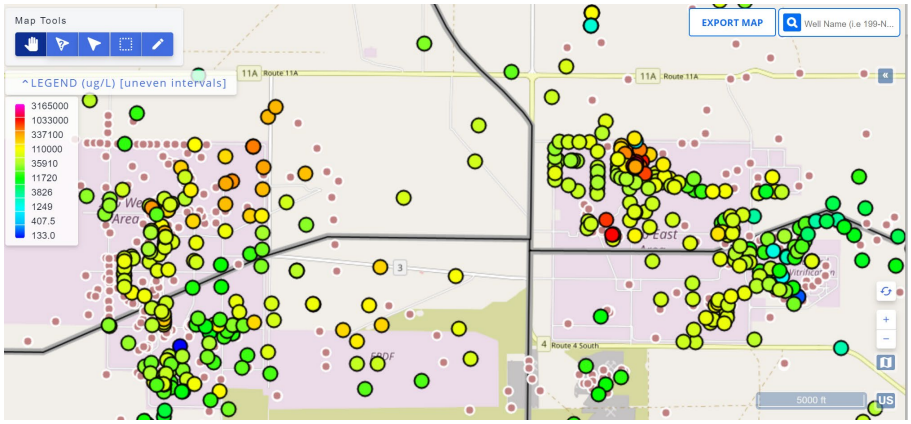

Figure 10 - 2022 Average nitrate concentrations (µg/L) at wells in the central plateau.

[1] https://www.hanford.gov/page.cfm/SoilGroundwaterAnnualReports

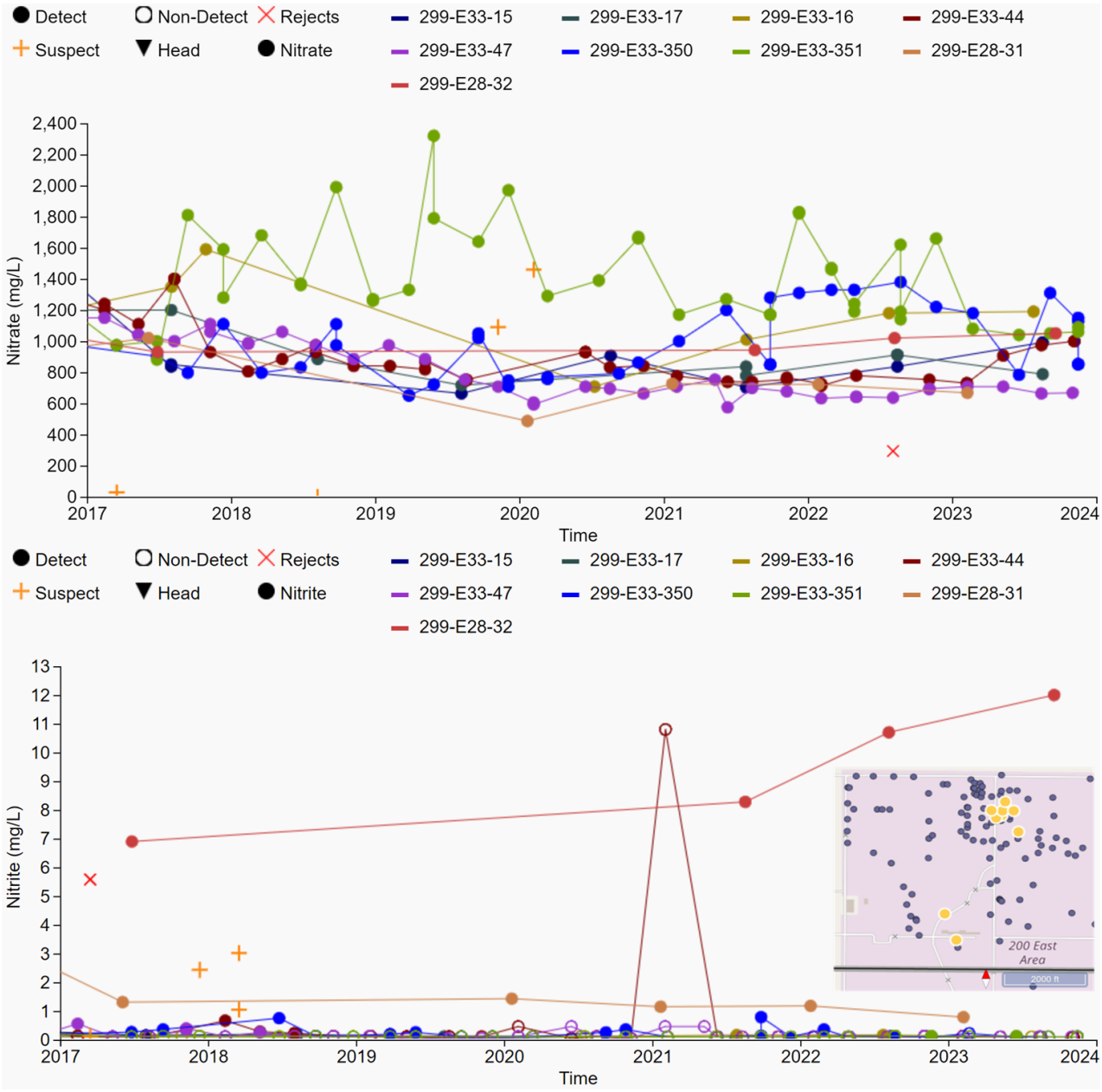

Figure 11 – Nitrate (top) and nitrite (bottom) concentrations for the 200 East wells marked in the inset map in yellow.

Table 4. Maximum nitrate and nitrite concentrations observed in 2022 for wells and aquifer tubes in the various areas of the Hanford, adapted from Table 1-8 of (Clark, 2023)). Bolded and italicized values indicate measurements that exceed the water quality standard.

Location	Type	Nitrate (mg/L)	Nitrite (mg/L)
Water Quality Standard		45	3.3
Site Maximum		1180	10.7
100-BC	Wells	37.1	N/A
	Aquifer Tubes	12.9	N/A
100-FR	Wells	***226***	N/A
	Aquifer Tubes	15.2	N/A
100-HR-D	Wells	27.4	N/A
	Aquifer Tubes	0.221	N/A
100-HR-H	Wells	***74.8***	0.164
	Aquifer Tubes	2.79	N/A
100-KR	Wells	***104***	0.164
	Aquifer Tubes	41.2	N/A
100-NR	Wells	***272***	1.91
	Aquifer Tubes	***64.6***	N/A
300-FF	Wells	***133***	0.131
	Aquifer Tubes	38.4	N/A
1100-EM and Offsite Wells		***137***	N/A
200-BP	Wells	***1180***	10.7
	Aquifer Tubes	N/A	N/A
200-PO	Wells	126	1.25
	Aquifer Tubes	33.8	N/A
200-UP	Wells	***237***	1.58
200-ZP	Wells	***518***	***4.47***

Bagwell et al. discuss how detection of nitrite in well data (Figure 12) is clear evidence of microbially catalyzed nitrate reduction to nitrite (Bagwell et al., 2019a) along with the nitrite spike in Figure 11. There is ample evidence that under the appropriate conditions both biotic and abiotic-biotic reductive degradation of carbon tetrachloride (CT) can occur in the Hanford subsurface. CT degradation mechanisms can be used degradation activity. Examination of available groundwater data, such as that in Figure 12, provides evidence that biotic CT degradation has occurred. Chloroform, (CF) concentration trends are an indicator of CT degradation by reductive dichlorination as CF can only be derived by the anaerobic degradation of CT in anoxic, reduced zones. Further reduction is evidenced by dichloromethane (DCM) which only originates from the degradation of CT (and CF) occurring in anoxic/reduced zones by reductive dechlorination. DCM can be used as a marker of recent degradation activity as it quickly metabolized to CO2 in oxic groundwater. Thus, detection of DCM in groundwater indicates recent biotic degradation in anoxic/reduced zones that must be within proximity to the wells where DCM is detected. Specifically, nitrite is also good indicator chemical for recent anoxic or reduced zone denitrification because nitrite is easily oxidized back to nitrate when exposed to oxic groundwater. The authors also note that nitrite may be more widespread than analysis results indicate because the detection

limits for nitrite are high due to the high nitrate concentrations for many wells, thus potentially masking low nitrite concentrations.

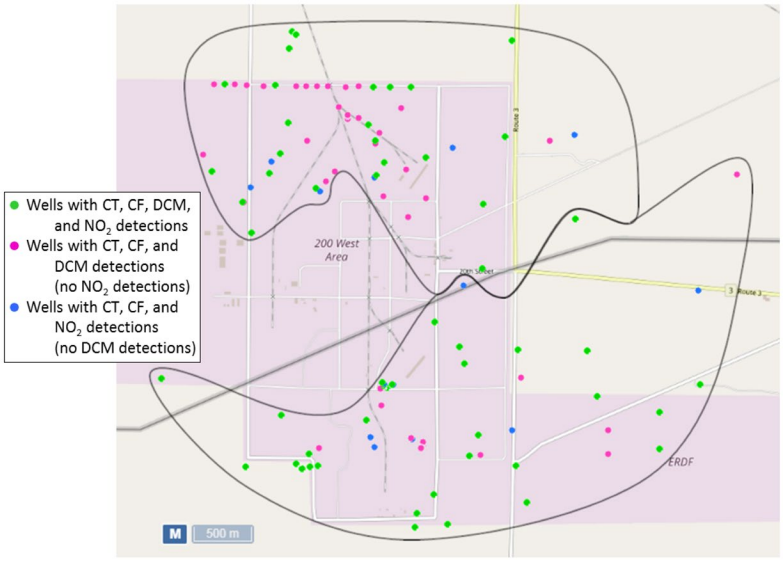

Figure 12. Locations of wells in the vicinity of the 200 West Area with detections of carbon tetrachloride (CT), chloroform (CF), dichloromethane (DCM), and/or nitrite (NO_2), adapted from (Bagwell et al., 2019a).

4.0 Nitrate in Processing and Waste Forms

This section will describe the behavior of nitrate and nitrite in two immobilization processes, vitrification and grouting, to provide context for how they would behave in the baseline flowsheet vs. a hypothetical grouted LAW flowsheet.

4.1 Behavior in Waste Processing and Vitrification

Nitrate can be removed from Hanford LAW above 400 °C (Kim et al., 2005). Prior works have looked at nitrate treatment in tank waste including denitrification using the nitrate to ammonia ceramic process (NAC) and hydrothermal approaches (Dell'Orco et al. 1993). These proposed processes are resource intensive (Mattus and Lee, 1993; Mattus et al., 1994) similar to other methods when the research area was active in the late 1980s and early 1990s (Cowan et al., 1987; Cox et al., 1992; Delegard et al., 1993; Elmore and Lawrence, 1996; Taylor et al., 1993).

For vitrification, the waste containing nitrates and nitrites is combined with glass-forming chemicals (GFCs) to create an aqueous/solid slurry called melter feed. The melter feed is charged into a liquid-fed ceramic melter (LFCM) at an operating temperature of 1150 °C, achieved by Joule heating of the glass melt. In these conditions, the melter feed forms a cold cap on the glass melt where heat transfer causes boiling of the slurry and chemical reactions to produce glass and off-gas. The glass product is poured into containers (or canisters) while the off-gas is directed through a system where it passes through treatment units to condense liquids and collect solid particulates before the remaining gas is exhausted (Buelt and Chapman, 1978).

During this vitrification process, nitrates and nitrites in the waste react with other components in the cold cap causing nitrogen to volatilize as several different gas species that travel with the other off--gases through the treatment system. The form and quantity of nitrogen-based off-gases vary depending on the amount of nitrates and nitrites in the initial waste and the composition of the melter feed, which will cause different reactions in the cold cap. Nitrate and nitrite can dictate the redox conditions in the melt (Ramsey et al., 1993). Often, a sugar reductant, sucrose, is added with GFCs to melter feeds to improve melting properties by promoting reactions with nitrate and nitrite (Appel et al., 2019; Kruger et al., 2013; Matlack et al., 2011). When the carbon and nitrogen reactions are complete, the product gas should be diatomic nitrogen, but other nitrogen species may be produced from incomplete reduction reactions (Appel et al., 2019; Matlack et al., 2016; Matlack et al., 2011). An example reaction between sugar and the sodium nitrate in the waste is:

$$C_{12}H_{22}O_{11} + 8\ NaNO_3 \rightarrow 8\ CO_2 + 4\ CO + 4\ N_2 + 11\ H_2O + 4\ Na_2O \quad (1)$$

Due to other deleterious effects of over-reduced conditions during vitrification, nitrogen reactions during nuclear waste vitrification are often incomplete. Evolved gas analysis methods such as Fourier Transform Infrared Spectroscopy and gas chromatography-mass spectrometry have shown that the primary product of incomplete reaction of nuclear waste simulant melter feed is NO, with lesser quantities of N_2O and other NO_x species (Appel et al., 2019; Lee et al., 2017; Matlack et al., 2016; Matlack et al., 2011; Rigby et al., 2023). Recovery analysis calculations reveal the balance of nitrogen gas product to be N_2 (Matlack et al., 2016). Alternative reductant sources in waste melter feeds or varying levels of sucrose have been tested, though results show that their greatest effect is on melting properties (foaming behavior and reduced metals in the glass melt) rather than nitrogen volatility (Appel et al., 2019; Matlack et al., 2016; Matlack et al., 2011; Rigby et al., 2022).

Once in the off-gas treatment system, the nitrogen gas species may condense with other off-gases in subsequent unit operations of the off-gas treatment train. The primary nitrogen-based gases that condense are NO_x in the form of nitrates and nitrites in the condensate solutions (Crawford, 2002), while N_2 and NO gases, which account for most of the nitrogen mass from the nitrates and nitrites in the initial waste, are exhausted from the system (Matlack et al., 2016). When the NO_x reaches the Selective Catalytic Reducer in WTP it reacts with a catalyst and ammonia to convert to dissolved ammonium and oxygen in the liquid effluent.

This effluent is discharged to the Liquid Effluent Retention Facility (LERF) for staging prior to processing at the Effluent Treatment Facility (ETF). These high levels of ammonium reaching ETF have been the focus of recent research to lessen the generation of ammonia in eventually processing of the ETF brine as a grout waste form (Abramowitz et al., 2021; Asmussen et al., 2023b; Gong et al., 2019, 2020). An inventory of nitrate (164,000 kg) was projected to be disposed in the IDF PA resulting from secondary wastes, which corresponds to ~0.3% of the total inventory present in the Hanford tanks (USDOE, 2018).

Nitrate and nitrite are expected to be volatilized and converted during vitrification. Their presence in the waste creates a downstream handling concern for ammonium. A residual amount of nitrate is projected to be disposed in the IDF in a secondary waste grout.

4.2 Nitrate and Nitrite Behavior in Grout Waste Forms

Unlike vitrification where nitrate and nitrite are converted in the melter, grouting as an ambient temperature process does not drive the same conversions. As such, the mass of nitrate and nitrite in the waste is transferred directly to the waste form. Due to the solubility of many nitrate and nitrite minerals, chemical retention of nitrate and nitrite in grouted waste forms is limited. Most sorption surfaces are negatively charged at the neutral to alkaline conditions common in grout; therefore, anions, like nitrate and nitrite, are not attracted to these surfaces. In grouted waste forms, a small and likely insignificant fraction of nitrate may be substituted into some secondary precipitation minerals (e.g., ettringite) (Ye, 2021). Geochemical speciation of Cast Stone porewater suggests that the majority of nitrate (and presumably nitrite) is contained in the porewater of the grout (Chen et al., 2021). Therefore, the pore structure of grouted materials offers the primary physical retention of nitrate and nitrite due to a disconnected, tortuous pore pathway – the longer and more tortuous the pathway, the slower the release. However, implementation and maintenance of these physical approaches to slow nitrate/nitrite release is limited to date.

Since there is little chemical retention for nitrates/nitrites, the principal methodologies for improving the overall retention of nitrate and nitrite are to: (1) limit exposure to a leaching solution, and (2) provide a longer diffusion pathway and smaller surface area for release (e.g., reduced porosity, reduced surface area to volume ratio of the waste package). Infiltration control through caps and other barriers can limit the volume of leaching solution in contact with grouted waste forms. Getters, like carbon and layered double hydroxides, are unlikely to be successful to improve nitrate retention due to competition from other anions in the waste streams (Skeen et al., 2020). Recent work with geopolymers has shown promise for improved nitrate retention when a simulant with a lower concentration was used (1mol/L Na vs >5 mol/L Na) (Abramowitz et al., 2021). Maximization of diffusion path and minimization of exposed surface area are best achieved by creation of bulk solidified materials.

The principal sources of uncertainty upon disposal include the amount of water infiltration in contact with the waste form and the potential for attenuation and dilution of leached nitrate and nitrite between the waste form and the point of compliance. Disposal environments that minimize infiltration (e.g., through

barriers or discontinuous pathways) are more likely to retain nitrate and nitrite from grouted waste forms. Peak concentrations of nitrate and nitrite in PA modeling of the IDF scale linearly to disposed inventory. A lower inventory placed in the IDF would lower overall concentrations in the subsurface. Therefore, any off-site disposal options where there is no pathway to potable water are good disposal candidates with respect to nitrate and nitrite retention as they remove IDF inventory and isolate nitrate and nitrite from water sources (Bates et al. 2022).

4.3 Targeting Nitrate Improvement in Grout

4.3.1 Grout Waste Form Performance Metric

In 2018, an effort was initiated to establish a performance metric target for grout in the IDF that could be used to benchmark laboratory grout performance based on leaching data. Performance metrics for four contaminants (Tc, I, nitrate, and Cr) were established (Asmussen et al., 2019) using modeling simulations of grouted LAW waste form performance in the IDF. The simulations varied the retention of the species within the grout waste form, but for nitrate and nitrite there was no presumed attenuation in the IDF backfill or the subsurface, which may be conservative. The performance metric was quantified as a retardation factor (R) based on the waste form retention capacity for the specific contaminant relative to a mobile (i.e., non-sorbing/non-reacting) species. The R value represents a minimum needed to maintain contaminant concentrations below the drinking water standard at the points of compliance 100 m down gradient from the IDF. For comparison purposes, R can be converted to a corresponding laboratory observed diffusivity value (D_{obs}). The R performance metric was determined through an iterative set of simulations representing grout waste within the IDF and varying the R-factor to observe changes in the predicted release from the IDF through reactive transport modeling. The outcome of this analysis is summarized in Figure 13. The standard established by the EPA for nitrate, is 10 mg/L as total nitrogen (EPA 2002b), this equals 44.3 mg/L of nitrate. This concentration at the point of compliance (100 m well down gradient of the IDF) was set as the initial target of the simulations. Subsequent simulations assumed one-tenth (4.4 mg/L) and one-hundredth (0.4 mg/L) of the water quality standard target. To meet the 44.3-mg/L target for nitrate, an R factor of 2 would be required, corresponding to an observed diffusivity of 2×10^{-9} cm^2/s. To achieve 4.4 mg/L, an R factor of 45 is needed and corresponds to an observed diffusivity of 6×10^{-11} cm^2/s. Finally, to achieve 0.44 mg/L, an R factor of 550 would be required, which would equal an observed diffusivity of 4×10^{-12} cm^2/s. These performance metrics have been used in recent years to assess the laboratory performance of grout waste forms related to nitrate and nitrite release.

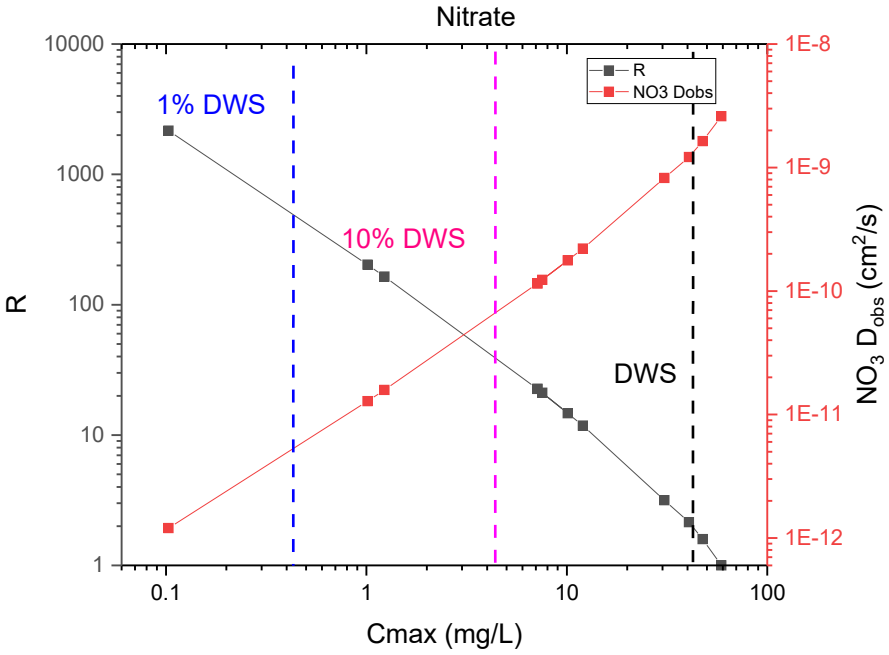

Figure 13 - Visualization of the R factor (black) used in the simulations and the resulting concentration of nitrate, determined at the POC in mg/L. The corresponding observed diffusivity that would be measured for a grout with a specific R factor is also shown (red). Dashed lines corresponding to the target concentrations are also provided from Asmussen et al. (2019).

4.3.2 Evaluation of Approaches to Impede Nitrate Release in IDF

An expert panel from PNNL, Savannah River National Laboratory, the Vitreous State Laboratory (VSL) at Catholic University, and WRPS performed an evaluation in 2020 to: (1) identify technical and regulatory limitations to treating and disposing of grouted LAW and (2) identify and evaluate a wide range of technical solutions to these limitations (Skeen et al., 2020). The analysis included technologies to allow inventory management and/or improve retention of iodine, technetium, and nitrate either in the waste packages, or within the IDF, and technologies to ensure regulated organics are below RCRA Land Disposal Restriction levels. An extensive list of technologies and engineering approaches was identified and subjected to an assessment by the team in 13 distinct technology categories. An uncertainty score was also developed for each technology by counting the number of technology maturation unknowns identified during group discussions.

From the study, pretreatment technologies were found for iodine and technetium, but no viable pretreatment options were identified for nitrate due to its large inventory and energy requirement of many of the technologies[1]. Other candidate nitrate and nitrite technologies have emerged including bed reforming (e.g., ScrollTherm process) which can also remove organics. In terms of active remediation or capture in the waste form, only two techniques, the addition of carbon-based getter and the use of layered double hydroxides, were identified as being potential methods to enhance nitrate retention in the waste form. Contaminant-specific engineered barrier technologies were assessed. The contaminant specific methods are of three general types: those that modify individual waste packages, those that modify the

[1] There is an on-going project in the DOE-EM Technology Development program at PNNL looking at denitrification through ultrasonic techniques.

backfill, and those that create a reactive barrier in the vadose or saturated zone below the disposal site. The technical method that was scored highest by the expert panel was the use of an iron-amended backfill to provide a reduction/sorption zone for nitrate and technetium. Methods to modify bulk transport properties in the waste form or the disposal facility were also assessed by the expert panel. Although there has been extensive characterization work on Cast Stone since its development, work on the development of formulation modifications and alternative formulations has been very limited. It was identified that there was substantial opportunity for optimization of this formulation to improve its performance (e.g., increase packing density) and also for the development of entirely different formulations, such as geopolymers (see Section 4.3.3 below). Specific to the disposal facility, improvements could be gained by increasing the physical size of the waste package or by reducing water infiltration. The use of a high-density polyethylene cap was rated highest by the expert panel, followed by improvements provided by increasing the size of the waste packages.

4.3.3 Grout Testing to Target Nitrate Improvement

Stemming from the technology evaluation, some efforts have targeted improving the retention of nitrate and other mobile anions in grout. The approach taken in these efforts was to lower the release of mobile species through modifying the transport properties of the waste form (e.g., increase packing density, decrease porosity) by using geopolymer formulations. The initial work in fiscal year (FY) 2021 evaluated neutral salt activated slag formulations, alkali silicate activated slag, a Portland cement formulation similar to ultra-high performance grout (UHPG), and Cast Stone (Gong and Pegg, 2022). The best performing formulations were the neutral salt activated slags (CSM0.40A4S and CSM0/40/A8S) and a UHPG (RPC-FSB45), giving observed diffusivities on the order of 5×10^{-11} cm^2/s when using a 1 mol/L Na simulant and 9×10^{-10} cm^2/s when using a 5.6 M Na simulant. These data showed nitrate release that was 5× lower than Na. Follow-on work in FY22 evaluated using cement-containing and cement-free Cast Stone, along with the prior formulations to compare mortar and pastes in the 5.6 M Na simulant. In these efforts, the nitrate release was similar for all samples, ranging between 2×10^{-9} cm^2/s and 7×10^{-9} cm^2/s, improving release by <2× when compared to Na. Nitrite behavior was comparable to nitrate. Further work in FY23 focused solely on the neutral salt activated slags with results similar to FY22. These studies have shown that nitrate and nitrite release can be lowered to below the performance metric target using geopolymers; however, repeatability of this leaching behavior has not yet been shown. The waste composition could play a significant factor in the level of release of nitrate/nitrite, as the presence of competing anions and overall concentration appears to play a role in overall nitrate/nitrite release rate (e.g., lowered observed diffusivity in tests using a 1 mol/L Na simulant compared with a 5.6 mol/L Na simulant in Gong et al. 2021 where the 1 mol/L simulant was a diluted version of the 5.6 mol/L simulant with respect to all species, including nitrate and nitrite).

Continued work on grout waste form improvement for nitrate and nitrite retention should be focused on reproducibility of results, driving to lower porosity, or the use of encapsulation barriers. Work on a getter for nitrate is of low priority due to high ionic competition.

4.3.4 Nitrate and Nitrite Behavior in Field Testing

A field-scale study of LAW waste form degradation is being conducted in large lysimeters (2-m diameter, 3-m deep) located at the IDF Test Platform facility on the Hanford (previously known as the field lysimeter test facility) (Bacon et al., 2018; Meyer et al., 2023). Three types of grout waste forms are currently installed in the lysimeters and being monitored for release of constituents, including nitrate and nitrite. The grouts consist of LAW simulant immobilized as Cast Stone (LAW-CS), WTP off-gas condensate (liquid secondary waste, LSW) simulant immobilized as Cast Stone (LSW-CS), and WTP off-

gas condensate simulant immobilized using a hydrated-lime-based formulation (LSW-HL). The concentration of the LAW simulant is ~2 mol/L nitrate, nitrite is 0.7 mol/L with 5910 µg/mL of total carbon (includes both organic and inorganic carbon). The concentration of the LSW simulant is ~0.5 mol/L nitrate, nitrite is 0.003 mol/L with 12 µg/mL of total carbon. Target compositions of the simulants are shown in Table 5, provided as the molar concentrations relative to the sodium ion content.

Table 5. Target compositions of the LAW (Asmussen et al. 2016) and WTP LSW (Um et al. 2016) simulants used for grout monolith preparation.

Major Anion/Cation, or Other Property	LAW Target[(a)]	LSW Target[(a)]
Na^+	1	1
Al^{3+}	0.065	-
Cl^-	0.015	0.02
NO_3^-	0.339	0.397
NO_2^-	0.121	0.003
SO_4^{2-}	0.018	0.847
K^+	0.008	-
PO_4^{3-}	0.002	-
F^-	-	0.003
pH	13.5	5.6
Total Carbon (µg/mL)	5910	12
Density (g/cm^3)	1.31	1.13

(a) mol species: mol Na, except for pH, density and total carbon

Monolithic grout waste forms were produced as circular cylinders, 19 cm tall and either 15 cm or 10 cm diameter. Two large and two small monoliths of a given formulation are installed adjacent to one another at three locations and two elevations within a lysimeter, as shown in Figure 14. Waste forms are in contact with sandy backfill soil obtained from the IDF excavation spoils pile. Each lysimeter is irrigated at a specific rate from mid-March thru mid-November and is covered to minimize evaporation from the soil surface. Automated irrigation began in March 2021. Porewater samplers[1] are located beneath each waste form location; drainage water beneath the waste forms can also be sampled. Quarterly sampling has been conducted in two lysimeters with grout waste forms; the irrigation flux is 50 cm/yr and 20 cm/yr for these lysimeters. A third lysimeter with grout waste forms began operation in October 2023 with an irrigation flux of 5 cm/yr. A control lysimeter without waste forms with irrigation at 50 cm/yr is also installed and sampled quarterly to help isolate the effects of the waste forms.

[1] One suction sampler and one fiberglass wick sampler are located about 10 cm beneath each waste form location and about 150 cm below ground surface in the control lysimeter.

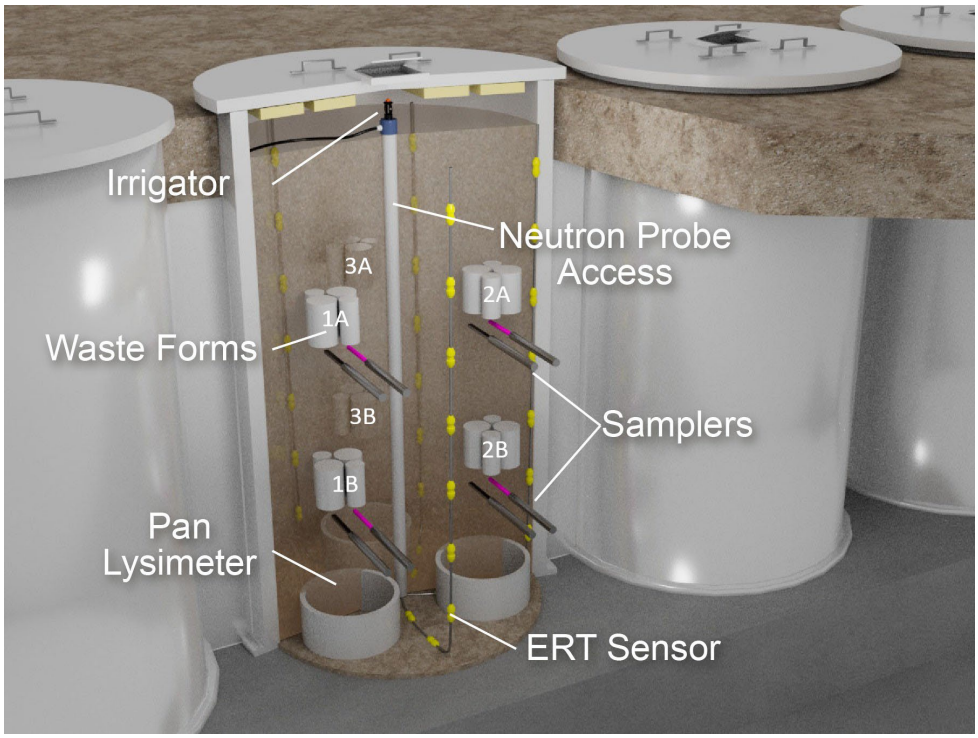

Figure 14. Cut-away view of a lysimeter at the IDF Test Platform showing three grout waste form locations (1, 2, and 3) at two elevations (A and B). Also shown are water samplers and pan lysimeters beneath the waste forms, the irrigation emitter, neutron probe access tube, lysimeter covers, and electrical resistivity tomography electrodes.

Water applied to the soil surface of the lysimeters consists of deionized Columbia River water mixed with a small amount of filtered raw river water. This results in irrigation water with an average pH of 6.8 and electrical conductivity of about 25 µS/cm. Average nitrate measured in the irrigation water is about 3 mg/L (as nitrate). As water flows down through the lysimeters it interacts with the soil in the control lysimeter and with the soil and waste forms in the lysimeters containing the three types of grout waste forms. Average nitrate concentrations[1] over time are shown in Figure 15 for the control lysimeter and for each of the grout waste form types in the lysimeters receiving 50 cm/yr and 20 cm/yr of irrigation (D9 and D10, respectively). Nitrate concentrations in the control lysimeter have reached an equilibrium value of about 20 mg/L and it is expected that by the time the irrigation water reached the waste form depth it has reached this concentration. Nitrate concentrations beneath the grout waste forms are significantly higher with initial values between 6,000 and 33,000 mg/L and the most recent values ranging from about 400 to 17,000 mg/L. Nitrate concentrations have generally decreased over time[2] and have consistently been the highest beneath the LAW-CS waste forms and the lowest beneath the LSW-CS waste forms.

Nitrite is a minor component of the LSW simulant and has been observed at low concentrations beneath the LSW-HL and LSW-CS waste forms, as shown in Figure 16. Missing values in the figure were reported as non-detects that are below estimated quantitation limits (EQLs) that ranged from 1 to 16 mg/L (EQLs for control lysimeter samples were between 0.1 and 1.6 mg/L). Nitrite is present in the LAW simulant at a molar concentration about one-third that of nitrate (25% on a mass basis) and appears in the

[1] Average concentration is calculated from samples obtained via the suction and wick samplers. For results beneath waste forms, the average includes samples from the A and B elevations.
[2] Initial decreases in concentrations in lysimeter D10 with subsequent increases may have been variations in background nitrate concentration while establishing the target irrigation rate.

pore water beneath the LAW-CS waste forms at a mass concentration about one-tenth that of nitrate (compare Figure 15 and Figure 16). Soil pore gas samples show that oxygen concentrations in the lysimeters have generally varied from 18 to 20 percent, indicating that oxidizing conditions are maintained. At this time, it is unclear what is leading to this change in ratio between collected nitrate and nitrite but maybe be driven by microbial conversions or other backfill interactions (it should be noted that some nitrifying bacteria can oxidize nitrite to nitrate, or conversely in anoxic conditions anaerobic ammonium oxidation can occur using nitrite to consume the ammonium and produce N_2, Kuenen 2008). A characterization of the microbial communities in the lysimeter cells and under each waste form type should be performed.

The lysimeter test will continue to supply valuable information on the release of nitrate and nitrite from grout waste forms and subsequent subsurface behavior. These data can be used to validate model projections of nitrate and nitrite behavior. As well, sequencing of the biological activity within the lysimeter units containing grout can give valuable insight into the extent of microbial conversion of nitrate and nitrite in Hanford environments and study correlations with carbon availability.

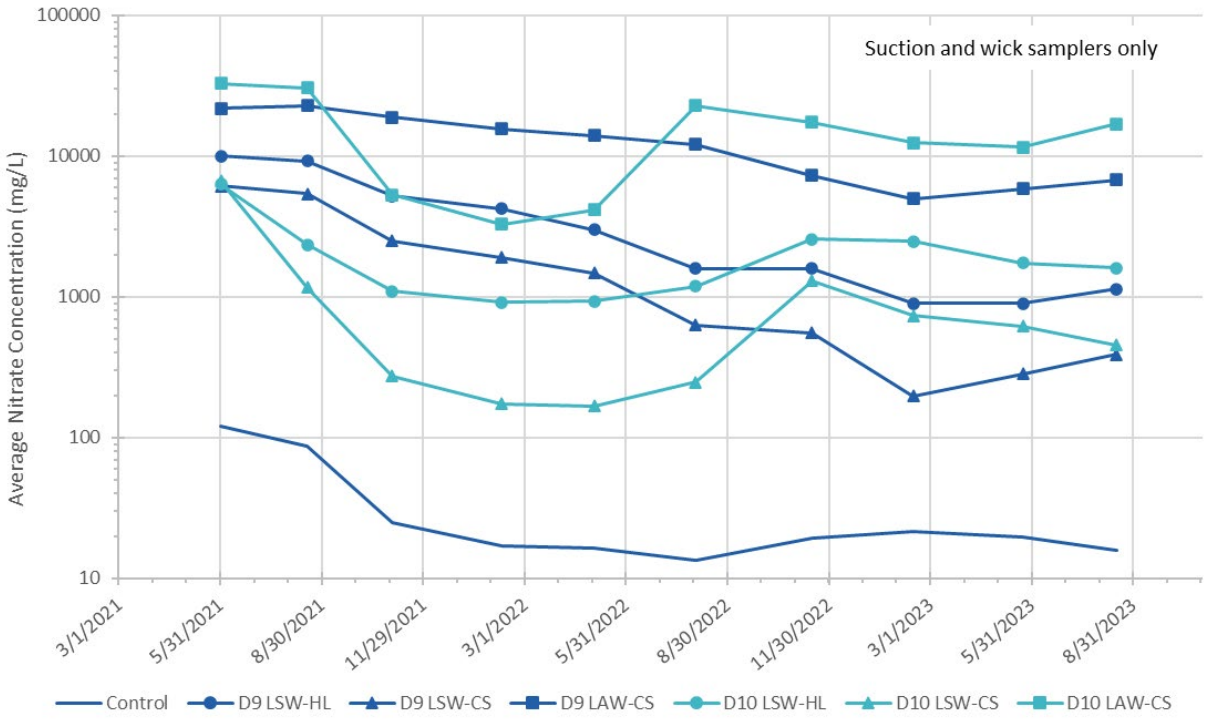

Figure 15. Average nitrate concentration in the control lysimeter and beneath grout waste forms in lysimeters D9 and D10 (50 cm/yr and 20 cm/yr irrigation, respectively).

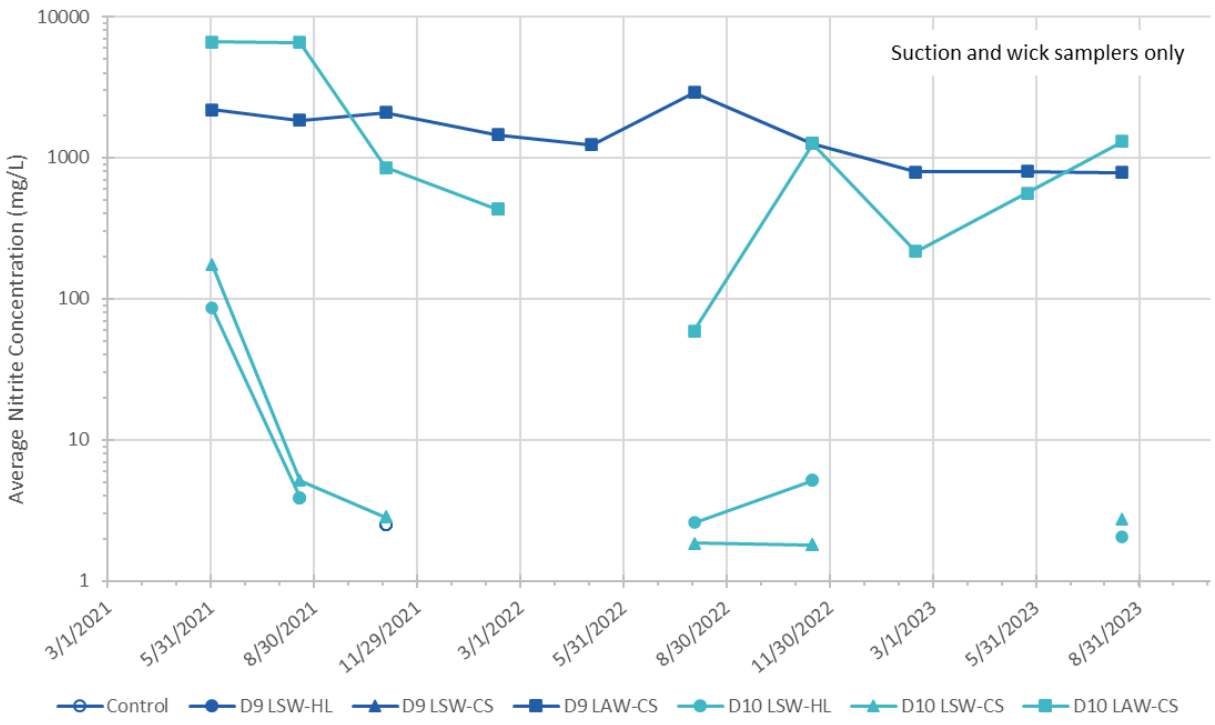

Figure 16. Average nitrite concentration in the control lysimeter and beneath grout waste forms in lysimeters D9 and D10 (50 cm/yr and 20 cm/yr irrigation, respectively).

5.0 Nitrate and Nitrite in the Hanford Subsurface

This section will give an overview of the known behavior of nitrate and nitrite in the Hanford subsurface relevant to environmental release from the IDF. The discussion includes information on the current understanding of nitrate and nitrite fate and transport in the Hanford perched, vadose, and saturated zones. There is also discussion on historical subsurface migration, active monitoring or remediation, reductive or mineral interactions, and biotic processes that occur as nitrate and nitrite migrate through the subsurface. The information captures the current state of knowledge of nitrate and nitrite behavior and what could be expected below the IDF in the vadose zone and saturated zone that are modeled in the IDF PA.

Under the neutral to slightly alkaline aqueous conditions present at Hanford (in the vadose zone and aquifer), nitrate displays no effective adsorption to sediments. The primary attenuation processes that can affect nitrate include subsurface water flow (dilution and dispersion), abiotic reduction by reactive mineral phases, and microbial conversion. While the bulk of the subsurface at Hanford is oxic, ample evidence shows that chemically reduced, anaerobic zones comprise a portion of the total aquifer volume (e.g., the Ringold formation) (Percak et al. 2014, Peretyazhko et a. 2012). These zones could represent "hot spots" for abiotic and microbial reduction mechanisms.

5.1 Nitrate and Nitrite in Perched Water Zones

Perched water zones are defined as a saturated zone that is not directly connected to the regional water table or lies above it (Freeze and Cherry 1979) that can contain water from natural or anthropogenic sources. Generally perched water zones are separated from the water table by unsaturated sediments and are relevant for environments with confined water and/or low recharge scenarios. The perched zones at Hanford are in similar sediments to the region below the IDF and low recharge is expected below the IDF as well. Specifically, Hanford has a perched water zone below the B-complex (Saslow et al. 2018, Demirkanli et al. 2018, Emerson et al. 2023, Serne et al. 2010, Truex et al. 2017). Quantifying the nitrate and nitrite inventory beneath the B-Complex perched zone is challenging because there is uncertainty in the multiple source locations, volumes, and intensities contributing to the perched zone (Demirkanli and Freedman, 2021; Oostrom et al., 2013; Serne et al., 2010; USDOE, 2020a). Currently the perched water zone beneath the B-Complex lacks characterization data for understanding not only the contaminant inventory, but also the lateral extent of this contamination (USDOE, 2020a). However, additional borehole installations are planned for the 200-DV-1 operable unit that will close this technical gap in characterization (Emerson et al. 2023). The perched zones can give valuable insights into the influence that applied remediation approaches.

5.2 Nitrate and Nitrite in the Vadose Zone

A vadose zone is the region between the surface and the water table where hydraulically unsaturated conditions exist; and the majority of the subsurface below the IDF is vadose zone. A background nitrate concentration of 52 mg/kg in Hanford Soil has been reported in the vadose, as compared to a measured nitrate concentration in uncontaminated ERDF pit sediments (40 ft depth) of 95 mg/kg (Table 6) (USDOE, 1993). Not enough data above detection limit was available at the time to calculate a background concentration for nitrite.

Measured nitrate concentrations in vadose zone pore water can be similar to the perched zone concentrations and likely much higher than groundwater. Note that some nitrate data available is for sediment measurements and must be converted to compare to water concentrations. There is only limited nitrate pore water data as these are based on water extractions from sediments beneath different waste sites in the 200 Area (Table 6). Most of the measured data beneath the B, S, and T complex, where the

components of the subsurface are similar to below the IDF, only have one or a few points, which is insufficient to describe a depth profile of nitrate.

Table 6 – Nitrate concentrations in 200 Area vadose zone sediments taken from water extraction measurements.

Sample Name, Depth	Sample Location	Nitrate (µg/g) dry	Data Source
C9507-B35434	T19 14C (CCUz)	77.2	1
C9507-B35443	T19 16C (CCUc)	83.6	1
C9507-B35461	T19 138’ (Ringold)	95.8	1
C9510-B361N1	T25 14C (H2/CCU)	6.33	1
C9512-B36177	S-9 8C (H1/2)	235.	1
C9512-B361F3	S-9 20C (H2)	9.35	1
C9552, 104.2–105.2	BY Cribs (H2)	3510	2
C9552, 134.1–135.1	BY Cribs (H2)	2500	2
C9552, 194.2–195.2	BY Cribs (CCUg)	2270	2
C9487-, 58.2–59.2	B7-AB (H2)	50.9	2
C9487, 134.1–135.1	B7-AB (H2)	6.13	2
C9487, 230.0–231.0	B7 AB (CCUz)	97.9	2
C9488, 230.0–231.0	B-7 (CCUz)	1360	2
ERDF pit, 40’	uncontaminated	95	2
C9497-B39M00	B-42 39C (CCUg)	3.72	3
C9513-B39X10	S-13 18E (H2/CCUz)	0.386	3
C9513-B39X55	S-13 25D (CCUc)	0.439	3
C9513-B39XC3	S-13 39D (Rwie)	0.495	3
C9555-B3DB67	T-3 57B (H2/CCUz)	6.07	3
C9555-B3BL58	T-3 31D (Rwie)	1.88	3
C9503-B39VR9	T-7 5C (H2/CCUz)	58.5	3
C9503-B39VT4	T-7 6B (CCUz/CCUc)	370	3
C9503-B39VY1	T-7 18C (Rwie)	1850.	3

1 (Truex et al., 2017)
2 (Szecsody et al., 2018)
3 (Demirkanli et al., 2018)

CCU = Cold Creek unit
CCUc = Cold Creek unit – caliche
CCU = Cold Creek unit – gravel dominated
CCUz = Cold Creek unit silt-dominated
H1 = Hanford formation unit 1
H2 = Hanford formation unit 2
Rwie = Ringold formation member of Wooded Island unit E

There are limited data sets of vadose zone nitrate concentration profiles with depth including: a) under the 216-A-37-1 crib, b) under A-AX farm, c) under the 216-S-13 crib, and d) under BC cribs. The 216-A-37-1 crib received 377 million liters of dilute ammonium hydroxide solution between 1977 and 1989 (Szecsody et al. 2020). A significant fraction of the ammonia was oxidized to nitrate, which reached

groundwater within 5-6 months of release. A characterization borehole (C4106) drilled in 2003 showed that a significant mass of nitrate (and possibly adsorbed ammonia or ammonia precipitates) remained in the first 100 feet of the vadose zone (Figure 17) with an order-of-magnitude higher concentration within the top 25 feet. It is likely that the nitrate plume extending to 100 ft depth is nitrate, but the shallow plume may include ammonia. An additional characterization borehole is planned for FY24.

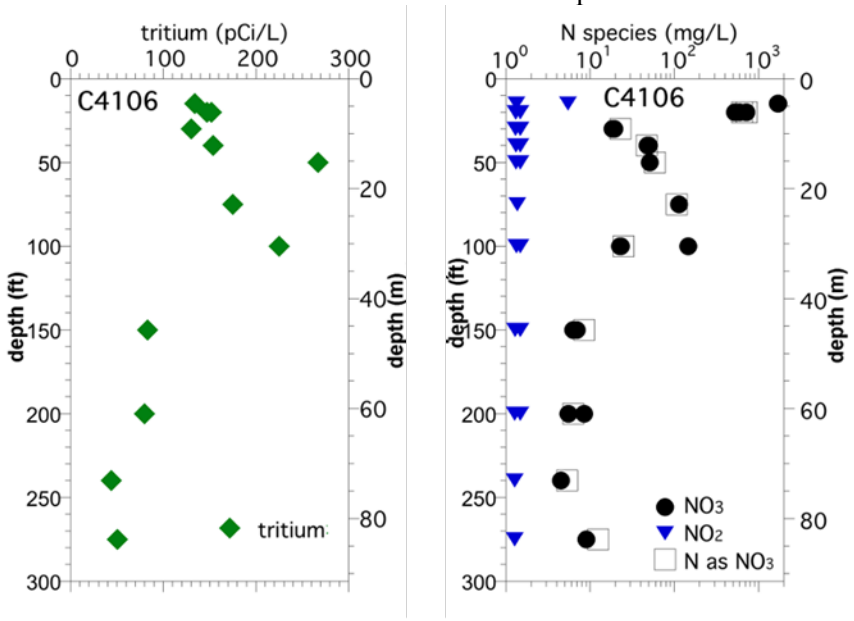

Figure 17 - Analysis from characterization borehole C4106 (drilled in 2003) at SE end of 216-A-37-1 crib: tritium (left), and nitrogen species (right) (Szecsody et al., 2020).

Characterization boreholes D0006 and D0008 drilled beneath the Waste Management Area (WMA) A-AX tank farm showed elevated nitrate near the surface (Figure 18, first 20 feet) and at a 260 to 290 ft depth. The deeper nitrate may be residual nitrate trapped in pore water from when the water table was elevated.

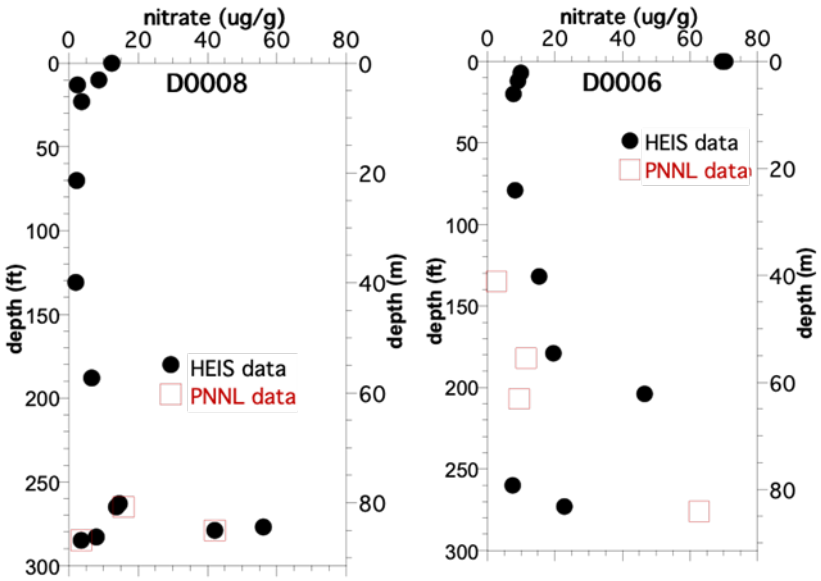

Figure 18 - Nitrate analysis with depth from characterization boreholes D0006 and D0008 in WMA A-AX tank farm (Szecsody et al., 2022).

The nitrate depth profile under the S-13 crib showed elevated concentrations at depths of <10 ft (3 m), 50 to70 ft (15 m to 21 m) and at ~200 ft (~60 m), with relatively low concentrations at other depths (Figure 19). Co-mingled organic contamination (methyl isobutyl ketone, MIBK, also shown in Figure 19) may be biodegraded and additionally reduce nitrate.

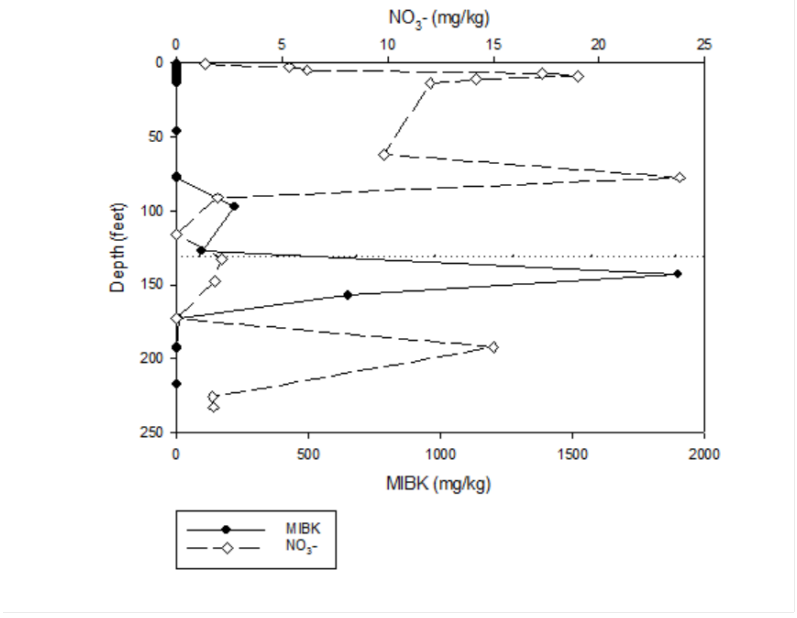

Figure 19 - Nitrate and methyl isobutyl ketone (MIBK) analysis with depth from characterization borehole C9513 in the 216-S-13 crib (Demirkanli et al., 2018). The horizontal dotted line indicates the intersection of the Hanford formation and the underlying Cold Creek Unit.

Finally, nitrate characterization in sediments under the BC cribs and associated electrical resistivity tomography (ERT) provides evidence for slow migration of nitrate in the Hanford vadose zone. Depth profiles of nitrate in four boreholes drilled in 2007 show multiple nitrate plumes at different depths

(Figure 20) due to the complex vertical and lateral infiltration of contaminants (including nitrate) from different tanks and trenches (Serne et al., 2009). Although these depth profiles provide high resolution nitrate concentrations that show as many as three peaks with depth (borehole C5923, at 80, 130, and 220 ft depth), associated 3-D ERT was needed to show that high conductivity water (predominantly Na and nitrate) migrated both vertically and horizontally from different leaks or discharges, which accounts for the multiple plumes with depth in these characterization boreholes (Johnson and Wellman, 2013). A comparison of subsurface electrical resistivity plumes taken in 2008 from a survey under the entire B-complex was compared to a separate 2022 survey (Robinson et al., 2023) shows no vertical migration of the nitrate plumes over the 14 years, within the ERT resolution. Water and contaminant migration through the vadose zone can be slow to rapid, dependent on several factors including the water discharge rate. The calculated migration time of water (and un-retarded nitrate) through the *natural* vadose zone (i.e., given 16 cm/year precipitation and a vegetated surface) is 7200 to 36,000 years (0.25 to 1.3 cm/yr infiltration, (Murphy et al., 1991), although migration is as fast as 5 months with a high waste discharge (between 30 gal/min and 60 gal/min of concentrated NH_4OH during the early portions of a processing campaign, which drastically slowed as the campaign progressed) (Buelt et al., 1988).

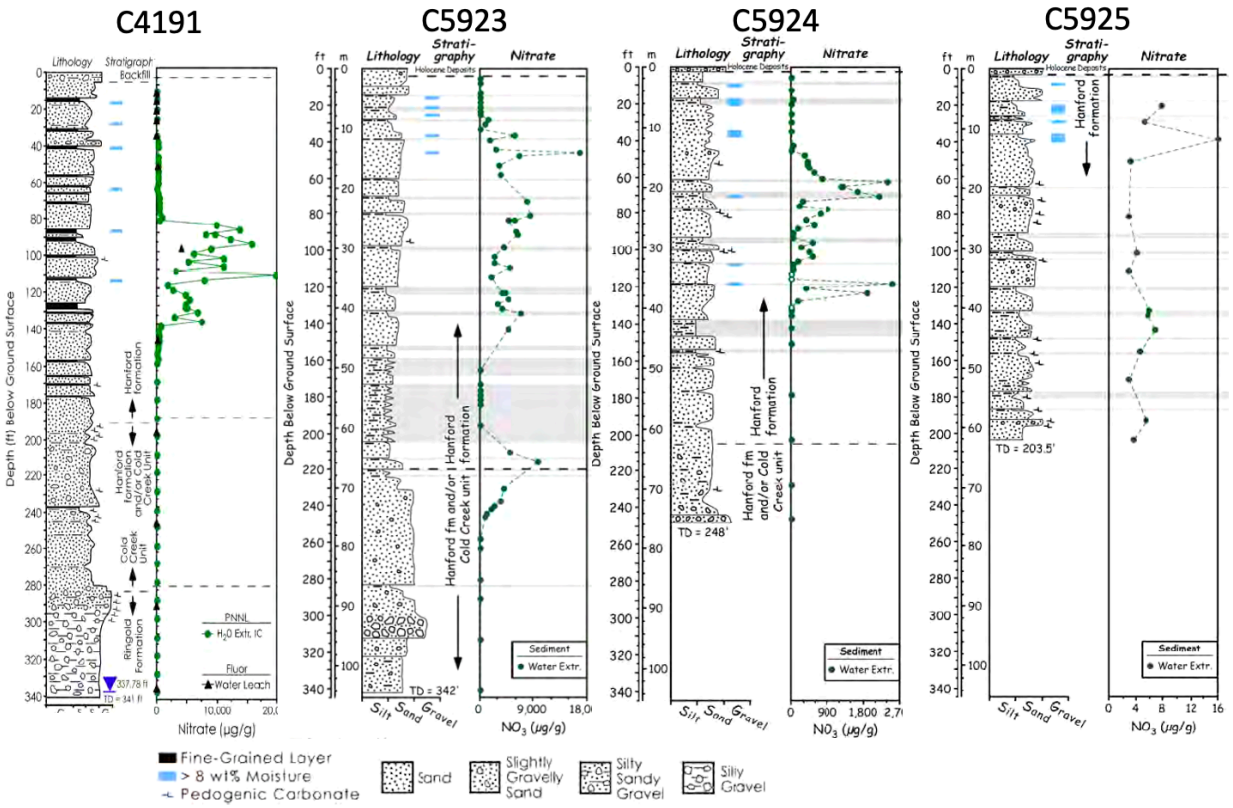

Figure 20 - Nitrate and stratigraphy vertical profiles under BC Cribs.

Nitrate has been tracked historically in the vadose zone and areas of alkaline liquid discharge have shown retardation in the movement of nitrogen species. It will likely take thousands of years for water transport through the vadose zone and historical data shows an associated slowed movement of nitrate under natural conditions.

5.3 Nitrate and Nitrite in the Saturated Zone

Upon reaching the saturated zone in the subsurface (water table) most COCs behave similarly. The following behavior was replicated in the 2018 IDF PA for the saturated zone below the IDF (USDOE, 2018). The concentrations of COCs in the saturated zone are dependent on the spatial and temporal arrival from the vadose zone source term. Once in the water table, the COCs quickly transport through the zone. There is assumed to be minimal transverse dispersion along the saturated zone and some vertical dispersion. Due to the relatively fast horizontal flow rate in the saturated zone the concentrations of COC's are reduced compared with the vadose zone. Placing an inventory of a COC (or majority thereof) into the saturated zone all at once can lead to increased dispersion in the saturated zone. However, spreading the inventory out can reduce the source term and spread the release across the vadose zone and saturated zone. The area of resulting contaminant plumes in the saturated zone are dependent on the size of the source term from the IDF liner system due to presumed limited transverse dispersion.

5.4 Current Remedial Actions at Hanford

This section provides information on remediation activities for nitrate at Hanford across the various operable units (OUs) to provide perspective on how nitrate has been treated at Hanford from previous releases to the subsurface. Remediation of subsurface contamination at Hanford has been active for decades with several reports summarizing approaches for specific contaminants, including nitrate (Beck and Duncan, 1993; BYRNES, 2008; Eberlein et al., 2013). The annual Hanford groundwater monitoring report for fiscal year 2022 (USDOE, 2022b) identifies the OUs in the River Corridor and Central Plateau that have ongoing or historical remediation objectives for nitrate and records of decision (ROD), remedial investigation (RI) or feasibility study (FS) (summarized in Table 5). Due to the limited amount of nitrite data, only a small subset of which is above detection limit, nitrogen present in the groundwater is typically assumed to be present as nitrate. Current nitrate remediation for most OUs in the River Corridor (Hanford 100 and 300 Areas) is addressed by monitored natural attenuation (MNA) when a remedial action for nitrate is required. MNA relies on natural attenuation processes, including physical (e.g., dispersion, dilution, volatilization), chemical (e.g., sorption, stabilization, transformation), or biological (e.g., biodegradation, stabilization) processes, that reduce the mass, toxicity, mobility, volume, or concentration of contaminants[1] (EPA, 1999). For the 100-KR-4 and 100-NR-2 OU, any nitrate removed is incidental due to treatment of other co-contaminants. In the Central Plateau (Hanford 200 Area), MNA or extraction for cleanup at the 200 West pump-and-treat (200W P&T) facility are used to meet identified remedial objectives or provide some incidental remediation of nitrate as a co-contaminant. In the case of the 200-ZP-1 OU, recent evaluations have initiated the transition from extraction to MNA remedial action as described below. These approaches in the different OUs show that despite the extensive releases of nitrate into the subsurface (as nitrate or ammonium hydroxide) many have progressed to MNA. As well, there has been some treatment of nitrate in treatment processes designed to target other contaminants. Therefore, there is a possibility that nitrate and nitrite released from the IDF could have a natural attenuation strategy.

[1] https://www.epa.gov/sites/default/files/2015-04/documents/a_citizens_guide_to_monitored_natural_attenuation.pdf

Table 7. Summary of Operable Units and remedial actions for nitrate in the Hanford's River Corridor and Central Plateau (Adapted from (USDOE, 2022b)).

Groundwater OU	Nitrate Source Term(s)	Current Groundwater Remediation	CERCLA Decision Status
River Corridor			
100-FR-3	- Pre-Hanford agriculture	MNA	ROD for final action signed in 2014
100-HR-3	- Gas condensate from D, DR, and H reactors - Septic and sewer systems - Pre-Hanford agriculture - Waste Sites receiving nitric acid	MNA	ROD for final action signed in 2018
100-KR-4	- Oxidation of ammonia in reactor gas dryer condensate	Co-contaminant, incidental remediation only	Interim ROD; Draft B RI report released for regulatory agency review in 2019; FS report released for regulatory agency review in 2020. ROD for final action anticipated in 2024.
100-NR-2	- Discharges to liquid waste disposal facilities (LWDFs) - Septic and sewer systems	Co-contaminant, incidental remediation only	Amended interim ROD signed in 2010. Draft B RI/FS report released for regulatory agency review in 2019.
300-FF-5	- 618-11 Burial Ground	MNA	ROD for final action signed in 2013
Central Plateau			
200-BP-5	- Liquid waste sites - Unplanned releases from 216-B-2 Ditches - Unplanned releases from WMA C - Discharge to Gable Mountain Pond	Groundwater extraction, Co-contaminant, incidental remediation only	Interim action ROD signed in 2021
200-PO-1	- Waste sites (Cribs, ponds, ditches) - Dust-suppression water percolation from WTP	None to date, pending interim action	Interim action ROD signed in 2021
200-UP-1	- WMA S-SX and U - Disposal Facilities Associated with U and REDOX Plants	MNA	ROD for interim action signed in 2012
200-ZP-1	- Liquid waste disposed to cribs near WMA T and 216-Z cribs and trenches	MNA	ROD for final remedial action signed in 2008
200-DV-1	- WMA B-BX-BY (200E Area) - WMAs T, TX-TY, S-SX (200W Area)	Perched water extraction	Implemented treatability test in 2011 and action memorandum in 2016; characterization of the deep vadose zone in progress.

In the 200-ZP-1 OU, nitrate remediation is in the process of transitioning from active remediation to MNA at the 200W P&T facility. Most nitrate in this OU persists at concentrations that are less than an order of magnitude above the cleanup level (45 mg/L as nitrate, 10 mg/L expressed as nitrogen). Assuming no continuing sources of nitrate persist, the amount of nitrate already removed from contaminated groundwater by *ex situ* biological treatment at the 200W P&T facility (through October 2019) may be sufficient to allow for the transition to MNA while still meeting the timeline for nitrate remediation specified in the 200-ZP-1 OU ROD. In October 2019, biological treatment at the 200W P&T facility was suspended to conduct an optimization study evaluating this facility configuration change for its potential to increase carbon tetrachloride treatment capacity and allow for MNA of nitrate (USDOE, 2020b, 2022a). Nearly 100 monitoring wells located within the 200-ZP-1 OU are being sampled on a monthly, quarterly, semiannual, or annual basis and analyzed by ion chromatography for nitrate and nitrite concentrations according to the study's sample and analysis plan (USDOE, 2019). Optimization testing is planned through at least fiscal year 2024, and the results of this study aim to provide a technical basis for modifying the P&T configuration. These results can continue to inform the likelihood of natural attenuation driven remediation of nitrate or nitrite in the subsurface below the IDF.

Prior releases of waste to the subsurface have generated nitrate and nitrite plumes. Prior P&T activities have shown remediation of nitrate and nitrite. Comparing the nitrate released to the subsurface in historical activities vs. projected releases from IDF could show potential for natural attenuation to consume nitrate and nitrite.

5.5 Factors Influencing Nitrate/Nitrite Migration in the Subsurface

5.5.1 Mineral Interactions

As anions, nitrate and nitrite are highly mobile in the Hanford subsurface and exhibit minimal sorptive interactions with Hanford sediment mineral phases that would retard their transport. The most likely mineral-mediated interactions involving nitrate and nitrite, e.g., dissolution and precipitation, occur initially upon discharge of the liquid to the subsurface. Tank waste at Hanford that has leaked into the subsurface is highly caustic, is highly concentrated (>1 mol/L Na), and in some cases persists at elevated temperatures (> 50 °C). As well, discharges have also included raw and decontaminated supernatants, select evaporator bottoms from processing decontaminated liquids and some dissolver liquids all of which are alkaline with high ionic content. These high-pH and high-salt liquids have similarities to the composition of leachates from grout waste forms. These high-pH and high-salt liquids have similarities to the composition of leachates from grout waste forms. These extreme solution conditions become highly reactive when they meet the contrasting circumneutral sediments in the Hanford subsurface that are comprised primarily of aluminosilicate minerals (Zachara et al., 2007). Laboratory studies performed to simulate waste/sediment reactions identify two distinct reaction zones that form downgradient from a source. The sediments evaluated in the study are similar to those found below the IDF (Qafoku et al., 2004; Wan et al., 2004; Zachara et al., 2007). In the first reaction zone, silicate and fine-grained aluminosilicates undergo dissolution reactions due to the presence and consumption of hydroxide. These dissolution reactions cause the pH to drop from approximately pH 14 (tank waste) to pH 11 – 12. At the boundary between this first zone and the second, a pH neutralization zone exists that is dictated by the volume of waste that is released at the source. As well, the pH in these regions will also be affected by the ingress of atmospheric CO_2, so comparisons to subsurface regions without waste discharges should be completed. In the pH neutralization zone, secondary precipitation of ettringite, gibbsite, cancrinite, sodalite, and other zeolitic, feldspathoid, and aluminosilicate phases release protons that continue to neutralize the tank waste (Ainsworth et al., 2005; Bickmore et al., 2001; Chorover et al., 2003; Deng et al., 2006; Um and Serne, 2005; Wang and Um, 2012). Phases precipitate on existing mineral surfaces and/or form colloids in the aqueous phase (Mashal et al., 2004). When the concentration of nitrate is elevated, the formation of nitrate-containing secondary phases occurs at an accelerated rate based on laboratory findings (Wan et al., 2004; Zhang et al., 2005). It is

unknown if similar processes occur from liquids contacting with or released from grout waste forms (also high pH and concentrated but this may be informed by lysimeter testing (Section 4.3.4). Very high nitrate concentrations in vadose zone sediments may be Na-nitrate precipitates (or other species like chromium-nitrates) as they are above solubility. For example, borehole C4191, at a 120' depth, shows values as high as 20,000 ug/g nitrate, which is approaching sodium nitrate solubility (Figure 20). If some of the nitrate is precipitated, then it is not slowly migrating downward with pore water in the vadose zone.

Historical work has shown that nitrate-containing phases can be generated from precipitation processes within the Hanford subsurface when contacting alkaline conditions. An evaluation of the likelihood of these processes resulting from IDF leachates would be valuable.

5.5.2 Microbial Conversion of Nitrate and Nitrite

Crucial to the behavior of nitrate and nitrite is the understanding of their microbial conversion in the subsurface, primarily the impact of denitrification and dissimilatory nitrate reduction to ammonia (DRNA) (Bagwell et al. 2019). Denitrification is a microbiological process that involves the multi-step reduction of nitrate to nitrite and then to gaseous nitrogenous products. Denitrifying microbes are ubiquitous in sedimentary environments, including industrial and nuclear waste impacted sites. Numerous laboratory studies and field demonstrations have used the inherent denitrifying capacity of subsurface environments for *in-situ* remediation of nitrate and co-contaminants, including at the Hanford, Oak Ridge Reservation, and other nuclear waste disposal sites around the world (Bagwell et al., 2019b; Lloyd and Renshaw, 2005; Safonov et al., 2018; Thorpe et al., 2012; Wu et al., 2010).

As an anaerobic process, denitrification activity will be the highest in low-O_2 subsurface regions (natural or engineered); however, some denitrifying bacteria can survive in aerobic conditions. Studies of Ringold Formation sediments from the 300 Area have been used to suggest that heterotrophic carbon metabolism is viable long-term in reducing sediments based on studies of varying oxygen and nitrate exposures (Percak-Dennett and Roden, 2014). Within low permeability zones (an oxidized top layer and a reduced sub layer from Hanford) denitrification rates were higher in the oxidized zone compared with a reduced zone sediment (Yan et al. 2016). Within these zones, N_2 was the end-product in the oxidized zone and N_2O was observed in the reduced zone as the rate of denitrification was faster in the oxidized zone driving more nitrate to the N_2 complete product. This behavior was attributed to colonies is the oxidized zone being more established and they have adapted to possessing the *nosZ* gene required for denitrification due to their access to nitrate. Whereas colonies in the reduced zone have had less access to nitrate due to its consumption in the upper layers, and as such, have not been driven to the same level of adaptation as in the oxidized zone. The results also implied that low-permeability zone sediments can be an important sink of nitrate and a potential secondary source of N_2O as a nitrate bio-reduction product in groundwater (Yan et al., 2016). Work is also ongoing to study *Paenibacillus* sp. from the 300 Area smear zone as it is likely to grow anaerobically with nitrate as the sole terminal electron acceptor, as it has shown prior reductive capability (Ahmed et al. 2012).

Microbial activity in the Hanford subsurface could also lead to conversion and removal of nitrate and nitrite, amongst other species (e.g., carbon tetrachloride) (Hooker et al., 1994; Skeen et al., 1995) (Bagwell et al., 2020; Koegler et al., 1989; Law et al., 2010; Sherwood et al., 1999; Skeen et al., 1994; Thorpe et al., 2012; Zhao et al., 2013). With one study concluding that "*Overall, it appeared that the Hanford subsurface possesses a microbial population able to transform CT and remove nitrate from the ground water"*. Separate studies from Hanford 300 Area sediments suggested that "*The qPCR and MPN analyses indicated a broadly distributed potential for nitrate reduction throughout the subsurface strata. The geochemical profiles, however, suggest that microbial nitrate reduction could be restricted to the strata just below the Hanford-Ringold contact, where O_2 becomes depleted,and nitrate is detectable. The denitrifying microbial populations in the 300 Area subsurface sediment were dominated by*

Ochrobactrum anthropi and Achromobacter sp., based on nosZ gene libraries (Lin et al., 2012a)". Spikes of hydrogen and nitrite in 300 Area groundwater have been observed suggesting that microbial driven oxidation of hydrogen was coupled to nitrate reduction, and in fact, *was suggested that nitrate was reduced beyond nitrite by Acidovorax spp (strain JHL-9) and this strain contains all the enzymes to completely reduce to nitrogen* (Lee JH et al. 2015). Samples from the 100-H area showed a HLN strain isolate that is nitrate reducing (Chakraborty et al., 2008; Han et al., 2010; Truex, M.J. et al., 2009) and also, in the 200 Area (Lee, JH et al. 2015). These studies have also isolated the *Pelosinus sp.* in reducing zones from the 300 Area and 100 Area that can reduce nitrate (Yang et al. 2019, Beller et al. 2013). As nitrate and radioiodine plumes at Hanford are comingled, a study of *Agrobacterium* strain DVZ35 showed removal of both iodate and nitrate. The addition of higher amounts of nitrate enhanced iodate removal (Lee et al., 2018). Whereas strains found at Hanford 300 Area (Acidovorax spp., Bradyrhizobium japonicum strain (strain 22)) have also been shown to be capable of denitrification (Lee et al. 2014, Benzine et al. 2013).

In the 1990's *in situ* bioremediation was deemed to be more economically feasible than *ex situ* treatment based on studies of joint CT and nitrate reduction and computer modeling efforts (Niemet and Semprini, 2005; Skeen et al., 1992; Skeen et al., 1993; Truex et al., 1994). It was shown that nitrate present with an acetate substrate increased CT removal (Niemet and Semprini, 2005). The injection of nitrate was shown to increase Cr removal via microbial activity in Hanford sediments (Zelaya, 2013). The *Acidovorax* spp. strain JHL-9 cultures isolated from colonized sand at Hanford showed reduction of technetium in the presence of denitrifying conditions and that nitrate assisted in growth of this strain in the presence of bicarbonate, H_2 and nitrate where nitrate was suggested to be converted to N_2 (Lee, J.H. et al., 2015). A similar investigation for the IDF would be of value to show if microbial activity can remove nitrate along with other co-contaminants; a process that could also be captured in long-term modeling.

Information on this possibility is gleaned from an analysis of the fluidized bed reactor (FBR) at the Hanford 200W P&T (Breedlove et al., 2011). Dissimilatory nitrate reduction to ammonia (DRNA), or ammonification, describes one pathway for the anaerobic reduction of nitrate. DNRA and denitrification (reduction of nitrate to nitrogenous gases) are distinct metabolic processes that compete for nitrate in the environment (Figure 21). The results are relevant to the FBR biological treatment system because, unlike denitrification, which results in the net loss of nitrogen, DNRA retains nitrogen in the system by converting it to a highly accessible (bioavailable) form, as soluble ammonia. DNRA in the FBR biological treatment system could be an important and continual source of ammonia at the 200W P&T Facility, contributing to biofouling of injection wells.

Denitrification is a more energetically favorable reaction than DNRA, but the enzymatic pathway is energetically expensive, giving a competitive advantage for DNRA bacteria. However, a preference for it can be attained with changes in water and sediment chemistry, fluid residence time, and groundwater–surface water exchange (Liu et al. 2017). It must be noted that while DNRA removed nitrate the ammonia generated could reoxidize to nitrate later. Strohm et al. (2007) illustrated this point through a series of growth studies on simple substrates that showed that DNRA produced 2× higher cell mass per mol of nitrate than denitrification. The published literature has clearly established the high frequency with which denitrifying activity (communities) in natural and engineered systems are overcome and replaced by DNRA activity (communities) over time (Kessler et al., 2018; Rivett et al., 2008; Tiedje et al., 1983; van den Berg et al., 2017), particularly in conditions when the organic carbon / nitrate ratio is high (Giblin et al., 2013; Strohm et al., 2007).

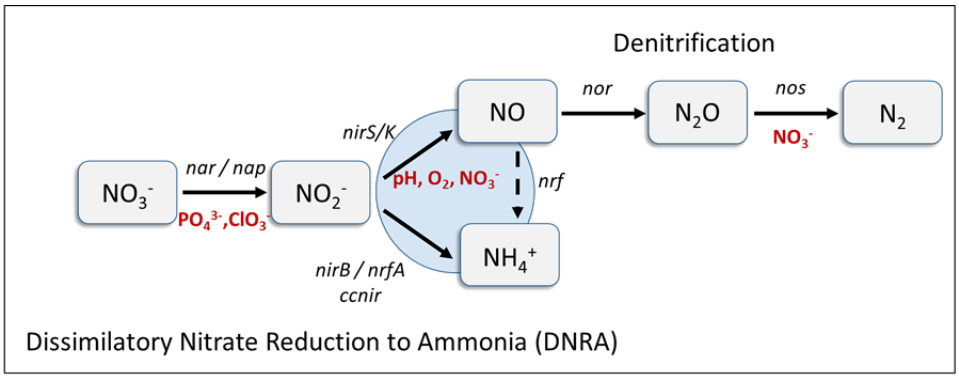

Figure 21 - Competing anaerobic nitrate reduction pathways. The enzymes that catalyze specific reactions are listed in italics. Relevant environmental regulators of key reactions are in red text and the pathway bifurcation (blue halo) is tightly controlled by a number of enzymatic and metabolic regulators.

Environmental conditions that tend to favor DNRA over denitrification include a consistent supply of organic carbon, carbon quality (fermentable substrates), low concentrations of nitrate, high C/N ratio, high temperatures, and variable pH, nitrite, and sulfide concentrations (Liu et al. 2017). The leachates from IDF in the scenarios considered in this report are unlikely to represent these conditions. Moreover, DNRA populations (and activity) are generally much less sensitive to changing environmental conditions than denitrifying bacteria (Rivett et al., 2008; van den Berg et al., 2017). The Hanford subsurface is oligotrophic (low in organic carbon) so on their own nitrate concentrations would need to be low to prefer DNRA, but what concentration defines “low” (and relative to organic carbon) remains unknown (Konopka et al. 2013).

Biologically driven denitrification remains an unrepresented pathway in IDF performance modeling, yet ample evidence of its occurrence in the Hanford subsurface exists. A focus should be placed on studying the rate of denitrification in IDF-relevant conditions, sources of organic carbon (and other electron donors) to drive microbial activity and correlating denitrification to subsurface transport in various geologies below the IDF. Doing so would allow this process to be represented in PA modeling.

5.5.3 Dispersion

Dispersion is a more dominant process in the saturated zone than the vadose zone due to the high horizontal flow in the saturated zone, see Section 5.3. It is presumed that there is limited transverse dispersion within the vadose zone below the IDF, and this was captured in the 2018 IDF PA. Unless zones within the subsurface can drive transverse dispersion this process will only impact concentrations within the saturated zone. Transverse dispersion is not currently included in the IDF PA.

6.0 Summary and Proposed Path Forward

6.1 Summary of Nitrate and Nitrite at Hanford

Based on the information above, the story of nitrate and nitrite from the tanks through disposal as a grouted waste form can be constructed with some uncertainties. The conceptual site model for contaminant attenuation in the 200 West Area aquifer (Central Plateau Area, includes both unconfined and confined aquifers) includes abiotic reduction and microbial conversion occurring in anoxic, reduced zones of low permeability (e.g., silt and clay lenses, Lower Ringold Mud Unit, Cold Creek Unit). There are numerous indicators that these zones exist and that conversion pathways are actively occurring for nitrate/nitrite, and for other priority contaminants (e.g., CT, chloroform, and reduction-oxidation active radionuclides) (Bagwell et al., 2019b; Neeway et al., 2019; Szecsody et al., 2020). Reliable indicators for contaminant (nitrate) reduction include site subsurface water data, characterization studies, remedy evaluations, and laboratory-based investigations (Lin et al., 2012b; Yan et al., 2016). Figure 22 presents the proposed full system summary for nitrate and nitrite at Hanford.

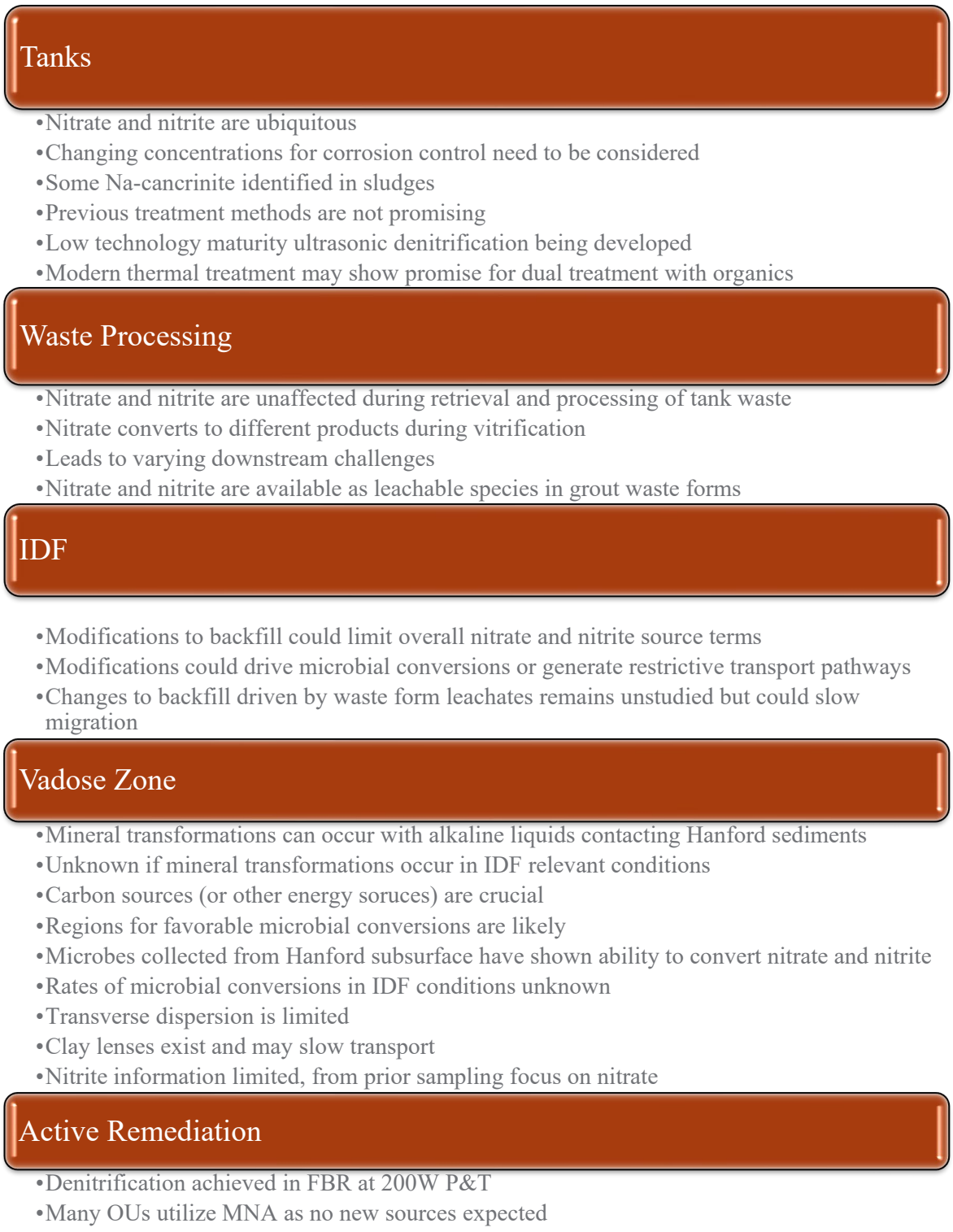

Figure 22 – Summary of nitrate and nitrite information at Hanford

6.2 Gap Assessment and Proposed Testing Approaches

Based on the conceptual model, several current uncertainties and gaps for nitrate and nitrite at Hanford are present. Closure of these gaps will provide further insight into nitrate and nitrite behavior that can be integrated into PA modeling of the IDF. An updated full system model of the IDF for a grouted waste form could possibly contain updated parameters accounting for significant natural attenuation processes in the subsurface and more accurately representing the fate of nitrate and nitrite resulting from a grouted LAW inventory in the IDF. From the evaluation of the relevant nitrate and nitrite information there are opportunities to better understand and predict the natural attenuation of nitrate in the subsurface below the IDF. Closing these gaps would allow for a decision to be made on whether any of the processes should be included in PA modeling of grout in the IDF and would also provide input parameters to represent the processes in the models. If natural attenuation is likely, and can be accounted for in PA modeling, the uncertainty around the disposal of a grouted LAW waste form in the IDF will be drastically reduced. The gaps, approach to their closure, and specific impact are presented in Table 8. High-priority items focus on addressing the uncertainty of the likelihood of natural attenuation (biotic or mineral based) in or below the IDF. A technically defensible reasoning would be required before developing the models specifically for the IDF. These modeling updates are addressed in the medium-priority items. Long-term priorities are those that are not an immediate need to assess if nitrate and nitrite removal in the subsurface is likely or for development of the model.

Table 8 – Summary of major gaps of nitrate and nitrite relevant to the IDF grouped by priority along with the proposed approach to close the gap and the resulting impact on the IDF performance assessment maintenance program.

Gap	Proposed Approach	Impact
High Priority		
Vadose Zone Are there stoichiometric correlations between the carbon inventory (both organic and inorganic) released from a grout waste form and the subsequent potential for biotic nitrate and nitrite removal? This also applies to other nutrients and electron donors released from the waste form (e.g., phosphate).	Organic and inorganic carbon release from grout waste forms is rarely tracked, yet, in the view of a natural attenuation mechanism for nitrate and nitrite, the availability of carbon (and other energy sources or nutrients) would play a significant role in biotic activity. This carbon could also arise from other waste forms in the IDF, e.g., activated carbon. A study should be performed to first document releases of carbon from grout waste forms related to nitrate release from the same waste forms. This would be followed by comparing transport of these compounds in relevant IDF subsurface conditions and compare with naturally available carbon sources in the Hanford subsurface. Data from the lysimeter can also inform the laboratory test results. Data from the lysimeter can inform/confirm laboratory test results.	Demonstrating that there is an adequate carbon source (or other energy sources) which travels simultaneously with nitrate released from a grout waste form to sustain biotic denitrification would build the technical defensibility of including subsurface biotic degradation of nitrate and nitrite in PA modeling.

Gap	Proposed Approach	Impact
Vadose Zone What are the rates of nitrate and nitrite conversion in different aqueous environments in the Hanford subsurface?	There have been cursory studies of microbial activity rates in Hanford environments, however, none in conditions relevant to the IDF subsurface or with liquids having contacted grout waste forms. Most data comes from the Ringold formation or Hanford saturated zone. A study should be performed to measure these denitrification rates in IDF-relevant conditions.	This study would give a sense of possible nitrate or nitrite conversion rates that can be coupled with COC migration and flow rates to assess the likelihood of conversion over time in or below the IDF. This assessment will inform the technical defensibility of nitrate and nitrite natural attenuation to be included in IDF PA modeling.
Vadose Zone Are there mineral precipitation reactions that occur in the IDF and subsurface sediments when contacted with an alkaline leachate from a grout waste form?	Prior evidence has shown the formation of a nitrate-cancrinite mineral phase occurred when waste was discharged to Hanford sand. Grout leachate is also highly alkaline and concentrated in salts. A laboratory effort should be performed to observe transformations of Hanford IDF sediments when contacting grout leachates (or estimated combined leachates that pool at the bottom of the IDF). The experiments would be supported with prior data to compare mineral changes from tank leaks vs. intentional discharges.	This effort would provide crucial information to support the technical defensibility of mineral incorporation of nitrate and nitrite in the IDF. Doing so would inform whether to include mineral incorporation of nitrate and nitrite in PA modeling.
Tanks How do nitrate to nitrite ratios from tanks and crib discharges correlate to existing and prior subsurface data?	Tracking previous conversions of nitrate and nitrite in the subsurface is challenging, but the ratios of nitrate and nitrite can be correlated with measured values in tanks and discharged wastes to see if any loss is observed. This could also employ isotope ratios to determine nitrate sources similar to prior efforts at Hanford.	This effort would fill a crucial information gap around the conversion of nitrate and nitrite in the Hanford subsurface by utilizing source term ratios from prior discharges. Specifically for nitrite, the available data on nitrite is limited as it was not a target of historical analyses, and many existing measurements are below detection limits. If existing data shows nitrite is lost in the subsurface (based on relative ratios to source term, or in experimental testing) it would build the technical defensibility for nitrite attenuation below the IDF.
IDF Can grout performance be shown to consistently lower nitrate and nitrite release using alternate	Continue testing of alternate grout formulations to assess improved nitrate and nitrite release.	Success in this development can show that the waste form alone can be suitable for mitigation of nitrate and nitrite release from the IDF

Gap	Proposed Approach	Impact
formulations or other methods?		
Mid-Range Priority		
Vadose Zone How does contaminant transport vary through the stratigraphy below various regions of the IDF.	The subsurface below the IDF is not consistent in current or future expansion locations. Contaminant transport may vary as species move between the different layers below the IDF. Laboratory studies and lysimeter tests could be used to replicate a scaled IDF subsurface and monitor contaminant transport across the system in waste form leachates.	This information can be used to develop a spatial geological model of the IDF subsurface that captures natural attenuation processes in specific locations.
Vadose Zone How does the 3D IDF subsurface correlate to the potential for natural attenuation?	There are features of the Hanford subsurface that could have enhanced attenuation or slowing of nitrate and nitrite, including clay lenses, anoxic zones, and zones with possible enhanced microbial conversion. Using borehole data, an updated 3D map below the IDF (current and future locations) should be produced to highlight zones of likely attenuation processes and correlate these zones to emplacement of a grouted inventory in the future.	This information can be used to develop a spatial geological model of the IDF subsurface that captures natural attenuation processes in specific locations. Such a model could help inform IDF operations to use advantageous placement of waste forms.
IDF Can grout performance be shown to consistently lower nitrate and nitrite release using alternate formulations or other methods?	Continue testing of alternate grout formulations to assess improved nitrate and nitrite release.	Success in this development can show that the waste form alone can be suitable for mitigation of nitrate and nitrite release from the IDF
Long-term Priority		
Waste Processing Is there a feasible technology to remove the nitrate and nitrite from tank waste during processing?	A technology development effort is underway under the EM-TD program investigating the ultrasonic removal of nitrate from Hanford tank waste. Further progression of this technology will be based on initial results. Other feasible technologies also exist including reforming processes that also destroy organics.	The extent of required nitrate removal may be large if subsurface attenuation or waste form management strategies are not feasible. Emerging results could change this ranking.
IDF How much additional nitrate and nitrite could theoretically be released from grout waste forms in the IDF and how does this compare to historical discharges?	A paper study can be performed to compare the mass of nitrate and nitrite remaining in the tanks that could be disposed at the IDF vs. the mass of nitrate and nitrite discharged previously into the subsurface that generated the existing plumes. Doing so could allow predictions of the migratory pathways of these species below the IDF and how the projected IDF inventory compares to existing plume inventories.	This mass balance exercise can help inform the development of transport models. It can assess the likelihood of nitrate co-mingling between existing plumes and any future nitrate release from the IDF, or co-mingling with other COCs.

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Appendix A - Expanded Nitrate Hanford Annotated Bibliography

A.1 Expanded Literature Review of Nitrate and Nitrite at Hanford

There are other studies around nitrate and nitrite specific to Hanford waste, waste processing, and subsurface behavior in the literature. While not directly tied to the IDF-related discussions above, the following section presents a short, annotated summary of these other Hanford-focused nitrate studies. The studies are presented in chronological order.

A.2 Microbial Studies

A study of Hanford site sandy loam for the activity of nitrifiers showed that nitrate reducer populations were always larger than denitrifiers and varied little with depth. While ammonium oxidizers decreased with depth and the concentration of nitrite oxidizers varied. A cyclic oxidation and reduction coupling of nitrate and nitrite was identified due the growth of nitrite oxidizers with time (Volz et al., 1975b). Similar results were seen in a shorter-term study where nitrate was reduced to nitrite with a rate of 0.013 – 0.046 µg N/h/g (Volz et al., 1975a).

Significant concentrations of nitrate-reducing bacteria have been identified in the riverbed hyporheic zones at the Hanford 100 Area along the Columbia River (Moser et al., 2003). Freeze collection of samples did little to impact the recovery of microbial samples.

Analysis of core samples below tank SX-108 showed denitrifying bacteria present in two of the seventeen samples analyzed (Fredrickson et al., 2004)

Nitrate has been shown to serve as an electron acceptor in the growth of Fe(II)-oxidizing bacteria in Hanford sediments (Alphaproteobacteria (Bradyrhizobium japonicum strains 22, is5, and in8p8), Betaproteobacteria (Cupriavidus necator strain A5-1, Dechloromonas agitata strain is5), and Actinobacteria (Nocardioides sp. strain in31) (Benzine et al., 2013) and possible links between pyrite oxidation and nitrate reduction (Percak-Dennett et al. 2017).

A.3 Nitrate Detection

Effectively quantifying nitrate in the Hanford subsurface has been on-going for many decades (Serne et al., 1975). These activities have included different examples in the literature.

Work has shown that reverse polarity capillary zone electrophoresis can be used to measure nitrate and nitrite concentrations in Hanford tank wastes (Okemgbo et al., 1999). The detection limit in this approach was ~50 µM.

Electrical conductivity in the subsurface can be used to link to nitrate concentrations for modeling purposes (Oostrom et al., 2017).

ERT has shown several examples of being a valuable tool in tracking plumes in the subsurface at Hanford, including nitrate plumes (Rucker, 2008; Rucker and Fink, 2007).

Raman spectroscopy can be used for nitrate detection (Crawford, 1997) and ion interactions results in a blue shift in the nitrate peak (Kocevska et al., 2022). These observations can be used to design sensors for waste processing monitoring, including in-tank nitrate and nitrite rations.

A.4 Nitrate in Tank Waste

The chemical interactions between nitrate, nitrite and organics (including ferrocyanide) have been studied to evaluate risks of unwanted chemical reactions within the tank wastes (COWLEY, 1999; Hunter et al., 1997; Scheele et al., 1993).

Nitrate is a crucial component to track in projecting the distribution coefficient of resins when studying the removal of Tc from tank wastes (Ashley et al., 1998). It also impacts the preparation of tank waste samples for analysis of organic species (Stromatt et al., 1993).

In the early phases of vitrification design at Hanford, the impact of possible conversion of ammonium to nitrate and nitrite in an over-reduced melt was studied (King and Bhattacharyya, 1996).

Recovery of sodium nitrate from Hanford wastes via crystallization has been shown as feasible without extracting large amounts of Cs (YANG and RANDOLPH, 1999).

Nitrate directly interferes with the uptake of Tc by Superlig 639 resin based on improved performance for Tc removal in Savannah River Site waste compared with simulated Hanford waste (Hassan et al., 2002; King et al., 2003; King et al., 2005). Nitrate also directly interferes with exchange sites in sodalites that can be used for Tc capture (Dickson et al., 2014) and with other resins (Rogers et al., 1997).

Nitrate cancrinite was identified in a sample of tank 241-AP-101 where Cs-137 became concentrated and matched well with a synthesized form in simulated tank waste (Buck and McNamara, 2004). These results matched with others tests of mineral transformations where nitrate can insert into cancrinite and sodalite (Zhao et al., 2004).

The amount of nitrate and nitrite present (up to 25 mol%) is a limiter on directly generating a hydroceramic waste form from LAW. At levels higher than this denitrification via calcining has been shown to be successful to generate a granular product that can then be immobilized (Bao et al., 2005).

Nitrate can cause aggregation of ferrihydrite in tank waste treatment processes and directly compete with target uptake species (e.g., Tc) (Wakoff and Nagy, 2004)

The solubility of sodium nitrate in tank waste can be predicted via a Gibbs-Duhem integration of water activity (Agnew et al. 2015).

Uranyl nitrate tributyl phosphate complexes have been identified in the tank wastes (Meznarich and Penchoff, 2021) which could impact processing and behavior upon releases to the subsurface. Pu-nitrate-tributyl phosphate species have also been observed (Baumer et al., 2022).

Nitrate is used as the counter-ion in chemical additions to remove radionuclides from tank wastes using Sr (Warrant et al., 2013), Ag (Asmussen et al., 2023a) and Fe (Wilmarth et al., 2001).

A.5 Nitrate in Subsurface

The impact of nitrate on an *in-situ* redox manipulation barrier's longevity for chromium removal showed the presence of nitrate did not limit function of the barrier (Szecsody et al., 2005; Truex, M. et al., 2009).

Nitrate microbial activity can also influence iodine speciation in the Hanford subsurface (Moser et al. 2016; Szecsody et al., 2017).

A.6 Nitrate in Other Studies

Nitrate has been used as a groundwater migration tracer in studies of contaminant migration relevant to salmon in the Columbia River (Geist et al., 1994).

In column tests studying colloid transport in Hanford sediments, nitrate was used as a conservative tracer where it displayed the expected behavior in both saturated and unsaturated conditions (Chen et al., 2005; Cherrey et al., 2003). Nitrate has been used as the conservative tracer in other Hanford studies as well (Murphy et al., 1991).

Lin et al 2012 used nitrate concentrations as indicators of water table rising and river intrusion in counting bacterial communities (Lin et al., 2012b; Yan et al., 2016).

The source of nitrate (and by association, nitrite) in the Hanford subsurface can be tracked via isotope ratios of nitrogen and oxygen (Singleton et al., 2005). This study showed that microbial activity in the soil column and buried caliche zone has generated nitrate. The difference arises from the chemical sources of nitrate. Nitrate from the waste processing is comprised of atmospheric oxygen while historical nitrate from agriculture gets the oxygen from water, inducing different ratios (Christensen et al., 2007; Conrad and Bill, 2008). The method of detection is driven by a biologically driven method (Woods et al., 2003).

Nitrate has been used to study hydrologic exchange in the Columbia River near Hanford and was used to identify increases due to agricultural discharges (Conner et al., 2021).

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