PNNL-14083

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Prepared for CH2M HILL Hanford Group, Inc., and
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under Contract DE-AC06-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RL01830

Printed in the United States of America

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Executive Summary

The overall goal of the Tank Farm Vadose Zone Project, led by CH2M HILL Hanford Group, Inc., is to define risks from past and future single-shell tank farm activities. To meet this goal, CH2M HILL Hanford Group, Inc., asked scientists from Pacific Northwest National Laboratory to perform detailed analyses on vadose zone sediments from within Waste Management Area B-BX-BY. This report is the first in a series of four reports to present the results of these analyses. Specifically, this report contains all the geologic, geochemical, and selected physical characterization data collected on vadose zone sediment recovered from borehole 299-E33-45 installed northeast of tank BX-102.

This report also presents interpretation of the data in the context of the sediment lithologies, the vertical extent of contamination, the migration potential of the contaminants, and the likely source of the contamination in the vadose zone, perched water and groundwater east of the BX tank farm. The information presented in this report supports the Waste Management Area B-BX-BY field investigation report prepared by CH2M HILL Hanford Group, Inc.(a)

Overall, the analyses identified common ion exchange and heterogeneous (solid phase-liquid solute) precipitation reactions as two mechanisms that influence the distribution of contaminants within that portion of the vadose zone affected by tank liquor. Significant indications of caustic alteration of the sediment mineralogy or porosity were not observed, but slightly elevated pH values between the depths of 79 to 141 ft below ground surface (bgs) were observed. X-ray diffraction measurements indicate no evidence of mineral alteration or precipitation resulting from the interaction of the tank liquor with the sediment. However, no samples were studied by scanning electron microscopy, a more sensitive technique for searching for faint evidence of caustic attack.

The analyses do not firmly suggest that the source of the contamination in the groundwater east of the BX tank farm is the 1951 overfill event at tank BX-102. However, evidence is convincing that the fluids from the overfill event are present in the vadose zone sediments at borehole 299-E33-45 to a depth of 170 ft bgs.

The near horizontally bedded, northeasterly dipping sediment likely caused horizontal flow of the migrating contaminants. At borehole 299-E33-45, there are several fine-grained lenses within the Hanford H2 unit at 74.5, 120, and 167 ft bgs that likely cause some horizontal spreading of percolating fluids. The 21-ft thick Plio-Pleistocene fine-grained silt/clay unit is also an important horizontal flow conduit as evidenced by the perched water zone between 227 and 232 ft bgs.

The following are the key findings of the detailed characterization of the borehole 299-E33-45 vadose zone sediments. The porewater electrical conductivity shows a two-lobed elevated plume. The shallower lobe, between 24.08 and 36.58 meters (79 and 120 feet) bgs, resides within the middle sand sequence in the Hanford H2 unit. The shallow lobe appears to pond on top of the fine-grained paleosol at 120 ft bgs. The more concentrated lobe resides between 45.72 and 52.73 m (150 and 173 ft) bgs with the most

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(a) Knepp AJ. 2002a. *Field Investigation Report for Waste Management Area B-BX-BY.* RPP-10098, CH2M HILL Hanford Group, Inc., Richland, Washington.

concentrated fluid between 150 and 160 ft bgs (within the Hanford H2 unit) perhaps ponding on the fine-grained wet zone (i.e., 167 to 169.8 ft bgs) at the bottom of the Hanford H2 unit. Thus, the leading edge of the tank overfill plume appears to reside at about 170 ft bgs which is well above the water table at 255 ft bgs.

High nitrate concentrations in borehole 299-E33-45 sediment start at the contact between the Hanford H1 and H2 units at 34 feet bgs and extend down into the fine-grained Plio-Pleistocene mud unit (PPlz) and perhaps extend all the way to the water table at 77.7 m (255 ft) bgs. The bulk of the water-extractable nitrate is bounded between two thin fine-grained lenses in the H2 middle sand sequence unit. The upper boundary is the fine-grained lens at 120 ft bgs and lower boundary is the fine-grained 2.5 ft-thick lens that forms the bottom of the Hanford H2 unit at 167 to 170 ft bgs. Nitrate concentrations reach 6150 mg/L or ~0.1M at 47.6 m (156.2 ft) bgs. However, there also appears to be somewhat elevated nitrate throughout the Hanford H3 unit at a fairly constant porewater concentration of 600 ± 200 mg/L. The nitrate in the PPlz unit porewater is slightly higher than the nitrate in the H3 unit. There is a decrease in porewater nitrate in the Plio-Pleistocene gravelly unit (PPlg) down to the capillary fringe zone where nitrate increases to values similar to those found in the groundwater. The nitrate data suggest that the BX-102 overfill fluids might have reached the groundwater. However, an alternate source of nitrate within and below the PPlz could be the nearby cribs and trenches after allowing horizontal transport within the perched water zone.

The significantly elevated uranium-238 concentrations first appear at 73.4 ft bgs in the Hanford H2 unit sediment just above the first thin lens (one-ft thick at 74.5 ft bgs). From about 90 ft to ~111 ft bgs, there is little indication that significantly elevated concentrations of uranium are present. Between 111 and 120 ft bgs, the uranium content in the sediment averages about 100 ppm. In the thin lens at 120 ft bgs, which may be a paleosol, the uranium concentration is very high (i.e., up to 1,649 ppm in the finest grained material from this sleeve). Below 120 ft bgs down to 145 ft bgs, the uranium content in the sediment is quite high (reaching values between 200 and 500 ppm). Between 145 and 167.2 ft bgs, in the lower portion of the H2 middle sand sequence, there are slightly elevated uranium concentrations (between 50 and 200 ppm). Within the fine-grained lens between 167.2 and 169.8 ft bgs, the uranium concentration increases again to values between 200 and 400 ppm. Below in the H3 lower sand sequence and the Plio-Pleistocene sediments, there is no significant indication of elevated uranium in the sediments. The in situ Kd values for uranium are distinctly higher in the PPlz and PPlg strata suggesting that no Hanford processing derived uranium is present (the high Kd values indicate the presence of only natural uranium that is much less water soluble in these deep vadose zone sediments).

The other major contaminant in the tank overfill fluid is technetium-99. Elevated concentrations of technetium-99 are found in the vadose zone between 120 and 167 ft bgs (within the middle sand sequence of H2). There appears to be a second less concentrated plume of technetium-99 within the contact between the H3 unit and the PPlz unit (i.e., 220 to 235 ft bgs). Both the acid extractable and water extractable data support this conclusion, however, the water extractable data are of higher quality. There is very good agreement between the technetium-99 concentrations found in the actual porewater and the dilution corrected sediment-water extracts in all regions and lithologies. Further, the technetium-99 concentration in the perched water also agrees with the nearby dilution corrected water extracts. There are obvious elevated concentrations of technetium-99 in the PPlz but not the PPlg unit down to the water table. It is also possible that the technetium-99 in the perched water and groundwater in the vicinity of borehole 299-E33-45 did not come from the overfilling of tank BX-102.

The water extractable cations suggest that an ion-exchange process dominates the major constituent porewater-sediment interactions in the borehole where tank fluid passed by or currently exists. The leading edge of the tank leak plume is enriched in alkaline earth cations that were displaced from the native sediment exchange sites. The interaction of the uranium present in the 1951 tank overfill fluids with the vadose zone sediments appears to include a combination of surface adsorption and discrete solid phase precipitation-dissolution with the precipitated uranium dominating. More mechanistic experiments are discussed in the Science and Technology Project contributions found in Appendix D of the Waste Management Area B-BX-BY field investigation report(a).

Based on a comparison of the depth of penetration of various contaminants and the percentages that are water leachable, it can be stated that uranium migrates slower than technetium-99 and nitrate. The technetium-99 desorption Kd data are consistently near zero, meaning that the technetium-99 is not interacting with the sediment. Despite the findings that only ten to thirty percent of the uranium is water leachable in 1:1 water extracts over a few days, the uranium desorption Kd values are still <3 mL/g in the entire zone where the bulk of the tank fluid currently resides.

In summary, the moisture content, pH, electrical conductivity, and the sodium, tritium, and uranium profiles do not suggest that the leading edge of the plume has penetrated below 170 ft bgs. In general, the majority of the ratios of constituents found in the porewater in the Hanford formation sediments are closer to those from the 1951 metals waste solution that escaped tank BX-102 during a cascading accident than to the other possible source, the 1970s BX-101 junction box leaks. The profiles (but not the ratios to other contaminants) of two constituents considered to be mobile, technetium-99 and nitrate, suggest that the leading edge of the plume may have penetrated all the way to groundwater. However, the ratios also suggest there may be other sources of these two mobile contaminants in the deep vadose zone. The perched water is a likely driving force to move fluids from other sources into the borehole environs. The technetium-99 to nitrate ratio for the perched water at 227 ft bgs is ~1.8 pCi/mg and for the groundwater at 258.7 ft bgs is 43 pCi/mg. This suggests that there may be a source of water, containing nitrate but not technetium, which is feeding the perched water zone. But this unknown water source has not changed the ratio in the surrounding sediments nor diluted the groundwater that is found only 21 ft deeper. The deep vadose, perched water, and groundwater data at borehole 299-E33-45 do not present a clear picture on what might be occurring in the Plio-Pleistocene unit.

Another unresolved issue is the depth of penetration of uranium and the 1951 tank overfill fluids. Based on the total uranium content in the vadose zone sediments, it is not considered that Hanford derived uranium has penetrated below the fine-grained lens separating the Hanford formation H2 unit from the H3 unit (~170 ft bgs). However, the in situ uranium Kd data suggest that Hanford derived uranium might have penetrated the entire Hanford formation down to the Plio-Pleistocene mud unit at ~220 ft bgs.

Acronyms and Abbreviations

ASA	American Society of Agronomy
ASTM	American Society for Testing and Materials
bgs	below ground surface
EC	electrical conductivity
EPA	Environmental Protection Agency (United States federal government regulatory organization)
FIR	Field Investigation Report
g	gravitational constant (980 cm^2/s)
GEA	gamma energy analysis
GPS	global positioning system
HCl	hydrochloric acid
HPGe	High-Purity Germanium
IC	ion chromatography
ICP	inductively coupled plasma (also called inductively coupled plasma – optical emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometer
ICP-OES	inductively coupled plasma – optical emission spectroscopy
Kd	distribution coefficient or sorption partition coefficient in units of mL/g
KUT	potassium, uranium, and thorium
MSL	mean sea level
PNNL	Pacific Northwest National Laboratory
PPlc	Plio-Pleistocene caliche layer
PPlg	Plio-Pleistocene gravelly sand or sandy gravel unit
PPlz	Plio-Pleistocene mud unit
QA	quality assurance
QC	quality control
RCRA	*Resource Conservation and Recovery Act*
REDOX	Reduction Oxidation Process (the second fuel reprocessing process used at the Hanford Site to extract plutonium)
SEM	scanning electron microscope
TEM	transmission electron microscopy
UFA	unsaturated flow apparatus (ultracentrifuge for squeezing porewater out of sediment)
UV	ultraviolet
WMA	Waste Management Area
XRD	X-ray diffraction
XRF	x-ray fluorescence (a technique to measure total element mass in solids)

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