CERTIFIED NO: 7016 0910 0001 0892 0079

Mr. Omer Shalev
U.S. Environmental Protection Agency
Region IX
75 Hawthorne Street
San Francisco, CA 94105

CERTIFIED NO: 7016 0910 0001 0892 0086

Ms. Roxanne Kwan
State of Hawaii Department of Health
Solid and Hazardous Waste Branch
2827 Waimano Home Road, Suite 100
Pearl City, HI 96782

Dear Mr. Shalev and Ms. Kwan:

SUBJECT: RESPONSE TO ENVIRONMENTAL PROTECTION AGENCY (EPA) AND STATE OF HAWAII DEPARTMENT OF HEALTH LETTER OF APRIL 22, 2019, COMMENTS ON ENVIRONMENTAL WORK AND DEVELOPMENT OF THE CONTAMINANT FATE AND TRANSPORT MODEL FOR THE RED HILL ADMINISTRATIVE ORDER ON CONSENT (AOC) STATEMENT OF WORK (SOW)

Enclosed are the response to comments from your letter dated April 22, 2019, Comments on Environmental Work and Development of the Contaminant Fate and Transport Model for the Red Hill AOC SOW. The enclosure includes two attachments. Attachment 1 to the enclosure is a summary of the multiple lines of evidence that addresses the specific comments in the April 22 letter. Attachment 2 to the enclosure is the slide deck of the "Multiple "Stacked" Impact Factors Analysis for Evaluation of Groundwater Impacts to Red Hill Monitoring Wells" that was presented to the Technical Working Group in July of 2019. Both attachments are referenced in the response enclosure, and it is hoped that their inclusion should help to increase the regulator’s understanding of the Navy’s position on the issues. The Navy appreciates the opportunity to provide clarifications and comments to help address any concerns. Please let us know if you have any further questions.
Should you have any questions, please contact Mr. Aaron Poentis of our Regional Environmental Department at (808) 471-3858 or at aaron.poentis@navy.mil.

Sincerely,

M. R. DELAO
Captain, CEC, U.S. Navy
Regional Engineer
By direction of the Commander

Enclosure: 1. Response to Comments, EPA and DOH letter of April 22, 2019, Comments on Environmental Work and Development of the Contaminant Fate and Transport Model for the Red Hill AOC SOW
Comments

The U.S. Environmental Protection Agency ("EPA") and Hawaii Department of Health ("DOH"), collectively the "Regulatory Agencies", are providing comments on several key issues for deliverables under development by the U.S. Department of the Navy ("Navy") and Defense Logistics Agency ("DLA") and its contractors to satisfy the requirements for Sections 6 and 7 of the SOW for the Red Hill Administrative Order on Consent ("AOC"). The Navy and DLA have made substantial progress in the evaluation of available data, acquisition of new data, and development of a groundwater flow model as a precursor to fate and transport analyses. Recent updates from the Navy and technical meetings on March 4 and March 13-14, 2019 regarding groundwater flow and pending fate and transport modeling efforts have been productive. A contaminant fate and transport model that carefully considers different potential release scenarios will lead to the development of appropriately protective release response plans.

To be useful, models - whether conceptual or numerical representations of groundwater flow and contaminant fate and transport - must incorporate site and area conditions to reasonably explain or simulate observed data, such as hydraulic responses to stresses or the patterns of detection of contaminants following releases. The Navy’s groundwater data is of generally good quality, but at the present time is relatively sparse. Given the highly complex subsurface conditions and a low density of monitoring wells at the Red Hill underground tank farm, the Regulatory Agencies will conservatively interpret data to ensure protection of human health and the environment.

Although we agree with much of the Navy’s interpretations, we continue to believe that the relatively sparse data available at present can also support the following interpretations:

1. Fuel-related detections reported in distal groundwater monitoring wells are potentially associated with releases from the tank farm;
2. Persistent, elevated concentrations of petroleum related contaminants in groundwater and soil vapor at the tank farm are consistent with the presence of a residual fuel source in the formation; and
3. Some fraction of the fuel released in 2014 may have reached groundwater, with the remainder retained as residual in the vadose zone and subject to natural attenuation processes.

The Regulatory Agencies received the Navy’s request dated March 6, 2019 for a response regarding the lines of evidence presented by the Navy at the February 21, 2019 technical working group meeting. Taken individually, the Navy has produced work that can support the lines of evidence presented, but other interpretations are also able to explain certain aspects of the observed data. The Regulatory Agencies are concerned that some of the Navy’s interpretations on the topics detailed below may lead to conclusions that are not at the present time adequately supported or sufficiently conservative.
A sophisticated monitoring network has been installed (and is being enhanced) which provides a large number of data for the site. The existing monitoring well network (and those wells currently being or soon to be installed) is adequate to bound the understanding of groundwater flow and contaminant migration relative to conditions at Red Hill. While significant heterogeneities exist in the subsurface, which may lead to localized potential contamination in areas where monitoring wells do not exist, multiple lines of evidence (LOEs) have been developed to support the Navy's conclusions. While any one LOE may be circumstantial, it is highly unlikely that all of these LOEs taken together are circumstantial when they all point to the same conclusions. The following conclusions are based on the analysis of available data and are described in Table 6-1 of Appendix B.8 in the June 2019 revision to the Conceptual Site Model (CSM) report (see Attachment 1):

1. Seven primary independent LOEs, along with 17 secondary LOEs (Section 1 Primary LOEs 1a – 1i of attached table) demonstrate that, based on existing data, there is no evidence of LNAPL near outlying monitoring wells. This is further supported by the multifactor/cluster analysis that was completed by the Navy and presented to the Agencies on July 26, 2019. The Navy completed these analyses as suggested by the Agencies at the March 14, 2019 face-to-face meeting (and described in the meeting summary). The July 26, 2019 multifactor/cluster analysis presented to the Agencies supplemented what is presented in Revision 01 of the CSM report.

2. Two additional independent primary LOEs, along with 1 secondary LOE (Section 1A Primary LOEs 1h and 1i of attached table), demonstrate that there is no evidence of impacts to the outlying wells from the 2014 release.

3. Five independent primary LOEs, along with 7 secondary LOEs (Section 3 Primary LOEs 3a-3e of the attached table), demonstrate that there is no evidence of groundwater impacts due to the 2014 fuel release.

4. Seven independent primary LOEs, along with 20 secondary LOEs (Section 2 2a-2g of the attached table), demonstrate that there is no evidence of LNAPL near Red Hill Shaft.

5. When the independent LOEs are considered collectively, the evidence is overwhelming that there are no distal impacts that indicate the presence of LNAPL.

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Comments

Responses to the three Regulatory interpretations are provided below:

1) As a specific response to the Agencies’ statement that “Fuel-related detections reported in distal groundwater monitoring wells are potentially associated with releases from the tank farm”: The Navy strongly disagrees based on the work described above (Section 1 of the attached LOE Table). Additional detail which indicates that TPH detections during the first 1-2 years are likely associated with drilling and well installation artifacts, rather than the facility, was provided during the July 26, 2019 AOC Technical Working Group Meeting (presentation attached). This was also presented to the Agencies on February 21, 2019.

2) As a specific response to the Agencies’ statement that “Persistent, elevated concentrations of petroleum related contaminants in groundwater and soil vapor at the tank farm are consistent with the presence of a residual fuel source in the formation,” the Navy agrees that there are likely residual sources in the vadose zone beneath some tanks. The Navy does not view the extremely low-level concentrations reported in groundwater at a few wells as “elevated concentrations.” The Navy has been very clear that there is likely residual hydrocarbon in the vadose zone beneath various tanks and has also been clear that there is a LNAPL source upgradient of RHMW02 (unrelated to the 2014 release) resulting in limited dissolved-phase impacts.

3) As a specific response to the Agencies’ statement that “Some fraction of the fuel released in 2014 may have reached groundwater, with the remainder retained as residual in the vadose zone and subject to natural attenuation processes,” the Navy believes that based on all the available data, there is no indication that fuel from the 2014 release reached groundwater (see LOE table, Section 3, in Attachment 1). However, as stated above, the Navy cannot rule out that there may have been very localized impacts that were not detected (as free product or evidenced by high dissolved concentrations) in the existing monitoring well network.

The Agencies conclude that there may be other interpretations of the data and, as previously discussed, the Navy welcomes a detailed technical discussion of those alternate conclusions by the Agencies that take into account (refute) the various LOEs that the Navy has presented. The Agencies’ suggestion that there may be alternate conclusions has not been supported by adequate technical justifications, information, or analyses provided by the Agencies to date. As discussed during several past meetings (e.g., July 26, 2019), if the Agencies can technically dispute any of the Navy’s LOEs or the results of the multifactor/cluster analysis, the Navy is willing to discuss those findings and potentially alter the conclusions that have been developed. To date, the Agencies’ position has been to say that any reported detection is an indication of contamination even though the Navy has found this conclusion to be unreliable and unrealistic based on rigorous analysis.
Comments

Topics of Concern:

1. **Total Petroleum Hydrocarbons ("TPH") and TPH Related Analyte Detections:** At Red Hill, TPH is often the most frequently detected group of compounds and provides interpretive utility. The analytic data set was prepared by certified labs using appropriate and accepted procedures, and, with some exceptions, the reported values are considered valid. TPH is an indication of petroleum impacts in groundwater, and as discussed in DOH guidance documents (HDOH, 2012, HDOH 2012c, HDOH 2016), the risk posed by dissolved-phase petroleum in groundwater can be informed by the range of TPH in addition to individual analytes such as benzene and naphthalene. While the Regulatory Agencies acknowledge that variance in the detection of TPH arises from many factors, including analytical method and differences between laboratories, the variance alone does not negate the value of the data and the pattern of repeated detections. Lab precision in TPH quantification does not imply that TPH detections are false positives; rather, there are other potential explanations for the observed distributions and behavior of TPH.

Response:

The Navy respectfully refers the Agencies to the DOH (2018) guidance *Collection and Use of Total Petroleum Hydrocarbon Data for the Risk-Based Evaluation of Petroleum Releases: Example Case Studies,* which describes common risk assessment problems and data lapses, one of which is “misinterpretation of baseline noise in gas chromatograph signals below 100 µg/L as TPH in groundwater or surface water samples.” As further discussed in the recent multifactor/cluster analysis meeting held July 26, 2019 with the AOC Parties (see Attachment 1 – Summary of Lines of Evidence and Attachment 2 – July 26, 2019 AOC Parties Technical Working Group meeting slide deck Multiple “Stacked” Impact Factors Analysis for Evaluation of Groundwater Impacts to Red Hill Monitoring Wells), it is evident that TPH detections in many wells for within 1 to 2 years after well installation were likely introduced during drilling despite the Navy drilling contractor’s use of food-grade lubricants and a drilling “make-up” water (using granular activated carbon) treatment system. In addition, later-year extremely low (< 18J µg/L) TPH signals in RHMW04 were determined not to be fuel-related based on chromatographic analysis. Based on this refined analysis, there is no meaningful evidence of fuel-related TPH in outlying wells.

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2. **Non-water Table Wells:** The Regulatory Agencies concur that there are several wells that, due to their construction and screened interval, are likely not representative of water table conditions. Those wells are, however, reflective of the overall local aquifer system and some exhibit analyte and biodegradation data that are of interpretive value. The Regulatory Agencies believe that all data locations should be considered.

**Response:**

The Navy agrees that data from all wells need to be considered, which is what the Navy continues to do. It is clear that certain wells are not part of the shallow unconfined basal aquifer system (such as Halawa Deep Monitor Well; RHMW11 Zones 6, 7, and 8; and RHMW07). This is further illustrated through the transfer function-noise (TFN) analysis evaluation conducted by the Navy and presented during the AOC Technical Working Group Webinar held in January 2019 as well as other meetings. As an example, this analysis shows no to very little apparent response to Red Hill Shaft or Halawa Shaft pumping conditions at RHMW07, indicating that this well has minimal connectivity with the basal aquifer and therefore is not representative of water table conditions. Groundwater chemistry data from these wells represent the formations from which they are sampled, even if this well is not part of the shallow unconfined basal aquifer system. New data show that there are relatively high heads in weathered basalt and saprolite zones in new wells and test boring (i.e., RHMW11 Zones 6, 7 and 8; RHMW12 [open hole]; RHMW13; RHMW14 Zones 4, 5, 6 and 7; and RHTB01 Zones 2, 3, and 4) recently installed in South Halawa Valley, and that the geology and hydrogeology of the materials overlying the regional basal aquifer in that area are quite complex.

3. **2014 Release Impact to Groundwater:** Although the data do not show widespread increases in contaminant levels in groundwater after the 2014 release, the Regulatory Agencies believe there is evidence to suggest that a portion of the 2014 JPB release may have reached groundwater. First, vapor data indicate possible transport to the northwest outside of the source zone monitoring array. Second, the detection behavior of TPH-diesel and naphthalene at RHMW02 suggests that either dissolved-phase entrainment of petroleum or fuel-related migration to the water table may have occurred near this well. Available data show that the 2014 release did not cause relatable increases in petroleum detections at Red Hill Shaft.
Response:

The Navy respectfully disagrees with the Agencies’ comment. The Navy does not see an indication of preferential vapor transport significantly to the northwest from the 2014 release. Rather, it appears that vapors spread out beneath tank 5 and at significantly lower concentrations under several nearby tanks after the release, likely due to advection related to the negative pressure in the access tunnels as well as other processes such as diffusion. This is demonstrated in the figure below showing distribution of soil vapor before and after the 2014 release. However, due to an absence of soil vapor monitoring points to the west, it is not clear how far vapors spread in that direction. As to the presence of dissolved-phase constituents near well RHMW02, the Navy does not discern a significant change in concentrations after the release as compared to concentrations prior to the release, thus (in part) indicating that the 2014 release did not impact groundwater in the vicinity of RHMW02. This is further reinforced by the multiple Section 3 LOEs (previously described herein) outlined in Revision 01 of the CSM report. With that said, there is a small possibility that localized groundwater impacts due to the 2014 release may have occurred outside of the areas that are currently monitored. However, even if this was the case, there is still no indication 1) that there were impacts from the 2014 release as detected at any existing monitoring well, or 2) that there was an impact to Red Hill Shaft.

![Figure 5: Average PID Values for 2013 (Prior to Jan. 2014 Tank 5 Release) and for 2014 (all values after the Tank 5 release)](image-url)

Notes: Each square represents the area around a tank (see top panel). The order of magnitude difference indicates the LNAPL migration zone was focused horizontally in the vicinity of Tank 5 but did not extend to the surrounding tanks. Each square is approximately 200 ft × 200 ft in area.
Comments

4. **Light Non-Aqueous Phase Liquid ("LNAPL") Presence:** Persistent detections of TPH and individual fuel constituents in groundwater are typically interpreted to result from the presence of an LNAPL source. Due to the frequency of elevated detections in RHMW01, RHMW02, and RHMW03, along with the occurrence of occasional detections in distal wells, the Regulatory Agencies conclude it is reasonable to assume that residual LNAPL is present in the subsurface from past releases. Furthermore, despite consensus on the anticipated dilution rates caused at Red Hill Shaft, trace levels of petroleum compounds have been detected in approximately 12% of the samples collected there. The Regulatory Agencies interpret this information as implying that Red Hill Shaft is a likely receptor, and that some LNAPL mass from the facility may be the cause of those detections. For the Red Hill groundwater system, dissolved-phase fuel impacts are not expected to travel further than approximately 200-ft from the LNAPL source mass, suggesting a relative distance of LNAPL distribution away from the tank farm. This 200-foot estimate is based on Red Hill characteristics reported by the Navy and is consistent with plume dimension studies. However, dissolved phase impacts have been detected further than 200 feet from the tank farm, thus atypical transport conditions, such as fast-track transport features (open voids, lava tubes), may also contribute to the detections observed at Red Hill Shaft.

The Navy's contaminant fate and transport model should recognize the interpretative value and magnitude of the distal detection data along with other indicators of residual contamination (for example, dissolved oxygen depletion), and the presence of an LNAPL mass distribution in the formation that would result in, or contribute to, observed groundwater impact patterns. The Navy should also include risk estimates for scenarios where vadose transport to groundwater is rapid, and those scenarios should consider petroleum detections reported at distal monitoring locations. The Navy's contaminant fate and transport model should also reflect the effects of cumulative assimilative capacity over time.

Response:

As previously discussed, the interpretation of groundwater chemistry related to the presence of LNAPL/dissolved-phase chemicals indicates that there is no evidence of LNAPL or dissolved-phase impacts to outlying wells or Red Hill Shaft (due to either groundwater or vapor-phase transport). This is based on all the LOEs as previously discussed (see Attachment 1) as well as the recent multifactor/cluster analysis (see Attachment 2) that counters the Agencies' interpretation of 12% of the samples from Red Hill Shaft having been impacted from prior fuel releases. The LLNL multi-site study found that the average benzene plume length was less than 200 feet and that 90% were less than 400 feet. The lack of discernable groundwater impacts described in the LOE table make the LLNL plume-length study irrelevant for this discussion. The Navy does concur that there have been groundwater impacts, primarily to RHMW02 and to a much lesser degree to RHMW01 (likely due to a pre-2014 LNAPL source upgradient of RHMW02).

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6 NAVFAC. March 2019 Fourth Quarter 2018 Quarterly Groundwater Monitoring Report, Red Hill Bulk Fuel Storage Facility, Joint Base Pearl Harbor- Hickam, O‘ahu, Hawai‘i, see Table 1-4


Comments

In addition, there is also evidence of groundwater impacts to RHMW03, most likely due to an older, highly weathered source. Finally, the apparent detections observed at Red Hill Shaft are likely due to sampling/laboratory issues as discussed in the CSM report, and are not indicative of a long plume. As described in the attached LOE table, there are 7 primary LOEs (Section 2 Primary LOEs 2a – 2g of attached table) indicating that contaminants from the Red Hill Tank Farm have not impacted Red Hill Shaft.

5. Electron Acceptor Depletion: To assess whether electron acceptors are depleted requires an understanding of typical ambient concentrations for these species in Hawaiian groundwater. The Navy has concluded that electron acceptors at some monitoring wells are not depleted by determining that concentrations are within the range indicated by a University of Hawaii and U.S. Geological Survey data set for Oahu that includes wells ranging from pristine to significantly contaminated. Based on a comparison with pristine background concentrations of various electron acceptors, the majority of the Red Hill monitoring network, including RHMW04, shows some level of biodegradation activity which may be attributable, in part, to the tank farm.

Response:

The Navy has conducted a thorough evaluation of electron acceptors. In particular (as described in the multifactor/cluster analysis and also as part of the presentation to the AOC Technical Working Group Meeting on July 26, 2019), the Navy completed a rigorous evaluation of various studies related to dissolved oxygen (DO). The USGS study *Ground-Water Quality and Its Relationship to Land Use on Oahu, 2001-01* (cited above as footnote 9) describes DO in “far-field monitoring wells” not impacted by groundwater contamination as having an average background DO concentration of 6.7 mg/L and an observed minimum background value of 4.7 mg/L. The results of background DO concentrations described in the USGS report are significantly different from the background concentrations (8 mg/L) described by the DOH in previous meetings, used as a threshold for identifying oxygen depletion, and subsequently as evidence of a petroleum source. In addition, this study and other studies indicate that basalts and saprolites containing reduced mineral species can cause localized depletion of oxygen in groundwater. Based on the USGS study, the range of DO described above was used (in part) to recalculate indicator values that were originally developed by the EPA’s contractor. A revised indicator analysis for DO, TPH, and other key chemicals was included in the multifactor analysis (presented at the July 26, 2019 meeting) and shows significantly elevated DO indicator values (indicative of impacts) for RHMW03, RHMW02, and RHMW01, and significantly lower DO indicator values for most of the remaining (basal aquifer) monitoring wells. In addition, the cluster analysis indicates that RHMW02 and RHMW01 are similar to each other and dissimilar to all other wells, and that RHMW03 is dissimilar to all wells. RHMW04 has zero to extremely small indicator values for a variety of constituents based on this analysis, demonstrating that this well has not been impacted by Red Hill operations.

The Navy presented these recent analyses to the Agencies on July 26, 2019. The Navy further welcomes any specific technical comments that the Agencies may have related to these new analyses.

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6. Potential Contaminant Transport Pathways Remain Uncharacterized: Current Navy presentations discount the possibility of groundwater flow from the Red Hill Ridge to the northwest. The stated rationale is that groundwater flows from areas of highest recharge to coastal areas or submarine discharge. However, it would be more technically correct to state that groundwater flows from areas of high hydraulic potential to areas of low hydraulic potential. Mink (1980)\(^1\) recognized that the Red Hill side of Halawa Valley has a higher hydraulic potential than the Halawa side of Halawa Valley. Contours of measured groundwater elevations prepared by the Navy\(^1\) and shown on the attached figures support Mink's hypothesis because they show very little gradient going down the axis of the Red Hill Ridge and a well-defined gradient to the northwest of the underground tank farms. Under certain conditions, particularly when Red Hill Shaft is not pumping, flow from under the upper tank farm to the northwest may occur given what is currently known about saprolite extent and groundwater use. Given the importance of this issue to the DOH Source Water Protection Program, DOH intends to provide additional technical information on this subject in a separate letter.

Response:
The Navy does not discount the possibility of local flow conditions toward the northwest or toward the southeast as noted in the data and depicted in Attachment 2 of the Agencies' comments. Hydrogeologic principles govern that groundwater flows from areas of highest recharge toward areas of lower recharge and discharge. However, it can take local deviations along the way governed by local heterogeneity. Hydraulic potentials and gradients are a result of this flow through the complicated geologic medium. A hydrogeologist can establish groundwater flows by evaluating the potential gradients along with the geologic anisotropy. Attachment 2 of the Agencies' comments cite a Navy document, suggesting that these figures were developed by the Navy. The Navy did not in fact create these groundwater elevation contour maps.

The contour maps of measured groundwater elevations locally at Red Hill developed by the Agencies clearly indicate that water levels are slightly higher (on the order of 0.1 foot) beneath the tank farm with lower water levels on both sides, indicating a local gradient to the northwest as well as to the southeast. Clinker zones at the water table that are aligned with the direction of lava flow can cause such localized deviations. This was demonstrated by the conceptual clinker model (interim Model #2), which indicated localized northwest direction flow gradients toward the high-conductivity clinker zone that drains the basalt. Conceptual clinker models will also be included in the ongoing modeling effort to demonstrate this behavior.


\(^{11}\) NAVFAC. 2018. Conceptual Site Model, Investigation and Remediation of Releases and Groundwater Protection and Evaluation, Red Hill Bulk Fuel Storage Facility, Joint Base Pearl Harbor-Hickam, O'ahu, Hawai'i. Figures 6-8 and 6-12
Comments

In addition, various heterogeneous model calibrations will be attempted to conservatively evaluate observed water level conditions at the site. This was described as part of the multi-model approach that the Navy is using. Furthermore, two different saprolite interpretations are being implemented in the models to evaluate the possibility of more regional northwest flow under conditions of minimal barrier impacts. New Westbay multi-level monitoring wells and test boring constructed in South Halawa Valley clearly indicate elevated heads in the saprolite as well as the basalts. These heads also appear to be consistent with heads reported as part of the geotechnical borings installed along S. Halawa Valley as part of the original H-3 alignment study. These elevated heads along the South Halawa valley axis will act as a hydraulic barrier to flow in shallow groundwater, preventing cross valley flow as hypothesized by the Agencies. Finally, the tuff cones (diatremes) in the Salt Lake Tuff Ring Complex are also being simulated with sensitivity to their hydrogeologic properties to observe whether they could cause a barrier to flow and a resulting redirection of cross-valley groundwater flow toward the northwest.

The inherent error in measuring absolute water levels could also explain the apparent local gradients, which should not be over-interpreted in a complex groundwater system especially in an area with such gentle gradients. The Navy has therefore conducted a TFN analysis to try to isolate stresses that impact the water level signals (e.g., barometric pressure, earth/ocean tide influences, rainfall recharge, pumping). The TFN analysis indicates that the strongest impact on water level in the Red Hill area is due to pumping at Red Hill Shaft. The TFN analysis was further used to develop unit pumping responses at the monitoring wells to improve calibration of the models. With all of these additional efforts expended toward evaluating and understanding the local gradients beneath Red Hill, as well as evaluating other impacts on regional flow, it is incorrect to suggest that the Navy is discounting it.

The Regulatory Agencies are primarily concerned about the potential risks associated with future fuel releases. The Navy’s conclusions regarding the topics listed above are not uniquely or exclusively supported by the evidence presented and may ultimately lead to release response actions that underestimate the risk posed by future releases. Given the existing uncertainties and complexities of the site, the Regulatory Agencies specifically request that the Navy bound transport and risk estimates in the models to include scenarios that appropriately recognize the alternate explanations covered in this letter.

We acknowledge the significant effort undertaken by the Navy and look forward to the progress anticipated over the next several months.

Response:

The Navy feels strongly that the existing monitoring well network (and those wells currently being or soon to be installed) is adequate to bound the understanding of groundwater flow and contaminant migration relative to conditions at Red Hill. The Agencies have not provided a technically based rebuttal to any LOE that has been presented relative to the extent of groundwater contamination. When this many LOEs all point to the same conclusion, the results are unique. The Navy is not discounting the small probability that contamination from past releases may have impacted small localized areas that are not currently monitored. However, even if this were the case, there is no indication that there have been impacts to any other monitoring well in the network or to Red Hill Shaft due to such potential sources.

The model scenarios that are currently being integrated into the multi-model approach include:

Conceptual Models for Multi-Model Evaluation

1. Homogeneous basalt
2. Alternate saprolite extent and depth below water table
3. Heterogeneous basalt
Comments

4. Heterogeneous basalt with alternate saprolite extent and depth below water table
5. Conceptual clinker zones
6. Caprock heterogeneity (K-values)
   a. Lower Kh and Kv for tuff
   b. Lower Kh and Kv for alluvium
7. Recharge and lateral inflow (USGS mapping of drought conditions)
8. Coastal marine discharge variability (more to Pearl Harbor and less offshore)
9. Lateral inflow from southeast boundary with discharge to Pearl Harbor and small discharge to offshore boundary

This multi-model approach allows the Navy to conservatively evaluate potential flow conditions, in an effort to address various risk considerations (e.g., potential impacts to Red Hill or Halawa Shaft).
Attachment 1:
Summary of Lines of Evidence
1. NO EVIDENCE OF LNAPL NEAR OUTLYING WELLS

1a. Naphthalene (by Itself) Is Not a Good Indicator for the Presence of LNAPL

   i. The very low detection limits for naphthalenes (e.g., 0.005 µg/L by CAS/ALS) are susceptible to interferences/artifacts and are inherently more variable.

   ii. There are sporadic detections of naphthalene at Outlying Wells. Incidence of detections correlates best with laboratories used rather than where detections occurred and at what concentrations.

      • Naphthalene detections during Fourth Quarter 2012 to First Quarter 2015 (Calscience/Eurofins) are suspect.
          Frequent detections of naphthalene from Fourth Quarter 2012 to Third Quarter 2014, then all detections stopped from Cal/Euro.

      • No coinciding detections of methylnaphthalenes

      The laboratory that followed after Calscience (i.e., CAS/ALS) did not detect naphthalene at a similar frequencies or concentrations, even though the reporting limit was an order of magnitude lower.

      • Approximately 60% of naphthalene detections in Outlying Wells occurred during the suspect period of Cal/Euro analysis. The remaining detections are highly sporadic.

      All naphthalenes were analyzed by EPA Method 8270 SIM at a time when only two ions were used to identify compounds. Three ions are required to have achieve robust identification.

1b. Electron acceptors are not depleted at Outlying Wells

   i. Oxidic conditions are present at Outlying Wells:

      • DO concentrations ranged from 5.09 to 9.31 mg/L (Fourth Quarter 2018) at Outlying Wells that are representative of water table chemistry.

      • RHMW07, RHMW11, and HDMW2253-03 are not representative of water table chemistry.

      The range of DO in Red Hill Outlying Wells is generally consistent with observed DO in O‘ahu wells.

      • Nitrate concentrations range from 2 to 5.5 mg/L (Fourth Quarter 2018) at Outlying Wells that are representative of water table chemistry, demonstrating that nitrate is not depleted.

      • Sulfate concentrations range from 6.9 to 51.3 mg/L (Fourth Quarter 2018) at Outlying Wells that are representative of water table chemistry, demonstrating that sulfate is not depleted.

      • Reducing conditions (ORP < 0 mV) are not present in Outlying Wells (Fourth Quarter 2018).

      • Apart from one sampling event at RHMW08, the ORP has been positive since Fourth Quarter 2016 at Outlying Wells representative of the water table.

1c. Metabolic by-products are not present at Outlying Wells

   i. Methane has not been detected in Outlying Wells representative of water table chemistry since Fourth Quarter 2016 (no methane data prior to this quarter).

   ii. Ferrous iron was not detected in RHMW04, RHMW05, RHMW08, RHMW09, RHMW10, and was detected below the limit of quantitation at RHMW06 (0.16 µg/mL) (Fourth Quarter 2018).

      • Since Fourth Quarter 2016, ferrous iron has either been nondetect or below the limit of quantitation in Outlying Wells representative of water table chemistry.

1d. There are not consistent coinciding detections of COPCs and non-COPCs (e.g., BTEX, methylnaphthalene, nonpyrogenic PAHs) with naphthalene

   i. BTEX were not detected in RHMW06, RHMW07, RHMW08, RHMW09, RHMW10, or all levels of RHMW11.

   ii. BTEX were detected infrequently (1-5 times) at the remaining Outlying Wells over the monitoring period, which is more indicative of field/laboratory artifacts.

      • Concentrations were often below the limit of quantitation and ranged from 0.07 J to 3.8 µg/L.

   iii. Non-COPC detections in Outlying Wells consisted mainly of compounds that are not associated with fuel: phthalates, halogenated VOCs, acetone, oxygenated compounds, and pyrogenic PAHs.

   iv. Non-COPCs that can be present in fuels, such as non-pyrogenic PAHs, were detected infrequently in Outlying Wells; detections occurred in two samples each in RHMW05 and RHMW07, and one sample in RHMW04, indicating field/laboratory artifact issues.

      • Non-pyrogenic PAHs were not detected in RHMW06, RHMW08, or RHMW09.
1. NO EVIDENCE OF LNAPL NEAR OUTLYING WELLS

<table>
<thead>
<tr>
<th>Primary LOE</th>
<th>Secondary LOEs</th>
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| **1e.** TPH should be assessed in the context of other COPCs and non-COPCs, as trend analyses are difficult because of inconsistent methodology and laboratories | i. TPH is a parameter defined by the method used.  
ii. TPH results can include hydrocarbons, metabolites/polar compounds and anything present that can be detected by the method.  
iii. TPH can be used as an indicator parameter for potential impact to groundwater, but the absolute values should be interpreted with caution. Changes can be method- and/or laboratory-related.  
   - TPH detection is not a direct indication of hydrocarbons in groundwater. |
| **1f.** TICs are not a good indicator of the presence of LNAPL in Outlying Wells | i. TIC identification and concentrations cannot be confirmed without comparison to a known standard.  
ii. Majority of TIC detections are not associated with fuels: phthalates, halogenated compounds, oxygen-containing compounds.  
   - These compounds are likely associated with field/laboratory contamination, well construction/maintenance, and/or historical or current activities at the site unrelated to fuel releases.  
iii. The only TIC hydrocarbon detections in Outlying Wells are trimethylbenzenes.  
   - Trimethylbenzene is expected to be found with other hydrocarbons if coming from a fuel/LNAPL; trimethylbenzene was the only TIC detected in Outlying Well samples.  
   - Trimethylbenzene was analyzed with Method 8260 in all Outlying Wells in 2017 and was not detected. |
| **1g.** Lead scavengers (1,2-dibromoethane and 1,2-dichloroethane) were not detected in Outlying Wells except for 1,2-dichloroethane in RHMW08 in 2017 | i. 1,2-dichloroethane was used in motor gasoline (not aviation gasoline). Motor gasoline was stored in Tank 17 prior to 1988. It is likely the detections of 1,2-dichloroethane in RHMW08 are from either fumigants or PVC impurity rather than motor gasoline.  
ii. To adequately evaluate lead in the environment, careful consideration should be given to the local range of background concentrations as well as filtering of water samples, since lead is a naturally occurring element. |

1A. No evidence of impact to Outlying Wells from 2014 fuel release (Red Hill discussed separately in LOE 2)

<table>
<thead>
<tr>
<th>Primary LOE</th>
<th>Secondary LOEs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1h.</strong> Continued sporadic detections of BTEX with no apparent increase in detection frequency after the 2014 fuel release</td>
<td></td>
</tr>
<tr>
<td><strong>1i.</strong> Continued sporadic detections of naphthalene with no apparent increase in detection frequency after 2014 fuel release</td>
<td>i. Apparent decrease in naphthalene detection frequency in Outlying Wells after the Fourth Quarter 2012 to Third Quarter 2014 period when Calscience/Eurofins stopped detecting naphthalene.</td>
</tr>
</tbody>
</table>
2. NO EVIDENCE OF LNAPL NEAR RED HILL SHAFT

**Primary LOE**

2a. Naphthalene (by itself) is not a good indicator of the presence of LNAPL near Red Hill Shaft

i. There are sporadic detections of naphthalene at Red Hill Shaft.
   - Naphthalene detections during Fourth Quarter 2012 to First Quarter 2015 (Calscience/Eurofins) are suspect.
     - Frequent detections of naphthalene from Fourth Quarter 2012 to Third Quarter 2014, then all detections dropped from Cal/Euro, indicating field/laboratory artifacts.
     - No coinciding detections of methylnaphthalenes.
     - The laboratory that followed Calscience (i.e., CAS/ALS) did not detect naphthalene at similar frequencies or concentrations even though the reporting limit was an order of magnitude lower.
     - The concentrations of naphthalene detected during Fourth Quarter 2012 to Third Quarter 2014 were similar to the concentrations detected in other Outlying Wells (e.g., HDMW2253-03, RHMW05). Similar concentrations would not be expected at these three wells with very different constructions:
       - Red Hill Shaft - Induced flow
       - HDMW2253-03 - Deep borehole with casing ~40 ft below the water table
       - RHMW05 - Screened across the water table
     - All naphthalenes were analyzed by EPA Method 8270 SIM at a time when only two ions were used to identify compounds. Three ions are required to have achieve robust identification (DoD and DOE 2017).
   ii. The very low detection limits for naphthalenes (e.g., 0.005 µg/L by CAS/ALS) are susceptible to interferences/artifacts and are inherently more variable.
   iii. Naphthalene detections often do not coincide with 1- and 2-methylnaphthalene or TPH detections, as would be expected if the detections were due to a nearby LNAPL source.

2b. Electron acceptors are not depleted at Red Hill Shaft

i. Oxidic conditions are present at Red Hill Shaft (DO = 8.7 mg/L during Fourth Quarter 2018 sampling event).
ii. Nitrate was 2.3 mg/L during Fourth Quarter 2018 sampling event and is not depleted.
iii. Sulfate was 15.6 mg/L during Fourth Quarter sampling event and is not depleted.
iv. Reducing conditions (ORP < 0 mV) were not present.

2c. Metabolic byproducts (methane and ferrous iron) were not detected in Red Hill Shaft (Fourth Quarter 2018)

i. Methane has been non-detect in Red Hill Shaft since Fourth Quarter 2016 (no methane data prior to this quarter).
ii. Ferrous iron has been most commonly non-detect in Red Hill Shaft since Fourth Quarter 2016, detected concentrations have ranged from 0.17 J to 0.34 mg/L.

2d. There are not consistent coinciding detections of COPCs and non-COPCs (e.g., BTEX, methylnaphthalene, nonpyrogenic PAHs) with naphthalene

i. BTEX have been detected in two samples (Fourth Quarter 2012 and Fourth Quarter 2018) and were not confirmed during the subsequent sampling events.
ii. Non-COPC detections in Red Hill Shaft consisted mainly of compounds that are not associated with fuel: phthalates, halogenated VOCs, acetone, oxygenated compounds, and pyrogenic PAHs.
iii. Non-COPCs related to fuel, non-pyrogenic PAHs, were detected in only one sample from Red Hill Shaft in Fourth Quarter 2005.

2e. TPH should be assessed in the context of other COPCs and non-COPCs as trend analysis is difficult because of inconsistent methodology and laboratories

i. TPH detections often did not coincide with detections of other COPCs.
ii. TPH is a parameter defined by the method used.
iii. TPH results can include hydrocarbons, metabolites/polar compounds, and anything present that can be detected by the method.
iv. TPH can be used as an indicator parameter or potential impact to groundwater, but the absolute values should be interpreted with caution.
   - Changes can be method- and/or laboratory-related.
   - TPH detection is not a direct indication of hydrocarbons in groundwater.
## 2. NO EVIDENCE OF LNAPL NEAR RED HILL SHAFT

<table>
<thead>
<tr>
<th>Primary LOE</th>
<th>Secondary LOEs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2f. TICs are not a good indicator of the presence of LNAPL in Outlying Wells</td>
<td>i. TIC identification and concentrations cannot be confirmed without comparison to a known standard.</td>
</tr>
<tr>
<td></td>
<td>ii. The majority of TIC detections are not associated with fuel: phthalates, halogenated compounds, oxygen-containing compounds.</td>
</tr>
<tr>
<td></td>
<td>• These compounds may be associated with field/laboratory contamination, well construction/maintenance, and/or historical or current activities at the site unrelated to fuel releases.</td>
</tr>
<tr>
<td></td>
<td>iii. TIC hydrocarbon detections in Red Hill Shaft are of trimethylbenzene and two other hydrocarbons (1,2,3,4,5-pentamethyl-cyclopentane, and 3,5,5-trimethyl-2-hexene).</td>
</tr>
<tr>
<td></td>
<td>• Trimethylbenzene would be expected to be found with other hydrocarbons if coming from a fuel/LNAPL; trimethylbenzene was the only TIC detected in Outlying Well samples.</td>
</tr>
<tr>
<td></td>
<td>• Trimethylbenzene was analyzed for with Method 8260 in Red Hill Shaft in 2017 and was not detected.</td>
</tr>
<tr>
<td></td>
<td>• The other TIC hydrocarbons were not detected in RHMW02 or RHMW01; detections are unlikely to be related to RHMW02.</td>
</tr>
<tr>
<td>2g. Lead scavengers (1,2-dibromoethane and 1,2-dichloroethane) have not been detected in Red Hill Shaft</td>
<td></td>
</tr>
</tbody>
</table>

## 3. NO EVIDENCE OF GROUNDWATER IMPACT FROM 2014 FUEL RELEASE

<table>
<thead>
<tr>
<th>Primary LOE</th>
<th>Secondary LOEs</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a. BTEX detection occurrences did not change in RHMW02 after the 2014 fuel release</td>
<td>i. A fresh source of LNAPL in RHMW02 vicinity would change the ratio as fresh fuel has a different signature than degraded fuel.</td>
</tr>
<tr>
<td></td>
<td>• In general, the parent PAH (COPC naphthalene) is less abundant than the sum of the corresponding alkylated PAHs (in this case, COPCs 1-methylnaphthalene and 2-methylnaphthalene, which are the two possible isomers of naphthalene with a methyl group substitution) from any petroleum sources.</td>
</tr>
<tr>
<td>3b. The ratio of methylnaphthalenes to naphthalene in RHMW02 did not change after the 2014 fuel release</td>
<td>i. TPH should be assessed in the context of other COPCs and non-COPCs, as trend analysis is difficult because of inconsistent methodology and laboratories.</td>
</tr>
<tr>
<td></td>
<td>• EPA Method 8015 is a guidance method and is not prescriptive, which results in significant variation in analysis between laboratories.</td>
</tr>
<tr>
<td></td>
<td>• Changes in analytical laboratory often coincide with sharp changes in detected TPH concentrations in RHMW02.</td>
</tr>
<tr>
<td>3c. TPH alone not good indicator of changes in water chemistry at RHMW02 after 2014 release</td>
<td>i. Results can include hydrocarbons, metabolites/polar compounds, and anything present detectable by the method.</td>
</tr>
<tr>
<td></td>
<td>• Concentrations/presence of TPH metabolites/polar compounds can be determined by using SGC.</td>
</tr>
<tr>
<td></td>
<td>• Polar compounds are more soluble than parent nonpolar compounds/hydrocarbons; therefore, the presence of polar compounds/metabolites can result in increased solubility of what is measured as TPH.</td>
</tr>
<tr>
<td></td>
<td>• Polar compounds/metabolites in RHMW02 are more soluble than parent hydrocarbons; what is measured as TPH is not indicative of the presence of LNAPL from a fresh release, but is indicative of an older nearby source.</td>
</tr>
<tr>
<td>3d. Measured TPH concentrations in RHMW02 are not a good indicator of the presence of LNAPL</td>
<td>i. The increased number of sampling events immediately following the 2014 fuel release results in an apparent increase in COPC detections. This is a result of more frequent sampling, not of an increase in TPH contamination in the groundwater.</td>
</tr>
<tr>
<td>3e. COPC detection signature did not change in RHMW02 after the 2014 fuel release</td>
<td>i. The increased number of sampling events immediately following the 2014 fuel release results in an apparent increase in COPC detections. This is a result of more frequent sampling, not of an increase in TPH contamination in the groundwater.</td>
</tr>
</tbody>
</table>
Multiple "Stacked" Impact Factors Analysis for Evaluation of Groundwater Impacts to Red Hill Monitoring Wells

Red Hill Bulk Fuel Storage Facility
July 2019
Road Map / Table of Contents

- **Background: Dissolved Oxygen (DO)**
  - National Background DO: Data from 26 Sites
  - DO in Other Basalt Aquifers
  - DO in Shallow Regional Groundwater Monitoring Wells on Oahu
  - Hawaii Example of Release Evaluation Using Dissolved O₂

- **Background: Total Petroleum Hydrocarbons**
  - Apparent First Years Drilling Effect
  - Air Rotary Drilling
  - Measuring Low TPH Concentrations

- **Multi-Factor Analysis**
  - Potential Impact Indicators
  - Network Clustering Analysis
  - Multi-Factor Evaluation
Road Map

• **Background: Dissolved Oxygen (DO)**
  - National Background DO: Data from 26 Sites
  - DO in Other Basalt Aquifers
  - DO in Shallow Regional Groundwater Monitoring Wells on Oahu
  - Hawaii Example of Release Evaluation Using Dissolved O$_2$

• **Background: Total Petroleum Hydrocarbons**

• **Multi-Factor Analysis**
Dissolved Oxygen Saturation: 26 Nationwide MNA Sites

Table 2-1: Background Dissolved Oxygen Data from 26 Monitored Natural Attenuation Studies (Wiedemeier et al., 1999)

<table>
<thead>
<tr>
<th>Month</th>
<th>Background Dissolved Oxygen Concentration (mg/L)</th>
<th>Greenwater Temperature (°C)</th>
<th>Theoretical Dissolved Oxygen Solubility (mg/L)</th>
<th>% Dissolved Oxygen Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hill AFB, UT - Site 870</td>
<td>5.9</td>
<td>18.7</td>
<td>9.4</td>
<td>63%</td>
</tr>
<tr>
<td>Battle Creek ANGB, MI - Site 5</td>
<td>6.9</td>
<td>14.9</td>
<td>10.2</td>
<td>88%</td>
</tr>
<tr>
<td>Madison ANGB, WI</td>
<td>7.1</td>
<td>11.1</td>
<td>11.1</td>
<td>64%</td>
</tr>
<tr>
<td>Elmendorf AFB, AK - Hangar 10</td>
<td>0.8</td>
<td>6.9</td>
<td>12.3</td>
<td>7%</td>
</tr>
<tr>
<td>Elmendorf AFB, AK - ST-41</td>
<td>12.6</td>
<td>7.1</td>
<td>12.2</td>
<td>103%</td>
</tr>
<tr>
<td>King Salmon AFB, AK - SS-12</td>
<td>10.9</td>
<td>7.5</td>
<td>12.1</td>
<td>90%</td>
</tr>
<tr>
<td>Eglin AFB, FL - POL Facility</td>
<td>3.8</td>
<td>26</td>
<td>8.2</td>
<td>49%</td>
</tr>
<tr>
<td>Patrick AFB, FL - Gas Station</td>
<td>3.7</td>
<td>26.1</td>
<td>8.2</td>
<td>49%</td>
</tr>
<tr>
<td>MacDill AFB, FL - Site 56</td>
<td>2.4</td>
<td>25.2</td>
<td>8.4</td>
<td>29%</td>
</tr>
<tr>
<td>MacDill AFB, FL - Pump House 75</td>
<td>2.1</td>
<td>26.3</td>
<td>8.2</td>
<td>29%</td>
</tr>
<tr>
<td>Myrtle Beach, SC - POL Facility</td>
<td>1.9</td>
<td>17.2</td>
<td>9.7</td>
<td>39%</td>
</tr>
<tr>
<td>Langley AFB, VA - Site SS04</td>
<td>5.0</td>
<td>15.5</td>
<td>9.3</td>
<td>54%</td>
</tr>
<tr>
<td>Langley AFB, VA - Site SS15</td>
<td>6.5</td>
<td>26.7</td>
<td>6.2</td>
<td>68%</td>
</tr>
<tr>
<td>Griffis AFB, NY - Pump House 5</td>
<td>6.5</td>
<td>14.9</td>
<td>10.2</td>
<td>64%</td>
</tr>
<tr>
<td>Pope AFB, NC - FPFA 84</td>
<td>8.5</td>
<td>16.8</td>
<td>9.8</td>
<td>63%</td>
</tr>
<tr>
<td>Seymour Johnson AFB, NC - Bldg 470</td>
<td>9.0</td>
<td>17.4</td>
<td>9.7</td>
<td>83%</td>
</tr>
<tr>
<td>Fairfield AFB, WA - Bldg 1212</td>
<td>9.3</td>
<td>12.1</td>
<td>10.9</td>
<td>68%</td>
</tr>
<tr>
<td>Eaker AFB, AR - Gas Station</td>
<td>8.2</td>
<td>14.5</td>
<td>10.3</td>
<td>69%</td>
</tr>
<tr>
<td>Dover AFB, DE - Site SS27/XYZ</td>
<td>8.3</td>
<td>14</td>
<td>10.4</td>
<td>69%</td>
</tr>
<tr>
<td>Bowling AFB, D.C. - Gas Center</td>
<td>7.5</td>
<td>20.3</td>
<td>9.1</td>
<td>82%</td>
</tr>
<tr>
<td>Corry AFB, NE - Tank 348</td>
<td>6.8</td>
<td>22.2</td>
<td>8.8</td>
<td>77%</td>
</tr>
<tr>
<td>Westover AFB, MA - Christmas Tree FTA</td>
<td>11.2</td>
<td>13.4</td>
<td>10.6</td>
<td>100%</td>
</tr>
<tr>
<td>Columbus AFB, MS - ST-24</td>
<td>8.5</td>
<td>20.6</td>
<td>9.1</td>
<td>94%</td>
</tr>
<tr>
<td>Shaw AFB, SC - Bldg 1613</td>
<td>7.9</td>
<td>22.6</td>
<td>8.7</td>
<td>90%</td>
</tr>
<tr>
<td>Travis AFB, CA - Gas Station</td>
<td>3.7</td>
<td>21.7</td>
<td>6.9</td>
<td>42%</td>
</tr>
<tr>
<td>Beale AFB, CA - UST Site</td>
<td>8.4</td>
<td>17.5</td>
<td>9.6</td>
<td>67%</td>
</tr>
</tbody>
</table>

Average

<table>
<thead>
<tr>
<th>Avg. Background DO (mg/L)</th>
<th>Avg. DO Solubility (mg/L)</th>
<th>Avg. DO Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7 mg/L</td>
<td>9.8 mg/L</td>
<td>68%</td>
</tr>
</tbody>
</table>
**DO Comparison Other Basalt Aquifers**

**Ground-Water Geochemistry of the Columbia Plateau Aquifer System, Washington, Oregon, and Idaho**

By W.C. Steinkampf and P.P. Hearn, Jr.

A contribution of the Eppel Aquifer System Analysis Program

U.S. Geological Survey
Open File Report 95-483

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### Dissolved Oxygen Data from Basalt Aquifers in Columbia Plateau (Steinkampf and Hearn, 1996)

<table>
<thead>
<tr>
<th>Basalt Hydrogeological Unit</th>
<th>Dissolved Oxygen Minimum (mg/L)</th>
<th>Dissolved Oxygen Maximum (mg/L)</th>
<th>Dissolved Oxygen Mean (mg/L)</th>
<th>Theoretical Dissolved Oxygen Saturation (mg/L)</th>
<th>Dissolved Oxygen Saturation (%)</th>
<th>Mean Groundwater Temperature (°C)</th>
<th>Number Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saddle Mountains</td>
<td>0.5</td>
<td>10</td>
<td>6.39</td>
<td>9.8</td>
<td>65%</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>Wanapum</td>
<td>0.1</td>
<td>10.6</td>
<td>5.5</td>
<td>10.3</td>
<td>53%</td>
<td>14.4</td>
<td>266</td>
</tr>
<tr>
<td>Grande Ronde</td>
<td>0.1</td>
<td>10.2</td>
<td>2.6</td>
<td>9.5</td>
<td>27%</td>
<td>18.3</td>
<td>160</td>
</tr>
</tbody>
</table>
DO Comparison To Other Basalt Aquifers

As groundwater moves through the aquifer along a flow path, the dissolved oxygen in the groundwater gradually is consumed by redox processes. Once all of the dissolved oxygen is consumed, other chemical species can accept electrons and become reduced. If nitrate is present, it will become the preferred electron acceptor, until it in turn is completely consumed.
Degradation of CFCs also can impart an old bias. Chlorofluorocarbons degrade in anaerobic environments under sulfate-reducing or methanogenic conditions (Plummer and Busenberg, 1999). Degradation does not appear probable in Oahu saturated aquifers because all ground-water samples contained dissolved oxygen and no methane. However, CFCs may degrade in parts of the unsaturated zone. Some exposures of red saprolite in the study area contain greenish-gray bands where iron has been reduced from its ferric state (red) to its ferrous state (green). This suggests that anaerobic reducing conditions existed in the saprolite, most likely within perched water bodies.
**Abstract**

During construction of a nuclear waste repository in basalt (NWRB), Eh conditions in the repository horizon will be perturbed as a result of air-saturation of groundwater, temporarily leading to redox conditions more oxidizing than in the undisturbed system. Performance assessment of an NWRB requires information on redox conditions, since they will greatly affect the corrosion rate of canisters and the solubility and transport of certain radionuclides. Experiments were conducted to evaluate rates of oxygen consumption and redox conditions in the basalt-water system under conditions expected in an NWRB. Two methods were used to obtain these data: (1) the As(III)/As(V) redox couple and (2) the measurement of dissolved oxygen levels in solution as a function of time. These experiments have provided evidence that basalt is effective in removing dissolved oxygen and in rapidly imposing reducing conditions on solutions. At 300°C, calculations showed that an upper limit on Eh of -400 ± 100 mV was attained in 11 days. The dissolved oxygen content of solutions from a 150°C experiment decreased from air-saturation (8.5-9 mg/L) to 0.4 mg/L after 8 days, while solutions maintained at 100°C for 130 days contained 1.8-1.9 mg/L dissolved oxygen.
Dissolved Oxygen Measurement Problems
Oct. / Nov. / Dec. 2016?

Key Point: Almost all DO measurements from Oct to Dec 2016 were depressed compared to previous and subsequent measurements, strongly supporting a conclusion that some type of calibration/measurement issues was the cause.

Dissolved Oxygen Concentration vs. Time Since Installation for Three Facility Monitoring Wells Drilled Near Saproite Zones. RHMW06 and RHMW07 were Completed in Oct. 2014; RHMW08 in Oct. 2016.

Monitoring Wells vs. Public Water Supply Wells

Monitoring Dissolved Oxygen in Ground Water: Some Basic Considerations

by Seth Rose and Austin Long

Anoxic water, the resulting sample will usually appear oxic. Valuable data that can be used to assess contaminant stability within the restricted anoxic zone(s) would be lost in this manner. Turbulence and the depressurization of deep ground water are other inherent problems associated with sampling from production wells. However, in many cases, production wells represent the only viable access to deep ground water and therefore must be considered as a sampling point of last resort.

No simple test can be given to assess the validity of any sampling method. However, if ground water samples are uniformly saturated (approach the maximum solubility of O₂ in water at a given salinity, temperature, and pressure), the sampling method might be considered suspect. Conversely, if samples from an unconfined aquifer

12
anoxic water, the resulting sample will usually appear oxic. Valuable data that can be used to assess contaminant stability within the restricted anoxic zone(s) would be lost in this manner. Turbulence and the depressurization of deep ground water are other inherent problems associated with sampling from production wells. However, in many cases, production wells represent the only viable access to deep ground water and therefore must be considered as a sampling point of last resort.

No simple test can be given to assess the validity of any sampling method. However, if ground water samples are uniformly saturated (approach the maximum solubility of $O_2$ in water at a given salinity, temperature, and pressure), the sampling method might be considered suspect. Conversely, if samples from an unconfined aquifer
Man-Made Non-COPCs in Outlying Wells
Detections, Sampling Artifacts, Lab Artifacts

**Halogenated VOCs:** chloromethane, bromomethane, bromodichloromethane, dibromochloromethane, trichloroethene (TCE), 1,2,4-trichlorobenzene (some of these halogenated VOCs could also be in groundwater due to past land use or chlorination, rather than a sampling/analytical artifact).

**Phthalates:** bis(2-ethylhexyl)phthalate, dimethyl phthalate

Percent Detections of Man-Made but non- Constituents of Potential Concern (non-COPCs) in Outlying Monitoring Wells at the Facility
Dissolved Oxygen in 15 USGS Upgradient, "Far-Field" Groundwater Monitoring Wells

Key Point:
USGS upgradient, "far-field" monitoring wells in regional study had:
- Average DO in shallow Oahu groundwater: 6.7 mg/L
- Minimum DO in shallow Oahu groundwater: 4.7 mg/L

Table 2-3: Background Dissolved Oxygen Data from 15 Upgradient, Far-Field Monitor

<table>
<thead>
<tr>
<th>USGS Upgradient, &quot;Far Field&quot; Monitoring Well</th>
<th>Dissolved Oxygen Concentration (mg/L)</th>
<th>% Dissolved Oxygen Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M01</td>
<td>6.5</td>
<td>77</td>
</tr>
<tr>
<td>M02</td>
<td>6.6</td>
<td>81</td>
</tr>
<tr>
<td>M03</td>
<td>4.7</td>
<td>57</td>
</tr>
<tr>
<td>M04</td>
<td>6.3</td>
<td>74</td>
</tr>
<tr>
<td>M05</td>
<td>6.8</td>
<td>82</td>
</tr>
<tr>
<td>M06</td>
<td>7.6</td>
<td>89</td>
</tr>
<tr>
<td>M07</td>
<td>7.2</td>
<td>86</td>
</tr>
<tr>
<td>M08</td>
<td>6.6</td>
<td>80</td>
</tr>
<tr>
<td>M09</td>
<td>6.6</td>
<td>83</td>
</tr>
<tr>
<td>M10</td>
<td>7.6</td>
<td>90</td>
</tr>
<tr>
<td>M11</td>
<td>7.6</td>
<td>94</td>
</tr>
<tr>
<td>M12</td>
<td>6.8</td>
<td>82</td>
</tr>
<tr>
<td>M13</td>
<td>7.1</td>
<td>85</td>
</tr>
<tr>
<td>M14</td>
<td>6.7</td>
<td>81</td>
</tr>
<tr>
<td>M15</td>
<td>6.1</td>
<td>73</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>6.7</strong></td>
<td><strong>81%</strong></td>
</tr>
</tbody>
</table>

Avg. Background DO (mg/L) 6.7 mg/L
Avg. DO Saturation 81%
Min. Background DO (mg/L) 4.7 mg/L
Comparing the typical landfill effects and leachate quality to the groundwater quality data presented in Table 1, no clear indication exists of landfill effects on groundwater quality at CMLF. While some constituent concentrations (such as sodium and chloride) are higher in downgradient well MW-2 compared to other wells, bicarbonate is higher in upgradient wells than in any of the downgradient wells. Data on chloride and sodium in groundwater should be used with caution because both ions are major components of sea water and spatial and temporal variability in the concentrations of these ions in basal aquifer groundwater, which occurs as a comparatively lower-density lens floating on comparatively higher-density sea water, are expected and have been described in the literature (Mink and Lau, 2006). In particular, chloride concentrations in groundwater in Hawaii is used as an indicator of sea water intrusion (Swain, 1973). As reflected in Table 1, the presence of sulfate and nitrate above reporting limits in all wells, the absence of dissolved iron, and the aerobic nature of the groundwater (positive redox values and several mg/L of dissolved oxygen) all suggest the lack of a water quality signature characteristic of releases from a MSWLF. Table 2 provides a comparison of these five key indicators in leachate and in groundwater.
Road Map

- **Background: Dissolved Oxygen (DO)**
  - National Background DO: Data from 26 Sites
  - DO in Other Basalt Aquifers
  - Shallow Regional Groundwater Monitoring Wells on Oahu
  - Hawaii Example of Release Evaluation Using Dissolved $O_2$

- **Background: Total Petroleum Hydrocarbons**
  - Apparent First Years Drilling Effect
  - Air Rotary Drilling
  - Measuring Low TPH Concentrations

- **Multi-Factor Analysis**
  - Potential Impact Indicators
  - Network Clustering Analysis
  - Multi-Factor Evaluation
Generalized Wilcoxon test – non-parametric statistical method to evaluate if two groups of left-censored chemical data are statistically different or similar

A general statistical rule is if the p-value is less than 0.05, then a statistically significant difference does exist at a 95% confidence level.

First year of combined TPH-d data (RHMW04 through RHMW10) showed a significant difference \((p < 0.05)\) vs. subsequent years.
Air Rotary Drilling Rigs
Key Component: Rotary Air Compressors and Hammers Lubricated by Oil

---

**Figure 8-31: Pressurized Air Discharge from an Air Rotary Assembly**

Left Photo: Compressed air is pumped down through the drill bit and driven upwards through the outside of the core barrel. Cuttings and compressed air are directed to a cyclone mechanism (on right) that dissipates air pressure and velocity and allows for cuttings collection in a driller below cyclone.

Right Photo: Rotary cutting bit.

---

**Primary Separation Filter for Rotary Air Compressor**

(vmacair.com)
AIR ROTARY DRILLING

RICHARD THRON, MGWC

1-(800) 760-9355  richardthron@yahoo.com

NGWA Video Excerpt:
https://www.youtube.com/watch?v=V9oAEbF-Nrl
0:00 to 0:04
41:00 to 42.08
Air Rotary Drilling: Rotary Air Compressors and Hammers Lubricated by Oil

**Methods**

- Most common methods of air rotary drilling
  - Air Drilling
  - Air Foam Drilling
  - Air Mist Drilling
  - Air Foam Gel Drilling
Could TPH Detects be Coming from Drilling?

Method. The air discharged from air compressors normally contains finely atomized lubricating oil. To help prevent this oil from contaminating monitoring well drill holes, compressor discharge filters must be installed and maintained during regular intervals on rigs used to drill monitoring wells. Air-discharge samples should be collected as reference samples for future comparison where hydrocarbon contamination is being studied. These samples are a necessity in applications where lubrication of down-the-hole hammers or other tools is essential. The use of foam additives to aid cuttings removal also can introduce organic contaminants into the monitoring system. These should be avoided, but where necessary, samples of the foaming agent must be taken as reference samples.

4.4 AirRotary

Rotary drilling involves the use of circulating fluids (i.e., mud, water, or air) to remove the drill cuttings and maintain an open hole as drilling progresses. Air rotary drilling forces air down the drill pipe and back up the borehole to remove the drill cuttings. The air rotary drilling technique is best suited for use in hard rock (versus unconsolidated or poorly consolidated materials).

Unless an oil-less compressor is used, there is always the risk of introducing some quantity of compressor oil into the borehole. This can occur even when oil-removing filters are used, because their effectiveness depends on careful maintenance. At best, the issue of whether oil has been introduced into the aquifer will remain suspect. There is generally no way to tell when compressor filters need changing because most drilling equipment have safety bypass valves that route the air around plugged filters.
Could TPH Detects be Coming from Drilling?

In hard, abrasive, consolidated rock, a down-the-hole hammer may be more appropriate than the air rotary method. In this method, compressed air is used to actuate and operate a pneumatic hammer as well as lift the cuttings to the surface and cool the hammer bit. One drawback of the down-the-hole hammer is that oil is required in the air stream to lubricate the hammer-actuating device, and this oil could potentially contaminate the soil in the vicinity of the borehole and the aquifer.

Hydrocarbon Contaminated Soils and Groundwater

chemistry, thereby distorting the true subsurface conditions. Air rotary drilling removes the concerns over formation clogging and drilling fluid effects by using compressed air to remove cuttings. It lacks the ability to maintain a stable borehole in unconsolidated formations although this may be somewhat mitigated by the addition of drilling fluids. The major limitations from a site assessment standpoint come from the potential for introduction of oils and contaminants into the well from poorly filtered air, the difficulty in collecting accurate samples, potential for vertical contaminant migration during drilling, and the risk of exposure for the drill crew to toxic volatile vapors when pockets of soil or water contami-
Low Level TPH Concentrations Observed in Drilling Water

- TPH identified in the water used for drilling.
  - An enhanced sampling program was developed to evaluate where the TPH was being introduced so that the problem could be isolated and addressed.
  - Most TPH hits were observed in drilling rig water outfall from the drill string (prior to entering the borehole).

- A review of the early TPH hits in RHMW10 clearly show that the TPH is likely due to a non-petroleum-based lubricant.

- Since TPH was a factor during the drilling of RHMW08, RHMW09, RHMW10, and RHMW14; it is likely that it also may have been a potential issue during the installation of all monitoring wells.

➢ Early detections of TPH are likely due to drilling and well installation.
➢ Low-level detections of TPH related to drilling are not uncommon and are a well-known issue within the industry.
### Drilling Water Data – TPH Detects Only

<table>
<thead>
<tr>
<th>Well ID</th>
<th>Sample Date</th>
<th>Sampling Point</th>
<th>TPH-g µg/L</th>
<th>TPH-9 µg/L</th>
<th>TPH-9 SGC µg/L</th>
<th>TPH-o µg/L</th>
<th>TPH-o SGC µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHMW08</td>
<td>9/7/2016</td>
<td>Rig Outfall</td>
<td>&lt; 18 U</td>
<td>170 J</td>
<td>520 J</td>
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<tr>
<td>RHMW08</td>
<td>9/26/2016</td>
<td>Rig Outfall</td>
<td>&lt; 18 U</td>
<td>85 J</td>
<td>150 J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>7/20/2016</td>
<td>Rig Outfall</td>
<td>&lt; 18 U</td>
<td>70 J</td>
<td>150 J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>7/29/2016</td>
<td>Water Truck Output</td>
<td>&lt; 25 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>8/12/2019</td>
<td>Rig Outfall</td>
<td>&lt; 15 U</td>
<td>48 U</td>
<td>48 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>1/6/1900</td>
<td>Municipal Hydrant</td>
<td>&lt; 18 U</td>
<td>180 J</td>
<td>220 J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>8/18/2016</td>
<td>Rig Outfall</td>
<td>&lt; 25 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>8/22/2016</td>
<td>Water Truck Output</td>
<td>&lt; 25 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>8/22/2016</td>
<td>Water Hose</td>
<td>&lt; 25 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW09</td>
<td>8/22/2016</td>
<td>Rig Outfall</td>
<td>&lt; 25 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW10</td>
<td>3/7/2017</td>
<td>Rig Outfall</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW10</td>
<td>3/28/2017</td>
<td>Rig Outfall</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW11</td>
<td>10/3/2017</td>
<td>Rig Outfall</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW14</td>
<td>1/11/2019</td>
<td>Municipal Hydrant</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW14</td>
<td>1/11/2019</td>
<td>Water Truck Output (pre-GAC)</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHMW14</td>
<td>1/11/2019</td>
<td>Rig Outfall (post-GAC)</td>
<td>&lt; 18 U</td>
<td>1,000 U</td>
<td>220 U</td>
<td>&lt; 40 U</td>
<td></td>
</tr>
<tr>
<td>RHMW14</td>
<td>1/22/2019</td>
<td>Water Hose (post-GAC)</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td>220 U</td>
<td>&lt; 40 U</td>
</tr>
<tr>
<td>RHMW14</td>
<td>1/22/2019</td>
<td>Rig Outfall (post-GAC)</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td>220 U</td>
<td>&lt; 40 U</td>
</tr>
<tr>
<td>RHMW14</td>
<td>2/18/2019</td>
<td>Water Hose (post-GAC)</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td>220 U</td>
<td>&lt; 40 U</td>
</tr>
<tr>
<td>RHMW14</td>
<td>2/18/2019</td>
<td>Rig Outfall (post-GAC)</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td>220 U</td>
<td>&lt; 40 U</td>
</tr>
<tr>
<td>RHMW15</td>
<td>12/1/2017</td>
<td>Rig Outfall</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td>220 U</td>
<td>&lt; 40 U</td>
</tr>
<tr>
<td>RHT301</td>
<td>3/7/2019</td>
<td>Rig Outfall (post-GAC)</td>
<td>&lt; 18 U</td>
<td>25 U</td>
<td>&lt; 25 U</td>
<td>220 U</td>
<td>&lt; 40 U</td>
</tr>
</tbody>
</table>

**Notes:**
- Bold: Detected value
- U: The compound was analyzed for but not detected above the stated limit
- J: Estimated value
- µg/L: micrograms per liter
- 1-MeN: 1-methylnaphthalene
- 2-MeN: 2-methylnaphthalene
- GAC: granular activated carbon
- N: naphthalene
- SGC: silica gel cleanup
- TPH-d: total petroleum hydrocarbons - diesel range organics
- TPH-g: total petroleum hydrocarbons - gasoline range organics
- TPH-o: total petroleum hydrocarbons - oil range organics

**SAMPLING POINTS**
- Water hose (post GAC) – water from the truck hose to the rig (some samples after GAC treatment (post-GAC)
- Rig outfall (post GAC) – water that has gone through the drilling rig/drill string (some of this was post-GAC before getting to the drilling rig) prior to entering the boring
- Municipal hydrant – water supply at the hydrant before going to the truck
- Water truck output (pre/post GAC) – water sample at the water truck (pre/post GAC treatment)

**Note:** Not all "rig outfall" or "water hose" samples collected under similar conditions and can either be:
1) collected after filtered through GAC (i.e., post-GAC sample [RHMW15-related samples and more recent]), or
2) was not run through GAC at all (potable water samples prior to RHMW15 drilling).
TPH in Outlying Wells: First Years Effect

Drilling Completed:
- Sept. 2005: RHMW04
- Oct. 2014: RHMW06, RHMW07
- Oct. 2016: RHMW08, RHMW09
- May 2017: RHMW10

Non-detect concentrations not plotted on Y-axis

Only 5 samples in RHMW04 in years 9 and 10
### Various laboratory limits for TPH-d

<table>
<thead>
<tr>
<th>Description</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (October 2016 to February 2019) Navy contracted laboratory MDL and LOD</td>
<td>13 and 25 μg/L</td>
</tr>
<tr>
<td>EPA Region 9 laboratory QL</td>
<td>150 μg/L</td>
</tr>
<tr>
<td>Typical routine Eurofins/Test America RL</td>
<td>100 μg/L</td>
</tr>
<tr>
<td>Historical Navy contract laboratories for the Facility monitoring DL</td>
<td>10 to 352 μg/L</td>
</tr>
<tr>
<td><strong>Concentration below which misinterpretation of baseline noise may cause data usability issues (DOH, 2018)</strong></td>
<td>100 μg/L</td>
</tr>
<tr>
<td><strong>Two RHMW04 TPH-d Detections</strong></td>
<td>10 J - 17 J μg/L</td>
</tr>
</tbody>
</table>

Notes: MDL* = method detection limit; LOD = limit of detection; QL = quantitation limit; RL = reporting limit, DL = detection limit; J = estimated value

* Laboratories can calculate MDLs that cannot be achieved in practice when very low spike levels are used.  
DoD Quality Systems Manual (QSM) (DoD and DOE 2017)
Are The Two Extremely Low Concentration Detections in RHMW04 After Year 2 Indications of Impact From Fuel Releases?

Anomalous Detections of “TPH”

“TPH” as measured using modified EPA Method 8015 is not sensitive to the actual constituents present in the sample, and therefore organic compounds other than petroleum can be quantified and reported by the laboratory in the GRO, DRO, and ORO ranges. VOCs such as chlorinated solvents can be reported as “TPHg/GRO.” Laboratory contamination can be reported in any of the TPH ranges. Natural organics and biodegradation by-products can be reported in the “TPHd/DRO” or “TPHmo/ORO” range. Semi-volatile organics such as coal tar or creosote can be reported as “TPHd/DRO” or “TPHmo/ORO.” These detections are often flagged by the laboratory as “does not match standard,” but the concentrations are reported anyway.

Important! It is important to review the chromatograms to evaluate the source of the anomalous detections, and not to assume that the reported detections are petroleum.

RHMW04 July 2014: Does not resemble any type of fuel pattern, dissolved fuel components, or biodegraded matter.

RHMW04 Jan. 2015: Obvious and often unavoidable over-integration of baseline noise.
Are The Two Extremely Low Concentration Detections in RHMW04 After Year 2 Indications of Impact From Fuel Releases?

Collection and Use of Total Petroleum Hydrocarbon Data for the Risk-Based Evaluation of Petroleum Releases

Example Case Studies

Last Updated: October 2018

Published by
Hawaii Department of Health
Hazard Evaluation and Emergency Response Office
Honolulu, Hawaii

4 COMMON RISK ASSESSMENT PROBLEMS AND DATA LAPSES

As noted in the case studies, existing TPH data might or might not be adequate for risk-based assessment of potential environmental concerns at a petroleum-release site. Common types of data lapses and data usability issues include:

- Reliance on BTEXN and PAH data (i.e., indicator compounds) alone for decision making in the absence of TPH characterization data for all media (i.e., soil, sediment, water, soil vapor and/or indoor air);
- Failure to document nature, location and potential environmental concerns posed by residual contamination;
- Absence of a detailed CSM and consideration of all current or potential sources, pathways and receptors;
- Focus of initial risk assessment on human direct exposure and lack of data collection and assessment of other potential concerns, including leaching, vapor intrusion, impacts to aquatic habitats, gross contamination, and related environmental concerns;
- Inability to assess degradation state of petroleum in groundwater due to lack of silica gel cleanup data;
- Inability to assess potential environmental concerns posed by polar, TPH-related metabolites due to lack of groundwater data that excludes silica gel cleanup;
- Bias of existing TPH soil data due to presence of tree sap, pine needles and other non-petroleum, organic material in samples and inadequate processing and analysis at the laboratory;
- Bias of existing TPH groundwater or surface water data due to presence of algae, dissolved organic carbon, fish oils and other non-petroleum, organic material in samples and inadequate processing and analysis at laboratory;
- Misinterpretation of baseline noise in gas chromatograph signals below 100 µg/L as TPH in groundwater or surface water samples;
- Use and interpretation of data from different analytical methods (for example, method 8015 vs. state-specific methods); and
- Limitations of data use due to elevated detection limits and laboratory reporting errors.

Additional problems associated with the use of historic data at petroleum release sites are discussed in individual case studies.
TPH Trends in Outlying Wells Explained by:
1) First Years Effect and 2) Low-Level (Non-Petroleum) Artifacts

Key Points: Multi-factor analysis should not use the first and possibly the second year of data, or data below 150 µg/L (EPA Region 9 TPH-d QL) or below 100 µg/L (HDOH).

*DOH Data Usability Warning: “Misinterpretation of baseline noise in gas chromatograph signals below 100 µg/L as TPH in groundwater….”

Drilling Completed:
Sept. 2005: RHMW04
Oct. 2014: RHMW06, RHMW07
Oct. 2016: RHMW08, RHMW09
May 2017: RHMW10

Only 5 samples in RHMW04 in years 9 and 10
Non-detect concentrations not plotted on Y-axis
Road Map

- **Background: Dissolved Oxygen (DO)**
  - National Background DO: Data from 26 Sites
  - DO in Other Basalt Aquifers
  - Shallow Regional Groundwater Monitoring Wells on Oahu
  - Hawaii Example of Release Evaluation Using Dissolved O₂

- **Background: Total Petroleum Hydrocarbons**
  - Apparent First Years Drilling Effect
  - Air Rotary Drilling
  - Measuring Low TPH Concentrations

- **Multi-Factor Analysis**
  - Potential Impact Indicators
  - Network Clustering Analysis
  - Multi-Factor Evaluation
Geochemistry Data for Multi-Factor Analysis

- **Field parameters**
  - Nitrate
  - Sulfate
  - Dissolved Oxygen
  - Methane

- **Chemical data**
  - TPH-d
  - TPH-o
  - TPH-g
  - Naphthalene
  - Methynaphthalenes
  - Benzene
  - Toluene
  - Ethylbenzene
  - Xylenes
Potential Impact Indicators
(Based on EPA Contractor's General Methodology)

- TPH-d, TPH-o, TPH-g, N, 1-MeN, 2-MeN, BTEX, and methane:
  - Unflagged detected concentration values → 1
  - U or UJ flagged data → 0
  - J flagged data → 0.5
  - Duplicate Sample Data

*Note: Naphthalene for impact indicators analysis is shown as "N" for subsequent slides

- DO, sulfate, and nitrogen

Concentrations → indicators

<table>
<thead>
<tr>
<th>Chemical parameters</th>
<th>Concentration for indicator = 0</th>
<th>Concentration for indicator = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>6.8</td>
<td>4.7</td>
</tr>
<tr>
<td>Sulfate</td>
<td>12.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.91</td>
<td>0.18</td>
</tr>
</tbody>
</table>

- Linear interpolation of indicators between two values
- All concentrations are mg/L
- Nitrogen (nitrite plus nitrate)
Data Considered in Sensitivity Analysis

- **Base Case:**
  - First 2 years of TPH data excluded
  - Cals/Euro lab data for naphthalene excluded
  - RHMW04 later year TPH not included since this was due to inherent issues with TPH measurements and not fuel-related.

- **Sensitivity Case 1:**
  - First year of the TPH data excluded (this is conservative since the first 2 years could have been excluded)
  - Cals/Euro lab data for naphthalene included – Detections are suspect since only found by this laboratory for most wells and not before/after
  - All available Red Hill Shaft data were included
  - RHMW04 later year TPH not included since this was due to inherent issues with TPH measurements and not fuel-related.

- **Sensitivity Case 2:**
  - All monitoring well data included
Spatial Distribution of Potential Impact Indicator Values (Base Case)
Network Clustering Analysis

What is network analysis?

It consists of three components:

- **Node**: data points for variables, multiple attributes (indices)
- **Edge**: similarity between nodes based on various factors, longer the edge the larger the difference
- **Community**: nodes that have similar attribute characteristics

![Diagram of network components]
Visualization of Communities from Clustering Analysis

- "R" was used to develop the network analysis
- Used pair-wise cosine similarity measures as a metric
- A graphical conceptual representation is developed by the program to describe similarity between communities.
- The length of edges between groups is not necessarily shown in the conceptual presentation
- The edge length within communities describes relative similarity between wells
**Base Case Clustering/Indicator Value Analysis (Similarity)**

**RHMW03**
- moderately high TPH-d indicator (heavier TPH range vs 01 and 02)
- High DO indicator value
- zero methane, nitrate, sulfate indicators
- very low N, and MeN indicators
- likely impacted by the Facility

**RHMW07, RHMW08, RHMW09, RHMW10, and Red Hill Shaft**
- TPH, N, 1-MeN, and 2-MeN indicator values are low or zeroes
- BTEX and methane indicator values are zeroes
- nitrate and sulfate are generally low
- DO indicator values are low at RHMW09 and RHMW10
- No consistently high indicators
- Likely not impacted by the Facility

**RHMW04, RHMW05, and RHMW06**
- TPH, N, 1-MeN, 2-MeN, and BTEX indicator values are low or zero.
- All methane indicators are zero
- The indicator values for DO, nitrate, and sulfate are generally low
- Likely not impacted by the Facility

**RHMW01, RHMW02**
- TPH indicator values and other degradation indicators are relatively high
- likely impacted by the Facility
**Sensitivity Analysis Relative to Similarity (All Cases)**

- RHMW01 and RHMW02 are in the same “community”
- RHMW03 is always in its own group with no similarity to any other well
- RHMW04, RHMW05, and RHMW06 are in the same “community”
- RHMW07, RHMW08 are always clustered in one group

**KEY POINT:** Outlying wells not in same community as near-tank wells.
Spatial Distribution of Clustering Network (Base Case)
Conclusions

- **Dissolved Oxygen and TPH Measurements**
  - DO is typically not near saturation. Upgradient, “far-field” USGS monitoring wells in Oahu average 6.7 mg/L and ranged between 4.7 – 7.6 mg/L.
  - TPH data from first 2 years likely representative of impacts from drilling, rather than releases from the Facility.
  - TPH results < 100 ug/L are not reliable (per DOH guidance).

- **Multiple Impact Factors Analysis**
  - The indicator analysis was performed consistent with EPA’s approach.
  - RHMW01, RHMW02, and RHMW03 are likely impacted by historical releases.
  - **None of the outlying wells’** groundwater quality data is similar to the groundwater quality data from the three impacted (near-tank) wells.