May 4, 2010

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Subject: **Type 1 Letter Report – Re-evaluation of the Tier 3 Risk Assessment/Groundwater Model & Proposed Course of Action**
Red Hill Bulk Fuels Storage Facility, Pearl Harbor, HI
Contract #N47408-04-D-8514, Task Order 54

INTRODUCTION

This Type 1 Report is required in accordance with the Red Hill Bulk Fuel Storage Facility Groundwater Protection Plan (TEC, 2008) as revised in 2009 (the Plan). In October 2008, concentrations of petroleum hydrocarbons in groundwater beneath the Red Hill Bulk Fuel Storage Facility (the Facility) exceeded levels associated with Category 4 status, as defined by the Plan. In accordance with the Plan, Category 4 status requires the United States (US) Navy to produce a Type 1 Report that documents the re-evaluation of the Tier 3 risk assessment and associated groundwater model (TEC, 2007a).

This Type 1 Letter Report is prepared for the Naval Fleet Engineering Service Center (NFESC) and the Pearl Harbor Naval Base Fleet Industrial Supply Center (FISC) by TEC Inc. (TEC) under contract N47408-04-D-8514, Task Order 54. Under Task Order 54, TEC is providing environmental compliance services associated with past releases of petroleum hydrocarbons to the subsurface bedrock and the underlying groundwater aquifer.

SITE DESCRIPTION AND BACKGROUND

The Facility includes twenty 12.5 million-gallon (Mgal) underground storage tanks (USTs) located within the Red Hill Ridge, Halawa Valley, Hawaii. The Facility also includes a series of tunnels and pipelines which deliver fuel to and from Pearl Harbor Naval Base (Figure 1). The Facility was constructed prior to World War II to support naval activities in the Pacific. Pertinent information regarding the Facility includes:

- The Facility is exempt from many of the Federal and State UST Program requirements because it was field-constructed;

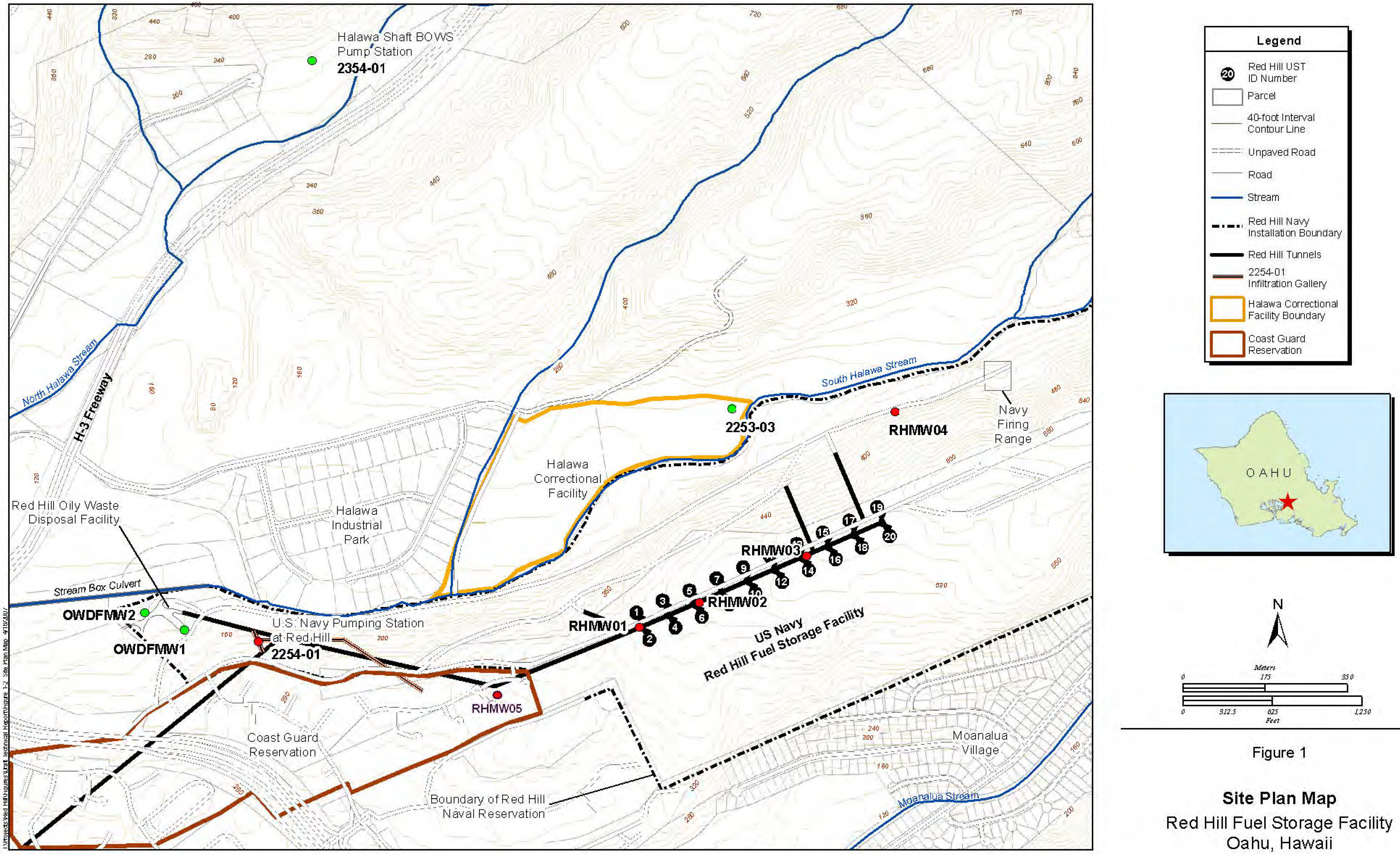

Figure 1

Site Plan Map

Red Hill Fuel Storage Facility
Oahu, Hawaii

- The Facility has stored diesel fuel, Navy Special Fuel Oil (NSFO), Navy Distillate (ND), Jet Propulsion Fuel 5 and 8 (JP-5 and JP-8), and F-76 (diesel marine fuel), and for a short time, aviation gasoline (AVGAS) and automobile gasoline (MOGAS) in selected USTs; and
- The Facility overlies the Waimalu and Moanalua aquifer systems, which are pumped extensively for potable water usage by the Honolulu Board of Water Supply (HBWS) and the Pearl Harbor Water System (PHWS).

Previous environmental investigations have determined that petroleum from past releases has migrated from the USTs to the underlying groundwater. A groundwater contaminant transport model was developed to evaluate the threat to surrounding potable water wells. In addition, a risk assessment was conducted to estimate current and future risk, based on the model. Current risk was found to be insignificant because petroleum had not migrated into nearby drinking water wells (Figure 2).

The US Navy Well 2254-01 pumps approximately 4.6 million gallons per day (mgd) of water from a water tunnel (infiltration gallery) that extends approximately 1,280 feet across the water table, southwest of the Facility. The US Navy developed the Plan (TEC, 2008) to mitigate this potential future threat. The Plan specifies quarterly groundwater monitoring at a network of wells within the Facility as well as site-specific action levels and specific mitigation actions when these action levels are observed.

In October of 2008, results for Total Petroleum Hydrocarbon, Diesel Range Organics (TPH-DRO) by United States Environmental Protection Agency (USEPA) Method 8015 from groundwater samples collected at RHMW02 were 4,540 μg/L in the primary sample and 6,300 μg/L in the duplicate sample for an average TPH-DRO concentration of 5,420 μg/L. This average concentration exceeded the site-specific action level of 4,500 μg/L, which is the solubility limit of TPH-DRO. These results triggered a Category 4 response action in accordance with the Plan. RHMW02 is located within the Facility lower access tunnel, approximately 2,060 feet from the US Navy Well 2254-01 infiltration gallery.

A Category 4 response is required by the Plan because high concentrations of petroleum contamination in groundwater are the risk driver at the Facility. Specifically, the results of the groundwater model and risk assessment (TEC, 2007a) indicate that for an imminent risk to occur, fuel would be within approximately 1,100 feet of the US Navy Well 2254-01 infiltration gallery.

This Type 1 Report provides the required Category 4 response as follows:

- Re-evaluate the Tier 3 Risk Assessment (TEC, 2007a);
- Re-evaluate the groundwater model assumptions and results (TEC, 2007b); and
- Provide a proposal to Hawaii Department of Health (HDOH) regarding a course of action.

A comprehensive re-evaluation of a risk assessment/groundwater model as required for this Type 1 Report is a complex task requiring a significant amount of field work and technical analysis. The completion of this field work and detailed technical evaluation was necessary before this Type 1 report could be issued.

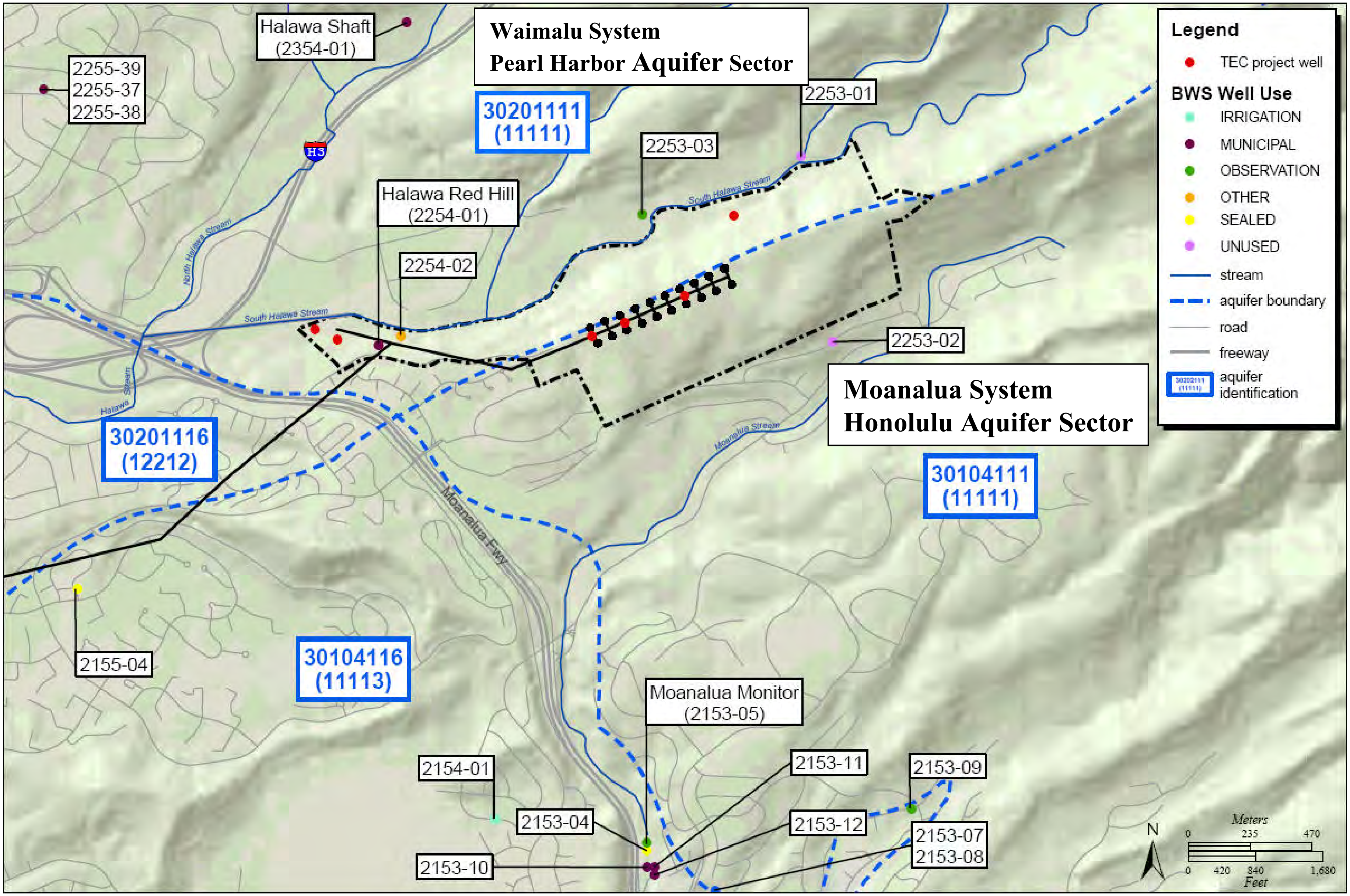

Figure 2.

Area Wells and Aquifer Systems

Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

In order to reassess the threat to water supply wells in the study area, the US Navy installed an additional groundwater monitoring well (RHMW05) between the Facility and the US Navy Well 2254-01 infiltration gallery, approximately 600 feet from the infiltration gallery. This well is now sampled quarterly with results included in the US Navy's quarterly reports to HDOH.

In addition, a sensitivity analysis was conducted on the risk assessment to determine the assumptions with the greatest potential for adversely impacting the results. The assumptions presented below were re-evaluated based on this sensitivity analysis. The site-specific risk-based levels (SSRBLs) presented in the Plan were based on the following Tier 3 Risk Assessment/groundwater model assumptions:

1. the concentration of dissolved fuel hydrocarbons in the groundwater as measured by USEPA Method 8015 is limited to 4,500 μg/L, the computed maximum solubility resulting from JP-5 fuel in direct contact with the groundwater surface;
2. the groundwater flows "mauka to makai"(i.e., mountain to ocean), a direction that places the US Navy Well 2254-01 directly down gradient from the USTs; and
3. the dissolved fuel hydrocarbons will degrade at a rate that was modeled using the reactive transport model code RT3D (the modeled bulk degradation rate was about 0.009 per day).

RE-EVALUATION EFFORTS IN RESPONSE TO THE CATEGORY 4 STATUS

The Category 4 results from the groundwater samples collected from RHMW02 in October 2008 during Round 13 by USEPA Method 8015 for TPH-DRO (4,540 μg/L; 6,300 μg/L in the duplicate sample; for an average of 5,420 μg/L) exceeded the calculated solubility limit of 4,500 μg/L for JP-5. These results and a Category 4 status given to RHMW02 necessitated a re-evaluation of the Facility Tier 3 Risk Assessment and groundwater model.

Re-evaluation of the Groundwater Flow Direction/Gradient

A study was undertaken to better understand the groundwater flow direction and gradient in the vicinity of the Facility. The SI report (TEC, 2007) reported a groundwater flow direction to the south when the pumps at the US Navy Well 2254-01 were off or operating at normal capacity, and a groundwater flow direction to the north-northwest when the pumps were operating at their maximum capacity. This was much different than the assumed "mauka to makai" flow direction of the west-southwest. To get a more accurate estimation of the groundwater flow direction, TEC contracted Pacific GPS to do a precision global positioning system (GPS) vertical survey of all wells that are not in the lower access tunnel, but were used in the 2006 aquifer test detailed in the SI report (TEC, 2007a).

The re-evaluation of the groundwater flow direction and gradient in the vicinity of the Red Hill Facility shows a local flow direction from the USTs toward the US Navy Well 2254-01 as expected. The gradient for this flow direction is approximately 0.00022 feet/feet. This evaluation also shows a regional component flowing to the northwest. The gradient for this flow direction is approximately 0.00028. The letter report detailing the groundwater flow/gradient study is included as Attachment A.

Re-evaluation of the Tier 3 Risk Assessment

Analytical results from RHMW02 collected during Round 13 (October 2008), placed RHMW02 in a Category 4 status as defined by the Plan. As discussed earlier, this prompted a re-evaluation of the groundwater flow direction and gradient because this data was used to prepare the associated groundwater flow/contaminant transport model used to support the Tier 3 Risk Assessment. In addition, a Tier 3 Risk Assessment re-evaluation was also conducted. The re-evaluation required an assessment regarding the assumption that the maximum solubility of JP-5 is 4,500 μg/L (Attachment B).

Although split samples from RHMW02 to be analyzed for TPH-DRO/TPH-gasoline range organics (GRO) and by the Massachusetts Department of Environmental Protection (MADEP) analytical protocol were not collected during Round 13, this was done during Round 16 (July 2009). Consequently, the results obtained from Round 16 allowed for a detailed comparison analysis of total TPH-DRO/TPH-GRO concentration verses the total MADEP volatile petroleum hydrocarbons (VPH)/extractable petroleum hydrocarbon (EPH) concentration (Attachment C). This comparison showed that an overall average of approximately 27 percent of the TPH-DRO result was from polar, non-fuel organic compounds.

This hypothesis is strengthened by an analysis of the TPH-DRO chromatographs for samples collected in January and February 2010. This TPH-DRO analysis showed that apparently non-fuel tentatively identified compounds (TICs) accounted for approximately 35 percent of the TPH-DRO concentration (Attachments B and D). These results strongly suggest that the TPH-DRO results for RHMW02 collected during Round 13 did not exceed the assumed maximum JP-5 solubility of 4,500 μg/L and that approximately 1/3 of the TPH-DRO reported concentration was likely from less toxic, non petroleum-related compounds (Attachment E).

The Tier 3 Risk Assessment also considered another critical factor of the groundwater/contaminant transport model (i.e., the simulated flow direction and gradient). As discussed in a previous section, a precision GPS elevation survey was done on all of the wells located out of the lower access tunnel that were used in the 2006 aquifer test. This data was used to compute the groundwater flow direction when the pumps at the US Navy Well 2254-01 were:

- Not in operation;
- Pumping at the maximum rate that could be sustained for five days; and
- Pumping at a rate closely resembling normal withdrawal from that well.

This analysis showed that there was flow in the assumed west-southwest direction parallel to the alignment of tanks, but it also showed a stronger flow component to the northwest. This deviation from the modeled groundwater flow direction and gradient does not significantly change the conclusions of the model. One of the sensitivity simulations performed and detailed in TEC (2007b) was a reduced flow scenario due to a drought.

This reduced flow beneath the UST source area to the infiltration gallery of US Navy Well 2254-01 was assessed. According to the model, the distance a dissolved plume traveled from a stationary free-product plume until natural attenuation had reduced the concentration to 100 μg/L was 1,170 feet for the base simulation, but was reduced to 1,090 feet for the lower-flow drought simulation. This establishes that the Tier 3 Risk Assessment/groundwater model, while not reflecting the entire groundwater flow field, does simulate the most conservative flow direction. Therefore, with respect to the potential risk to the US Navy Well 2254-01, the results of the Tier 3 Risk Assessment (TEC, 2007b) still remain valid. This is because the Tier 3 Risk Assessment assumes a worst case scenario, that the dominant groundwater flow direction places the infiltration gallery of 2254-01 directly down gradient from the USTs.

PROPOSED FUTURE COURSE OF ACTION

TPH-DRO results at RHMW02 exceeding the computed maximum solubility of JP-5 have occurred twice during the history of the groundwater monitoring program associated with the Facility. It is expected this situation will occur again in the future. If this does occur, a detailed chromatograph TICs evaluation similar to that done for the Round 18 samples should be requested from the lab. If the results indicate that the TPH fraction due to fuel hydrocarbons does exceed the computed solubility of JP-5 (4,500 μg/L), another re-evaluation of the Tier 3 Risk Assessment/groundwater model should be done.

This re-evaluation should consist of investigating the validity of the 4,500 mg/L solubility limit and re-computing the distance from the edge of a free product plume to TPH-GRO/TPH-DRO compliance using the measured TPH concentration and a degradation rate of 0.007 per day. This is an average degradation rate computed using results from 23 Air Force fuel contaminated sites (Wiedemeier et al., 1999). Using this data, new SSRBLs could be established for the monitoring wells based on distance from the eastern end of the infiltration gallery for US Navy Well 2254-01.

It is further recommended that at least one more round of split samples be collected for TPH-GRO/TPH-DRO and MADEP VPH/TPH analysis. This will help establish whether TPH-DRO concentrations that may be measured at the Facility’s non-potable wells (RHMW01, RHMW02, RHMW03, and RHMW05) are from fuel hydrocarbons or from polar, less toxic, non-fuel organic compounds.

Of the wells previously listed, RHMW05 is of greatest concern because its TPH-DRO results have been consistently greater than the HDOH environmental action levels (EALs). Therefore, due to the close proximity of RHMW05 (i.e., located between RHMW01 and the US Navy Well 2254-01, approximately 600 feet from the US Navy Well 2254-01), modified SSRBLs for TPH-DRO and TPH-GRO for this well should be established and the Plan revised as appropriate.

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Wiedemeier, T.H., J.S. Rifai, C.J. Newell, and J.T. Wilson. 1999. Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. J. Wiley and Sons, Inc.

Attachment A

Groundwater Letter Report

April 15, 2010

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Subject: **Groundwater Flow Direction/Gradient and Tier 3 Risk Assessment Re-evaluation Letter Report**
Red Hill Bulk Fuel Storage Facility, Pearl Harbor, HI
Contract #N47408-04-D-8514, Task Order 54

1.1 INTRODUCTION

This Letter Report was prepared for the Naval Fleet Engineering Service Center (NFESC) and the Pearl Harbor Naval Base Fleet Industrial Supply Center (FISC) by TEC Inc. (TEC) under contract N47408-04-D-8514, Task Order 0054. Under Task Order 0054, TEC is providing environmental compliance services to FISC at the Red Hill Bulk Fuel Storage Facility (the Facility), associated with past releases of petroleum hydrocarbons to the subsurface bedrock and underlying groundwater aquifer.

1.2 SITE DESCRIPTION

The Facility includes twenty 12.5 million-gallons (Mgal) underground storage tanks (USTs) located within Red Hill Ridge, Halawa Valley, Hawaii. The Facility also includes a series of tunnels and pipelines that deliver fuel to and from Pearl Harbor Naval Base (Figure 1). The Facility was constructed prior to World War II to support United States Naval activities in the Pacific.

The USTs were constructed in the field using mining techniques, and are exempt from many Federal and State UST program requirements due to the field-constructed nature of the tanks. According to records, the main fuel types stored at the Facility have been diesel oil, Navy Special Fuel Oil (NSFO), Navy Distillate (ND), Jet Propulsion Fuels 5 and 8 (JP-5 and JP-8), and F-76 (diesel marine fuel). In addition, Tank 17 contained Aviation Gasoline (AVGAS) and Motor Gasoline (MOGAS) between 1964 and 1969, and Tank 18 contained AVGAS between 1964 and 1968. A review of the Facility records, which were classified until 1995, has identified an ongoing maintenance and repair program conducted by the United States (U.S.) Navy. Environmental studies conducted between 1995 and the present (AMEC Earth and

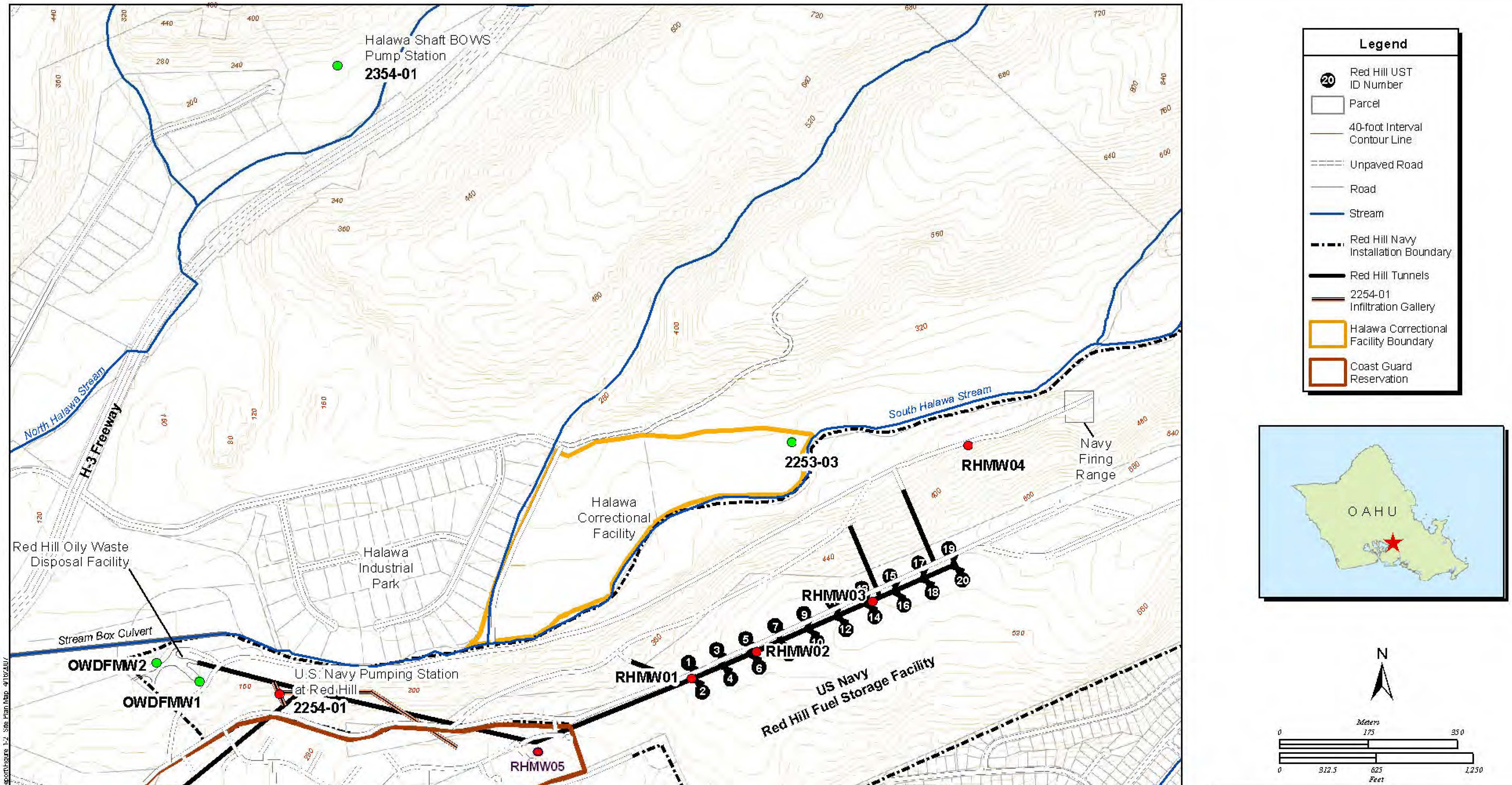

Figure 1

Site Plan Map

Red Hill Fuel Storage Facility
Oahu, Hawaii

Environmental Inc. [AMEC], 2002; Dawson Group Inc. [Dawson], 1995; TEC Inc., 2007; and others) have identified petroleum under a number of these USTs in soil vapor, rock samples, and groundwater that has been categorized as a drinking water resource by the HDOH (Mink and Lau, 1990). This poses a potential threat to downgradient drinking water wells.

The Facility is approximately 100 feet above the basal water table on the boundary of the Waimalu and Moanalua Aquifer Systems of the Pearl Harbor and Honolulu Aquifer Sector, respectively. Both aquifers are sources of potable water for several public water systems, including the Honolulu Board of Water Supply (HBWS) well 2354-01 (Halawa Shaft); wells 2153-10, 2153-12, and 2153-22 (HBWS Moanalua wells); and the U.S. Navy Well 2254-01 (Figure 2). Most notably, the U.S. Navy Well 2254-01, located approximately 3,000 feet from Facility USTs, is permitted to pump 4.6 million gallons per day (mgd) of potable water from a submerged infiltration tunnel which extends approximately 1,280 feet across the water table and supplies the Pearl Harbor Water System. Historical estimates of the hydraulic gradient within these aquifers assumed that the U.S. Navy Well 2254-01 is located directly downgradient from the Facility and is at the greatest risk for contamination from fuel releases from the Facility.

1.3 BACKGROUND

1.3.1 Summary of Previous Gradient Analysis

EarthTech (EarthTech, 2000) performed gradient analysis using wells at the Oily Waste Disposal Facility (OWDF) installed for a Remedial Investigation (RI). This analysis showed a groundwater flow direction that varied from nearly due east to northeast, depending on the magnitude of the groundwater withdrawal from the U.S. Navy Well 2254-01. The gradient varied from 0.00038 to 0.00048 ft/ft. TEC (TEC, 2007) did a gradient analysis based on wells located in the Facility. This analysis showed a groundwater flow direction to the north-northwest when the drinking water well pumps were operating at full capacity (approximately 304 degrees from north) and to the south when the pumps were not in operation (approximately 179 degrees from north). The previous site conceptual model assumed that groundwater in the area flowed parallel to the Red Hill Ridge (approximately 240 degrees from north) without the influence of pumping, and in the direction of the U.S. Navy well 2254-01 infiltration gallery (approximately 270 degrees from north) when U.S. Navy well 2254-01 is pumping at full capacity.

Both of these analyses used wells that were relatively closely spaced where the distance between wells varied from 815 ft to 4490 ft. Since groundwater gradients in the study area are relatively small, usually on the order of 2×10^{-4} ft/ft to 4×10^{-4} ft/ft, a small error in the measurement of the groundwater elevation at any well can result in a significant shift of the computed groundwater flow direction from the true value. Also, only using on-site wells does not show the influence of the regional groundwater flow direction and gradient in the area.

An analysis of the regional groundwater flow in the study area was conducted as part of the aquifer test and modeling performed by TEC and the University of Hawaii (UH) by Rotzoll and El-Kadi (Rotzoll and El-Kadi, 2006). This test included wells owned by the HBWS and State of Hawaii Commission on Water Resources Management (CWRM), as well as the on-site wells. For this regional test, four on-site wells (OWDF-MW1, RHMW02, RHMW03, and RHM04) and three regional wells (Halawa Deep Observation well, CWRM Deep Monitoring Well, and

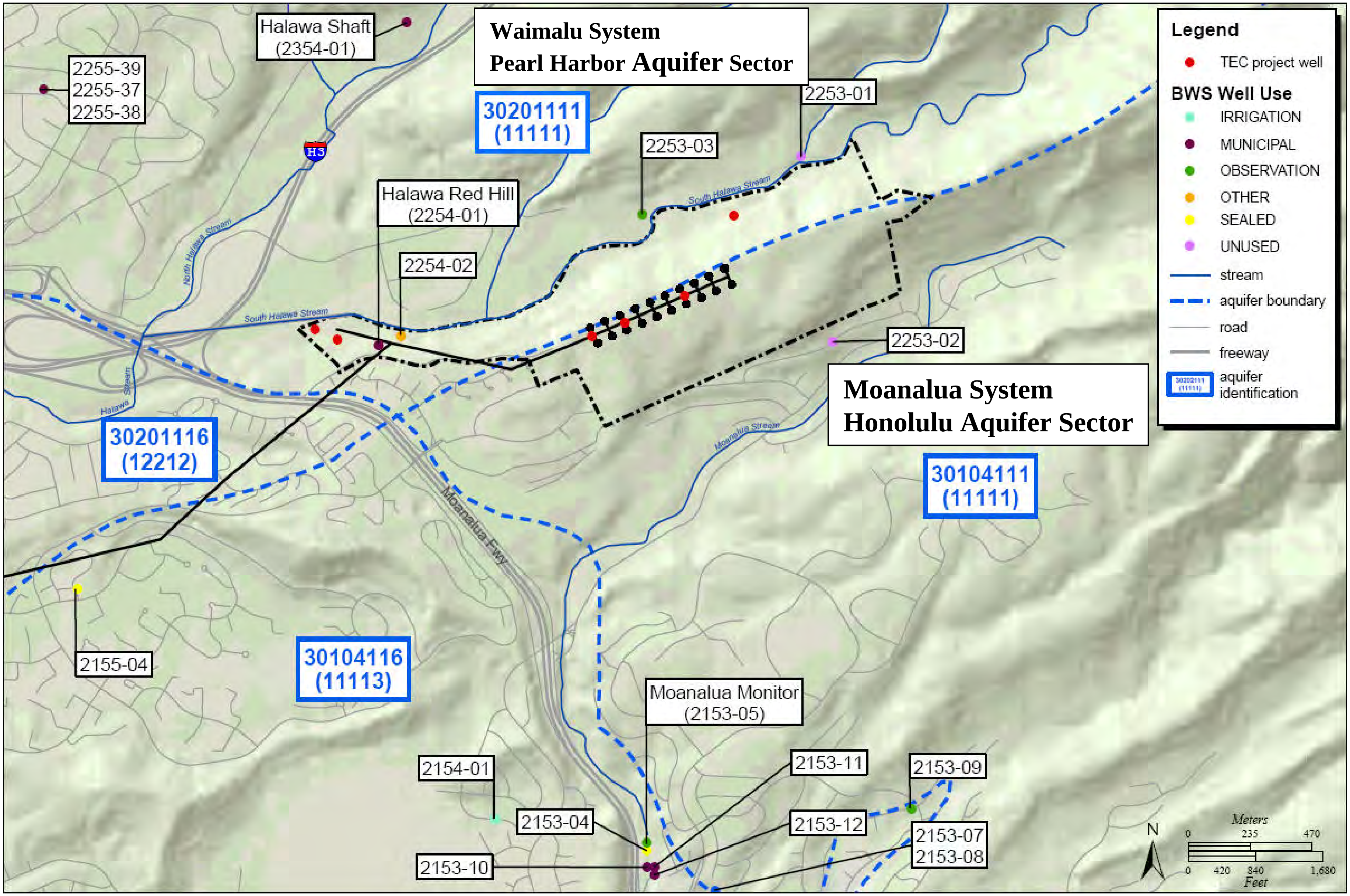

Figure 2.
Area Wells and Aquifer Systems
Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

TAMC-MW2 well) were instrumented with pressure sensing data loggers that provided long-term water elevation versus time data at each well. This data was augmented by daily averaged water table elevations measured at two HBWS wells, one in Moanalua Valley (Manaiki Observation Well) and the other in north Halawa Valley (Halawa Shallow Observation Well). Figure 3 shows the location of the wells used in this aquifer test.

During the test, the pumps at the U.S. Navy Well 2254-01 infiltration gallery were shut off for five days, and then pumped at a maximum sustainable rate for four days. The goal of the test was to estimate the hydraulic parameters of the aquifer by matching the field measured water table variations with the output of the groundwater flow model. A good match was developed between the measured and simulated variations in water table elevation, but there were significant differences in the absolute value of the water table elevation. In the report (Rotzoll and El-Kadi, 2006), these differences were noted in the graphs as offset values used to superimpose the model results on the measured data (Figure 4). One potential source of the difference between the absolute values of measured and simulated water levels was thought to be potential errors in TOC elevation measurements from the various wells used in the study. For example, the TOC elevations used for the three HBWS observation wells had been measured at different times from the TOC elevation for the CWRM Deep Monitoring Well. These wells did not have a single control point of reference or common datum. Also, water level data from these off-site wells were used to calibrate the regional flow model that defined the simulated flow regime in the study area, therefore, any error related to an inconsistent datum would have an effect on the absolute water table elevations in the calibrated model.

It was also noted that inconsistent reference points, or other errors associated with prior surveys, would affect the calculated hydraulic gradient direction and magnitude, which were inconsistent with expected results (see above).

1.4 SURVEY OF REGIONAL AND ON-SITE WELL TOC ELEVATIONS

To resolve the uncertainties associated with inconsistent survey reference points and the resulting effects on groundwater flow direction, a set of surveys was conducted to reference all measurements to a common datum. This was done with a Global Positioning System (GPS) survey for wells capable of receiving a satellite signal, and an optical survey to tie the GPS survey to the wells located in the lower access tunnel within the Facility.

On September 29, 2009, Pacific GPS was contracted by the U.S. Navy through TEC to survey the TOC elevation of all wells with a clear view of the sky using GPS technology. The Pacific GPS report is included as Attachment A to this letter report. A short summary of the process and results are given here. As part of the study, a base station GPS instrument was placed near OWDF-MW1. This provided a known location to reference all other GPS measurements (a common datum). GPS signals are altered by atmospheric conditions, which must be accounted for to get the most accurate measurements. Data recorded at a GPS base station at a known location allows the effect of atmospheric distortion to be calculated and removed from the GPS signals collected at unknown locations, thus providing an atmospheric correction.

During the study, the base station was in radio communication with the “rover” station, which measured the northing, easting, and elevation of the other wells. During the course of the survey,

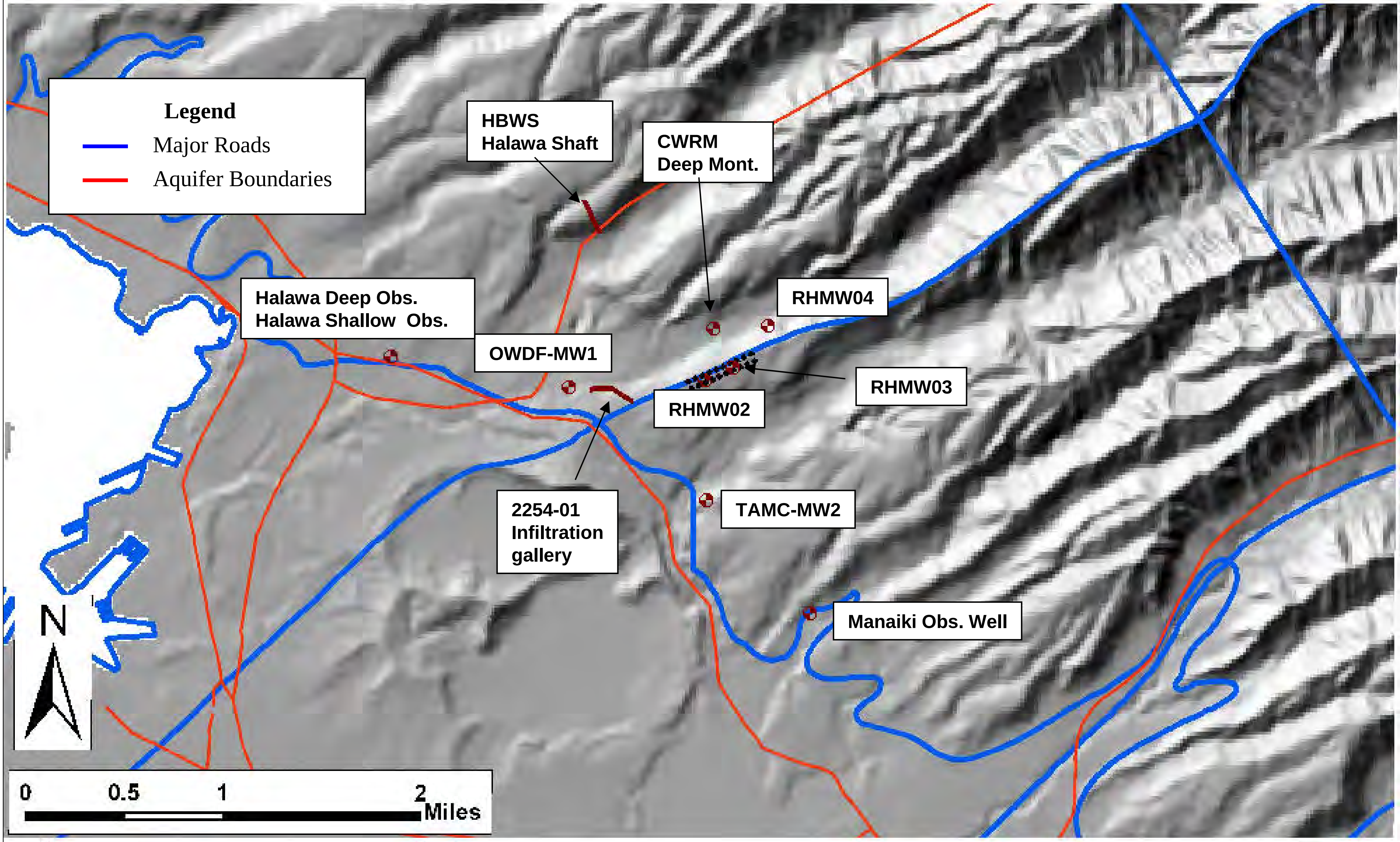

Figure 3

Locations of Wells Used in the 2006 Aquifer Test and Current Groundwater Flow Direction Analysis

Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

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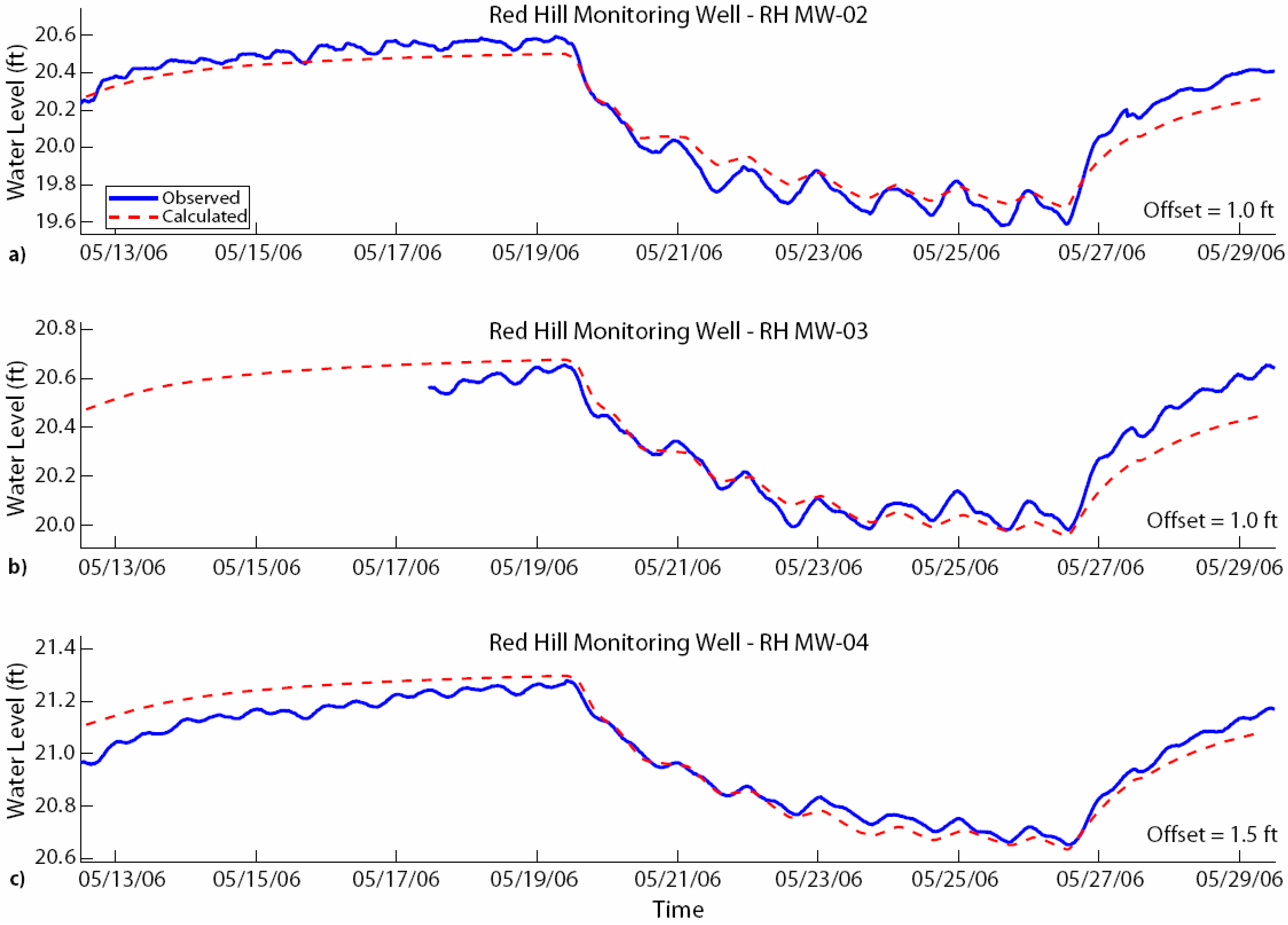

Figure 4

Offset Required to Match Simulated Water Levels to Measured Water Levels (Rotzoll and El-Kadi, 2006)

Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

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a recently validated survey bench mark, monument CHIGUI, was found near the site. The elevation of a temporary bench mark outside of Adit 3 was established in relationship to monument CHIGUI, becoming the central reference point or common datum for this survey. Table 1 below shows the assumed elevation and revised elevation of each surveyed point. For the purposes of the groundwater gradient evaluation it was important that all wells were referenced to a common datum. The datum selected for this study was Mean Tidal that was used for benchmark CHIGUI. Prior to the submission of the project summary report, the difference between the Mean Tidal vertical datum and NAVD 29 Mean Sea Level datum will be investigated and all TOC elevations will be referenced the NAVD 29 Mean Sea Level datum.

Table 1. GPS Survey Results Compared With Previously Surveyed TOC Elevations

Well Name	**State Well No.**	**2006 TOC Elev.**	**2009 GPS TOC Elev.**	**Elevation Difference**
Datum		**NAVD 29 Mean Sea Level**	**Mean tidal**	
		(ft above datum)	**(ft above datum)**	**(ft)**
RHMW04	-	313.03	312.34	-0.69
OWDF-MW1	-	138.94	138.38	-0.56
TAMC MW-2	-	179.91**	179.65	-0.26
CWRM Deep Mont. Well	2253-03	226.68	226.96	0.28
Halawa Deep Obs. Well	2255-40	60.00**	60.43	0.43
Halawa Shallow Obs. Well	2255-33	58.01	58.24	0.23
Manaiki Obs. Well	2153-09	61.05	61.26	0.21
Note: ** indicates estimated TOCs used in 2006 data set, not based on survey data.				

Notes:

GPS – Global Positioning System
TOC – Top of Casing
No.- Number
Elev.- Elevation
NAVD 29 – North American Vertical Datum, 1929
ft.- feet

The new GPS survey with the common datum resulted in changes in the relative TOC elevations between measured wells as shown in Table 1. For example following the survey, the water elevation difference between RHMW04 and OWDF-MW1 changed by 0.13 ft, whereas, the water elevation difference between RHMW04 and the CWRM Deep Monitoring Well changed by 0.97 ft. TEC could not find reliable elevation data for TAMC-MW2 and Halawa Deep Observation Well for the 2006 data set, so the previously used elevations were estimates. The 2009 GPS survey data are considered survey grade for these locations.

Table 2. Comparison of TOC elevations Used since 2006 and the Updated TOC Elevations Based on the GPS Survey and the 2009 Optical Survey

Well Name	2006 TOC Elev.	2010 Optical Elev.	Elevation Difference
Datum	**NAVD 29 Mean Sea Level**	**Mean tidal**	
	(ft above datum)	**(ft above datum)**	**(ft)**
OWDF-MW1	138.94	138.38	-0.56
RHMW01	102.51	102.27	-0.24
RHMW02	105.01	104.76	-0.25
RHMW03	121.31	121.06	-0.25
RHMW05	NA	101.55	NA

Notes:

GPS – Global Positioning System
TOC – Top of Casing
No.- Number
Elev.- Elevation
NAVD 29 – North American Vertical Datum, 1929
ft.- feet

On March 21 and March 22, 2010, a closed-loop optical survey was conducted of RHMW01 and RHMW05 within the Facility tunnel using OMDF-MW1 as the reference elevation. RHMW01 was also surveyed as part of the Remedial Investigation in 2006, as were RHMW02 and RHMW03. The 2006 TOC elevations of RHMW02 and RHMW03 were adjusted based on the elevation difference measured between the 2006 and 2010 surveys of well RHMW01. The results of the 2006 and the 2010 surveys are included with this report as Attachments B and C respectively.

1.5 REVISED GROUNDWATER FLOW DIRECTION AND GRADIENT

1.5.1 Geometric Calculations

The recent GPS and optical surveys referenced the TOC measuring point at each surveyed well to a common vertical datum. Using the revised TOC elevation data, the on-site groundwater flow direction and gradient were re-evaluated using previously collected groundwater elevation measurements. This was done for the three different pumping conditions created during the 2006 aquifer test (TEC, 2007). The data were collected during the following conditions and dates:

- May 18, 2006 when the pump in the U.S. Navy Well 2254-01 had been shut off for 5 days;
- May 25, 2006 when the pumps in the U.S. Navy Well 2254-01 had been pumping a maximum sustainable rate of approximately 10 mgd for 4 days; and
- May 30, 2006 when the pumps in the U.S. Navy Well 2254-01 had been pumping at a normal rate (about 4 mgd) for 5 days.

The groundwater flow direction and gradient computed from on-site wells were evaluated and compared to that computed in 2007 (TEC, 2007). The analysis was done using the EPA gradient calculation website (http://www.epa.gov/athens/learn2model/part-two/onsite/gradient4plus-ns.html). Wells RHMW02, RHMW03, RHMW04, and OWDF-MW1 were used in this analysis. These are the same wells used in the previous TEC report (2007) except that OWDF-MW1 was used instead of the U.S. Navy Well 2254-01. This was done because the EPA gradient calculation website assumes the data entered are from point sources and the water level measured at U.S. Navy Well 2254-01 is reflective of the water level in the infiltration gallery, a long linear source. Table 3 below compares the two sets of flow direction and gradient calculations for the dates selected.

Table 3. Groundwater Flow Direction and Gradient for Wells Located on the Facility Computed in 2006 and 2010

Date	**(TEC, 2006)**		**(TEC, 2010)**	
	Flow Direction[1]	**Gradient (ft/ft)**	**Flow Direction**[1]	**Gradient (ft/ft)**
May 18, 2006	180	0.00051	270	0.000089
May 25, 2006	306	0.0024	270	0.00015
May 30, 2006	184	0.00051	270	0.000093

Notes:

[1] – degrees measured from north, clockwise

ft/ft – Hydraulic gradient as feet per feet, rise to run

The substitution of OWDF-MW1 for 2254-01 excludes the large localized water level variations in 2254-01 that result from pump drawdown. With the revised TOC elevations and excluding the monitoring well 2254-01, the groundwater flow direction is to the west and the gradient is much shallower. To properly include the impact of the drinking water shaft on the water table elevation requires a two-dimensional contouring program, as described below.

1.5.2 Two-Dimensional Contouring

Calculating groundwater flow direction and gradient assumes that the points fit nicely into a plane. In reality this is rarely the case and the Red Hill region is no exception. To get a more accurate representation of the groundwater elevation surface, the well data were contoured using the Triangular Irregular Network (TIN) module of the Groundwater Modeling System (GMS). This software is actually a suite of the leading groundwater modeling codes. The MODFLOW and RT3D modules of GMS were used to perform the Tier 3 risk analysis modeling for this site (TEC, 2007). For the problem at hand, a polygon was digitized that encompassed the wells that were used in the regional flow analysis. The polygon was converted to TIN and the water level data from the wells was interpolated to the TIN using the natural neighbor method (Figure 5). This method looks "beyond" the boundary of the enveloping polygon to prevent errors at the edge of the TIN. Data for May 18, 25, and 30, 2006 were contoured and are shown in Figures 6 through 8 respectively. Water levels used for the contouring were from wells:

- OWDF-MW1;

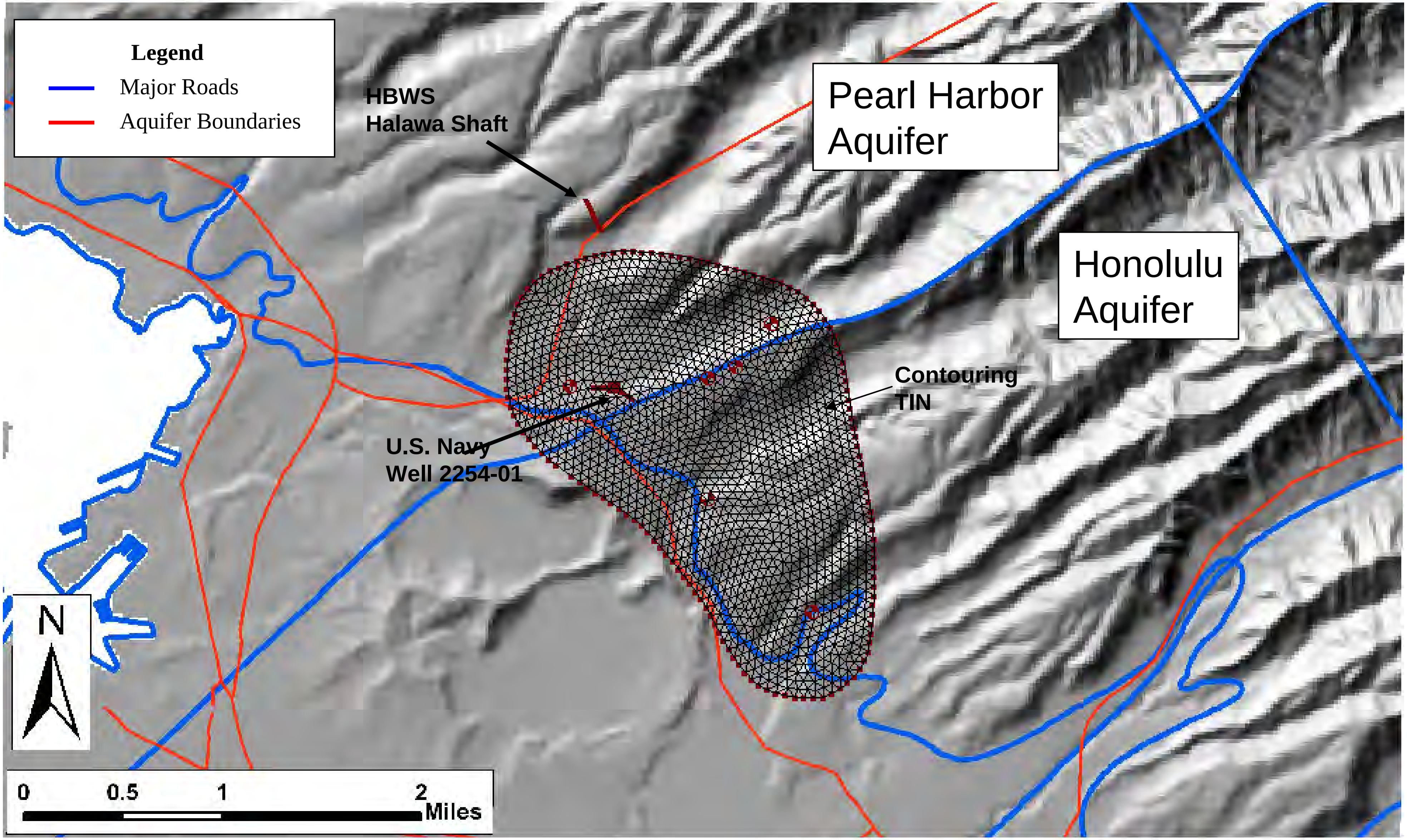

Figure 5.
TIN Used to Contour the Water Table at the Red Hill Region
Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

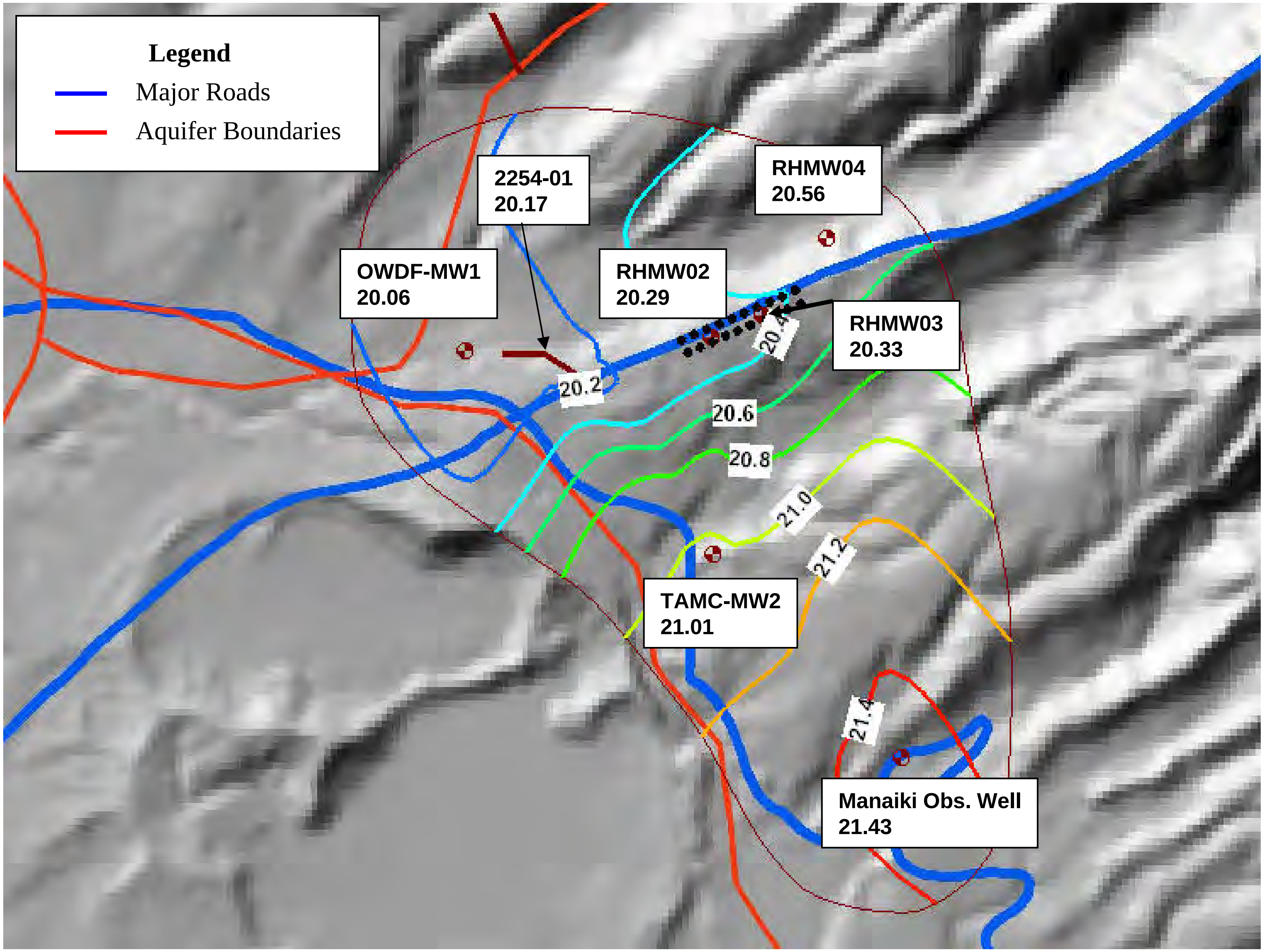

Figure 6.
Groundwater Elevation Contours Based on Water Levels Measured On May 18, 2006 (contour labels and groundwater elevations at each well shown in ft above mean tidal datum)
Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

N

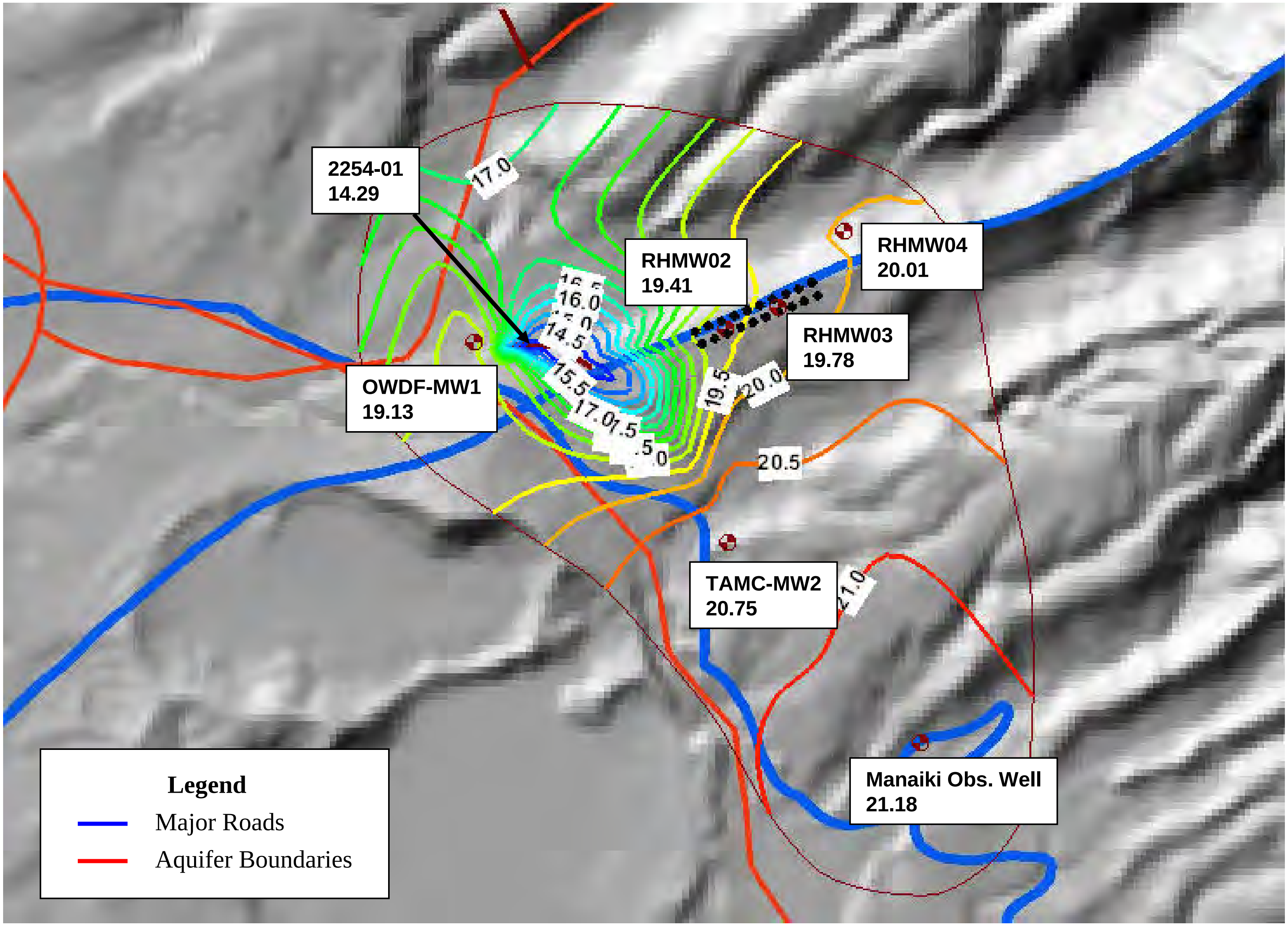

Figure 7.
Groundwater Elevation Contours Based on Water Levels Measured On May 25, 2006 (contour labels and groundwater elevations at each well shown in ft above mean tidal datum)

Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

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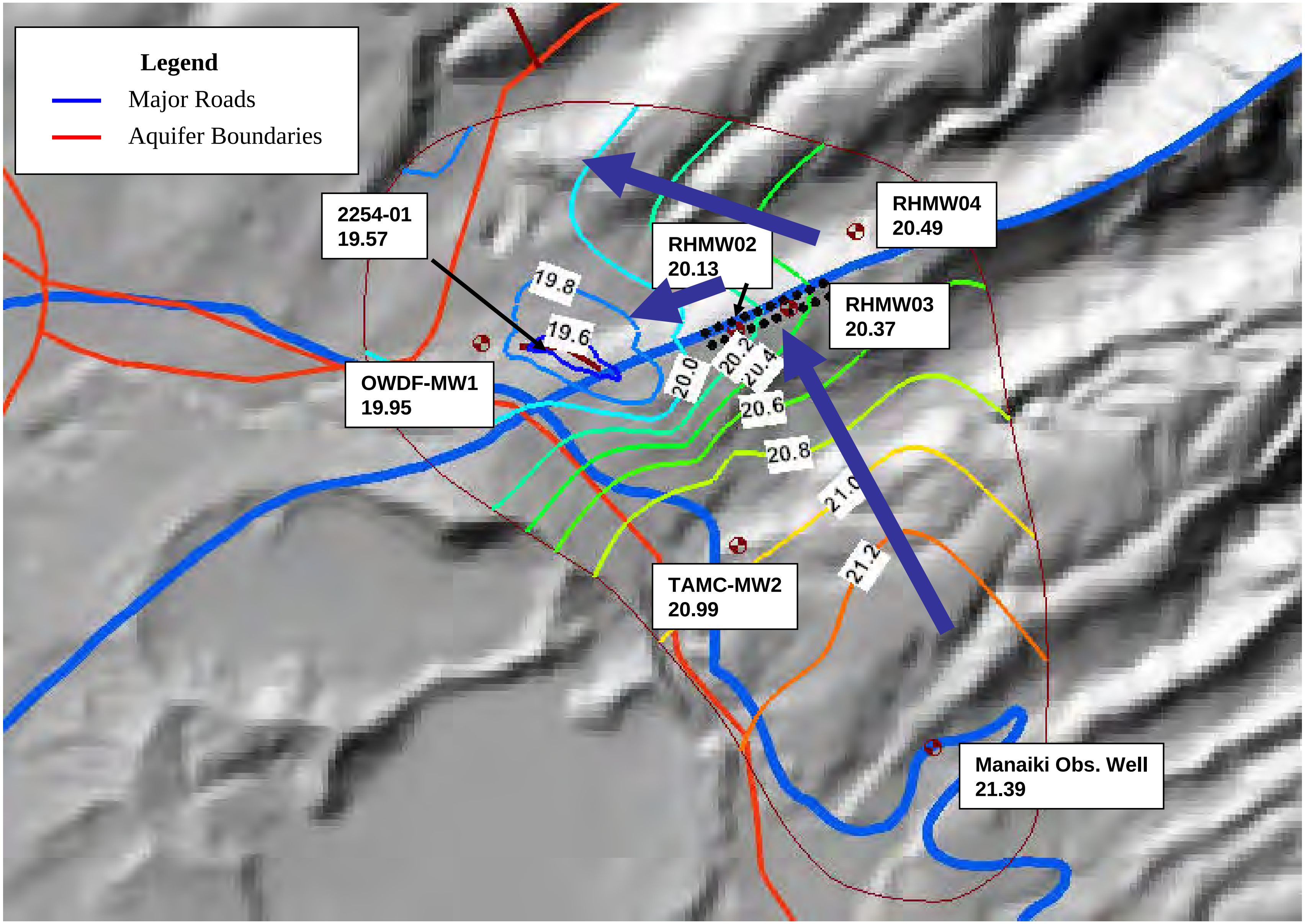

Figure 8.
Groundwater Elevation Contours Based on Water Levels Measured On May 30, 2006 (contour labels and groundwater elevations at each well shown in ft above mean tidal datum) (Blue arrows show interpreted groundwater flow directions)
Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

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- U.S. Navy Well 2254-01 (represented as a shaft by a series of closely spaced data points);
- RHMW02;
- RHMW03;
- RHMW04;
- TAMC-MW2; and
- The Manaiki Observation Well.

The Halawa observation wells were not included because there is an intervening flow barrier, probably the north Halawa valley fill, between these wells and the Facility, as observed in results of the 2006 aquifer test (TEC, 2007). CWRM Deep Monitoring Well was not included because of questionable water level elevations measured at this well. A recent evaluation of measurements taken during the 2006 aquifer test has shown a two-foot difference between the water elevations measured in the main CWRM well and co-located piezometer. The cause of this discrepancy has not been determined.

Assuming that the aquifer directly beneath the study area is horizontally isotropic, in which the hydraulic conductivity is the same regardless of the flow direction, groundwater will flow in a direction perpendicular to the groundwater equal-elevation contours. The data set is sparse, particularly at the southeast end of the polygon, but a generalized flow pattern becomes evident. In Figure 6, the data show that groundwater flows from southeast to the northwest.

Figure 7 shows the water table surface on May 25, 2006, when the pumps in the infiltration gallery at U.S. Navy Well 2254-01 are pumping at full capacity (approximately 10 mgd). As shown, there is a significant drawdown at the infiltration gallery increasing the southwestly groundwater flow component. However, a west-northwest regional flow component is evident in the vicinity of the USTs.

Figure 8 shows the water table surface on May 30, 2006, when pumps at the U.S. Navy Well 2254-01 were operating at normal capacity (approximately 4 mgd). On this figure arrows are drawn to show the dominant groundwater flow directions. In the vicinity of the USTs, as before, the gradient indicates a regional component of groundwater flow to the west northwest and a local component to the southwest. The gradient east of the Facility is approximately 0.00028 to the northwest. At the Facility and U.S. Navy Well 2254-01 there is a localized gradient of approximately 0.00022 to the southwest, less than one-tenth of the magnitude of the regional gradient.

1.6 IMPLICATIONS FOR THE TIER 3 RISK ASSESSMENT

The revised groundwater flow direction and gradient does not invalidate the Tier 3 Risk Assessment detailed in Appendix K of TEC (2007) that evaluates the Navy drinking water well 2254-01 as the receptor of concern. The groundwater model is the key component of the Tier 3 risk assessment that required re-evaluation based on recent information. Other assumptions and calculations used in the Tier 3 model have not changed. The model assumes a “mauka to makai” flow that runs parallel to the alignment of tanks, placing the northeast portion of the drinking water well 2254-01 directly down gradient from the underground storage tanks (USTs). This is the most conservative approach and most protective of the drinking water source.

The northwest regional flow places the HBWS Halawa Shaft, a major drinking water source for south Oahu, down gradient from the USTs. Results from a regional groundwater test in 2006 indicate no good hydraulic connection between wells on the northern edge of Halawa Valley and pumping from U.S. Navy Well 2254-01. Figure 9 shows the water levels monitored during the aquifer test. All wells monitored showed a good response to the induced drawdown at U.S. Navy Well 2254-01 (blue-green line) except the Halawa Deep and Shallow Observation wells. Figure 10 shows the well arrangement for this test and the locations of the valley fills that may pose a barrier to groundwater flow. The probable cause of this poor connection is thick sediments that have filled in the North Halawa Valley to depths well below the water table. In addition, the modeled natural attenuation rate indicates that the HBWS Halawa Shaft would not be threatened from a petroleum release from the Facility unless a free product plume moved in the direction of the HBWS Halawa Shaft. To date no free product plume has been detected.

1.7 CONCLUSIONS AND RECOMMENDATIONS

A re-evaluation of the groundwater flow direction and gradient in the vicinity of the Red Hill Facility shows a local flow direction from the USTs toward the drinking water well 2254-01 as expected. The gradient for this flow direction is approximately 0.00022 ft/ft. This evaluation also shows a regional component flowing to the northwest. The gradient for this flow direction is approximately 0.00028. With respect to the potential impact to the U.S. Navy Well 2254-01, the results of the Tier 3 Risk Assessment (TEC, 2007) still remain valid. It assumes a worst case scenario that the dominant groundwater flow direction places the infiltration gallery of 2254-01 directly down gradient from the USTs.

The northwest regional component of the groundwater flow may be transporting a petroleum plume or dissolved hydrocarbons in a direction that is not currently being monitored. Currently there are no compliance wells between the Halawa Shaft and the Facility to evaluate this possibility. For the HBWS Halawa Shaft to be threatened by contamination from the Facility a free product plume would have to be present within approximately 1200 ft of this drinking water source. The CWRM Deep Monitoring Well is not suitable for detecting a free product plume since the solid casing of this well extends about 50 ft below the water table. RHMW04 is not ideally located to monitor a northwest plume because it is located northeast of the USTs. In order to ensure petroleum components are not moving off-site along the northwest groundwater flow direction, it is recommended that at least two monitoring wells be installed to monitor any contamination that may be migrating off-site in that direction.

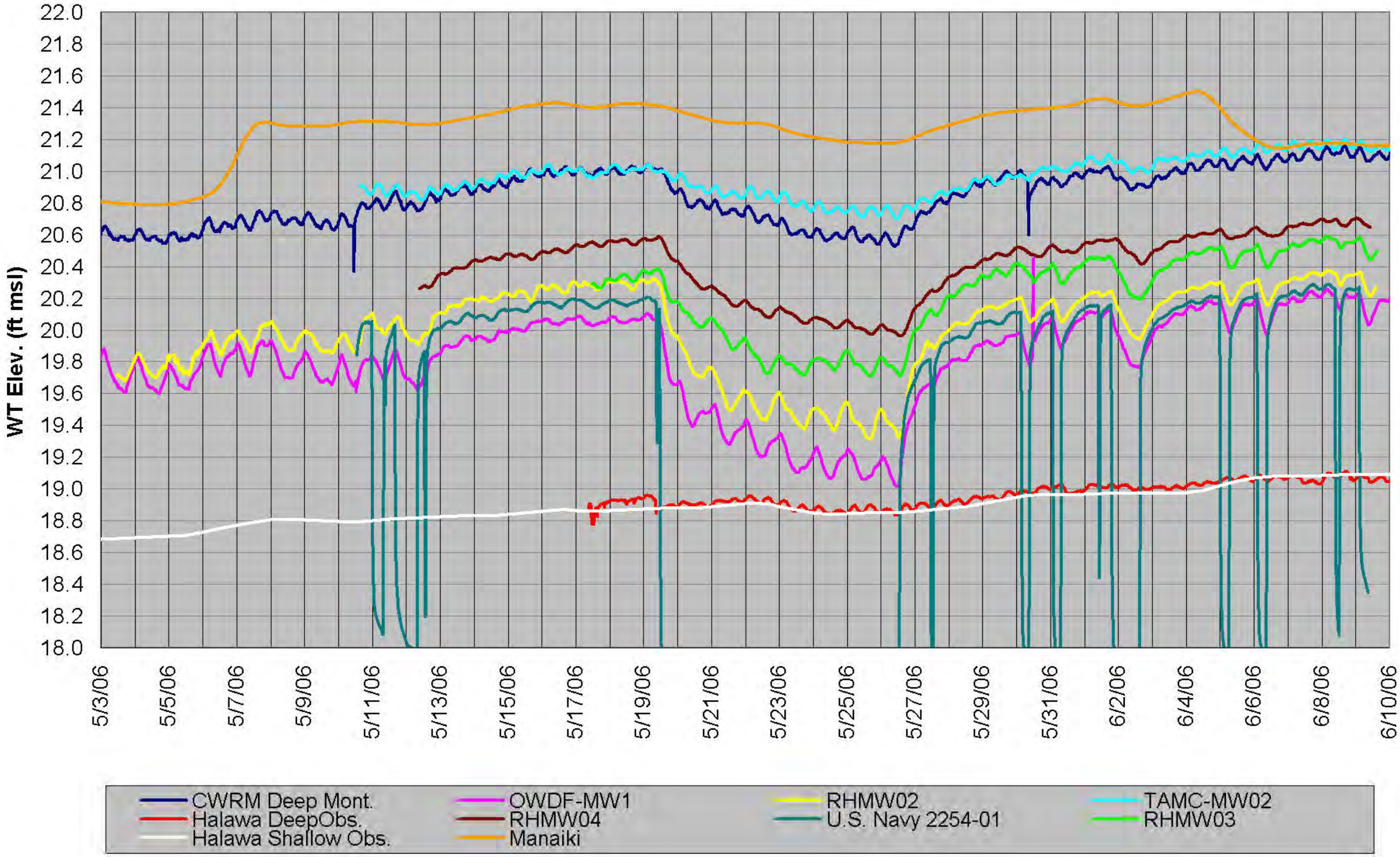

Figure 9.

Recorded Water Levels in Wells Monitored During the May 2006 Aquifer Test at Red Hill Updated Using New TOC Elevations

Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

N

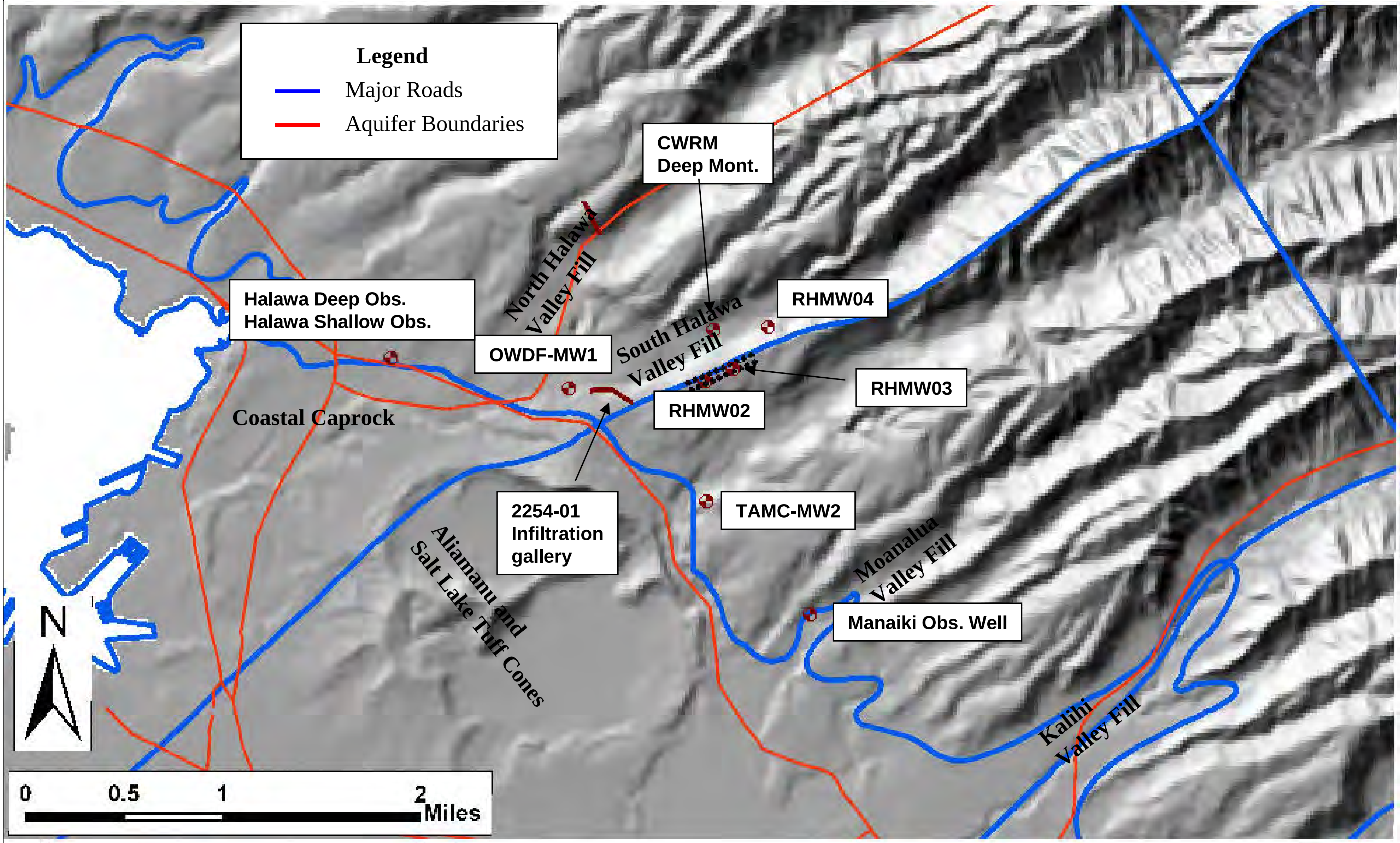

Figure 10
Locations of Monitoring and Observations Wells, and the Locations of Potential Barriers to Groundwater Flow
Groundwater Gradient Study Red Hill Bulk Fuel Storage Facility, Pearl Harbor, Hawaii

This letter report presents an interpretation of the groundwater flow direction and gradient in the Red Hill Bulk Fuel Storage Facility study area and surrounding region. The surrounding areas were included to assess what influence regional flow might have on contaminant transport from the facility. If you have any questions, please contact me at (808) 528-1445 or Rick Adkisson at that number or via his cell phone at (865) 742-2181.

Sincerely,
TEC Inc.

Robert B. Whittier
Senior Hydrogeologist

Att: Attachments A, B, and C

cc: Raelynn Della Salla
Robert Campbell
Carol Vollmer

References

AMEC, 2002. Red Hill Bulk Fuel Storage Facility Investigation Report, Prepared for NAVFAC Pacific, August 2002.

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Mink, J.F. and L. L. Lau, 1990. Aquifer Identification and Classification for O’ahu: Ground-Water Protection Strategy for Hawaii. Water Resources Research Center, University of Hawaii at Manoa. February 1990. Revised

TEC, 2007. Red Hill Bulk Fuel Storage Facility Final Technical Report, Pearl Harbor, Hawaii. Prepared for NAVFAC Pacific. 142 pages and Appendices. August 2007

Attachment A

GPS Elevation Survey of Red Hill Area Wells

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info@pacificgps.com

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October 13, 2009

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RE: ELEVATION SURVEY, RED HILL FUEL STORAGE FACILITIES

Bob and Richard,

This letter presents our findings for the elevation survey performed at the well heads located on and around the Red Hill area. The survey was performed using Trimble's survey grade GPS systems including an R7GNSS base station and R8GNSS rover receiver. The data was processed in Trimble Business Center software, version 2.1.

A GPS Base station was setup in the middle of the project area, close to well OWDFMW1. An RTK survey was conducted for each point with a minimum occupation time of 5 minutes at each well location except for the Maniki well. The Maniki well position was derived by collecting two independent 5 minute static survey sessions and post processing this data with GPS data collected at the base station. The vertical precision value is derived based on a 95% confidence level.

Observation locations were taken on the "north notch" of each well casing, where feasible. The well elevations for 2255-40, Halawa Shallow, and Maniki were calculated by taking a GPS observation at a location in the immediate vicinity and utilizing a level between the well casings and observation points.

Table 1 presents the well and associated point elevations in Hawaii State Plane, Zone 3, NAD 83 coordinates and both WGS-84 ellipsoidal heights (referenced to NAD 83) and Local Tidal elevations. The ellipsoidal heights were determined by the GPS observations. Local Tidal elevations were determined by referencing NGS class I monument CHIGUI and using Geoid model GEOID03. The NGS monument CHIGUI datasheet is attached for reference.

As a check for our base station location, a five hour static observation was recorded at the base and processed using the NGS Online Positioning User Service (OPUS). The OPUS results were based on rapid ephemeris information and were within our GPS derived base position by 0.032 feet in the vertical direction.

Table 1 - Red Hill Well Elevation Survey, (US Survey feet)

Well or Point Name	Northing	Easting	Local Tidal Elevation	Ellipsoid Height	Vertical precision	Description
ADIT3	74266.086	1671830.745	116.19	169.58	0.016	Nail in asphalt west of tunnel
RHMW04	75743.087	1677348.858	312.34	365.72	0.059	North Notch
OWDFMW1	74113.189	1672000.653	138.38	191.77	0.043	North Notch
2253-03	75654.495	1675870.469	226.96	280.34	0.046	North Notch
USGS Monument	74940.778	1667222.854	59.36	112.75	0.036	Monument at well 2255-40
2255-40			60.43	113.82	0.043	well casing
Halawa Shallow			58.24	111.62	0.043	well casing
TBM Maniki	68011.522	1678441.522	61.05	114.44	0.039	Nail 5' NW of Hydrant
Maniki			61.26	114.65	0.046	well casing
TAMC MW-2	71048.658	1675661.519	179.65	233.04	0.033	North Notch
Mon CHIGUI	73997.195	1668571.178	83.76	137.15	class 1	Monument, from datasheet
GPS Base Station	74143.366	1672049.537	137.38	190.76	0.032	Nail, NE of OWDFMW1

An updated Geoid model, GEOID 09, was recently made available by the National Geodetic Survey. The elevation difference between models GEOID03 and GEOID09 vary from 0.49 to 0.54 feet in the study area. Table 2 lists the values for GEOID03 and GEOID09 and the difference in values for each location.

Table 2 - Red Hill Well, Geoid Values (US Survey Feet)			
Well or Point Name	**GEOID 03 Height**	**GEOID 09 Height**	**GEOID03 - GEOID09**
ADIT3	51.90	51.37	0.53
RHMW04	52.19	51.64	0.54
OWDFMW1	51.90	51.37	0.53
2253-03	52.11	51.58	0.53
USGS Monument	51.75	51.21	0.54
2255-40	51.75	51.21	0.54
Halawa Shallow	51.75	51.21	0.54
TBM Maniki	51.91	51.41	0.50
Maniki	51.91	51.41	0.50
TAMC MW-2	51.90	51.41	0.49
Mon CHIGUI	51.77	51.23	0.54
GPS Base Station	51.90	51.37	0.53

Thank you for the opportunity to assist you in this project. Please call or email with any questions or comments.

Sincerely,

Ryan McGrath

Ryan McGrath
Director of Survey
Pacific GPS
(808) 538-7477
mcgrath@pacificgps.com

Attachment B

2006 Survey of On-Site Wells

2006 On-Site Well Survey

Horizontal Datum: NAD 83
Pearl Harbor Control Network Hawaii State Plane
Vertical Datum: NAVD 29 Mean Sea Level
Unit: Feet

Point Number	Northing	Easting	Elevation	Description
1	75742.64	1677345.57		RHMW-04
			312.83	RHMW-04 ground
			313.03	RHMW-04 top casing
			312.57	RHMW-04 top gauge

2	74041.08	1675059.16		RHMW-01
			102.33	RHMW-01 conc
			102.51	RHMW-01 top of casing
			102.41	RHMW-01 gauge

3	74282.05	1675639.24		RHMW-02
			105.64	RHMW-02 conc
			105.67	RHMW-02 top cover
			105.01	RHMW-02 gauge

4	74610.90	1676391.37		RHMW-03
			122.06	RHMW-03 conc
			122.11	RHMW-03 top rim
			121.31	RHMW-03 gauge

5	74006.92	1672560.73		2254-01
			105.79	2254-01 top cover
			105.76	2254-01 gauge "N"
			105.75	2254-01 gauge "S"

6	74202.61	1671757.38		MW9
			116.79	MW9 brass disk
			116.20	MW9 ground
			119.35	MW9 top casing
			118.91	MW9 gauge

7	74112.75	1671997.36		MW8
			138.94	MW8 top casing
			136.66	MW8 conc.
			138.57	MW8 gauge

Attachment C

Results of 2010 Optical Survey

RED HILL FUEL STORAGE FACILITIES, NAVFAC PACIFIC

DESCRIPTION	NORTHING	EASTING	ELEVATION	
ADIT3	74266.09	1671830.75	116.19	
ENTER	74222.06	1672009.76	114.50	Mag Nail at Entrance
OWDFMW1	74113.19	1672000.65	138.35	Top of 4" PVC
RHMW01	74041.12	1675062.48	102.32	Top of Cover
			102.21	Top of 1" PVC
RHMW05	73690.63	1674268.20	101.97	Top of Cover
			101.52	Top of 2" PVC

Note:
Units: U.S. Feet

Coordinates were established from Stations ADIT3 and GPS Base Station as established by Pacific GPS.

Elevations are based on a local tide and are referred to Station ADIT3 having an elevation of 116.19 feet as established by Pacific GPS.

Underlined elevation was established by RMTC using differential leveling from Station ADIT3.

2010 On-Site Well Survey

Attachment B

Risk Assessment/Groundwater Re-evaluation Considerations

Tier 3 Risk Assessment/Groundwater Re-evaluation Considerations

The Facility SSRBL (i.e., 4,500 μg/L for TPH) established by the Tier 3 Risk Assessment/groundwater model (Tier 3 RAGWM) was based on the following assumptions:

1. the concentration of dissolved fuel hydrocarbons in the groundwater is limited to 4,500 μg/L, the computed maximum solubility resulting from JP-5 fuel in direct contact with the groundwater surface;
2. that the groundwater flows “mauka to makai”(i.e., mountain to ocean), a direction that places the U.S. Navy Well 2254-01 directly down gradient from the USTs; and
3. the dissolved fuel hydrocarbons will degrade at a rate that was modeled using the reactive transport model code RT3D (the modeled bulk degradation rate was about 0.009 per day).

A TPH-DRO average concentration observed during Round 13 (October 2008) between the normal and duplicate sample of 5,420 μg/L at RHMW02 tends to indicate that Assumption 2 above could be invalid because no free product has been measured during monthly monitoring. To answer these and other related questions, a re-evaluation of the Tier 3 RAGWM was performed. This re-evaluation looked at three basic questions:

1. Is the assumption that 4,500 μg/L is the maximum possible TPH concentration resulting from a release of JP-5 to the water table still valid?
2. Was the modeled groundwater flow direction correct?
3. If either of the two preceding assumptions is found to be invalid, what impact does this have on the risk posed to drinking water sources by contamination from the USTs at the Facility?

If Assumption 1 above is correct, the October 2008 TPH-DRO average concentration of 5,420 μg/L implies that petroleum product was directly in contact with groundwater in the vicinity of RHMW02 and that groundwater samples at that RHMW02 may contain un-dissolved product. However, oil-water interface measurements collected at RHMW02 did not detect measurable product at this location. If Assumption 1 was determined to be invalid, this would indicate that the modeled distance a dissolved plume would travel beyond a stabilized free-product plume prior to the TPH concentration degrading to less than the HDOH EAL concentrations could be erroneous.

Question 1 - Maximum TPH Solubility Assessment

To answer these questions, various studies and evaluations were undertaken. The first study involved dual analysis of the groundwater collected from certain Facility wells. This included the TPH-DRO and TPH-GRO analysis that has been part of field sampling protocol since long-term monitoring started at the Facility. A second analysis was done using a protocol developed by the Massachusetts Department of Environmental Protection (MADEP) [MADEP, 2002]. This analysis breaks down TPH into two categories with each divided into three different fractions based on a range of carbon numbers (C). The breakdown is as follows:

- Volatile Petroleum Hydrocarbons (VPH) includes the TPH compounds that range from C5 to C12 and are subdivided into:
    - C5-C8 aliphatics
    - C9-C10 aromatics

    - C9-12 aliphatics, but omits benzene, ethylbenzene, toluene, xylenes, (BTEX) methyl tert-butyl ether (MTBE), and naphthalene
- Extractable Petroleum Hydrocarbon (EPH) includes TPH compounds that range from C9 through C26 and are subdivided into:
    - C11-C22 aromatics
    - C9-C18 aliphatics
    - C19-C36 aliphatics, but omits the 17 polycyclic aromatic hydrocarbons (PAHs) analyzed using Method SW8270SIM

The MADEP VPH analysis covers a slightly larger carbon range than TPH-GRO (VPH covers C5-C12, while TPH-GRO covers C6-C10). The MADEP EPH analysis covers the carbon range of C9-C36, while TPH-DRO is generally limited to the carbon range of C9-C26.

Another major difference between TPH-DRO analyzed using method SW8015B and MADEP EPH analysis is a silica gel filtering step. Fuel hydrocarbons that dissolve into groundwater from fuels are non-polar while naturally occurring organics and less toxic hydrocarbon breakdown byproducts are polar compounds. The MADEP EPH analysis adds a silica gel column in the analysis string that removes the polar compounds from the sample aliquot effectively removing these interfering, less toxic breakdown compounds.

In Round 16 (July 2009), the US Navy included MADEP VPH/EPH fractionation analyses along with TPH, to better understand the chemistry of the TPH plume under the Facility, and to re-assess the risk associated with the plume. Additional TPH fractions can be evaluated for risk because MADEP has determined toxicity reference doses (RfDs) for these specific fractions that make up the TPH-GRO and TPH-middle distillate ranges (TPH-DRO). For Round 16, MADEP fractions for VPH and EPH were measured along with TPH-GRO and TPH-DRO in split samples from RHMW01, RHMW02, and RHMW03.

The results from samples collected at RHMW02 showed that an overall average of approximately 27 percent of the TPH-DRO result was from polar, non-fuel organic compounds (Table 1). If this 27% average was used to adjust the observed average for only fuel-related compounds, then the TPH-DRO Round 13 concentration of 5,420 µg/L would be reduced to 3,957 µg/L. This analysis strongly suggests the actual observed concentration of fuel hydrocarbons at RHMW02 is less than the computed maximum solubility of 4,500 µg/L. Therefore, the established SSRBL for TPH of 4,500 µg/L appears to be valid.

Table 1. Total Petroleum Concentrations, MADEP Compared to USEPA Method 8015

Monitor Well ID[1]	MADEP VPH[2] (μg/L)	TPH-GRO[4] (μg/L)	MADEP EPH[3] (μg/L)	TPH-DRO[5] (μg/L)	Average[6] Percent Non-Fuel Compounds
RHMW02 and RHMW02D	Average VPH 455	<30	Average EPH 545	1,375	27%

[1] RHMW02D is the field duplicate sample of RHMW02
[2] MADEP VPH – Massachusetts Department of Environmental Protection Volatile Petroleum Hydrocarbons (VPH)
[3] MADEP EPH – Massachusetts Department of Environmental Protection Extractable Petroleum Hydrocarbons (EPH)
[4] TPH-GRO – Total Petroleum Hydrocarbons, Gasoline Range Organics by USEPA Method 8015 Modified
[5] TPH-DRO – Total Petroleum Hydrocarbons, Diesel Range Organics by USEPA Method 8015 Modified
[6] Average Percent Non-Fuel Compounds computed by [1,375 – (455 + 545)/1,375] x 100 = 27% average percentage of Non-Fuel Compounds
μg/L – Micrograms per liter
<30 – The compound was not detected, the value is the method detection limit

Further evidence of interference from non-fuel hydrocarbons [i.e., tentatively identified compounds (TICs)] was found during Round 18 sampling conducted initially in January 2010, with resample events at RHMW02 for TPH-DRO only conducted in February and March 2010 (Attachment D).

The TPH-DRO chromatographs were reviewed and it was found that a significant fraction of the measured concentration was from TICs that were not associated with fuel hydrocarbons. Table 2 indicates that on average, non-fuel related compounds accounted for approximately 35 percent of the total TPH-DRO concentrations. This data further supports the validity of the established SSRBL for TPH of 4,500 μg/L.

Table 2. Contribution of TICs to TPH-DRO Results

Well	Date	TPH-DRO (μg/L)	TPH-DRO Corrected for TICs (μg/L)	Percent Non-Fuel Compounds
RHMW02	1/26/2010	2,130	1,740	18.3%
RHMW02D	1/26/2010	3,410	2,110	38.1%
RHMW02	2/23/2010	8,650	3,470	59.9%
RHMW02D	2/23/2010	6,910	2,930	57.6%
RHMW02	3/30/2010	2,630	2,630	0.0%
RHMW02D	3/30/2010	2,350	2,350	0.0%
RHMW05	1/26/2010	2,060	541	73.7%
Overall Total Average	**-**	**-**	**-**	**35%**

A related consideration pertains to the toxicity of the non-fuel organic compounds. The non-fuel hydrocarbon fraction of the TPH-DRO results that were captured by the silica gel column during the MADEP EPH analysis should be considered when evaluating relative toxicity. In a letter report to the Air Force by Zemo and Associates (2008) (Attachment E), it was estimated that the toxicity of the polar organics filtered out by the MADEP EPH analysis are approximately 24 times less toxic than the most toxic fraction of the petroleum-related compounds.

In summary, polar compounds that likely make up a significant fraction of the highest historically detected TPH-DRO concentrations at RHMW02 pose a much lower health risk than petroleum hydrocarbons being monitored from the Facility. In addition, these polar compounds and/or TICs provide an explanation as to why, absent detailed analysis, the calculated JP-5 solubility SSRBL for TPH of 4,500 μg/L seemed to have been exceeded during the Facility groundwater sampling Rounds 13 and 18 without the observation of free product in that monitoring well. Thus, the established SSRBL for TPH of 4,500 μg/L still appears to be valid.

Question 2 – Modeled GW Flow Direction & Question 3 – Validity of the Tier 3 Risk Assessment

As indicated in Attachment A, the revised groundwater flow direction and gradient validates and supports the existing Tier 3 Risk Assessment. This is because, with respect to the potential risk to the US Navy Well 2254-01, the results of the Tier 3 Risk Assessment are still valid since it assumes a worst case scenario that the dominant groundwater flow direction places the US Navy Well 2254-01 infiltration gallery directly down gradient from the USTs.

Attachment C

MADEP Letter Report

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March 26, 2010

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Subject: MADEP Risk Assessment Letter Report
Red Hill, Pearl Harbor, HI
Contract #N47408-04-D-8514, Task Order 54

1.1 INTRODUCTION

This Letter Report was prepared for the Naval Fleet Engineering Service Center (NFESC) and the Pearl Harbor Naval Base Fleet Industrial Supply Center (FISC) by TEC Inc. (TEC) under contract N47408-04-D-8514, Task Order 0054. As part of Task Order 0054, TEC is providing environmental compliance services to FISC at the Red Hill Bulk Fuel Storage Facility (the Facility), associated with past releases of petroleum hydrocarbons to the subsurface bedrock and underlying groundwater aquifer.

1.2 SITE DESCRIPTION

The Facility includes twenty - 12.5 million gallon (Mgal) underground storage tanks (USTs) located within the Red Hill Ridge, Halawa Valley, Hawaii. The Facility also includes a series of tunnels and pipelines which deliver fuel to and from Pearl Harbor Naval Base (Figure 1). The Facility was constructed prior to World War II to support naval activities in the Pacific.

The USTs were constructed in the field using mining techniques, and are deferred from many Federal and State UST program requirements. According to records, the main fuel types stored at the Facility have been diesel oil, Navy Special Fuel Oil (NSFO), Navy Distillate (ND), Jet Propulsion Fuel 5 and 8 (JP-5 and JP-8), and F-76 (diesel marine fuel). In addition, Tank 17 contained Aviation Gasoline (AVGAS) and Motor Gasoline (MOGAS) between 1964 and 1969; and Tank 18 contained AVGAS between 1964 and 1968.

A review of the Facility records, which were classified until 1995, indicated that several USTs have been repaired over the years and may have released petroleum to the environment. This situation could potentially threaten drinking water aquifers. The Facility is approximately 100 feet above the basal groundwater table on the boundary of the Waimalu and Moanalua Aquifer Systems of the Pearl Harbor and Honolulu Aquifer Sector, respectively.

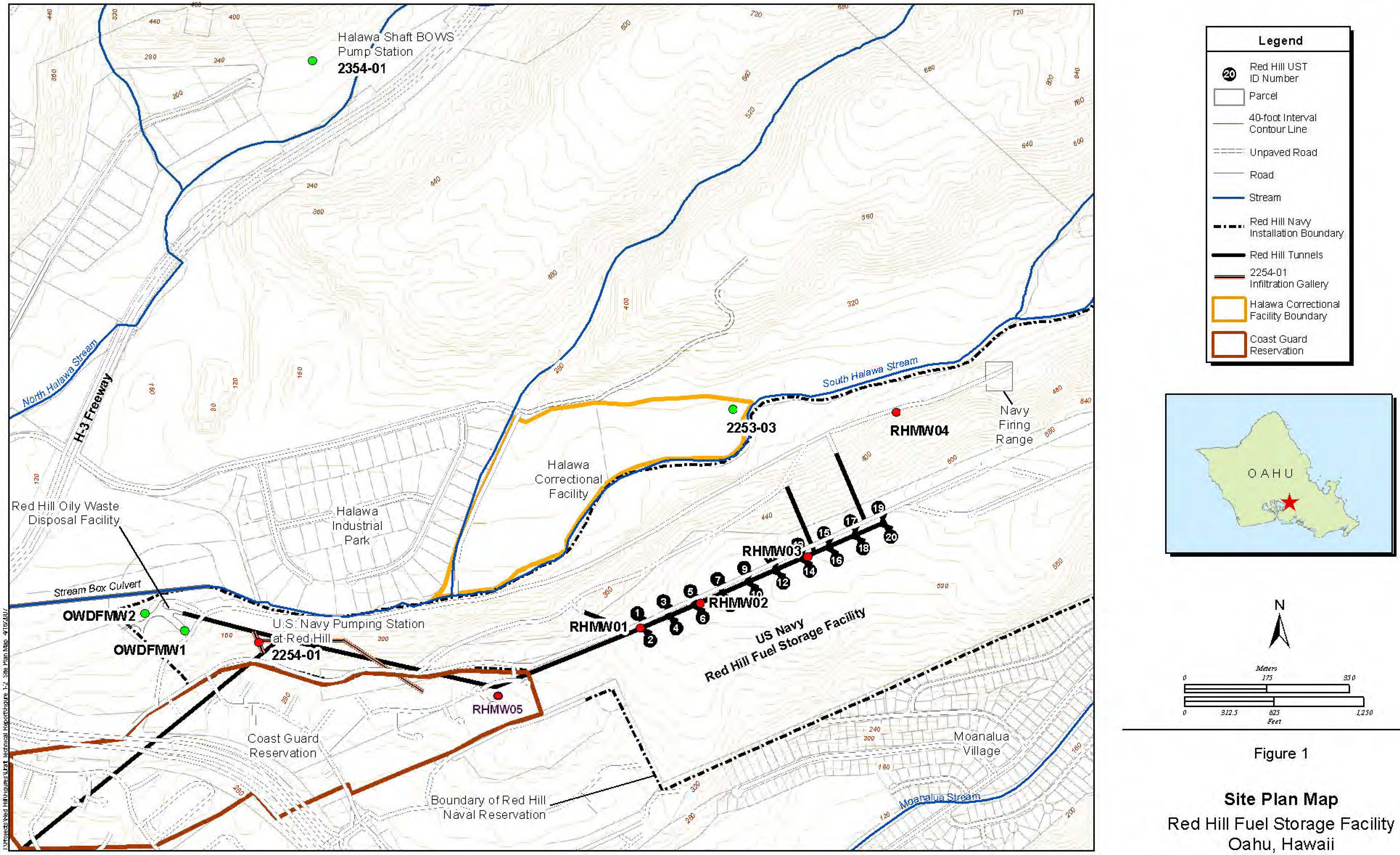


Figure 1

Site Plan Map

Red Hill Fuel Storage Facility
Oahu, Hawaii

Both aquifers are sources of potable water for several public water systems (Figure 2). Most notably, the U.S. Navy Well 2254-01, is located approximately 3,000 feet from Facility USTs and is permitted to pump approximately 4.6 million gallons per day (mgd) of potable water from a submerged infiltration tunnel. This tunnel extends approximately 1,280 feet across the water table and supplies the Pearl Harbor Water System.

1.3 BACKGROUND

1.3.1 Summary of Previous Investigations

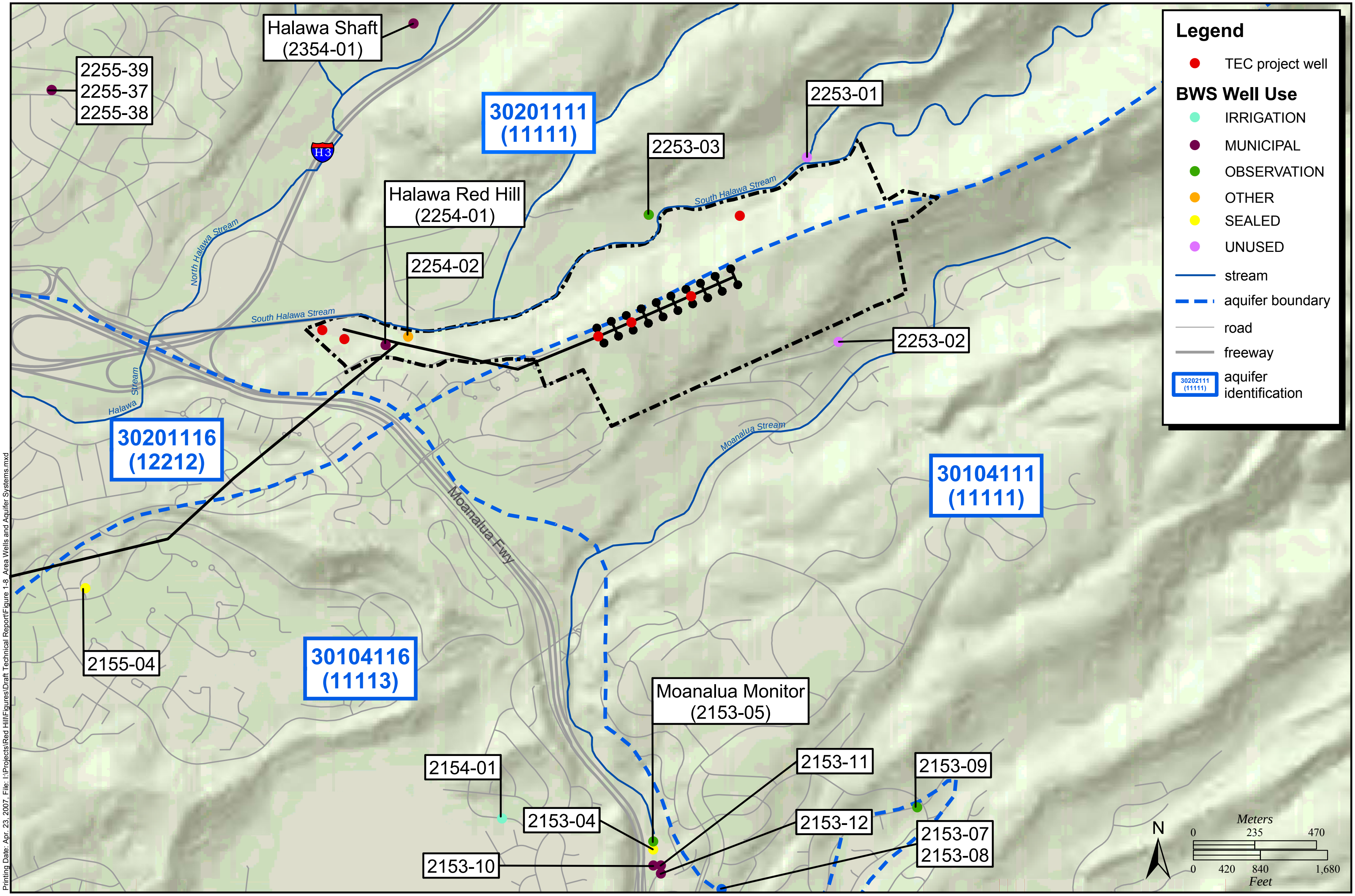
In 2002, the U.S. Navy initiated a Site Investigation (SI), conducted by AMEC Earth and Environmental, Inc. (*AMEC. 2002. Red Hill Bulk Fuel Storage Facility Investigation Report,* Prepared for NAVFAC Pacific, August 2002) at the Facility. Rock core samples were collected from directly beneath the Facility USTs and groundwater samples were collected from a single well installed within the lower access tunnel. Results indicated that petroleum had been released from Facility USTs, as observed in core samples, and in groundwater samples. After evaluating the results of the SI, the State of Hawaii, Department of Health (HDOH), Solid and Hazardous Waste Branch (SHWB) requested that quarterly groundwater monitoring commence, a Tier 3 risk assessment be conducted to evaluate the risk to the U.S. Navy pumping well at Red Hill, and a contingency plan be developed to ensure the protection of the U.S. Navy pumping well at Red Hill from future contamination.

The U.S. Navy initiated quarterly groundwater sampling at the existing monitoring well (formerly MW1, currently RHMW01) and at the U.S. Navy well 2254-01. Dawson Group, Inc. (*Dawson Group, Inc. 2006. Fourth Quarter 2005 Groundwater Sampling Report, Red Hill Fuel Storage Facility, Hawaii*. February 2006) conducted the first four sampling events in February 2005, June 2005, September 2005, and December 2005 (Rounds 1 through 4).

1.3.1.1 TEC Inc. Site Investigation and Risk Assessment (2004 to 2006)

In 2004, TEC was tasked to conduct a SI, Risk Assessment, and produce a contingency plan in the event that contamination from the Facility required closure of nearby drinking water wells. As part of this site investigation, groundwater monitoring well RHMW02 was installed directly upgradient from Tanks 5 and 6, and groundwater monitoring well RHMW03 was installed directly upgradient of Tanks 13 and 14. RHMW04 was installed in a location assumed to be upgradient of the tanks to measure background concentrations of contamination to ensure an offsite plume is not contributing to the contamination detected at the Facility. In addition, groundwater monitoring well RHMW2254-01 was installed within the U.S. Navy Well 2254-01 infiltration gallery.

The purpose of installing these additional wells was to divide the Facility into three groundwater sections so that inadvertent fuel releases from each section could be detected by the associated well. Two additional rounds of groundwater samples (Round 5 and 6) were collected and analyzed for risk assessment purposes. Groundwater samples were analyzed for Volatile Organic Compounds (VOCs) by United State Environmental Protection Agency (USEPA) Method SW 8260B, Total Petroleum Hydrocarbons quantified as Gasoline Range Organics (TPH-GRO) and Diesel Range Organics (TPH-DRO) by USEPA Method SW8015B, Semi-Volatile Organic Compounds (SVOCs) by USEPA Method SW8270C, and lead by USEPA Method SW6010B. Samples were validated for decision making and risk assessment.



Printing Date: Apr. 23, 2007, File: I:\Projects\Red Hill\Figures\Draft Technical Report\Figure 1-8. Area Wells and Aquifer Systems.mxd

Figure 2
Area Wells and Aquifer Systems
Red Hill Fuel Storage Facility
Oahu, Hawaii

TEC inc

Source Data:
City & County of Honolulu,
GIS base layers
DLNR Board of Water Supply,
2005 water supply well IDs

In 2006, TEC conducted a Tier 1, Tier 2, and Tier 3 Human Health Risk Assessment for the Facility using the results from the SI described above (*TEC, 2007. Red Hill Bulk Fuel Storage Facility, Final Technical Report, Pearl Harbor, Hawaii.* August 2007). The Tier 1 risk screening assessment was conducted for groundwater to determine compounds of potential concern (COPCs).

The Tier 1 risk assessment determined that groundwater beneath the Facility did not meet standards for residential potable water use and that naphthalene, TPH-GRO, tetrachloroethylene, 1,2,-dichloroethylene, trichloroethyelene, and lead should be evaluated further as COPCs.

A Tier 2 Risk Assessment was conducted to evaluate migration pathways for contaminants. It was determined that there was no potential seepage of leachate or product to the ground surface or surface water in the vicinity of the Facility because the underlying water table is between 80 and 220 feet below the surrounding valley floors. The risk assessment also concluded that the soil vapor migration pathway was not a significant concern. Finally, it was determined that since groundwater is not used directly beneath the Facility; there were no current risks associated with hydrocarbon concentrations detected in monitoring wells located within the Facility.

Several potable water production wells are located within a 1.5 mile radius from the Facility. The Honolulu Board of Water Supply (HBWS) Halawa Shaft (2354-01) is approximately 5,000 feet to the northwest of the Facility. HBWS Moanalua Wells (2153-10, -11 and -12) are located approximately 8,500 feet south of the Facility. The U. S. Navy drinking water well 2254-01 is located approximately 4,000 feet to the west of the Facility. Groundwater sample results from RHMW 2254-01 indicated that this pathway was not complete at that time.

In order to evaluate the potential for these groundwater supply wells to be contaminated in the future from leaking USTs at the Facility, TEC conducted a Tier 3 assessment of future risk to these potable water production wells. A site-specific conceptual model was used that considered particle mass degradation of hydrocarbon compounds in both oxygenated and anaerobic groundwater. TEC used the Reactive Multispecies Transport in 3-Dimensions (RT3D) to model solute (i.e., dissolved contaminant) transport and natural attenuation of hydrocarbons utilizing the groundwater flow solution produced by the MODFlow modeling code.

RT3D models the natural attenuation of hydrocarbons using the stochiometry of the chemical reactions and estimated kinetic constants that govern the rate at which these chemical reactions occur. The model inputs were based on experimental or empirically defined values for chemicals of concern (COCs). Based on screening assessments of transport properties, worst case initial concentrations, and chemical toxicities or action levels, TEC determined that for the fuel currently stored at the Facility, benzene and TPH (i.e., TPH-DRO and TPH-GRO) were the pertinent COCs because these would be observed first in the U.S. Navy Well 2254-01 at levels of concern.

The results of the Tier 3 Risk Assessment indicated that fuel product must be present on the groundwater in a plume extending to within approximately 1,100 feet of the U.S. Navy Well 2254-01 infiltration gallery in order for dissolved contaminants in groundwater to present a potentially unacceptable risk to the Pearl Harbor Water System. The model indicated that TPH would be the first COC to reach unacceptable concentrations in this scenario.

Action levels in groundwater from monitoring wells within the Facility were set at the solubility limit of TPH and benzene (assuming that JP-5 was the fuel released), as a way of estimating whether fuel was present on the water table nearby. JP-5 COC Action Levels from this study are contained in the Facility's Groundwater Protection Plan (*TEC, 2008. Red Hill Bulk Fuel Storage Facility, Final Groundwater Protection Plan, Pearl Harbor, Hawaii.* January 2008) as site-specific risk based levels (SSRBLs) and presented below. These site-specific Action Levels or SSRBLs were based upon the assumption that fuel (i.e., free product) would be present on groundwater at Facility monitoring wells:

- The site-specific Action Level (solubility limit) for TPH resulting from a JP-5 release was 4.5 milligrams per liter (mg/L); and
- The site-specific Action Level (solubility limit) for benzene resulting from a JP-5 release was 0.75 mg/L.

1.3.1.2 TEC Inc. Long-Term Groundwater Monitoring (2006-2009)

Based on release response requirements from HDOH, the U.S. Navy has conducted quarterly groundwater monitoring events following the SI (*TEC, 2007. Red Hill Bulk Fuel Storage Facility, Final Technical Report, Pearl Harbor, Hawaii.* August 2007). A total of 16 Rounds of groundwater monitoring have been conducted through July 2009. Prior to Round 16, samples were analyzed for TPH-DRO and TPH-GRO by USEPA Method 8015, VOCs by USEPA Method 8260, Polynuclear Aromatic Hydrocarbons (PAHs) by USEPA Method 8270C SIM, and dissolved lead by USEPA Method 8020. Results from these rounds have indicated TPH-DRO is consistently present in RHMW02 and RHMW01. In Round 13, TPH-DRO exceeded the Groundwater Protection Plan Category 4 Action Level, which required the U.S. Navy to evaluate concentrations in surrounding wells, and install an additional monitoring well (RHMW05) between the Facility and the U.S. Navy Well 2254-01.

In Round 16 (July 2009), the U.S. Navy included fractionation analyses for TPH by the protocol developed by Massachusetts Department of Environmental Protection (MADEP), *Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach*, Policy #WSC-02-411 (MADEP, 2002), to better understand the chemistry of the TPH plume under the Facility, and to re-assess the risk associated with these plumes.

Additional TPH fractions can be evaluated for risk because MADEP has determined toxicity reference doses (RfDs) for these specific fractions that make up the TPH-gasolines and TPH-middle distillate ranges (including diesel). For Round 16, MADEP fractions for Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH) were measured along with TPH-GRO and TPH-DRO in split samples from RHMW01, RHMW02, and RHMW03.

The results are provided for comparison in Table 1 below.

Table 1. Total Petroleum Concentrations, MADEP Compared to USEPA Method 8015

Monitor Well ID	MADEP VPH (µg/L)		TPH-GRO (µg/L)	MADEP EPH (µg/L)		TPH-DRO (µg/L)
RHMW01	Total VPH	<100	<30	Total EPH	<100	248
	C5-C8 Aliphatics	<100		C11-C22 Aromatics	<100	
	C9-C10 Aromatics	<100		C19-C36 Aliphatics	<100	
	C9-C12 Aliphatics	<100		C9-C18 Aliphatics	<100	
RHMW02	Total VPH	420	<30	Total EPH	540	1,450
	C5-C8 Aliphatics	<100		C11-C22 Aromatics	270	
	C9-C10 Aromatics	420		C19-C36 Aliphatics	<100	
	C9-C12 Aliphatics	<100		C9-C18 Aliphatics	270	
RHMW02D[1]	Total VPH	490	<30	Total EPH	550	1,300
	C5-C8 Aliphatics	<100		C11-C12 Aromatics	280	
	C9-C10 Aromatics	490		C19-C36 Aliphatics	<100	
	C9-C12 Aliphatics	<100		C9-C18 Aliphatics	270	
RHMW03	Total VPH	<100	<30	Total EPH	<100	<150
	C5-C8 Aliphatics	<100		C11-C22 Aromatics	<100	
	C9-C10 Aromatics	<100		C19-C36 Aliphatics	<100	
	C9-C12 Aliphatics	<100		C9-C18 Aliphatics	<100	

[1] RHMW02D is the field duplicate sample of RHMW02
MADEP VPH – Massachusetts Department of Environmental Protection Volatile Petroleum Hydrocarbons (VPH)
MADEP EPH – Massachusetts Department of Environmental Protection Extractable Petroleum Hydrocarbons (EPH)
TPH-GRO – Total Petroleum Hydrocarbons, Gasoline Range Organics by USEPA Method 8015 Modified
TPH-DRO – Total Petroleum Hydrocarbons, Diesel Range Organics by USEPA Method 8015 Modified
µg/L – Micrograms per liter
<100 – The compound was not detected, the value is the method detection limit

1.3.2 MADEP EPH/VPH versus USEPA Method 8015 Modified TPH-DRO/GRO

In order to estimate risk associated with TPH as a mixture, MADEP derived toxicity-based reference doses for specific fractions of EPH and VPH. In addition, MADEP developed specific testing methodologies to ensure that they were measuring the correct fraction and not other components of the mixture that were not petroleum hydrocarbons. In the development of EALs for petroleum mixtures in groundwater, HDOH used toxicity factors developed by MADEP as an approximation of toxicity factors for more widely available EPA Method 8015 Modified (TPH-DRO and TPH-GRO) (HDOH, 2005). Attachment 1 provides additional discussion regarding MADEP vs. Method 8015 analytical methods.

In general, MADEP VPH analytical results should approximate TPH-GRO analysis results, and MADEP EPH analytical results should approximate TPH-DRO analysis results. However, there are several variations in the methods that can account for observed differences in concentrations associated with these analytical methods as described below:

EPH vs. TPH-DRO:

1. EPH Method measures extractable hydrocarbons from C9 to C36, but does not include 17 PAHs. TPH-DRO includes the 17 PAH and is generally limited to C9 through C26 extractable hydrocarbons.
2. The EPH Method includes a silica gel cleanup to remove biogenic interferences that can cause high biases or “false positives”. This clean-up process removes polar compound

interferences such as breakdown products (e.g., oils, sugars, and fatty acids) from the extract without affecting the non-polar petroleum hydrocarbons. This silica gel cleanup is used because older fuel releases degrade over time and the resulting non-hydrocarbon breakdown products are significantly less toxic than the parent hydrocarbons. Because the TPH-DRO analytical method does not include the silica gel cleanup process, TPH-DRO analytical results may include these polar compounds breakdown products that are not extractable petroleum hydrocarbons. The inclusion of these breakdown products tends to bias the TPH-DRO method results higher than EPH method results.

3. Differing calibration standards between laboratories.
4. Variability associated with split samples.

VPH vs. TPH-GRO

1. Differences in the VPH and TPH-GRO analytical results may be associated with differences in the carbon range for the different analyses (e.g., since TPH-DRO analyses overlaps the VPH analyses with respect to the carbon range, this can result in VPH detectable results being expressed as TPH-DRO, not TPH-GRO; see Table 1, RHMW02 and RHMW02D results). In addition, VPH measures the volatile hydrocarbons from C5 to C12, but does not include BTEX, MtBE, or naphthalene. TPH-GRO results includes BTEX, MtBE, and naphthalene.
2. Differing calibration standards between laboratories.
3. Variability associated with split samples.

In summary, the lack of silica gel cleanup or similar removal of polar compounds may cause the TPH-DRO analytical method to report results that are significantly greater than what would be reported as part of the EPH analytical method under certain circumstances.

Table 2 provides values of physical and chemical properties for MADEP fractions.

Table 2. Recommended VPH/EPH Fractional Properties for Modeling Purposes

MADEP Petroleum Fractions	Equivalent Carbon Number (EC)	Molecular Weight	Vapor Pressure (atms)	Solubility in Water (µg/L)	Henry's Constant, H (dimension - less)	Partition Coeff, Koc (mL/g)	Diffusion Coeff (cm^2/s)	
							air w	ater
C5-C8 Aliphatics	6.5	93	0.10	11,000	54	2265	0.08	1 x 10^{-5}
C9-C12 Aliphatics	10.5	149	8.7 x 10^{-4}	70	65	1.5 x 10^{5}	0.07	1 x 10^{-5}
C9-C10 Aromatics	9.5	120	2.9 x 10^{-3}	51,000	0.33	1778	0.07	1 x 10^{-5}
C9-C18 Aliphatics	12	170	1.4 x 10^{-4}	10	69	6.8 x 10^{5}	0.07	5 x 10^{-6}
C19-C36 Aliphatics	considered immobile							
C11-C22 Aromatics	14	150	3.2 x 10-^{5}	5800 0.03	5000		0.06	1 x 10^{-5}

1.4 HDOH REGULATORY UPDATES AND ASSOCIATED STUDIES

Information obtained from recent U.S. Air Force environmental investigations in Hawaii indicate favorable results when using TPH fractionation methods, such as those presented by MADEP (MADEP, 2002) while conducting quantitative risk assessments for TPH in groundwater that is drinking water. At these sites, when comparing TPH-DRO and EPH groundwater split sample data, TPH-DRO results tend to be higher than the EPH results. This data indicates that the TPH-DRO analytical method may be over estimating the associated site risk for older release sites where the hydrocarbons have been degraded in the groundwater. As mentioned above, this can occur because with EPH analyses, the polar, non-hydrocarbon degradation products are filtered out with silica gel, whereas with the TPH-DRO analyses, these non-hydrocarbon significantly less toxic breakdown products are not removed prior to the analysis.

Prior to 2005, HDOH did not consider TPH toxicity in risk based groundwater studies, rather concentrations of TPH were considered only in cases of gross contamination and concentrations of TPH constituents (e.g., benzene, toluene, ethylbenzene, xylenes and/or naphthalene [BTEXN]), were evaluated for risk. Hawaii Administrative Rules (HAR) Chapter 11-281, Subchapter 7, Release Response Action presented Table 1-1a and 1-1b, Tier 1 Action Levels for Soil and Groundwater with "NS" (No Standard) for TPH-residual fuels (oil and grease), TPH middle distillates (diesel and kerosene), and TPH-gasolines for groundwater where drinking water is threatened.

In May 2005, HDOH published *Screening For Environmental Concerns At Sites With Contaminated Soil and Groundwater*, (HDOH, 2005), which included Environmental Action Levels (EALs) for TPH-middle distillates (including diesel) and TPH-gasolines in groundwater used for drinking based on the nuisance taste and odor. These levels were set at 100 microgram per liter (µg/L), for each, with non-drinking water EALs set at 2,000 µg/L for TPH-gasolines and 5,000 µg/L for TPH-middle distillates (including diesel). These values were still not risk-based, and could not be used to quantify risk.

In 2008, HDOH updated their EALs for TPH-middle distillates and TPH-gasolines in *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (HDOH, 2008). This document was based on studies conducted by the Massachusetts Department of Environmental Protection (MADEP, 2002). HDOH risk-based EALs for TPH for groundwater that is drinking water were revised to 100 µg/L for TPH-gasolines and 210 µg/L for TPH-middle distillates (including diesel).

In setting these EALs, HDOH generally assumed that the components of each TPH mixture consisted of the most toxic fractions. However, measuring the amount of each fraction using the MADEP method allows a more precise determination of risk that does not assume the highest chemical toxicity by default. For example, in Table 1 monitoring well RHMW02 had an EPH that consisted of roughly equal amounts of C11-C22 aromatics and C9-C18 aliphatics. The C9-C18 aliphatic fraction has oral and inhalation toxicities, as measured by a reference dose (RfD; a factor that can be interpreted as a "safe" dose) over three times higher than the C11-C22 aromatic fraction. Thus, a lower risk is determined for this sample.

There is considerable evidence that the TPH-DRO analytical method provides results that are biased high, particularly when measuring older fuel releases. As mentioned above, older fuel releases degrade, and the resulting non-hydrocarbon breakdown products are significantly less toxic than the parent hydrocarbons. However, as previously discussed, MADEP EPH analytical methodologies for TPH-middle distillates (including diesel) include a silica gel filtration process that removes non-hydrocarbon components, while the TPH-DRO method does not.

In a recent environmental investigation conducted for the U.S. Air Force (TEC 2008. *Supplemental Remedial Investigation Report at ST18, Hickam POL Site, Oahu, Hawaii July 2008*), aviation gasoline (AVGAS) was released from the Hickam Air Force Base Petroleum, Oils and Lubricants (POL) pipelines that have been inactive since the mid 1950's. Analytical results from TPH-DRO and TPH-GRO analysis (Method 8015) indicated that a large TPH-middle distillate plume was present, where a TPH-gasoline plume was expected. To resolve this issue, the U.S. Air Force compared TPH-DRO and MADEP EPH results in ten affected wells during two semi-annual rounds of sample collection at the site (i.e., Rounds 3 and 4) to assess fractional toxicity differences, as well as to better understand the potential high bias for the middle distillate results from the TPH-DRO analyses. In Round 3, MADEP EPH concentrations were approximately half the TPH-DRO concentrations in the six wells in which both were detected. This indicated that approximately half the TPH-DRO component was not from hydrocarbons, but most likely less toxic breakdown products from the degraded fuel. Similar results were obtained from the Round 4 comparison.

This may have significance at the Facility, since fuel releases are expected to have occurred in the past, which may result in a significant amount of the compounds found in the TPH-DRO analysis being less toxic breakdown products. Conversely, if a recent release was sampled, it would be expected that the TPH-DRO and EPH concentrations would approximate each other, since no non-hydrocarbon breakdown products would be present to bias the TPH-DRO result toward higher concentrations.

1.5 RISK ANALYSIS AT THE FACILITY USING MADEP FRACTIONATION METHODS

For the purposes of this Letter Report, a Tier 1 Human Health Risk Screening Assessment is conducted below, based on the conservative assumption that the groundwater beneath the Facility is potable water used by residents. Table 3 and Table 4 indicate that for Round 16 groundwater sampling only TPH-gasolines and TPH-middle distillates (including diesel) are COPCs. All others are not detected or detected at less than the HDOH EAL screening criteria.

All COPCs detected in groundwater underlying the Facility are non-carcinogens. Non-carcinogenic risk is determined through the calculation of a ratio, the hazard quotient (HQ), which is the ratio of intake to an RfD (i.e., an intake without an appreciable risk of deleterious effects during a lifetime). The simplified formula to calculate an HQ is:

HQ = CDI/RfD where:
HQ = Hazard quotient;
CDI = Calculated average daily intake of COPC (mg/kg-day); and
RfD = Reference dose (mg/kg-day).

The CDI for potable water exposure is calculated using measured concentrations and the EPA Region IX default exposure assumptions and the formula for establishing PRGs (USEPA, 2004). It includes oral intake and inhalation during water use such as showering.

USEPA generally considers an HQ of 1.0 or less to be acceptable. EALs and PRGs can be developed for non-carcinogens by selecting an HQ of 1.0 and then back-calculating an

Table 3. Analytical Results for MADEP Sampling Report (Round 16, July 15, 2009), Red Hill Fuel Storage Facility Pearl Harbor Hawaii

Method	Chemical	HDOH Drinking Water EALs[1] for Human Toxicity UG/L	HDOH Groundwater Gross Contamination EALs[2] UG/L	RHMW01 UG/L July 15, 2009				RHMW02 UG/L July 15, 2009				RHMW02D UG/L July 15, 2009				RHMW03 UG/L July 15, 2009				RHMW05 UG/L July 15, 2009				RHMW2254-01 UG/L July 15, 2009			
				Result	Q	MDL	RL	Result	Q	MDL	RL	Result	Q	MDL	RL	Result	Q	MDL	RL	Result	Q	MDL	RL	Result	Q	MDL	RL
8015B (Petroleum)	TPH as DIESEL RANGE ORGANICS	210	100	***248***	F	161	430	***1450***		150	400	***1300***		150	400	ND	U	150	400	***491***		158	421	ND	U	163	435
	TPH as GASOLINE RANGE ORGANICS	100	100	ND	U	30	100	ND	U	30	100	ND	U	30	100	ND	U	30	100	ND	U	30	100	ND	U	30	100
8270C SIM (PAHs)	1-METHYLNAPHTHALENE	4.7	10	***9.44***		0.158	0.526	***13.2***		0.156	0.521	***10.6***		0.165	0.549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	2-METHYLNAPHTHALENE	24	10	3.07		0.158	0.526	3.66		0.156	0.521	2.58		0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	ACENAPHTHENE	370	20	0.18		0.0158	0.0526	0.235		0.0156	0.0521	0.213		0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	ACENAPHTHYLENE	240	2000	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	ANTHRACENE	1800	22	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	BENZO(a)ANTHRACENE	0.092	4.7	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	BENZO(a)PYRENE	0.2	0.81	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	BENZO(b)FLUORANTHENE	0.092	0.75	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	BENZO(g,h,i)PERYLENE	1500	0.13	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	BENZO(k)FLUORANTHENE	0.92	0.4	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	CHRYSENE	9.2	1	0.0159	F	0.0158	0.0526	0.0162	F	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	DIBENZ(a,h)ANTHRACENE	0.0092	0.52	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	FLUORANTHENE	1500	130	0.0263	F	0.0158	0.0526	0.0247	F	0.0156	0.0521	0.0199	F	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	FLUORENE	240	950	0.0952		0.0158	0.0526	0.115		0.0156	0.0521	0.108		0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	INDENO(1,2,3-c,d)PYRENE	0.092	0.095	ND	U	0.0158	0.0526	ND	U	0.0156	0.0521	ND	U	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	NAPHTHALENE	17	21	5.61		0.326	1.05	8.37		0.323	1.04	6.71		0.341	1.1	ND	U	0.0326	0.105	ND	U	0.0341	0.11	ND	U	0.0341	0.11
	PHENANTHRENE	240	410	0.0349	F	0.0158	0.0526	0.0304	F	0.0156	0.0521	0.0291	F	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
	PYRENE	180	68	0.027	F	0.0158	0.0526	0.0272	F	0.0156	0.0521	0.0189	F	0.0165	0.0549	ND	U	0.0158	0.0526	ND	U	0.0165	0.0549	ND	U	0.0165	0.0549
8260B (VOCs)	1,1,1,2-TETRACHLOROETHANE	0.52	50000	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	1,1,1-TRICHLOROETHANE	200	970	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,1,2,2-TETRACHLOROETHANE	0.067	500	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	1,1,2-TRICHLOROETHANE	5	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,1-DICHLOROETHANE	2.4	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,2,3-TRICHLOROPROPANE (TCP)	0.6	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,2,4-TRICHLOROBENZENE	70	3000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,2-DIBROMO-3-CHLOROPROPANE (DBCP)	0.04	10	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2
	1,2-DIBROMOETHANE (EDB)	0.0065	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,2-DICHLOROBENZENE	600	10	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,2-DICHLOROETHANE	0.15	7000	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	1,2-DICHLOROPROPANE	5	10	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,3-DICHLOROBENZENE	180	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	1,4-DICHLOROBENZENE	75	5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	ACETONE	22000	20000	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	65		3.1	10	ND	U	3.1	10
	BENZENE	5	170	ND	U	0.12	0.4	ND	U	0.12	0.4	ND	U	0.12	0.4	ND	U	0.12	0.4	ND	U	0.12	0.4	ND	U	0.12	0.4
	BROMODICHLOROMETHANE	0.22	50000	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	BROMOFORM	100	510	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	BROMOMETHANE	8.7	50000	ND	U	0.94	3	ND	U	0.94	3	ND	U	0.94	3	ND	U	0.94	3	ND	U	0.94	3	ND	U	0.94	3
	CARBON TETRACHLORIDE	5	520	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	CHLOROBENZENE	100	50	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	CHLOROETHANE	8600	16	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	CHLOROFORM	70	2400	ND	U	0.3	1	ND	U	0.3	1	ND	U	0.3	1	ND	U	0.3	1	ND	U	0.3	1	ND	U	0.3	1
	CHLOROMETHANE	1.8	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	cis-1,2-DICHLOROETHYLENE	70	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	cis-1,3-DICHLOROPROPENE	0.43	50000	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	DIBROMOCHLOROMETHANE	0.16	50000	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5	ND	U	0.15	0.5
	ETHYLBENZENE	700	30	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	HEXACHLOROBUTADIENE	0.86	6	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	M,P-XYLENE (SUM OF ISOMERS)	10000	20	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2
	METHYL ETHYL KETONE (2-BUTANONE)	7100	8400	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10
	METHYL ISOBUTYL KETONE (4-METHYL-2-PENTANONE)	2000	1300	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10	ND	U	3.1	10
	METHYLENE CHLORIDE	4.8	9100	ND	U	1	5	ND	U	1	5	ND	U	1	5	ND	U	1	5	ND	U	1	5	ND	U	1	5
	NAPHTHALENE	17	21	ND	U	0.62	2	10.1		0.62	2	11.2		0.62	2	ND	U	0.62	2	ND	U	0.62	2	ND	U	0.62	2
	STYRENE	100	10	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	TETRACHLOROETHYLENE(PCE)	5	170	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	TOLUENE	1000	40	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	trans-1,2-DICHLOROETHENE	100	260	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	TRICHLOROETHYLENE (TCE)	5	310	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
	VINYL CHLORIDE	2	3400	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1
6020	LEAD	15	50000	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1	ND	U	0.31	1

PAHs - Polynuclear aromatic hydrocarbons
VOCs - Volatile organic compounds
UG/L - Micrograms per Liter
Q - Data qualifier
U - Indicates that the compound was analyzed for but not detected at or above the stated limit
F - Indicates that the compound was identified but the concentration was above the MDL and below the RL
200 - Result exceeds one or both HDOH EALs

MDL - Method detection limit
RL - Reporting limit
TPH - Total petroleum hydrocarbons
ND - Indicates that the compound was not detected above the stated method detection limit

[1] Final Drinking Water Action Levels for Human Toxicity, Table D-3a, *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater*, HDOH, 2009

[2] Groundwater Gross Contamination Action Levels, Table G-1, *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater*, HDOH, 2009

Table 4. MADEP Analytical Results for MADEP Sampling Report (Round 16, July 15, 2009), Red Hill Fuel Storage Facility, Pearl Harbor, Hawaii

Method	Chemical	HDOH Drinking Water EALs[1] for Human Toxicity UG/L	HDOH Groundwater Gross Contamination EALs[2] UG/L	RHMW01 UG/L July 15, 2009				RHMW02 UG/L July 15, 2009				RHMW02D UG/L July 15, 2009				RHMW03 UG/L July 15, 2009			
				Result	Q	MDL	RL	Result	Q	MDL	RL	Result	Q	MDL	RL	Result	Q	MDL	RL
MADEP EPH	EXTRACTABLE PETROLEUM HYDROCARBONS C11-C22 AROMATIC			ND	U	100	100	***270***		100	100	***280***		100	100	ND	U	100	100
	EXTRACTABLE PETROLEUM HYDROCARBONS C19-C36 ALIPHATIC			ND	U	100	100	ND	U	100	100	ND	U	100	100	ND	U	100	100
	EXTRACTABLE PETROLEUM HYDROCARBONS C9-C18 ALIPHATIC			ND	U	100	100	***270***		100	100	***270***		100	100	ND	U	100	100
	TOTAL EXTRACTABLE PETROLEUM HYDROCARBONS			ND	U	100	100	***540***		100	100	***550***		100	100	ND	U	100	100
MADEP PAHs	2-METHYLNAPHTHALENE	24	10	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	ACENAPHTHENE	370	20	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	ACENAPHTHYLENE	240	2000	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	ANTHRACENE	1800	22	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	BENZO(a)ANTHRACENE	0.092	4.7	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	BENZO(a)PYRENE	0.2	0.81	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	BENZO(b)FLUORANTHENE	0.092	0.75	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	BENZO(g,h,i)PERYLENE	1500	0.13	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	BENZO(k)FLUORANTHENE	0.92	0.4	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	CHRYSENE	9.2	1	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	FLUORANTHENE	1500	130	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	FLUORENE	240	950	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	INDENO(1,2,3-cd)PYRENE+DIBENZ(a,h)ANTHRACENE			ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	NAPHTHALENE	17	21	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	PHENANTHRENE	240	410	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	PYRENE	180	68	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
MADEP VPH	VOLATILE PETROLEUM HYDROCARBONS C5-C8 ALIPHATIC			ND	U	100	100	ND	U	100	100	ND	U	100	100	ND	U	100	100
	VOLATILE PETROLEUM HYDROCARBONS C9-C10 AROMATIC			ND	U	100	100	***420***		100	100	***490***		100	100	ND	U	100	100
	VOLATILE PETROLEUM HYDROCARBONS C9-C12 ALIPHATIC			ND	U	100	100	ND	U	100	100	ND	U	100	100	ND	U	100	100
	TOTAL VOLATILE PETROLEUM HYDROCARBONS			ND	U	100	100	***420***		100	100	***490***		100	100	ND	U	100	100
MADEP BTEX-M	BENZENE	5	170	ND	U	5	5	ND	U	5	5	ND	U	5	5	ND	U	5	5
	ETHYLBENZENE	700	30	ND	U	5	5	ND	U	5	5	ND	U	5	5	ND	U	5	5
	M,P-XYLENE (SUM OF ISOMERS)	10000	20	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	NAPHTHALENE	17	21	ND	U	10	10	ND	U	10	10	ND	U	10	10	ND	U	10	10
	O-XYLENE (1,2-DIMETHYLBENZENE)			ND	U	5	5	ND	U	5	5	ND	U	5	5	ND	U	5	5
	tert-BUTYL METHYL ETHER			ND	U	5	5	ND	U	5	5	ND	U	5	5	ND	U	5	5
	TOLUENE	1000	40	ND	U	5	5	ND	U	5	5	ND	U	5	5	ND	U	5	5

MADEP EPH - Massachusetts Department of Environmental Protection Extractable Petroleum Hydrocarbons
MADEP VPH - Massachusetts Department of Environmental Protection Volatile Petroleum Hydrocarbons
UG/L - Micrograms per Liter
Q - Data qualifier
U - Indicates that the compound was analyzed for but not detected at or above the stated limit
200 Result exceeds the laboratory method detection limit

MDL - Method detection limit
RL - Reporting limit
ND - Indicates that the compound was not detected above the stated method detection limit

[1] Final Drinking Water Action Levels for Human Toxicity, Table D-3a, *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater*, HDOH, 2009

[2] Groundwater Gross Contamination Action Levels, Table G-1, *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater*, HDOH, 2009

acceptable concentration using standard exposure parameters. For multiple chemicals or fractions at an exposure point (e.g. for a monitoring well) a Hazard Index (HI) is calculated by summing the HQs.

1.5.1.1 Direct Exposure Risk Results

For purposes of this risk assessment, the MADEP results from Round 16 are used for the definitive evaluation of risk because it is assumed that greater accuracy is achieved when evaluating more specific components of petroleum, versus the broad categories of TPH-GRO and TPH-DRO.

MADEP fractions were only observed above the detection limit at RHMW02, in both the normal and duplicate sample (Table 1). Direct exposure risk calculations and for this sample are shown in Table 5. For the potential future residential scenario of groundwater use as potable water, MADEP VPH and MADEP EPH exceeded an HQ of 1.0 for monitoring well RHMW02, thus indicating a potential non-carcinogenic risk.

- The HQ at RHMW02 for MADEP VPH ranged between 4.4 and 5.1 based entirely on C9-C10 Aromatics detected in the normal (420 µg/L) and duplicate (490 µg/L) sample.
- The HQ at RHMW02 for MADEP EPH was 3.5, based on C9-C18 Aliphatics Aromatics detected in the normal (270 µg/L) and duplicate (270 µg/L) sample, and C11-C22 Aromatics (270 µg/L in the normal and 280 µg/L in the duplicate samples).
- The total HI for these samples ranged from 8.0 for the normal sample to 8.7 for the duplicate sample.

Although an HI of 8.0 to 8.7 represents a potentially unacceptable risk if observed in the Pearl Harbor Water System, it represents actual risk only if these same concentrations were to migrate to the U.S. Navy Well 2254-01, or if potable water wells were installed within the maximum concentrations associated with the plume. In the July 2009 Round 16 sampling event, MADEP fractions were not detected in the sample from RHMW01 (located between RHMW02 and the U.S. Navy Well 2254-01). MADEP analyses were not conducted at RHMW05 (between RHMW01 and U.S. Navy Well 2254-01) or at RHMW2254-01 (located within the U.S. Navy Well 2254-01 infiltration gallery)

Table 5. Risk Estimates for Groundwater, RHMW02 Round 16

Risk Calculation Equation*	$TC = \frac{THQ \times BWa \times ATn \times 1000\ ug/mg}{EFr \times EDr\ [(IRWa/RfDo) + (VFw \times IRAa/RfDi)]}$						
Risk Parameter Identification	VPH			EPH			
	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	C9-C18 Aliphatics	C19-C36 Aliphatics	C11-C22 Aromatics	
THQ =Target Hazard Quotient	1	1	1	1	1	1	
Bwa = Adult Body Weight (kg)	70	70	70	70	70	70	
Atn = Averaging Time (d)	10950	10950	10950	10950	10950	10950	
Efr = Exposure Frequency (d/y)	350	350	350	350	350	350	
Edr = Exposure Duration (y)	30	30	30	30	30	30	
IRWa = Adult Water Ingestion Rate (L/d)	2	2	2	2	2	2	
RfDo = Oral Reference Dose (mg/kg-d)	0.04	0.1	0.03	0.1	2	0.03	
VFW = Volatilization factor	0.5	0.5	0.5	0.5	0.5	0.5	
IRAa Adult Air Ingestion Rate (m3/d)	20	20	20	20	20	20	
RfDi = Inhalation Reference Dose (mg/kg-d)	0.05714	0.05714	0.014285	0.05714	NA	0.014285	
TC = Target Concentration for HQ of 1 (ug/L)	324	374	95	374	73000	95	
Monitor Well Sample Identification	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	C9-C18 Aliphatics	C19-C36 Aromatics	C11-C22 Aromatics	
	Input Concentrations (ug/L)						
RHMW02			420	270		270	
RHMW02D			490	270		280	Hazard Index Summation
	Calculated Hazard Quotients						
RHMW02			4.4	0.7		2.8	8.0**
RHMW02D			5.1	0.7		2.8	8.7**

* To calculate the baseline risk HQ (versus the target HQ) the formula is rearranged and uses the measured concentrations.
** Represent rounded values.

1.6 CONCLUSIONS AND RECOMMENDATIONS

Since 2005, revisions to regulatory requirements and environmental investigations in Hawaii associated with hydrocarbons in groundwater have provided new perspective on evaluating risk at these sites.

At the Facility, the U.S. Navy has an extremely important mission in supplying fuel to the Pacific Fleet. This is complicated by environmental issues associated with past hydrocarbon releases to the underlying drinking water aquifer. Prior to groundwater monitoring Round 16 in July 2009, the site-specific groundwater model and Action Levels associated with the past and hypothetical future petroleum releases from the site were based in part on results from USEPA Method 8015 Modified for TPH-GRO and TPH-DRO.

As discussed in the previous sections of this document, MADEP fractionation methods for VPH and EPH may be more relevant for quantifying risk associated with petroleum mixtures and in determining when specific actions should be taken to mitigate future releases. For example, the Round 16 sample result for TPH-DRO at RHMW01 (248 μg/L) indicated that the EAL for TPH-middle distillates (210 μg/L) were exceeded at this location, whereas no MADEP fractions were detected in this sample. MADEP fractionation analysis provides advantages over the traditional TPH analysis. First it divides the gasoline and middle distillate range TPH analysis in three sub-fractions for each range. This provides more accurate health risk analysis. The second advantage is that only the petroleum hydrocarbons are included in analytical results.

Round 16 results seem to indicate that in all but one of the wells tested, the TPH results were probably petroleum breakdown products or from some non-petroleum source. This ambiguity in TPH results is somewhat problematic regarding petroleum contaminant groundwater monitoring at the facility. The consistent future use of MADEP fraction analysis may be able to resolve uncertainties associated with Facility TPH results.

The Tier 1 Human Health Risk Assessment conducted on MADEP factional results indicated that groundwater underlying RHMW02 exceeded the acceptable HI of 1.0 by a factor of approximately 8, assuming the most conservative residential potable water scenario. However, MADEP fractions were not detected in samples from RHMW01 or RHMW03 within the Facility. RHMW01 is located directly southwest of Tanks 1 and 2, and currently assumed to be hydrologically downgradient from all USTs in the Facility and upgradient from the U.S. Navy Well 2254-01.

The absence of detectable MADEP fractions in RHMW01 may indicate that contaminants are not migrating in significant concentrations toward the U.S. Navy Well 2254-01 under July 2009 conditions. The assumed groundwater flow direction is the worst case scenario for contaminant transport from beneath the tanks to the drinking water well. Any significant divergence from this groundwater flow direction would move contamination away from the drinking water well.

Based on observations described in this letter report, it is recommended that consideration be given to including MADEP analyses in the analytical groundwater monitoring program. Using the combination of TPH-GRO/TPH-DRO and VPH/EPH analytical results, will allow a more thorough assessment regarding actual petroleum contaminant risks posed by the Facility to the U.S. Navy Well 2254-01 or other area drinking water supply wells.

However, using a different analytical method to evaluate Facility risk requires the concurrence of HDOH. Therefore, it is recommended that the Navy and TEC consider entering into discussions with HDOH to use MADEP fractionation analysis to supplement the current TPH analysis with the possibility of at some point, replacing TPH analysis with the MADEP analytical methodology.

Please don’t hesitate to contact me if you have any questions regarding this Letter Report at either 808-528-1445 or my cell at 865-742-2181.

Sincerely,

Rick Adkisson

TEC Project Manager

ATTACHMENT 1
Differences Between MADEP and 8015C Analytical Methods

Differences Between MADEP and 8015C Analytical Methods

There are basic differences between analytical method 8015C and the MADEP method that can result in differing results for split samples analyzed by both methods. A general explanation of the methods is helpful in order to understand these differences.

Petroleum hydrocarbons in the environment, especially older weathered samples, are complex mixtures of not only aliphatic and aromatic hydrocarbons, but also breakdown products of petroleum and other organic materials. Total petroleum hydrocarbon (TPH) analytical methods such as 8015, MADEP, and others are non-specific methods that attempt not to identify and quantify individual compounds, but rather measure all purgeable or extractable hydrocarbon compounds within a "range" that corresponds to the boiling points of hydrocarbons. These boiling point ranges generally correspond to gasoline and diesel. Quantification of the amount of either gasoline range (GRO or VPH) or diesel range (DRO or EPH) petroleum hydrocarbons in a sample is accomplished by summing the individual concentrations of all compounds detected within specified ranges. It is the definition of these ranges that gives rise to most of the significant differences between the 8015C and MADEP VPH results.

By definition, method 8015C specifies the quantification range of GRO from C6 – C10 (n-hexane to n-decane). This corresponds to compounds that elute from a chromatographic column between 2-methylpentane and 1,2,4-trimethylbenzene. MADEP defines VPH as ranging from C5 – C12 (n-pentane to n-dodecane), which corresponds to those compounds that elute from n-pentane up to naphthalene. The attached set of chromatograms illustrates the effect of the differing ranges. The top figure is a reference chromatogram showing the retention times of the four compounds that define the two ranges, and the lower figure shows an actual sample. Note that there are petroleum hydrocarbons that elute after 1,2,4-trimethybenzene, but before naphthalene. These compounds would not be quantified in an 8015C analysis, but would be quantified in a MADEP VPH analysis. This is why 8015C GRO results could be reported at lower concentrations than MADEP VPH results.

Beyond this very simplistic explanation, there are other more significant discriminators between the two methods. The Hawaii Department of Health (HDOH) has approved the use of MADEP analytical methods at Air Force sites within Hawaii that have residual contamination from historic fuel releases. This is primarily because the MADEP methods prescribe a cleanup/fractionation step (EPH only) and results are obtained and presented separately for aliphatic and aromatic compounds according to ranges: C5 – C8; C8 – C12; C9 – C18; and C19 – C36 for aliphatic compounds and C9-C10 and C11 – C22 for aromatic compounds. Thus, the MADEP method provides much greater specificity than is typically achieved through 8015C methodology.

Given the increased specificity and the required silica gel cleanup, the MADEP method may provide greater insight into not only the age of the petroleum hydrocarbons (many petroleum breakdown products will be removed from the extract during the silica gel cleanup), but also provide indications as to how site conditions may be changing over time. TPH methods will only present trends (increasing/decreasing TPH concentrations) while the greater number of “analyte” ranges in MADEP results allows for analysis of shifts to heavier or to lighter range hydrocarbons as well.

Finally, the MADEP VPH and EPH methods were “designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons.” As described in **INTERIM FINAL PETROLEUM REPORT: DEVELOPMENT OF HEALTH-BASED ALTERNATIVE TO THE TOTAL PETROLEUM HYDROCARBON (TPH) PARAMETER**, (prepared for the Bureau of Waste Site Cleanup, Massachusetts Department of Environmental Protection by Office of Research and Standards Massachusetts Department of Environmental Protection) . This approach provides for:

> “…an alternative approach to the analysis and interpretation of the "TPH" parameter used at oil contaminated waste sites. The alternative can be used to perform site-specific risk assessments or to develop health-based cleanup standards for petroleum hydrocarbons. Rather than quantifying the entire range of petroleum hydrocarbons as one mass, a technique is used which divides the broad chemical classes of petroleum hydrocarbons (alkanes, cycloalkanes, alkenes and aromatics) into subgroups of compounds based on numbers of carbon atoms in the compounds in each subgroup and translates the masses of compounds in each specific segment into discrete estimates of health risk for specified exposure scenarios.”

Standard 8015 analysis does not provide the chemical divisions necessary to conduct analogous calculations.

Because of the greater specificity that the MADEP analytical method provides, it is recommended that the Navy and TEC consider entering into discussions with HDOH to use MADEP fractionation analysis to supplement the current TPH analysis with the possibility of at some point, replacing TPH analysis with the MADEP analytical methodology. By collecting split-samples to be analyzed by method 8015C and the MADEP method, this would allow for the establishment of baseline results for each method. Then at some point, pending HDOH approval, analysis by method 8015C could possibly be discontinued since the MADEP analytical method provides more information than the 8015 method.

Report Date: 05-Nov-2009 16:07:02 Chrom Revision: 1.1 26-Oct-2009 10:54:26

Preliminary Report

Data File: \\wessvr06\chromdata\InstG.i\20090723-1.b\G17160.D
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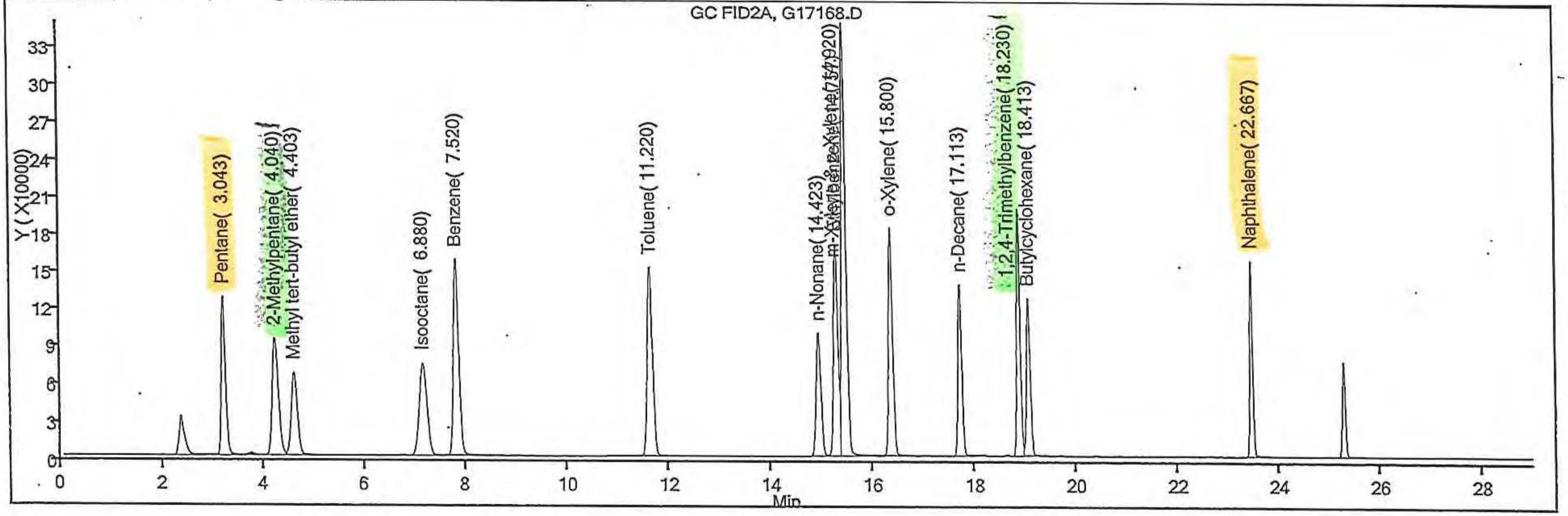
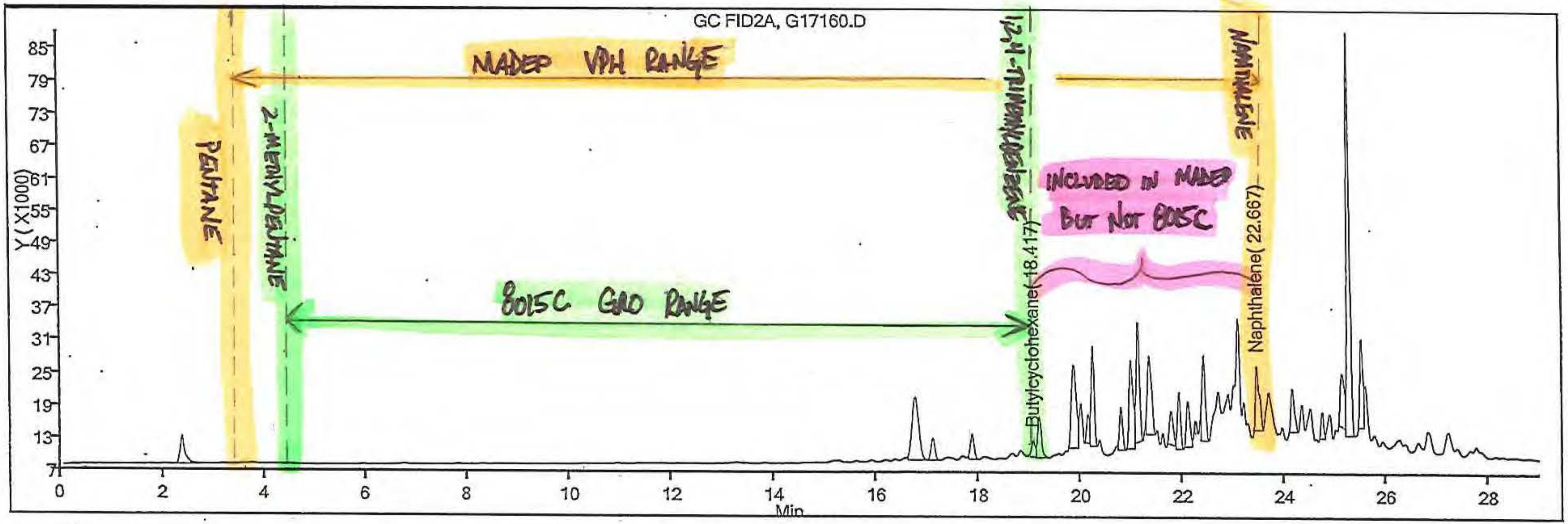
Lims Batch ID: 46964 Lims Sample ID: 20





Attachment D

TICs Memorandum

April 19, 2010

January 2010 Sampling Event at the Red Hill Facility

TPH-DRO at RHMW02

The January 2010 total petroleum hydrocarbon, diesel range organics (TPH-DRO) results at RHMW02 were significantly impacted by two large peaks identified by the laboratory as caprolactam and DEET. These tentatively identified compound (TIC) peaks were reported as part of the TPH-DRO result because according to the analytical method, all peaks within the diesel range must be quantified. However, these TICs are apparently unrelated to Red Hill Bulk Fuels Storage Facility (Facility) stored fuels. Caprolactam is a monomer used to produce “Nylon 6” and is found in plastics and possibly in paints and floor polishes. DEET is a pesticide commonly used as an insect repellent.

Neither of these TIC compounds was detected as part of the laboratory extraction or instrument quality control process (e.g., method blanks, instrument blanks, and laboratory control spikes). Also, caprolactam and DEET are not used or found in the SGS laboratory that performed the analysis. Therefore, the TICs are not laboratory introduced contaminants. In addition, the same field personnel performed the January sampling and their sampling approach was identical to that used in previous Facility sampling events. Furthermore, the field personnel were extremely careful and cognizant not to introduce any contaminants to the collected and/or shipped samples. Consequently, it is not believed that the TICs were introduced via the analytical or sampling/shipping process.

As shown in Table 1, these two significant TIC peaks (i.e., identified by the laboratory as caprolactam and DEET) contributed significantly to the reported TPH-DRO results. Although the TPH-DRO analytical method requires that all peaks in the diesel range be quantified for the “officially reported” TPH-DRO result, Table 1 estimates what the respective TPH-DRO concentrations would have been without the two TIC peaks. The reprocessing or re-quantification results were provided by the laboratory. These “adjusted concentrations” more closely represent what would be anticipated with normal and duplicate samples.

Table 1 – January 2010 RHMW02 Analytical Results**

January 2010 Results	Official TPH-DRO Result (μg/L)	Estimated TPH-DRO Result without the two TIC peaks included (μg/L)
RHMW02	2,130	1,740
RHMW02D (duplicate sample)	3,410	2,110

Table 1 Note: ** TICs are "tentatively identified" compounds. The TPH-DRO analytical method is not specific (i.e., is designed to quantify any and all organic compounds within the diesel range). By scanning the TPH-DRO extract via GC/MS, unknown peaks have been "tentatively identified" (i.e., without the benefit of "neat" standards and the use of specific methods designed to accurately quantify the particular TIC peaks "identified"). Therefore, although the TICs are believed to be the "identified" compounds, there is some inherent uncertainty associated with this identification process. This uncertainty is why the "officially reported" TPH-DRO result must quantify all the organic compounds within the TPH-DRO range.

In summary, these TICs from the January 2010 sampling event are apparently not attributable to stored fuels at the Facility, they are not laboratory contaminants, and it is unlikely that they were introduced by the sampling/shipping process.

TPH-DRO at RHMW05

Similar to RHMW02, the January 2010 TPH-DRO result for RHMW05 was significantly impacted by two large peaks identified by the laboratory as caprolactam and DEET. These TIC peaks were reported as part of the TPH-DRO result because according to the analytical method, all peaks within the diesel range must be quantified. However as mentioned above, these TICs are apparently unrelated to Facility stored fuels. Caprolactam is a monomer used to produce "Nylon 6" and is found in plastics and possibly in paints and floor polishes. DEET is a pesticide commonly used as an insect repellent.

As with RHMW02, neither of these TIC compounds was detected as part of the laboratory extraction or instrument quality control process (e.g., method blanks, instrument blanks, and laboratory control spikes). Also, caprolactam and DEET are not used or found in the SGS laboratory that performed the analysis. Therefore, the TICs are not laboratory introduced contaminants. In addition, the same field personnel performed the January sampling and their sampling approach was identical to that used in previous Facility sampling events. Furthermore, the field personnel were extremely careful and cognizant not to introduce any contaminants to the collected and/or shipped samples. Consequently, it is not believed that the TICs were introduced via the analytical or sampling/shipping process.

As shown in Table 2, these two significant TIC peaks contributed significantly to the reported TPH-DRO results. Although the TPH-DRO analytical method requires that all peaks in the diesel range be quantified for the "officially reported" TPH-DRO result, Table 2 estimates what the respective TPH-DRO concentrations would have been without the two TIC peaks. The reprocessing or re-quantification results were provided by the laboratory.

Table 2 – January 2010 RHMW05 Analytical Results**

January 2010 Results	Official TPH-DRO Result (μg/L)	Estimated TPH-DRO Result without the two TIC peaks included (μg/L)
RHMW05	2,060	541

Table 2 Note: ** TICs are "tentatively identified" compounds. The TPH-DRO analytical method is not specific (i.e., is designed to quantify any and all organic compounds within the diesel range). By scanning the TPH-DRO extract via GC/MS, unknown peaks have been "tentatively identified" (i.e., without the benefit of "neat" standards and the use of specific methods designed to accurately quantify the particular TIC peaks "identified"). Therefore, although the TICs are believed to be the "identified" compounds, there is some inherent uncertainty associated with this identification process. This uncertainty is why the "officially reported" TPH-DRO result must quantify all the organic compounds within the TPH-DRO range.

In summary, these TICs from the January 2010 sampling event are apparently not attributable to stored fuels at the Facility, they are not laboratory contaminants, and it is unlikely that they were introduced by the sampling/shipping process.

February 2010 Re-sampling Event at the Red Hill Facility

TPH-DRO at RHMW02

Per the Facility Groundwater Protection Plan, because of the January 2010 results for RHMW02, the monitoring well was re-sampled in February 2010 for TPH-DRO. The February 2010 TPH-DRO results for RHMW02 were significantly impacted by three relatively large TIC peaks. The first peak (i.e., likely caprolactum) provided the largest TIC contribution toward the "officially reported" TPH-DRO concentration. The second peak was initially thought to be DEET, but following additional analyses, was identified to likely be dodecanoic acid. The third TIC peak was not able to be identified, even after subsequent analyses.

These three TIC peaks were reported as part of the TPH-DRO result because according to the analytical method, all peaks within the diesel range must be quantified. Caprolactam is a monomer used to produce "Nylon 6" and would be found in plastics and possibly in paints and floor polishes. Dodecanoic acid is not used or found in the SGS laboratory and was not found as part of the laboratory quality control process (e.g., instrument and method blanks), thus is not a laboratory contaminant. The third TIC peak that contributed to the "officially reported" TPH-DRO concentration could not be identified, even given subsequent analyses.

Chromatograms from the February laboratory data depict the two TIC peaks (i.e., identified as caprolactam and dodecanoic acid) that apparently are unrelated to Facility stored fuels and the third unknown TIC compound. The three peaks are summarized on the chromatograph as follows:

- The first peak marked (~2 minutes) should be caprolactam/nylon6. This is the largest TIC peak and is the major TIC contributor to the "officially reported" TPH-DRO result.
- The second peak marked (~4 minutes) was initially thought to be DEET, but following subsequent analysis was identified as likely to be dodecanoic acid.

- The third peak marked (~6.6 minutes) is an unidentified/unknown compound (i.e., not identifiable following an 8270 analytical method TIC library search). This peak was also present on the chromatograms for the January 2010 TPH-DRO sample results, but was much smaller and did not significantly influence the "officially reported" January TPH-DRO results.

Note that none of these three TIC peaks appear as part of the associated laboratory quality control process (e.g., method blanks and instrument blanks).

Table 3 depicts the "official reported" TPH-DRO results that include all three TIC peaks described above. Table 3 also estimates what the TPH-DRO results would be in the event that the three TIC peaks (i.e., likely caprolactam, dodecanoic acid, and an unknown compound) were not present. This reprocessing or re-quantification of the chromatograms was performed by the laboratory.

Table 3 – February 2010 RHMW02 Analytical Results**

February 2010 Results	**Official TPH-DRO Result (µg/L)**	**Estimated TPH-DRO Result without the three major TIC peaks included (µg/L)**
RHMW02	8,650	3,470
RHMW02D (duplicate sample)	6,910	2,930

Table 3 Note: ** TICs are "tentatively identified" compounds. The TPH-DRO analytical method is not specific (i.e., is designed to quantify any and all organic compounds within the diesel range). By scanning the TPH-DRO extract via GC/MS, unknown peaks have been "tentatively identified" (i.e., without the benefit of "neat" standards and the use of specific methods designed to accurately quantify the particular TIC peaks "identified"). Therefore, although the TICs are believed to be the "identified" compounds, there is some inherent uncertainty associated with this identification process. This uncertainty is why the "officially reported" TPH-DRO result must quantify all the organic compounds within the TPH-DRO range.

In summary, for the February analytical results, the first two TICs (and possibly the third TIC) are apparently not attributable to stored fuels at the Facility and they are likely not laboratory contaminants. Also, it is believed that none of these three TIC peaks have been significant contaminants of past Facility TPH-DRO reported concentrations prior to the January and February 2010 sampling events. In addition, the same field personnel performed the February sampling and their sampling approach was identical to that used in previous Facility sampling events. Furthermore, the field personnel were extremely careful and cognizant not to introduce any contaminants to the collected and/or shipped samples. Consequently, TEC does not believe that the TICs were introduced via the analytical or sampling/shipping process.

One identifiable variable that occurred during the January and February sampling events that was not true with earlier rounds was the ongoing process of dismantling/removing temporary PVC collection pipelines and the demobilization of various equipment and supplies from the tunnel complex. It is unclear how or if these occurrences may have had any effect/influence on the January and February 2010 TPH-DRO results.

March 2010 Re-sampling Event at the Red Hill Facility

TPH-DRO at RHMW02

Per the Facility Groundwater Protection Plan, because of the February 2010 results for RHMW02, the monitoring well was re-sampled in March 2010 for TPH-DRO. These sampling results (normal and duplicate samples) did not show large concentrations of the TICs described above that are apparently non-fuel related. Furthermore, the TPH-DRO concentrations more closely approximate the levels that have been historically observed from RHMW02. Table 4 presents the RHMW02 TPH-DRO March 2010 results.

Table 4 – March 2010 RHMW02 Analytical Results

March 2010 Results	Official TPH-DRO Result (µg/L)
RHMW02	2,630
RHMW02D (duplicate sample)	2,350

Please feel free to contact me if you have any questions or comments on my cell phone at 865-742-2181.

Sincerely,

Rick Adkisson

Rick Adkisson
TEC, Project Manager

Attachment E

Assessment of Potential Toxicity Posed by Polar Byproducts

Zemo & Associates LLC
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Incline Village, NV 89451
775-831-6179; dazemo@zemoassociates.com

FINAL DRAFT

July 11, 2008

Mr. Jeff Hart, R.G.
Principal, Senior Project Manager
TEC Inc.
1001 Bishop Street, Suite 1400
Honolulu, HI 96813

Subject: Assessment of Potential Toxicity Posed by Polar Byproducts Resulting from Biodegradation of Petroleum Hydrocarbons
Hickam Air Force Base, Pearl City, Hawaii

Dear Mr. Hart:

This letter presents a summary of findings regarding the potential toxicity posed by polar compounds dissolved in groundwater that result from intrinsic biodegradation of petroleum hydrocarbons. Polar compounds in the semivolatile range have been detected in groundwater associated with a historic gasoline release at Hickam Air Force Base, Site 18, Pearl City, Hawaii. The Hawaii Department of Health (HDOH) has requested that the Air Force justify the use of the Massachusetts Department of Environmental Protection (MADEP) fractionated analysis for Extractable Petroleum Hydrocarbons (EPH), which does not measure the polar component, to calculate risk associated with the middle distillate petroleum fraction in groundwater at ST18. The HDOH alternative risk calculation approach has been to assume that the middle distillate petroleum fraction can be measured using the United States Environmental Protection Agency (USEPA) Method 8015 modified, which includes the polar component, and then assumes the maximum toxicity (based on the C_{11} to C_{22} aromatics petroleum fraction) for the entire mixture to calculate risk. Evidence presented in this letter favors the use of the MADEP analysis and fractions for determining risk, and justifies the assumption that the toxicity associated with the polar component is negligible compared to the petroleum fraction. On this basis, this letter presents the following:

1. A primer regarding the chemistry of petroleum hydrocarbons and their polar biodegradation byproducts;
2. An assessment of the analytical methods and technical issues associated with both MADEP and USEPA Method 8015mod protocols for petroleum mixtures;
3. A description of the potential toxicities of the petroleum fractions as defined by MADEP compared to the potential toxicities of the polar biodegradation byproducts; and
4. Conclusions that support the use of the MADEP fractionated analysis for risk assessment purposes rather than the USEPA Method 8015mod analysis because the

potential toxicity posed by the polar compounds appears to be negligible compared to the C_{11} to C_{22} aromatics petroleum fraction.

Chemistry of Petroleum Hydrocarbons and Biodegradation Byproducts

Petroleum hydrocarbons such as crude oils and fuel products are composed primarily of aliphatic and aromatic hydrocarbons, which consist of carbon and hydrogen atoms and are non-polar in their molecular structure. Crude oils and heavier petroleum products such as heavy fuel oils can contain large heterocyclic molecules with nitrogen, sulfur, or oxygen in their structure (called NSOs), which have increased polarity. Lighter products such as aviation gasoline and automotive gasoline (generally C_4 to C_{12}) and jet fuels (generally C_8 to C_{18}) contain virtually no NSOs and therefore virtually no polar molecules, exclusive of additives [Chevron 2000, 2004; Zemo and Foote 2003]. The environmental fate of the individual petroleum hydrocarbon constituents and the fuel product mixtures is a function of molecular class (aliphatic vs. aromatic) and molecular size. With respect to water solubility, it is well established that the aliphatics have very low pure-component water solubilities that decrease exponentially with increasing molecule size (e.g., the water solubility of the C_5 to C_8 aliphatics fraction is 11 milligrams per liter [mg/l], and the water solubility of the C_9 to C_{18} aliphatics fraction is 0.010 mg/l) [MADEP 2002]. The aromatics are more water soluble, but their pure-component solubilities also decrease exponentially with increasing molecule size (e.g., the water solubility of the C_9 to C_{10} aromatics fraction is 51 mg/l, and the water solubility of the C_{11} to C_{22} aromatics fraction is 5.8 mg/l) [MADEP 2002]. Within a fuel mixture, the pure-component solubility of a constituent or a fraction is reduced in proportion to its mole-fraction within the mixture, resulting in its “effective solubility”. Based on published data, the hydrocarbons in the total measurable water-soluble fraction of fresh fuel products are limited to the small aliphatics (less than C_8) and the aromatics up to about C_{14} [Zemo and Foote 2003].

The microbial biodegradation of petroleum hydrocarbons has been extensively studied due to the wide interest in monitored natural attenuation. When petroleum hydrocarbons biodegrade, the hydrocarbon molecules are destroyed by sequential oxidation reactions that start with the formation of alcohols and proceed to various aliphatic and aromatic organic acids and ultimately to carbon dioxide and water; intermediate metabolites can include phenols, ketones and aldehydes [Dragun 1988; Barcelona et al 1995]. All of these families of constituents are polar in their molecular structure, and therefore are very soluble in groundwater. Because the sequential oxidation processes proceed at different rates in different portions of a plume due to availability of electron acceptors, the specific polar constituents present in the groundwater will vary with time and space. These polar constituents will accumulate where groundwater is anoxic, but have been shown to oxidize relatively quickly in the presence of oxygenated water [Cozzarelli et al 1994; Cozzarelli and Baedecker 1996; Eganhouse et al 1993].

Analytical Methods and Technical Issues

To assess the concentrations of each of the target petroleum fractions, MADEP developed an analytical method that is divided into volatile (purgeable) and extractable petroleum fractions (VPH/EPH). For the EPH method, the sample is separated into aliphatic and aromatic fractions via a series of solvent exchanges and using a silica gel column. Silica gel is a highly polar material and therefore attracts other polar compounds, and the use of a silica gel column to fractionate or clean up samples to reduce interference from non-target analytes is a long-standing EPA method. Because petroleum hydrocarbons are not polar, they are eluted off of the silica gel column with the respective solvents. Multiple studies have shown that this MADEP analytical method provided acceptable recoveries of the petroleum hydrocarbons present in the sample. Although it was not a primary focus of the method, fractionating the sample into aliphatic and aromatic hydrocarbons on the silica gel column also isolated the polar non-hydrocarbons that may be present in the sample by retaining them on the silica gel.

It is widely known that polar non-hydrocarbons are measured as extractable total petroleum hydrocarbons (e.g., diesel range organics [DRO]; total extractable petroleum hydrocarbons [TEPH]) when methods that do not incorporate a routine silica gel cleanup are used (e.g., USEPA Method 8015mod) [Zemo and Foote 2003]. This is because the flame ionization detector is not specific to petroleum (it measures all of the organics in the sample), and the semivolatile polar compounds can elute in the apparent C_{10} to C_{30} range. It has been demonstrated that at sites where groundwater was in contact with biodegraded petroleum, up to 100% of the DRO concentration resulted from polar compounds [Zemo and Foote 2003]. Thus, groundwater downgradient from a biodegrading gasoline source can contain measureable "DRO" concentrations even though there are no dissolved petroleum hydrocarbons in the groundwater sample.

Potential Toxicities of the Petroleum Fractions

The potential toxicities of the various petroleum fractions were extensively studied in the mid-1990s, and were codified into risk-based regulatory programs in several states. Of note is the work performed by the MADEP. MADEP divided the potential ranges of petroleum hydrocarbons into volatile fractions (VPH) and extractable fractions (EPH). Each of these large fractions is further subdivided into the aromatics and the aliphatic hydrocarbons, which are further subdivided into carbon ranges (molecule size). To assess potential risk to human health posed by the extractable fraction of petroleum, MADEP requires evaluation of the polycyclic aromatic hydrocarbons (PAHs) individually, and then groups the remaining hydrocarbons as the C_{11} to C_{22} aromatics, the C_9 to C_{18} aliphatics, and the C_{19} to C_{36} aliphatics [MADEP 2003]. After extensive review of the toxicological literature, MADEP has assigned toxicity properties to each of these petroleum hydrocarbon fractions based on either a single surrogate petroleum constituent or the properties of a surrogate petroleum mixture [MADEP 2003]. The toxicity of the C_{11} to C_{22} aromatics fraction is based on pyrene, with an oral reference dose (RfD) of 0.03 milligrams per kilogram per day (mg/kg/day); the toxicity of the C_9 to C_{18} aliphatics fraction is based on laboratory-prepared petroleum mixtures, with an oral RfD of 0.1 mg/kg/day; and the toxicity of the C_{19} to C_{36} aliphatics fraction is based on white mineral oils, with an oral RfD of 2. The uncertainty factors applied when developing each of these RfDs were 3000, 1000, and 100, respectively. MADEP updates these RfDs periodically when new petroleum toxicological studies become available; values shown are the most current (2003).

Potential and Relative Toxicity Posed by the Polar Compounds

The potential risk to human health posed by the polar biodegradation byproducts has not been well studied due to (1) the large number of individual compounds that may be present, (2) the transient nature of which compounds may be present, (3) the difficulty in analyzing many of these families of compounds, and (4) the assumption that compounds with the polar molecular structures would generally be less toxic than the petroleum target compounds (primarily the aromatics). While it is impossible to know exactly which specific compounds are present at a particular point in time, a practical approach is to estimate the risk posed by these polar compounds in a general way by evaluating the available data regarding the toxicities of constituents that are representatives of each of these families of polar compounds. For example, the 2008 USEPA Regions 3, 6 and 9 Preliminary Remedial Goals (PRG) document shows RfDs for four alcohols, three organic acids, two aldehydes, seven phenols and five ketones that may plausibly result from the biodegradation of petroleum hydrocarbons. The table below summarizes the range of oral RfDs for each of the families of polar compounds for the plausible biodegradation byproducts; the average of the oral RfDs (rounded to a single significant figure) is also presented for each family of compounds.

Polar Family	No. of Plausible Constituents with PRG	Range of Oral RfDs	Factor to RfD of 0.03 (C_{11} to C_{22} aromatics)
Alcohols	4	0.1 to 0.5 (Avg 0.3)	3 to 17 (Avg 10)
Organic Acids	4	0.9 to 4 (Avg 2)	30 to 133 (Avg 77)
Aldehydes	2	0.1 to 0.2 (Avg 0.2)	3 to 6 (Avg 5)
Phenols	7	0.0006 to 0.3 (Avg 0.06)	0.02 to 10 (Avg 2)
Ketones	5	0.08 to 5 (Avg 1)	3 to 167 (Avg 43)

Notes:
Alcohols – Methanol, n-butanol, isobutyl alcohol, benzyl alcohol.
Acids – Formic acid, acetic acid, benzoic acid.
Aldehydes – Formaldehyde, benzaldehyde.
Phenols – Phenol, 2,4-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethlyphenol, m-cresol, o-cresol, p-cresol.
Ketones – Acetone, cyclohexanone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone.

The most toxic of the extractable petroleum fractions, the C_{11} to C_{22} aromatics, has an oral RfD of 0.03. The polar families have oral RfDs that are a factor of about 3 to 167 times higher (less toxic), except for the phenols, which range from a factor of 0.02 to 10 higher. The alkylated phenols have RfDs that are lower or are about the same as the C_{11} to C_{22} aromatics. Importantly, the phenols, as well as the aldehydes and ketones, are intermediate metabolites that would likely be present in relatively small amounts and for relatively short time periods. The alcohols and organic acids are likely the most predominant polar families present in groundwater associated with a biodegrading petroleum source; the organic acids have been shown to range from about 30% to more than 50% of the total dissolved organic carbon [Thorn and Aiken 1998; Cozzarelli et al 1994; Eganhouse et al 1993]. Four of the five polar compound families have RfDs ranging from about 0.1 to 5, which is a factor of about 3 to 167 times higher compared to the RfD of 0.03 for the C_{11} to C_{22} aromatics. In addition, using the “average” oral RfD for each polar compound family and conservatively assuming that each family comprises 20% of the total mixture (i.e., giving each family equal weight),the overall average oral RfD for these five polar compound families is 0.7, which is a factor of 24 higher than 0.03. Based on this evaluation, it is reasonable to conclude that, in general, the toxicities of the polar biodegradation byproducts to human receptors are likely significantly lower (1/3 to less than 1/100, with an average of about 1/24) than the C_{11} to C_{22} aromatics petroleum fraction.

The potential toxicity posed by the polar biodegradation byproducts to aquatic ecological receptors has been the subject of a several peer-reviewed studies. The effects from the Exxon Valdez oil spill have been studied and it was concluded that although the polar oxidation products of petroleum hydrocarbons demonstrated some toxicity, they posed little actual risk to the marine organisms because of their high solubility, which results in rapid attenuation in the water column [Wolfe et al 1996]. Furthermore, it was pointed out that independent surveys showed that sediment toxicity in Prince William Sound declined in only two years to near background levels between 1989 (year of the spill) and 1991 [Wolfe et al 1996]. Other studies have shown that the polar compounds in the water-accommodated fraction from a biodegrading petroleum source demonstrated toxicity, but the response is highly variable depending on which taxonomic group and which species were tested [Neff et al 2000; Middaugh et al 1996; Middaugh et al 1998; Shelton et al 1999; Carls et al 1999;Heintz et al 1999]. It is also important to note that the microcosms and columns used in the various studies may have also been impacted by ammonia and sulfide resulting from the petroleum biodegradation, both of which are highly toxic to marine organisms [Page et al 2002]. In summary, although there may be measureable aquatic toxicity associated with the polar compounds resulting from oxidative biodegradation of petroleum, the actual risk is likely very low because the polar compounds are not expected to be persistent in surface waters.

Conclusions

The constituents in groundwater measured as part of the USEPA Method 8015mod (TPH-DRO) analysis and that are removed by the silica gel cleanup are not extractable petroleum hydrocarbons, but rather are biodegradation byproducts that are polar in their molecular structure. These polar compounds include alcohols, organic acids, phenols, ketones and aldehydes, with the alcohols and organic acids likely being the most predominant. The polar compounds are not persistent in oxygenated groundwater. The potential toxicity to human health posed by these polar compounds is not well studied, but based on available data for plausible representatives of four of the five families of polar compounds with PRGs, it is likely that they are less toxic than the C_{11} to C_{22} aromatics fraction by a factor of 3 to 167 (1/3 to less than 1/100 as toxic). Using the overall average RfD for all five families, which conservatively gives each family equal weight, the polar compounds may be less toxic than the C_{11} to C_{22} aromatics fraction by a factor of 24 (1/24 as toxic). Therefore, defaulting to the toxicity of the C_{11} to C_{22} aromatics petroleum fraction as currently requested by HDOH is unjustifiably conservative to assess the risk posed by the polar compounds. With respect to the potential toxicity posed by the polar biodegradation byproducts to aquatic receptors, these compounds appear to result in toxic effects in laboratory studies; however, the polar compounds are not expected to be persistent in surface water and therefore the actual risk is likely very low.

In summary, this evaluation supports the use of the MADEP fractionated analysis to assess risk rather than the USEPA Method 8015mod analysis because the potential toxicity posed by the polar components appears to be negligible compared to the toxicity of the C_{11} to C_{22} aromatics petroleum fraction.

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