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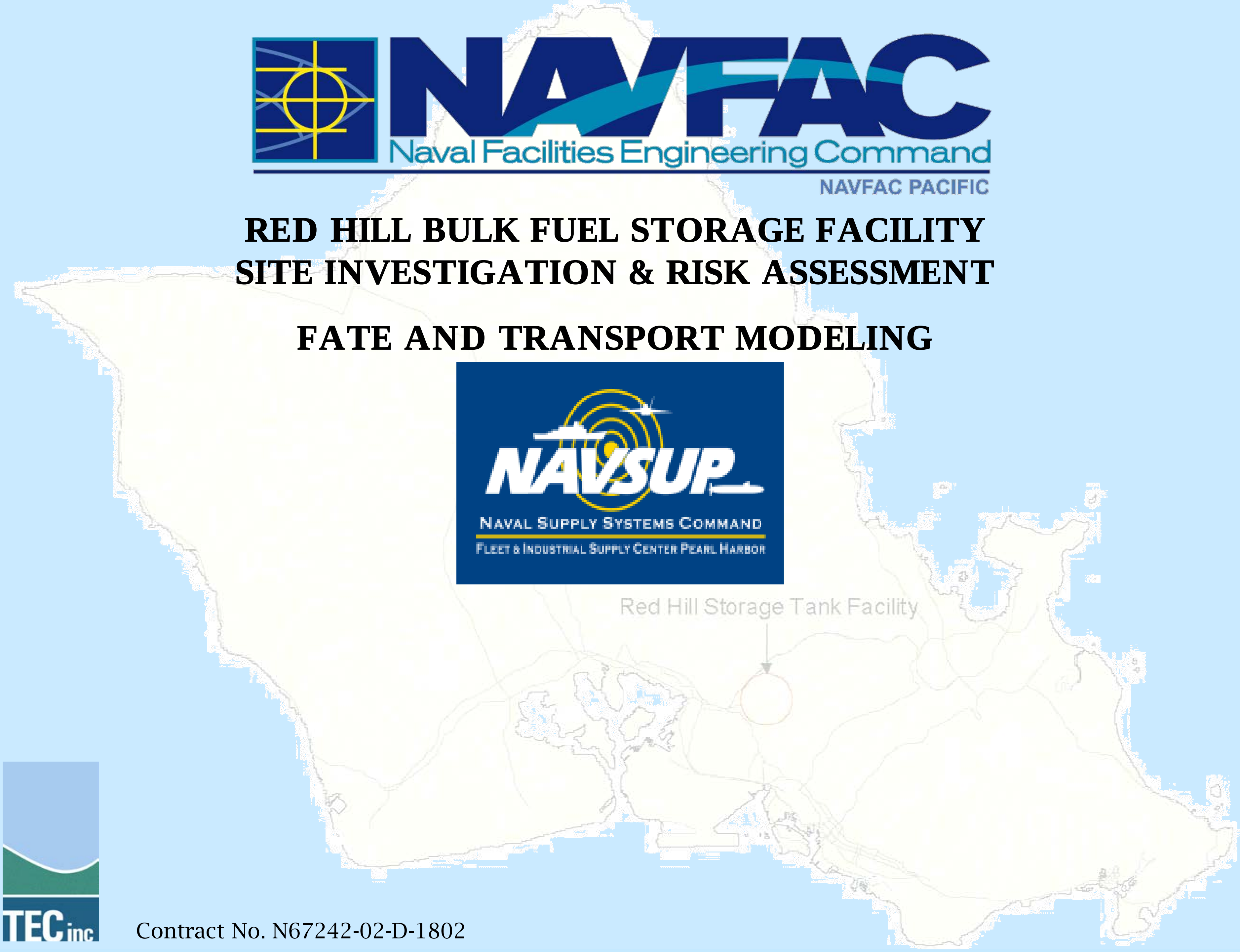
RED HILL BULK FUEL STORAGE FACILITY
SITE INVESTIGATION & RISK ASSESSMENT

FATE AND TRANSPORT MODELING

NAVSUP
NAVAL SUPPLY SYSTEMS COMMAND
FLEET & INDUSTRIAL SUPPLY CENTER PEARL HARBOR



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Contract No. N67242-02-D-1802

Contaminant Fate and Transport
U.S. Navy Red Hill Bulk Fuel Storage Facility, Hawaii

- First a disclaimer
  - This presentation summarizes the modeling done by TEC, Inc in support of an environmental investigation at the Red Hill Bulk Fuel Storage Facility
  - **It does not reflect** the views and opinions of the Hawaii Department of Health nor has it been vetted by HDOH
  - Partly taken from a presentation prepared for NAVFAC at the end of the project in 2007

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Contaminant Fate and Transport
U.S. Navy Red Hill Bulk Fuel Storage Facility, Hawaii

- Presentation purpose
  - Brief USN and EPA on 2007 Fate and Transport Model
    - Methods used
    - Overview of results
    - Gaps and uncertainties

Contaminant Fate and Transport
U.S. Navy Red Hill Bulk Fuel Storage Facility, Hawaii

- Background
  - 2005 – 2007 TEC, Inc. performed an environmental site investigation at the Red Hill Bulk Fuel Storage Facility
    - Installed 3 new wells and a monitoring point (increased network from 2 to 6)
    - Soil vapor monitoring pilot study
    - Eight rounds of groundwater sampling
    - **Hydrogeologic study**
      - Aquifer response test
      - Groundwater flow model
      - **Contaminant fate and transport model**

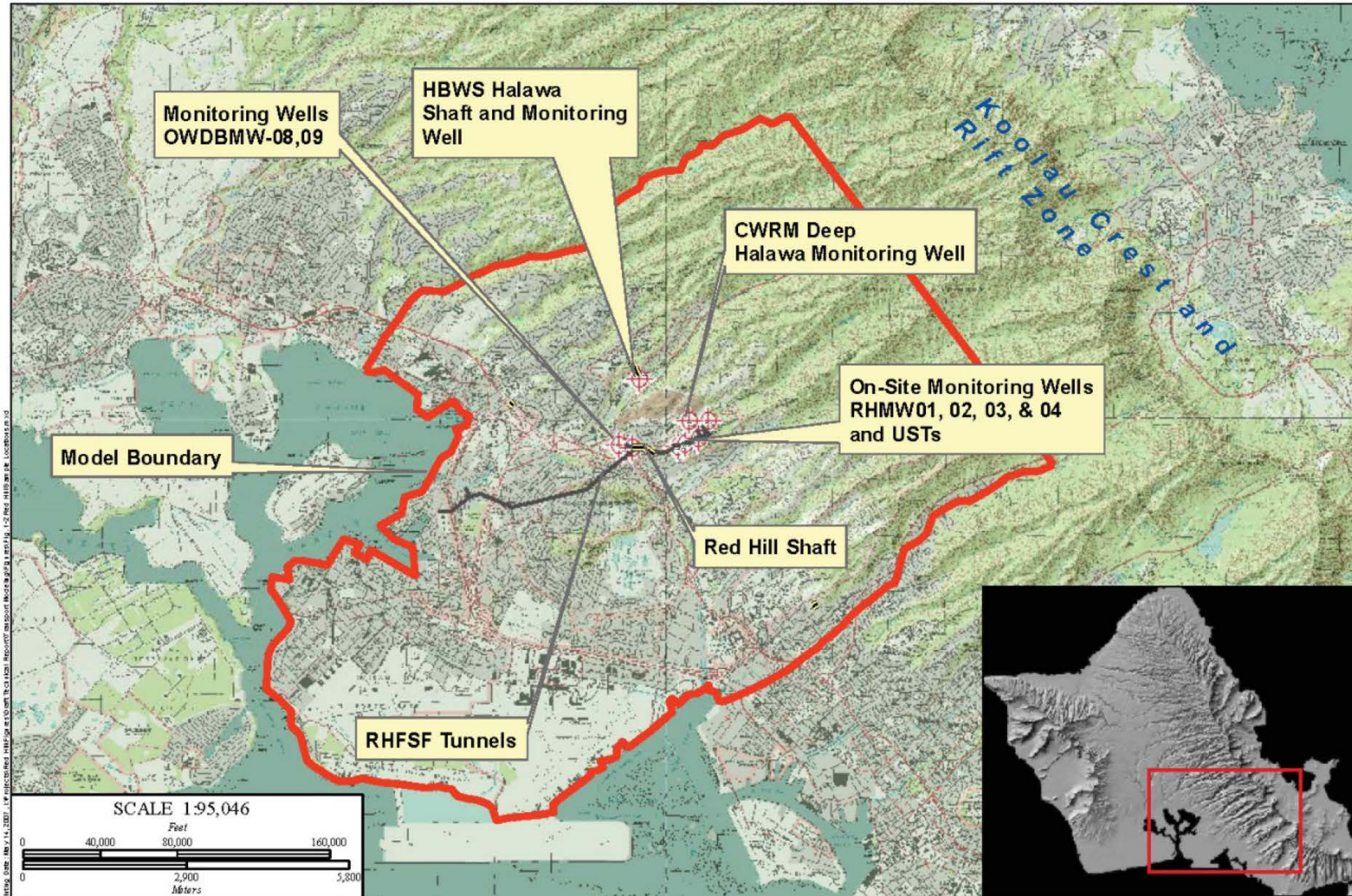
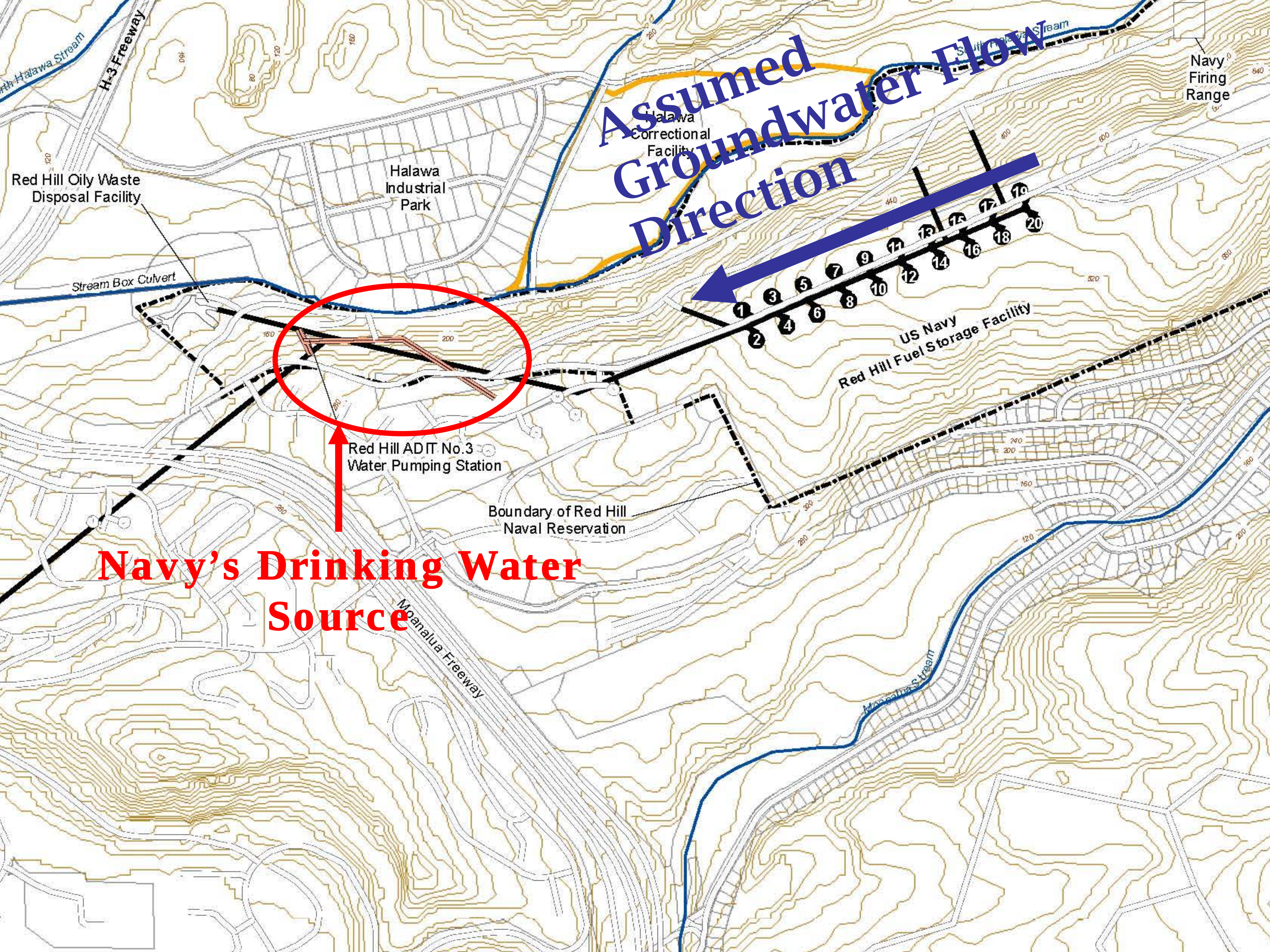


Figure 1-1
Map of Important Site Features



Assumed Groundwater Flow Direction
Navy's Drinking Water Source
Red Hill ADIT No.3
Water Pumping Station
Red Hill Oily Waste
Disposal Facility
Halawa
Industrial
Park
Halawa
Correctional
Facility
Navy
Firing
Range
Stream Box Culvert
US Navy
Red Hill Fuel Storage Facility
Boundary of Red Hill
Naval Reservation
H-3 Freeway
Moanalua Freeway
South Halawa Stream
Moanalua Stream
1
2
3
4
5
6
7
8
9
10
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19
20

Contaminant Fate and Transport

U.S. Navy Red Hill Bulk Fuel Storage Facility, Hawaii

Fate and Transport Modeling

- Modeling purpose
  - Tier 3 risk assessment
    - Establish site specific risk based limit for selected compounds of concern
    - Difficult to meet MCLs or EALs in the groundwater beneath the tanks
    - EALs for Species Evaluated
      - Benzene – 0.005 mg/L
      - Total Petroleum Hydrocarbons (TPH) – EAL – 0.100 mg/L
      - Must show compliance at drinking water source
    - Establish SSRBLs to ensure compliance at receptors of concern
- Modeling Question:
  - "How close can an LNAPL plume get to the Red Hill Shaft without exceeding MCL or EAL?"

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- What this model **DOESN'T** do:
  - Simulate the LNAPL migration in the vadose zone
  - Simulate the LNAPL migration along the water table
- What the model **DOES** do:
  - Estimate the degradation rate of dissolved contamination
  - Provide the foundation for Site Specific Risk Based Remediation Action Level (SSRBL)

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U.S. Navy Red Hill Bulk Fuel Storage Facility, Hawaii

Modeling Steps

- Select modeling code
- Identify requisite parameters
- Acquire or estimate requisite parameters
- Build conceptual model
- Convert conceptual model to grid
- Run model
- Make need adjustments (calibration, sensitivity)
- Interpret results

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Modeling Approach

- Select modeling code
  - Compatible with MODFLOW
    - MODPATH, MT3D, RT3D
  - MODPATH
    - Particle tracking, good for delineating zones of contribution and estimating groundwater velocity
    - No dispersion
  - MT3D
    - Simultaneously simulate transport of multiple species
    - Include dispersion, sorption, first order decay
    - Some challenges in acquiring needed parameters
  - RT3D
    - Similar to MT3D but can simulate the sequential biodegradation steps
    - Very challenging to get required parameters!

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U.S. Navy Red Hill Bulk Fuel Storage Facility, Hawaii

Modeling Approach - Selected modeling codes

- MODPATH
  - Delineating well capture zones
  - Estimating groundwater velocity
    - Estimate hydrocarbon degradation rates
- RT3D
  - Able to simulate the sequential degradation of the selected compounds
  - Focus of this presentation

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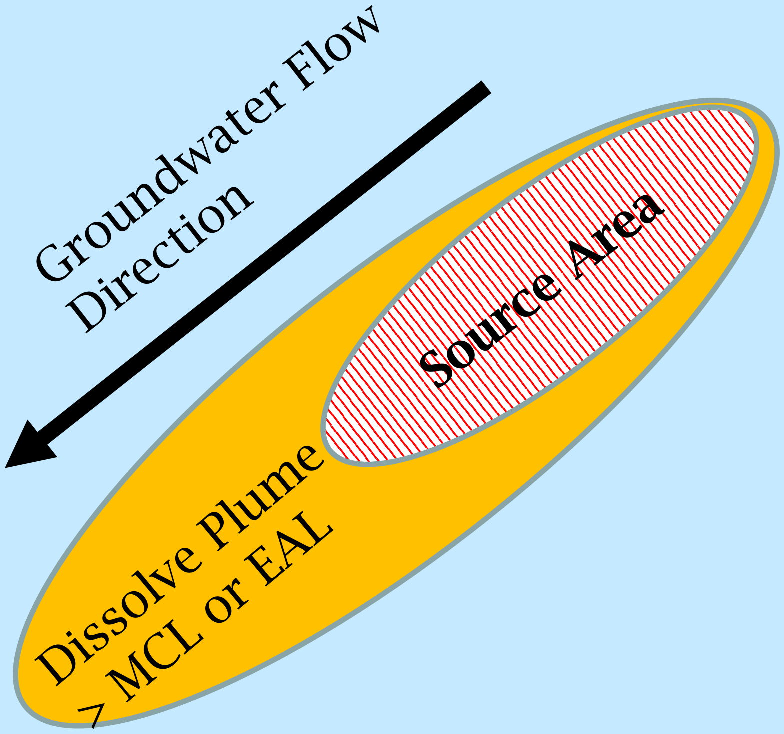

Modeling Approach

- Model source area as an immobile LNAPL Plume
- Simulate microbial mediated degradation in the dissolved plume
- Estimate distance dissolved plume travels prior to degrading to < MCL or EAL

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Modeling Approach

- RT3D required parameters
  - Dispersivity
    - What is dispersivity?
    - Estimated from rock core logs (50 ft) and USGS reports (250 ft)
    - Geometric mean 112 ft;
    - Estimated Lahaina Tracer Test Value - 82 ft (for comparison)
  - Sorption
    - Assumed to be zero
    - Conservative assumption
    - Likely not completely true
  - Natural Attenuation Parameters
    - Concentrations
    - Consumptive rate
    - Reaction rates and coefficients

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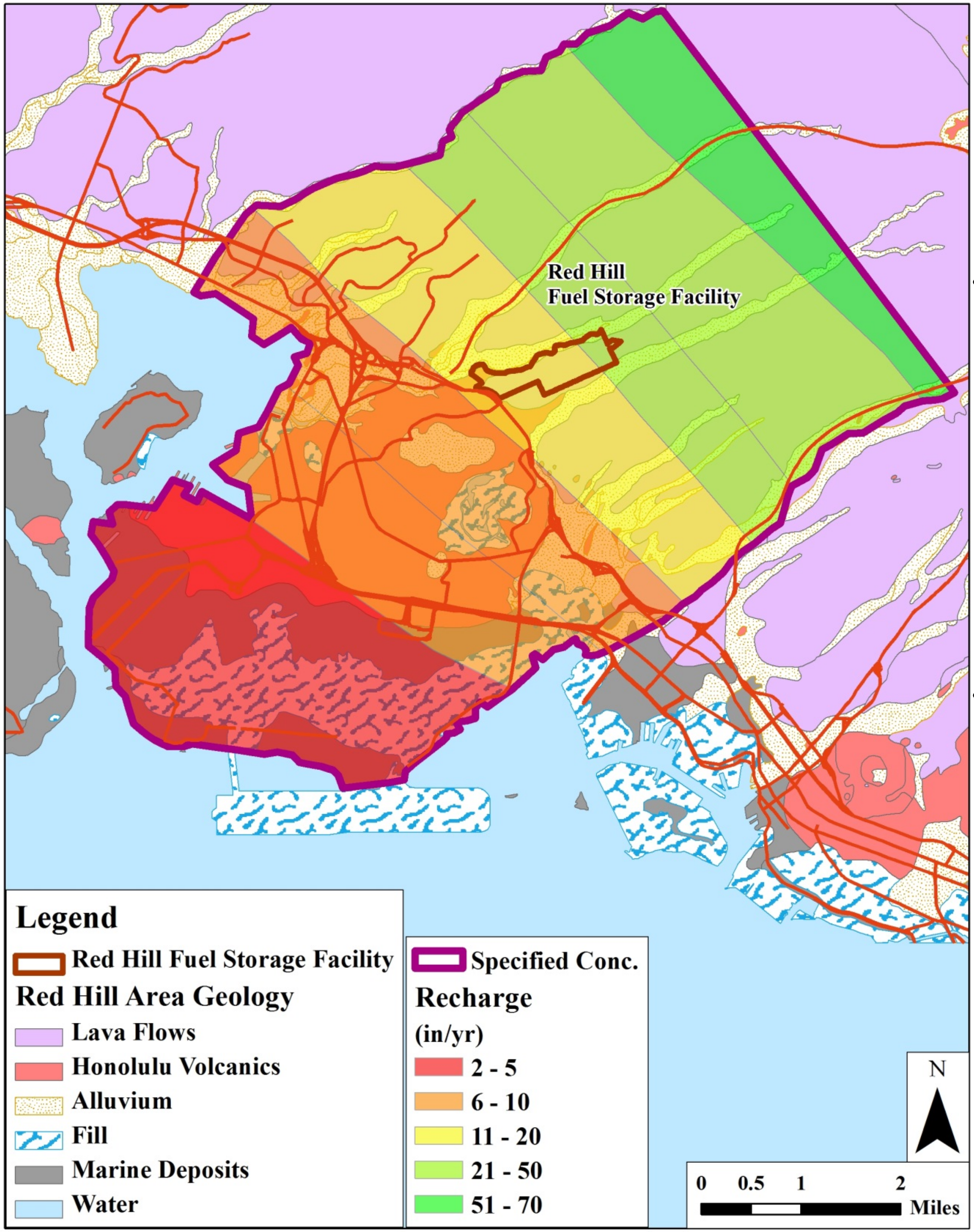
Acquire or estimate required parameters

- Select contaminants
  - TPH – high measured concentration
  - Benzene – mobility and toxicity
- Initial contaminant concentration
- Natural Attenuation Parameters (NAP)
  - Background and initial concentrations
  - Reaction rate coefficients
  - Stoichiometry coefficients
  - Must be modified from BTEX package values
    - Simulating TPH and Benzene so values different



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- Boundaries
  - Water table
  - Kalihi Valley
  - Marginal dike zone
  - Waiawa Valley
  - Shoreline
  - Midpoint of the freshwater/saltwater transition zone
- Model Boundary Conditions
  - Specified source area
    - Immobile LNAPL plume
  - Specified contaminant & NAP concentrations
    - At the lateral boundaries
    - In the recharge

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Initial Contaminant Concentration

Contaminant concentration = solubility

- $C_e = MF_a * S$
- Where:
  - C_e = effective solubility concentration (mg/L)
  - MF_a = Mole fraction of compound "a" in the fuel (unitless)
  - S = the pure phase solubility of the compound (mg/L)
- JP-5
  - 41 identified compounds (from American Petroleum Institute [API])
  - Only accounted for 41% weight percent of fuel
  - See Appendix A of F&T model report
  - Benzene not listed
    - Could be as much as 0.02 weight percent

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LNAPL Plume dissolution

- $MF_a = WF_a * \rho_{JP-5} / Mw_a$

- Where:
  - MF_a = the mole fraction of compound a (unitless);
  - WF_a = the weight fraction of the compound (unitless)
    - Value given in API fuel compositions
  - ρ_{JP-5} = the density of JP-5 (g/L);
  - MW_a – the molecular weight of compound a (g/mole).

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Results of dissolve phase calculations

Compound	Molecular Weight (g/mole)	Weight Fraction (percent)	Density (Kg/L)	Mole Fraction (unitless)	Pure Phase Solubility (mg/L)	Effective Solubility (mg/L)
Benzene[1]	**78.1**	**0.02**	**0.880**	**0.0004**	**1780**	**0.75**
Ethylbenzene[1]	92.4	0.01	0.870	0.0002	152	0.035
Toluene[1]	106.2	0.05	0.870	0.001	515	0.50
Xylenes	106.2	0.2	0.880	0.003	198	0.59
BTEX Total	NA	0.28		0.0046	NA	1.87
TPH	**NA**	**100**	**0.820**	**1.00**	**NA**	**4.5**
					ATSDR* estimated JP-5 solubility	5.0

1- weight fraction estimated

***Agency for Toxic Substances and Disease Registry**

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Natural Attenuation Parameters (NAP) and the Reactions That Occur

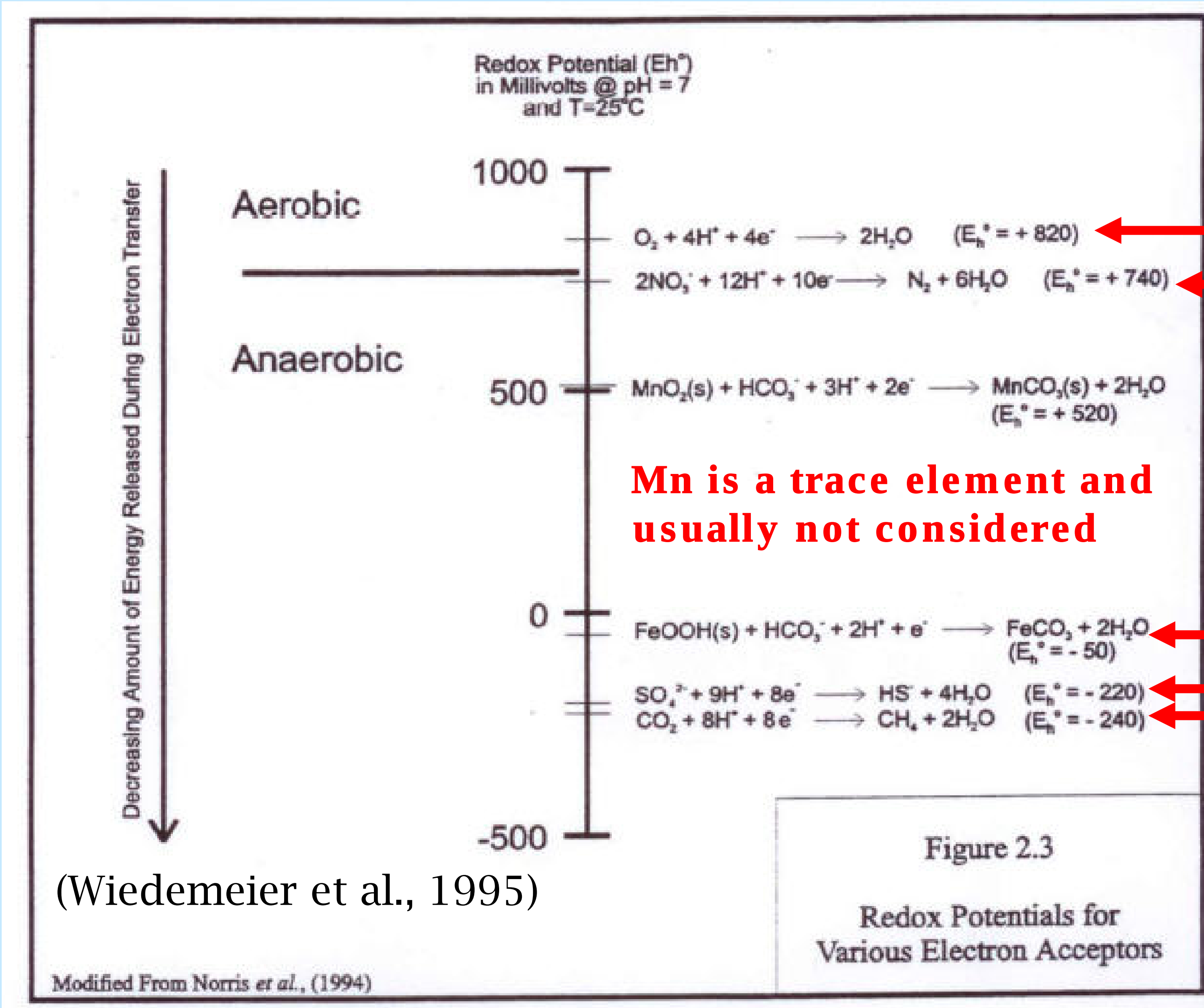

Figure 2.3

Redox Potentials for Various Electron Acceptors

1st O_2

2nd NO_3

3rd Fe^{3+}

4th SO_4

5th CO_2

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NAP Parameters

- Background concentration of each natural attenuation species
- Stoichiometry of natural attenuation reaction
  - Must be modified from BTEX package since simulated Benzene and TPH
  - See Appendix A
- Rate constants for each natural attenuation species
  - O_2, NO_3, Fe^{3+}, SO_4, CO_2
  - Used rates Lu et al, (1999), Hill AFB study

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Initial and background NAP Concentrations

Parameter	RHMW04 (mg/L)	RHMW01 (mg/L)	RHMW02 (mg/L)	RHMW03 (mg/L)	RHS (mg/L)	Modeled Conc. (mg/L)
Dissolved Oxygen	8.0	1.9	1.2	1.8	8.3	8.0
Nitrate[1]	0.5	0.0	0.2	1.1	0.6	1.0
Ferrous Iron[2]	0.03	3.1	2.5	0.9	0.1	6
Sulfate[1]	9.6	0.5	12.5	27.8	NT	25
Methane[2]	0.0	0.08	1.4	0.0	NT	3

NT – Not taken
RHS - Red Hill Shaft
1 Regional value
2 Maximum value measured at Hickam POL and RHFSF sites

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Calculated Stoichiometry Coefficients for TPH

NAP Species	Stoichiometry Coefficient for BTEX	Stoichiometry Coefficient for TPH
Oxygen	3.14	3.24
Nitrate	4.9	5.02
Ferrous Iron	21.8	22.7
Sulfate	4.7	4.86
Methane	0.78	0.81

mg-NAP (used or produced)/mg-TPH consumed

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Fate and Transport Modeling

- Model Simulations
  - Base – estimate proximity of LNAPL to RHS and still be compliant at the Red Hill Shaft
    - TPH
    - Benzene
  - Plume size
    - Step-wise increase in width and length
  - Infiltration only
    - Simulate the impact on groundwater of recharge moving through contamination in the unsaturated zone
  - Reaction rates

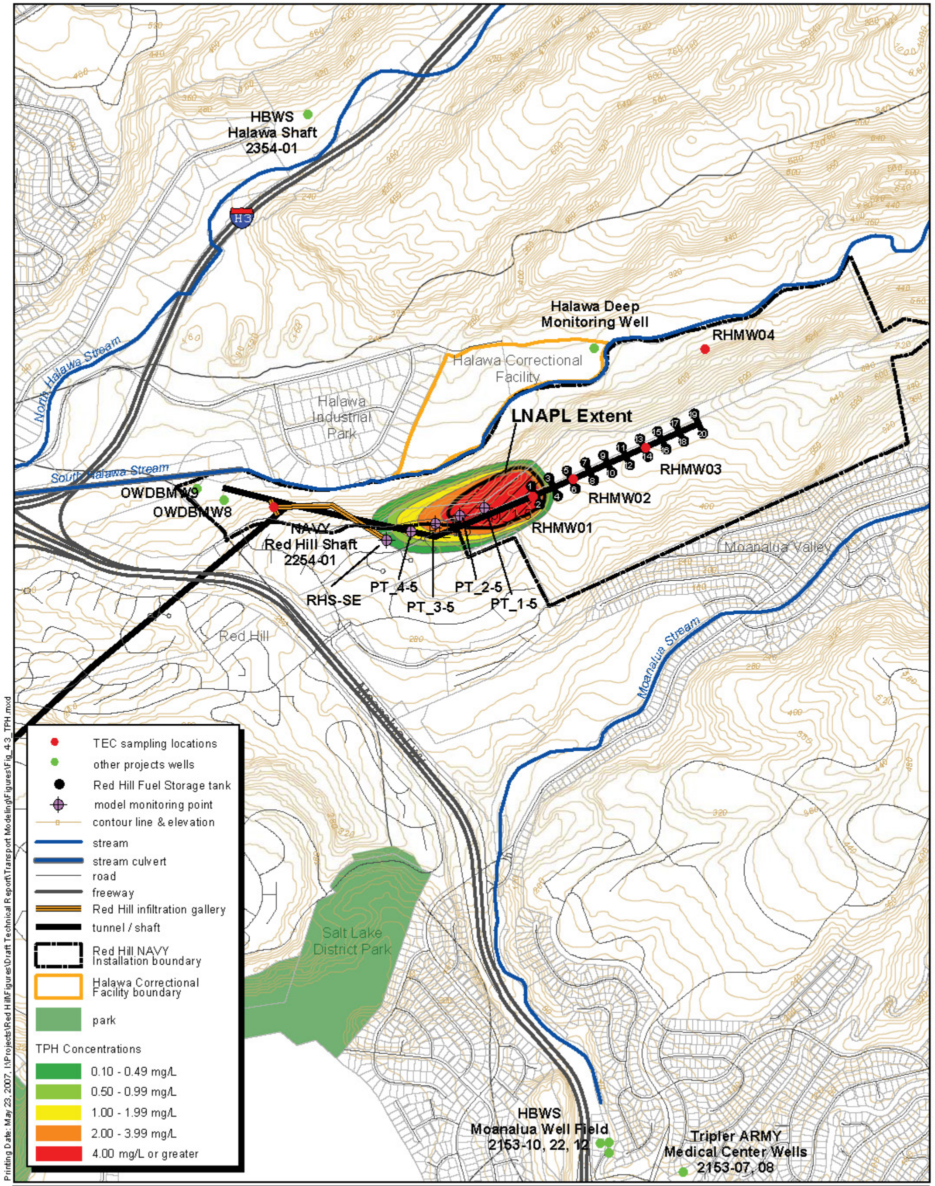

Figure 4-3
TPH Concentration Distribution When the TAL is Exceeded at the RHS

Fate and Transport Model Results

Total Petroleum Hydrocarbons

- LNAPL footprint red hatched oval
- Results
  - LNAPL must pass extend to point mid-way between RHMW01 and RHMW05 for an exceedance to occur at the RHS
- TPH Dissolution Rate
  - 2.7 mg/d/ft^2
  - Compared favorably with analytical model
    - Wiedeimerer et al (1995)

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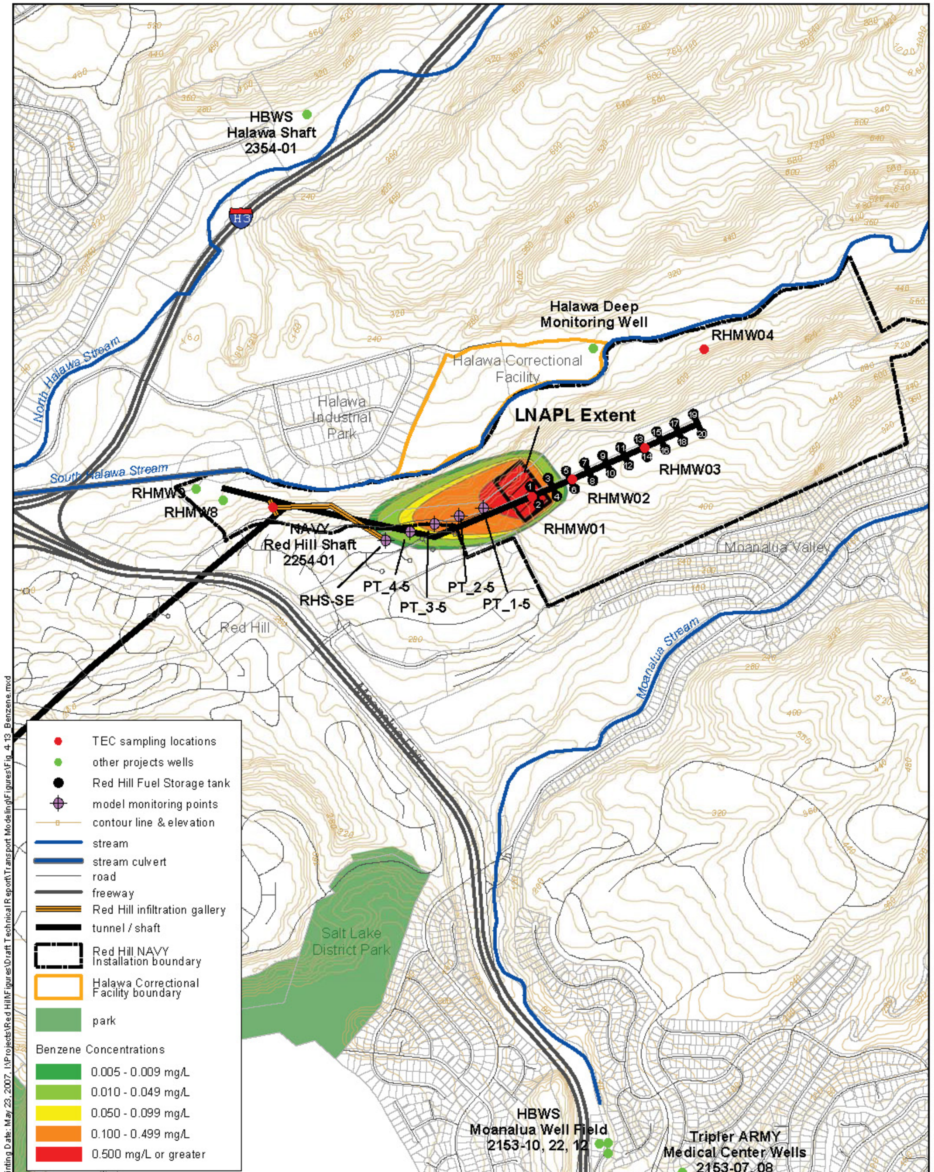


Figure 4-13
Benzene Concentration Distribution
for the Benzene Compliance Simulation

Fate and Transport Model Results

Benzene

- Results
  - An LNAPL plume that reaches just beyond RHMW01 could cause an exceedance at the RHS
- Concentration must be reduced by a factor of 150
  - TPH, only requires a 45 fold reduction
- But only infrequent, trace Benzene detections
  - Perhaps not a major risk driver

Sensitivity Analysis

- Plume geometry
  - Varied source area width and length
  - Results

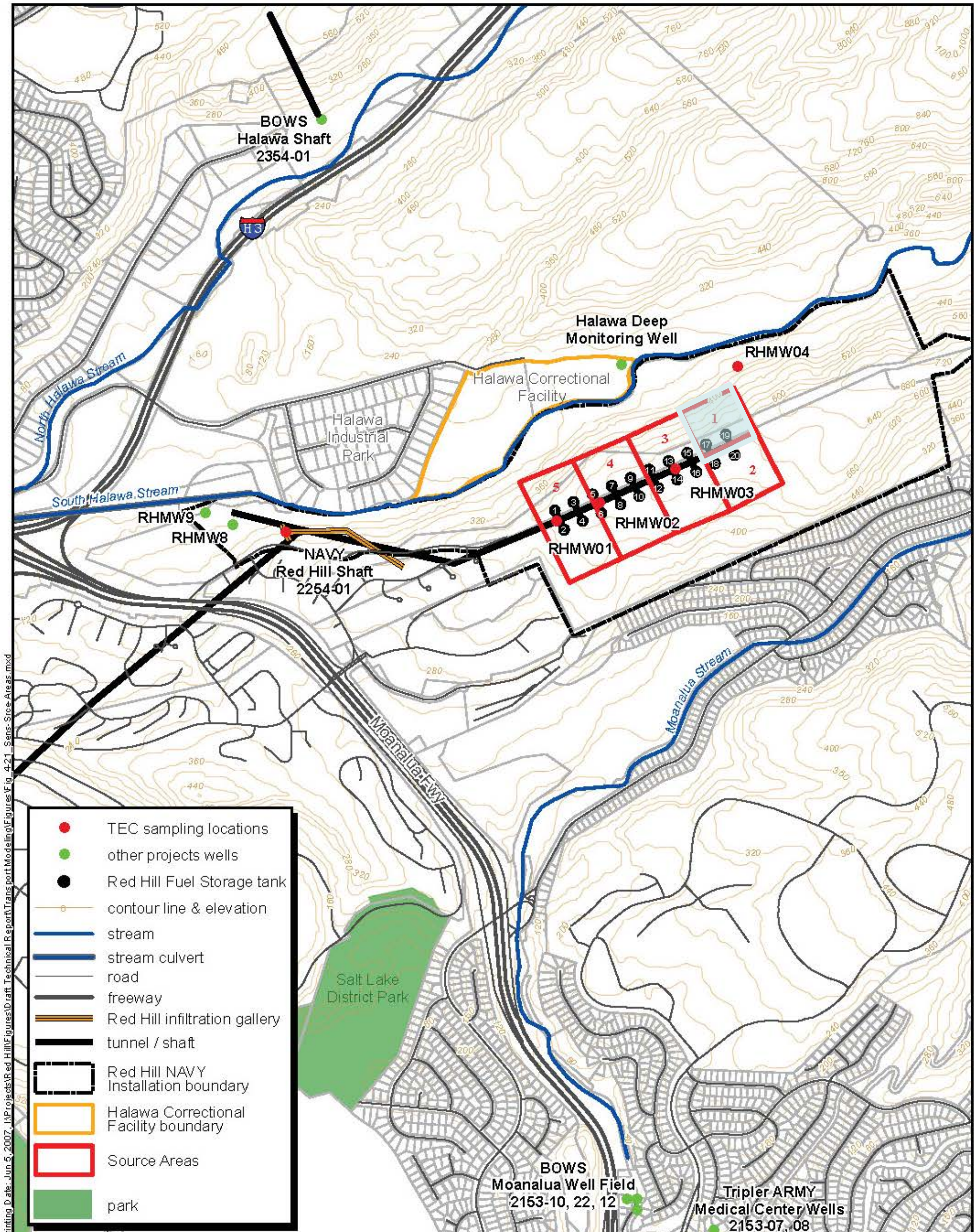
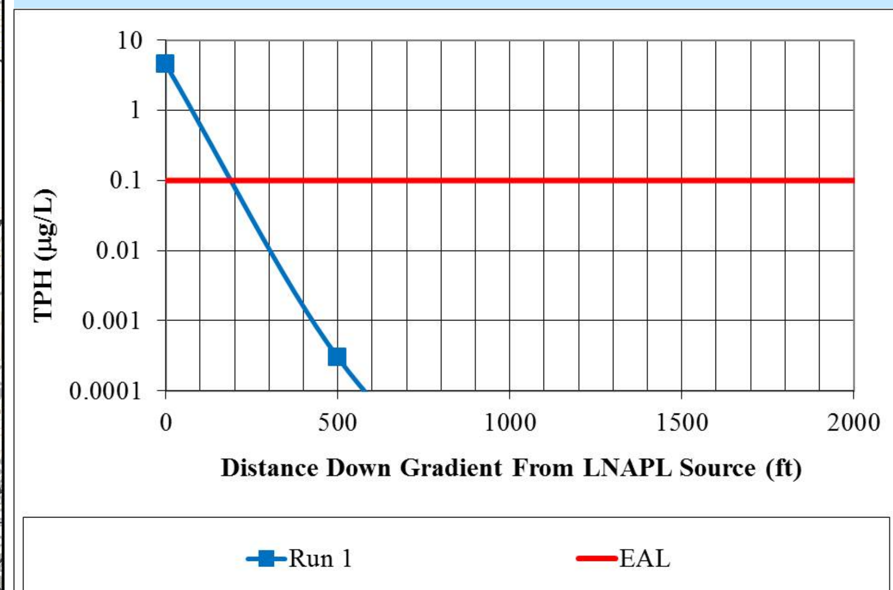


Figure 4-21
Source Areas for the Sensitivity Simulations



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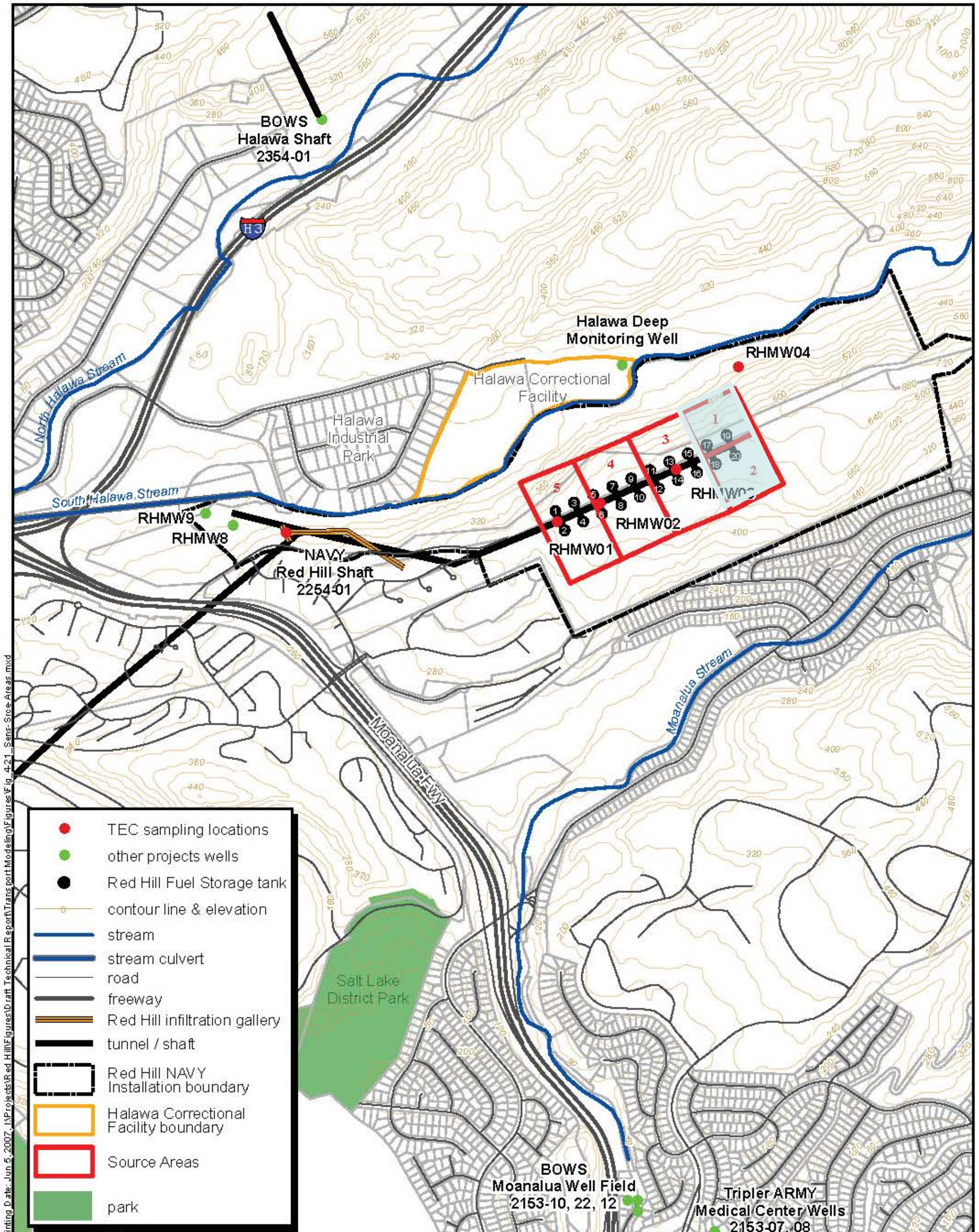
Sensitivity Analysis

- Plume geometry
  - Varied source area width and length
  - Results
    - Width is important



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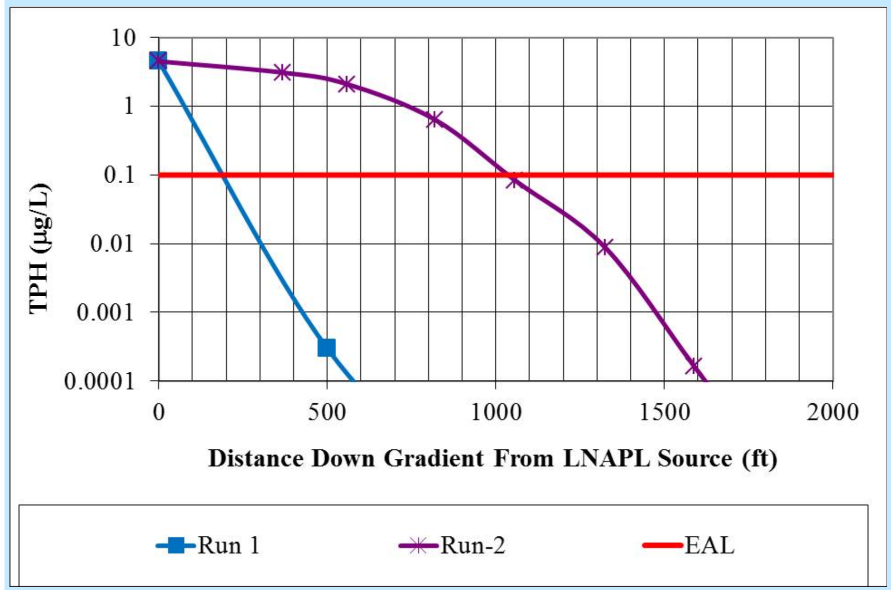

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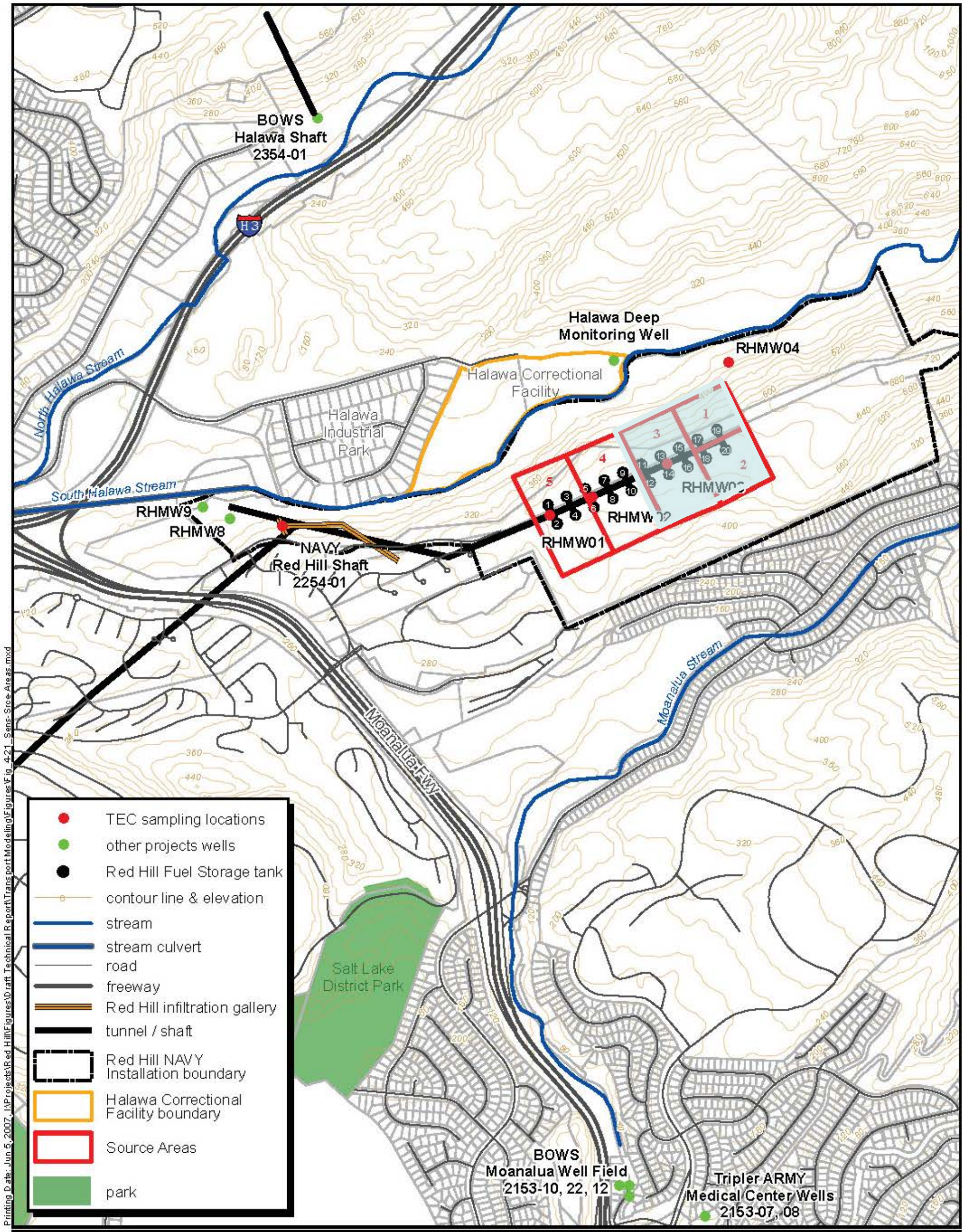
Sensitivity Analysis

- Plume geometry
  - Varied source area width and length
  - Results
    - Width is important
    - Little change as Length increased
    - Solubility limted



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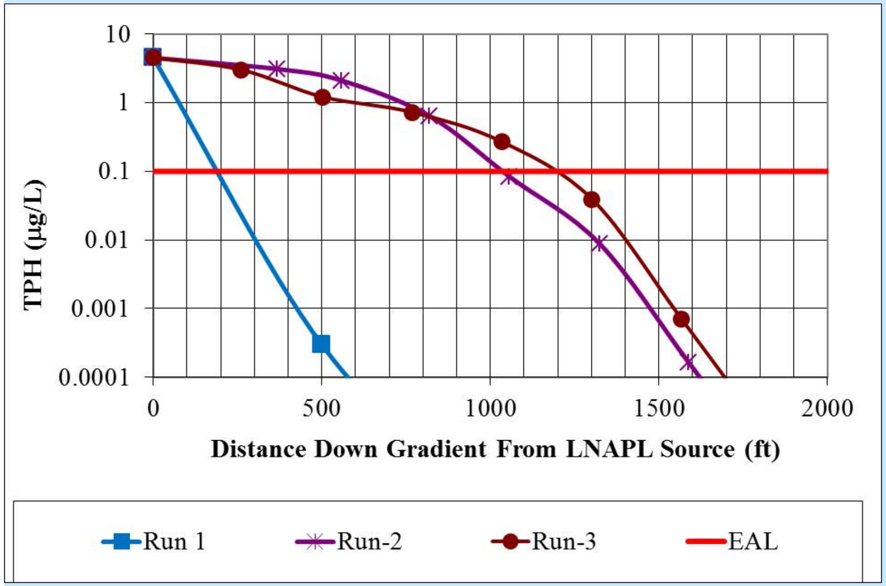

Sensitivity Analysis

- Recharge – with contamination from the unsaturated zone

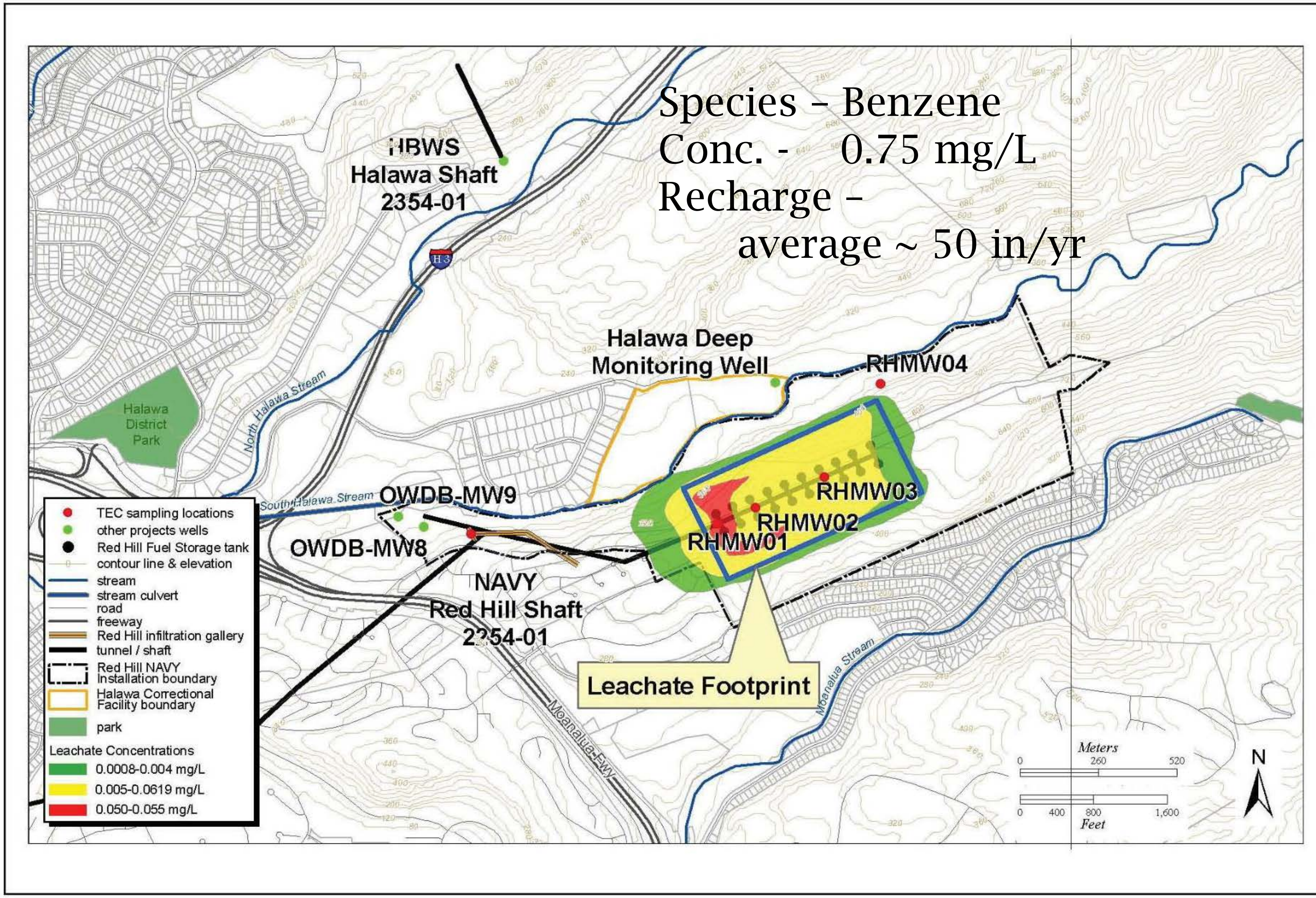

Figure 4-24. Benzene Contours for the Maximum Leachate Scenario
Red Hill Fuel Storage Facility
Oahu, Hawaii

Contaminant Fate and Transport

U.S. Navy Red Hill Bulk Fuel Storage Facility, Hawaii

Fate and Transport Modeling

NATURAL ATTENUATION

- Is natural attenuation of petroleum hydrocarbons occurring?
- Distribution of selected NAPs
  - Modeled vs.
  - Measured
- Is knowing the NAP reaction rates important?

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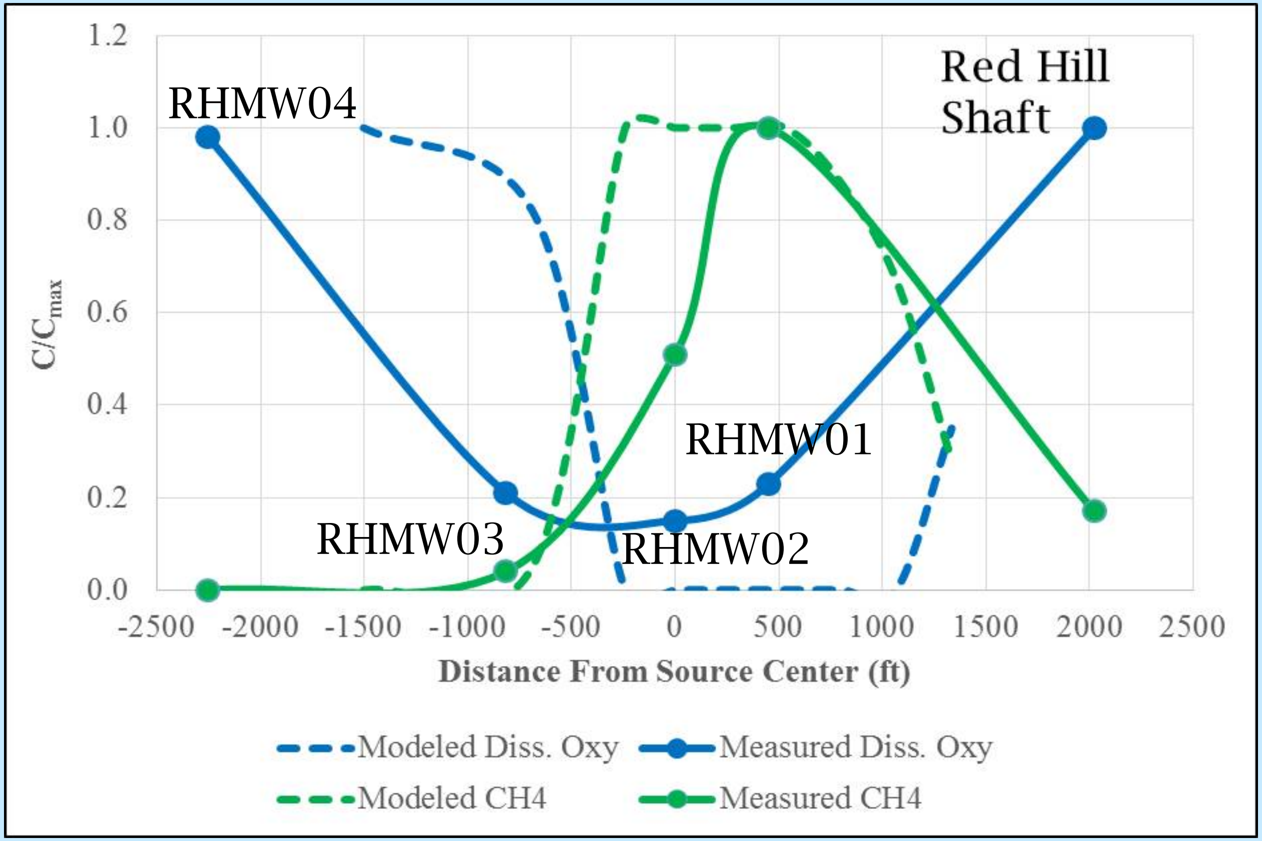

NAP Distribution

- Diss. Oxy
  - Dissolved oxygen
- CH4
  - Methane
- Dashed lines
  - Modeled conc.
- Solid lines
  - Measured
- Center of plume at RHMW02
- Similar traces
  - Natural attenuation is occurring
  - Rates are kinetic

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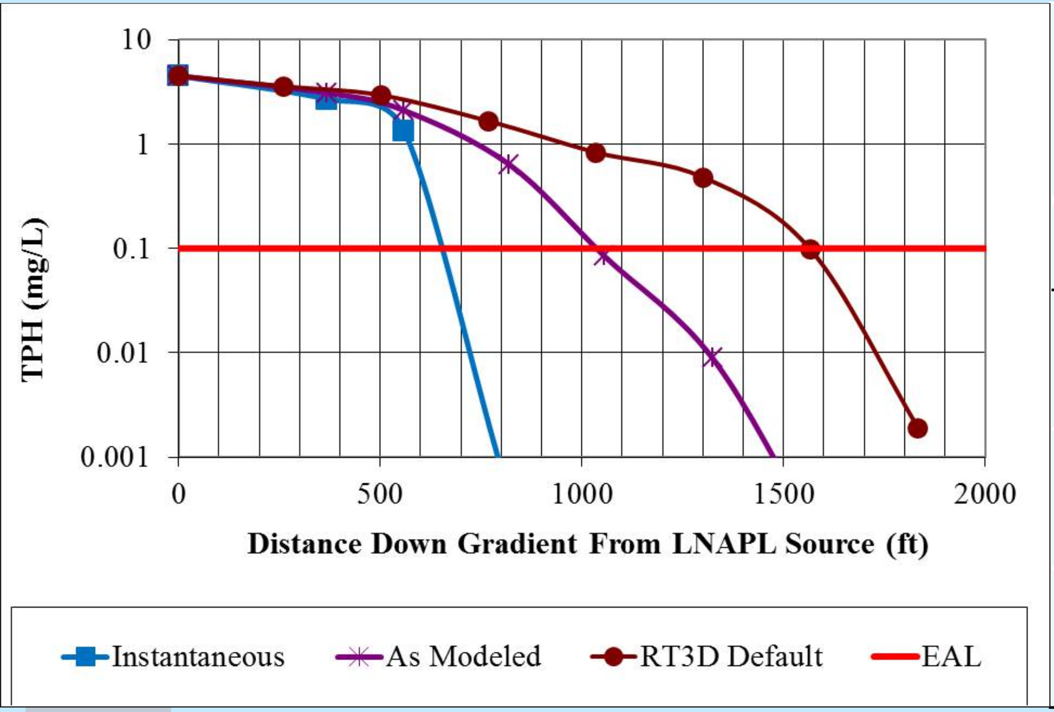
Sensitivity to Changes in Reaction Rate Coefficients



Scenario	Distance To Compliance	First Order Degradation Rate
	(ft)	(d^{-1})
Instan-taneous	530	0.020
As Modeled	1170	0.010
RT3D Default	1610	0.007

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- Modeling Conclusions
  - Jet fuels solubility is relatively low
    - TPH Solubility of ~5 Parts per Million (mg/L)
    - Benzene Content Low, 0.7 mg/L Maximum
      - **May be much less**
  - Red Hill dissolved contamination is not extremely mobile
  - Natural attenuation reduces TPH concentrations to < EAL over distances of 1000 – 2000 ft
  - Properly characterizing NAP reaction rates is important if doing RT3D modeling

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Fate and Transport Modeling

- Uncertainties
  - Actual solubility of JP-5 & 8
    - One analysis lists JP-8 solubility as 12 mg/L
  - Stoichiometry
    - Bulk rate of NAP utilization
  - Reaction rates and coefficients
    - Data indicates knowing these are important
  - Groundwater flow paths

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Fate and Transport Modeling

- Data Gaps (things we can measure)
  - Actual solubility of JP-5 & 8
  - Groundwater velocity
  - Aquifer dispersion characteristics
  - Bulk petroleum degradation rates
  - Which compounds are the primary risk drivers?
    - Benzene may not be a risk driver

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Fate and Transport Modeling

- Recommendations
  - Perform fuel solubility tests
    - Basis for SSRBLs
  - Tracer test
    - Groundwater velocity
    - Aquifer dispersion characteristics
  - Use tracer test to estimate contaminant retardation and decay
  - Geochemistry
    - Regional NAP concentrations (best to include all major ions and silica)
    - Selected stable isotopes
      - Sulfur (in sulfate)
      - O&H isotopes
      - Can be used to constrain flow paths
  - Again, these are recommendations from myself
    - **Not DOH recommendations**

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Thank You and Aloha

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