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From: Roger Brewer, PhD
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Subject: *Estimates of Contaminant Types and Concentrations in Joint Base Pearl Harbor Hickam Drinking Water System Following November 2021 Release of Jet Fuel from Red Hill Fuel Facility*

This memorandum summaries previous notes on estimates of the nature and magnitude of contamination of groundwater drawn into the Joint Base Pearl Harbor Hickam (JBPHH) drinking water system via the Red Hill Shaft following the November 20, 2021, release of JP-5 jet fuel from the Navy's Red Hill Bulk Fuel Storage Facility. Several thousand gallons of JP-5 jet fuel are estimated to have been drawn into the JBPHH drinking water system supply well at Red Hill following breakage of a fire suppression system pipe in Adit 3 of the facility (Cavanaugh 2022; USDN 2022a). The fuel had been unknowingly pumped into the fire suppression system following a May 6, 2021, release during the transfer of fuel between storage tanks in another area of the facility.

Estimates of maximum contaminant concentrations based on the solubility of individual JP-5 components and mixing (emulsion) of droplets of the fuel with water as it was drawn into the JBPHH drinking water system are presented. This information should assist in assessment of exposure and potential health effects of affected persons at JBPHH. More detailed testing of fuel samples from the Red Hill facility and discussions with outside petroleum experts is currently underway. This memorandum as well as HODH action levels JP-5 in tapwater will be updated as appropriate following completion of these tests and reviews, anticipated in late spring 2023.

Exposure Pathways of Concern

Exposure to petroleum in tapwater can occur via direct ingestion of tapwater, dermal contact during bathing and inhalation of vapors during bathing (see HIDOH 2017, 2022; USEPA 2021). Dermal exposure focuses the uptake of more soluble and less volatile aromatic carbon range compounds that could penetrate the skin during bathing. Highly volatile aliphatic compounds are assumed to be rapidly emitted from the water (USEPA 2021). Degraded, hydrocarbon-related compounds are assumed to pose a similar health risk as the parent hydrocarbon compounds (HIDOH 2017, 2022; CAEPA 2019).

Contaminants of Potential Concern

Health risk posed by JP-5 and other petroleum fuels is assessed in terms of three components: 1) Individually targeted compounds such as benzene, toluene, ethylbenzene, xylenes, methylnaphthalenes and naphthalene (BTEXMN); 2) Non-specific compounds associated with aliphatic and aromatic carbon ranges and 3) Hydrocarbon-related degradation products. The latter includes complex mixtures of degradation products associated with the partial oxidation of BTEXMN- and carbon range compounds, referred to as "Hydrocarbon Oxidation Products (HOPs)."

Under HIDOH guidance, HOPs compounds are assumed to have a similar toxicity as the original, parent hydrocarbon compounds (HIDOH 2017; see also Mohler et al. 2013; Zemo et al. 2013; CAEPA 2019). The sum of non-degraded carbon ranges and hydrocarbon-related degradation products is collectively reported as "Total Petroleum Hydrocarbon (TPH)" Consideration of this mixture of non-specific compounds in assessment of health risk is required under HIDOH guidance (HIDOH 2022).

Composition of JP-5 Jet Fuel

Petroleum Hydrocarbons

Jet fuel is composed of refined hydrocarbons and additives used to stabilize or enhance the performance of the fuel. Table 1 presents the relative makeup of older JP-5 jet fuel (1990s to early 2000s) and more modern JP-5 fuel in terms of BTEXMN and aliphatic and aromatic carbon ranges.

Data for older formulations were only available at the time that the HIDOH TPH action levels for JP-5 were developed (HIDOH 2022). Testing of more current formulations of JP-5 by Newfields on behalf of HIDOH indicate significantly lower concentrations of in xylenes and methylnaphthalenes in current JP-5 and a corresponding increase in C8-C18 aliphatics (see Table 1; Newfields 2022).

The relative BTEXMN and carbon range makeup of more modern JP-5 fuel is assumed to be more representative of the fuel that was released at the Navy's Red Hill facility in 2021. The HIDOH JP-5 action levels will be updated based on the newer data as well as testing of actual fuel from the Red Hill facility currently underway.

Additives

A summary of other additives used in JP-5 fuel is provided in Attachment A. The fuel stored at the Red Hill facility has been confirmed by the Navy to contain antioxidants, corrosion inhibitor/lubricity improver, and Fuel System Icing Inhibitor (USDN 2022b). A detailed list of specific chemicals and concentrations of the additives has not been provided by the Navy. Compounds noted in Table 2 are based on information for jet fuel additives provided in Department of Defense (DoD) fuel specifications (e.g., DoD 1999, 2011, 2016) and include:

- Diethylene Glycol Monomethyl Ether (Fuel System Icing Inhibitor),
- 2,6-Di-Tert-Butyl-4-Methylphenol (Antioxidant),
- Linoleic acid dimers (Lubricity Improver).

A more detailed review of these and other potential additives in the fuel stored at the Red Hill facility is currently underway.

Other Potential Contaminants

The Navy reportedly used the surfactant Simple Green to clean the floors and walls of Adit 3 following the November 2021 release of JP-5 jet fuel. An unspecified amount of water was used. Surfactants such as Simple Green are highly soluble and can enhance the emulsification, mixing and mobility of petroleum in water.

It is possible that groundwater in the vicinity of the Red Hill Shaft was also contaminated with this product. Indicator compounds associated with the presence of Simple Green were not to my knowledge included in testing of groundwater in the vicinity of the Red Hill Shaft following the November 2021 release.

Estimated Contaminant Levels in Groundwater

Table 3 presents estimates of the types and magnitude of contaminants in groundwater in the vicinity of the Red Hill water supply shaft following the November 21, 2021, release of JP-5 jet fuel. Estimations for concentrations of both dissolved-phase fuel and emulsified fuel in groundwater are provided.

Comparison to risk-based action levels for individual contaminants is included in Table 3 for reference. The action levels represent concentrations of contaminants in tapwater that are considered to not pose a health risk over several years of exposure ("chronic health risk"). Risk-based action levels for exposure over very short time periods – days or weeks, are not currently available ("acute health risk").

Dissolved-Phase Fuel in Groundwater

Dissolved-phase concentrations of individual JP-5 jet fuel components in groundwater in the immediately vicinity of the November 2021 release were calculated based on the effective solubility of the component in water (see also HIDOH 2022). Effective solubility is calculated as:

$$C_i = \left(\frac{w_i \times 0.01}{MW_i} \times MW_{ave}\right) \times S_i. \quad \text{Eq 1).}$$

Where:

Ci = Effective solubility of the compound;
Si = Pure component solubility.
wi =Weight percent of the constituent in the mixture (converted to a fraction);
MWi = Average molecular weight of the constituent; and
MWave = Average molecular weight of the mixture.

Physiochemical constants for individual components used in the equation are provided in Attachment B. An average molecular weight for JP-5 fuel of 185 was assumed for the calculations (NRC 1996).

The effective solubilities are assumed to reflect the maximum, dissolved-phase concentration of hydrocarbons and additives in water that is in direct contact with fresh product. The sum of the calculated, effective solubilities predicts a concentration of dissolved-phase hydrocarbons in water in contact with fresh JP-5 of 6.1 mg/L (see Table 3). This is in agreement with the general, total solubility of middle distillate fuels in water (HIDOH 2017).

Predicted concentrations of BTEXMN are lower than that presented in the April 2022, TPH action level memorandum due to a lower concentration of these compounds in more modern JP-5 jet fuel (see HIDOH 2022). The predicted concentration of non-specific, >C8 aromatics is correspondingly higher.

The high concentration of dissolved-phase Diethylene Glycol Monomethyl Ether (DiEGME or methyl carbitol) noted in Table 3 is due to the complete solubility (miscibility) of this compound in water. This compound would have been quickly drawn into groundwater in contact with JP-5 fuel and is likely to have entered the Red Hill Shaft drinking water system ahead of less soluble and less mobile, petroleum contaminants.

Emulsified Fuel in Groundwater

Residents reported sheens on tapwater prior to disconnection of the Red Hill Shaft well from the JBPHH drinking water system. This suggests the presence of emulsified fuel in the water. For comparison, Table 3 includes a calculation of contaminant concentrations in water that contains 0.015% emulsified fuel (150 mg/L; see following section). This is intended to reflect elevated concentrations of TPH reported for samples of groundwater collected within the Red Hill Shaft immediately following the November 2021 release.

Under this scenario, concentrations of dissolved-phase contaminants in the water could approach those noted in Table 3. The combined mixture of emulsified and dissolved-phase fuel would represent the highest exposure and health risk to JBPHH residents.

Red Hill Shaft Groundwater Data

A total concentration of jet fuel-related compounds in groundwater (TPH) of 142 mg/L was reported for a sample collected from the Red Hill Shaft tunnel on December 8, 2021 (monitoring well RHMW2254-01). This exceeds the solubility of jet fuel (typically 5-10 mg/L) and is indicative of emulsified droplets of fuel in the water. Benzene was not detected at a detection limit of 0.2 µg/L. Ethylbenzene, toluene and xylenes were reported at concentrations of 0.63 µg/L, 0.11 µg/L and 7.2 µg/L, respectively.

The relative proportions of BTEX compounds reasonably matches that predicted by their content in modern JP-5 fuel and estimations of effective solubility. The low concentrations with respect to that predicted for the reported level of TPH reported for the sample suggests that much of the BTEX had already degraded (compare predictive effective solubilities in Table 3). The degradation products would have been included under the umbrella analysis for TPH.

The fuel system icing inhibitor DiEGME (2-(2 methoxyethoxy)-ethanol) was reported at a concentration of 32 mg/L in a Navy sample collected from the "Adit 3 Sump" on December 21, 2021, several weeks after the release. DiEGME has a half-life of approximately 15 days (EC 2009), suggesting that the concentration in the groundwater could have been significantly higher immediately following the November 21, 2021, release.

Groundwater Entering JBPHH Drinking Water System

Concentrations of emulsified and dissolved-phase JP-5 fuel estimated and reported for groundwater in the vicinity of the Red Hill Shaft drinking water shaft would likely have been diluted by deeper and/or cleaner groundwater pulled into the well during active pumping. The presence of strong vapors and sheens on tapwater by JBPHH residents suggests that slugs of relatively undiluted, contaminated groundwater could have been drawn into the drinking water system at some points in time.

Assessment of Health Risk

Estimation of emulsified and dissolved-phase contaminants in groundwater in the vicinity of the Red Hill Shaft provides a starting point for estimation of contaminant concentrations in tapwater within JBPHH and exposure of residents following the November 2021 release of JP-5 at the bulk fuel storage facility. A comparison of the effective solubilities of JP-5 components to risk-based action levels suggests that lower-toxicity, fuel system icing inhibitor compounds such as diethylene glycol monomethyl ether could pose the most significant health risk from exposure to contaminated water. This is due to the enhanced solubility of these compounds and the resulting high, relative dissolved-phase concentration in groundwater in comparison to other compounds.

Non-specific aromatic compounds included under >C-8 aromatics also pose an increased, relative risk in combination with individually targeted compounds such as BTEX and PAHs. Degraded BTEX and PAH compounds are assumed to have the same toxicity as the parent compounds under HIDOH guidance (HIDOH 2017, 2022). Related polar degradation products will be collectively reported under "Total Petroleum Hydrocarbon (TPH)" using standard laboratory analytical techniques and in the absence of silica gel cleanup (e.g., USEPA Method 8015M). Relatively high concentrations of degraded compounds could remain in water in the absence of significant concentrations of individual BTEX and PAH compounds. This emphasizes the need to consider TPH data in assessment of health risk. Cumulative and synergistic health effects posed by the total mixture of fresh and degraded contaminants in the tapwater should also be considered.

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Table 1. Relative makeup of JP-5 fuel based on later 1990s to early 2000s fuel specifications in versus makeup of more modern formulations.

Chemical/ Carbon Range	[1]Relative Carbon Range Makeup of 1990s-2000s Formulations of JP-5 Jet Fuel	[2]Relative Carbon Range Makeup of Current Formulations of JP-5 Jet Fuel
Total BTEXMN:	11%	1.8%
Total Carbon Ranges:	89%	98.2%
Benzene	0.03%	0.00%
Toluene	0.10%	0.03%
Ethylbenzene	0.00%	0.05%
Xylenes	4.6%	0.25%
1-Methylnaphthalene	3.5%	0.35%
2-Methylnaphthalene	0.0%	0.48%
Naphthalene	3.0%	0.69%
C5-C8 Aliphatics	12%	0.42%
>C8-C18 Aliphatics	68%	79%
>C18-C32 Aliphatics	0.0%	0.0%
>C8 Aromatics	9.0%	19%

Notes:

1. Relative makeup of JP-5 neat fuel based on summary review of Department of Defense military fuel specification requirements (USDOD 1998, 2004, 2016) provided by the US Navy (Mumy 2021). Used to prepare April 2022 and earlier HIDHOH TPH EALs for JP-5 (HIDOH 2022).

2. Default makeup of JP-5 neat fuel based on testing of modern JP-5 fuel (after Newfields 2022). This is assumed to be more representative of fuel stored at the Navy's Red Hill facility and released in 2021. Note the significant reduction in xylenes and methylnaphthalenes in current JP-5 and the corresponding increase in C8-C18 aliphatics.

Table 2. Example additives stated by the Navy to be present in JP-5 fuel stored at the Red Hill facility.

Purpose	Example Compounds	Estimated Concentration In JP-5 Fuel
[1]Fuel System Icing Inhibitor (FSII)	• Diethylene glycol monomethyl ether (DEGMME)	0.11% (1,100 mg/L)
[1]Antioxidants	• 2,6-Di-tert-butyl-4-methylphenol • 2,4-dimethyl-6-tert-butylphenol • Mixed methyl and dimethyl tert-butylphenols	0.0024% (24 mg/L)
[2]Corrosion Inhibitor/ Lubricity Improver	• Linoleic acid dimers	0.0054% (54 mg/L)

1. Reference: MIL-DTL-5624W (DoD 1999, 2016).
2. Reference: Flake et. al (2014); see also MIL-PRF-25017H (DoD 2011). Specific chemicals used in JP-5 proprietary.

Table 3. Estimated makeup and maximum concentration of JP-5 related contaminants in groundwater in the vicinity of the Red Hill Shaft intake following the November 2021 release.

	Compound	[1]Estimated Weight Percent Makeup of JP-5 Jet Fuel	[3]Concentration in Water Containing 0.015% Emulsified JP-5 (µg/L)	[4]Estimated Maximum Dissolved-Phase Concentration in Water (µg/L)	[5]Tapwater Action Level (µg/L)	Notes
[1]JP-5 Fuel	Benzene	0.004%	5.9	168	5.0	Tapwater Action levels for individual compounds from HIDOH 2017.
	Toluene	0.025%	38	267	1,000	
	Ethylbenzene	0.049%	74	145	700	
	Xylenes	0.25%	374	775	10,000	
	1-Methylnaphthalene	0.48%	722	162	27	
	2-Methylnaphthalene	0.69%	1,035	221	34	
	Naphthalene	0.35%	524	156	17	
	C5-C8 Aliphatics	0.42%	634	75	266	Sum of carbon range data compared to April 2022 HIDOH action level for JP-5 in tapwater.
	>C8-C18 Aliphatics	79%	118,533	58		
	>C18-C32 Aliphatics	0.0%	0	0.0		
	>C8 Aromatics	19%	28,062	4,074		
	Total Hydrocarbons (ug/L):		150,000	6,101		
[2]JP-5 Additives	Diethylene Glycol Monomethyl Ether (Fuel System Icing Inhibitor)	0.11%	1,100	1,695,833	800	DoD Fuel Spec MIL-DTL-5624W (DoD 2016). Fuel System Ice Inhibitor used in JP-5 jet fuel at a concentration of up to 0.11% (1,100 mg/L). 100% soluble in water (miscible). Not included in HIDOH EALs. USEPA Tapwater Screening Level noted (USEPA 2022).
	2,6-Di-Tert-Butyl-4-Methylphenol (Antioxidant)	0.0024%	24	1.2	3.4	Antioxidant noted in DoD Fuel Spec MIL-DTL-5624W (DoD 2016). Specific compounds used in JP-5 at Red Hill not provided by Navy. Not included in HIDOH EALs. USEPA Tapwater Screening Level noted (USEPA 2022).
	Linoleic acid dimers (Lubricity Improver)	0.0054%	54	0.005	(not available)	Often used as a Lubricant Improver in petroleum fuels (Flake 2014). Assumed low-toxicity (Flake 2014)? Low solubility and low concentration in fuel.
Other	Simple Green (cleaning agent)	(not applicable)	(not applicable)	(unknown)	(not available)	Reportedly used in cleaning of floor and walls of Adit 3 following November 2021 release of JP-5 jet fuel. Assumed low-toxicity but can enhance emulsification and mobility of fuel in groundwater.

Table 3 (cont.). Estimated makeup and maximum concentration of JP-5 related contaminants in groundwater in the vicinity of the Red Hill Shaft intake following the November 2021 release.

Notes:
1. Chemical makeup of JP-5 based on analytical data for generic sample of JP-5 (Newfields 2022). Additives not tested for in sample.
2. Types of additives confirmed by Navy to be present in JP-5 fuel stored at the Red Hill facility (USDN 2022b). Estimated percent makeup in fuel based on Department of Defense fuel specifications (see text). Specific additive compounds in JP-5 fuel stored at Red Hill not disclosed but assumed to be similar to those noted in fuel specifications.
3. For example only. Intended to reflect maximum concentration of TPH reported for groundwater samples collected in Red Hill drinking water supply shaft immediately following release (see text).
4. Predicted initial dissolved-phase concentration of contaminant in water that is in contact with fresh product (effective solubility).
5. Refer to Table D-3a in HIDOH Environmental Action Level guidance for individual compounds (HIDOH 2017). Action level for dissolved JP-5 in tapwater from HIDOH (2022). Action levels for example additives taken from USEPA Regional Screening Levels guidance (USEPA 2022). The action levels represent concentrations of contaminants in tapwater that are considered to not pose a health risk over several years of exposure ("chronic health risk"). Risk-based action levels for exposure over very short time periods – days or weeks ("acute health risk") are not currently available but would presumably be higher.

Attachment A: Summary of Potential Additives in JP-5 Fuel Stored at Red Hill Bulk Fuel Storage Facility (UAEPA 2016)

Attachment B: Physiochemical Constants used in Calculation of Effective Solubilities

	Chemical/ Carbon Range	[1]Molecular Weight	[1]Pure Component Solubility (mg/L)	[2]Estimated Weight Percent Makeup of JP-5 Jet Fuel	[3]Effective Solubility (mg/L)
	Benzene	78	1,790	0.004%	0.17
	Toluene	92	526	0.025%	0.27
	Ethylbenzene	106	169	0.049%	0.15
	Xylenes	106	178	0.25%	0.78
	1-Methylnaphthalene	142	25.8	0.48%	0.16
	2-Methylnaphthalene	142	24.6	0.69%	0.22
	Naphthalene	128	31	0.35%	0.16
C5-C8 Aliphatics	**C5-C6 Aliphatics**	81	36	0.046%	0.04
	>C6-C8 Aliphatics	100	5.4	0.38%	0.04
>C8-C18 Aliphatics	**>C8-C10 Aliphatics**	130	0.43	7.3%	0.04
	>C10-C12 Aliphatics	160	0.03	34%	0.01
	>C12-C16 Aliphatics	200	7.6E-04	38%	2.7E-04
	>C16-C21 Aliphatics	270	2.5E-06	0.27%	4.7E-09
>C18-C32 Aliphatics	**>C21-C32 Aliphatics**	400	1.5E-11	0.00%	0.00
>C8 Aromatics	**>C8-C10 Aromatics**	120	65	0.90%	0.90
	>C10-C12 Aromatics	130	25	6.7%	2.4
	>C12-C16 Aromatics	150	5.8	11%	0.78
	>C16-C21 Aromatics	190	0.65	0.20%	1.3E-03
	>C21-C32 Aromatics	240	6.6E-03	0.00%	0.00
[4,5]Additives	**Diethylene glycol monomethyl ether (DiEGME)**	120	1.0E+06	0.11%	1,696
	2,6-Di-tert-butyl-4-methylphenol	220	60	0.0024%	0.0012
	Linoleic Acid	280	1.39E-01	0.0054%	5.0E-06
			Sum BTEXN:	**1.8%**	**1.9**
			Sum Carbon Ranges:	**98.2%**	**4.2**
			Sum BTEXN+ Carbon Ranges:	**100%**	**6.1**

Attachment B (cont.). Physiochemical Constants used in Calculation of Effective Solubilities

Notes:

1. Physiochemical constants for petroleum fuel components from to HIDOH (2022) Technical Memorandum for JP-5 tapwater action levels.
2. Chemical makeup of JP-5 based on analytical data for generic sample of JP-5 (Newfields 2022). Additives not tested for in sample. Additional review pending.
3. Refer to text for calculation of effective solubility.
4. Types of additives confirmed by Navy to be present in JP-5 fuel stored at the Red Hill facility (USDN 2022b). Estimated percent makeup in fuel based on Department of Defense fuel specifications (see text). Specific additive compounds in JP-5 fuel stored at Red Hill not disclosed but assumed to be similar to those noted in fuel specifications.
5. Constants for DEGMME (CAS# 111-77-03) and 2,6-Di-tert-butyl-4-methylphenol (CAS# 128-37-0) taken from USEPA Regional Screening Levels guidance (USEPA 2022). Constants for linoleic acids (CAS# 60-33-3) taken from GESTIS Substance Database as referenced in Wikipedia (accessed 2/3/23; https://en.wikipedia.org/wiki/Linoleic_acid#cite_note-GESTIS-3)