



**DEPARTMENT OF THE NAVY**

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Mr. Bob Pallarino  
U.S. Environmental Protection Agency, Region 9  
75 Hawthorne Street  
San Francisco, CA 94105

Mr. Steven Y.K. Chang, P.E., Chief  
State of Hawaii Department of Health  
Solid and Hazardous Waste Branch  
919 Ala Moana Boulevard, Room 210  
Honolulu, HI 96814

Dear Mr. Pallarino and Mr. Chang:

**SUBJECT: NAVY'S RESPONSE TO SPLIT SAMPLING RESULTS FROM FIRST QUARTER 2017, ADMINISTRATIVE ORDER ON CONSENT STATEMENT OF WORK SECTION 6 AND SECTION 7, RED HILL BULK FUEL STORAGE FACILITY (RED HILL), JOINT BASE PEARL HARBOR-HICKAM, OAHU, HAWAII**

The Navy is in receipt of the September 12, 2017 correspondence that details the split sampling analysis performed by the United States Environmental Protection Agency (EPA) Region 9 and Hawaii Department of Health (DOH) (herein collectively referred to as the "Regulatory Agencies") for groundwater samples collected by the Navy with field oversight from DOH from January 2017 to March 2017. Based on the split sampling results outlined in the September 12, 2017 letter, it is the Navy's understanding that results for the chemical compounds and parameters analyzed by the EPA Region 9 Laboratory are consistent with the Navy's contracted laboratory aside from the differences for nitrate and TPH-DRO. The Navy also wants to expeditiously determine the cause in analytical differences between the two labs and is taking steps to further evaluate the split sampling analysis, specifically addressing the differences in laboratory results for total petroleum hydrocarbon diesel-range organics (TPH-DRO) as this is considered a chemical of potential concern (COPC).

The Navy shares the Regulatory Agencies' commitment to provide accurate and quality data to protect groundwater resources and resolving this issue as expeditiously as possible. In order to generate environmental data of known and documented quality, the Navy utilizes a Department of Defense (DoD) Environmental Laboratory Accreditation Program (ELAP) accredited analytical laboratory. DoD ELAP certification includes standard operating procedure (SOP) reviews and verification of compliance with stringent performance and protocol requirements detailed in the DoD Quality Systems Manual (QSM) (DoD 2017). Additionally, analytical laboratory results generated by the Navy's contracted laboratory undergo independent third-party data validation by a separate contractor to ensure compliance with the analytical method and the DoD QSM. The Navy also understands that the EPA Region 9 Laboratory undergoes a similar level of scrutiny. The Navy believes that the process detailed in this letter will help resolve these differences in reported concentrations of TPH-DRO in order to increase confidence in the analytical results.

Petroleum hydrocarbons are unique in environmental site assessment and management since petroleum hydrocarbons are a complex mixture of chemical compounds comprised of thousands of compounds with carbon chain lengths ranging from 3 to 40 carbons. Following a petroleum hydrocarbon release into the environment, the complex petroleum mixtures are subject to change due to a multitude of processes commonly referred to as weathering (e.g., volatilization, dissolution, biodegradation, oxidation, etc.). Assessment of these complex mixtures is conducted through the estimation of TPH, which is generally the total amount of petroleum-based hydrocarbons extracted and quantified by a particular analytical method in a given environmental matrix (e.g., water, soil, sediment, etc.).

TPH analytical methods vary in scope to a great extent, with each providing results within a particular range, while some results may be nonspecific in certain cases. Hence, understanding how the laboratory analysis was carried out for TPH is crucial for appropriate interpretation of the results obtained. Furthermore, there is no federal or EPA method developed specifically for TPH. EPA SW-846 Method 8015C includes guidelines for TPH. These guidelines were added to an analytical method that was originally developed for non-halogenated compounds by gas chromatography (GC)/flame ionization detector (FID). Most TPH analytical methods in use cite this method and qualify it as "modified".

While this analytical method provides quality assurance and quality control (QA/QC) guidelines for TPH analysis, this method does not mandate specific steps in the analysis and each analytical laboratory has multiple options that could be utilized which may lead to differing analytical results between laboratories. For example, within the framework of TPH analysis presented as guidance under EPA SW-846 Method 8015C, sample preparation, extraction, clean-up, concentration, separation, and quantification as well as calibration standards may vary between laboratories. Hydrocarbon extraction and analytical efficiency are not identical for each laboratory's implementation of EPA SW-846 Method 8015C, and may produce different TPH concentrations. The details in each step are critical, as the results are dependent on the method; thus, TPH results from different laboratories can vary. The best way to achieve consistent and comparable TPH results by different laboratories is to ensure that the laboratories are using the same extraction solvent, preparation steps, type of calibration standard, carbon range, and quantitation protocol.

Similarly, the nitrate concentrations reported by the two laboratories are influenced by laboratory-specific details in steps of nitrate analysis performed using EPA Method 300.0 (e.g., sample preparation, calibration, quantification, etc.). Additionally, nitrate may undergo denitrification and, if so, is converted to dinitrogen ( $N_2$ ) in a short period of time; thus, nitrate only has a 48-hour method-recommended hold time. This short hold time combined with the difference between laboratory analyses times from sample collection may also contribute to analytical result differences.

During the split sampling, the following efforts were made by the EPA Region 9 Laboratory and the Navy's contracted laboratory to have consistency in the protocol for TPH analysis: (1) use of EPA SW-846 Method 8015 as guidance to analyze TPH-DRO and TPH-residual/oil/lube-oil range organics (RRO); (2) reporting TPH ranges in accordance with the DOH Technical Guidance Manual (DOH 2016b); and (3) use of the same extraction solvent. However, in evaluating the split sampling data, it was observed that several laboratory protocols varied including but not limited to: (1) volume of groundwater used per sample during extraction; (2) extraction methodology; (3) calibration standards; and (4) calibration range. These protocol differences may have contributed to the observed concentration differences for TPH-DRO. For example, in regards to extraction methodology, if a laboratory does not adequately solvent-rinse the sample containers after decanting the sample volume into the extraction vessel, there may be less TPH extracted due to undissolved petroleum potentially adhering to the sample container, which may lead to a lower concentration value for that sample.

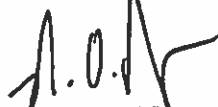
While the aforementioned presents possible reasons for the observed differences in laboratory results for TPH-DRO, the Navy recommends the following actions to further evaluate the split sampling results and to identify resolutions:

1. Following the Navy's review of the Level IV data packages received from the EPA on September 22, 2017, the Navy requests follow-on discussion with the EPA Quality Assurance Office regarding analytical options utilized in each step of the TPH analysis.
2. In order to obtain a more definitive understanding of the analytical differences between the EPA Region 9 Laboratory and the Navy's contracted laboratory, the Navy requests third-party validation of EPA Region 9 Laboratory Level IV data packages be performed as soon as possible utilizing identical validation criteria used in validation of analytical laboratory results generated by the Navy's contracted laboratory.
3. As part of the third-party validation process, the Navy requests single- and/or double-blinded performance testing sample analysis be performed by EPA Region 9 Laboratory and the Navy's contracted laboratory.
  - EPA Region 9 Laboratory and the Navy's contracted laboratory analyze up to three (3) single- or double-blind TPH-DRO performance testing (PT) samples provided by a third-party vendor utilizing analytical protocols used by each laboratory during the January 2017, February 2017, and March 2017 split sampling events. Performing PT sample analysis will help allow for evaluation of any laboratory bias (low or high) in analyzing TPH in groundwater; and three PT samples will provide sufficient data points to determine a trend.
  - EPA Region 9 Laboratory and the Navy's contracted laboratory analyze a single- or double-blind TPH-DRO PT sample provided by a third-party vendor utilizing each laboratory's analytical protocols modified to have identical initial sample extraction volumes (i.e., 1 liter). Modifying the laboratories' analytical methods to have identical initial sample extraction volumes will allow for evaluation of concentration variability due to different initial sample extraction volumes.
4. To address potential issues related to sample volume and extraction, collection of additional split sampling data is needed from upcoming groundwater sampling events. Additional split sampling will include the following:
  - Collect split groundwater samples from select monitoring wells (i.e., RHMW01, RHMW02, and RHMW03) to be analyzed by the EPA Region 9 Laboratory and the Navy's contracted laboratory for TPH-DRO and TPH-RRO, with and without silica gel cleanup, utilizing EPA Method 8015 with the analytical protocols modified to have identical initial sample extraction volume (i.e., 1 liter). Modifying the laboratories' analytical methods to have identical initial sample extraction volumes will allow for evaluation of any concentration variability due to different initial sample extraction volumes. Additionally, analysis with and without silica gel cleanup will allow for evaluation of what is being measured as TPH (i.e., hydrocarbons from fuels) and potential contribution of polar material from fuel degradation to differences reported concentrations for TPH-DRO. Analysis with and without silica gel cleanup may also reduce uncertainties in identification of fuel type that may be present in groundwater. Presence of these polar compounds may cause misidentification of the fuel type(s) (e.g., diesel, jet fuel, etc.) in the groundwater.
  - Collect split groundwater samples from select monitoring wells (i.e., RHMW01, RHMW02, and RHMW03) to be analyzed by the EPA Region 9 Laboratory and the Navy's contracted laboratory for polyaromatic hydrocarbons (PAHs) utilizing EPA Method 8270 SIM. Concentrations of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene were generally consistent between the two laboratories, thus PAHs are likely suitable markers of consistent dissolved COPC concentrations in sample volumes sent to each laboratory.

Upon evaluation of the Level IV data packages, the third-party validation of these data packages, and the aforementioned analysis of PT and split samples, the Navy will expeditiously prepare a formal response on the cause of the laboratory differences in TPH-DRO. The Navy's ability to perform a complete evaluation is contingent on availability of this information. The Navy appreciates the Regulatory Agencies' support to address our shared interest in evaluating these laboratory differences.

If you have any questions, please contact Aaron Y. Poentis of our Regional Environmental Department at (808) 471-3858 or at [aaron.poentis@navy.mil](mailto:aaron.poentis@navy.mil).

Sincerely,



R. D. HAYES, III  
Captain, CEC, U.S. Navy  
Regional Engineer  
By direction of the  
Commander

References:

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