Technical Review

Of

Technical Memorandum:

Joint Base Pearl Harbor-Hickam (JBPHH) Water Distribution System (System):

Lines of Evidence (LOEs) Regarding Total Petroleum Hydrocarbon (TPH) Detections during Long-Term Monitoring (LTM)

Prepared for:

The Honolulu Board of Water Supply (BWS)

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Executive Summary

Due to a JP-5 leakage event in 2021 from the Red Hill storage farm, water samples from the JBPHH were monitored in seven Long Term Monitoring (LTM) segments. During the monitoring process it was noted that some zones had an increase in the frequency of low-level TPH detections. This increase in frequency was especially noticed in some zones during LTM 6. The Department of the Navy, the Environmental Protection Agency and the Hawaii Department of Health formed a task force to identify the cause of this apparent increase in TPH observations. The conclusion of the interagency team was:

1. The increase was not due to contamination by JP-5 from Red Hill or any other source of TPH from Red Hill.
2. The increase was due to contamination from the laboratory during the sample preparation procedure and from a reaction of the surrogate chemical with residual chlorine.

Some background information is useful to understand this discussion. Method 8015[1], a method from the EPA's SW-846 method compendium[2], was used to analyze the extracted water samples. This method was developed to analyze samples for the presence of fuels such as gasoline, diesel or oil. Method 8015 is a technique that measures any organic chemical that can burn. Because it responds to any flammable chemical and not just fuel related chemicals, it is considered a non-specific method and can suffer from interfering chemicals. It measures the amount of a fuel by how large the signal is and uses a metric called retention time to distinguish between gas, diesel or oil, which all have different retention times. Therefore, when a sample contains chemicals with the same retention time of, for example, diesel, then the system reports out a number that is assumed to be from diesel but in fact may not be. This is called a false positive result. The task force concluded that the increase in TPH detections was a false positive and that there is no TPH in the water samples.

To prepare the sample for this type of analysis, it is usually necessary to extract and concentrate the components from the sample matrix to minimize interference from the matrix and improve the detection limit. The method used to prepare the samples for this project was Method 3510C, also from the EPA's method compendium. In Chapter 4 of the SW-846 compendium[3], it is stated that drinking water samples should be treated to remove the residual chlorine before extracting the sample. This is done to prevent chlorine from having any unwanted reactions with chemicals that may be present in the sample. When extracting a sample with this method, a single compound, called a surrogate, is added prior to extraction to monitor how complete the extraction was. Often these chemicals react with residual chlorine if it is not removed before the surrogate is added. Method 8015 uses a chemical called o-Terphenyl as the surrogate.

The sample collection process for this project should have had a sample preservation procedure to remove residual chlorine but this was not done and may indicate a non-compliance with method 3510C[4].

The laboratory has determined what signal intensity is detectable and not simply noise and what concentration of fuel that corresponds to. This is the method detection limit (MDL). The laboratory has also established a fuel concentration that may be quantitated accurately. This is the Method Reporting Limit (MRL). A sample may have a small amount of fuel that is below the MRL and above the MDL so that it is suspected that something is in the sample, but its concentration cannot be known with certainty. These types of results are often caused by contamination issues or method artifacts and not from the target analyte. Results that are between the MDL and the MRL are qualified by the laboratory by placing a "J" next to the reported number. These are the types of results that were observed with increasing frequency during the JBPHH monitoring project.

Samples called method blanks (MB) originate at the analytical laboratory and are extracted and analyzed at the same time as the samples. This is done to gain information about contamination coming from the analytical process, whether it is from the extraction process or an artifact of the analysis. If the result from the MB is below the MDL it can be demonstrated that there is little to no contamination from the laboratory.

With low-level detections that are between the MDL and the MRL, it is possible that a combination of contamination from the sampling and analysis process can result in enough signal to be reported even though there is no fuel in the sample. In the Tech Memorandum, the case is made that the sum of laboratory contamination and from peaks arising from reactions of the surrogate with chlorine come to a total signal that is above the MDL.

A technical peer review of the report and its conclusions was requested to ensure an unbiased evaluation of the Tech Memorandum conclusions. The following are the findings of the technical review:

1. The review of the raw data supports the conclusion that the increase in TPH detections was not due to JP-5 but the data does not rule out the presence of other trace level fuels in the sample or the possibility of contamination during the sample collection procedure.

2. A review of the method blank data from several zones and across all of the LTMs shows that the majority of the blanks showed undetectable amounts of TPH. Therefore, the contribution of blank contamination was below the MDL for most of the samples taken. While there is some contribution to the total signal from the MB, it is small and more importantly it is constant for most of the samples taken during the LTMs. If the blank area was a cause of the increase observed in LTM 6 then there should have been an observed increase in MB contamination for extraction batches during that time, but none was observed. The MB results were consistently free from contamination. Extractions where there was a MB with a signal above the MDL did occur but happened in only a few numbers of extractions and were randomly distributed. There was no systematic pattern to MB results above the MDL. There is no evidence to support the conclusion that laboratory contamination contributed to the increased frequency of TPH detections.

3. A review of the peaks from the reaction products between chlorine and the surrogate indicate the size of the peak is fairly constant across all zones and LTMs. The surrogate concentration was the same throughout LTMs 1-6, therefore, the contribution to the total TPH signal from the chlorinated surrogate is expected to be constant. The reactions with the surrogate would not result in an increased frequency of TPH detections. The signal from these compounds would be constant during the entire sampling period. As with the MB, the chlorinated surrogate peaks do contribute to the total area of TPH, but this contribution is constant and does not support the conclusion that the increase in the frequency of TPH detections is caused by chlorinating the surrogate.

4. The Tech Memorandum discusses a relationship between the residual chlorine amount and the frequency of TPH observations, concluding that increased chlorine residual caused an increase in the amount of chlorinated surrogate but when the size of the actual chlorinated surrogate peak is plotted versus time and zone, there is no obvious correlation. The size of the chlorinated surrogate is fairly constant and does not support the conclusion that this is the cause of the increased frequency of TPH detections. It is possible that there is another cause for the correlation between residual chlorine and TPH detections, but it is unlikely due to reactions with the surrogate, the main conclusion from the task force.

5. Laboratory contamination and chlorinated surrogate compounds did contribute to the total TPH signal in all of the samples analyzed during this monitoring project. However, there are a large number of samples from all zones and all LTMs that did not have a detectable TPH signal. If contamination and chlorinated surrogate caused enough signal to be above the MDL, then all samples would have had a low level TPH detection. Therefore, the raw data suggests that there may be another cause for the observed increase in TPH observations.

6. A new method was created that is designed to reduce laboratory contamination by using a microextraction and a reduced surrogate concentration, which resulted in a decrease in the frequency of TPH detections, but these changes may have masked another cause for the increased TPH observations. An option to improve data comparability would be to follow the sampling preservation guidelines outlined in Chapter 4 of SW846 and continue to use the existing analytical method.

7. The extraction and analysis methods both refer to the SW-846 method compendium for proper sample collection, preservation and handling procedures. The compendium recommends that samples with residual chlorine should be preserved with sodium thiosulfate to remove residual chlorine but this guidance was not followed.

List of Acronyms

DBP – Disinfectant By Product. These are chemicals formed by the reaction of disinfectants such as chlorine with organic compounds in water such as humic substances.

DRO – Diesel range organics. A term used to refer to a group of hydrocarbons that typically comprise diesel fuels.

GAC – Graphitized Activated Carbon. This material is used to absorb organic chemicals from water and is frequently used to remove contaminants from drinking water sources.

GC/FID – Gas Chromatography Flame Ionization Detection. The gas chromatograph is an instrument that is used to separate chemicals in a sample from the matrix and any other chemicals in the sample. The flame ionization detector is placed and the exit flow of the gas chromatograph and has a flame between two charged plates. When a chemical exits the chromatograph, it is burned in the flame. The resulting ions are measured as an electrical current between the two plates. The signal from this detector is proportional to the amount of material that exits the chromatograph.

GRO – Gas range organics. A term used to refer to a group of hydrocarbons that typically comprise gasoline.

JBPHH – Joint Base Pearl Harbor Hickham

LOE – Lines of Evidence. A list of possible reasons for the observations of increased frequency of TPH in the samples.

LTM – Long Term Monitoring. This monitoring effort was done in seven sampling segments. Segment 1 is March 2022. Segment 2 is April 2022. Segment 3 May 2022. Segment 4 June-Dec., 2022. Segment 5 is Jan-June, 2023. Segment 6 is July-Dec, 2023. Segment 7 is Jan-March, 2024.

MB – Method Blank. A sample prepared from a similar matrix to that being tested that is provided by the laboratory and known to be free of the target analyte and any other contamination. In this case, a sample of de-ionized water, which is certified to a certain grade of purity. The function of the method blank is to demonstrate that there are no impurities that would interfere with the measurement that are coming from the sample preparation or analysis procedures.

MDL – Method Detection Limit. The concentration of an analyte that can be observed above the noise level of the analytical method. Typically, a signal that has a signal to noise ration of 3 is considered to be at the detection limit of the method.

MEQ – Microextraction technique. This is a method to extract aqueous samples using substantially less water and extraction solvents. Typically, 40mL of water are used for this type of extraction.

MRL – Method Reporting Limit. The concentration of an analyte that can be reported with known accuracy.

ORO – Oil range organics. A term used to refer to a group of hydrocarbons that typically comprise oils and greases.

SME – Subject Matter Expert. A person with a significant amount of experience and knowledge in the area of discussion.

SF – Separatory Funnel extraction. This is the standard procedure used in EPA methods for extracting organic chemicals from water. A separatory funnel allows water to be extracted with solvents that are more dense than water, and not soluble in water. The solvent is drained from the bottom of the funnel and allows for multiple extractions of the sample to achieve a high extraction efficiency. This type of extraction is usually performed with 1 liter of water.

SW-846 – A group of documents created by the United States Environmental Protection Agency that describe sample collection and analytical procedures that have been proven to provide reliable data for the analysis of environmental samples.

TPH – Total Petroleum Hydrocarbons

Introduction

In mid-2023 an increase in low level Total Petroleum Hydrocarbons (TPH) was observed in samples from the long-term monitoring program at JBPHH[5]. This monitoring program was instituted to monitor for contamination of the drinking water from either the November 2021 release of JP-5 or any other contamination that might be in the system from decades of proximity to fuel and or other hydrocarbon sources.

The cause of the increased low level TPH results that were observed in the laboratory data was studied by a group of Subject Matter Experts (SME) from the Department of the Navy, the Environmental Protection Agency, the State of Hawaii Department of Health and contractors used by the Navy for the monitoring project. The team evaluated the following hypotheses:

A. The low level TPH results were not associated with the JP-5 release in 2021.
B. The TPH observations were not associated with any other hydrocarbon release into the JBPHH system.

C. The detections were caused by laboratory error, in particular blank contamination, and failure to use a dechlorinating reagent prior to sample extraction.

The interagency team considered the following six discussion points to evaluate the proposed hypotheses. These were titled Lines of Evidence (LOE):

1. Distribution of TPH results among the drinking water zones in the JBPHH and how the TPH results varied across the period of monitoring.
2. The team performed a hydraulic modeling analysis of the water to understand how water from one zone could be affected by water from another zone.
3. The team evaluated the analytical method that was used to provide the TPH results.
4. The team developed a new analytical method to control and or decrease some of the possible sources of TPH that were being observed. The new method minimized glassware and reagents and it was expected that it would produce less TPH observations above the method detection limit. This method was then compared to the original method.
5. The team evaluated the data to look for compounds that they expected would be in the water from JP-5 contamination.
6. The team performed a statistical analysis of the data to determine if there was a relationship between reagents and chlorine levels.

Discussion

LOE 1: Spatial and Temporal Distribution of TPH Results

There are 18 different drinking water zones that were used to determine how the TPH results were distributed across the JBPHH water system. These zones were divided into four different types of zones:

- Those with water only from the Waiawa source, which is not expected to have any concentration of TPH.
- Those with water from both the Waiawa source and the Red Hill source. This water could potentially have some residual TPH from the 2021 spill.
- Those with mostly water from the Red Hill source. This would be expected to have the most impact from the 2021 spill.
- Those with water that is treated with a Granular Activated Carbon unit which has been demonstrated to remove TPH from water. This water would be expected have no TPH present.

The reason to evaluate the distribution of TPH across all zones is because if the TPH results were randomly observed then it would be unlikely that the TPH is coming from the Red Hill shaft. Additionally, if TPH was observed in the GAC zones, it would indicate that there is

contamination during the measurement process as the water should have no TPH after GAC treatment. These conclusions would be accurate if the only source of TPH contamination was from Red Hill but if there were other sources of TPH in the JBPHH system, looking at random TPH detections or TPH in the GAC zones would not provide an explanation for these observations.

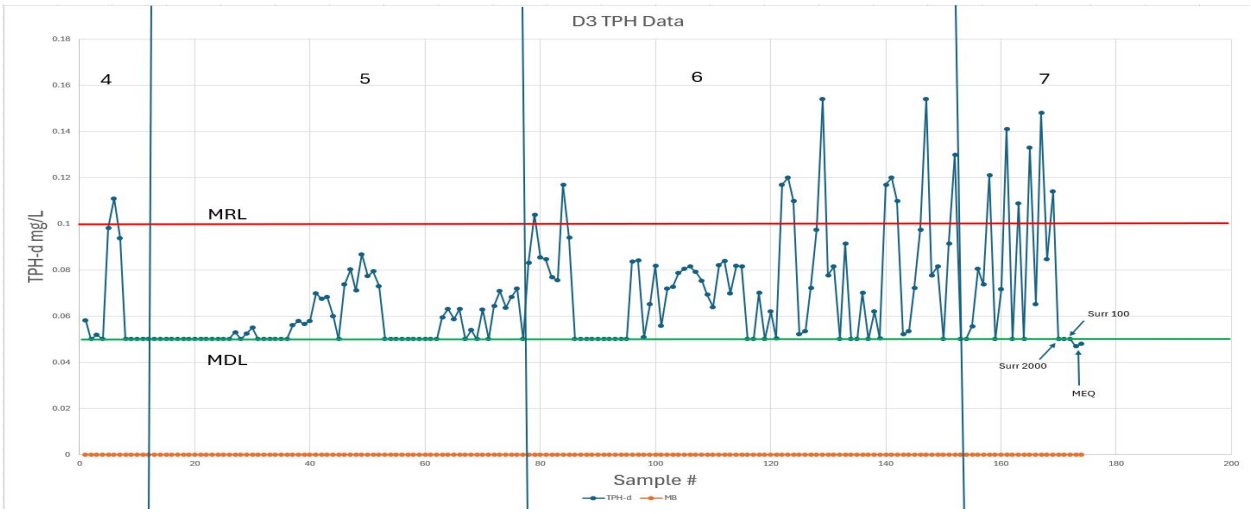

Fig 1. Zone D3 (Red Hill and Waiawa) TPH results for LTM 4, 5, 6 and 7. Results show the increase in LTM 6 compared to earlier LTM.

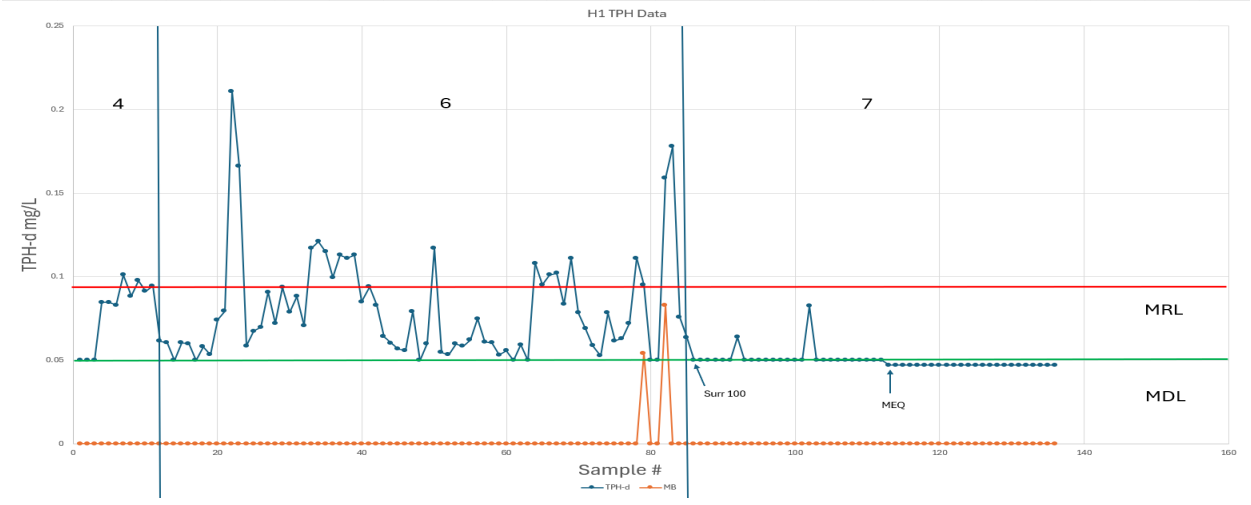

Fig 2. Zone H1(GAC Treated) TPH results for LTM 4, 6 and 7. Results show no apparent differences from one LTM to the other. In LTM the method was changed.

In figures 1 and 2, both the sample TPH (blue trace) and the method blank TPH (orange trace) are shown. For the method blanks if the reported result was shown on the data sheet as 0.05U or as ND, the result plotted was 0. This was done to more clearly show any blank results that were above the MDL. In these graphs, the red trace is the method reporting limit (MRL) of 0.08mg/L and the green trace is the method detection limit (MDL) of 0.052mg/L. For the sample results, if there is a data point on the line then that result was an undetected amount of TPH. So, only those points above the green line were samples that were found to have any TPH in them. Those points above the red line were reported as TPH without qualification.

The data in the figures show that the distribution across time is different for these two zones and does not agree with the task team finding that all zones have similar TPH patterns. Similar TPH patterns would be expected if the signals were arising solely from laboratory contamination as many of these zones were sampled in a similar time frame. The data also shows that not all zones showed an increase in LTM 6. The H1 zone has fairly consistent TPH results throughout the sampling period until the method was changed to reduce the surrogate concentration from 2000mg/L to 100 mg/L.

This data does not support the hypothesis that the TPH results were similar spatially or temporally. There were differences yet this was cited several times as support for the final conclusion that there was no petrogenic source of the TPH results.

LOE 2: Hydraulic Modeling of the JBPHH System Following the November 2021 Release

The hydraulic modeling supports the conclusion that water from each shaft does not communicate with each other. Because the release in 2021 only affected the Red Hill shaft, water from the Waiawa shaft should not result in TPH detections unless there is another source of hydrocarbons in those zones supplied by the Waiawa shaft or in the distribution system.

LOE 3: Detailed Review of the Analytical Methods Used to Identify and Quantify TPH

Method 8015 is an analytical method that is performed using gas chromatography flame ionization detection (GC/FID). The FID detector produces a signal when any flammable compound elutes out of the GC column and is considered a non-specific technique. It has been used to measure gas range organics (GRO), diesel range organics (DRO) and oil range organics (ORO) for several years. The method uses a retention time range to measure the amount of GRO, DRO or ORO but because the method is non-specific, any compound or compounds that elutes from the GC column in the retention time range of one of the fuel types will be measured as that fuel. This can lead to reporting TPH results that are not actually hydrocarbons but some other chemical.

Several observations regarding the analytical procedure were reported in the tech memorandum and will be discussed in the order that they were presented.

In evaluation of method 8015 by the interagency team, it was noted that the method was not developed as a drinking water method. However, SW-846 Compendium (Update VI), Chapter 4: Organic Analytes, Table 4-1 (page 11) clearly states that aqueous samples WITH residual chlorine present should be preserved with thiosulfate. The method calls for the addition of 3mL 10% sodium thiosulfate per liter of water collected. This guidance applies to all aqueous organic extraction methods listed in SW-846, including Method 3510C, the method used for this project. Problems with unwanted reactions are directly related to incorrect sample preservation practices for this matrix.

The team found that the majority of the TPH results were between the MDL and the MRL, which is accurate, but this does not necessarily indicate that the laboratory was having difficulty meeting the MDL. In fact, the MDL data from figures 1 and 2 indicate that the majority of the method blanks were below the MDL. This does not support the conclusion that the laboratory was having difficulty meeting the MDL. Two other explanations for the low-level TPH detections are that there was sample contamination at the point of collecting the sample and the other explanation is that there is a low concentration of TPH or other chemical in the sample.

One of the issues with any analytical method is that, as the MDL is approached, any additional signal can result in a sample being above the MDL. This is especially of concern for less specific methods such as 8015 that use a retention time range for quantitation.

Method blank samples are used by the laboratory to ensure that any contamination from laboratory glassware, reagents or chemists do not impact the final sample results. In figure 3, a typical method blank sample from LTM 1 is shown. This blank demonstrates a very clean laboratory sample preparation, and it would not be expected that the sample results would

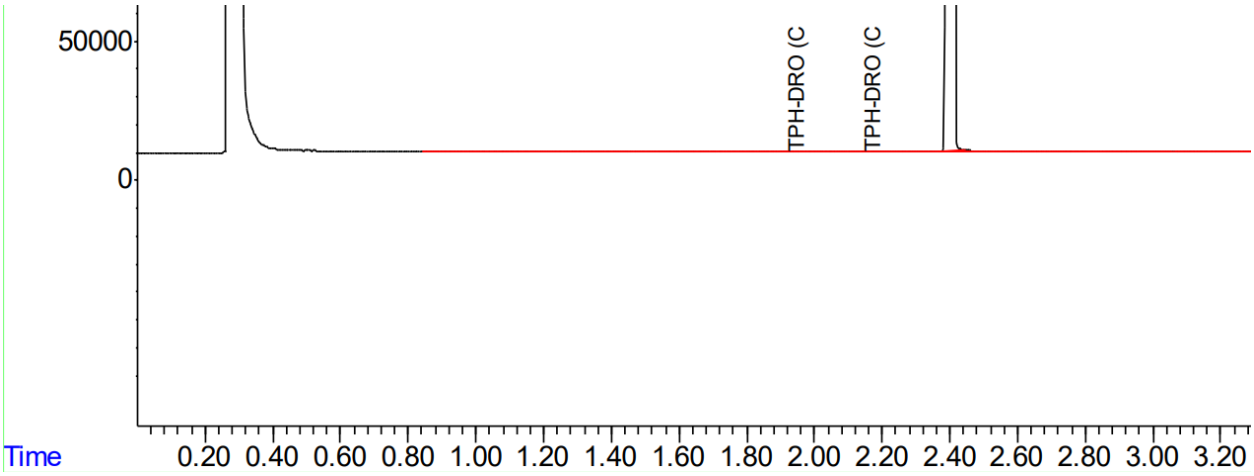

Fig 3. Blank OP21424 from SDG DA43252, Zone F2, LTM 1

be impacted by the laboratory sample preparation procedure. Two samples that are associated with blank OP21242 (blank shown in Fig. 3) are shown in Figure 4. The top chromatogram is from sample number 1 and the reported TPH for this sample was 0.052U, indicating that there was no TPH observed in this sample. The bottom chromatogram is from sample 4. This sample

was reported to have a TPH concentration of 0.102mg/L. When the method blank shows no contamination and most samples associated with that preparation batch also show no TPH it must be concluded that there is a detectable amount of some chemical in the sample.

Three features in the top chromatogram of figure 4 are noteworthy. The first is the four small peaks observed between 1 and 1.3 minutes. These peaks are observed in all of the samples and are most likely disinfectant byproducts (DBP)[6].

The second feature is the small peaks that are just to the right side of the surrogate peak, which is the peak at 2.4 minutes. These peaks, along with the four other small peaks are all integrated and do contribute some area to the TPH signal, but in this situation the area measured was below the MDL.

The third feature is the peak at a retention time of 2.78 minutes. This peak is from the halogenation of the surrogate and was also observed in all of the samples. The surrogate was spiked at 2000mg/L, a very large concentration compared to a TPH signal of approximately 0.1mg/L and as there was no dechlorination step in the sample preparation, it is expected that some reactions with reagents will occur, and indeed they were observed.

The data in the lower trace in Figure 4 show a chromatogram from a sample that had a reportable amount of TPH. Along with the four DBP peaks, there is also the halogenated surrogate peak. However, the largest peak is at a retention time of 2.4 minutes, just to the right of the surrogate peak. This peak was identified by the interagency team as hexadecanoic acid, also known as palmitic acid and is widely used in lotions and cosmetics.

The hexadecenoic acid peak was observed in many samples throughout the sampling period and is possibly due to contamination during sampling with a smaller contribution from the laboratory. Finally, there are several other peaks in the chromatogram, and these are unidentified, but it is possible that these are from TPH hydrocarbons. While no hydrocarbon hump is observed, it is well known that heavily weathered fuels often exhibit just a few peaks from persistent compounds[7]. These peaks may be from weathered fuel, but this cannot be proven without mass spectral data to confirm the peak identities.

The data in Figures 3 and 4 provide an example of a situation where the method blank demonstrated that the laboratory could prepare the samples without contamination. This blank was associated with 19 samples, four of which had reported TPH values above the MDL.

The interagency team found that ghost peaks, or peaks that are formed due to the sample preparation procedure, occurred. It was noted that the ghost peaks were observed in samples that had reportable TPH and those that did not have reportable TPH. The surrogate level for LTMs 1-6 were 2000mg/L and a generally consistent sized peak at a relative retention time from the surrogate (RRT) of 1.15 was observed in all drinking water samples. This peak was not present in blanks, blank spikes or calibration samples because there was no chlorine in those samples. This results in a situation where those samples that have residual chlorine have peaks from the halogenation reaction that contribute to the total area of the TPH integration that were not in the

calibration samples and therefore these peaks are quantitated as TPH, but they are actually not hydrocarbon peaks.

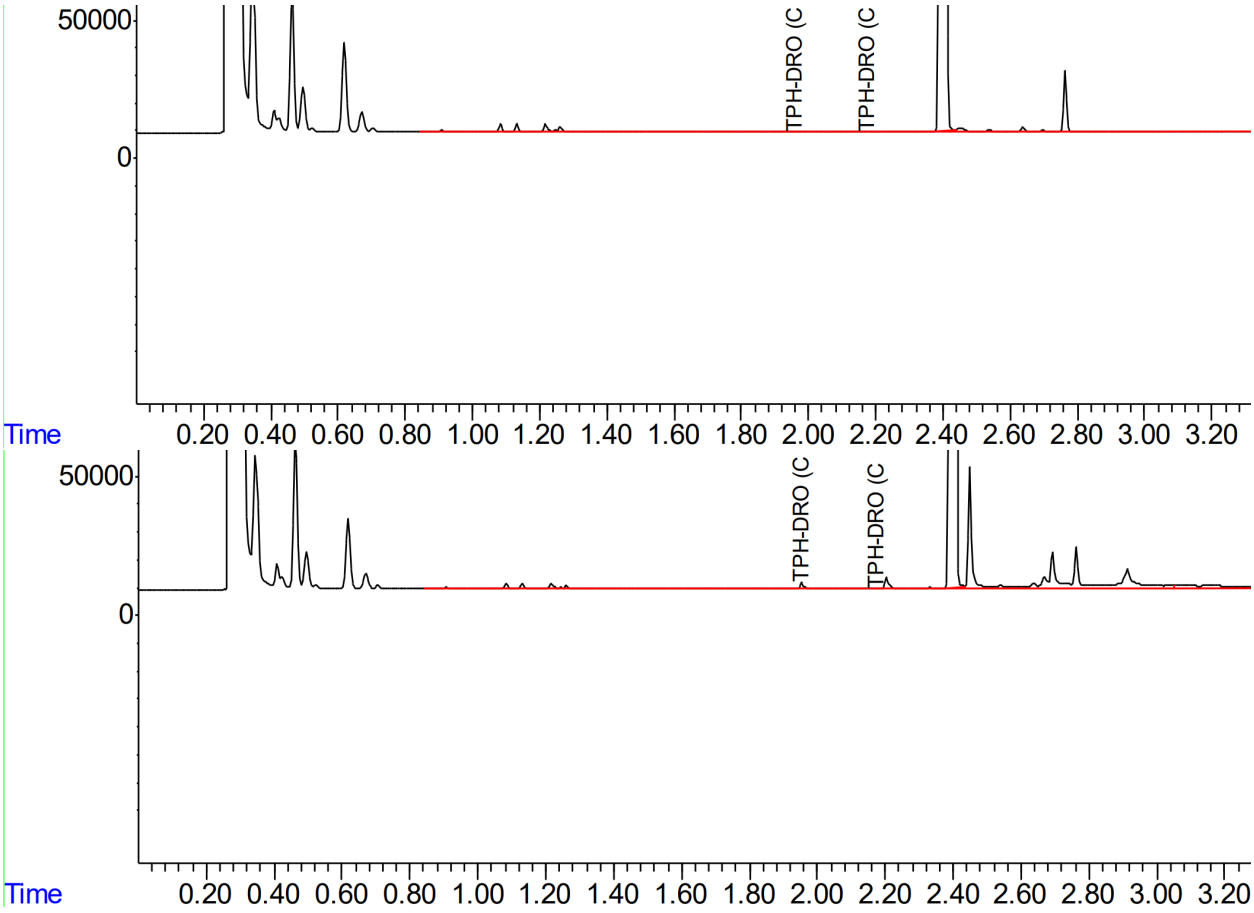

Figure 4. SDG DA43252. Top trace is sample 1 and there was no TPH above the MDL. Bottom trace is sample 4. This sample had a reported TPH concentration of 0.102mg/L.

The interagency team concluded that a combination of ghost peaks and blank contamination resulted in a systemic treatment effect that is not associated with JP-5 or other fuel related TPHs. While the data supports the statement that the TPH that has been observed is not from JP-5, it does not support the statement that the TPH peaks are non-fuel related.

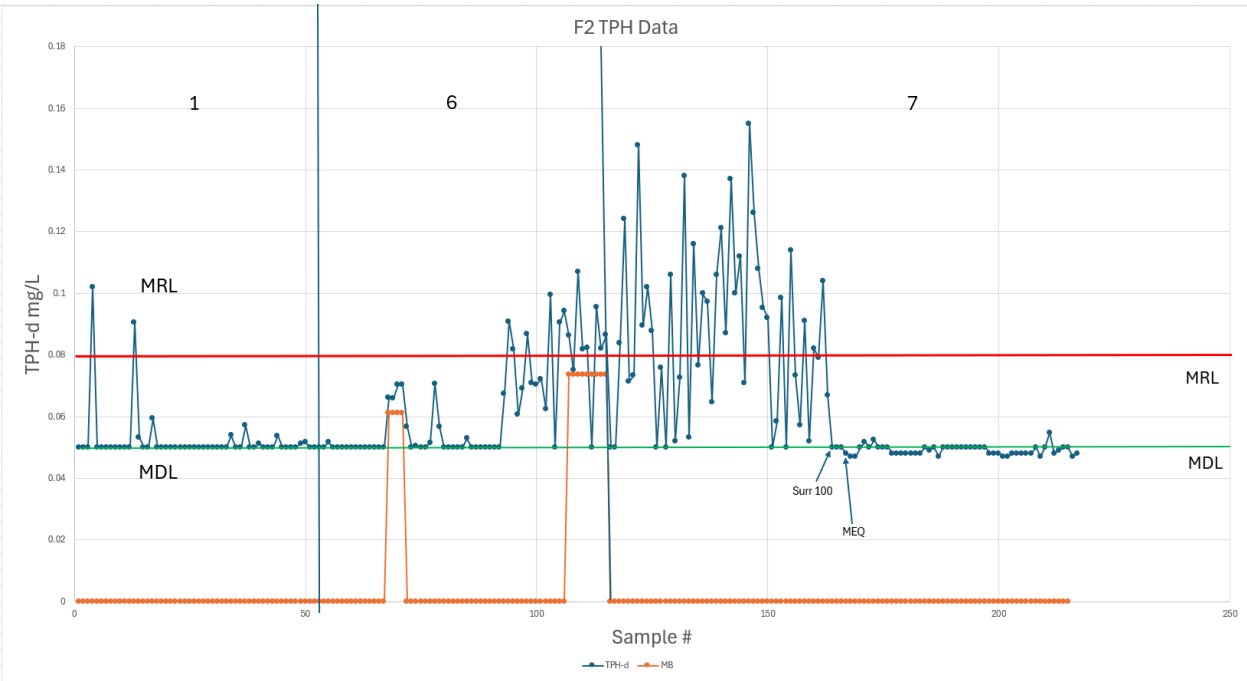

Fig. 5. TPH results for zone F2. This data shows two method blanks with TPH detections above the MDL. The data also show a pattern to the TPH results.

Figure 5 shows the results for samples from the F2 zone in LTMs 1, 6 and 7. The results are generally clean until the mid-point of LTM 6. With no change to the analytical method, something changed halfway through LTM 6 that resulted in an increase of TPH detections. The data prior to the sampling date of August 31, 2023, indicate most results below the MDL and two of the sample batches with reportable TPH are associated with a contaminated method blank. Beginning with the August 31, 2023, sampling date, samples mostly had reportable TPH results. If there was a systemic treatment effect, this pattern should not have been observed, the TPH should have been above the MDL consistently throughout the LTM period.

There are only two method blanks for this sampling period where TPH levels above the MDL were observed. This indicates that laboratory contamination is not a chronic problem. All of these samples had a surrogate concentration of 2000mg/L and were not dechlorinated, but until the late August sampling event, the was a very low rate of TPH detections. If Ghost peaks were one of the main causes of TPH observations then the TPH detects should have been constant throughout the LTM timeframe.

One remarkable feature of the samples after August 31 is that there was an increase in the size of the hexadecenoic acid peak and an increase in peaks in the retention time range from 2.5 to 3.2 minutes. The increase in area from these peaks are the cause for the increased TPH results. The identity of these peaks cannot be determined with 8015 data but TPH as the cause cannot be ruled out as the associated method blanks are clean.

The TPH data did return to below MDL levels when the surrogate concentration was lowered from 2000mg/L to 100mg/L. Lowering the surrogate would be expected to lower the total TPH observed but does not explain why an excursion occurred in late August. Such a change to the method does have the effect of minimizing an unexplained observation.

LOE 4: Side-By-Side Comparison of Laboratory Results using Sample Preparation using Separatory Funnels Without Dechlorination Versus Micro-Extraction with Quenching

A new method was developed to address the observed increase in TPH detections. The new method uses a microextraction (MEQ) procedure from the SW-846 compendium, Method 3511[8]. Because it was suspected that the increase in TPH observations was related to laboratory contamination issues and a lack of dechlorination with the separatory funnel method (SF), an extraction method was sought that used less glassware, less reagent and added a dechlorination step. In addition to using the microextraction, a dechlorinating step using thiosulfate the surrogate concentration was lowered by a factor of 20 and the extraction solvent was changed resulting in an entirely new sample preparation procedure. Based on the data from LTM 1 and 3, it appeared that the original method was performing satisfactorily, and a change should not have been required unless something in the entire sample collecting and sample analysis process changed.

One major difference between the two methods is the amount of material injected on-column. For example, a compound present at a concentration of 0.05mg/L in the sample would result in 50ng injected on the column using the SF method. Using the MEQ method, the amount injected on column drops to 34ng, approximately 30% less analyte. If the instrument had sufficient sensitivity to detect 34ng then this reduction of on-column amount should not be an issue but if the instrument did not have the ability to measure 34ng of material, then a peak that was observed in the SF method would not be observed in the MEQ method. This may become an important factor as the concentration of 0.05mg/L is at the MDL and presumably, concentrations lower than this are not detectable. The MEQ method has been demonstrated to provide accurate results at matrix spike concentrations but no data, such as injections of standards at the MDL have been presented to verify that MDL can be verified. In addition, before changing to a new method, equivalency should be demonstrated as outlined in USEPA guidance[9].

Ultimately, a case has not been made for the need for a new method. It is demonstrated in Figures 1, 2 and 5 that there are several zones that have many samples with no TPH detected which clearly shows that the method is capable of generating TPH free results. If the issue was related to a lack of dechlorination when a high surrogate concentration was used or if there was a problem with laboratory contamination, then TPH detections should have been far more consistent throughout the LTM periods. The team did note that the TPH detections were caused by halogenated surrogate and, while this is certainly a contributing factor it is not the only factor or the most important factor causing the increase in TPH detections. The MEQ method may simply look cleaner because less material is being loaded onto the column.

The MEQ method may be capable of meeting the project Data Quality Objectives (DQO), and certainly drinking water samples should be dechlorinated but an explanation that is more consistent with the observed data for the TPH detections should be provided before changing to a new method.

LOE: Absence of Indicator Compounds Associated with JP-5

The sample data from method 524.2 consistently indicate a lack of GRO in the samples. In addition, the data from samples analyzed using Method 8015 indicate peaks contributing to the TPH result are out of the retention time range of JP-5. It is likely that the TPH results observed during the LTM are not due to the presence of JP-5, but it cannot be known that the TPH detects are from non-petrogenic sources as stated in the conclusion, without further data being acquired.

The TPH detection concentrations were low, mostly lower than the MRL. Therefore, it would be expected that ion signals from such a low concentration would be small and may not be detectable. To draw any conclusions from the lack of indicator ions it would be necessary to spike samples with hydrocarbon standards at the MDL and then analyze them by method 525. Without this data, there is no way to know how low of a concentration of TPH can be found by looking for characteristic ions.

It is also possible that the TPH that was observed in the samples was due to older, more weathered sources. If this were the case, looking for the hydrocarbons listed in Table D-1 in the Tech Memorandum may not be useful as many of those compounds may have dissipated. It would be better to look for the known persistent compounds from heavily weathered fuels. To provide useful data for demonstrating the lack of fuel related signal, spiking studies would be required with a set of compounds shown to be persistent in weathered fuels to know how low of a concentration it would be possible to detect. Without data to demonstrate that concentrations in the range seen in these samples (between the MDL and MRL) can be observed in the GC/MS trace, looking for indicator compounds does not provide convincing evidence for the lack of fuel related compounds.

LOE: Statistical Analysis of TPH Data, Chlorine Residuals, and Surrogate Doses

The key findings indicate that the odds of observing an increased TPH are due to either increased residual chlorine and or high surrogate doses. The other key finding was that the frequency of TPH detections increased in the second half of LTM 6. The conclusion was made that the data over two years strongly support the hypothesis that halogenated byproducts are the main cause of the TPH detections. The data does not support their conclusion however and will be discussed in detail.

The team discussed the effect of thiosulfate addition in Appendix C and on page 14 in the Tech Memorandum. There is no question that the surrogate is being halogenated and the peak at a

RRT of 1.15 was seen in virtually all of the sample results that were reviewed. An example of this shown in Figure 6., a chromatogram from Zone F2, sampled on 3/24/2022.

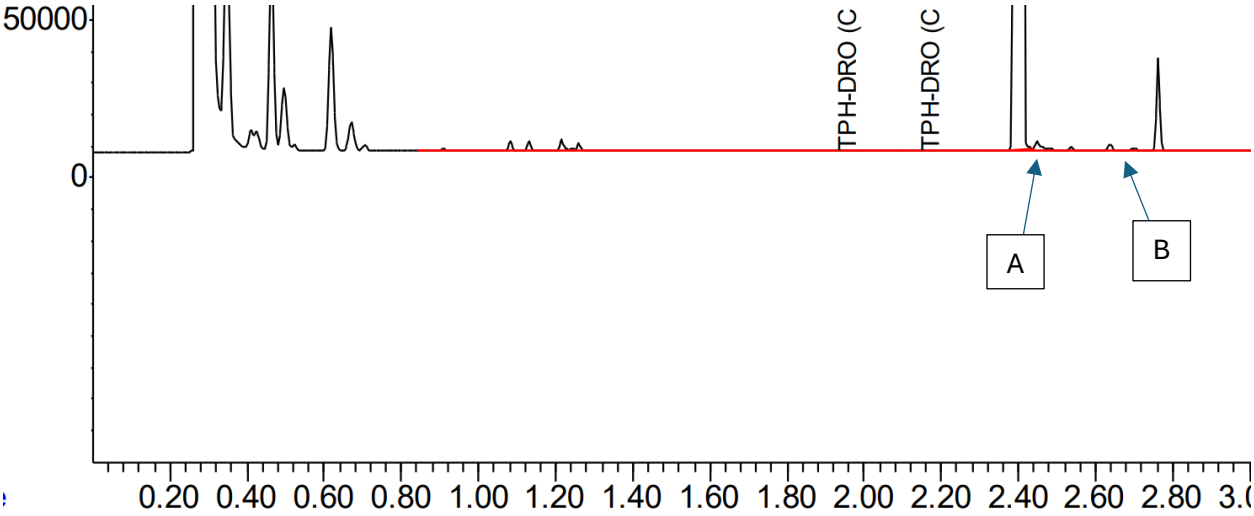

Figure 6. Sample DA43255-35, LTM 2, Sampled 3/24/2022. One main halogenated surrogate peak, very small hexadecenoic acid peak

The peak with a retention time of 2.78 is from a reaction of the surrogate with residual chlorine. The identity was given as a brominated o-Terphenyl, but this identification is difficult to understand because the water is disinfected with chlorine. That this is halogenated is not in question, but the correct identification should be made. There is no mass spectrum for this peak in the report and it is not possible to verify the statement that this is a brominated compound instead of a chlorinated compound.

The peaks in Figure 6 labelled B are also caused by reactions of the surrogate with residual chlorine but are much smaller than the main halogenated peak. The peak labelled A is from the sample prep, either as an impurity in the surrogate standard or from the procedure but is small in comparison to the halogenated peak at 2.78 minutes. This sample had an undetected amount of TPH.

This pattern was common in many the samples in all the zones and throughout the LTM period. This demonstrates the consistency of the reaction of the surrogate with the residual chlorine. The issue is not that halogenated peaks are formed, the uncertainty in the conclusion is that the kinetics of the chlorination are constant and if the cause of the increased TPH observations was from halogenated surrogate then there should always have been TPH observed above the MDL during the LTM because the surrogate was always present at 2000mg/L.

It was noted that changes in the residual chlorine resulted in changes in the observed amount of halogenated surrogate and also in the number of TPH detections. The data in Figure 6 were from

a time period where the residual chlorine was shown to be 0.49mg/L (pg. F4, Tech Mem.) and the halogenated peak is approximately 50,000 counts.

The chromatogram in Figure 7 is from Zone F2 and was taken during LTM 5 when the residual chlorine was 0.41mg/L (pg F4, Tech Mem.), the lowest amount of residual chlorine during the LTM period. The pattern and height of the halogenated peaks is very similar to that observed when the residual chlorine was at 0.49.

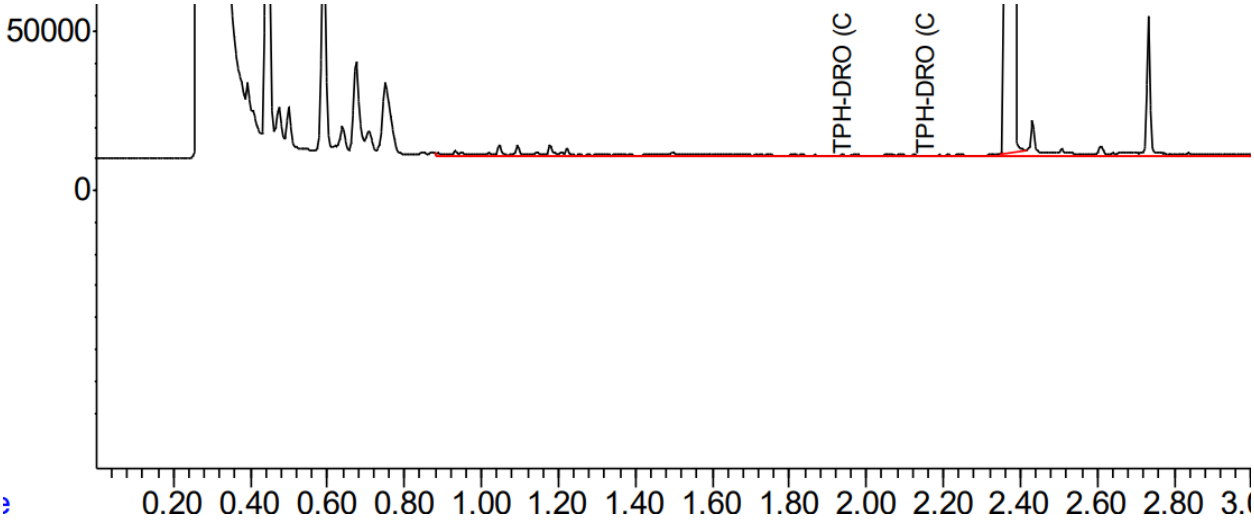

Figure 7. Sample DA53302-16, LTM 5, sampled 2/1/2023.

The chromatogram shown in Figure 8 is from Zone H1, one of the GAC treated zones. The sample was taken in LTM 6 when the residual chlorine was 0.5mg/L. This chromatogram has the halogenated peak (RRT 1.15, RT 2.6)

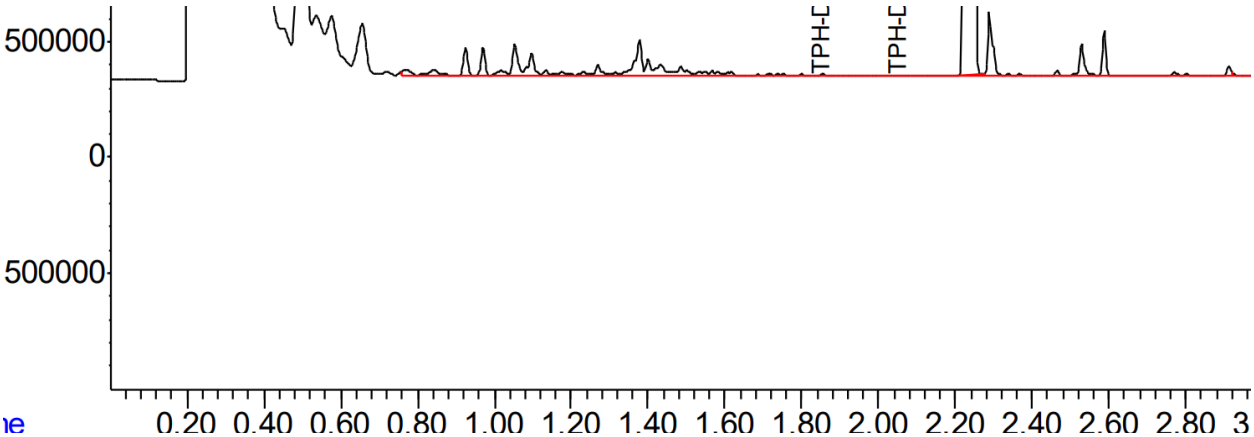

Figure 8. Sample DA58860-21, LTM 6, sampled 9/25/2023.

as expected, but this peak is approximately the same intensity as those from other LTMs. This demonstrates that the halogenated surrogate amount is not affected by changes in the residual chlorine.

A large peak at a RT of approximately 2.53, is much larger than those previously seen and it is possible that there is a peak co-eluting with any minor halogenated peak. The other halogenated peaks have been shown to be consistently small in relation to the main halogenated peak, thus a change in relative peak amounts is not expected. There is also a much larger peak at RT 2.4 which has been identified as hexadecanoic acid (pg D-7, Tech Mem.). In addition, there are peaks around RT 1.4 that are not the four DBP peaks. This sample had a TPH value of 0.0593, which is above the MDL but below the MRL and is a good example of how the data from low level TPH results appears. In this sample, the halogenated peak is a contributor to the total TPH area but not the main reason for a TPH above the MDL as the size of the halogenated surrogate peak is about the same size as been observed in other samples where the TPH result was below the MDL. The method blank for this sample batch was 0.052U, below the MDL but the blank chromatogram did have a peak at RT 2.53, which supports a co-eluting peak as a cause for the increase of the peak relative to the halogenated surrogate peak.

The data in Figures 6, 7 and 8 demonstrate that the size of the halogenated surrogate peak does not vary noticeably with residual chlorine and so, even though there is a statistical correlation between residual chlorine and TPH results above the MDL, there may be other factors that are the actual cause.

An alternate hypothesis to explain the increased TPH is possible but was not discussed in the Tech Memorandum. Looking at the TPH results shown in Figure 5, it can be seen that there is an abrupt increase in TPH values starting about halfway through LTM 6. A sample chromatogram from the sample just before the TPH spike is shown in Figure 9. This is a chromatogram from DA57431-21, sampled on 8/2/23.

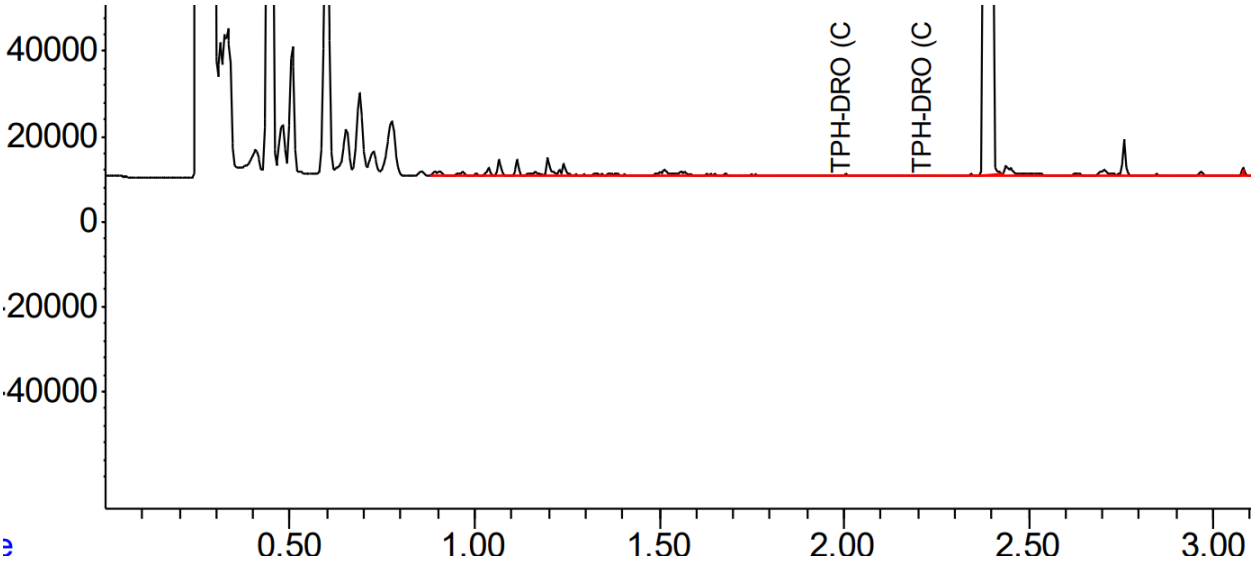

Figure 9. DA57431-21, Zone F2, LTM 6, Sampled 8/2/2023.

The chromatogram has the halogenated surrogate, the DBP peaks and a small peak to the right of the surrogate. The result for this sample was below the MDL. The method blank for this set of samples was similarly without peaks.

The chromatogram for the next sample taken in this zone is shown in Figure 10. This is from DA58265 and was sampled on August 31, 2023. There are several peaks that are present in this sample that are not present in the samples taken on August 2. There is the usual halogenated peak but there is also a hexadecanoic acid peak that is much larger than the halogenated surrogate peak and a peak at approximately 2.54 minutes. Both of

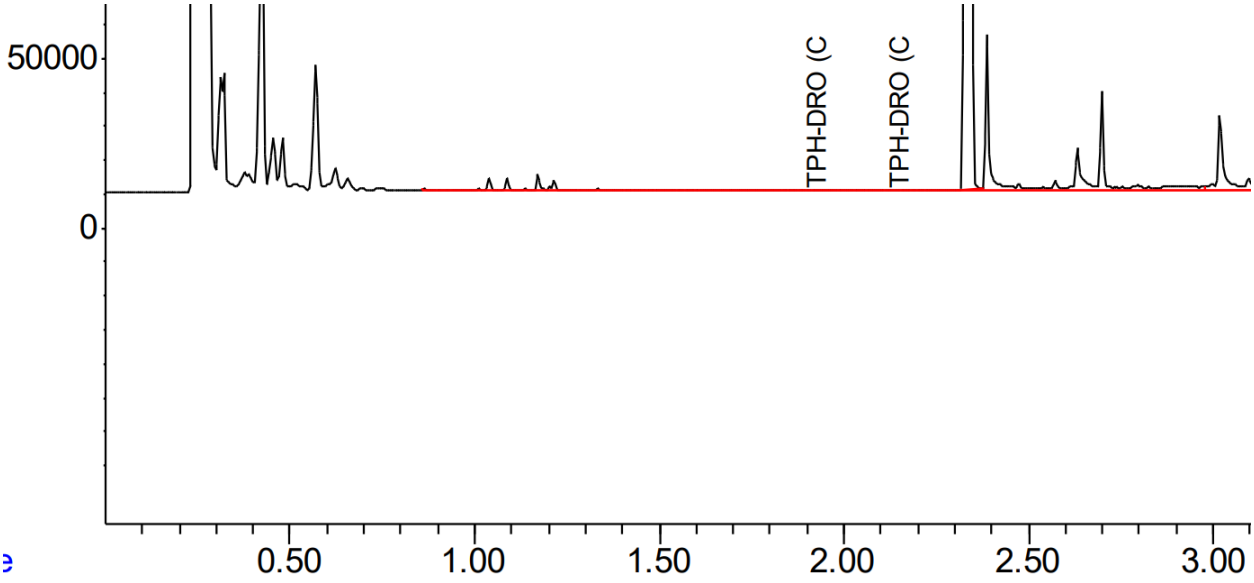

Figure 10. DA58265-1, Zone F2, LTM 6, Sampled 8/31/2023.

these peaks are observed in the blank, but they are smaller than those in the sample. The blank for this batch of samples is shown in Figure 11 for comparison. The TPH result for this sample was 0.0675, above the MDL but below the MRL. This pattern becomes increasingly

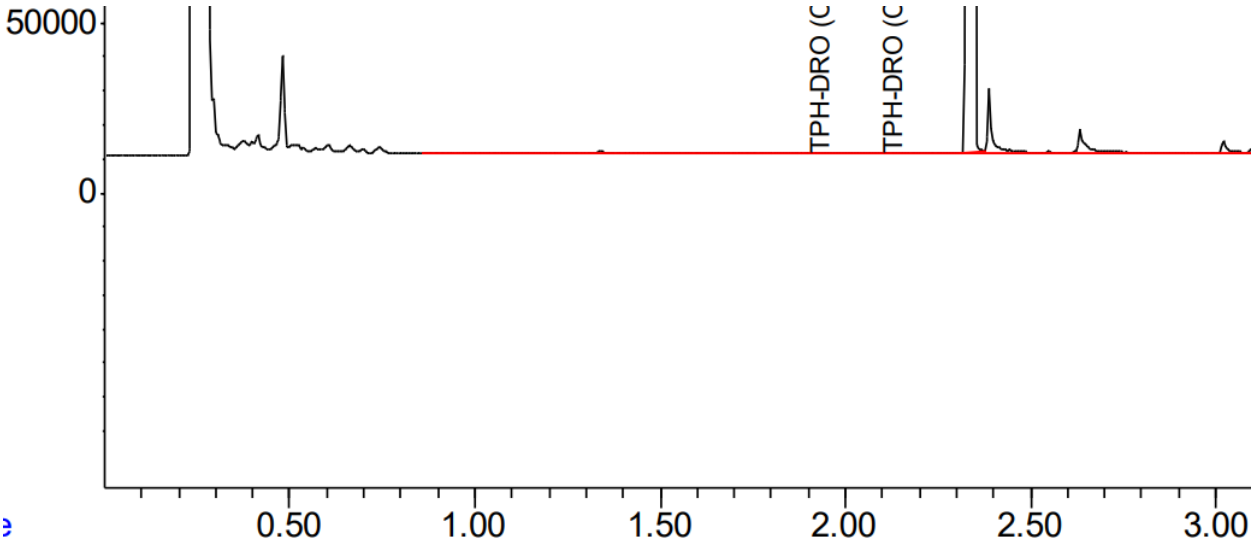

Figure 11. Method Blank OP24261.

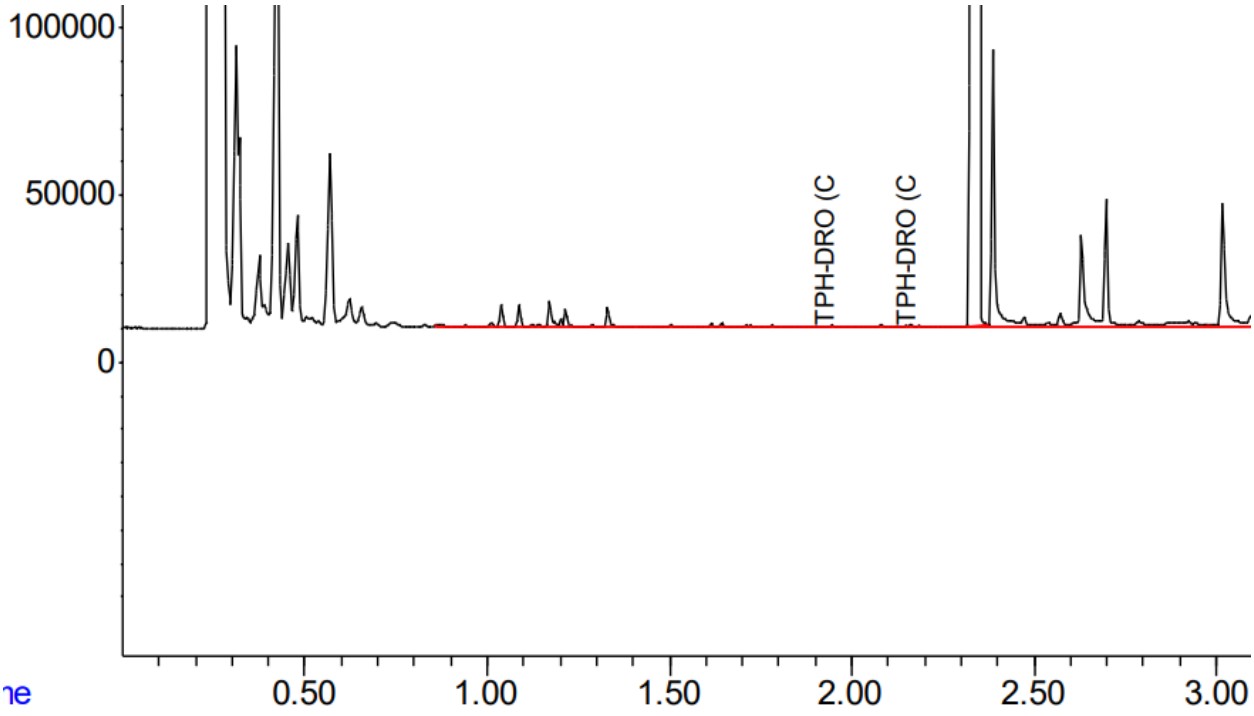

Figure 12. DA58265-11, Zone F2, LTM 6, Sampled 8/31/2023.

pronounced with other samples in the batch. For example, the chromatogram shown in Figure 12 shows the halogenated surrogate peak at approximately 2.58 minutes and 50000 counts high,

which is the same as this peak in most other samples. Note that the y axis in this figure is 100,000 counts because the hexadecanoic acid peak is approximately twice as large as in sample 1 from this same batch. There is also a large peak at approximately 3 minutes. This has been identified as octadecanoic acid by the interagency team (Tech Mem. Pg D-7). It is the presence of the hexadecanoic acid and octadecanoic acid peaks that are most likely the cause of this sample having a reported TPH value of 0.0944 and not due to halogenation of the surrogate.

The data in figures 10 – 12 show examples where the laboratory Method Blank was relatively clean, but the samples had TPH results above the MDL. Hexadecanoic and octadecanoic acids are common ingredients in lotions, cosmetics and sunscreens. One possibility is that there is contamination of the sample at the point of collection. This data indicates that the laboratory is not the main contributor to the TPH results nor is the halogenated surrogate.

Method Compliance, Data Defensibility and Data Useability

Method compliance is an important consideration because it establishes the reliability of the analytical data. EPA methods have been carefully validated and used for decades, and many of the problems with the methods that have arisen have been documented and solutions for avoidance of these problems are described. The compliant use of these methods also makes comparison of data sampled over long periods of time possible as it is a means to control analytical variables.

In the case of the JBPHH project, the compliance of the laboratory for the analytical method 8015C and the extraction method 3510C were evaluated. Both methods were performed in compliance with the written method, but both methods reference Chapter 4 of the SW 846 Method Compendium for sample collection, preservation and handling instructions. The correct sample preservation guidelines were not followed. Sample collection and preservation are of particular importance to the overall quality of the data because if samples are not collected properly, preserved properly or handled correctly, any analytical results would be meaningless even when the analysis was performed correctly.

Section 6.0, Method 3510C and section 8.0, Method 8015C requires that Chapter 4 of the SW-846 compendium be consulted for sample preservation procedures. As shown in Figure 13, samples containing residual levels of chlorine are required to be preserved with sodium thiosulfate. The samples from the JBPHH are drinking water samples and, therefore, contain residual chlorine and should have been preserved with thiosulfate at the time of sample collection but this was not performed. Because the samples were not preserved as directed in Chapter 4, these samples are not compliant with the preservation requirements of Method 3510C or Method 8015C. From the perspective of data validation, the lack of proper sample preservation would invalidate these results.

TABLE 4-1 (continued)
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES[a]

		preservatives and analyze as soon as possible.	
SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES AND HERBICIDES			
Sample Matrix	Container[1]	Preservative[2]	Holding Time[3]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	Cool to 0 - 6 °C.	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to 0 - 6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Add 3 mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to 0 - 6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.

Figure 13. SW-846 Chapter 4, Table 4-1. This table shows guidance for preserving samples with residual chlorine.

Another important reason for performing sample analysis in compliance with the EPA methods is because these data may be used in legal situations and the quality and accuracy of the data must be able to be defended. When data are used in this manner, every aspect of the process, from sample collection to the final report, is scrutinized to ensure that the analytical data is beyond dispute. Any failure to fully follow the method guidelines and procedures may result in the data being found inadmissible. Any failure to fully and completely document the entire process from sample collection through sample analysis can also make the data inadmissible.

Because the samples collected for TPH analysis for the JBPHH project were not preserved per the guidelines in SW-846, this data would not be legally defensible as the quality of the results would be open to questions about the effect of not following the recommended sample preservation guidelines. An example of how the sample preservation process may introduce uncertainty into the results can be found when considering how chlorine reacts with diesel fuel components. It is known, for example, that aliphatic hydrocarbon fractions from diesel are less soluble than the aromatic fractions. The diesel aliphatic fractions are also less reactive in the presence of chlorine than the aromatic fractions[10]. These fractions do react with chlorine, but the rate of reaction for all diesel components is not well understood or documented, leading to a situation where it cannot be stated with certainty how any TPH in this sample may have reacted with chlorine. Because the exact nature of the potential contamination is not fully known and the way that the components react, there is uncertainty related to the fate of any low-level TPH contamination in the samples. As a result, the reliability of this data could be questioned. This data set would not be considered defensible from a data validation perspective.

The last topic to consider is whether the results are scientifically accurate, thus making the data usable even when it is not defensible. In this case, there is a large body of data related to the reaction of aromatic hydrocarbon compounds with aqueous chlorine. There is little data related to the reaction of heavy aliphatic compounds, greater than C_6, but it is expected that compounds larger than C_6 are less reactive. Therefore, it is expected that if there was TPH in the sample, it would be expected to be observed at some concentration, but it is difficult to know at what concentration TPH contamination could be observed when the samples are stored in the presence of residual chlorine. Because it is known that reactions with fuel components can and do occur in aqueous samples containing residual chlorine, but the extent and rate of the reactions is not well understood there can be no certainty in the results. If there was a low level of TPH in the sample but enough components reacted with the residual chlorine to reduce the signal to below the MDL, then a situation could exist where there were amounts of TPH above the MDL in the sample with no TPH reported due to degradation of the analytes. While such a situation is highly unlikely because most of the aliphatic hydrocarbons would not be expected to react substantially with the residual chlorine, it cannot be stated with certainty that there was no TPH above the MDL. Without spiking drinking water samples at the MDL and studying the effect of long term contact with residual chlorine, it cannot be known how the low-level TPH results were impacted by the residual chlorine. This makes it difficult to have complete confidence in the existing data. Another way to consider the usability of this data would be to understand how much confidence there would be in the analytical data from Method 524 or 525 if the samples had not been dechlorinated. Those data would not be accepted in any circumstance because they are not compliant with the method. This is no different than the situation for Method 8015 in these circumstances where the method also requires dechlorination for drinking water samples. The data to this point should be, at the least, qualified.

Conclusions

The conclusions from the Technical Memorandum are that chlorination of the surrogate was the cause of an increase in TPH observations. A review of the data indicates that this is not accurate as demonstrated by a careful review of the raw data.

When the TPH results are plotted by sample, it appears that different zones have different shapes from other zones and also not every zone had a rise in TPH during LTM 6. This is not in agreement with the conclusion that the special and temporal data was the same for all zones.

The laboratory method blanks throughout the sampling period are mostly clean. There are some small peaks in many of the blanks, but the total area of these peaks does not result in an area count that is above the MDL, which results in these blanks having a U qualifier indicating that the blank had undetectable amounts of TPH. While the presence of these peaks is not sufficient

to result in a B flag, they do contribute to the total TPH area and along with other non-TPH peaks may result in a combined area that results in a TPH number greater than the MDL.

The surrogate is reacting with residual chlorine to form at least one halogenated compound that was observed in all of the drinking water samples and possibly a couple of other less abundant halogenated compounds, but the identity is uncertain for the smaller peaks because they were not present in all of the drinking water samples. The Tech Memorandum identified the main peak as a brominated surrogate but did not supply mass spectral data to support that conclusion and it seems unlikely that the surrogate would be brominated instead of chlorinated. This should be verified as it creates uncertainty in the conclusion from the panel.

The Tech Memorandum concludes that halogenated byproducts are the cause of the TPH detections. The data does not support this conclusion. There is no doubt that halogenation is occurring, and it was elegantly demonstrated that these peaks were gone when no surrogate was spiked and that these peaks were gone when the sample was treated with thiosulfate. What is not clear is if these halogenated peaks are the main cause of the TPH detections. If the samples had been collected following the guidelines in SW-846 for aqueous samples with residual chlorine, the TPH increase may still have been observed because there was no measurable change in sample blank response and the surrogate was always used at 2000mg/L throughout the LTM period.

It appears that the sample may be contaminated during sampling because most of the samples with elevated TPH had large hexadecanoic acid peaks and in some cases octadecanoic acid peaks which may come from contaminated sample collection equipment.

The presence of low-level hydrocarbons cannot be completely ruled out because there were samples with elevated TPH that had peaks that were not the acids or the halogenated peaks yet still had a reportable TPH result. It does appear that sampling contamination may be a larger cause for the observed increase in TPH.

The full cause for the increase in observed TPH results should be more carefully evaluated before using a new method. It is never desirable to have a significant analytical method change in the middle of a monitoring program due to difficulties in comparing results. The simplest corrective action would be to follow the sample preservation guidelines presented in SW-846 Chapter 4, with no other changes to sample collection, extraction or analysis. Because there would be no other changes to the analytical process this approach would introduce the least amount of uncertainty when comparing analytical results across the LTM periods.

The MEQ method uses a smaller concentration factor, a lower surrogate dose and a different extraction solvent, which are significant method alterations and may make data comparisons difficult. Before considering a method change, a valid method detection limit study should be performed and the laboratory should verify the calculated MDL through the analysis of samples spiked at the MDL and analyzed. This would unambiguously demonstrate that the MDL can be achieved using the new method. Use of the MEQ method has resulted in samples with fewer

TPH results above the MDL than were observed for that zone in LTM 6. However, these results are not fully conclusive because there were sample batches collected in LTM 7 and prepared with the standard method that did not have reportable TPH results. If there was an event of increased TPH in LTM 6, it appears to have cleared by LTM 7 and all sample prep methods produce clean samples. A clear reason for the increased TPH results observed in LTM 6 has not been convincingly identified in the Tech Memorandum because the conditions of analysis did not change during the entire sampling event, therefore it is not due to halogenated surrogate or blank contamination. For this reason, a more supportable cause for the increase in observed TPH should be identified before changing methods.

Finally, the observed TPH results are quite small as noted in the Tech Memorandum. When this is the case, every small contribution to the total peak area moves the total area closer to being over the MDL amount. In this situation, calibration samples do not have peaks from preparation contaminants, halogenation of surrogates or small impurities in a very large surrogate concentration. This creates a situation where a change in any one of these, or even a small increase in actual TPH in the sample would put the result over the MDL. Any effort to remove these peaks is an important step towards improving the quality of the analytical results. Therefore, at a minimum, adding a thiosulfate step to the existing procedure in accordance with the SW846 guidelines and lowering the surrogate concentration to a lower concentration are good practices analytically and will improve the ability of the method to detect TPH in the sample.

Any method modifications, however, should not be made without careful evaluation to demonstrate adequacy and equivalency to the current method.

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