Field Investigation of the Chemistry and Toxicity of TPH in Petroleum Vapors: Implications for Potential Vapor Intrusion Hazards

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Note: This report was updated in December 2012 to correct a typographical error in Section 4 (example naphthalene indoor air goal corrected to 0.072 $\mu g/m^3$) and to clarify in Section 6.2 that "TPH" for both gasoline and diesel/middle distillates vapors is reported as the sum of C5 to C12 (Summa canisters) or C5 to C18 (sorbent tubes) compounds minus BTEX and naphthalene.

Executive Summary

This report presents a field-based investigation of the chemistry and toxicity of vapors associated with subsurface, petroleum-contaminated soil and groundwater. The project was carried out by staff of the Hawaiʻi Department of Health (HDOH), Hazard Evaluation and Emergency Response office (HEER) with assistance from Hickam Air Force Base in Honolulu as well as a number of local and mainland-based consultants. The study focuses on the nature of vapors in the immediate source area of petroleum contamination. The fate and transport of vapors away from the source area was not directly evaluated.

Particular emphasis is placed on the study of the aliphatic and aromatic, carbon range makeup of Total Petroleum Hydrocarbon (TPH) vapors and the potential for TPH to drive potential vapor intrusion hazards (“risks”) over individual compounds such as benzene, toluene, ethylbenzene, xylenes and naphthalene (BTEXN) and methane. For the purposes of this study, TPH represents the sum of non-specific, aliphatic and aromatic hydrocarbon compounds exclusive targeted, individual compounds. An evaluation of both TPH and targeted, individual compounds is required under HDOH guidance (HDOH 2009, 2011).

Five study sites in Hawaiʻi were targeted for the collection and detailed analysis of soil gas associated with petroleum-contaminated soil and groundwater. Each of the sites was known through prior investigations to be heavily contaminated. Fuels released at the sites ranged from gasolines, including AVGAS and JP-4 jet fuel, to middle distillates, including diesel fuel and JP-8 jet fuel. Several of the study sites are suspected to be contaminated with both gasolines and middle distillates. Pipeline releases with widespread contamination and existing soil vapor monitoring points were targeted in order to ensure that vapors would be encountered and to minimize field sample collection costs.

Key study questions addressed as part of this study included:

1. How are the chemistry and toxicity of petroleum vapors characterized and evaluated?
2. What is the overall composition of vapors emitted from fresh fuels and petroleum-contaminated soil and groundwater in terms of non-specific, TPH compounds and traditionally targeted, individual compounds such as benzene?
3. What is the chemical makeup of the non-specific, TPH component of petroleum vapors in terms of aliphatic and aromatic carbon range compounds?
4. What is the average or weighted toxicity (e.g., noncancer Reference Concentration) of vapor-phase TPH at a given site in terms of the overall carbon range makeup of the vapors?

5. What is the critical ratio of TPH to benzene in indoor air or soil gas (and TPH to other, targeted compounds) where the potential noncancer hazard posed by TPH overrides the cancer risk or noncancer hazard posed by the individual compound?
6. Do the results of the study indicate that there are conditions where risk-based decision making for potential vapor intrusion concerns would be based on or driven by the noncancer TPH hazard rather than the cancer risk and/or noncancer hazard ("risk") posed by individual compounds? and
7. Based on the findings of this study, is an update to the 2008 HDOH indoor air and soil gas air action levels for TPH warranted?

As summarized below and discussed in detail in this report, the answer to the latter two questions is clearly "Yes." The vapor intrusion risk (in general terms) posed by the non-specific, TPH component of petroleum vapors can override the risk posed by posed by individual compounds such as benzene due to its overwhelming dominance of vapor phase compounds. This is especially true for contamination associated with diesel or similar middle distillate fuels. The results also indicated that the 2008 HDOH indoor air and soil gas air action levels for TPH were based on an overly conservative assumption of TPH composition and needed to be revised (included in the Fall 2011 update of the HEER office EHE guidance; HDH 2011).

The field investigation was designed to help answer these questions and to update HDOH soil gas action levels for TPH. A limited number of vapor samples were also collected over containers of fresh fuels for comparison to soil gas data from the targeted study sites. Summa canisters were used to collect vapor samples during the first phase of the study. Laboratories reported that they cannot fully recover >C12 aliphatic and >C10 aromatic compounds from canisters, however, which could be of concern at middle distillate-release sites. Both Summa canister and sorbent tube samples were therefore collected during the second phase of the study. Sorbent tube TPH and carbon range data were used to evaluate the presence of heavy, vapor-phase aliphatic compounds and aromatic compounds in the samples that might have been missed in the Summa canister data. Field methods for the collection of soil gas samples and tests for leaks in the sampling train were also evaluated.

1. How are the chemistry and toxicity of petroleum vapors characterized and evaluated?

Petroleum vapors are evaluated in terms of a limited number of individual compounds (e.g., benzene, ethylbenzene, toluene, xylenes and naphthalene or BTEXN) and non-specific compounds collectively reported as TPH. The chemistry and toxicity of vapor-phase TPH is evaluated in terms of three groups of aliphatic and aromatic carbon range compounds:

- C5-C8 aliphatics,
- C9-C18 aliphatics, and
- C9-C16 aromatics.

Inhalation toxicity factors or “Reference Concentrations (RfCs)” published by USEPA were used to develop fraction-specific action levels for indoor air and subslab, soil gas based on the sample approach used by HDOH for individual compounds. For example, a residential, indoor air action level of 630 $\mu g/m^3$ was calculated for C5-C8 aliphatics, based on an RfC of 600 $\mu g/m^3$. An indoor action level of 100 $\mu g/m^3$ was calculated for both C9-C18 aliphatics and C9-C16 aromatics based on an RfC of 100 $\mu g/m^3$. This is because C9-C18 aliphatic and C9-C16 aromatic components of TPH are considered to be slightly more toxic than C5-C8 aliphatics. Correlative soil gas action levels for potential vapor intrusion hazards are set at 1,000 times the indoor air action level (HDOH 2011).

The overall, average toxicity of TPH in a vapor plume can be evaluated in terms of the relative makeup and contribution of the targeted carbon ranges to the total TPH. An initial evaluation of TPH carbon range makeup allows for development of site-specific screening levels for TPH in soil gas without the need for carbon range analysis of each sample collected. Conservative assumptions regarding TPH composition can also allow development of risk-based action levels for more widespread use, such as those published by the HEER office.

2. What is the overall composition of vapors emitted from fresh fuels and petroleum-contaminated soil and groundwater in terms of non-specific, TPH compounds and traditionally targeted, individual compounds such as benzene?

TPH compounds dominated petroleum vapors at all sites investigated during the study, with the exception of a former gas manufacturing site (GASCO) where benzene and naphthalene were produced for commercial purposes. [Note that for the purposes of this project, “TPH” for both gasoline (“TPHg) and diesel/middle distillates (“TPHd”) was reported as the sum of vapor-phase, C5 to C12 (Summa canisters) or C5 to C18 (sorbent tubes) compounds minus BTEX and naphthalene.] Vapors collected over containers of fresh, gasoline and middle distillate fuels were characterized by 86-96% TPH and 4-14% BTEXN (dominated by TEX). Soil gas samples collected from study sites show an even greater dominance of TPH, with less than 1% of the total vapors generally attributable to BTEXN. Although the data are limited, the reduction of aromatic BTEXN compounds in subsurface vapors at the study sites could reflect preferential removal of vapor-phase aromatic compounds over aliphatic compounds due to a greater affinity for soil moisture and resulting higher susceptibility to biodegradation. Note that vapor-phase, aliphatic compounds are also highly biodegradable in the subsurface, as illustrated by the rapid attenuation of TPH in general away from source areas at petroleum-contaminated sites. Aromatics appear to be even more efficiently removed from soil vapors, however.

Although data are limited, a higher proportion of total BTEXN was reported in vapors collected over fresh fuels in comparison to soil gas samples collected at aged-release sites. The ratio of TPH to benzene for vapors collected over fresh fuels was in turn relatively low, ranging from approximately 50:1 to 300:1 and not that significantly different between gasoline, JP-8 and diesel fuel. This suggests that either TPH or benzene could drive vapor intrusion risks for fresh fuels, again depending on the carbon range chemistry and associated toxicity of the TPH and the target risk used to screen benzene. As the ratio decreases, however, the chance that benzene will drive vapor intrusion concerns over TPH increases.

The average ratio of TPH to benzene was significantly higher in soil gas samples collected at the study sites, ranging from an average of approximately 1,500:1 at the Hickam AFB VP26 site (JP-4/AVGAS) site to over 18,000:1 at both the Hickam AFB SP43 site (mix of gasolines and middle distillates) and the Honolulu Harbor Fishing Village site (primarily diesel and other middle distillates). The average TPH:Benzene ratio exceeded 2,000:1 at the three sites were diesel and other middle distillate contamination was known to be present. This indicates TPH will dominate vapor intrusion risks at these sites over benzene and other individual VOCs regardless of the actual carbon range makeup of the TPH or the use of a conservative, target risk for benzene. The average TPH:Benzene ratio at an aged, gasoline release site included in the study also exceeded the critical ratio of 2,000:1 (>9,000:1; Hickam AFB ST03). This could be associated with a preferential removal of vapor-phase, aromatic compounds over aliphatic compounds at aged release sites in comparison to vapors from fresh fuels. Although data are limited and this could simply be related to the original fuels released, other consultants have reported similar findings.

3. What is the chemical makeup of the non-specific, TPH component of petroleum vapors in terms of aliphatic and aromatic carbon range compounds?

4. What is the average or weighted toxicity (e.g., noncancer Reference Concentration) of vapor-phase TPH at a given site in terms of the overall carbon range makeup of the vapors?

5. What is the critical ratio of TPH to benzene in indoor air or soil gas (and TPH to other, targeted compounds) where the potential noncancer hazard posed by TPH overrides the cancer risk or noncancer hazard posed by the individual compound?

A comparison of the highest-possible indoor air action level for TPH (e.g., 630 $\mu g/m^3$, assuming 100% C5-C8 aliphatics) to the most conservative soil gas action level for benzene (e.g., 0.31 $\mu g/m^3$, based on a 10^{-6} cancer risk) suggests that TPH will *always* drive vapor intrusion risk over benzene if the ratio of TPH to benzene in indoor air or soil gas exceeds approximately 2,000:1 (rounded from 2,032:1). This “critical ratio” is an important and very useful screening tool that represents the point at which the collective mass of vapor-phase TPH aliphatic and aromatic compounds will overwhelm the risk posed by benzene, even though the relative toxicity of the latter is substantially greater. Either TPH *or* benzene could drive potential vapor intrusions concerns below a TPH:Benzene ratio of 2,000:1, depending on the actual carbon range makeup of the TPH and the target risk used to evaluate benzene. Note that this depends in part on the toxicity factors assigned to individual carbon range fractions. The relative risk posed by TPH could increase or decrease if alternative toxicity factors for TPH carbon ranges were used. Note that exceeding the critical ratio does not in itself imply that the TPH in soil vapors poses an actual vapor intrusion risk, since this will be governed by the concentration of TPH and individual VOCs present in the soil vapors, the location of the vapor plume with respect to nearby or future buildings, building design and related factors.

Similar “critical TPH ratios” were calculated for other targeted compounds (i.e., TEXN). The ratio increases for compounds that are more toxic than benzene (e.g., naphthalene critical ratio 8,800:1) and decreases for compounds that are less toxic (e.g., toluene critical ratio 0.6:1). In other words, a higher proportion of TPH in soil gas (or indoor air) is required to overwhelm the vapor intrusion risk posed by an individual compound as the toxicity of the targeted compound increases. Based on this approach, the results of the study suggest that ethylbenzene, toluene and xylenes are unlikely to significantly contribute to vapor intrusion risks at petroleum-contaminated sites in comparison to either TPH or benzene due to their relatively low proportion of the total vapors present their lower toxicity. Naphthalene was not detected above laboratory reporting limits in the majority of the samples outside of samples over containers of fresh JP-8 and diesel. This suggests that naphthalene has limited use as a tool to screen for potential vapor intrusion hazards at petroleum-contaminated sites in Hawai‘i. Methylnaphthalene data were still pending at the date of this draft report but are anticipated to be similar to naphthalene.

6. Do the results of the study indicate that there are conditions where risk-based decision making for potential vapor intrusion concerns would be based on or driven by the noncancer TPH hazard rather than the cancer risk and/or noncancer hazard (“risk”) posed by individual compounds?

The study indicated benzene generally drives risk at the scale of an individual compound and that TEXN data are not reliable, stand-alone indicators of potential vapor intrusion hazards. For benzene, the above question could be rephrased to ask: *Can benzene soil gas data be used as a standalone tool to screen for potential vapor intrusion hazards at petroleum-contaminated sites, in the absence of TPH data?* The answer for benzene varies based on a number of factors, including: 1) The type and original composition of the fuel released, 2) The proportion of vapor-phase TPH to benzene, 3) The carbon range makeup of the TPH and 4) The target risk applied to benzene.

Based on the dominance of C5-C8 aliphatics and the relatively low ratio of TPH to benzene in vapors collected over fresh gasoline, benzene could be used as a stand-alone indicator of potential vapor intrusion hazards even if a less conservative, target cancer risk 10^{-5} were applied. For example, a benzene indoor air action level 3.1 $\mu g/m^3$ and a subslab, soil gas action level 3,100 $\mu g/m^3$ can be used as stand-alone tool to evaluate potential vapor intrusion hazards). If the reported concentration of benzene in indoor air or soil gas meets these action levels then the noncancer risk posed by the TPH component of the soil gas will likewise not exceed a Hazard Quotient of 1.0. Based on (very limited) vapor samples collected over fresh diesel fuel and JP-8 jet fuel, benzene could still be used as a standalone tool to screen for vapor intrusion provided that a target cancer risk of 10^{-6} was applied (e.g., target benzene indoor air action level 0.31 $\mu g/m^3$ and soil gas action level 310 $\mu g/m^3$).

The use of benzene as a stand-alone tool to screen for potential vapor intrusion hazards was less clear cut in the field. Soil gas data from two, gasoline-release sites included in the study identified significantly lower proportions of benzene relative to TPH in comparison with vapors from fresh fuel samples. At the Hickam AFB VP26 site, benzene was still adequate as a stand-alone tool to screen for potential vapor intrusion hazards but only if a target cancer risk of 10^{-6} was applied. Significant vapors were being emitted from this site, with concentrations of TPH in soil gas over 100,000,000 µg/m^3 reported for some samples and benzene up to 470,000 µg/m^3 reported (average TPH:Benzene ratio 1,500). A vapor intrusion soil gas action level of 560,000 µg/m^3 was calculated for this site.

At the forty year-old, Hickam ST03 gasoline release site (major break in a JP-4/AVGAS pipeline), however, the amount of benzene in soil gas samples was so low (average TPH:Benzene ratio >9,000:1) and the toxicity of the TPH so high (weighted RfC 211 µg/m^3) that TPH could still pose a significant vapor intrusion risk even if very conservative action levels were applied to benzene. A soil gas action level of 220,000 µg/m^3 was calculated for the site. Vapor concentrations in the source area of this site were significantly lower than identified for the more recent release at the Hickam VP26 site, however, with a maximum TPH soil gas concentration of just under 1,000,000 µg/m^3 reported. Benzene was not reported above a detection level of 42 µg/m^3 in the same sample. This suggests that the original JP-4 or AVGAS fuel contained a very low proportion of benzene or benzene and/or a significant, preferential removal of aromatics over aliphatics due to biodegradation is taking place at the site. A bioventing remedial action was also underway at this site and may have affected the TPH and BTEXN composition of the vapors.

Vapor intrusion risks at sites where diesel or other middle distillate fuels were present were consistently driven by TPH, regardless of the target risk used to screen for benzene. This is due to both a lower relative proportion of benzene in soil gas in comparison to TPH and an increased toxicity of the TPH due to the increased proportion of vapor-phase, C9-C12 aliphatic compounds. Naphthalene (and most likely methylnaphthalenes) was rarely identified above laboratory detection levels or did not make up a significant enough proportion of the total vapors present to drive vapor intrusion risks over TPH.

7. Is an update to the 2008 HDOH soil gas action levels for TPH warranted?

Revisions of the 2008 HDOH indoor air and soil gas action levels for TPH were incorporated into the Fall 2011 update of the HEER office EHE guidance, based on an initial review of data from this study (HDOH 2011). The 2008 action levels were based on an overly conservative assumption of the C9-C12+ aromatic carbon range compound component of TPH vapors, as well as the use of outdated toxicity factors.

In the subject study, TPH vapors collected over fresh fuels and in soil gas at all of the study sites were dominated by aliphatic compounds. Sorbent tube data indicated a minimal amount of C12 and higher aliphatic and aromatic compounds in the samples. Vapors collected over containers of fresh gasoline contained only traces of C9-C12 aliphatic compounds reported (98-99% C5-C8 aliphatics). Vapors collected over fresh diesel were dominated by C5-C8 aliphatics, with moderate proportions of C9-C12 aliphatics (14 and 21% for Summa canister samples and up to 35% for a sorbent tube sample). Aromatic compounds >C10 were present in only trace amounts in the gasoline samples (<1% in the Summa canister samples and 2% in the sorbent tube samples) and only slightly higher in vapors collected over fresh JP-8 and diesel (2-5%).

Weighted TPH Reference Concentrations and associated indoor air and soil as action levels based on the carbon range makeup of the TPH follow a similar trend. The weighted TPH RfC and associated action levels calculated for vapors collected over fresh gasoline and for soil gas associated with a relatively recent, gasoline-contaminated site (e.g., Hickam AFB VP26 and Honolulu Harbor OU1C) approach those for C5-C8 aliphatics (e.g., TPH RfC 400 to 600 $\mu g/m^3$). The weighted TPH RfC and associated action levels calculated for vapors collected over diesel and JP-8 and for soil gas associated with sites dominated by diesel or other middle distillate fuels (e.g., Honolulu Harbor Fishing Village) approach those for the more toxic, C9-C12 aliphatic compounds (e.g., TPH RfC 100 to 200 $\mu g/m^3$) and are reflective of the higher proportion of these compounds in the vapors. The weighted toxicity factor calculated for the Honolulu Fishing Village site was used as a reference for updates to the HDOH soil gas action levels for TPH.

Study site Hickam AFB ST03, a forty year-old gasoline pipeline release, is again an exception. Although highly variable, TPH in soil gas samples collected from the site were on average composed of 35% C9-C12 and very atypical of fresh gasoline. The age of the release and the type of fuel released is known with a high degree of certainty. A weighted RfC of 211 $\mu g/m^3$ and indoor air action level of 220 $\mu g/m^3$ was calculated for the site, similar to what might be calculated for a relatively fresh diesel release.

Summary

In summary, the results of this study support the need for quantitative evaluation of TPH in soil gas in order to accurately evaluate vapor intrusion risks posed by subsurface, petroleum-contaminated soil and groundwater. Benzene (and other individual VOCs) could potentially be used as a standalone tool to screen soil gas data for vapor intrusion concerns at gasoline-contaminated, provided that a conservative target risk and associated indoor air and soil gas action levels are applied (e.g., 10^{-6} cancer risk). Vapor intrusion hazards could be driven by TPH over benzene at some gasoline-contaminated sites, however, due to the preferential removal of aromatics through biodegradation at aged sites and/or a low proportion of benzene and other aromatics in the original fuel released. This issue requires further study.

The TPH component of vapors drove vapor intrusion risk over benzene and other individual VOCs at the study sites where diesel fuel and other middle distillates had been released. The potential presence of co-mingled diesel or other middle distillate fuels at typical petroleum-release sites and the apparent preferential removal of benzene and other aromatics from vapors at aged releases suggest that it would be prudent to collect and evaluate TPH soil gas data at all petroleum-release sites (required in HDOH guidance; HODH 2009, 2011).

Results from this study indicate that C5-C8 aliphatic compounds can make up a significant if not dominant fraction of the total TPH present in vapors associated with diesel and other middle distillate fuels. This is important, since current laboratory protocols typically require that they report “TPHdiesel” in any media as the sum of C10 to approximately C24 hydrocarbon compounds. Excluding the contribution of C5-C8 aliphatics to the total concentration of TPH reported in air or soil vapor samples associated with middle distillate fuels would be inappropriate, however. To address this problem, laboratories should be instructed to report TPH in air or vapor samples as: 1) The sum of C5-C12 compounds for whole-air samples (e.g., summa canister samples and TO-15 lab methods), with the understanding that aromatics can only be confidently summed to C10 and 2) The sum of C5-C18 for samples collected using a sorbent media, with the understanding that aromatics can only be confidently summed to C16 (e.g., sorbent tubes and TO-17 lab methods), regardless of whether the samples are associated with gasolines or middle distillates. Designation of chromatogram patterns as “gasoline range” (e.g., C5-C12) or “diesel range” (e.g., C10-C24) compounds with respect to traditional, laboratory methods for TPH in soil or water is not applicable to air and vapor samples and is not necessary or recommended. The reported concentration of TPH can then be compared to HDOH soil gas action levels. The sum of concentrations of individual, target analytes such as BTEX and naphthalene that will be evaluated separate can be subtracted from the reported concentration of TPH in order to avoid double counting, although this is not likely to make a significant difference in the final concentration.

It is important to note that the results of this study reflect in part both the composition of the petroleum fuels produced or otherwise used in Hawaiʻi as well as environmental conditions at release sites. The vapor signatures reported in this study for TPH carbon range fractions (i.e., proportions of non-specific, TPH aliphatics to aromatics) are likely to be similar to sites outside of Hawaiʻi. The BTEXN component of the vapors and the relative proportion of TPH to individual compounds could vary dramatically, however, depending on the blending process used by the refinery that produced the fuel. For example, MTBE is not widely added to fuels in Hawaiʻi. The BTEXN component of fuels used (and released) in Hawaiʻi can differ dramatically, however, depending on the processes used by the two refineries that operate here. Weathering of fuel over time can also significantly affect the both the TPH and individual compound signatures in soil vapors. Temperatures of subsurface soil and groundwater could affect both vapor concentrations and composition. For example, vapor emissions from contaminated soil and groundwater is likely to be greater in Hawaiʻi versus Alaska, due to the higher average subsurface temperature here. Higher subsurface temperatures could also promote more rapid biodegradation, however. This emphasizes the need for site-specific data.

This study was not intended to evaluate actual vapor intrusion risks at the study sites where soil vapor samples were collected. Significant vapor intrusion impacts have not been identified at any of the sites. Factors that control long-term, vapor intrusion problems include the vertical or lateral distance of a building from heavily contaminated soil or groundwater, building design and ventilation and in particular biodegradation of the source area over time. Natural biodegradation of petroleum in contaminated soil and groundwater will significantly reduce the long-term vapor-intrusion risk of subsurface contamination in comparison to soil contaminated with an equal amount of chlorinated solvents. Note, however, that default indoor air:soil gas attenuation factors incorporated into HEER soil gas action levels are intended to apply to subslab soil vapors at the point that the vapors are about to be drawn into the affected building. Given the assumed, short transit time of the vapor through building slab (e.g., via gaps around utilities, likely to be seconds or minutes), any reduction in VOC concentrations due to biodegradation will be negligible.

The results of this study were recently used to update HEER office indoor air and soil gas action levels for TPH (HDOH 2011). As discussed in the report, secondary objectives of the study included an evaluation of the design of vapor monitoring points, leak detection methods, the overall representativeness of soil vapor data using current sample collection methods and the fate and transport of petroleum vapors in the subsurface. These topics will continue to be evaluated in future studies and incorporated into updates of the HEER Technical Guidance Manual.

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1 BACKGROUND

The intrusion of vapors into existing or future buildings is one of several potential environmental hazards posed by petroleum-contaminated soil and groundwater (refer to HDOH 2009, 2011). Vapors emitted from subsurface petroleum contamination will diffuse upwards (and outwards) from the source area. If an overlying building is under pressured in comparison to area immediately beneath the floor (e.g., in the fill material under a slab or in the crawl space under a post-and-pier structure), then vapors that diffuse into this area could be advectively drawn into the building via cracks or utility gaps in the floor and mix with indoor air.

The ratio of the concentration of a chemical in indoor air after mixing (excluding background from indoor sources) to the original concentration of the chemical in vapors immediately beneath the building slab (or in the crawl space) is referred to for the purposes of this report as the "Attenuation Factor." Vapor intrusion is of particular concern in colder climates where heating of buildings can lead to relatively low indoor air pressures and high rates of vapor flux through building floors. This combined with poor ventilation of the buildings to reduce heating costs can lead to substantial vapor intrusion problems. The risk of vapor intrusion in Hawai'i is generally much lower, since buildings tend to be air-conditioned and over pressured or windows routinely kept open for ventilation. Even air conditioned buildings can become under pressured under windy conditions, however, so potential vapor intrusion hazards cannot be completely ruled out. As a conservative measure, HEER office guidance assumes a default Indoor Air:Subslab Soil Gas Attenuation Factor of 0.001 for residential homes (e.g., 1,000-fold dilution of subslab vapors) and 0.0005 for commercial/industrial buildings (e.g., 2,000 fold dilution of subslab vapors; see HDOH 2011).

The HEER office *Environmental Hazard Evaluation* guidance ("EHE" guidance; HDOH 2011) and *Technical Guidance Manual* ("TGM;" HDOH 2009) recommends that soil gas samples be collected at sites with petroleum contaminated soil and groundwater in order to evaluate potential vapor intrusion hazards. Ideally, samples are collected immediately beneath the slab of an existing building or immediately under paved areas. Deeper samples may also be useful in some cases (e.g., to evaluate upward attenuation of vapors from the source area). HDOH guidance requires that soil gas samples from petroleum-contaminated sites be tested for Total Petroleum Hydrocarbons (TPH, or equivalent) as well as targeted individual compounds, including benzene, toluene, ethylbenzene and xylenes and naphthalene (BTEXN). Concentrations of the latter are subtracted from the reported TPH if this is not done by the lab. Methane levels must also be evaluated. Site soil gas data are compared to action levels for potential vapor intrusion hazards published by HDOH. If the reported concentrations of TPH and targeted compounds are below action levels then no further action is generally needed, although periodic monitoring may be required. If action levels are exceeded then further action is necessary, as described in HDOH guidance.

Soil gas action levels for TPH originally published by the HEER office in 2005 and again in 2008 are noted in Table 1 (HDOH 2008, updated in 2011). The action levels were based on conservative assumptions regarding the toxicity and overall predominance of TPH in soil gas at petroleum release sites. A default, noncancer inhalation Reference Concentration (RfC) of 50 µg/m^3 was assigned for TPH vapors associated with gasolines, based on the most conservative RfC for carbon range fractions published by the Massachusetts Department of Environmental Protection (C11-C22 aromatics; MADEP 2003). A slightly less toxic mixture of aliphatics and aromatics was assumed for vapors associated with diesel and other middle distillate fuels, resulting in a default RfC of 110 µg/m^3 (discussed in Appendix 1 of the 2008 EHE guidance). The TPH action levels were also based on a conservative, noncancer Hazard Quotient of 0.5 for calculation of TPH risk-based action levels. This was done in order to take into account the cumulative, noncancer risk posed by targeted, individual compounds (i.e., TPH + BTEXN).

These assumptions were intentionally conservative, given the lack of field data and published information on the chemistry and toxicity of TPH in soil vapors available at that time. Guidance on the use of TPH carbon range fractions to more accurately evaluate the chemistry and toxicity of TPH in subsurface vapors was published by the environmental office of Hickam Air Force Base Air Force in Honolulu and their consultant in 2009 and updated in 2011 (Parsons 2011). Soil gas action levels for individual carbon ranges are included in the guidance (based on Massachusetts DEP toxicity factors). The Air Force and its consultants also began to collect TPH carbon range soil gas data for petroleum releases associated with its operations in Hawai‘i.

The Air Force data, as well as data from other sites, confirmed that vapors associated with petroleum fuels of all types were overwhelmingly dominated by TPH aliphatics, with BTEXN and other aromatic compounds making up only a minor component of the total vapors present. This suggested that an update of the HDOH TPH soil gas action levels was warranted and served as the impetus for the study described in this report. The resulting information was ultimately used to update the HEER office guidance on potential vapor intrusion hazards associated with petroleum-contaminated soil and groundwater (HDOH 2011), with a focus on updates to risk-based soil gas screening levels for “Total Petroleum Hydrocarbon” or “TPH” in soil gas.

2 STUDY OBJECTIVES

The objective of this project was to evaluate the chemistry and toxicity of the non compound-specific, aliphatic and aromatic component of vapors associated with subsurface petroleum contamination. Key study questions formulated as part of this study included:

1. How are the chemistry and toxicity of petroleum vapors characterized and evaluated?
2. What is the overall composition of vapors emitted from fresh fuels and petroleum-contaminated soil and groundwater in terms of non-specific, TPH compounds and traditionally targeted, individual compounds such as benzene?
3. What is the chemical makeup of the non-specific, TPH component of petroleum vapors in terms of aliphatic and aromatic carbon range compounds?
4. What is the average or weighted toxicity (e.g., noncancer Reference Concentration) of vapor-phase TPH at a given site in terms of the overall carbon range makeup of the vapors?
5. What is the critical ratio of TPH to benzene in soil gas (and TPH to other, targeted compounds) where the potential noncancer hazard posed by TPH overrides the cancer risk or noncancer hazard posed by the individual compound?
6. Do site data indicate that there are conditions where risk-based decision making for potential vapor intrusion concerns would be based on or driven by the noncancer TPH hazard rather than the cancer risk and/or noncancer hazard ("risk") posed by individual compounds? and
7. Based on the findings of this study, is an update to the 2008 HDOH indoor air and soil gas air action levels for TPH warranted?

A field investigation was designed to help answer these questions and in particular the potential for non-specific, aliphatic and aromatic compounds in soil gas to pose potential vapor intrusion hazards at petroleum-release sites even though benzene and naphthalene are below levels of concern. The locations of sites included in the study are noted in Figure 1. As described in Section 4, soil gas samples were collected at key petroleum release sites in Hawai'i and submitted for detailed, carbon range testing as well as BTEXN and a small number of other, individual compounds. Sample collection was carried out between May and October 2011 by staff of the Hawaiʻi Department of Health (HDOH) Hazard Evaluation and Emergency Response (HEER) office with assistance by staff of the Underground Storage Tank (UST) section of the HDOH Solid and Hazardous Waste Branch.

Answering and addressing the study questions required a review of the chemical makeup of petroleum fuels, especially in terms of carbon range fractions. The next section provides a brief over view of this topic with references for additional details.

Note that this study does not address biodegradation of petroleum vapors as the vapors migrate away from the source area. The study focused instead on the initial chemistry and toxicity of petroleum vapors *in the immediate source area*. The fate and transport of vapors in the vadose zone represents the next, important step in evaluation of the vapor intrusion threat posed by petroleum-contaminated soil and groundwater. Petroleum is highly biodegradable in the subsurface under aerobic conditions (see discussion in HDOH 2011). Recent field studies and modeling efforts have suggested that ten meters or less of clean soil (i.e., TPH <100 mg/kg) is adequate under most circumstances to reduce petroleum vapor concentrations to below levels of concern for potential vapor intrusion hazards, regardless of the mass or concentration of petroleum in underlying soil, the presence of free product on groundwater or the design and vulnerability of overlying buildings (e.g., Abreu et. al 2009, API 2010, McHugh 2010). This issue will be discussed in more detail in updates to Section 7 of the HEER office *Technical Guidance Manual* (Soil Vapor and Indoor Air Sampling Guidance, anticipated Fall 2012).

3 TPH CARBON RANGE FRACTIONS

The study was initiated with a review of risk-based methods for evaluation of TPH in soil gas. As discussed in this section, this included the selection of target carbon range fractions and associate toxicity factors as well as development of risk-based action levels for indoor air and soil gas. These toxicity factors and action levels were used to evaluate soil gas data collected at the study sites. A brief discussion of the chemistry of petroleum fuels is provided in Appendix 1 of the HEER office EHE guidance and included in Attachment 1 of this report. Models used to develop risk-based action levels for Total Petroleum Hydrocarbons (TPH) in soil, soil gas and groundwater is also described in the EHE document.

Petroleum is a complex mixture of hundreds of different compounds composed of hydrogen and carbon (i.e., "hydrocarbon" compounds). For the purposes of this study, petroleum mixtures are subdivided into "gasolines", "middles distillates" and "residual fuels", following the methodology used by the American Petroleum Institute (API 1994). Gasolines include commercial gasoline used in autos and aviation fuels such as AVGAS. Middle distillates include common diesel fuel, kerosene and jet fuels such as JP-8. Jet fuel JP-4 is a mixture of gasoline and kerosene. Most of the largest subsurface petroleum releases in Hawaiʻi are associated with jet fuels. Several of these sites were targeted for the study.

The general carbon range makeup of common petroleum fuels is depicted in Figures 2a. Non-specific, aliphatic and aromatic compounds collectively reported as Total Petroleum Hydrocarbons or “TPH” make up the overwhelming majority of the hydrocarbon mass in fuels and in vapors emitted from fuels (e.g., refer to Hartman 1998). As documented in this study, individual, “indicator” compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) as well as naphthalene and other targeted polyaromatic hydrocarbons (PAHs) make up only a small percentage of the total mass of hydrocarbon compounds in fuels and in vapors.

The TPH component of petroleum can be further subdivided into groups or “fractions” of aliphatic and aromatic compounds based on the number of carbon molecules in compounds within that range (Figure 2b; e.g., TPHCWG 1998; MADEP 1997, 2002, 2003; WADOE 2006). An overview of the carbon range method published by Massachusetts is provided in Attachment 2. Representative fate and transport parameter values and toxicity factors are then assigned to each fraction, allowing for risk-based action levels to be developed in the same manner as done for individual chemicals. Carbon range fractions established by Massachusetts are the most commonly referenced and have been incorporated into past editions of the HEER office EHE guidance and associated action levels (see Figure 2b, MADEP 2002; see also HDOH 2011):

- C5-C8 aliphatics;
- C9-C12 aliphatics;
- C13-C18 aliphatics;
- C19-C36 aliphatics;

- C9-C10 aromatics;
- C11-C22 aromatics.

Physiochemical constants assigned to each carbon range are summarized in Table 2 (after MADEP 2002). Each of the carbon ranges can have an associated vapor-phase component in air or soil gas. The dominance of petroleum-related vapors by lighter-weight aliphatics (e.g., C5-C16 aliphatics) can be predicted by the typical carbon range makeup of fuels and theoretical partitioning between fuels and air based on the physiochemical constants noted in Table 2 (e.g., Hartman 1998). Aliphatic compounds will preferentially remain in the vapor phase, as indicated by a Henry Law Constant greater than one (ratio of vapor-phase component to dissolved-phase component).

The Henry's Law Constants for aromatic compounds such as BTEXN, in contrast, are consistently less than one (see Table 2). This indicates that aromatic compounds will preferentially partition into soil moisture. As a result, these compounds will also be more susceptible to bacteria-driven biodegradation. As discussed below, this may explain increased TPH:Benzene ratios in soil gas samples collected from the study sites in comparison to TPH:Benzene ratios for vapors collected over a limited number of fresh fuel samples (i.e., preferential loss of vapor-phase aromatics at aged releases due to biodegradation).

An evaluation of vapor-phase TPH in terms of vapor intrusion risk depends in part on the toxicity factors assigned to individual carbon range fractions. The relative risk posed by TPH could increase or decrease if other toxicity factor values are used. A number of organizations and agencies have published toxicity factors for carbon ranges (see Table 3). A consortium of regulators, oil companies and private consultants lead by the Air Force and referred to as the "TPH Criteria Working Group" published a thorough summary of the carbon range chemistry of petroleum fuels in the late 1990s and assigned preliminary toxicity factors to each fraction (TPHCWG 1998). The Massachusetts Department of Environmental Protection (MADEP), which was preparing similar guidance at the time, published initial guidance during the same time period and last updated their toxicity factors for carbon range fractions in 2003. The Washington Department of Ecology published TPH carbon range guidance in 2005 and 2006 using a slightly different approach but again including toxicity factors for targeted carbon range fractions (WADE 2006). The USEPA National Center for Environmental Assessment published a detailed review of TPH carbon range toxicity and recommended Provisional Peer-Reviewed Toxicity Values (PPRTVs) in 2009 (USEPA 2009). The California EPA Department of Toxics Substances Control also published guidance and proposed toxicity factors similar to those proposed by MADEP in 2009 (CalEPA 2009; currently withdrawn pending review of the USEPA report).

The PPRTV toxicity factors published by the USEPA in 2009 were ultimately selected for use in the Fall 2011 update of the HEER office EHE guidance and calculation of risk-based, Environmental Action Levels for individual carbon ranges and TPH in general (EALs, HDOH

2011). Note that PPRTV values are routinely used by USEPA and other agencies to develop screening levels in the absence of more thoroughly reviewed toxicity factors, including calculation of USEPA Regional Screening Levels (see USEPA 1012). From a toxicity standpoint, vapor-phase compounds can be combined into three fractions: C5-C8 aliphatics, C9-C18 aliphatics and C11-C16 aromatics (Figure 2c). Risk-based indoor air and soil gas action levels for individual TPH carbon ranges are provided in Table 4 (see also Appendix 1 of the 2011 EHE guidance). Action levels for C5-C8 aliphatics are the least stringent (e.g., indoor air action level 630 µg/m^3), reflecting the higher inhalation Reference Concentration assigned to this fraction of 600 µg/m^3. Action levels for C9-C18 aliphatics and C9-C16 aromatics are most stringent, reflecting the lower Reference Concentration of 100 µg/m^3 common to both fractions and generating an identical indoor air action level of 100 µg/m^3, after rounding. The action levels are based on a target, noncancer hazard quotient of 1.0. Cancer- and noncancer-based action levels for benzene and naphthalene based on alternative target risks are provided for comparison in Tables 5a and 5b. As discussed in the next section, a comparison of TPH action levels to action levels for individual compounds provides a useful screening tool to quickly determine if the former might drive vapor intrusion over the latter at a site.

The use of TPH soil gas data is generally preferable for initial screening of petroleum-contaminated sites due to the added cost the limited number of laboratories that can provide vapor-phase carbon range data. The following equation can be used to calculate weighted inhalation Reference Concentration (RfC) for TPH based on the site-specific carbon range makeup of TPH in soil gas or indoor air (see Appendix 1 of HDOH 2011 EHE guidance):

$$\text{Weighted RfC }(\mu\text{g/m}^3) = \frac{1}{\left[\frac{(Fraction\ C5\ to\ C8\ Aliphatics)}{C5\ to\ C8\ Aliphatics\ RfC} + \frac{(Fraction\ C9\ to\ C18\ Aliphatics)}{C9\ to\ C18\ Aliphatics\ RfC} + \frac{(Fraction\ C9\ to\ C16\ Aromatics)}{C9\ to\ C16\ Aromatics\ RfC}\right]}$$

As discussed in Section 6, this approach was used in the study to estimated weighted TPH toxicity factors (RfCs) and associated indoor air and soil gas action levels for each of the sites included in the study. As also discussed, vapor-phase aliphatic compounds >C12 and aromatic compounds >C10 did not represent a significant component of any of the samples collected. This allowed a reasonable estimation of TPH RfCs based on Summa canister data limited to C5-C12 aliphatic compounds and C9-C10 aromatic compounds (heavier compounds not extractable from canisters).

4 TPH:INDIVIDUAL COMPOUND CRITICAL RATIOS

The relative risk posed by two (or more) different chemicals under a given exposure pathway (e.g., vapor intrusion) is in part a function of concentration and toxicity. The risk posed by exposure to high concentrations of a chemical with a relatively low toxicity can exceed the risk posed by exposure to low concentrations of a highly toxic chemical. For example, TPH is significantly less toxic than benzene based on a simple comparison of indoor air action levels (see Tables 4 and 5a&b). At some critical ratio of TPH to benzene, however, the sheer mass of TPH will override the risk posed by benzene and TPH will "drive" vapor intrusion risk. In these cases, consideration of only benzene to screen or remediate a site will not be sufficient, since the remaining TPH could still pose a vapor intrusion risk. Note that exceeding the critical ratio does not in itself imply that the TPH in soil vapors poses an actual vapor intrusion risk, since this will be governed by the concentration of TPH and individual VOCs present in the soil vapors, the location of the vapor plume with respect to nearby or future buildings, building design and related factors (refer to HDOH 2011).

The point at which the transition from benzene to TPH as the primary risk driver occurs is the ratio of target TPH action level to the target benzene action level (see Tables 4 and 5a&b). (Note that the term "risk" is used in a generic fashion to denote "noncancer hazard" and/or "excess cancer risk.") This provides a very simple and quick tool to determine the potential significance of TPH as a vapor intrusion risk driver at a site where both TPH and benzene soil gas data are available. The same method can be used for TEX and naphthalene, although the former and in most cases the latter are unlikely to drive vapor intrusion risk at a site over TPH or benzene based on the results of the study discussed in this report.

As noted in Tables 4 and 5a, action levels for TPH in indoor air or soil gas can be up to 2,000 times higher than action levels for benzene (e.g., maximum TPH carbon range indoor air action level of 630 µg/m^3 divided by most conservative benzene indoor air action level of 0.31 µg/m^3 = 2,032). Similarly, action levels for TPH can be almost 8,800 times higher than action levels for naphthalene (maximum TPH indoor air action level of 630 µg/m^3 divided by minimum naphthalene indoor air action level of 0.072 µg/m^3).

These ratios can be used to initially screen soil gas data from a site and determine if TPH will or could drive potential vapor intrusion risks over benzene and/or naphthalene (Table 6a and 6b). For example, if the TPH:Benzene ratio exceeds approximately 2,000:1 at a site then TPH will *always* drive vapor intrusion risk over benzene, regardless of the carbon range makeup of the TPH (i.e., even if TPH composed of 100% C5-C8 aliphatics) and even if a very conservative benzene action level is used (i.e., based on an excess cancer risk of 10^{-6} or one-in-a-million). The same is true when the TPH:Naphthalene ratio exceeds 8,800:1. In such cases, TPH vapors could still pose a vapor intrusion risk when concentrations of individual met their respective action levels.

In a similar manner, benzene will *always* drive risk when the TPH:Benzene ratio is less than approximately three (Table 6a), the ratio of the lowest possible TPH action level (100,000 µg/m^3 for 100% C9-C12 aliphatics) to the highest acceptable benzene action level (31,000 µg/m^3, coincidentally based on both an excess cancer risk of 10^{-4} *and* a noncancer Hazard Quotient of 1.0). The equivalent TPH:Naphthalene ratio for instances where the latter will always drive vapor intrusion risk is 32 (point at which the naphthalene noncancer Hazard Quotient will exceed 1.0; see Table 6b).

For TPH:Benzene and TPH:Naphthalene ratios in between the ratios noted above (e.g. 2,000:1 to for benzene and 8,800:1 for naphthalene) in Tables 6a and 6b, either TPH or the individual chemical could drive vapor intrusion risk. This will ultimately depend on the actual carbon range chemistry of the TPH and the associated toxicity and the target risk used to screen for benzene and naphthalene. Less TPH is required to overwhelm the risk posed by an individual chemical as the proportion of more toxic, C9-C18 aliphatics (or C9-C16 aromatics) increases. As discussed below, this was used as a tool to initially screen soil gas data collected from the study site and also to screen TPH versus benzene data from other sites. As discussed below, naphthalene was rarely detected in soil gas samples from most sites and appears to be less useful in vapor intrusion studies.

Similar ratios at which TPH will always drive vapor intrusion risk ratios can be calculated for other, targeted individual compounds such as ethylbenzene, toluene, xylenes and methylnaphthalenes. A summary of critical ratios for these compounds is provided Table 6c. A lower critical ratio reflects a lower toxicity for the individual compound. For example, A proportion of TPH that exceeds just 650 times that of ethylbenzene is required for TPH to *always* drive vapor intrusion risk over ethylbenzene, even when the TPH is dominated by relatively low-toxicity C5-C8 aliphatics. The chemical 1-methylnaphthalene is more toxic, but TPH will dominate risks posed by this chemical when the TPH:1-methylnaphthalene ratio exceeds 2,200:1. Toluene is the least toxic, targeted individual compound. TPH will *always* drive vapor intrusion risk over toluene when the concentration of TPH in soil gas (or indoor air) exceeds just 60% of the concentration of toluene (critical ratio 0.6:1).

The next step of the study involved the selection of key, petroleum-contaminated sites and the collection of soil gas samples from the sites. The carbon range Reference Concentrations and action levels and critical ratios of TPH to targeted, individual compounds presented in this section were used to evaluate soil data collected at these sites.

5 SELECTION OF STUDY SITES

A survey of petroleum release sites overseen by the HDOH HEER office and the UST office was carried out to identify potential candidates for the collection of soil gas samples. An attempt was made to incorporate a variety of fuel types, ranging from gasolines to diesel fuel and other middle distillate fuels. Budget constraints were anticipated to restrict testing to approximately 20 to 25 samples for each of the two field phases of the study. Three to five samples per site were deemed desirable, with the potential for sample collection from five to eight sites. Sites with existing soil vapor monitoring points were preferentially targeted in order to minimize field costs. Site access was also considered.

Six, previously investigated petroleum-release sites were initially selected for inclusion in the study (see Figure 1 and Table 7a):

- Hickam AFB Site VP26;
- Honolulu Harbor OU1C;
- Hickam AFB Site ST03;
- Fishing Village;
- Aloha Petroleum–School Street; and
- GASCO.

Two phases of sample collection were carried out. The first phase focused on the collection of Summa samples and identification of sites with sufficient levels of petroleum vapors for more detailed, followup sample collection and analyses using sorbent tubes. The six sites selected included an operating service station and four sites associated with fuel pipeline releases (Hickam AFB SP43 not included). The sites represented a mix of gasoline and diesel fuel releases, with larger releases associated with pipelines that transported jet fuels to military bases on the island. While the extent and magnitude of contamination may not be representative of typical underground storage tank (UST) release sites, the chemistry of the petroleum vapors should be similar. For comparison, soil gas samples were also collected from the GASCO site in Honolulu, a former manufactured gas plant facility that is known to be heavily contaminated with benzene and naphthalene, two of the main products that were produced at the facility. Vapor samples were also collected over open containers of fresh gasoline and diesel fuel.

Soil gas and/or groundwater contamination maps from published reports for each site were used to initially target vapor monitoring points for sample collection (Figures 3-9, see references in Table 7a). The targeted sample points are noted on the maps. The depth to groundwater at the sites ranged from five to twenty feet below the ground surface (bgs). An exception was Hickam AFB ST03 (Site D), a significant pipeline release of JP-4 jet fuel (mix of gasoline and kerosene) that impacted groundwater at a depth over 500 feet bgs (see Figure 6). Soil vapor monitoring had been installed from the surface to groundwater. Samples collected as part of this project were collected from fixed monitoring points at depths of 250 to 490 feet. This site had also undergone a bioventing pilot study, where ambient air was pumped into the vadose zone to provide oxygen and enhance biodegradation. Oxygen levels at the vapor points had returned to normal (i.e., <5%) at the time that the samples were collected.

Four of the originally sampled samples sites were carried through to the second phase of sample collection. Soil gas results for the active service station site were non-detect, due mostly likely to vapor extraction remedial actions carried out since discovery of the release but also potentially due to heavy rainfall on the day of sample collection. The GASCO site was not resampled in the second phase of field work since it is not representative of typical petroleum releases. Hickam AFB site SP43, another jet fuel pipeline release site, was added. As was the case for the majority for the other sites, the depth to groundwater at SP43 was very shallow (less than ten feet bgs) and the soil gas samples were collected very close to source areas. The final sites included in the primary study were therefore as follows:

- Hickam AFB Site VP26 (Site A);
- Honolulu Harbor OU1C (Site B);
- Hickam AFB Site SP43 (Site C);
- Hickam AFB Site ST03 (Site D); and
- Fishing Village (Site E).

The purpose of this study was to obtain general information on the chemical makeup of vapors at petroleum-contaminated sites. The most heavily impacted areas of the sites were intentionally targeted for sample collection. **The data collected and discussed below are not intended to be representative of overall site conditions or potential vapor intrusion hazards at the sites.** More detailed investigations of the sites are being carried out separately by the responsible parties, under the oversight of HDOH. A generic designation was assigned to each of the sites for use in discussions of data subsequently collected at the sites (see above list; Site B, Site B, etc.).

Information regarding the nature of contamination (e.g., vadose zone soils and/or product on groundwater), vapor point identification number and depth to groundwater at the five, key study sites is summarized in Table 7b. Vapor points for most sites were installed in soil (including saprolite, marine sediments or fill material) and situated within five to fifteen feet of contaminated soil and/or groundwater. Vapor points at the Hickam AFB ST03 site were installed in basalt. As discussed above, sample points within or within a few feet of the source media were intentionally targeted in order to obtain data on the chemistry of petroleum vapors at the source. Consultants familiar with the Hickam AFB ST03 site suggested that some of the vapor probes could be as much as fifty to seventy-five feet or more from free product trapped in the basalt or on groundwater, even though reported levels of petroleum vapors at the points was extremely high.

Reports referenced in Table 7a and associated with the HEER office case file for the site include more detailed data for other measurements collected at the vapor points and project areas, including oxygen, carbon dioxide and methane levels over time. A summary of this information and review of degradation, vapor fate and transport, etc., was beyond the scope of this study but is being evaluated at several of the subject sites by the responsible parties and their consultants.

Additional vapor samples were collected over open containers of fresh gasoline and diesel fuel as well as JP-8 jet fuel. A limited number of auto exhaust samples were collected to determine if petroleum vapors associated with exhaust have a distinct signature in comparison to vapors from fresh fuel. Based on the few samples collected, it appears that the TPH:BTEX ratio for exhaust could be higher than typically observed for vapors from pure fuels. In the future, and with additional research, this could assist in determining the origin of petroleum vapors identified in the shallow subsurface or indoor or ambient air. As discussed below, sorbent tube samples were collected in addition to Summa samples during the second phase of the study.

6 SAMPLE COLLECTION AND ANALYSIS

6.1 SAMPLE COLLECTION

As discussed below, Summa canisters were used to collect soil vapor samples during Phase I of the study. Both Summa canisters and sorbent tubes were used to collect samples during Phase II of the study. Based on discussions with Air Toxics and other laboratories, Summa canister sample analysis methods are also only able to report up to C10 aromatic and C12 aliphatic compounds. Heavier compounds cannot be adequately extracted from the canisters after sample collection. Published data for headspace samples collected over different fuel types have suggested that a significant fraction of petroleum vapors could be dominated by these compounds, especially C12+ aliphatics (e.g., e.g., >10% and even >50%; see Hayes 2007). If so, then reliance of traditional Summa canister methods for the collection and analysis of soil gas samples (e.g., TO3 and TO15 methods) could significantly underestimate of actual concentration of TPH in soil gas samples and subsequently underestimate potential vapor intrusion risk.

In such cases the use of sorbent tube sample collection and analysis methods would be required to more accurately determine TPH concentrations. As discussed below, this was evaluated at the target study sites through the co-collection of both Summa canister and sorbent tube samples at each vapor point during Phase II of the field program.

6.2 TARGET ANALYTES

6.2.1 PRIMARY TARGET ANALYTES

The primary target analytes for the study included the following:

- C5-8 aliphatic compounds;
- C9-C12 aliphatic compounds;
- C13-C18 aliphatic compounds (Phase II only);
- C9-C10 aromatic compounds;
- C11-C16 aromatic compounds (Phase II study only);
- TPHgasoline (Phase II only)
- TPHdiesel (Phase II only)
- Benzene, toluene, ethylbenzene, xylenes (BTEX);
- Naphthalene.

All samples were analyzed by Air Toxics laboratory in Folsom, California. The sum of C2-4 aliphatics, hexane and additional volatile organic chemicals (VOCs, e.g., methylnaphthalenes) were reported for selected samples. The data were not directly used as part of this study but may be of use at a later time. Helium was reported as part of the leak tests. Although biodegradation was not a focus of this study, carbon dioxide and methane were also reported. Oxygen was recorded in the field at some vapor monitoring points, although not consistently due to equipment problems (also available from previous soil gas studies carried out at the sites).

6.2.2 Reporting TPH for Middle Distillate Vapors

The concentration of "TPH" in soil and groundwater is traditionally reported as "TPHgasoline," "TPHdiesel" and "TPHresidual fuels" or similar nomenclature. These terms reflect a specified range of carbon compounds that make up the bulk of the noted fuel type. For example TPH is typically quantified as the sum of C5-C12 compounds for gasolines, C10 to C24 for diesel/middle distillates and C24 to C35 for heavy fuels (actual ranges may vary slightly between laboratory methods and individual labs). From the standpoint of a laboratory, a request to test a media for a specific fuel type is interpreted as a request to quantify the total mass of hydrocarbon compounds within a pre-specific range of the gas chromatograph spectrum (with or without subtraction of individual, targeted compounds such as BTEX).

This works reasonably well for petroleum in soil, since the TPH in the soil presumably reflects the same range hydrocarbon compounds that dominate in the original fuel. Exclusion of the relatively minor component of lighter-end, C5-C9 aliphatic compounds present in diesel fuel from the laboratory analysis will not cause the total concentration of TPH in the soil sample to be significantly underestimated.

This approach can be inappropriate for quantification of TPHdiesel in water or, in the case of this study, for quantification of TPH in soil vapors. This is because the proportion of lighter-range, C5-C9 aliphatic compounds in vapors (or air in general) can be significantly greater than the proportion of these compounds in the original fuel. Exclusion of these compounds from the laboratory analysis can lead to a significant, under reporting of the actual concentration of TPH in the sample. For example, diesel fuel typically contains <1-2% C5-C8 aliphatic compounds (IDEM 2010, ODEQ 2003 TPHCWG 1997). Excluding these compounds from the reported concentration of TPH in diesel-contaminated soil is not significant. Results from this study, however, indicate that C5-C8 aliphatic compounds in diesel vapors can indeed make up a significant if not dominant fraction of the total TPH present. This is due to the higher volatility of these compounds and their propensity to partition out of fuel and into air rather than water (refer to Table 2). Excluding the contribution of C5-C8 aliphatic compounds to the total concentration of TPH reported in diesel vapors, for example by requesting that the lab report the concentration of "TPHdiesel" in the samples as might reasonably be done for soil, would be inappropriate from a risk assessment standpoint.

This was accounted for in the study by requiring that the laboratory report "TPHdiesel" in the samples as the sum of sum of vapor-phase, C5 to C12 (Summa canisters) or C5 to C18 (sorbent tubes) compounds minus BTEX and naphthalene. The fact that diesel vapors can be dominated by "gasoline-range" compounds can be confusing to non-chemists in the field who are requesting analysis of soil vapor samples from a laboratory. Both the terminology and laboratory methods for TPH in air and soil vapors need to be updated to make the nature of data reported more transparent. Future updates to HDOH guidance will simply recommend that TPH be reported as the sum of C5-C12 compounds for whole-air samples (e.g., summa canister samples and TO-15 lab methods) and C5-C18 for samples collected using sorbent materials (e.g., sorbent tubes and TO-17 lab methods). The same problem is likely to exist for reporting of TPHdiesel in water samples.

6.3 CARBON RANGE LABORATORY ANALYSIS OF SOIL GAS

A vapor-phase analytical procedure developed by the laboratory and referred to as "MA-APH" was used to quantify targeted carbon range concentrations in the samples. Although the procedure is proprietary, a summary of the basic aspects of the method provided by Air Toxics is included in Attachment 3. Chromatograph elution times for key carbon range markers using both Summa canister and sorbent tube samples are noted in Table 8 of the main report. The laboratory method is similar to the approach developed by the Massachusetts DEP for carbon range analysis of soil and water samples.

6.4 PHASE I SAMPLE COLLECTION AND ANALYSIS

6.4.1 STUDY SITES

Six sites were initially targeted for sample collection during Phase I of the study (see Table 7a):

- Hickam AFB Site VP26;
- Honolulu Harbor OU1C;
- Hickam AFB Site ST03;
- Fishing Village;
- Aloha Petroleum–School Street; and
- GASCO.

Each of the sites was known through past investigations to be heavily contaminated with a range of petroleum fuels. Soil vapor data were also available for most of the sites, including carbon range data at the Hickam Air Force Base sites. Vapor samples were also collected over open containers of gasoline and diesel fuel.

6.4.2 SOIL GAS SAMPLE COLLECTION

Soil gas samples were collected from targeted sites between May and August 2011 for Phase I of the study. The locations of vapor points used to collect samples at the study sites are noted in Figures 3-9. The soil vapor monitoring points were typically constructed of ¼ inch Teflon tubing with a wire mesh screen installed at the targeted subsurface horizon. Sample screen points were typically located within five to twenty feet of known, contaminated soil or groundwater. Surface completions of well points varied between the sites and even within a given site and ranged from flush-mounted traffic boxes with or without valves for vapor ports to temporary concrete plugs over well points with unions included for hookup to sample collection equipment (e.g., see Figures 10-11).

One sample was collected from each targeted monitoring point using a one-liter Summa canister. Summa canisters and flow meters were pre-ordered and provided by Air Toxics laboratory in Folsom, California. Flow meters were typically pre-set to 53.3 ml/minute (15 minute samples), although some samples collected in areas of known higher permeability soils were collected using flow rates of 125 ml/minute (approximately eight minute samples) and 200 ml/minute (five minute samples).

A PID was typically used to purge vapor monitoring points of at least three volumes of tubing volumes and until PID readings stabilized (flow rate 200 ml/minute; Figure 10). This was relatively easy to accomplish given the shallow depth to groundwater at most targeted sites (five to twenty feet bgs). Purging was accomplished by calculating the volume of the vapor point tubing and punning the PID an appropriate amount of time to remove at least three air volumes. In some cases additional purging was carried out until the PID reached a stable reading for total vapors present. In cases of tight formations, the PID would automatically switch off if an excess vacuum was applied, likewise indicating that vapor point had been adequately purged. The final Total VOC reading was recorded for each sample as was oxygen, although less consistently due to problems with the field meter. An electric pump was used by the Hickam AFB consultant to purge the vapor monitoring wells at Site ST03, where vapor wells were up to 500 feet deep (approximate depth to groundwater). A Tedlar bag sample was collected by the consultant after purging was completed and PID readings recorded.

The Summa sampling train was prepared by connecting the canister to the flow controller and attaching a six- to twelve-inch length of ¼ inch Teflon tubing to the top of the controller. A short length (typically <three inches) of flexible tubing (e.g., Tygon) was used to connect the Teflon tubing to the vapor monitoring point at well points. If the well point was completed with a union and Swage Lok then a small length of Teflon tubing was attached and a small length of flexible tubing was used to attached the to the sampling train and allow a point to pinch the monitoring point shut if needed (see Figure 11). Vapor monitoring points were fitted with valves at some sites that allowed the well point to be closed without the need to include a short length of flexible tubing.

Polyethylene and other flexible tubing (e.g., Tygon) are known to absorb VOCs during sample collection. The short lengths used to collect samples during the study are not anticipated to have significantly affected concentrations or ratios of targeted VOCs originally in soil vapors, especially given the elevated levels of petroleum vapors at the study sites. The need to minimize or even eliminate the use of potentially sorptive tubing will be discussed in upcoming updates to the HEER office Technical Guidance Manual.

Vapor samples were collected over open containers of gasoline and diesel fuel. Samples were collected by placing a short length of ¼” Teflon tubing from the flow controller adjacent to the top of the container and opening the valve on the canister a target vacuum of -5mm Hg was reached. This allowed more significant dilution of the vapors in comparison to a traditional, headspace test using baggies or a jar with a only a small opening. This was done in part to help ensure that the sorbent tube samples did not become saturated. Trace levels of petroleum in ambient air were also not anticipated to significantly affect overall ratios of targeted carbon range compounds and targeted individual VOCs (e.g., ambient air typically <1,000 µg/m^3 TPH and 1-5 µg/m^3 benzene).

6.4.3 *LEAK DETECTION*

Leak detection was carried out during Phase I of the study by covering the entire Summa canister sample train a large, plastic garbage bag and using this as a helium shroud (Figure 12). The shroud was fitted to the ground surface to the extent feasible and then filled with helium. (Note that "party grade" helium such as that used in this study has been reported to contain trace amounts of benzene and other petroleum compounds which could be released into the sample if a significant leak occurred, although not at concentrations anticipated to exceed soil gas action levels.) A helium concentration inside the shroud of 10-30% was targeted and measured base on the use of a field helium meter at some sites. A detection of helium in the Summa sample would reflect a leak somewhere along the sampling train.

This leak detection approach was carried out for all samples collected during Phase I of the study. Note that although the leakage of ambient air into a Summa canister would affect the reported concentrations of VOCs in the sample, it would not significantly affect the relative ratios of targeted carbon ranges, which was the primary objective of the study. Anticipated levels of TPH in the samples based on previous testing (e.g., >100,000 µg/m^3) were orders of magnitude above potential concentrations in outdoor air (typically <100 µg/m^3). A moderate leakage of the ambient air into the Summa canister (e.g., <10%) would not significantly alter these ratios.

After helium was released into the shroud the valve to the Summa canister was opened and the soil gas sample was collected. Additional helium was released into the shroud as needed to keep it reasonably inflated. In some cases a field meter was used by a consultant to monitor the level of helium in the shroud.

This approach worked adequately for some sample points but not for others. Fitting the bag shroud over the sampling train was awkward and inefficient in many cases, especially for points with flush-mounted traffic boxes where an adequately tight seal against the ground surface could not be obtained. Keeping the bag inflated and stable on windy days was also difficult. In one case the tubing came undone during sample collection at the juncture of the Teflon and flexible tubing but went unnoticed under the bag. A consultant brought a shroud made with a five-gallon, plastic bucket to one site as an alternative (Figure 13, also discussed in the HEER TGM) but the combined Summa canister and flow controller was too tall to fit under the bucket. As discussed below, an alternative leak detection method was used during Phase II of the study based on further discussions with consultants. A summary of this approach is provided in Attachment 4.

6.4.4 SAMPLE ANALYSIS

Samples were shipped to Air Toxics for analysis. The following analyses were carried out on each sample (primary analytes noted):

- TO-15 Massachusetts APH (GC/MS; targeted carbon ranges, BTEX and naphthalene);
- ASTM 1945M (C2-4 hydrocarbons, helium, CO2, methane);
- TO-15 (GC/MS; TPHg).

The concentration of TPHg (based on a gasoline standard) reported using Method TO-15 is based on the full range of C5-C24, vapor-phase compounds. Sample collection methods and analyses were slightly modified during phase II of the study, as summarized below. Data for C2-4 hydrocarbons, helium, CO2 and methane are included in Attachment 6 but not summarized in the main tables of the report.

6.5 PHASE II SAMPLE COLLECTION AND ANALYSIS

6.5.1 TARGETED SITES

Five sites were targeted for the collection of additional soil gas during Phase II of the study (see Figure 1 and Tables 7a&b):

- Hickam AFB Site VP26 (Site A);
- Honolulu Harbor OU1C (Site B);
- Hickam AFB Site SP43 (Site C);
- Hickam AFB Site ST03 (Site D); and
- Fishing Village (Site E).

Four of the six, Phase I sites were retained and a JP-4 and JP-8 release site at Hickam Air Force Base was added (Hickam AFB Site SP43/Site C). Samples were collected from the same vapor monitoring points used in Phase I of the study. An exception was well point B8 at the VP26 [HAFB-VP26-B08(21)]. This monitoring point was not resampled during Phase II of the study due to the similarity with the other four sample points at this site a need to reduce analytical costs. Vapor points used for Hickam AFB Site SP43 are noted in Figure 5. The Aloha Petroleum gas station was dropped due to a lack of significant petroleum vapors in any of the samples collected during Phase I of the study. The GASCO site (former manufactured gas plant) was not resampled since it is not typical of petroleum-release sites. A significant amount of soil gas data is available for this site in other investigation reports.

An alternative leak detection approach was used, however, as described below. Additional vapor samples were collected over open containers of gasoline, diesel fuel and JP-8 jet fuel. Samples were again collected by placing a ¼ inch Teflon tubing from the flow controller adjacent to the container lid and opening the valve on the canister a target vacuum of -5mm Hg was reached.

6.5.2 *SUMMA CANISTER SAMPLE COLLECTION AND LEAK DETECTION*

Vapor points were purged and field data recorded in the same manner as done during Phase I of the study. The Summa sample was collected immediately after purging. The sampling train was connected to the vapor points in the same manner as described before.

An alternative and ultimately much more efficient leak detection approach was used during Phase II of the study. This included the use of a small (3.25 quart), see-through Tuperware plastic bowl as a helium shroud (Figure 14). The following steps were followed for each of the samples collected (see also Attachment 4):

1) Thread Teflon tubing from flow controller through the Tupperware shroud with precut holes (see photos in Attachment 4);
2) Connect the Summa sampling train to the well monitoring point;
3) Close well point valve or pinch flexible connector tubing shut;
4) Carry out a "shut-in" test by opening Summa canister valve and monitoring vacuum gauge on flow controller to check Summa canister and flow controller connections (main locations of potential leaks; no significant leaks assumed if vacuum holds for sixty seconds);
5) Recheck Summa canister and flow controller connections if a leak is detected and repeat vacuum-hold test until the vacuum gage indicates tight sampling train connections;
6) Open monitoring point valve (or unpinch tubing) and place Tupperware shroud over well point, fill with helium;
7) Open Summa canister valve and collect sample (e.g., until vacuum gage reads 3-5 mmHg);
8) Reclosed vapor monitoring point valve or pinch flexible tubing closed to prevent ambient air from being drawn into the well point;
9) Disconnect Summa sampling train from well point.

If a drop in the vacuum pressure was identified during the shut-in test then the Summa canister valve was immediately closed and the connections checked and tightened as needed. If the vacuum on the Summa canister dropped below 25 mm Hg then the canister would have been replaced, although this was not necessary for any of the samples collected. The sorbent tube sampling train was connected to the well point immediately following collection of the Summa canister sample and a second sample was collected as described in following section.

This approach has an advantage over a large shroud in its simplicity and the immediate identification of a significant leak at the canister and flow controller connections. Only one leak was identified in the field and was due to a faulty connection between the Summa canister and the flow controller. A leak around well point itself was indicated if helium was identified in the sample by the laboratory. A helium meter could also have been used in the field to monitor for leaks at the well point during sample collect but was not available (see figures in Attachment 4).

Addition notes on leak detection methods for soil gas samples will be included in future updates of the HEER office Technical Guidance Manual (HDOH 2009).

In Step 8, the monitoring point valve or the flexible tubing connected pinched shut immediately after collection of the Summa canister sample and before the canister connection was undone (see Attachment 4). This prevented the potential backflow of ambient air into the well tubing due to a residual vacuum in the soil where the sample was extracted.

6.5.3 SORBENT TUBE SAMPLE COLLECTION

Sorbent Tube Preparation

A sorbent tube sample was collected from each vapor point in addition to a Summa canister sample (see Figure 15). Existing soil gas data for the selected study sites were discussed with Air Toxics laboratory staff prior to the initiation of field work. This information allowed the laboratory to identify the most appropriate sorbent materials for the site in order to adequately capture targeted compounds. As discussed below, this also helped to establish the maximum volume of vapors that could be drawn without risk of saturating the tubes. This was particularly important for petroleum-contaminated sites, given the wide carbon range and sorptive properties of compounds in the vapors anticipated to be present.

Sorbent tube methods for the collection of vapor-phase samples were originally developed for indoor air and relatively low concentrations of volatile, organic compounds (e.g., 10s or 100s $\mu g/m^3$). In the case of the TO-17 method proposed for the study, for example, a single tube pack with a series of three, increasingly sorptive materials is used to capture VOCs in air that is pulled though the tube. The concentration of the VOC in the air sample is calculated as the mass of the compound sorbed divided by the volume of air pulled through the tube.

The collection of high-concentration, soil gas samples (e.g., 1,000s to 1,000,000s $\mu g/m^3$ total VOCs) posed two inter-related field and laboratory issues – potential saturation of the sorbent material and potential breakthrough of vapors due to saturation and/or an excessively fast sample draw rate. Methods to address these potential concerns were developed and incorporated into field sample collection and laboratory analysis procedures. As discussed in the summary section of this report, the procedures implemented in general worked well to minimize field laboratory error and provide TO-17 data that were reasonably comparable to concurrent Summa canister data for the same vapor point.

TO-17 Soil Gas Sample Volume

The maximum volume of soil gas that could be drawn through the sorbent tubes without saturating the sorbent material was a critical issue for the study. Saturation of the sorbent material and preferential breakthrough of light or heavy compounds could introduce error into estimates of carbon range and individual compound ratios in the vapors. Sorbent materials and packing arrangements typically used for low-concentration, air samples where one-liter or larger samples are typically drawn would be quickly overwhelmed and become saturated if a similar volume of soil gas with high-concentrations of VOCs were drawn through the tubes.

The laboratory initially suggested a maximum sample draw volume of only five to ten milliliters based on the anticipated, very high concentrations of TPH and other VOCs in the soil gas. While ideal from a laboratory perspective, this was considered to be too small to be representative of field conditions (although the same argument might be made for one- and even six-liter samples and the topic of a potential followup study). Perhaps more importantly, such a small volume is highly prone to field error if the vapor point tubing is not adequately purged of ambient air. The ¼ inch tubing used to collect the samples contained approximately 15 milliliters of air volume per meter length. The depth of sample collection points ranged from one to two meters at the Hickam AFB SP43 site and the Honolulu Harbor Fishing Village and OU1C sites, five to ten meters at the Hickam AFB VP26 site and over one-hundred meters at the Hickam AFB ST03 site. A small residual vacuum at a well point after collection of the Summa sample could potentially draw in an amount of ambient air that exceeded the subsequent draw volume of the sorbent tube sample and result in what in essence was simply a sample of ambient air rather than subsurface vapors.

After a further review of optimal sorbent packing materials and arrangements, the laboratory was able to prepare TO-17 sorbent tubes that could be used to collect high-concentration vapor samples with no anticipated breakthrough provided that no more than 50 milliliters of soil gas were drawn through the tubes. While still not ideal with respect to sample volume and representativeness, the concurrent collection of a Summa canister sample at each point would provide a means to check sorbent tube sample data for potential field error. As mentioned above and described in more detail below, field sample collection procedures were also designed to minimize the potential for ambient air to be drawn into sample tubing prior to collection of a sorbent tube sample.

TO-17 Soil Gas Sample Draw Rate

Although the sorbent material and sample draw rate were believed to have been optimized, concern was still expressed by some consultants in regards to potential breakthrough of VOCs due to an excessively fast sample draw rate. Discussions with labs suggested that breakthrough associated with the speed at which the soil gas was drawn through the sorbent tube draw rate was unlikely if the draw rate was kept below 200 ml/minute. As discussed below, a draw rate of approximately 100 ml/minute was adhered to in the field through the gradual collection of a 50ml sample over a period of thirty seconds. As also discussed below, potential breakthrough was directly evaluated by adding a second, downstream sorbent tube to the sampling train (Tube B). This tube was analyzed for the same list of target compounds separately from the upstream tube to confirm that significant breakthrough (e.g., >10% total TPH mass) had not occurred.

Sample Collection

Sorbent tubes soil gas samples were collected using a 60ml syringe with a three-way valve (supplied by Air Toxics). The sampling train is shown in Figure 15. Two sorbent tubes, rather than the traditional single tube, were used and connected using a union joint. The first tube (Tube A, closest to well point) was intended to fully capture petroleum vapors in the sample drawn from a well point. The second tube (Tube B) was added to the sampling train and tested in order to verify that breakthrough did not occur, since this would result in an underestimation of vapor concentrations using just the first tube and potentially distorting the ratios of carbon ranges and individual compounds in the vapor. The downstream tube is connected to the well point with a short length of flexible tubing in the same manner as done for the Summa canister sampling train.

A simple leak detection test of the sorbent tube sampling train was carried out by closing the well point valve or pinching the flexible connector tubing shut. The handle of the syringe was then gently pulled back and held ten to fifteen seconds to see if air was pulled into the syringe (making sure the three-way valve was set to allow flow from the vapor point). If not, then the syringe connection to the sorbent tubes and the sorbent tube connection to the well point were assumed to be tight. The well point itself was not tested for leaks, since this had already been done during collection of the Summa canister sample. This could have been carried out using the Tupperware shroud noted above if a Summa sample had not been initially collected, however. (Note that there would be some concern about the sample representativeness given the small sorbent tube draw volume). Obtaining a tight connection of the sorbent sample sampling train to the vapor point was relatively easy and no leaks were detected in the field using this approach. As was the case for the Summa canister sampling train, this approach has an advantage over a large shroud in its simplicity and the immediate identification of a significant leak.

6.5.4 SAMPLE ANALYSIS

Samples were shipped to Air Toxics for analysis. The following analyses were carried out on each sample (primary analytes noted):

Summa Canister Samples:

- TO-15 Massachusetts APH (GC/MS; targeted carbon ranges, BTEX and naphthalene or “BTEXN,” TPHg);
- ASTM 1945M (C2-4 hydrocarbons, helium, CO2, methane);
- TO-15 (GC/MS; TPHg);
- TO-3 (GC/FID);

Sorbent Tube Samples:

- TO-17 Massachusetts APH (GC/MS; targeted carbon ranges, BTEX and naphthalene, 1&2-methylnaphthalenes, TPHg, TPHd).

The concentration of TPHg (based on a gasoline standard) reported for Summa canister samples is based on the full range of C5-C24, vapor-phase compounds for Methods TO-3, TO-15 and TO-17. The concentration of TPHd reported for sorbent tube samples using Method TO-17 only included C10-C24 compounds, however. The laboratory stated that this is the range generally requested by clients for TPH vapors at diesel and other middle distillate sites. As discussed in Section 8, this proved problematic given the high proportion of C5-C8 aliphatics in soil gas at the middle distillate sites evaluated in this study. Data for C2-4 hydrocarbons, helium, CO2 and methane are again included in Attachment 6 but not summarized in the main tables of the report.

The lab was subsequently requested to report both 1- and 2-methylnaphthalenes for the Phase II sorbent tube samples. Methylnaphthalenes were not identified above method reporting limits in most of the samples and were therefore not carried through in the detailed review of vapor study data (see TO-17 data in Attachment 6).

7 RESULTS AND ANALYSIS

Results of the study are presented in terms of the questions and topics posed in the introduction:

- TPH versus BTEXN Composition of Soil Gas;
- TPH:Benzene Ratios at Other Sites;
- TPH Carbon Range Chemistry and Weighted Inhalation Toxicity;
- Results of Leak Tests; and
- Evaluation of Sorbent Tube Breakthrough.

A discussion of the relative vapor intrusion risk posed by TPH versus benzene and other individual compounds at the study sites is presented in Section 7.

Sample data are summarized in Tables 9-21. A comparison of the TPH versus BTEXN makeup of the vapor samples and initial implications for vapor intrusion risk drivers is provided in the next section. This is followed by a summary and discussion of the carbon range composition of the TPH and a more detailed assessment of TPH versus benzene or naphthalene as the risk driver at the study sites. Chromatograms for samples from key sites were obtained as part of the study and are presented in Attachment 5. Laboratory reports for the samples collected during the study are provided in Attachment 6.

7.1 TPH VERSUS BTEXN COMPOSITION OF SOIL GAS

A summary of TPH and BTEXN Summa canister data for vapors collected over fresh fuels and soil gas samples collected at targeted study sites is provided in Tables 9, 10 and 11. These data help to answer two of the key questions posed at the beginning of the study:

- What is the typical proportion of TPH in petroleum vapors in comparison to targeted, individual volatile organic compounds (VOCs) such as benzene and naphthalene?

And, at least at a initial screening level,

- Is the proportion of TPH sufficiently large in some cases for TPH to drive vapor intrusion over benzene, naphthalene and other targeted, individual VOCs?

Detailed carbon range data are required to full answer the second question. As discussed in Section 3, however, an initial review of the ratio of TPH to individual, targeted compounds such as benzene and naphthalene can shed some light on the potential for the TPH component of soil vapors to drive vapor intrusion risk.

Data from Summa canister samples are used to initially address these two questions. Concurrent sorbent tube data for co-located samples are discussed below in the summary of TPH carbon range data. As discussed in Section 5, reliance on Summa data risks under reporting the true concentration of TPH in the samples, since aromatic compounds >C10 and aliphatic compounds

>C12 cannot be adequately extracted from the canisters. The degree that this affected the Summa canister samples is also discussed in the below summary carbon range data.

Table 9 presents a summary of TPH versus BTEXN vapor data for the Phase I and Phase II samples. Tables 10 and 11 present the relative proportion of TPH versus BTEXN in individual samples and for each study site as a whole. It is clear from the data that non-specific, TPH compounds dominate the vapors. Vapors collected over containers of fresh fuels were characterized by 86-96% TPH and only 4-14% total BTEXN (dominated by TEX). The BTEXN percentages presented in Table 11 reflect the average of all samples collected at the site during the two phases of the study. Note that use of one-half the MRL to estimated total BTEXN does not significantly affect the observation that total BTEXN in soil vapors on average makes up a very small percentage of the total petroleum vapors present.

Soil gas samples collected from study sites show an even greater dominance of TPH, with less than 1% of the total vapors generally attributable to BTEXN. Although the data are limited, the reduction of aromatic BTEXN compounds in subsurface vapors at the study sites could reflect a preferential biodegradation of aromatic compounds in comparison to aliphatic compounds that dominate the TPH fraction of the vapors. This assumes that the BTEXN component of the fuels released at the site were similar to the fresh fuels included in this study. This is of course not known, and an apparent reduction of total BTEXN in vapors over time is of course very speculative. Note that vapor-phase, aliphatic compounds are also highly biodegradable in the subsurface, as illustrated by the rapid attenuation of TPH in general away from source areas at petroleum-contaminated sites. Aromatics appear to be even more efficiently removed from soil vapors, however. Additional evaluation of this issue is warranted in future studies.

Total BTEXN in the range of 1-4% for samples collecte4d from Hickam AFB Site ST03 in October 2011 (Site D) could indicate an undocumented release of fresher fuel, although samples collected in July 2011 were 1% or less BTEXN (see Tables 10 and 11). Bioventing pilot tests had been carried out at the at the site several months previous to the collection of samples for this study but a sufficient amount of time was allowed for re-equilibration of subsurface vapors, based on discussions with the Hickam AFB consultant who was also collecting samples at the site when the HEER office samples were collected. It is possible that this was stripping fresh, BTEX-enriched vapors from free product. Alternatively, this could reflect differences in weathering and biodegradation in different areas of the plume. This issue was not evaluated in detail, but the data highlight the likely spatial and temporal heterogeneity of petroleum vapors in the subsurface and potential problems associated with one-time sampling events.

A comparison of TPH versus benzene and naphthalene data for key sites based on Summa canister samples is presented in Table 12. A summary of average vapor ratios for fresh fuels and soil gas samples collected at the study sites is provided in Tables 13a and 13b. Naphthalene was not detected above laboratory reporting limits in the majority of the samples outside of samples over containers of fresh JP-8 and diesel. This suggests that naphthalene has limited use as a tool to screen for potential vapor intrusion hazards at petroleum-contaminated sites. For the sites included in this study, TPH and Benzene data are far more useful. Note that analytical detection limits for naphthalene were typically higher than detection limits for other individual VOCs by a factor of two to ten. This does not affect the overall conclusions of the study.

A significant variability between samples collected from different sites and even between samples collected from the same sites is apparent in the date (see Table 12 and 13). The ratio of TPH to benzene for vapors collected over fresh fuels is relatively low, ranging between approximately 50:1 and 300:1 and not that significantly different between gasoline, JP-8 and diesel fuel. This reflects a relatively high proportion of benzene in the vapors. Based on comparison to the TPH:Benzene critical ratios in Table 6a, this initially suggests that either TPH or benzene could drive vapor intrusion risks for vapors from the fresh fuels sampled. Whether TPH or benzene ultimately drives risk depend on the carbon range-weighted toxicity of the TPH and the target risk applied to benzene. This is discussed below and reviewed in more detail in Section 7.

Note the even lower ratio of TPH to benzene in both the gasoline and diesel exhaust samples (see Tables 10 and 12, 4:4 to 7:1). This seems to reflect a much more significantly more efficient combustion of aliphatic compounds in comparison to aromatic compounds, as further discussed in the section of this report that discusses carbon range data. Although data are obviously limited, comparison to the TPH:Benzene ratios in Table 6a suggests that benzene will almost certainly drive inhalation risk for fresh auto exhaust vapors. Naphthalene was again not detected.

Soil gas samples collected from the Hickam AFB VP26 AVGAS site (Site A) are the most gasoline-like within the study group, in comparison with vapors collected over fresh samples of gasoline. The TPH:Benzene ratio at two of the well points was consistently below 1,000:1, indicating moderately high proportion of benzene (although not as high as observed for fresh fuels). Reported levels of TPH approached 100,000,000 $\mu g/m^3$ in some samples (see Table 9). The ratio of TPH:Benzene in the other two well points was consistently over 1,000:1 and up to 5,000:1, indicating a reduced proportion of benzene. This may reflect differences in degradation and/or the presence of JP-4 and middle distillate fuel in these areas. (JP-4 is a mix of a gasoline and kerosene mixture.) Based on comparison to Table 6a, this suggests that either TPH or benzene could drive vapor intrusion risks given the average TPH:Benzene ratio of approximately 1,500:1 (see Table 13a). In areas where the TPH:Benzene ration exceeds the critical ratio of 2,032:1, however, TPH will *always* drive vapor intrusion risk over benzene due to its overwhelming proportion in the vapors.

The average ratio of TPH to benzene was significantly higher in soil gas samples collected from the four other study sites (Honolulu Harbor Site OU1C/Site B; Hickam AFB Site SP43/Site C; Hickam AFB Site ST03/Site D, Honolulu Harbor Fishing Village/Site E; see Tables 9 and 13a). This suggests a reduced proportion of benzene in the original fuels released and/or a preferential reduction of benzene in vapors as the release aged. (Note that from a vapor intrusion standpoint, the exact cause of the low benzene component of the vapors, e.g., original fuel composition and/or biodegradation, is not relevant.) The ratio of TPH to benzene in samples collected at the Honolulu Harbor OU1C site (Site B) was between 3,000:1 and 5,000:1 when benzene was detectable within the overwhelming mass of TPH compounds, with an average of approximately 4,000:1. As discussed below, the TPH carbon range signature for the samples suggests a dominance of gasoline-related fuels (i.e., TPH dominated by C5-C8 aliphatics). Benzene was only detected in two of the five soil gas samples collected at Hickam AFB Site SP43 (Site C), with TPH:Benzene ratios in both cases well over 10,000:1 and reported concentrations of TPH approaching 40,000,000 µg/m^3. The ratio of TPH to benzene exceeds 18,000:1 in samples collected from Hickam AFB Site SP43 (Site C) and the Fishing Village site at Honolulu Harbor (Site D). Both of these sites are suspected to include a large component of middle distillate fuels, including JP-8 and/or diesel fuel. The ratio of TPH:Benzene in the samples collected from all four of these sites imply that TPH would drive vapor intrusion risk over benzene even if a conservative, 10^{-6} cancer risk is applied to benzene (see Table 13a).

Moderate levels of naphthalene in vapors collected over fresh fuels suggest that either TPH or naphthalene could drive inhalation risk, depending on the carbon range chemistry and toxicity of the TPH component of the vapors (see Table 9). Naphthalene was not reported in soil gas samples collected at Hickam AFB Site VP26 (Site A; JP4 /AVGAS release), Honolulu Harbor OU1C (Site B; mixed fuels) or Hickam AFB Site ST03 (Site D; JP4/AVGAS). Naphthalene was detected in two of the five soil gas samples collected at Hickam Site SP43 (Site C; JP-8 +/- SP-4), with an average TPH:Naphthalene ratio of approximately 6,300:1. Although this suggests that either TPH or naphthalene could hypothetically drive vapor intrusion risk, the ratio is approach the critical point of 8,800:1 where TPH will drive risks over naphthalene even if a target risk of 10^{-6} is used for the latter (see also Table 13b). Overall, the lack of detections or analytical data for naphthalene appears to limit its usefulness in vapor intrusion studies.

7.2 TPH:BENZENE RATIOS AT OTHER SITES

Ratios of TPH to benzene from soil gas samples collected by consultants at other sites in Hawaiʻi are noted in Table 14. (Again, the data are presented for example purposes only and are not intended to be representative of overall site conditions of the potential for actual vapor intrusion threats.) The ratios are similar to those calculated as part of this study. Releases primarily associated with gasolines are characterized by TPH:Benzene ratios between 100:1 and 1,000:1 (e.g., samples collected from Hickam AFB Site SS156-E). Based on the data obtained in this study, benzene would be an adequate indicator of vapor intrusion risk provided that a target risk of 10^{-6} was adhered to. Data are highly variable, however. This is also highlighted by data from other sites reviewed during this study (see Table 14). Previous soil gas data from the Aloha Petroleum gas station site (assumed gasoline-only release) included in this study indicated TPH:Benzene ratios in soil gas that ranged from approximately 200:1 to 13,000:1 (see reference in Table 7a). In the latter case TPH would clearly drive vapor intrusion risk over benzene.

TPH:Benzene ratios for soil gas samples collected at the ConocoPhillips fuel terminal site are also highly variable, ranging from a low of 42:1 to a high of over 7,000:1. This site was known to be heavily contaminated with gasoline. In some areas of the site benzene almost certainly drives vapor intrusion risk; in other areas vapor intrusion risk is clearly driven by TPH. This could indicate an unidentified mixture of gasoline and diesel releases at the sites. Both benzene and TPH soil gas data clearly identified vapor intrusion risks, however.

TPH clearly drives vapor intrusion risk at most sites dominated by middle distillates release, with average TPH:Benzene ratios well over 10,000 (see Table 14; e.g., Hickam AFB Sites SS156-J and CG110). This includes a soil gas sample from a localized area of stoddard solvent contamination at a dry cleaner (Hakuyosha dry cleaner).

Apparent exceptions include the Challenger Loop diesel/JP-8 site. In this case TPH in soil gas is well below the Fall 2011 HDOH residential vapor intrusion action level of 130,000 µg/m3 but naphthalene is marginally above the vapor intrusion action level of 72 µg/m^3 at some well points. This assumes, however, that the TPH soil gas data are accurate. As discussed in the next section, laboratories typically report only C10 and higher compounds for TPH in soil gas samples collected at diesel sites, even though data collected during this study suggest that C5-C8 aliphatics could make up a substantial component of the total TPH vapors. Naphthalene also appears to play a role in vapor intrusion risk along with benzene at the Hickam AFB SS156-E gasoline site, where both compounds marginally exceed vapor intrusion action levels but the reported level of TPH is very low. Again, however, historical under reporting of TPH in soil gas samples by the laboratory at middle distillate-release sites is likely.

Each of these examples highlights the importance of considering TPH, benzene and in some cases even naphthalene in soil gas for an accurate evaluation of vapor intrusion hazards at sites with petroleum-contaminated soil and groundwater. Selecting the appropriate lab method for TPH is also important, as discussed in Section 8.

7.3 TPH CARBON RANGE CHEMISTRY AND WEIGHTED INHALATION TOXICITY

An evaluation of the TPH versus BTEXN component of petroleum vapors for fresh fuels and aged release sites demonstrated the dominance of TPH in comparison to targeted, individual compounds. A better understanding of the carbon range chemistry and toxicity of the TPH is required to determine if TPH indeed drives vapor intrusion risk over benzene and other traditionally targeted, individual compounds. This was evaluated under the second set of questions posed at the beginning of the study:

- What is the aliphatic and aromatic, carbon range makeup of the TPH?
- Does the carbon range makeup vary with different fuel types or with respect to fresh versus weathered fuels?

- Is the proportion of volatile compounds greater than C10 (aromatics) or C12 (aliphatics) significant enough to warrant the use of sorbent tube (vs Summa canister) methods for the collection and analysis of soil gas samples?
- What is the weighted toxicity of TPH based on the carbon range makeup, after subtracting separately targeted compounds such as benzene and naphthalene?
- Is an update to the current HDOH soil gas action levels for TPH warranted?

TPH carbon range data were obtained for all vapor samples in order to help answer these questions, based on both Summa canister and sorbent tube sample collection techniques.

A summary of the reported concentrations of carbon ranges in samples collected in Summa canisters is presented in Table 15. The relative carbon range percentage in samples is noted in Table 16. A summary of the average carbon range makeup of TPH in the samples is presented in Table 17a. The relative contribution of individual carbon ranges to the total TPH noncancer hazard is summarized in Table 17b. The relative contribution to noncancer hazard for each carbon range was calculated as (Summa data and target carbon ranges):

$$= \frac{\frac{(Fraction\ Carbon\ Range)}{Carbon\ Range\ RfC}}{\left[\frac{(Fraction\ C5\ to\ C8\ Aliphatics)}{C5\ to\ C8\ Aliphatics\ RfC} + \frac{(Fraction\ C9\ to\ C18\ Aliphatics)}{C9\ to\ C18\ Aliphatics\ RfC} + \frac{(Fraction\ C9\ to\ C16\ Aromatics)}{C9\ to\ C16\ Aromatics\ RfC}\right]}$$

Tables 18 through 20 present similar carbon range data for sorbent tube samples collected immediately after the Summa canister samples during Phase II of the study. Example gas chromatograms for samples collected from each site and pie charts that depict the average TPH carbon range makeup of soil gas are included in Figures 16 through 31. A full set of chromatograms for Summa canister samples and sorbent tube samples is included in Attachment 5. Laboratory reports for carbon range data are provided in Attachment 6.

In general there is good agreement between Summa canister and sorbent tube carbon range data. Reference Concentrations (RfCs) for inhalation toxicity were calculated for each sample and the study sites as a whole, based on the weighted, carbon range makeup of the TPH vapors (see Section 3). The weighted RfCs do not consider the BTEXN component of vapors, which are evaluated separately for potential vapor intrusion risks. Estimations of weighted TPH RfCs and related decisions regarding potential vapor intrusion hazards at a site would not be significantly different using either set of data. Most interesting, and perhaps surprising given limited data to suggest the contrary, was the general lack of aromatic compounds >C10 and in particular the lack of >C12 aliphatic compounds both in vapors over fresh fuels and soil gas from aged, middle distillate release sites (see Tables 17a and 20a). This is clearly evident in gas chromatographs for sorbent tube samples (see also Attachment 5).

TPH vapors in all of the samples are dominated by aliphatic compounds (see Tables 15 and 18). Vapors collected over containers of fresh gasoline contained only traces of C9-C12+ aliphatics and C9-C10+ aromatics (98-99% C5-C8 aliphatics). Vapors collected over fresh diesel were also dominated by C5-C8 aliphatics in two of three samples, with moderate proportions of C9-C12+ aliphatics (14 and 21% for Summa canister samples and 35% for a single sorbent tube sample). C10-C11+ aromatics were present in only trace amounts in the gasoline samples (<1% in the Summa canister samples and 2% in the sorbent tube samples). C10-C11+ aromatics were slightly higher in vapors collected over fresh JP-8 and diesel (2-5%). Weighted inhalation TPH RfCs follow a similar trend, with RfCs and associated action levels for gasoline vapors similar to the RfC for C5-C8 aliphatics (e.g., 600 $\mu g/m^3$). Inhalation toxicity RfCs for middle distillate vapors are closer to the RfC for C9-C12 aliphatics of 100 $\mu g/m^3$ and therefore more “toxic” than TPH vapors emitted from gasolines. This is an important observation. Disregarding the BTEXN component, TPH vapors associate with diesel and other middle distillate fuels will necessarily exhibit a higher toxicity than vapors from gasoline due to a higher proportion of C9-C12 aliphatics. With respect to actual vapor intrusion hazards, however, this will be partially offset by a comparative reduction in the overall mass and concentration of vapor emitted due to the lower volatility of middle distillate fuels.

A diesel vapor sample (Diesel #2) collected in a Summa canister was reported to contain 9.7% C9-C11 aromatics. Unlike the other two diesel vapor samples, this sample was also dominated by C9-C12 aliphatics (57%). This was significantly higher than the other two diesel vapor samples (maximum 35% C9-12+ aliphatics). The reason for this discrepancy is unknown but could reflect a different source of the fuel or even a difference in the temperature of the fuels when the samples were collected (not recorded but estimated to range between 70 and 85 degrees Fahrenheit).

The carbon range data demonstrates a progressive transition between the study sites from vapors dominated by C5-C8 aliphatics (e.g., Hickam AFB Site VP26/Site A, associated with gasoline) to vapors dominated by C9-C12+ aliphatics (e.g., Honolulu Harbor Fishing Village/Site E; associated with middle distillates). This is identifiable in the gas chromatograms by a progressive shift of the detected mass of petroleum compounds to the right (i.e., towards longer elution times; see figures for each site and chromatograms in Attachment 5). Soil gas samples collected from the Hickam AFB VP26 site (Site A) are dominated by C5-C8 aliphatics (96-98%) with only minor amounts of C9+ aliphatics and C10+ aromatics. This agrees with the known release of AVGAS gasoline fuels at the site. Samples from the Honolulu Harbor OU1C site (Site B) were also dominated by C5-C8 aliphatics (approximately 90%) but show a small but distinct signature of C9-C12 aliphatic compounds in soil gas for both Summa and sorbent tube samples (7-9%). This is presumed to be related to co-located releases of gasolines and middle distillate fuels at the site. Weighted TPH RfCs for these two sites are in the range of 400 to 500 $\mu g/m^3$, however, and reflective of the less toxic makeup of gasoline-range aliphatics in comparison to middle distillate vapors. Indoor air and ultimately soil gas TPH action levels calculated for these sites would also approach action levels for C5-C8 aliphatics (see Table 4).

Soil gas samples collected at the Hickam AFB SP43 site (Site C) exhibit a distinct, TPH signature for the presence of middle distillate fuels. As noted in Tables 17b and 20b, moderate levels of C9-C12 aliphatic in the samples contributed to a relatively low, weighted TPH RfC and associated indoor air and soil gas action levels (e.g., average, weighted TPH RfC 251 µg/m^3 based on Summa canister data). An even lower TPH RfC was calculated for soil gas samples from Hickam AFB Site ST03 (Site C) due to an average TPH composition of over 30% C9-C12 aliphatic compounds (average, weighted TPH RfC 211 µg/m^3). This seems to confirm the suspected release of JP-4 jet fuel due to a pipeline break in the mid 1970s.

The Fishing Village site (Site D) is located in the same general vicinity of the Honolulu Harbor as site OU1C. The TPH in samples collected from this site was distinctly dominated by heavier, C9 to C12 aliphatics related to a separate release of diesel fuel and possible JP-8 jet fuel (see Tables 15 and 18). A weighted RfC of 127 µg/m3 was calculated for the site based on the average carbon range makeup of TPH vapors measured in Summa canister samples (see Table 17a). A corresponding, weighted TPH RfC of 161 µg/m^3 was calculated based on sorbent tube sample data collected at the same time as the second round of Summa canister samples. These were the lowest (i.e., most stringent) TPH RfCs calculated for the samples collected during the study.

7.4 RESULTS OF LEAK TESTS

A significant leak was positively identified for only one sample, HAFB ST03 B58 (422), collected during the first phase of the study and was identified in the field. The leak test for this sample was carried out using a helium-filled garbage bag that covered the entire sampling train. The tubing to the vapor monitoring point was inadvertently pulled apart during a check of the Summa canister as the sample was being collected. A concentration of 19% helium was reported for the sample by the laboratory, similar to the target concentration for the shroud based on a field helium meter. Petroleum vapor concentrations in the sample were, however, high enough to permit calculation of the relative proportions of targeted aliphatic and aromatic carbon range fractions and ratios of TPH to benzene and other individual aromatic compounds (e.g., sum of carbon range fractions = 80,200 µg/m^3).

Sorbent tube samples were collected immediately after Summa canister samples at each well point during Phase II of the study. A simple leak test was carried out for sorbent tube sampling trains prior to sample collection by connecting the sampling train to the well point, pinching the well point tubing closed or closing the well point valve and attempting to draw a sample into the syringe by pulling on the handle (see Section 5 and Figure 15). All sampling trains appeared to be tight in the field.

The sorbent tube data agreed reasonably well with data for Summa canister samples that were collected immediately prior to the sorbent tube samples. Nonetheless, the dramatic difference between Summa TPH data and sorbent tube TPH data for sample HAFB-SP43-VMP17 suggests that ambient air was drawn into the well point prior to collection of the latter sample. In this sample, TPH calculated as the sum of the carbon ranges was 6,530,000 µg/m^3 for Summa canister sample but only 12,210 µg/m^3 for the sorbent tube data. This suggests that ambient air was drawn into the sorbent tube sampling train before or during sample collection. Even so, and as discussed below, the relative percentage of carbon range fractions reported for the sample agreed very well with the relative proportions of fraction calculated for the Summa canister sample.

7.5 EVALUATION OF SORBENT TUBE BREAKTHROUGH

A summary of data for paired sorbent tubes connected in series to evaluate potential breakthrough is presented in Table 21 (see also Figure 15). Tube A represents the tube closest to the vapor sampling point. Tube B represents the tube placed between Tube A and the sampling syringe in order to check for breakthrough from the first tube. The percent breakthrough noted in the table represents the concentration of TPH reported in Tube B divided by the sum of the TPH reported for both Tubes A and B. The summary assumes that all TPH reported in Tube B resulted from breakthrough in Tube A, rather than contamination of the original packing material or to exposure to TPH in ambient air during preparation of the TO-17 sampling train.

No breakthrough was identified in nineteen of the twenty-four sorbent tube samples collected (see Table 21; i.e., TPH compounds not detected in the downstream Tube B). Insignificant breakthrough, defined as <10% of the total TPH in Tube B for the purpose of this study (also referenced in HEER office guidance; HDOH 2011), was indentified for three of the high-concentration samples (JP-8 vapor sample and soil gas samples HAFB-VP26-B05(18)-HDOH, HH-OU1C-MW22R and HAFB-ST03-B58 (347)). The only significant, apparent breakthrough occurred in a single, relatively low-concentration soil gas sample (and FV-GP-01-HDOH#2; 41% of total TPH in Tube B). This is perplexing, given the low concentration of TPH at these monitoring points in comparison to other samples (low TPH concentration confirmed by concurrent Summa canister data). Concentrations of toluene, xylenes and naphthalene reported in Tube B were also similar to concentrations reported in Tube A. This suggests that the tubes may not have been lined up correctly during sample collection (arrow on tube must point to sample collection device) or that the tubes were not packed properly at the laboratory. With this one exception, breakthrough was not a significant problem for even very high-concentration soil gas samples.

8 TPH VERSUS INDIVIDUAL VOCS AS VAPOR INTRUSION RISK DRIVERS

The carbon range makeup and toxicity of TPH in vapors over fresh fuels and in soil gas samples collected at the study sites allows for a more detailed evaluation of TPH as a potential risk driver over benzene and individual, targeted compounds and sheds light on the final and ultimate question posed in the study:

- "Do the results of the study indicate that there are conditions where risk-based decision making for potential vapor intrusion concerns would be based on or driven by the noncancer TPH hazard rather than the cancer risk and/or noncancer hazard ("risk") posed by individual compounds?"

Soil gas data collected during the study highlighted benzene over naphthalene (rarely detected) as the most important challenger to TPH as a risk driver. The above question can be restated as:

- "Will the noncancer, vapor intrusion risk posed by the TPH component of soil gas still exceed a target Hazard Quotient of 1.0 when the benzene meets a target cancer risk level?"

Based on the results of this study the answer to both questions can undoubtedly be "Yes" under common site conditions. The noncancer risk or "Hazard Quotient" posed by TPH vapors when the concentration of benzene in indoor air or soil gas meets a specified, target cancer risk can be calculated as follows:

$$TPH\ noncancer\ HQ = \frac{\mathrm{TPH}(_{\mathrm{equivalent\ concentration}})}{\mathrm{TPH\ Action\ Level}}$$

where the term "$\mathrm{TPH}(_{\mathrm{equivalent\ concentration}})$" is the equivalent, vapor-phase concentration of TPH at a specified concentration of benzene (either indoor air or soil gas). This is calculated based on the site-specific (or sample-specific) ratio of TPH to Benzene multiplied by the target benzene action level for the same media:

$$\mathrm{TPH}(_{\mathrm{equivalent\ conentration}}) = \mathrm{Site\ Specific\ TPH{:}\ Benzene\ Ratio} \times \mathrm{Target\ Benzene\ Concentration.}$$

A noncancer Hazard Quotient greater than 1.0 suggests that TPH will drive vapor intrusion risk over benzene. This type of evaluation was carried out for each of the study sites.

Tables 22 and 23 illustrate the noncancer risk (Hazard Quotient) posed by TPH in vapors from fresh fuels and soil gas samples collected from at study sites in comparison to benzene at different target cancer risks. Table 22 reflects the carbon range chemistry and associated TPH toxicity based on Summa canister samples. Table 23 reflects carbon range data and TPH toxicity based on the sorbent tube samples. **As stated earlier, the soil gas data obtained during the study are not intended or assumed to be representative of overall conditions at the sites where the samples were collected.** The samples were intentionally collected the most heavily impacted areas of the sites and in areas where releases of middle distillate fuels were suspected. Actual vapor intrusion impacts to buildings have not been identified at any of the sites included in the study.

As can be in the tables, the Summa canister and sorbent tube data are in relatively good agreement. Boxes highlighted in green indicate conditions where benzene will drive vapor intrusion risk over TPH. Boxes highlighted in red indicate conditions where TPH will drive vapor intrusion risk over benzene. For example, benzene drives vapor intrusion risk for all fresh fuel samples and for samples collected from Hickam AFB Site VP26 (Site A) if a target cancer risk of 10^{-6} is applied. TPH takes precedence over benzene for fresh gasoline vapors if a less conservative, target risk of 10^{-4} is applied to the latter (i.e., Hazard Quotient >1.0). TPH will drive vapor intrusion risks over benzene for vapors from the fresh JP-8 and diesel fuel samples and for samples collected from Hickam AFB Site VP26 if a target risk of 10^{-5} is applied to benzene (i.e., TPH could still pose a vapor intrusion risk even if benzene in soil gas meets a target risk of 10^{-5}).

Especially telling is the observation that TPH will still pose a vapor intrusion risk at the latter four study sites *even if benzene in soil gas meets a target cancer risk of* 10^{-6}. This reflects the small amount of benzene present in the soil gas in comparison to TPH (i.e., high TPH:Benzene ratio) as well as the increased toxicity of the TPH vapors due to the presence of vapor-phase, C9-C12+ aliphatic compounds.

The relationship between TPH and benzene as vapor intrusion risk drivers can also be depicted graphically. Figures 32-39 depict the average, relative vapor intrusion risk posed by TPH in vapors at a target risk for benzene of 10^{-6} (typically the most conservative target risk used) for each group of samples collected. A TPH Hazard Quotient of 1.0 (left side of graphs) is set equal to a benzene target risk of 10^{-6} (right side of graphs). A TPH Hazard Quotient below 1.0 when the concentration of benzene equals a 10^{-6} risk indicates that benzene drives vapor intrusion concerns if this target risk is applied. This is the case for all of the fresh fuel vapors and for samples collected from the Hickam AFB VP26 site. A TPH Hazard Quotient above 1.0 when the concentration of benzene equals a 10^{-6} risk indicates that TPH drives vapor intrusion hazards even when the benzene target risk is conservatively set to 10^{-6}. This is the case for the four remaining study sites.

The tables and figures were generated based on the equations noted above. For example, an average TPH:Benzene ratio of 170:1 was calculated for vapor samples collected over fresh gasoline based on Summa canister data (see Table 22). Assume for a given site that benzene is present in soil gas at a concentration that met a 10^{-6} risk for vapor intrusion, or 310 µg/m^3 (see Table 5a). At the noted ratio, the corresponding concentration of TPH would be 170-times this concentration or 52,700 µg/m^3. This is well below the soil gas action level of 590,000 µg/m^3 calculated for vapors over fresh gasoline based on the carbon range makeup of the TPH (see Table 17a) and reflects a noncancer Hazard Quotient of less than 0.1, well below the target of 1.0 (see Table 22). This means that a site that meets a benzene soil gas action level of 310 µg/m^3 will also meet a TPH noncancer hazard quotient of 1.0. In the case of a remedial action at a site with these TPH and benzene characteristics, reducing benzene in soil gas to a target cleanup of 310 µg/m^3 would adequately address potential vapor intrusion hazards posed by TPH in petroleum vapors at the site. This is depicted graphically for the vapor samples from fresh gasoline in Figure 32.

TPH would also be adequately addressed if benzene in soil gas met an action level of 3,100 µg/m^3, based on target risk of 10^{-5}, since the corresponding concentration of TPH in soil gas of 527,000 µg/m^3 (i.e., 3,100 µg/m^3 times 170) would still be below the vapor intrusion action level of 590,000 µg/m^3 (HQ=0.9 based on the sample data). Reducing benzene in soil gas to a target cleanup of 3,100 µg/m^3 would adequately address potential vapor intrusion hazards posed by TPH in petroleum vapors at the site. In this example of vapors associated with fresh gasoline, it therefore can be stated that benzene “drives” potential vapor intrusion hazards over TPH down to a target risk of 10^{-5}. There is no need to consider TPH provided that benzene in soil gas meets this target risk, since the associated noncancer Hazard Quotient would be less than 1.0.

This does not hold true if action levels that reflect a target risk of only 10^{-4} are used to screen benzene in soil gas at a site with these TPH and benzene characteristics, however. The corresponding soil gas action level under HDOH guidance would be 31,000 µg/m^3. At a TPH:Benzene ratio of 170:1, the corresponding concentration of TPH in soil gas would be 5,270,000 µg/m^3, well above the action level of 590,000 µg/m^3. As noted in Table 22, the corresponding vapor intrusion Hazard Quotient for TPH under this scenario would be 8.9, well above the target of 1.0. Reducing benzene in soil gas to a target cleanup of 31,000 µg/m^3 would *not* adequately address potential vapor intrusion hazards posed by TPH in petroleum vapors at the site. TPH will drive potential vapor intrusion hazards over benzene if a cancer risk of only 10^{-4} is used for the latter.

This highlights the need to apply a relatively conservative target risk to screen benzene in soil vapors at gasoline-contaminated sites for potential vapor intrusion concerns. For study sites where diesel or other middle distillate fuels were present, TPH will drive vapor intrusion risk over benzene even if a conservative target cancer risk is applied.

Ethylbenzene and naphthalene, like benzene, are also considered to be carcinogens and have similarly low indoor air and soil gas action levels. As previously discussed, naphthalene was not detected above laboratory reporting limits in most of the samples and could not be used as an indicator of vapor intrusion risk (see Table 9). Ethylbenzene was detected in a larger number of samples. The indoor air action level for ethylbenzene at a 10^{-6} excess cancer risk is 0.97 µg/m^3 (residential soil gas action level 970 µg/m^3), approximately three times higher than the benzene indoor air action level of 0.31 µg/m^3 (soil gas action level 310 µg/m$^{3;}$ HDOH 2011). This means that ethylbenzene would need to be present at more than three times the concentration of benzene in order to drive vapor intrusion risk over the latter. This was not the case for gasoline fuel vapor samples and for samples collected from gasoline dominated sites such as Hickam AFB Site VP26 (Site A) and Honolulu Harbor Site OU1C (Site B). Benzene dominated ethylbenzene at these sites.

Ethylbenzene was present on one of three vapor samples collected over fresh diesel fuel, however (DIESEL#3, see Table 9). Ethylbenzene was also present at more than three times the concentration of benzene in samples collected from Hickam AFB Sites SP43 (Site C) and ST03 (Site D), where mixes of gasolines and middle distillates were released. In each of these cases, the vapor intrusion risk posed by ethylbenzene will outweigh the risk posed by benzene. Based on a comparison of the C5-C8 aliphatic soil gas action level of 630,000 µg/m^3 (least stringent TPH action level) to the most stringent ethylbenzene soil gas action level of 970 µg/m^3 (based on a 10^{-6} excess cancer risk), TPH will, however, drive vapor intrusion risk over ethylbenzene whenever the TPH:Ethylbenzene ratio is greater than 650:1 (630,000 µg/970 µg/m^3 m^3/). As summarized in Table 24, this was the case for the average of all but the vapor samples collected over fresh gasoline and diesel fuel. TPH would drive potential vapor intrusion threats for all of the samples collected even when ethylbenzene concentrations in soil gas (or indoor air) met a 10^{-6} cancer risk. This supports the need to evaluate TPH data at these sites in additional to individual chemicals. Although not presented in detail, this is also the case for xylenes (critical TPH:Xylenes ratio of 30:1) and toluene (critical TPH:Toluene ratio of 0.6) due to their much lower toxicity and significantly higher soil gas action levels (e.g., 21,000 µg/m^3 and 1,000,000 µg/m^3 for residential scenarios, respectively; HDOH 2011).

Based on the samples collected, TPH and/or benzene will therefore be the primary risk drivers at sites with petroleum-contaminated soil or groundwater, as summarized in Table 25. The primary driver for potential vapor intrusion threats is TPH, rather than benzene, for soil gas samples collected from sites collected with diesel fuel or other middle distillate fuels.

9 MEASUREMENT OF TPH IN SOIL GAS

The results of the study support the need to include an evaluation of the TPH component of soil gas as part of vapor intrusion investigations at petroleum-contaminated sites. This can be done by requesting specific aliphatic and aromatic carbon range data from the laboratory and treating each fraction as a separate entity, as done for individual compounds such as benzene (e.g., see Table 4). Very few labs are currently set up to report carbon range fractions in soil gas, however, and a standard lab method has not been fully established. Reporting of individual carbon range fractions in soil gas is also more expensive than traditional TPH (approximately $300 per sample in this study, including BTEX and naphthalene).

As an alternative, TPH (excluding BTEXN and any other targeted, individual compounds) can be reported and compared to risk-based screening levels for vapor intrusion hazards based on an assumed, carbon range makeup of the TPH vapors. For example, HDOH guidance presents a TPH soil gas action level of 130,000 $\mu g/m^3$ for sites where unrestricted (e.g., residential) current or future use is desired and 370,000 $\mu g/m^3$ for commercial/industrial sites (HDOH 2011; see discussion of HDOH TPH soil gas screening levels in Attachment 1). These action levels conservatively assume a high component of C9-C12 aliphatics in TPH vapors, with the default TPH RfC based on soil gas data Summa from the Honolulu Harbor Fishing Village diesel site (RfC 127 $\mu g/m^3$).

As presented in this report, a more detailed evaluation of the carbon range makeup of TPH vapors can be carried out as needed based on an initial comparison of TPH soil gas data to published action levels. Site-specific action levels could be up to five-times higher than the default, HDOH action levels if the TPH component of petroleum vapors is in fact dominated by less toxic, C5-C8 aliphatics. This is likely to be the case at sites where only gasoline-related fuels have been released.

The concentration of TPH in soil gas can be estimated through a number of different laboratory methods. A limited comparison of different methods was included as part of this study. Five different methods for calculation of TPH concentrations in soil gas were evaluated during the second phase of the investigation, using two different sample collection methods:

Summa canister samples:

- TO-3 (GC/FID);
- TO-15 (GC/MS);
- Sum of individual, MA-APH carbon ranges (GC/MS);

Sorbent tube samples:

- TO-17 (GC/MS);
- Sum of individual, MA-APH carbon ranges (GC/MS).

A comparison of estimated gasoline-range (e.g., C5-C12) TPH concentrations using different lab methods for samples collected during the second phase of the study is presented in Table 26a and 26b. Reported concentrations of TPHg are summarized in Table 26a. Data for TPHd are presented for comparison. In Table 26b, the concentration of TPHg reported under a specific lab method is divided by the highest concentration of TPHg reported for that sample overall in order to generate relative TPHg concentrations.

As noted in Table 26b and Figure 40, concentrations of TPHg reported under Method TO-15 for Summa canisters were consistently higher than concentrations of TPHg reported under other test methods. Agreement between TPHg reported as the sum of individual carbon ranges using Methods TO-15 and TO-17 was better in most cases and on average less than 40% of the highest TPH concentration reported for a given sample.

Discussions with the laboratory (Air Toxic) suggested that the TO-15 analysis may not have been adequately calibrated to the other methods. The sum of the individual carbon range fractions is assumed to be the most accurate. This issue warrants further evaluation, however.

On an individual sample basis, the different TPH methods consistently flagged samples that failed HDOH soil gas action levels for vapor intrusion concerns (e.g., 130,000 µg/m^3 for unrestricted land use). Exceptions were HAFB-VMP17, where ambient air was apparently introduced into the well point before the sorbent tube sample was collected or the sample train was otherwise leaking. The vapor sample collected over the container of fresh diesel (Diesel#3) is more problematic. The concentration of TPH calculated as the sum of the Summa canister carbon range fractions is far lower than the concentration reported for the correlative sorbent tube sample using Method TO-17 as well as concentration of TPH reported for the Summa canister sample using Method TO-3. The difference is not significantly attributable to the presence of C13 and higher aliphatics in the sample that were not included in the concentration of TPH reported for the Summa canister sample (only reports C5-C12). If this were soil gas data from a commercial/industrial site then the Summa carbon range data would have suggested an absence of vapor intrusion problems while TPH as calculated by other methods would have identified a problem. This supports the need for multiple soil gas samples to characterize a site, as well as the concurrent collection of Summa canister samples if low-volume (e.g., less than one liter) sorbent tube samples are to be collected. The data also support the need to report the full range of C5-C24 compounds for TPH at diesel and other middle distillate sites.

The concentration of vapor-phase TPH based on TO-3 (GC/FID) analysis of Summa canister samples agreed reasonably well with the TO-17 data (GC/MS), including the sum of individual carbon ranges and estimated TPH. Several consultants and laboratory personnel expressed concern about the limitations of TO-3 for other than general screening, however, due to the lowered sensitivity of the method.

The results of this study highlight the need to include the full range of C5-C24 compounds in vapors for TPH reported as both gasoline and diesel. This is routinely done for TPHg or equivalent tests for gasoline-related vapors. Laboratories might only report TPHd as the sum of C10-C24 compounds, however. During this study, relatively high proportions of C5-C8 aliphatic compounds were indentified both in vapors collected over fresh diesel fuel and JP-8 jet fuel as well as at sites where releases of middle distillate fuels were known to have occurred. Reporting TPH as only the sum of C10 to C24 compounds would have significantly under estimated the total concentration of TPH in the vapors, and subsequently underestimated the potential vapor intrusion risk.

Use of sorbent tubes to estimate the concentration of TPH and individual compounds in soil gas at heavily contaminated sites can be problematic. The sorbent material used in the tubes is susceptible to saturation and breakthrough or other interferences with sample analysis. Discussions with the laboratory prior to collection of high-concentration, vapor samples during this study allow the laboratory to optimize the sorbent materials used in the tubes. A maximum sample draw volume of 50ml was also set. As a result, significant breakthrough was only reported for one sample. The mass of petroleum vapors collected in the upstream sorbent tube (Tube A) for a soil gas sample collected at Hickam AFB Site VP26 [HAFB-VP26-B05(24)-HDOH] overwhelmed the ability of the laboratory to quantity TPHg in the sample. A maximum reporting level of 37,000,000 $\mu g/m^3$ was instead provided by the laboratory (see Table 26). No breakthrough was reported for this sample (see Table 21). Concentrations of individual carbon range fractions were also reported (see Table 18).

Note that variability based on the laboratory method selected is not restricted to TPH. As summarized in Table 27, reported concentrations of benzene in the Phase I samples was also moderately to highly variable based on the method used. Concentrations reported using method TO-3 were consistently significantly higher than those reported using TO-15 or TO-17. This is in part due to the high concentration of petroleum vapors in the samples, with most of the TO-3 data flagged “Reported value may be biased due to apparent matrix interferences” by the laboratory. Lab methods for VOCs are being further evaluated by the HEER office.

10 SUMMARY

The study was designed to address the following question: “Is the proportion of TPH in vapors sufficiently large in some cases for TPH to drive vapor intrusion over benzene, naphthalene and other targeted, individual VOCs?” Based on the data collected the answer to this question is clearly “Yes” for the samples collected in this study, and especially for samples collected from sites contaminated with diesel and other middle distillate fuels (see Table 25).

The results of the study highlight the need to consider the TPH component of vapors at petroleum-contaminated sites in addition to BTEX and naphthalene in order to accurately quantify and evaluate potential vapor intrusion risks posed by contaminated soil and groundwater. TPH aliphatic compounds dominate vapors associated with both gasolines and middle distillates fuels (e.g., diesel), with BTEXN making up less than one-percent of the total vapors for most of the samples collected. The vapor intrusion risk posed by the TPH component of subsurface vapors equaled (samples from one site) or exceeded (samples from four sites) the risk posed by benzene and other individual, targeted compounds, including naphthalene at each of the five sites included in the study. This was due to both a relatively low proportion of benzene and other aromatic compounds in vapors in comparison to TPH in the samples collected as well as an increasing proportion of more toxic, C9-C18 aliphatic compounds in vapors associated with middle distillate fuels. A reduced proportion of BTEXN compounds in soil gas samples in comparison to vapor samples collected over fresh fuels could be related to a preferential partitioning of aromatic compounds into soil moisture, as predicted by partitioning models, and/or to preferential biodegradation of these compounds in the vadose zone (also focused in soil moisture). Note that vapor-phase, aliphatic compounds are also highly biodegradable in the subsurface, as illustrated by the rapid attenuation of TPH in general away from source areas at petroleum-contaminated sites. Aromatics appear to be even more efficiently removed from soil vapors, however.

The study suggests that reliance on benzene in soil gas to screen gasoline-contaminated sites for potential vapor intrusion concerns may be adequate provided that a typical and reasonably conservative, target cancer risk is applied (e.g., 10^{-5} to 10^{-6} cancer risk). This applied to samples collected from only one of the five study sites investigated - Hickam AFB VP26 (Site A) Remediation of a hypothetical site with a similar petroleum vapor signature to reduce benzene-related vapor intrusion risk to a 10^{-6} cancer risk would adequately address noncancer risks posed by the TPH component of soil vapors. Remediation of the site based on a less conservative, target risk for benzene would leave levels of TPH in soil vapors that still posed a vapor intrusion concern, even through benzene had been adequately addressed. It is interesting to note, however, the a reduction of TPH levels in soil gas to meet a target, noncancer Hazard Quotient of 1.0 would be sufficient to address vapor intrusion concerns even if benzene data were not collected.

Soil gas data indicated that the TPH component of samples collected at the four, remaining study sites could pose significant vapor intrusion risks even if the level of benzene in vapors were reduced to meet a target, 10^{-6} cancer risk. This is due to a significantly lower proportion of benzene in soil vapors combined with an increase in the toxicity of TPH vapors related to the presence of heavier, vapor-phase aliphatics (C9-C12+) associated with the presence of diesel and other middle distillate fuels (see Table13a and Tables 15-17). A consideration of TPH in soil gas as part of vapor intrusion investigations at middle distillate release sites is therefore critical.

TPH soil gas data and conservative, risk-based action levels for soil gas provide an important and easy-to-use tool to screen petroleum-contaminated sites for potential vapor intrusion concerns. Detailed carbon range data can be collected as needed to establish site-specific and most likely less conservative action levels for remedial purposes if needed. In this study, TO-15 analysis of Summa canister samples consistently yielded the highest and most conservative estimate of TPH concentrations, on average twice as high as Method TO-3 and the sum of individual TPH carbon ranges for the same samples and for concurrently collected sorbent tube samples. Several consultants expressed concern over the reliance on TO-3 to report TPH in soil gas due to its decreased sensitivity in comparison to TO-15. Heavily contaminated sites were intentionally selected for the study and significant vapor intrusion concerns would have been identified for all samples collected from the key study sites based on TPH data regardless of the laboratory method used.

The relative proportion of carbon range fractions and estimates of weighted, vapor-phase TPH toxicity were reasonably similar between Summa samples and sorbent tube samples. Sorbent tube methods did not indicate a significant proportion of >C12 aliphatics or >C10 aromatics in any of the samples (maximum 10% and 1%, respectively, in vapors collected over fresh diesel). This suggests that TPH data for Summa canister samples would have been adequate to evaluate potential vapor intrusion concerns at each of the study sites.

Limitations of sorbent tubes include the need to use very small sample draw volumes at heavily contaminated sites in order to avoid saturation of the sorbent material. Sample draws were limited to 50ml based on the anticipated concentration of vapors at the sites included in this study and discussions with the laboratory. The potential for ambient air to be drawn into the vapor monitoring point after purging poses a risk that the resulting sorbent tube data may not be representative of site conditions. This was addressed in the field by collecting a concurrent Summa canister sample from each well point and by closing the well point prior to disconnection of the Summa canister sampling train. Additional carbon range data for middle distillate sites are needed before the use of sorbent tubes at diesel and other middle distillate sites can be completely negated.

Naphthalene was rarely reported in soil gas samples (even at diesel sites) and was not a reliable indicator of potential vapor intrusion hazards. Naphthalene was marginally above soil gas action levels for vapor intrusion in samples collected at one site when TPH was below action levels, suggesting that it should still be included as a target analyte in soil gas investigations. Ethylbenzene was present in significant enough concentrations in samples collected from several sites with mixed, gasoline and middle distillate fuels to contribute to potential vapor intrusion risk. Ethylbenzene was also present in significantly higher concentrations than benzene in one of three vapor samples collected over fresh diesel fuel. Xylenes and toluene were not significant risk drivers in samples collected at any of the sites included in the study in comparison to TPH and benzene. This suggests that TPH and/or benzene will in most cases be the primary risk drivers for vapor intrusion at sites with petroleum-contaminated soil and groundwater. The study suggests that naphthalene and ethylbenzene can still contribute to vapor intrusion risks, however, and should continue to be included as contaminants of potential concern in vapor intrusion investigations.

Results from this study indicate that C5-C8 aliphatic compounds can make up a significant if not dominant fraction of the total TPH present in vapors associated with diesel and other middle distillate fuels. This is important, since current laboratory protocols typically require that they report “TPHdiesel” in any media as the sum of C10 to approximately C24 hydrocarbon compounds. Excluding the contribution of C5-C8 aliphatics to the total concentration of TPH reported in air or soil vapor samples associated with middle distillate fuels would be inappropriate, however. To address this problem, laboratories should be instructed to report TPH in air or vapor samples as: 1) The sum of C5-C12 compounds for whole-air samples (e.g., summa canister samples and TO-15 lab methods), with the understanding that aromatics can only be confidently summed to C10 and 2) The sum of C5-C18 for samples collected using a sorbent media, with the understanding that aromatics can only be confidently summed to C16 (e.g., sorbent tubes and TO-17 lab methods), regardless of whether the samples are associated with gasolines or middle distillates. Designation of chromatogram patterns as “gasoline range” (e.g., C5-C12) or “diesel range” (e.g., C10-C24) compounds with respect to traditional, laboratory methods for TPH in soil or water is not applicable to air and vapor samples and is not necessary or recommended. The reported concentration of TPH can then be compared to HDOH soil gas action levels. The sum of concentrations of individual, target analytes such as BTEX and naphthalene that will be evaluated separate can be subtracted from the reported concentration of TPH in order to avoid double counting, although this is not likely to make a significant difference in the final concentration.

The results of this study will be used to update the section of the HEER Technical Guidance Manual that discusses the collection and analysis of soil gas at petroleum-contaminated sites. An update of this section is anticipated to be completed in 2012. The conclusions of this study are based on the selection of inhalation toxicity factors for individual, TPH carbon ranges. The use of alternative, published toxicity factors may indicate either an increased vapor intrusion risk posed by the TPH component of soil vapors (e.g., MADEP 2003) or a decreased risk (e.g., TPHCWG 1998, WADOE 2006).

It is important to note that the soil gas data collected during this study reflect in part the composition of the petroleum fuels produced or otherwise used in Hawaiʻi. The vapor signatures reported in this study for TPH carbon range fractions (i.e., proportions of non-specific, TPH aliphatics to aromatics) are likely to be similar to sites outside of the State. The proportions and identified ratios of TPH to individual compounds such as benzene and naphthalene could vary dramatically, however, depending on the blending processes used by different refineries. Fuel blends in Hawai‘i can also differ dramatically between the two refineries that operate here. Weathering of fuel over time can also significantly affect the both the TPH and individual VOC signatures in soil vapors. Temperatures of subsurface soil and groundwater could affect both vapor concentrations and composition (e.g., average Hawai‘i versus Alaska). Other factors, including the average temperature of vadose zone soils and groundwater, could also affect the nature of vapors emitted from subsurface sources (e.g., see Chin 2012).

This study does not address biodegradation of petroleum vapors as the vapors migrate away from the source area. The fate and transport of vapors in the vadose zone represents the next, important step in evaluation of the vapor intrusion threat posed by petroleum-contaminated soil and groundwater. This issue will be discussed in more detail in updates to Section 7 of the HEER office *Technical Guidance Manual* (Soil Vapor and Indoor Air Sampling Guidance, anticipated September 2012).

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Table 1. Previous HDOH toxicity factors and indoor air and soil gas action levels for TPH (HDOH 2008).

[1]Fuel Type	RfC (µg/m³)	[2]Indoor Air (µg/m³)		[2,3]Subslab Soil Gas (µg/m³)	
		Residential	**Commercial/ Industrial**	**Residential**	**Commercial/ Industrial**
TPH(gasolines)	50	26	37	26,000	73,000
TPH(middle distillates)	110	57	80	57,000	160,000

1. Middle distillates include diesel fuel, Stoddard solvent, JP-8 jet fuel, etc.
2. Based on exposure assumptions in HDOH EHE guidance and a target Hazard Quotient of 0.5 (see HDOH 2008 & 2011).
3. Based on a residential indoor air:subslab soil gas attenuation factor of 1/1,000 and a commercial/industrial attenuation factor of 1/2,000 (see HDOH 2008 & 2011).

Table 2a. Default physiochemical constants for carbon range fractions (after MADEP 2002).

***Chemical/ Carbon Range**	**Molecular Weight**	**Vapor Pressure (atms)**	**Solubility in Water (mg/L)**	**Henry's Constant, H (dimensionless)**	**Partition Coeff, Koc (cm^3/g)**	**Diffusion Coefficient (cm2/s)**	
						air	**water**
Benzene	78	0.1	1,790	0.23	146	0.09	1×10^{-5}
Ethylbenzene	106	0.01	169	0.32	446	0.068	8.5×10^{-6}
Toluene	92	0.04	526	0.27	234	0.078	9.2×10^{-6}
Xylenes	106	0.01	161	0.29	375	0.068	8.4×10^{-6}
Naphthalene	128	1.0×10^{-4}	30	0.018	1,540	0.06	8.4×10^{-6}
C5-C8 Aliphatics	93	0.1	11,000	54	2,265	0.08	1×10^{-5}
C9-C12 Aliphatics	149	8.7×10^{-4}	70	65	150,000	0.07	1×10^{-5}
C9-C18 Aliphatics	170	1.4×10^{-4}	10	69	680,000	0.07	5.0×10^{-6}
C19-C36 Aliphatics	280	1.1×10^{-6}	0.0000015	110	4.0×10^{-8}	-	-
C9-C10 Aromatics	120	2.9×10^{-3}	51,000	0.33	1,778	0.07	1×10^{-5}
C11-C22 Aromatics	150	3.2×10^{-5}	5,800	0.03	5,000	0.06	1×10^{-5}

*Constants for BTEXN from USEPA RSL guidance (USEPA 2011, see Appendix 1 of the HDOH EHE guidance, HDOH 2011); vapor pressures from TOXNET (NLM 2012). Carbon range values from Massachusetts DEP (MADEP 2002) except C19-C36 Aliphatics (TPHCWG 1997, based on EC>16-35 aliphatics).

Table 2b. Theoretical partitioning of targeted VOCs and carbon range fractions in vadose-zone soils.

Chemical/ Carbon Range	**[1]Clean Sand**			**[2]Silty Sand**		
	Sorbed To Soil Particles	**Dissolved In Pore Water**	**Vapor In Soil Pore Space**	**Sorbed To Soil Particles**	**Dissolved In Pore Water**	**Vapor In Soil Pore Space**
Benzene	4.0%	67.1%	29.0%	29.2%	49.5%	21.3%
Ethylbenzene	18.4%	50.6%	31.0%	69.3%	19.1%	11.7%
Toluene	10.7%	58.9%	30.4%	54.6%	30.0%	15.5%
Xylenes	20.6%	50.6%	28.8%	72.2%	17.7%	10.1%
Naphthalene	53.4%	44.9%	1.7%	92.0%	7.7%	0.3%
C5-C8 Aliphatics	2.1%	0.9%	96.9%	18.0%	0.8%	81.2%
C9-C12 Aliphatics	54.7%	0.4%	44.9%	92.4%	0.1%	7.6%
C9-C18 Aliphatics	83.8%	0.1%	16.1%	98.1%	0.0%	1.9%
C19-C36 Aliphatics	99.9%	0.0%	0.1%	100.0%	0.0%	0.0%
C9-C10 Aromatics	52.3%	29.4%	18.4%	91.6%	5.2%	3.2%
C11-C22 Aromatics	82.6%	16.5%	0.9%	97.9%	2.0%	0.1%

1. Clean Sand: TOC=0.0001, Air-Filled Porosity=28%, Water-Fill Porosity=15%.
2. Silty Sand: TOC=0.001, Air-Filled Porosity=28%, Water-Fill Porosity=15%.

Table 3. Published inhalation toxicity factors for petroleum aliphatic and aromatic carbon ranges.

Reference		**RfC (mg/m3)**	**RfC µg/m3**
TPH Working Group (1998)			
(C5-C8) Aliphatics		18.4	18,400
(C9-C18) Aliphatics		1.0	1,000
(C9-C16) Aromatics		0.2	200
Massachusetts DEP (2003)			
(C5-C8) Aliphatics		0.2	200
(C9-C18) Aliphatics		0.2	200
(C9-C18) Aromatics		0.05	50
[1]Washington DOE (2006)	**[1]RfDinh (mg/kg-day)**		
(C5-C8) Aliphatics	1.7	6.0	5,950
(C9-C16) Aliphatics	0.085	0.3	298
(C9-C10) Aromatics	0.114	0.399	399
(C11-C12) Aromatics (naphthalene)	0.00086	0.003	3.0
(C13-C16) Aromatics	0.05	0.2	175
[2]CalEPA-DTSC (2009)			
(C5-C8) Aliphatics		0.7	700
(C9-C18) Aliphatics		0.3	300
(C9-16) Aromatics		0.05	50
[3]USEPA/NCEA (2009)			
(C5-C8) Aliphatics (noncancer)		0.6	600
(C9-C18) Aliphatics		0.1	100
(C9-C16) Aromatics		0.1	100

1. Inhalation Reference Dose published by Washington DOE converted to a Reference Concentration: RfC (mg/m^3) = RfD (mg/kg-day) x70kg x (1/20m3-day).
2. California EPA toxicity factors withdrawn in 2010 pending review of USEPA document and potential revision.
3. USEPA NCEA toxicity factors selected for calculation of HDOH risk-based indoor air and soil gas action levels.

Table 4. Indoor air and soil gas action levels for vapor-phase carbon ranges based on USEPA-NCEA inhalation Reference Concentrations (see Table 2).

Carbon Range	**RfC ($\mu g/m^3$)**	**[1]Indoor Air ($\mu g/m^3$)**		**[2]Subslab Soil Gas ($\mu g/m^3$)**	
		Residential	**Commercial/ Industrial**	**Residential**	**Commercial/ Industrial**
C5-C8 Aliphatics	600	630	880	630,000	176,000
C9-C18 Aliphatics	100	100	150	100,000	300,000
C9-C16 Aromatics	100	100	150	100,000	300,000

1. Based on exposure assumptions in HDOH EHE guidance and a target Hazard Quotient of 1.0 (see HDOH 2011).

2. Based on a residential indoor air:subslab soil gas attenuation factor of 1/1,000 and a commercial/industrial attenuation factor of 1/2,000 (see HDOH 2011).

Table 5a. Benzene and naphthalene indoor air and soil gas action levels based on cancer health risk.

Chemical	IUR $(\mu g/m^3)^{-1}$	Target Cancer Risk	[1]Indoor Air ($\mu g/m^3$) Residential	[1]Indoor Air ($\mu g/m^3$) Commercial/ Industrial	[1,2]Subslab Soil Gas ($\mu g/m^3$) Residential	[1,2]Subslab Soil Gas ($\mu g/m^3$) Commercial/ Industrial
Benzene	7.8E-06	10^{-6}	0.31	0.52	310	1,040
		10^{-5}	3.1	5.2	3,100	10,400
		10^{-4}	31	52	31,000	100,400
Naphthalene	3.48E-05	10^{-6}	0.072	0.12	72	240
		10^{-5}	0.72	1.2	720	2,400
		10^{-4}	7.2	12	7,200	24,000

1. Based on exposure assumptions in HDOH EHE guidance (see HDOH 2011).
2. Based on a residential indoor air:subslab soil gas attenuation factor of 1/1,000 and a commercial/industrial attenuation factor of 1/2,000 (see HDOH 2011).

Table 5b. Benzene and naphthalene indoor air and soil gas action levels based on noncancer health risk.

Chemical	RfC ($\mu g/m^3$)	Target HQ	[1]Indoor Air ($\mu g/m^3$) Residential	[1]Indoor Air ($\mu g/m^3$) Commercial/ Industrial	[1,2]Subslab Soil Gas ($\mu g/m^3$) Residential	[1,2]Subslab Soil Gas ($\mu g/m^3$) Commercial/ Industrial
Benzene	30	1.0	31	44	31,000	88,000
Naphthalene	3.0	1.0	3.1	4.4	3,100	8,800

1. Based on exposure assumptions in HDOH EHE guidance (see HDOH 2011).
2. Based on a residential indoor air:subslab soil gas attenuation factor of 1/1,000 and a commercial/industrial attenuation factor of 1/2,000 (see HDOH 2011).

Table 6a. TPH versus benzene as the primary vapor intrusion risk driver.

TPH:Benzene Soil Gas Ratio	**Risk Driver**
>2,000:1	TPH will always drives vapor intrusion hazards over benzene (TPH HQ will exceed 1.0 when benzene ECR risk is 10^{-6}).
16:1 to 2,000:1	TPH Carbon Range data recommended. TPH could drive vapor intrusion hazards depending on carbon range makeup and benzene target risk (TPH HQ could exceed 1.0 even though benzene ECR risk is not exceeded).
<3:1	Benzene will always drive vapor intrusion risk over TPH (Benzene ECR will exceed 10^{-4} and HQ will exceed 1.0 when TPH HQ is 1.0)

Table 6b. TPH versus naphthalene as the primary vapor intrusion risk driver.

TPH:Naphthalene Soil Gas Ratio	**Risk Driver**
>8,800:1	TPH will always drives vapor intrusion hazards over naphthalene (TPH HQ will exceed 1.0 when naphthalene ECR risk is 10^{-6}).
32:1 to 8,800:1	TPH could drive vapor intrusion hazards depending on carbon range makeup and naphthalene target risk (TPH HQ could exceed 1.0 even though naphthalene ECR risk is not exceeded).
<32:1	Naphthalene will always drive vapor intrusion risk over TPH (Naphthalene noncancer HQ will exceed 1.0 when TPH HQ is 1.0)

Table 6c. Summary of critical ratio where TPH will always drive vapor intrusion risk over versus noted, individual compound.

VOC	**[1]Indoor Air Action Level (µg/m^3)**	**[2]Critical TPH:VOC Ratio**
Naphthalene	0.072	8,800:1
1-Methylnaphthalene	0.29	2,200:1
Benzene	0.31	2,000:1
Ethylbenzene	0.97	650:1
Xylenes	21	30:1
Toluene	1,000	0.6:1

1. Based on 10^{-6} cancer risk for naphthalene, benzene, 1-methylnaphthalene and ethylbenzene and noncancer Hazard Quotient of 1.0 for toluene and xylenes. VOCs listed in order or relative toxicity.

2. Risk posed by TPH aliphatics and aromatics sufficient to overwhelm risk posed individual compound due to overwhelming proportion of TPH in vapor.

Table 7a. Sites selected for collection of soil gas samples.

Site Name (sampling phase)	[1]Location	Suspected Fuel Type Released	Notes	Site Overview Reports
[2]Aloha Petroleum (Phase I)	School Street, Honolulu	Gasoline	Operating service station	Soil Gas Investigation, Aloha Petroleum, Ltd., 1841 Palolo Avenue, Honolulu, Hawai'i, 2008.
[3]GASCO (Phase I)	616 Iwilei Road, Honolulu	Benzene, naphthalene, diesel fuel	Former manufactured gas plant	Remedial Investigation Report, Former GASCO Facility, 616 Iwilei Road, Honolulu, April 1, 2009.
[3]HAFB IRP Site VP26 (Phase I & II)	Aiea	JP-4/AVGAS	Fuel pipeline release	Draft Work Plan Addendum for Treatability Study at IRP Site ST02/Valve Pit 26, Hickam POL Pipeline, Oahu, Hawaii, April 7, 2011.
[3]OU1C (Phase I & II)	Honolulu Harbor Pier 24 area	Mixture gasolines and middle distillates	Fuel pipeline release	Operable Units OU1C LNAPL and Soil Gas Investigation, Supplemental Remedial Investigation Report, Honolulu, Hawai'i, June 2008.
[3]HAFB IRP Site SP43 (Phase II)	Hickam Air Force Base, Honolulu	JP-8	Fuel pipeline release	Investigation/Remediation of Air Mobility Command Stripper Pit Site No. 43, Hickam Air Force Base Oahu, Hawai'i, September 30, 2010
[3]HAFB IRP Site ST03 (Phase I & II)	Mililani,	MOGAS, AVGAS, JP-4	Fuel pipeline release (mid 1970s)	Work Plan for Phase 2 Remedial Investigation and Treatability Study at IRP Site ST03, Hickam AFB, Honolulu, Hawai'i, July 2009.
[3]Fishing Village (Phase I & II)	Honolulu Harbor Piers36-38 area	Diesel	UST and/or pipeline releases	Soil Gas Monitoring Report, Domestic Commercial Fishing Village Site, Honolulu, May 2010.

Table 7a (cont.). Sites selected for collection of soil gas samples.

Site Name (sampling phase)	**[1]Location**	**Suspected Fuel Type Released**	**Notes**	**Site Overview Reports**
Other				
Fresh Gasoline Vapors (Phase I & II)	-	Gasoline	Vapors over fresh fuel	-
Fresh Diesel Vapors (Phase I & II)	-	Diesel #2	Vapors over fresh fuel	-
Fresh JP-8 Vapors (Phase II)	-	Jet Fuel #8	Vapors over fresh fuel	-
Gasoline Auto Exhaust (Phase II)	-	Gasoline	Vapors from exhaust	-
Diesel Auto Exhaust (Phase II)	-	Diesel #2Exhaust	Vapors from exhaust	-

1. All sites located on the island of O‘ahu, Hawai‘i (see Figure 1).
2. UST office lead case.
3. HEER office lead case.

Table 7b. Depth and proximity of soil gas sampling point to source area at final, primary study sites.

Site	Sample ID	[1]Primary Source of Vapors at Sampling Point	Surface Cover at Sampling Point	[2]Soil Vapor Point Depth (feet bgs)	[3]Estimated Distance to Vapor Source (feet)	Depth to Groundwater (feet bgs)
Hickam AFB VP26 (Site A)	HAFB-VP26-B05(18)-HDOH	VZS, GW	Soil	-18’	<15’	-30’
	HAFB-VP26-B05(24)-HDOH	VZS, GW	Soil	-24’	<6’	-30’
	HAFB-VP26-B07(20)-HDOH	VZS, GW	Soil	-20’	<10’	-30’
	HAFB-VP26-B07(25)-HDOH	VZS, GW	Soil	-25’	<5’	-30’
Honolulu Harbor OU1C (Site B)	HH-OU1C-MW10SG	GW	Asphalt	-2.3’	<5’	-6’
	HH-OU1C-MW22R	GW	Asphalt	-2.3’	<5’	-6’
	HH-OU1C-OTNS1	GW	Asphalt	-1.8’	<5’	-6’
Hickam AFB SP43 (Site C)	HAFB-SP43-VMP10	GW	Soil	-2.5’	<5’	-6’
	HAFB-SP43-VMP11	GW	Soil	-2.5’	<5’	-5’
	HAFB-SP43-VMP12	GW	Soil	-2.5’	<5’	-7’
	HAFB-SP43-VMP16	GW	Soil	-2.5’	<5’	-6’
	HAFB-SP43-VMP17	GW	Soil	-2.5’	<5’	-5’
Hickam AFB ST03 (Site D)	HAFB-ST03-B58 (347)	VZS?	Soil	-347’	<50’?	-540’
	HAFB-ST03-B58 (422)	VZS?	Soil	-422’	<50’?	-540
	HAFB-ST03-B58 (492)	VZS?	Soil	-492’	<50’?	-540
	HAFB-ST03-B59 (388)	VZS?, GW	Soil	-388 to -538’	<50’?	-540
Fishing Village (Site E)	FV-GP-01-HDOH	GW	Asphalt	-1 to -5’	<5’	-5’
	FV-GP-08-HDOH	GW	Asphalt	-1 to -5’	<5’	-5’
	FV-GP-16R-HDOH	GW	Asphalt	-1 to -5’	<5’	-5’

1. Assumed primary source of vapors at sampling point based on site investigation reports (VZS=vadose-zone soils, GW=free product and/or dissolved-phase petroleum at water table).

2. Top of six-inch screen noted for discrete sample points.

3. Distance to product in basalt and/or on groundwater uncertain at Site D due to depth and limited number of borings.

Table 8. Elution/retention times for targeted VOCs and chemical markers use to define carbon ranges.

Target Chemical/ Carbon Range	**Marker Chemical(s) on Chromatogram**	**Elution/Retention Time (minutes)**	
		TO-15	**TO-17**
C5 aliphatics	Isopentane	7.445	3.302
C9 aliphatics	Nonane	20.240	11.121
C13 aliphatics	Dodecane	23.134	15.457
C18 aliphatics	Octadecane	NA	21.037
C24 aliphatics	Tetracosane	NA	24.991
C9 aromatics	o-Xylene	20.238	10.844
C11 aromatics	Naphthalene	23.060	14.978
C16 aromatics	Octadecane	NA	21.037
Benzene	“”	14.779	5.565
Ethylbenzene	“”	19.704	10.128
Toluene	“”	17.997	8.022
Xylenes	“”	M/P :19.816 O :20.138	M/P :10.321 O :10.744
Naphthalene	“”	23.160	15.078
1-Methylnaphthalene	“”	NA	16.549
2-Methylnaphthalene	“”	NA	16.370
TPHg (C5-C12)	Isopentane & Nonane	7.445 to 23.134	3.302 to 11.121
TPHg (C5-C24)	Isopentane & Tetracosane	NA	3.302 to 24.991
[1]TPHd (C5-C24)	Isopentane & Tetracosane	NA	3.302 to 24.991
[2]TPHd (C10-C24)	Nonane & Tetracosane	NA	12.671 to 24.991

1. Request lab to report TPHd as C5 to C24 to ensure inclusion of C5-C8 aliphatics.

2. Not recommended, excludes potential C5-C8 aliphatics in diesel and other middle distillate vapors.

Table 9. Summary of TPH and BTEXN vapor data based on Summa canister data.

Site	**Sample ID**	**[1]TPH ($\mu g/m^3$)**	**[2]Benzene ($\mu g/m^3$)**	**[2]Toluene ($\mu g/m^3$)**	**[2]Ethylbenzene ($\mu g/m^3$)**	**[2]Xylenes ($\mu g/m^3$)**	**[2]Naphthalene ($\mu g/m^3$)**
Fresh Fuels and Auto Exhaust	Gasoline #1	261,985,000	5,100,000	28,000,000	2,100,000	7,300,000	ND (<500,000)
	Gasoline #2	8,342,000	29,000	130,000	11,000	49,000	ND (<26,000)
	Gasoline Exhaust	27,540	4,700	6,400	1,000	5,200	ND (<200)
	JP8#1	6,010,000	20,000	62,000	22,000	115,000	6,100
	Diesel#1	1,195,000	16,000	42,000	9,700	31,800	730
	Diesel#2	974,000	2,900	21,000	6,000	37,000	3,500
	Diesel#3	208,200	1,000	850	4,000	3,800	120
	Diesel Exhaust	62	14	4.6	ND (<3)	ND (<6)	ND (<16)
Site A (May 2011)	HAFB-VP26-B05(18)-HDOH	49,412,000	29,000	ND (<4,800)	14,000	ND (<9,600)	ND (<25,000)
	HAFB-VP26-B05(24)-HDOH	94,275,000	470,000	ND (<240,000)	ND (<240,000)	ND (<240,000)	ND (<300,000)
	HAFB-VP26-B07(20)-HDOH	38,267,500	58,000	ND (<230)	40,000	545	ND (<1,200)
	HAFB-VP26-B07(25)-HDOH	100,396,000	19,000	ND (<4,600)	9,200	ND (<9,200)	ND (<24,000)
Site A (October 2011)	HAFB-VP26-B05(18)-HDOH	49,412,000	40,000	ND (<2,000)	18,000	ND (<2,000)	ND (<11,000)
	HAFB-VP26-B05(24)-HDOH	94,275,000	280,000	ND (<50,000)	ND (<50,000)	ND (<100,000)	ND (<260,000)
	HAFB-VP26-B07(20)-HDOH	38,267,500	84,000	ND (<4,800)	37,000	ND (<9,600)	ND (<15,000)
	HAFB-VP26-B07(25)-HDOH	100,396,000	45,000	ND (<6,300)	20,000	ND (<12,600)	ND (<33,000)
Site B (August 2011)	HH-OU1C-MW10SG	63,835,000	12,000	3,600	ND (<3,100)	ND (<6,200)	ND (<16,000)
	HH-OU1C-MW22R	23,217,000	7,700	ND (<1,900)	ND (<1,900)	ND (<3,800)	ND (<10,000)
	HH-OU1C-OTNS1	902,700	ND (<300)	ND (<500)	ND (<500)	ND (<1,000)	ND (<1,600)
Site B (October 2011)	HH-OU1C-MW10SG	67,017,000	16,000	ND (<6,700)	ND (<6,700)	ND (<13,400)	ND (<35,000)
	HH-OU1C-MW22R	65,304,100	ND (<16,000)	ND (<16,000)	ND (<16,000)	ND (<32,000)	ND (<85,000)
	HH-OU1C-OTNS1	699	ND (<3.1)	ND (<3.1)	ND (<3.1)	ND (<6.2)	ND (<16)

Table 9 (cont.). Summary of TPH vs BTEXN data based on Summa canister data.

Site	Sample ID	[1]TPH (µg/m^3)	[2]Benzene (µg/m3)	[2]Toluene (µg/m^3)	[2]Ethylbenzene (µg/m^3)	[2]Xylenes (µg/m^3)	[2]Naphthalene (µg/m3)
Site C (October 2011)	HAFB-SP43-VMP10	19,520,000	1,600	ND (<490)	7,200	ND (<980)	4,000
	HAFB-SP43-VMP11	19,982,000	ND (<480)	ND (<480)	41,000	ND (<960)	2,600
	HAFB-SP43-VMP12	2,158	ND (<4.8)	ND (<4.8)	ND (<4.8)	ND (<4.8)	ND (<50)
	HAFB-SP43-VMP16	37,830,000	1,500	ND (<500)	1,600	ND (<1,000)	ND (<2,600)
	HAFB-SP43-VMP17	6,530,000	ND (<500)	ND (<490)	6,000	ND (<980)	ND (<2,600)
Site D (July 2011)	HAFB-ST03-B58 (347)	173,340	22	400	140	1,260	ND (<100)
	HAFB-ST03-B58 (422)	80,200	14	210	54	329	ND (<65)
	HAFB-ST03-B58 (492)	530,850	79	680	240	2,120	ND (<340)
	HAFB-ST03-B59 (388)	510,700	32	550	170	1,080	ND (<330)
Site D (October 2011)	HAFB-ST03-B58 (347)	624,000	ND (<32)	110	510	13,400	ND (<160)
	HAFB-ST03-B58 (422)	944,000	ND (<43)	130	620	15,600	ND (<220)
	HAFB-ST03-B58 (492)	898,000	ND (<42)	160	720	19,000	ND (<220)
	HAFB-ST03-B59 (388)	72,000	180	360	120	2,420	140
Site E (May 2011)	FV-GP-01-HDOH	89,600	ND (<28)	ND (<28)	ND (<28)	ND (<28)	ND (<150)
	FV-GP-08-HDOH	3,781,000	50	67	110	638	50
	FV-GP-16R-HDOH	5,923,000	ND (<490)	ND (<490)	ND (<490)	ND (<980)	ND (<2,600)
Site E (Oct 2011)	FV-GP-01-HDOH	28,472	ND (<4.7)	ND (<4.7)	ND (<4.7)	ND (<9.4)	ND (<150)
	FV-GP-08-HDOH	1,609,700	49	51	ND (<48)	ND (<96)	125
	FV-GP-16R-HDOH	6,917,000	ND (<490)	ND (<490)	ND (<490)	ND (<980)	ND (<2,600)

Notes

1. TPH calculated as sum of individual carbon ranges; excludes BTEXN.
2. Benzene and naphthalene concentrations as reported in MA-APH test data.

Table 10. Summary of relative proportion of TPH versus total BTEXN vapor data based on Summa canister data.

Site	**Sample ID**	**[1]TPH (µg/m^3)**	**[2]Sum of BTEXN (µg/m3)**	**Percent TPH**	**Percent BTEXN**	**Comments**
Fresh Fuels and Auto Exhaust	Gasoline #1	261,985,000	42,750,000	86.0%	14.0%	Vapors collected over various fuels and directly from auto exhaust
	Gasoline #2	8,342,000	232,000	97.3%	2.7%	
	Gasoline Exhaust	27,540	17,380	61.3%	38.7%	
	JP8#1	6,010,000	225,100	96.4%	3.6%	
	Diesel#1	1,195,000	100,750	92.2%	7.8%	
	Diesel#2	974,000	70,400	93.3%	6.7%	
	Diesel#3	208,200	9,770	95.5%	4.5%	
	Diesel Exhaust	62	30	67.1%	32.9%	
Site A (May 2011)	HAFB-VP26-B05(18)-HDOH	49,412,000	62,700	99.9%	0.1%	JP-4/AVGAS
	HAFB-VP26-B05(24)-HDOH	94,275,000	1,600,000	98.3%	1.7%	
	HAFB-VP26-B07(20)-HDOH	38,267,500	99,260	99.7%	0.3%	
	HAFB-VP26-B07(25)-HDOH	100,396,000	47,100	100.0%	0.0%	
Site A (October 2011)	HAFB-VP26-B05(18)-HDOH	49,412,000	66,500	99.9%	0.1%	
	HAFB-VP26-B05(24)-HDOH	94,275,000	510,000	99.5%	0.5%	
	HAFB-VP26-B07(20)-HDOH	38,267,500	132,850	99.7%	0.3%	
	HAFB-VP26-B07(25)-HDOH	100,396,000	90,950	99.9%	0.1%	
Site B (August 2011)	HH-OU1C-MW10SG	63,835,000	28,250	100.0%	0.0%	Mix diesel, fuel oil & gasoline
	HH-OU1C-MW22R	23,217,000	16,500	99.9%	0.1%	
	HH-OU1C-OTNS1	902,700	2,050	99.8%	0.2%	
Site B (October 2011)	HH-OU1C-MW10SG	67,017,000	46,900	99.9%	0.1%	
	HH-OU1C-MW22R	65,304,100	82,500	99.9%	0.1%	
	HH-OU1C-OTNS1	699	16	97.8%	2.2%	

Table 10 (cont.). Summary of relative proportion of TPH versus total BTEXN vapor data based on Summa canister data.

Site	Sample ID	[1]TPH (µg/m^3)	[2]Sum of BTEXN (µg/m3)	Percent TPH	Percent BTEXN	Comments
Site C (October 2011)	HAFB-SP43-VMP10	19,520,000	13,535	99.9%	0.1%	JP-4 + JP-8
	HAFB-SP43-VMP11	19,982,000	44,560	99.8%	0.2%	
	HAFB-SP43-VMP12	2,158	22	99.0%	1.0%	
	HAFB-SP43-VMP16	37,830,000	5,150	100.0%	0.0%	
	HAFB-SP43-VMP17	6,530,000	8,285	99.9%	0.1%	
Site D (July 2011)	HAFB-ST03-B58 (347)	173,340	1,872	98.9%	1.1%	JP-4/AVGAS, JP-8
	HAFB-ST03-B58 (422)	80,200	640	99.2%	0.8%	
	HAFB-ST03-B58 (492)	530,850	3,289	99.4%	0.6%	
	HAFB-ST03-B59 (388)	510,700	1,997	99.6%	0.4%	
Site D (October 2011)	HAFB-ST03-B58 (347)	624,000	14,116	97.8%	2.2%	
	HAFB-ST03-B58 (422)	944,000	16,592	98.3%	1.7%	
	HAFB-ST03-B58 (492)	898,000	20,011	97.8%	2.2%	
	HAFB-ST03-B59 (388)	72,000	3,220	95.7%	4.3%	
Site E (May 2011)	FV-GP-01-HDOH	89,600	145	99.8%	0.2%	Diesel; May 2011 TPH based on sum of carbon ranges (no TO-15 analysis)
	FV-GP-08-HDOH	3,781,000	865	100.0%	0.0%	
	FV-GP-16R-HDOH	5,923,000	2,525	100.0%	0.0%	
Site E (Oct 2011)	FV-GP-01-HDOH	28,472	21	99.9%	0.1%	
	FV-GP-08-HDOH	1,609,700	297	100.0%	0.0%	
	FV-GP-16R-HDOH	6,917,000	2,280	100.0%	0.0%	

Average for Sites (excluding fuel vapors): 99.4% 0.6%

Notes

1. TPH calculated as sum of individual carbon ranges; excludes BTEXN.
2. Sum of reported benzene, toluene, ethylbenzene, xylenes and naphthalene (BTEXN); NDs summed as 1/2 the method reporting level (see Table 9).

Table 11. Average TPH versus BTEXN composition for fuel vapor and soil gas samples from key sites based on Summa canister data.

Site/Fuel Type	**Average Soil Gas Composition (TO-15 Data)**	
	TPH	**[1]BTEXN**
Gasoline (Fresh Vapors)	91.6%	8.4%
Diesel (Fresh Vapors)	93.7%	6.3%
JP-8 (Fresh Vapors)	96.4%	3.6%
Site A (JP-4/AVGAS)	99.6%	0.4%
Site B (mixed fuels)	99.5%	0.5%
Site C (JP-8 +/- JP-4)	99.7%	0.3%
Site D (JP-4/AVGAS)	98.3%	1.7%
Site E (diesel)	99.9%	0.1%

1. NDs summed as 1/2 the method reporting level for estimation of total BTEXN (see Tables 9 and 10).

Table 12. TPH vs benzene and naphthalene data based on Summa canister data.

Site	**Sample ID**	**[1]TPH (µg/m^3)**	**[2]Benzene (µg/m^3)**	**[2]Naphthalene (µg/m^3)**	**[1]TPH: Benzene Ratio**	**[1]TPH: Naphthalene Ratio**
Fresh Fuels and Auto Exhaust	Gasoline #1	261,985,000	5,100,000	ND (<500,000)	51:1	>524:1
	Gasoline #2	8,342,000	29,000	ND (<26,000)	288:1	>321:1
	Gasoline Exhaust	27,540	4,700	ND (<200)	7.1:1	>138:1
	JP8#1	6,010,000	20,000	6,100	301:1	985:1
	Diesel#1	1,195,000	16,000	730	75:1	1,637:1
	Diesel#2	974,000	2,900	3,500	336:1	278:1
	Diesel#3	208,200	1,000	120	208:1	1,735:1
	Diesel Exhaust	62	14	ND (<16)	4.4:1	>3.8:1
Site A (May 2011)	HAFB-VP26-B05(18)-HDOH	49,412,000	29,000	ND (<25,000)	1,704:1	>1,976:1
	HAFB-VP26-B05(24)-HDOH	94,275,000	470,000	ND (<,300,000)	201:1	>73:1
	HAFB-VP26-B07(20)-HDOH	38,267,500	58,000	ND (<1,200)	660:1	>31,890:1
	HAFB-VP26-B07(25)-HDOH	100,396,000	19,000	ND (<24,000)	5,284:1	>4,183:1
Site A (October 2011)	HAFB-VP26-B05(18)-HDOH	49,412,000	40,000	ND (<11,000)	1,235:1	>4,492:1
	HAFB-VP26-B05(24)-HDOH	94,275,000	280,000	ND (<260,000)	337:1	>363:1
	HAFB-VP26-B07(20)-HDOH	38,267,500	84,000	ND (<15,000)	456:1	>2,551:1
	HAFB-VP26-B07(25)-HDOH	100,396,000	45,000	ND (<33,000)	2,231:1	>3,042:1
Site B (August 2011)	HH-OU1C-MW10SG	63,835,000	12,000	ND (<16,000)	5,320:1	>3,990:1
	HH-OU1C-MW22R	23,217,000	7,700	ND (<10,000)	3,015:1	>2,322:1
	HH-OU1C-OTNS1	902,700	ND (<300)	ND (<1,600)	>3,009:1	>564:1
Site B (October 2011)	HH-OU1C-MW10SG	67,017,000	16,000	ND (<35,000)	4,189:1	>1,915:1
	HH-OU1C-MW22R	65,304,100	ND (<16,000)	ND (<85,000)	>4,082:1	>768:1
	HH-OU1C-OTNS1	699	ND (<3.1)	ND (<16)	>225:1	>44:1

Table 12 (cont.). TPH vs benzene and naphthalene data based on Summa canister data.

Site	Sample ID	[1]TPH (µg/m^3)	[2]Benzene (µg/m^3)	[2]Naphthalene (µg/m^3)	[1]TPH: Benzene Ratio	[1]TPH: Naphthalene Ratio
Site C	HAFB-SP43-VMP10	19,520,000	1,600	4,000	12,200:1	4,880:1
	HAFB-SP43-VMP11	19,982,000	ND (<480)	2,600	>41,629:1	7,685:1
	HAFB-SP43-VMP12	2,158	ND (<4.8)	ND (<50)	>450:1	>43:1
	HAFB-SP43-VMP16	37,830,000	1,500	ND (<2,600)	25,220:1	>14,550:1
	HAFB-SP43-VMP17	6,530,000	ND (<500)	ND (<2,600)	>13,060:1	>2,512:1
Site D (July 2011)	HAFB-ST03-B58 (347)	173,340	22	ND (<100)	7,879:1	>1,733:1
	HAFB-ST03-B58 (422)	80,200	14	ND (<65)	5,729:1	>1,234:1
	HAFB-ST03-B58 (492)	530,850	79	ND (<340)	6,720:1	>1,561:1
	HAFB-ST03-B59 (388)	510,700	32	ND (<330)	16,213:1	>1,548:1
Site D (October 2011)	HAFB-ST03-B58 (347)	624,000	ND (<32)	ND (<160)	>19,500:1	>3,900:1
	HAFB-ST03-B58 (422)	944,000	ND (<43)	ND (<220)	>21,953:1	>4,291:1
	HAFB-ST03-B58 (492)	898,000	ND (<42)	ND (<220)	>21,381:1	>4,082:1
	HAFB-ST03-B59 (388)	72,000	180	140	400:1	514:1
Site E (May 2011)	FV-GP-01-HDOH	89,600	ND (<28)	ND (<150)	>3,200:1	>597:1
	FV-GP-08-HDOH	3,781,000	865	50	75,620:1	6,302:1
	FV-GP-16R-HDOH	5,923,000	ND (<500)	ND (<2,600)	>11,846:1	>2,278:1
Site E (Oct 2011)	FV-GP-01-HDOH	28,472	ND (<4.7)	ND (<150)	>6,058:1	>190:1
	FV-GP-08-HDOH	1,609,700	49	125	32,851:1	12,878:1
	FV-GP-16R-HDOH	6,917,000	ND (<245)	ND (<2,600)	>28,233:1	>2,660:1

Table 12 (cont.). TPH vs benzene and naphthalene data based on Summa canister data.

Site	Sample ID	[1]TPH (µg/m³)	[2]Benzene (µg/m³)	[2]Naphthalene (µg/m³)	[1]TPH: Benzene Ratio	[1]TPH: Naphthalene Ratio
[3]GASCO (former MGP that produced benzene & naphthalene)	G-IPB20-HDOH	ND (2,500)	34,000	430	<0.1:1	<5.8
	G-IPH11-HDOH	ND (<840,000)	9,700,000	ND (<81,000)	<0.1:1	-
	G-IPH19-HDOH	689	480	ND (<26)	1.4:1	>28:1
	G-IP28-HDOH	ND (<1,340,000)	22,000,000	ND (<410,000)	<0.1:1	-
	G-SG12-HDOH	4,220	ND (<13)	ND (<70)	>325:1	>60:1
[3]Aloha Petroleum School Street (gasolines)	A-SV04-HDOH	52	ND (<4.4)	ND (<24)	-	-
	A-SVO13-HDOH	66	10	ND (<24)	6.6	-
	A-AS4-HDOH	62	ND (<4.2)	ND (<24)	-	-

Notes

Red: Not detected, laboratory Reporting Limit noted.

1. TPH calculated as sum of individual carbon ranges; excludes BTEXN.

2. Benzene and naphthalene concentrations as reported in MA-APH test data.

3. GASCO and Aloha Petroleum site data not carried forward for additional evaluation (see Section 5). TPH ratios not calculated for Aloha Petroleum site data due to non-detects for some individual TPH carbon ranges and low to non-detect levels of benzene and naphthalene.

Table 13a. Average TPH and benzene ratios for fuel vapor samples and samples from key sites and potential vapor intrusion risk driver based on Summa canister data.

Site/Fuel Type	**[1]TPH:Benzene Ratio**	**Vapor Intrusion Risk Driver (see Table 6a)**
Gasoline (Fresh Vapors)	170:1	TPH *could* drive vapor intrusion hazards depending on carbon range makeup and benzene target risk.
Diesel (Fresh Vapors)	206:1	TPH *could* drive vapor intrusion hazards depending on carbon range makeup and benzene target risk.
JP-8 (Fresh Vapors)	301:1	TPH *could* drive vapor intrusion hazards depending on carbon range makeup and benzene target risk.
Site A (JP-4/AVGAS)	1,513:1	TPH *could* drive vapor intrusion hazards depending on carbon range makeup and benzene target risk.
Site B (mixed fuels)	4,174:1	[2]TPH drives vapor intrusion hazards over benzene.
Site C (JP-8 +/- JP-4)	18,710:1	[2]TPH drives vapor intrusion hazards over benzene.
Site D (JP-4/AVGAS)	9,135:1	[2]TPH drives vapor intrusion hazards over benzene.
Site E (diesel)	54,236:1	[2]TPH drives vapor intrusion hazards over benzene.

1. See Table 9, TPH base on sum of Summa carbon range data. Average ratio for samples where both TPH and benzene were reported; individual samples with ND for benzene not included.
2. TPH noncancer Hazard Quotient for vapor intrusion will exceed 1.0 even though benzene risk is $<10^{-6}$.

Table 13b. Average TPH and naphthalene ratios for fuel vapor samples and samples from key sites and potential vapor intrusion risk driver based on Summa canister data.

Site/Fuel Type	[1]TPH:Naphthalene Ratio	Vapor Intrusion Risk Driver (see Table 6b)
Gasoline (Fresh Vapors)	-	Naphthalene not detected.
Diesel (Fresh Vapors)	1,217:1	TPH *could* drive vapor intrusion hazards depending on carbon range makeup and naphthalene target risk.
JP-8 (Fresh Vapors)	985:1	TPH *could* drive vapor intrusion hazards depending on carbon range makeup and naphthalene target risk.
Site A (JP-4/AVGAS)	-	Naphthalene not detected.
Site B (mixed fuels)	-	Naphthalene not detected.
Site C (JP-8 +/- JP-4)	6,283:1	TPH *could* drive vapor intrusion hazards depending on carbon range makeup and naphthalene target risk.
Site D (JP-4/AVGAS)	-	Naphthalene not detected.
Site E (diesel)	44,249:1	[2]TPH drives vapor intrusion hazards over naphthalene.

1. See Table 9; TPH base on sum of Summa carbon range data. Average ratio for samples where both TPH and naphthalene were reported; individual samples with ND for naphthalene not included.
2. TPH noncancer Hazard Quotient for vapor intrusion will exceed 1.0 even though naphthalene risk is $<10^{-6}$.

Table 14. Example TPH vs benzene and naphthalene data for other petroleum sites in Hawai‘i.

Site (see reference)	**Sample ID**	**[1]TPH ($\mu g/m^3$)**	**[1]Benzene ($\mu g/m^3$)**	**[1]Naphthalene ($\mu g/m^3$)**	**[2]TPH: Benzene Ratio**	**[2]TPH: Naphthalene Ratio**
[1]Hickam AFB SS156-J (mix gasolines & middle distillates)	VMP05	60,000,000	11,000	10,000	5,455:1	6,000:1
	VMP06	82,000,000	5,600	810	14,643:1	101,235:1
	VMP07	68,000,000	860	ND (<45)	79,070:1	>1,511,111:1
	VMP08	43,000,000	260	ND (<89)	165,385:1	>483,146:1
	VMP10	84,000,000	150,000	5,400	560:1	15,556:1
[1]Hickam AFB SS156-E (gasolines)	VMP30	3,000	5.2	34	577:1	88:1
	VMP31	3,500	2.7	44	1,296:1	80:1
	VMP32	3,600	9.7	33	371:1	109:1
	VMP33	3,900	16	27	244:1	144:1
	VMP34	3,000	4.9	40	612:1	75:1
	VMP3	39,000	130	ND (<30)	300:1	>1,300:1
	VMP04	620,000	1,800	51	344:1	12,157:1
	VMP08	6,900	19	28	363:1	246:1
	VMP09	1,000	2.2	48	455:1	21:1
	VMP10	98,000	250	ND (<30)	392:1	>3,267:1
	MP3-SS156E (14' bgs)	390,000,000	2,200,000	ND (< 17,000)	195:1	<22,941:1
[2]Hakuyosha Dry Cleaner (stoddard)	B1-SV	9,000	ND (<34)	-	>265:1	-
	B4-SV	1,300,000	ND (<1,800)	-	>722:1	-
	B8-SV1	1,200	ND (<32)	-	>38:1	-
	B10-SV	1,600	ND (<32)	-	>50:1	-
	B12-SV	8,200	ND (<32)	-	>256:1	-
[3]Challenger Loop, Pearl Harbor NB (middle distillates)	SG-1	4,880	1.3	39	3,754:1	125:1
	SG-2	4,596	1.3	ND (<27)	3,535:1	>170:1
	SG-3	4,534	0.9	ND (<25)	5,152:1	>181:1
	SG-4	4,719	1.7	ND (<26)	2,776:1	>182:1
	SG-5	4,152	ND (<0.7)	ND (<24)	>6,106:1	>173:1

Table 14 (cont.). Example TPH vs benzene and naphthalene data for other petroleum sites in Hawaiʻi.

Site (see reference)	**Sample ID**	**[1]TPH (µg/m^3)**	**[1]Benzene (µg/m^3)**	**[1]Naphthalene (µg/m^3)**	**[2]TPH: Benzene Ratio**	**[2]TPH: Naphthalene Ratio**
[4]Aloha Gas Station (gasolines)	S1	17,100,000	1,300	-	13,154:1	-
	S2	6,300,000	17,200	-	366:1	-
	S4	75,600	390	-	194:1	-
	S5	185,000	114	-	1,623:1	-
	S6	144,000	241	-	598:1	-
[5]ConocoPhillps Fuel Terminal (mix gasolines & middle distillates)	EVT-005	15,902,000	63,804	-	249:1	-
	EVT-007	194,356,000	2,010,000	-	97:1	-
	EV-014	106,012,000	382,822	-	277:1	-
	EV-025	14,577,000	350,920	-	42:1	-
	EVT-002	21,202,000	8,933	-	2,373:1	-
	EVT-012	5,742,000	766	-	7,496:1	-
	EV-026	27,828,000	23,607	-	1,179:1	-
	EV-041	3,500,000	650	-	5,385:1	-
[6]Kamehameha Schools Lipoa Place (gasoline-diesel mix?)	SV07	28,000	ND (<17.0)	3.4	>1,647:1	8,235:1
	SV10	74,000	900	20	82:1	3,700:1
	SV11	2,300,000	ND (<360)	ND (<2.2)	>6,389:1	>1,045,455:1
	SV13	140,000	ND (<52)	4	>2,692:1	>36,842:1
	SV14	180,000	670	13	269:1	>13,846:1
[7]Hickam AFB Bldg 1760 (gasoline)	SG002	965,300	5,037	43	192:1	22,449:1
	SG004	20,853	142	2.9	147:1	7,191:1
[8]Hickam AFB Bldg CG110 (middle distillates)	SG05	8,790,000	6	1,000	1,598,182:1	8,790:1
	SG06	18,400,000	12	150	1,600,000:1	122,667:1

a. TPH generally reported as TPHgasoline and includes BTEXN; data usually based on TO-15 Summa canister analysis but varies between sites; TPH noted for Hickam AFB Bldg 1760 calculated as sum of individual carbon ranges.

b. Benzene and naphthalene respectively subtracted from TPH for calculation of ratios.

Table 14 (cont.). TPH vs benzene and naphthalene data for other petroleum sites in Hawai‘i.

Note: For example only; not intended to be representative of overall conditions at subject site.

References

1. Record of Decision and Response Action Memorandum Spill Site 156 Feasibility Study, Proposed Plan, and Record of Decision/Response Action Memorandum, Hickam AFB, Honolulu, Hawai'i, November 2009.
2. Limited Site Investigation, Hakuyosha International Inc., Honolulu, Hawai'i, June 2007.
3. Environmental Hazard Evaluation Report, Challenger Loop Site, Hickam AFB, Honolulu, Hawai'i, April 2007.
4. Soil Gas Investigation, Aloha Petroleum, Ltd., 1841 Palolo Avenue, Honolulu, Hawai'i, 2008.
5. Site Characterization, Former ConocoPhillips Terminal, Honolulu, Honolulu, Hawai'i, September 2007
6. DRAFT Soil Vapor Assessment (May 2011), 98-121 Lipoa Place, Aiea, Oahu, Hawai'i.
7. Additional Site Characterization Report for Building 1760, Hickam AFB, Honolulu, Hawai'i, November 2009.
8. Final Remedial Investigation Report for Site CG110 (March 9, 2007), Hickam AFB, Honolulu, Hawai'i, Appendix H, Complete Processed Data Listings, Table 5.

Table 15. Reported TPH carbon range concentrations in TO-15 Summa canister soil gas samples.

Site	**Sample ID**	**Reported Carbon Range Concentrations (Summa samples)**			
		C9-10 Aromatics ($\mu g/m^3$)	**C5-8 Aliphatics ($\mu g/m^3$)**	**C9-12 Aliphatics ($\mu g/m^3$)**	**Sum Carbon Ranges ($\mu g/m^3$)**
Fresh Fuels and Auto Exhaust	Gasoline#1	1,700,000	260,000,000	285,000	261,985,000
	Gasoline #2	12,000	8,200,000	130,000	8,342,000
	Gasoline Exhaust	2,200	25,000	340	27,540
	JP8#1	210,000	4,500,000	1,300,000	6,010,000
	Diesel#1	25,000	1,000,000	170,000	1,195,000
	Diesel#2	94,000	320,000	560,000	974,000
	Diesel#3	5,200	160,000	43,000	208,200
	Diesel Exhaust	ND (<18)	45	ND (<18)	54
Site A (JP-4/AVGAS) (May 2011)	HAFB-VP26-B05(18)-HDOH	12,000	18,000,000	330,000	18,342,000
	HAFB-VP26-B05(24)-HDOH	1,200,000	160,000,000	1,400,000	162,600,000
	HAFB-VP26-B07(20)-HDOH	8,000	12,000,000	220,000	12,228,000
	HAFB-VP26-B07(25)-HDOH	11,500	58,000,000	78,000	58,089,500
Site A (JP-4/AVGAS) (October 2011)	HAFB-VP26-B05(18)	12,000	48,000,000	1,400,000	49,412,000
	HAFB-VP26-B05(24)	125,000	94,000,000	150,000	94,275,000
	HAFB-VP26-B07(20)	7,500	38,000,000	260,000	38,267,500
	HAFB-VP26-B07(25)	16,000	100,000,000	380,000	100,396,000
Site B (mixed fuels) (August 2011)	HH-OU1C-MW10SG	35,000	62,000,000	1,800,000	63,835,000
	HH-OU1C-MW22R	17,000	22,000,000	1,200,000	23,217,000
	HH-OU1C-OTNS1	2,700	740,000	160,000	902,700
Site B (mixed fuels) (October 2011)	HH-OU1C-MW10SG	17,000	66,000,000	1,000,000	67,017,000
	HH-OU1C-MW22R	4,100	63,000,000	2,300,000	65,304,100
	HH-OU1C-OTNS1	8.0	620	71	699

Table 15 (cont.). Reported TPH carbon range concentrations in TO-15 Summa canister soil gas samples.

		Reported Carbon Range Concentrations (Summa samples)			
Site	**Sample ID**	**C9-10 Aromatics $(\mu g/m^3)$**	**C5-8 Aliphatics $(\mu g/m^3)$**	**C9-12 Aliphatics $(\mu g/m^3)$**	**Sum Carbon Ranges $(\mu g/m^3)$**
Site C (JP-8 +/- JP-4)	HAFB-SP43-VMP10	120,000	13,000,000	6,400,000	19,520,000
	HAFB-SP43-VMP11	82,000	14,000,000	5,900,000	19,982,000
	HAFB-SP43-VMP12	28	1,500	630	2,158
	HAFB-SP43-VMP16	130,000	32,000,000	5,700,000	37,830,000
	HAFB-SP43-VMP17	30,000	4,600,000	1,900,000	6,530,000
Site D (JP-4/AVGAS) (July 2011)	HAFB-ST03-B58 (347)	340	130,000	43,000	173,340
	HAFB-ST03-B58 (422)	200	64,000	16,000	80,200
	HAFB-ST03-B58 (492)	850	420,000	110,000	530,850
	HAFB-ST03-B59 (388)	700	410,000	100,000	510,700
Site D (JP-4/AVGAS) (October 2011)	HAFB-ST03-B58 (347)	44,000	320,000	260,000	624,000
	HAFB-ST03-B58 (422)	44,000	450,000	450,000	944,000
	HAFB-ST03-B58 (492)	58,000	460,000	380,000	898,000
	HAFB-ST03-B59 (388)	10,000	30,000	32,000	72,000
Site E (diesel) (May 2011)	FV-GP-01-HDOH	1,200	9,400	79,000	89,600
	FV-GP-08-HDOH	61,000	520,000	3,200,000	3,781,000
	FV-GP-16R-HDOH	23,000	1,100,000	4,800,000	5,923,000
	FV-GP-17-HDOH	310	7,000	11,000	18,310
Site E (diesel) (Oct 2011)	FV-GP-01-HDOH#2	72	8,400	20,000	28,472
	FV-GP-08-HDOH#2	9,700	680,000	920,000	1,609,700
	FV-GP-16R-HDOH#2	17,000	1,700,000	5,200,000	6,917,000

Red: Laboratory Reporting Limit noted or 1/2 MRL used for summation of carbon range data if other carbon ranges detected.

Table 16. Relative TPH carbon range concentrations in Summa canister soil gas samples and equivalent, weighted inhalation reference Concentration (RfC).

		Relative Carbon Range Composition (Summa samples)			
Site	**Sample ID**	**C9-10 Aromatics (RfC=100 $\mu g/m^3$)**	**C5-8 Aliphatics (RfC=600 $\mu g/m^3$)**	**C9-12 Aliphatics (RfC=100 $\mu g/m^3$)**	**[1]Weighted TPH RfC ($\mu g/m^3$)**
Fresh Fuels and Auto Exhaust	Gasoline#1	0.6%	99%	0.1%	578
	Gasoline #2	0.1%	98%	1.6%	553
	Gasoline Exhaust	8%	91%	1%	411
	JP8#1	3.5%	75%	22%	266
	Diesel#1	2.1%	84%	14%	330
	Diesel#2	9.7%	33%	57%	138
	Diesel#3	2.5%	77%	21%	278
	Diesel Exhaust	12%	73%	15%	256
Site A (JP-4/AVGAS) (May 2011)	HAFB-VP26-B05(18)-HDOH	0.1%	98%	1.8%	549
	HAFB-VP26-B05(24)-HDOH	0.7%	98%	0.9%	556
	HAFB-VP26-B07(20)-HDOH	0.1%	98%	1.8%	549
	HAFB-VP26-B07(25)-HDOH	0.0%	100%	0.1%	595
	HAFB-VP26-B08(21)-HDOH	0.1%	88%	12%	373
Site A (JP-4/AVGAS) (October 2011)	HAFB-VP26-B05(18)	0.0%	97%	2.8%	525
	HAFB-VP26-B05(24)	0.1%	100%	0.2%	591
	HAFB-VP26-B07(20)	0.0%	99%	0.7%	580
	HAFB-VP26-B07(25)	0.0%	100%	0.4%	588
Site B (mixed fuels) (August 2011)	HH-OU1C-MW10SG	0.1%	97%	3%	525
	HH-OU1C-MW22R	0.1%	95%	5%	475
	HH-OU1C-OTNS1	0.3%	82%	18%	316
Site B (mixed fuels) (October 2011)	HH-OU1C-MW10SG	0.0%	98%	1.5%	558
	HH-OU1C-MW22R	0.0%	96%	3.5%	510
	HH-OU1C-OTNS1	1.1%	89%	10%	383

Table 16 (cont.). Relative TPH carbon range concentrations in Summa canister soil gas samples and equivalent, weighted inhalation reference Concentration (RfC).

		Relative Carbon Range Composition (Summa samples)			
Site	**Sample ID**	**C9-10 Aromatics (RfC=100 µg/m^3)**	**C5-8 Aliphatics (RfC=600 µg/m^3)**	**C9-12 Aliphatics (RfC=100 µg/m^3)**	**[1]Weighted TPH RfC (µg/m^3)**
Site C (JP-8 +/- JP-4)	HAFB-SP43-VMP10	0.6%	67%	33%	225
	HAFB-SP43-VMP11	0.4%	70%	30%	240
	HAFB-SP43-VMP12	1.3%	70%	29%	238
	HAFB-SP43-VMP16	0.3%	85%	15%	339
	HAFB-SP43-VMP17	0.5%	70%	29%	242
Site D (JP-4/AVGAS) (July 2011)	HAFB-ST03-B58 (347)	0.2%	75%	25%	267
	HAFB-ST03-B58 (422)	0.2%	80%	20%	299
	HAFB-ST03-B58 (492)	0.2%	79%	21%	294
	HAFB-ST03-B59 (388)	0.1%	80%	20%	302
Site D (JP-4/AVGAS) (October 2011)	HAFB-ST03-B58 (347)	7.1%	51%	42%	175
	HAFB-ST03-B58 (422)	4.7%	48%	48%	166
	HAFB-ST03-B58 (492)	6.5%	51%	42%	174
	HAFB-ST03-B59 (388)	14%	42%	44%	153
Site E (diesel) (May 2011)	FV-GP-01-HDOH	1.3%	10%	88%	110
	FV-GP-08-HDOH	1.6%	14%	85%	113
	FV-GP-16R-HDOH	0.4%	19%	81%	118
	FV-GP-17-HDOH	1.7%	38%	60%	147
Site E (diesel) (Oct 2011)	FV-GP-01-HDOH#2	0.3%	30%	70%	133
	FV-GP-08-HDOH#2	0.6%	42%	57%	154
	FV-GP-16R-HDOH#2	0.2%	25%	75%	126

Red: Not detected, relative percentage based on 1/2 MRL.

Table 17a. Summary of average TPH carbon range composition for fuels and samples from key sites based on Summa canister samples.

Site/Fuel Type	Average Carbon Range Composition (Summa Canister Data) Aromatics C9-10	Aliphatics C5-8	Aliphatics C9-12	[1]Weighted RfC (µg/m^3)	[2]Indoor Air Action Level Residential (µg/m^3)	[3]Soil gas Action Level Residential (µg/m^3)	[2]Indoor Air Action Level C/I (µg/m^3)	[3]Soil gas Action Level C/I (µg/m^3)
Gasoline (Fresh Vapors)	0.4%	99%	0.8%	565	590	590,000	820	1,649,000
Diesel (Fresh Vapors)	4.7%	64%	31%	216	250	250,000	230	631,000
JP-8 (Fresh Vapors)	0.6%	67%	33%	225	230	230,000	330	657,000
Site A (JP-4/AVGAS)	0.2%	96%	3.3%	510	530	530,000	740	1,480,000
Site B (mixed fuels)	0.3%	93%	6.8%	443	460	460,000	650	1,240,000
Site C (JP-8 +/- JP-4)	0.6%	72%	27%	251	260	260,000	370	733,000
Site D (JP-4/AVGAS)	4.1%	63%	33%	211	220	220,000	310	616,000
Site E (diesel)	0.9%	25%	74%	127	130	130,000	190	371,000

1. Based on 2009 USEPA-NCEA Reference Concentrations for individual carbon ranges (C9+ aromatics = 100 µg/m^3, C5-C8 aliphatics = 600 µg/m^3, C9+ aliphatics = 100 µg/m^3).
2. Based on model and exposure parameter assumptions discussed in the HEER office EHE guidance (HDOH 2011).
3. Soil gas action levels based indoor air:subslab soil gas attenuation factor of 0.001 (1/1,000) for residential structures and 0.0005 (1/2,000) for commercial/industrial structures (HDOH 2011).

Table 17b. Relative contribution of target carbon ranges to total TPH noncancer hazard (average of Summa canister data).

	Relative Contribution to Total TPH Noncancer Hazard (TO-15 Data)		
	Aromatics	**Aliphatics**	
Site/Fuel Type	**C9-10**	**C5-8**	**C9-12**
Gasoline (Fresh Vapors)	2.3%	93%	4.9%
Diesel (Fresh Vapors)	10%	22%	67%
JP-8 (Fresh Vapors)	1.4%	24%	75%
Site A (JP-4/AVGAS)	1.1%	81%	18%
Site B (mixed fuels)	1.2%	69%	31%
Site C (JP-8 +/- JP-4)	1.6%	29%	69%
Site D (JP-4/AVGAS)	8.8%	21%	70%
Site E (diesel)	1.1%	5.1%	95%

Table 18. Reported TPH carbon range concentrations in sorbent tube soil gas samples.

		Reported Carbon Range Concentrations (μg/m^3)					
		Aromatics		**Aliphatics**			**Sum Carbon Ranges**
Site	**Sample ID**	**C9-10**	**C11-C16**	**C5-8**	**C9-12**	**C13-18**	
Fresh Fuels and Auto Exhaust	Gasoline #2 (A)	340,000	20,000	16,000,000	7,000	20,000	16,387,000
	Gasoline Exhaust (A)	1,250	5,000	34,000	34,000	5,000	79,250
	JP8#1 (A)	190,000	17,000	1,800,000	1,300,000	150,000	3,457,000
	Diesel#3-HDOH (A)	23,000	5,000	470,000	190,000	78,000	766,000
	Diesel Exhaust (A)	ND (<500)	ND (<2000)	ND (<460)	ND (<700)	ND (<2000)	ND (<5,660)
Site A (JP-4/AVGAS)	HAFB-VP26-B05(18)-HDOH (A)	9,300	4,000	12,000,000	750,000	4,000	12,767,300
	HAFB-VP26-B05(24)-HDOH (A)	17,000	4,000	64,000,000	430,000	4,000	64,455,000
	HAFB-VP26-B07(20)-HDOH (A)	5,400	4,000	13,000,000	180,000	4,000	13,193,400
	HAFB-VP26-B07(25)-HDOH (A)	5,200	4,000	29,000,000	220,000	4,000	29,233,200
Site B (mixed fuels)	HH-OU1C-MW10SG (A)	31,000	4,000	35,000,000	1,900,000	13,000	36,948,000
	HH-OU1C-MW22R (A)	110,000	4,000	20,000,000	2,800,000	120,000	23,034,000
	HH-OU1C-OTNS1 (A)	ND (<500)	ND (<2000)	ND (<460)	ND (<700)	ND (<2000)	ND (<5,660)
Site C (JP-8 +/- JP-4)	HAFB-SP43-VMP10 (A)	180,000	4,000	13,000,000	650,000	66,000	13,900,000
	HAFB-SP43-VMP11 (A)	140,000	4,000	17,000,000	6,200,000	100,000	23,444,000
	HAFB-SP43-VMP12 (A)	ND (<500)	ND (<2000)	ND (<460)	ND (<700)	ND (<2000)	ND (<5,660)
	HAFB-SP43-VMP16 (A)	130,000	1,000	26,000,000	4,600,000	12,000	30,743,000
	HAFB-SP43-VMP17 (A)	210	850	7,500	2,800	850	12,210

Table 18 (cont.). Reported TPH carbon range concentrations in sorbent tube soil gas samples.

Site	**Sample ID**	**Reported Carbon Range Concentrations (µg/m³)**					
		Aromatics		**Aliphatics**			**Sum Carbon Ranges**
		C9-10	**C11-C16**	**C5-8**	**C9-12**	**C13-18**	
Site D (JP-4/AVGAS)	HAFB-ST03-B58 (347) (A)	110,000	1,000	830,000	580,000	4,800	1,525,800
	HAFB-ST03-B58 (422) (A)	92,000	1,000	850,000	590,000	3,600	1,536,600
	HAFB-ST03-B58 (492) (A)	100,000	1,000	870,000	640,000	7,000	1,618,000
	HAFB-ST03-B59 (388) (A)	7,600	1,000	120,000	38,000	2,400	169,000
Site E (diesel)	FV-GP-01-HDOH (A)	210	850	11,000	13,000	850	25,910
	FV-GP-08-HDOH (A)	11,000	1,000	900,000	640,000	6,000	1,558,000
	FV-GP-16R-HDOH (A)	32,000	4,000	3,200,000	5,500,000	130,000	8,866,000

Red: Not detected, laboratory Reporting Limit noted or 1/2 MRL used for summation of carbon range data if other carbon ranges detected.

Table 19. Relative TPH carbon range concentrations in sorbent tube soil gas samples and equivalent, weighted inhalation Reference Concentration (RfC).

		Relative Carbon Range Composition					**[2]Weighted TPH RfC ($\mu g/m^3$)**
		Aromatics		**Aliphatics**			
Site	**Sample ID**	**C9-10**	**C11-C16**	**C5-8**	**C9-12**	**C13-18**	
Fresh Fuels and Auto Exhaust	Gasoline #2 (A)	2.1%	0.1%	98%	0.0%	0.0%	537
	Gasoline Exhaust (A)	1.6%	6.0%	43%	43%	6.3%	156
	JP8#1 (A)	5.5%	0.5%	52%	38%	4.3%	177
	Diesel#3-HDOH (A)	3.0%	1.0%	61%	25%	10%	205
	Diesel Exhaust (A)	-	-	-	-	-	-
Site A (JP-4/AVGAS)	HAFB-VP26-B05(18)-HDOH (A)	0.1%	0.0%	94.0%	5.9%	0.0%	461
	HAFB-VP26-B05(24)-HDOH (A)	0.0%	0.0%	99.3%	0.7%	0.0%	580
	HAFB-VP26-B07(20)-HDOH (A)	0.0%	0.0%	98.5%	1.4%	0.0%	559
	HAFB-VP26-B07(25)-HDOH (A)	0.0%	0.0%	99.2%	0.8%	0.0%	577
Site B (mixed fuels)	HH-OU1C-MW10SG (A)	0.1%	0.0%	94.7%	5.1%	0.0%	475
	HH-OU1C-MW22R (A)	0.5%	0.0%	86.8%	12.2%	0.5%	362
	HH-OU1C-OTNS1 (A)	-	-	-	-	-	-
Site C (JP-8 +/- JP-4)	HAFB-SP43-VMP10 (A)	1.3%	0.0%	94%	5%	0.5%	453
	HAFB-SP43-VMP11 (A)	0.6%	0.0%	73%	26%	0.4%	253
	HAFB-SP43-VMP12 (A)	-	-	-	-	-	-
	HAFB-SP43-VMP16 (A)	0.4%	0.0%	85%	15%	0.04%	339
	HAFB-SP43-VMP17 (A)	1.7%	7.0%	61%	23%	7.0%	205
Site D (JP-4/AVGAS)	HAFB-ST03-B58 (347) (A)	7.2%	0.1%	54.4%	38.0%	0.3%	183
	HAFB-ST03-B58 (422) (A)	6.0%	0.1%	55.3%	38.4%	0.2%	186
	HAFB-ST03-B58 (492) (A)	6.2%	0.1%	53.8%	39.6%	0.4%	181
	HAFB-ST03-B59 (388) (A)	4.5%	0.6%	71.0%	22.5%	1.4%	245
Site E (diesel)	FV-GP-01-HDOH (A)	0.8%	3.3%	42%	50%	3.3%	155
	FV-GP-08-HDOH (A)	0.7%	0.1%	58%	41%	0.4%	193
	FV-GP-16R-HDOH (A)	0.4%	0.0%	36%	62%	1.5%	143

Red: Not detected, relative percentage based on 1/2 MRL.

Table 20a. Summary of average TPH carbon range composition for fuels and samples from key sites based on sorbent tube samples.

Site/Fuel Type	**Average Carbon Range Composition (Sorbent Tube Data)**					**[1]Weighted RfC (µg/m³)**	**[2]Indoor Air Action Level Residential (µg/m³)**	**[3]Soil gas Action Level Residential (µg/m³)**	**[2]Indoor Air Action Level C/I (µg/m³)**	**[3]Soil gas Action Level C/I (µg/m³)**
	Aromatics		**Aliphatics**							
	C9-10	**C11-C16**	**C5-8**	**C9-12**	**C13-18**					
Gasoline (Fresh Vapors)	2.1%	0.1%	98%	0.0%	0.1%	537	560	560,000	780	1,568,000
Diesel (Fresh Vapors)	3.0%	0.7%	61.4%	24.8%	10.2%	205	210	210,000	300	599,000
JP-8 (Fresh Vapors)	5.5%	0.5%	52%	38%	4.3%	177	180	180,000	260	517,000
Site A (JP-4/AVGAS)	0.0%	0.0%	98%	2.2%	0.0%	539	560	560,000	790	1,574,000
Site B (mixed fuels)	0.3%	0.0%	91%	8.6%	0.3%	411	430	430,000	600	1,200,000
Site C (JP-8 +/- JP-4)	1.0%	1.8%	78%	17%	2.0%	286	300	300,000	420	835,000
Site D (JP-4/AVGAS)	6.0%	0.2%	59%	35%	0.6%	196	200	200,000	290	572,000
Site E (diesel)	0.6%	1.1%	45%	51%	1.7%	161	170	170,000	240	470,000

1. Based on 2009 USEPA-NCEA Reference Concentrations for individual carbon ranges (C9+ aromatics = 100 µg/m³, C5-C8 aliphatics = 600 µg/m³, C9+ aliphatics = 100 µg/m³).

2. Based on model and exposure parameter assumptions discussed in the HEER office EHE guidance (HDOH 2011).

Table 20b. Relative contribution of target carbon ranges to total TPH noncancer hazard (average of sorbent tube data).

Site/Fuel Type	Relative Contribution to Total TPH Noncancer Hazard (TO-17 Data)				
	Aromatics		**Aliphatics**		
	C9-10	**C11-C16**	**C5-8**	**C9-12**	**C13-18**
Gasoline (Fresh Vapors)	12%	0.7%	87%	0.2%	0.7%
Diesel (Fresh Vapors)	6.2%	1.3%	20%	51%	21%
JP-8 (Fresh Vapors)	9.8%	0.9%	15%	67%	7.7%
Site A (JP-4/AVGAS)	0.2%	0.1%	87%	12%	0.1%
Site B (mixed fuels)	1.2%	0.1%	61%	37%	1.2%
Site C (JP-8 +/- JP-4)	2.9%	5.1%	36%	50%	5.7%
Site D (JP-4/AVGAS)	12%	0.4%	18%	68%	1.2%
Site E (diesel)	1.0%	1.8%	12%	84%	2.8%

Table 21. Comparison of series sorbent tube samples for potential breakthrough (Tube A closest to well point).

Site	**Sample ID**	**Highest of TPHg and TPHd ($\mu g/m^3$)**		**Total TPH (Tube A+Tube B)**	**[1]Percent Breakthrough**
		Upstream (Tube A)	**Downstream (Tube B)**		
Fresh Fuels and Auto Exhaust	Gasoline #2	20,000,000	ND (100,000)	-	-
	Gasoline Exhaust	310,000	ND (100,000)	-	-
	JP8#1	2,100,000	120,000	2,220,000	5.4%
	Diesel#3-HDOH	2,000,000	ND (100,000)	-	-
	Diesel Exhaust	160,000	ND (100,000)	-	-
Site A (JP-4/AVGAS)	HAFB-VP26-B05(18)-HDOH	19,000,000	33,000	19,033,000	0.2%
	HAFB-VP26-B05(24)-HDOH	>37,000,000	ND (20,000)	-	-
	HAFB-VP26-B07(20)-HDOH	14,000,000	ND (20,000)	-	-
	HAFB-VP26-B07(25)-HDOH	29,000,000	ND (20,000)	-	-
Site B (mixed fuels)	HH-OU1C-MW10SG	30,000,000	ND (20,000)	-	-
	HH-OU1C-MW22R	29,000,000	39,000	29,039,000	0.1%
	HH-OU1C-OTNS1	ND (20,000)	ND (20,000)	-	-
Site C (JP-8 +/- JP-4)	HAFB-SP43-VMP10	18,000,000	ND (20,000)	-	-
	HAFB-SP43-VMP11	4,600,000	ND (20,000)	-	-
	HAFB-SP43-VMP12	ND (20,000)	ND (20,000)	-	-
	HAFB-SP43-VMP16	26,000,000	ND (20,000)	-	-
	HAFB-SP43-VMP17	20,000	ND (17,000)	-	-

Table 21 (cont.). Comparison of series sorbent tube samples for potential breakthrough (Tube A closest to well point).

Site	Sample ID	Sum of Detected TPH Carbon Range Fractions ($\mu g/m^3$)		Total TPH (Tube A+Tube B)	[1]Percent Breakthrough
		Upstream (Tube A)	Downstream (Tube B)		
Site D (JP-4/AVGAS) (October 2011)	HAFB-ST03-B58 (347)	1,600,000	26,000	1,626,000	1.6%
	HAFB-ST03-B58 (422)	1,600,000	ND (20,000)	-	-
	HAFB-ST03-B58 (492)	1,600,000	ND (20,000)	-	-
	HAFB-ST03-B59 (388)	180,000	ND (20,000)	-	-
Site E (diesel) (Oct 2011)	FV-GP-01-HDOH#2	27,000	19,000	46,000	41%
	FV-GP-08-HDOH#2	860,000	ND (20,000)	-	-
	FV-GP-16R-HDOH#2	10,000,000	ND (20,000)	-	-

1. Reported TPH in Tube B (downstream tube, closest to sampling syringe) divided by sum of TPH reported in Tube A plus Tube B.

Table 22. Vapor intrusion risk posed by TPH in soil gas at different target risks for benzene based on the average TPH carbon range makeup and TPH:Benzene ratio in vapor samples collected over fresh fuel or soil gas samples from key study sites based on comparison to Summa canister carbon range data.

			[3]TPH Vapor Intrusion Risk (HQ) at noted Benzene Concentration and Risk (Based on MA-APH Summa data)			
Site/Fuel Type	**[1]Average Soil Gas TPH:Benzene Ratio**	**[2]TPH Indoor Air Action Level ($\mu g/m^3$)**	**Benzene= 31 $\mu g/m^3$ (VI Risk=10^{-4})**	**Benzene= 3.1 $\mu g/m^3$ (VI Risk=10^{-5})**	**Benzene= 0.31 $\mu g/m^3$ (VI Risk=10^{-6})**	**[4]Vapor Intrusion Risk Driver**
Gasoline (Fresh Vapors)	170:1	590	8.9	0.9	0.1	TPH begins to drive vapor intrusion risk when benzene in soil gas or indoor exceeds a cancer risk of 10^{-4}.
Diesel (Fresh Vapors)	206:1	230	28	2.8	0.3	TPH begins to drive vapor intrusion risk as benzene in soil gas or indoor approaches a cancer risk of 10^{-5}.
JP-8 (Fresh Vapors)	301:1	230	41	4.1	0.4	
Site A (JP-4/AVGAS)	1,513:1	530	89	8.9	0.9	TPH begins to drive vapor intrusion risk when benzene in soil gas or indoor exceeds a cancer risk of 10^{-6}.
Site B (mixed fuels)	4,174:1	460	281	28	2.8	TPH drives vapor intrusion risk even when benzene in soil gas or indoor air is below a cancer risk of 10^{-6}.
Site C (JP-8 +/- JP-4)	18,710:1	260	2,231	223	22	
Site D (JP-4/AVGAS)	9,135:1	220	1,287	129	13	
Site E (diesel)	18,611:1	130	4,438	444	44	

1. See Tables 12 and 13a; TPH calculated as sum of carbon range data for Summa canister samples (does not consider >C10 aromatics or >C12 aliphatics).
2. See Table 17. Based on weighted TPH toxicity using Summa canister carbon range data and a noncancer Hazard Quotient of 1.0.
3. TPH vapor intrusion noncancer hazard quotient = (Soil Gas TPH:Benzene Ratio x Benzene Concentration)/TPH Indoor Air Action Level. Benzene indoor air action levels presented and discussed in HEER EHE guidance (HDOH 2011).
4. TPH drives vapor intrusion risk when HQ>1.0 at noted target benzene concentration and risk.

Table 23. Vapor intrusion risk posed by TPH in soil gas at different target risks for benzene based on the average TPH carbon range makeup and TPH:Benzene ratio in vapor samples collected over fresh fuel or soil gas samples from key study sites based on comparison to sorbent tube carbon range data.

			[3]TPH Vapor Intrusion Risk (HQ) at noted Benzene Concentration and Risk (Based on MA-APH sorbent tube data)			
Site/Fuel Type	**[1]Average Soil Gas TPH:Benzene Ratio**	**[2]TPH Indoor Air Action Level (µg/m^3)**	**Benzene= 31 µg/m^3 (VI Risk=10^{-4})**	**Benzene= 3.1 µg/m^3 (VI Risk=10^{-5})**	**Benzene= 0.31 µg/m^3 (VI Risk=10^{-6})**	**[4]Vapor Intrusion Risk Driver**
Gasoline (Fresh Vapors)	152:1	560	8.4	0.8	0.1	TPH begins to drive vapor intrusion risk when benzene in soil gas or indoor exceeds a cancer risk of 10^{-4}.
Diesel (Fresh Vapors)	389:1	210	57	5.7	0.6	TPH begins to drive vapor intrusion risk as benzene in soil gas or indoor approaches a cancer risk of 10^{-5}.
JP-8 (Fresh Vapors)	247:1	180	42	4.2	0.4	
Site A (JP-4/AVGAS)	965:1	560	53	5.3	0.5	
Site B (mixed fuels)	5,514:1	430	398	40	4.0	TPH drives vapor intrusion risk even when benzene in soil gas or indoor air is below a cancer risk of 10^{-6}.
Site C (JP-8 +/- JP-4)	12,772:1	300	1,320	132	13	
Site D (JP-4/AVGAS)	12,915:1	200	2,002	200	20	
Site E (diesel)	20,570:1	170	3,751	375	38	

1. See Tables 9 and 15. Average of benzene data based on Summa canister samples divided by TPH calculated as sum of carbon range data for sorbent tube samples (includes consideration of >C10 aromatics or >C12 aliphatics).
2. See Tables 19 and 20. Based on weighted TPH toxicity using sorbent tube carbon range data and a noncancer Hazard Quotient of 1.0.
3. TPH vapor intrusion noncancer hazard quotient = (Soil Gas TPH:Benzene Ratio x Benzene Concentration)/TPH Indoor Air Action Level. Benzene indoor air action levels presented and discussed in HEER EHE guidance (HDOH 2011).
4. TPH drives vapor intrusion risk when HQ>1.0 at noted target benzene concentration and risk.

Table 24. Vapor intrusion risk posed by TPH in soil gas at different target risks for ethylbenzene based on the average TPH carbon range makeup and TPH:Ethylbenzene ratio in vapor samples collected over fresh fuel or soil gas samples from key study sites based on comparison to Summa canister carbon range data.

			[1]TPH Vapor Intrusion Hazard Quotient vs Ethylbenzene Concentration and Risk			
Site/Fuel Type	**[1]TPH: Ethylbenzene Ratio (Summa data)**	**[1]TPH Indoor Air Action Level (µg/m^3)**	**Ethylbenzene =97 µg/m^3 (VI Risk=10^{-4})**	**Ethylbenzene =9.7 µg/m^3 (VI Risk=10^{-5})**	**Ethylbenzene =0.97 µg/m^3 (VI Risk=10^{-6})**	**Vapor Intrusion Risk Driver**
Gasoline (Fresh Vapors)	442:1	590	73	7.3	0.7	TPH begins to drive vapor intrusion risk as ethylbenzene in soil gas or indoor approaches a cancer risk of 10^{-5}.
Diesel (Fresh Vapors)	113:1	230	47	4.7	0.5	
JP-8 (Fresh Vapors)	273:1	230	115	12	1.2	TPH begins to drive vapor intrusion risk when ethylbenzene in soil gas or indoor air is below a cancer risk of 10^{-6}.
Site A (JP-4/AVGAS)	4,033:1	530	738	74	7.4	
Site B (mixed fuels)	-	460	-	-	-	
Site C (JP-8 +/- JP-4)	6,983:1	260	2,605	261	26	
Site D (JP-4/AVGAS)	1,567:1	220	691	69	6.9	
Site E (diesel)	34,373:1	130	25,647	2,565	256	

1. See Table 9; TPH calculated as sum of carbon range data for Summa canister tube samples (does not includes consideration of >C10 aromatics or >C12 aliphatics).
2. See Table 17. Based on weighted TPH toxicity using Summa canister carbon range data and a noncancer Hazard Quotient of 1.0.
3. TPH vapor intrusion noncancer hazard quotient = (Soil Gas TPH:Ethylbenzene Ratio x Ethylbenzene Concentration)/TPH Indoor Air Action Level. Ethylbenzene indoor air action levels presented and discussed in HEER EHE guidance (HDOH 2011).
4. TPH drives vapor intrusion risk when HQ>1.0 at noted target ethylbenzene concentration and risk.

Table 25. Summary of TPH versus benzene as the vapor intrusion risk driver for vapors over fresh fuel and samples collected at key study sites.

Site/Fuel Type	**Vapor Intrusion Risk Driver**	
	TPH Drives Risk	**[1]Benzene Drives Risk**
Gasoline (Fresh Vapors)		X
Diesel (Fresh Vapors)		X
JP-8 (Fresh Vapors)		X
Site A (JP-4/AVGAS)	X	X
Site B (mixed fuels)	X	
Site C (JP-8 +/- JP-4)	X	
Site D (JP-4/AVGAS)	X	
Site E (diesel)	X	

1. Assuming a minimum, target benzene cancer risk of 10^{-5} for fresh fuels and 10^{-6} for aged release sites..

Table 26a. Comparison of laboratory methods for Total Petroleum Hydrocarbons (TPH) in soil gas samples (Phase II data).

Sample ID	**TO-3 (TPHg)**	**TO-15 (TPHg)**	**TO-17 (TPHg)**	**[1]TO-17 (TPHd)**	**TO-15 MA-APH (sum of carbon ranges)**	**TO-17 MA-APH (sum of carbon ranges)**
Gasoline #2	3,800,000	26,000,000	20,000,000	ND (<400,000)	8,342,000	16,387,000
JP8#1	7,200,000	14,000,000	2,100,000	380,000	6,010,000	3,457,000
Diesel#3-HDOH	540,000	570,000	1,100,000	2,000,000	208,200	766,000
HAFB-SP43-VMP10	22,000,000	40,000,000	18,000,000	730,000	19,520,000	13,900,000
HAFB-SP43-VMP11	30,000,000	45,000,000	4,600,000	710,000	19,982,000	23,444,000
HAFB-SP43-VMP12	3,200	6,100	10,000	ND (<20,000)	2,158	ND (<5,660)
HAFB-SP43-VMP16	82,000,000	86,000,000	26,000,000	320,000	37,830,000	30,743,000
HAFB-SP43-VMP17	8,000,000	11,000,000	20,000	ND (<17,000)	6,530,000	12,210
FV-GP-01-HDOH	39,000	53,000	27,000	ND (<17,000)	28,472	25,910
FV-GP-08-HDOH	2,200,000	2,700,000	860,000	130,000	1,609,700	1,558,000
FV-GP-16R-HDOH	6,100,000	13,000,000	10,000,000	890,000	6,917,000	8,866,000
HAFB-VP26-B05(18)-HDOH	46,000,000	130,000,000	19,000,000	ND (<80,000)	49,412,000	12,767,300
HAFB-VP26-B05(24)-HDOH	320,000,000	270,000,000	37,000,000	ND (<80,000)	94,275,000	64,455,000
HAFB-VP26-B07(20)-HDOH	42,000,000	110,000,000	14,000,000	ND (<80,000)	38,267,500	13,193,400
HAFB-VP26-B07(25)-HDOH	140,000,000	300,000,000	29,000,000	ND (<80,000)	100,396,000	29,233,200
HAFB-ST03-B58 (347)	1,400,000	1,800,000	1,600,000	1,200,000	624,000	1,525,800
HAFB-ST03-B58 (422)	1,700,000	2,400,000	1,600,000	1,100,000	944,000	1,536,600
HAFB-ST03-B58 (492)	1,700,000	2,600,000	1,600,000	1,200,000	898,000	1,618,000
HAFB-ST03-B59 (388)	180,000	220,000	180,000	170,000	72,000	169,000
HH-OU1C-MW10SG	100,000,000	220,000,000	30,000,000	170,000	67,017,000	36,948,000
HH-OU1C-MW22R	39,000,000	180,000,000	29,000,000	710,000	65,304,100	23,034,000
HH-OU1C-OTNS1	2,100	2,100	ND (<20,000)	ND (<20,000)	699	ND (<5,660)

Notes

1. TO-17 TPHdiesel data provided for reference only. Note that the reported concentration of TPHd in the vapor sample collected over fresh diesel was higher than the reported concentration of TPHg for the same sample, calibrated to a gasoline standard.

Table 26b. Relative proportion of reported TPHg with respect to highest concentration reported for that sample (see also Figure 40).

Sample ID	**TO-3 (TPHg)**	**TO-15 (TPHg)**	**TO-17 (TPHg)**	**TO-17 (TPHd)**	**TO-15 MA-APH (sum of carbon ranges)**	**TO-17 MA-APH (sum of carbon ranges)**
Gasoline #2	0.1	1.0	0.8	-	0.3	0.6
JP8#1	0.5	1.0	0.2	-	0.4	0.2
Diesel#3-HDOH	0.5	0.5	1.0	-	0.2	0.7
HAFB-SP43-VMP10	0.6	1.0	0.5	-	0.5	0.3
HAFB-SP43-VMP11	0.7	1.0	0.1	-	0.4	0.5
HAFB-SP43-VMP12	0.3	0.6	1.0	-	0.2	0.6
HAFB-SP43-VMP16	1.0	1.0	0.3	-	0.4	0.4
HAFB-SP43-VMP17	0.7	1.0	0.0	-	0.6	0.0
FV-GP-01-HDOH	0.7	1.0	0.5	-	0.5	0.5
FV-GP-08-HDOH	0.8	1.0	0.3	-	0.6	0.6
FV-GP-16R-HDOH	0.5	1.0	0.8	-	0.5	0.7
HAFB-VP26-B05(18)-HDOH	0.4	1.0	0.1	-	0.4	0.1
HAFB-VP26-B05(24)-HDOH	1.0	0.8	0.1	-	0.3	0.2
HAFB-VP26-B07(20)-HDOH	0.4	1.0	0.1	-	0.3	0.1
HAFB-VP26-B07(25)-HDOH	0.5	1.0	0.1	-	0.3	0.1
HAFB-ST03-B58 (347)	0.8	1.0	0.9	-	0.3	0.8
HAFB-ST03-B58 (422)	0.7	1.0	0.7	-	0.4	0.6
HAFB-ST03-B58 (492)	0.7	1.0	0.6	-	0.3	0.6
HAFB-ST03-B59 (388)	0.8	1.0	0.8	-	0.3	0.8
HH-OU1C-MW10SG	0.5	1.0	0.1	-	0.3	0.2
HH-OU1C-MW22R	0.2	1.0	0.2	-	0.4	0.1
HH-OU1C-OTNS1	0.1	0.1	1.0	-	0.0	0.3
Average:	0.6	0.9	0.5		0.4	0.4

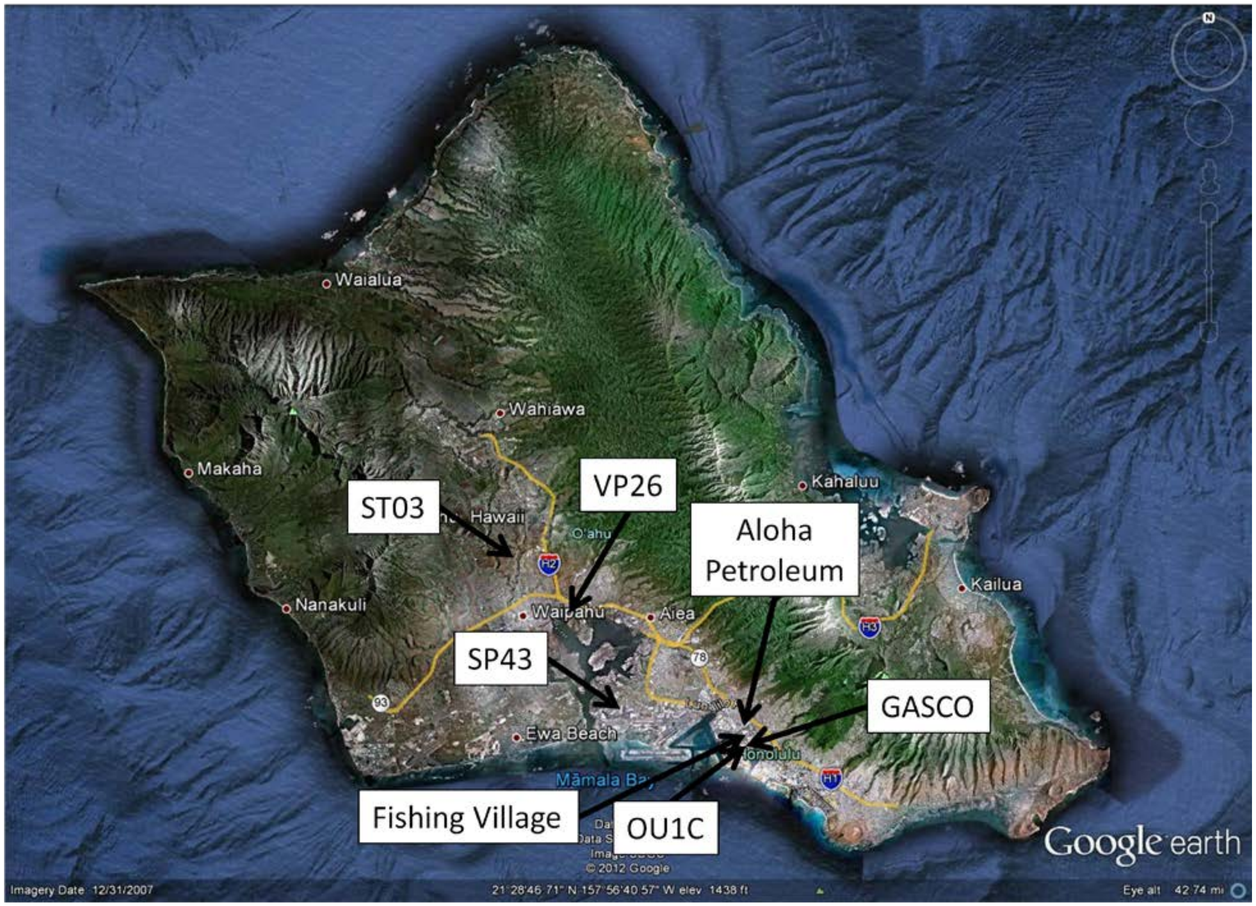
Table 27. Comparison of laboratory methods for benzene in soil gas samples (Phase II data).

Site	Sample ID	[1]TO-15 Benzene ($\mu g/m^3$)	[2]TO-17 Benzene ($\mu g/m^3$)	[3]TO-3 Benzene ($\mu g/m^3$)
Fresh Fuels and Auto Exhaust	Gasoline #2	29,000	340,000	28,000
	Gasoline Exhaust	4,700	3,900	5,400
	JP8#1	20,000	7,600	19,000
	Diesel#3	1,000	2,800	2,000
	Diesel Exhaust	14	430	36
Site A (October 2011)	HAFB-VP26-B05(18)-HDOH	40,000	16,000	150,000
	HAFB-VP26-B05(24)-HDOH	280,000	620,000	1,000,000
	HAFB-VP26-B07(20)-HDOH	84,000	35,000	180,000
	HAFB-VP26-B07(25)-HDOH	45,000	22,000	700,000
Site B (October 2011)	HH-OU1C-MW10SG	16,000	10,000	360,000
	HH-OU1C-MW22R	16,000	3,600	130,000
	HH-OU1C-OTNS1	3.1	64	34
Site C	HAFB-SP43-VMP10	1,600	1,700	500
	HAFB-SP43-VMP11	480	750	11,000
	HAFB-SP43-VMP12	4.8	80	3.8
	HAFB-SP43-VMP16	1,500	1,200	1,600
	HAFB-SP43-VMP17	500	53	160
Site D (October 2011)	HAFB-ST03-B58 (347)	32	81	42
	HAFB-ST03-B58 (422)	43	91	500
	HAFB-ST03-B58 (492)	42	130	750
	HAFB-ST03-B59 (388)	180	70	580
Site E (Oct 2011)	FV-GP-01-HDOH	4.7	100	96
	FV-GP-08-HDOH	49	320	2,400
	FV-GP-16R-HDOH	245	260	2,200

Notes:

1. Benzene reported for Summa canister sample using TO-15 (reported with MA-APH data; see Table 9 and Attachment 6).
2. Benzene reported for sorbent tube sample using TO-17 (reported with MA-APH data; see Attachment 6).
3. Benzene reported for Summa canister sample using TO-3 (see Attachment 6). Most TO-3 benzene data qualified by laboratory: "Reported value may be biased due to apparent matrix interferences."

Figure 1. Project site locations. All sites located on O‘ahu, Hawai‘i.



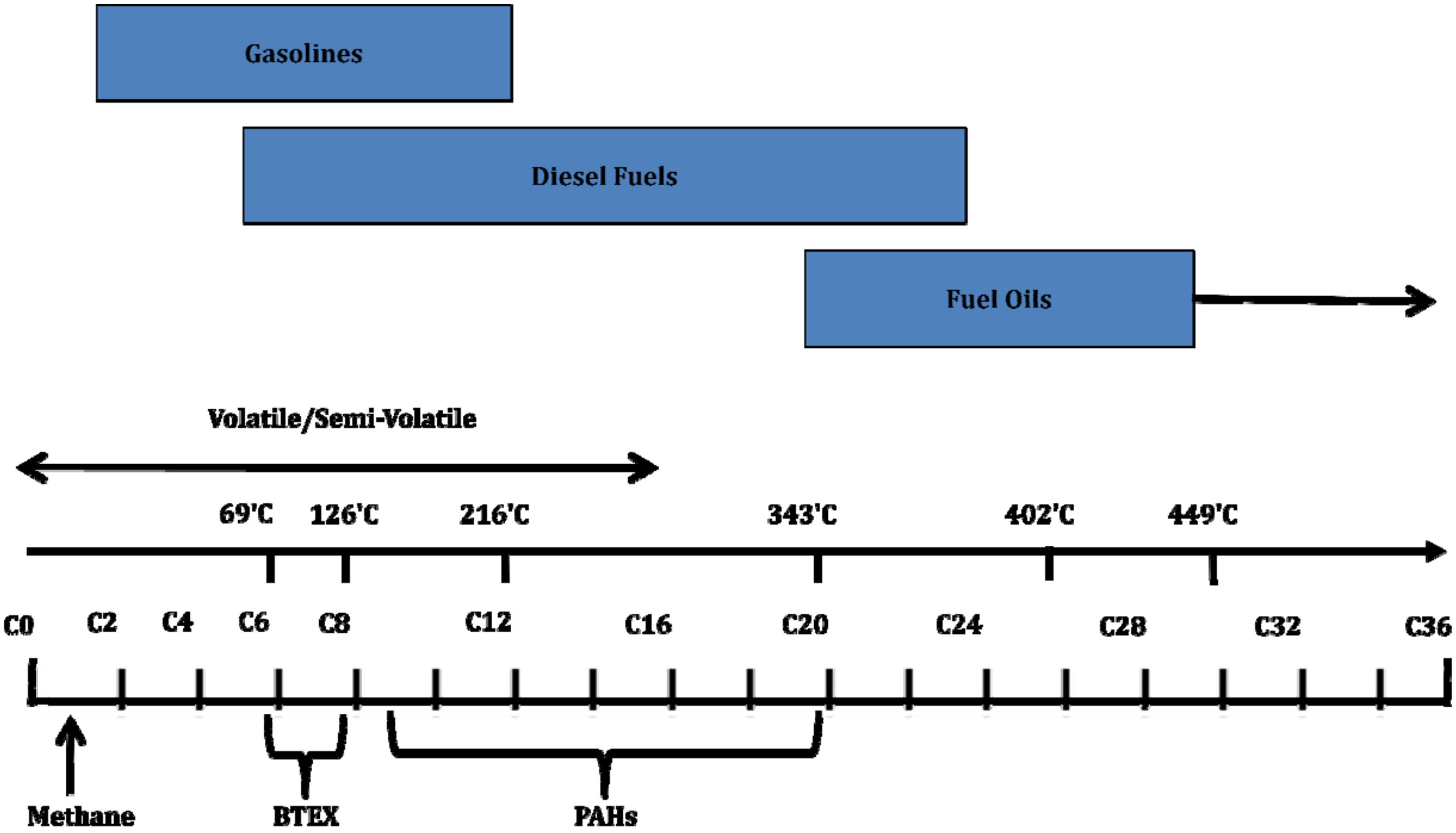


Figure 2a. Composition of typical petroleum fuels with respect to the number of carbon molecules in individual compounds.

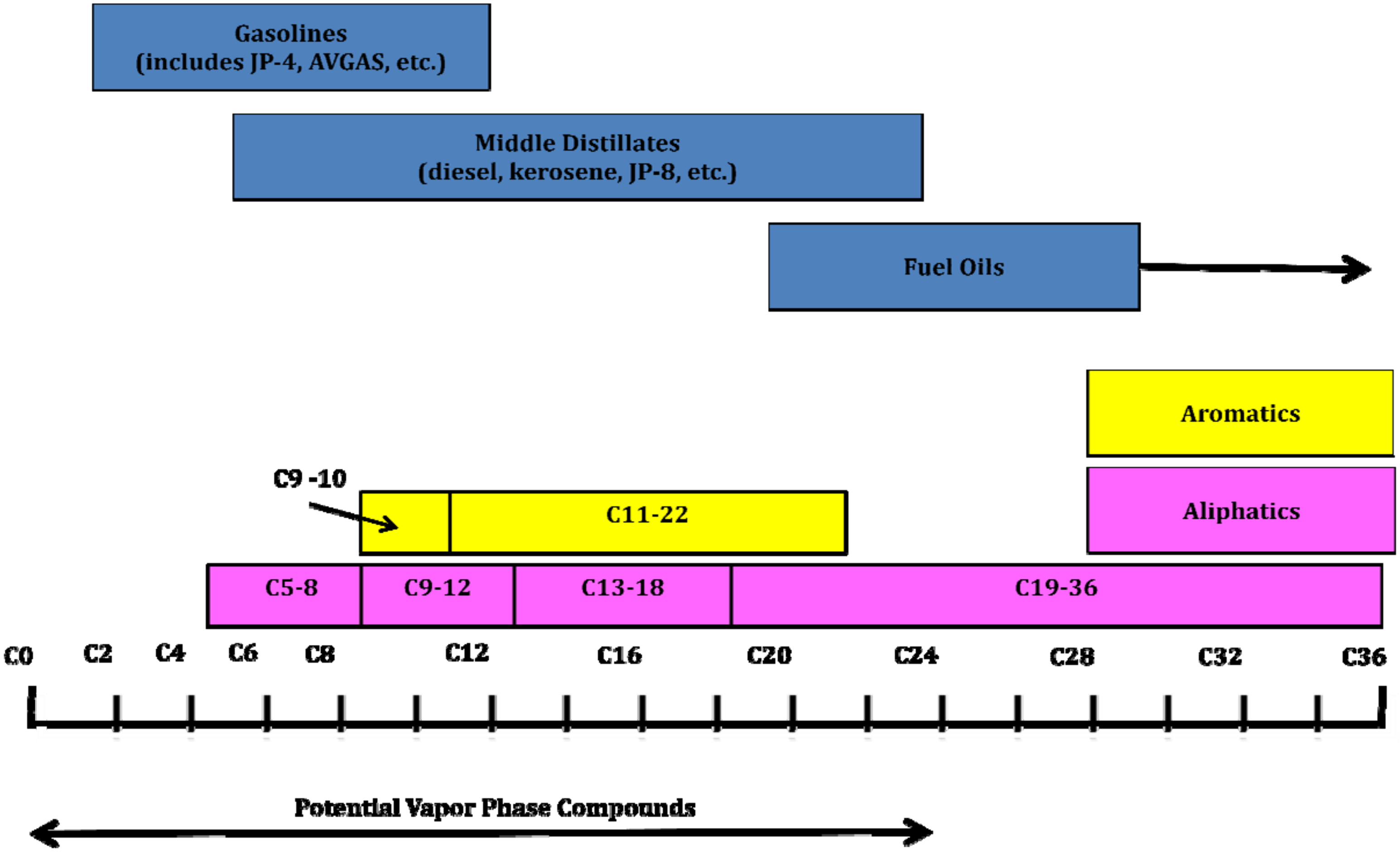


Figure 2b. Massachusetts DEP TPH Carbon Ranges. “TPH” represents the sum of individual aromatic and aliphatic carbon range fractions, excluding BTEX, naphthalene and other individually targeted compounds. Vapor-phase TPH is typically dominated by C5-C8 and C9-C12 aliphatic compounds.

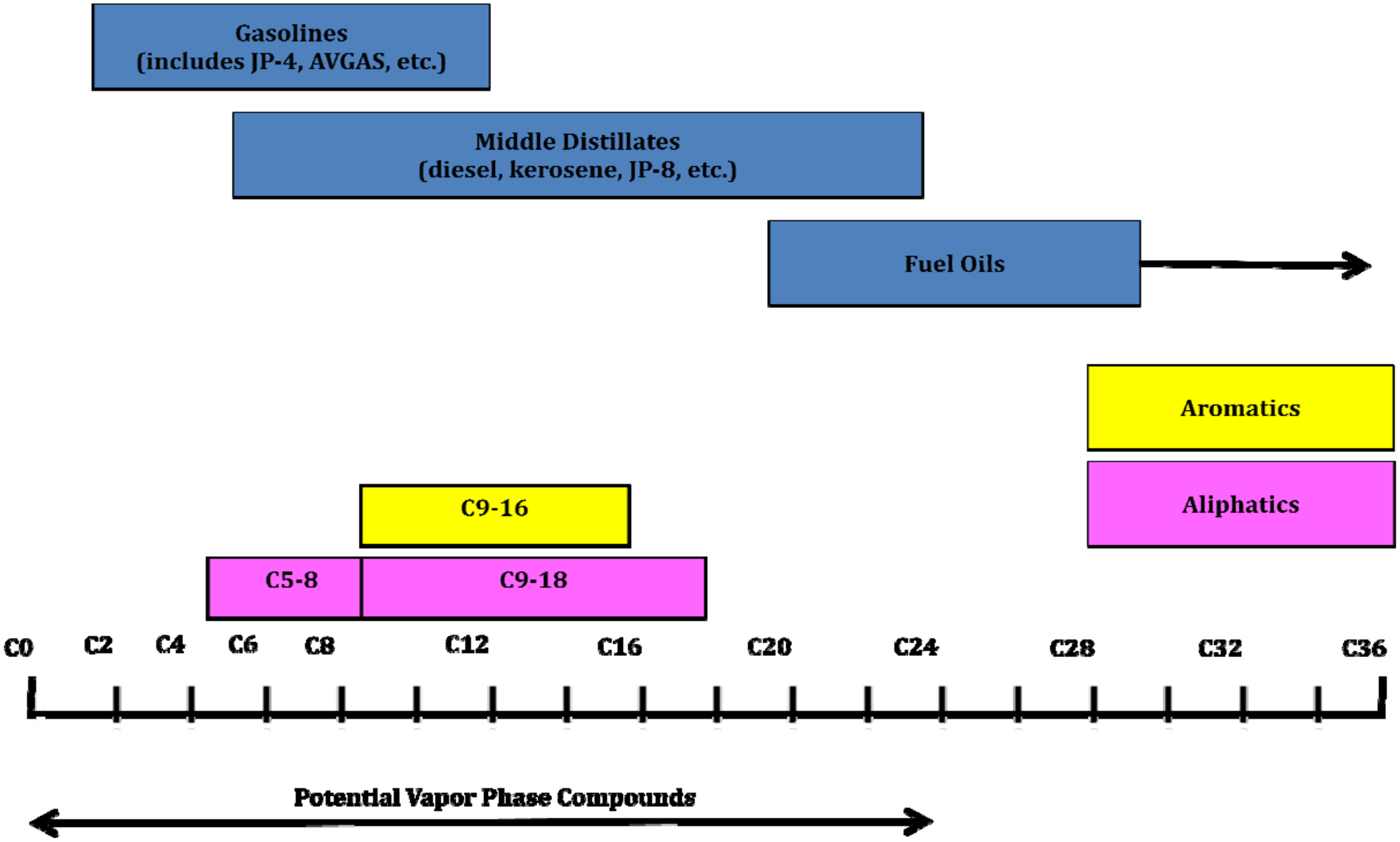
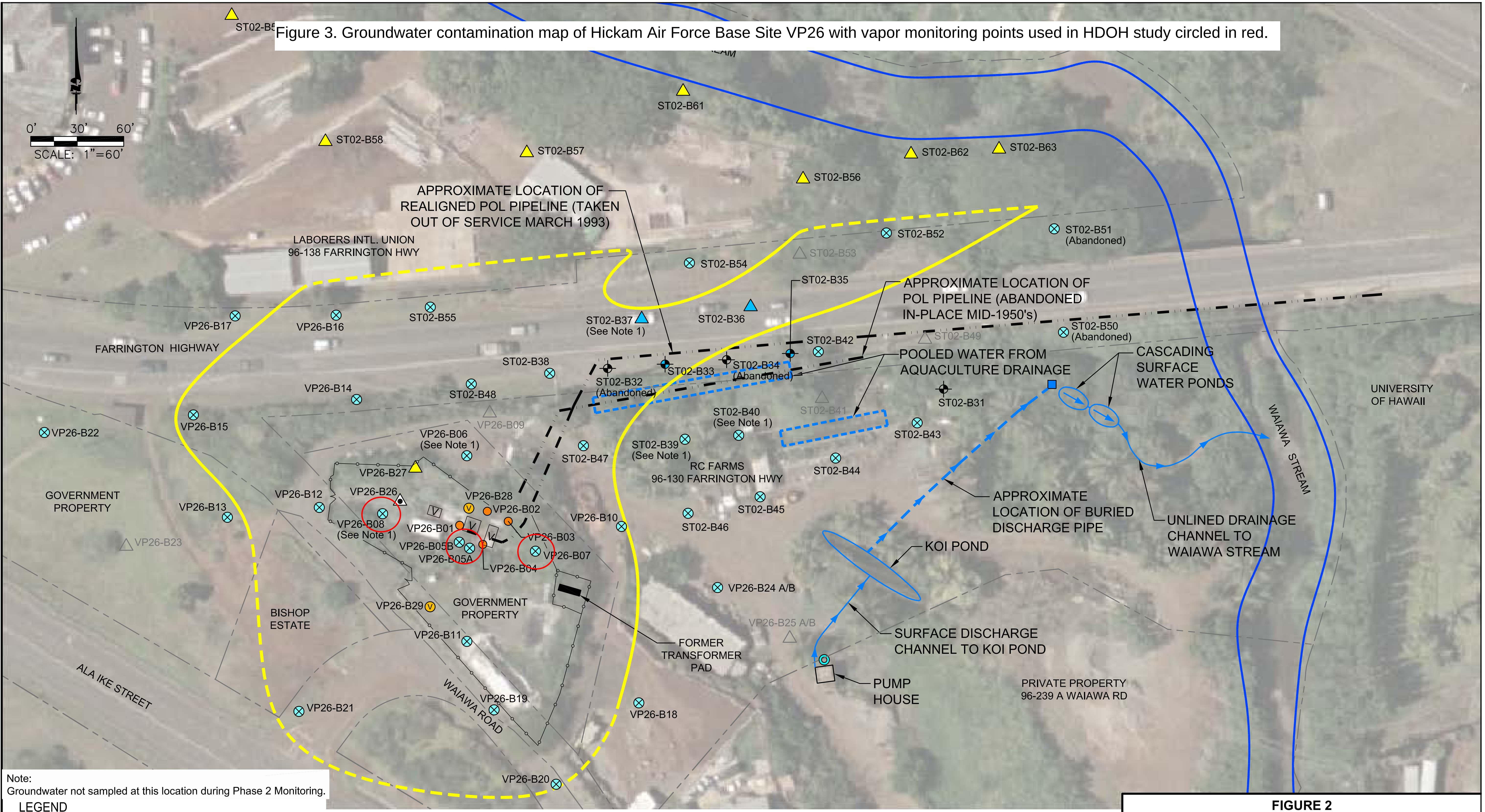


Figure 2c. Target vapor-phase aliphatic and aromatic carbon range fractions.

Figure 3. Groundwater contamination map of Hickam Air Force Base Site VP26 with vapor monitoring points used in HDOH study circled in red.



Note:
Groundwater not sampled at this location during Phase 2 Monitoring.

LEGEND

- ⊕ Phase 1 Soil, Soil Vapor, and Groundwater Sampling Location with Permanent MW Installation
- ⊕ Phase 1 Monitoring Wells Sampled during Phase 2
- ● Phase 1 Soil and Soil Vapor Sampling Location
- ⊗ Phase 2 Sampling Location and Installed Groundwater Monitoring Well
- V Valve Pit
- ▲ Phase 2 Soil and Groundwater "Grab Sample" Location
- ▲ Proposed Additional Phase 2 Soil and Groundwater Sampling Location
- △ Proposed Phase 2 Soil and Groundwater Sampling Location - Not Sampled
- ▲ Proposed LNAPL Recovery Well
- V Bioventing Well
- ■ Koi Pond Effluent Transition To Surface Flow
- ◎ Active Irrigation Well
- Estimated extent of groundwater contamination following the Phase 2 investigation matching or exceeding 2008 EALs (dotted line represents undefined extent)
- Approximate location of stream bank
- Approximate Location of POL Pipeline
- Approximate Property Boundary
- Chainlink Fence

FIGURE 2

SITE LAYOUT AND PROPOSED ADDITIONAL PHASE 2 RI SAMPLING LOCATIONS ST02 AND VP26 IRP SITE ST02

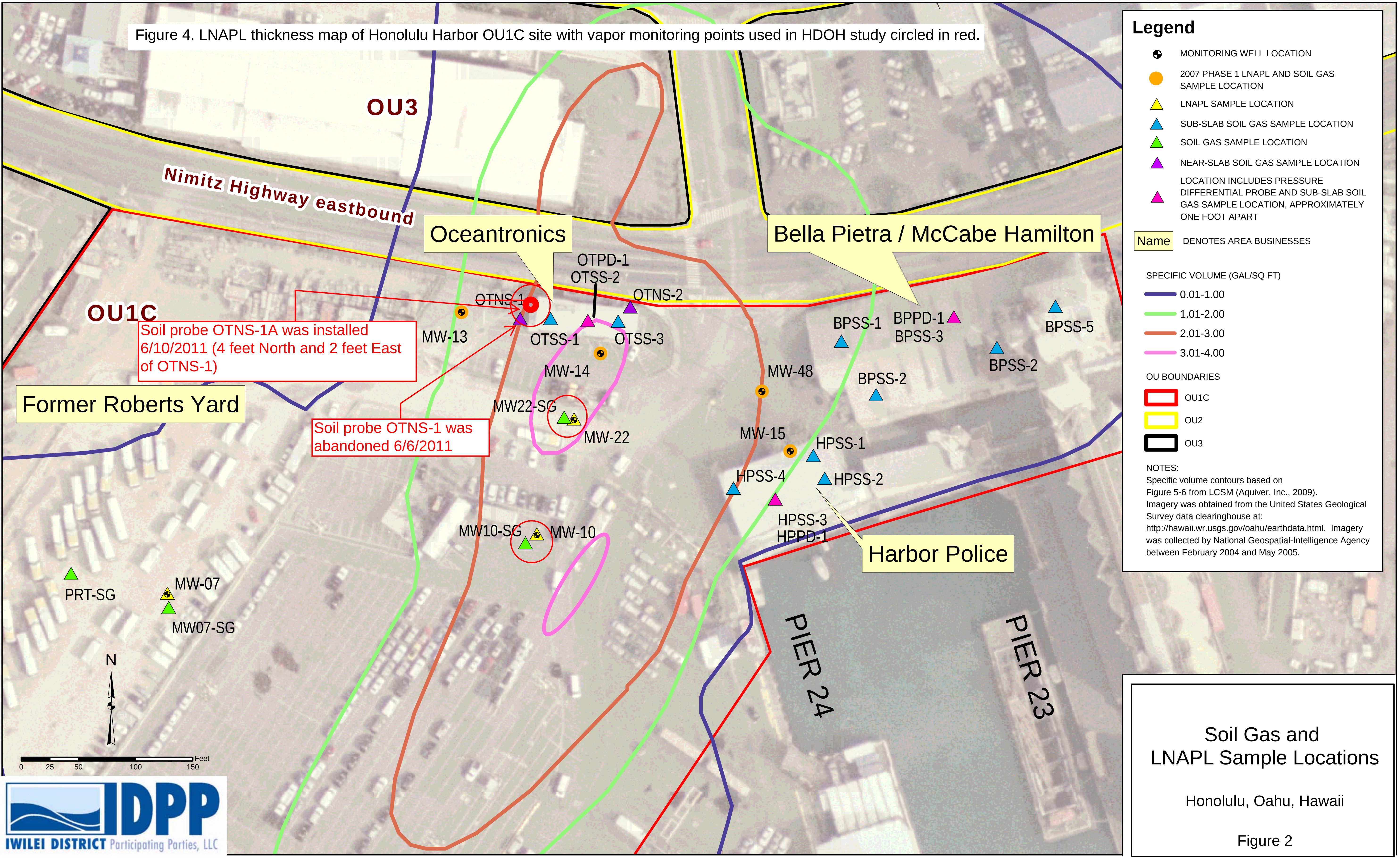
Hickam POL Pipeline, Oahu, Hawaii

PARSONS

Honolulu, Hawaii

S:\ES\REMED\746859 – HPOL PH 2 RI – 4P08 T048\02000 – MEETINGS AND WORK PLAN\WORK PLAN\ADDENDUM #1 – TS\FIGURES\ST02-P2WP-PSUR-1010-2.DWG 3/21/11 SDM

Figure 4. LNAPL thickness map of Honolulu Harbor OU1C site with vapor monitoring points used in HDOH study circled in red.



Soil probe OTNS-1A was installed 6/10/2011 (4 feet North and 2 feet East of OTNS-1)

Soil probe OTNS-1 was abandoned 6/6/2011

Legend

● MONITORING WELL LOCATION

● 2007 PHASE 1 LNAPL AND SOIL GAS SAMPLE LOCATION

▲ LNAPL SAMPLE LOCATION

▲ SUB-SLAB SOIL GAS SAMPLE LOCATION

▲ SOIL GAS SAMPLE LOCATION

▲ NEAR-SLAB SOIL GAS SAMPLE LOCATION

▲ LOCATION INCLUDES PRESSURE DIFFERENTIAL PROBE AND SUB-SLAB SOIL GAS SAMPLE LOCATION, APPROXIMATELY ONE FOOT APART

Name DENOTES AREA BUSINESSES

SPECIFIC VOLUME (GAL/SQ FT)

— 0.01-1.00

— 1.01-2.00

— 2.01-3.00

— 3.01-4.00

OU BOUNDARIES

🟥 OU1C

🟨 OU2

⬛ OU3

NOTES:
Specific volume contours based on Figure 5-6 from LCSM (Aquiver, Inc., 2009).
Imagery was obtained from the United States Geological Survey data clearinghouse at: http://hawaii.wr.usgs.gov/oahu/earthdata.html. Imagery was collected by National Geospatial-Intelligence Agency between February 2004 and May 2005.

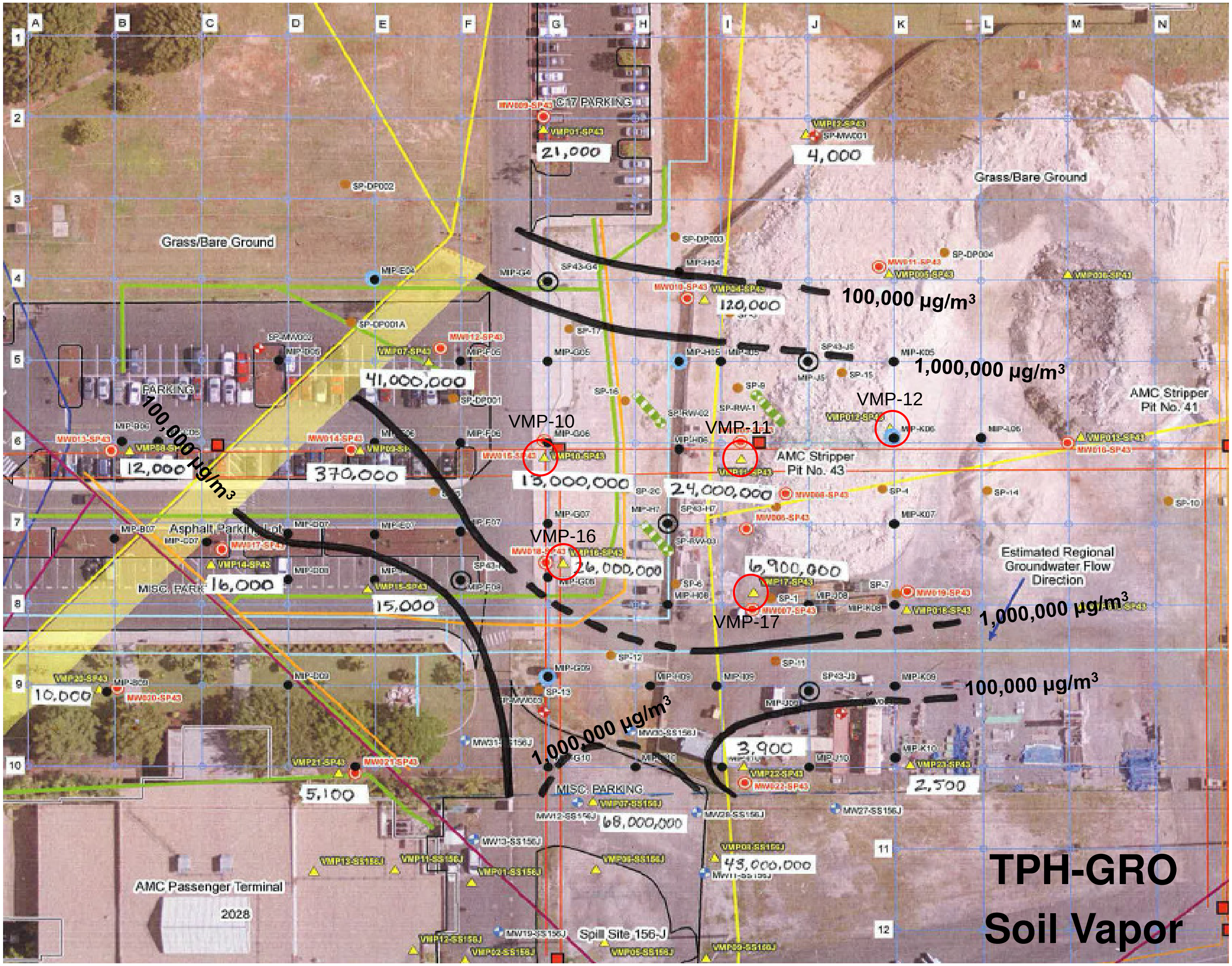
Soil Gas and
LNAPL Sample Locations

Honolulu, Oahu, Hawaii

Figure 2

Prepared by: URS Corp. J:\IDPP_Project\av_project\60_SoilGasInvestigation\Phase2\Fig2_OU1C_DOTHarbors_SoilGasLocs_081009.mxd ssm 10-16-09

Figure 5. TPHg soil gas map of Hickam Air Force Base Site SP43 with vapor monitoring points used in HDOH study circled in red.



S:\ES\REMED\747579 – HICKAM ST03 PH 3 RI\02000 – MEETINGS AND WORK PLANS\WORK PLANS\PRE- DRAFT\WP\FIGURES\CAD\HICK-ST03LAYOUT3.DWG 2/28/11 SDM

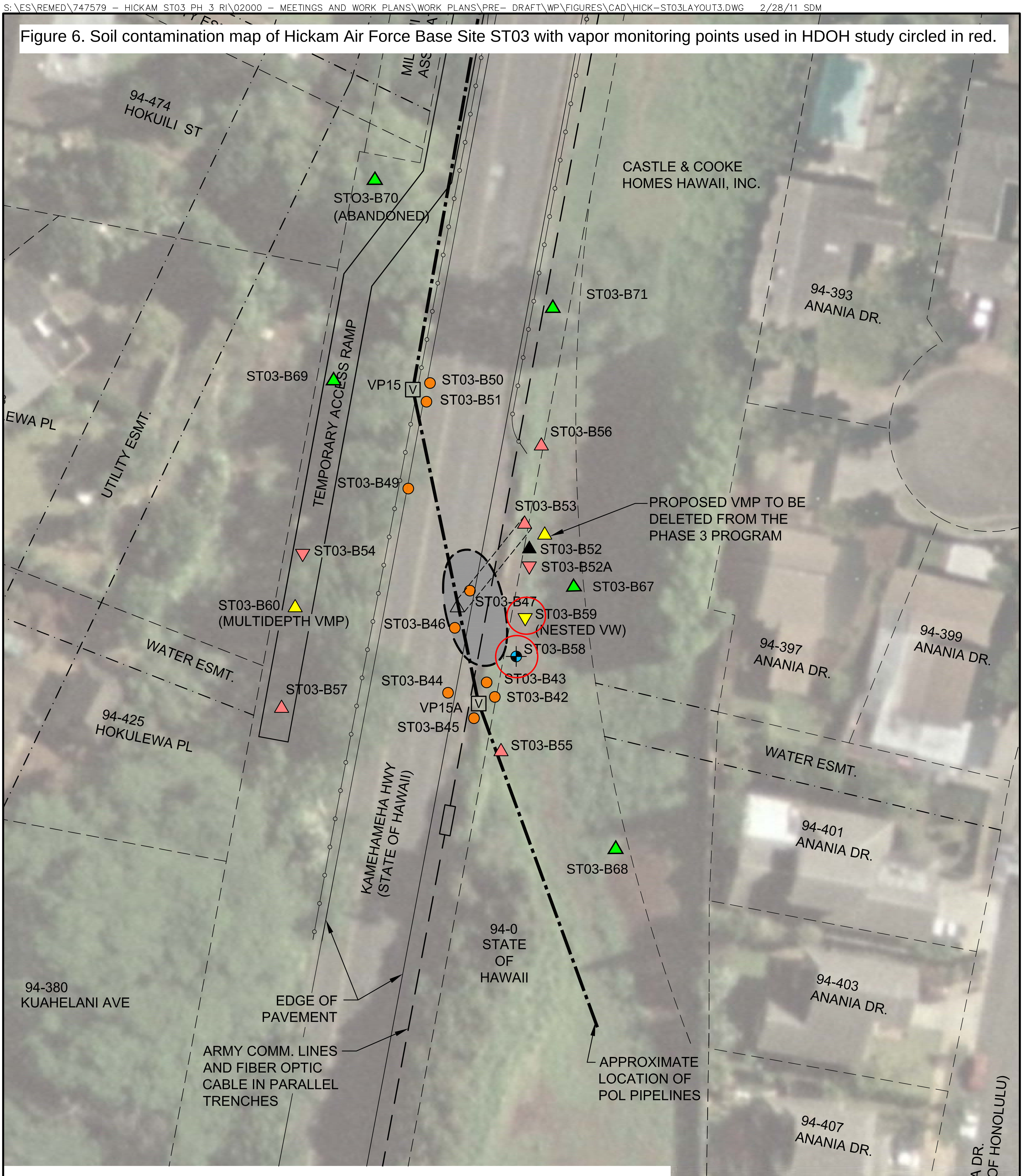


Figure 6. Soil contamination map of Hickam Air Force Base Site ST03 with vapor monitoring points used in HDOH study circled in red.

LEGEND

⊕	Phase 3 Boring and Monitoring Well
△	Phase 3 Boring and Multidepth VMP
▽	Phase 3 Boring and Nested VW
━ · ━	Approximate Location of POL Pipelines
— — —	Approximate Property Boundary
— · —	Approximate Easement Boundary
–o–o–	Guardrail
— —	Buried Utility Line
▭	Utility Box
V	Valve Pit
●	Estimated Extent of Soil Contamination Exceeding Tier 1 EALs
●	Phase 1 RI Soil and Soil Vapor Sampling Location (Installed in Jan/Feb 2008)
▲	Phase 2 RI Soil and Soil Vapor Sampling Location (Installed in Sept/Oct 2009) Completed as a Vapor Monitoring Point
▼	Phase 2 RI Soil and Soil Vapor Sampling Location (Installed in Sept/Oct 2009) Completed as a Vent Well
▲	Abandoned Phase 2 RI Soil Sampling Location (Installed in Sept/Oct 2009)
△	Angled Boring (red triangle indicates boring location at ground surface; open triangle indicates termination of boring at subsurface depth).
▲	Phase 2 RI Soil Sampling Location (Installed Oct/Nov 2010)

Notes:

1. Surveyed coordinates for Phase 1 Remedial Investigation (RI) locations are in WGS 84, UTM Zone 4N (meters), and were provided by Ace Land Surveying, LLC., Honolulu, HI.
2. Geo-referenced aerial imagery obtained from USGS Earth Data Imagery website http://hawaii.wr.usgs.gov/oahu/earthdata.html (projected in UTM).
3. Geo-referenced property boundaries obtained from City and County of Honolulu, Dept. of Permitting & Planning website – http://gis.hicentral.com (as of October, 2008; projected in UTM).
4. Surveyed coordinates for Phase 2 RI locations are in WGS 84, UTM Zone 4N (meters), and were provided by Hawaii Engineering Group, Inc., Honolulu, HI.

N

0' 20' 40'

SCALE: 1"=40'

FIGURE 1

SITE LAYOUT AND SAMPLING LOCATIONS SUBSITE ST03

Phase 3 RI/TS at Subsite ST03
Hickam POL Pipeline
Oahu, Hawaii

PARSONS

Honolulu, Hawaii

Figure 7. TPHg soil gas map of Fishing Village site with vapor monitoring points used in HDOH study circled in black.

Soil Gas Monitoring Report - May 2010
Honolulu Harbor, Domestic Commercial Fishing Village

FIGURE 5-4
CURRENT TPH-g SOIL GAS LEVELS

FINDINGS AND CONCLUSIONS

Page 5-6

Figure 8. Groundwater TPH gasoline map of the School Street Aloha Petroleum site with vapor monitoring points used in HDOH study circled in red.

Notes:

This figure represents one interpretation of contaminant migration; other interpretations are possible.

Groundwater sample data presented in this figure were collected December 20 through 30, 2010.

There is no DOH GAL for TPH-G.

Where two monitoring wells were completed adjacent to each other, and at different screened intervals, the data from the well exhibiting the highest concetration was used for contouring.

J indicates an estimated value. Analyte detected at a level less than the Reporting Limit (RL) and greater than or equal to the Method Detection Limit (MDL).

Distribution of TPH-G
in Groundwater

RELEASE RESPONSE REPORT - 4TH QUARTER 2010
Aloha Petroleum, Ltd. – Island Mini Mart
1403 North School Street - Honolulu, Hawaii

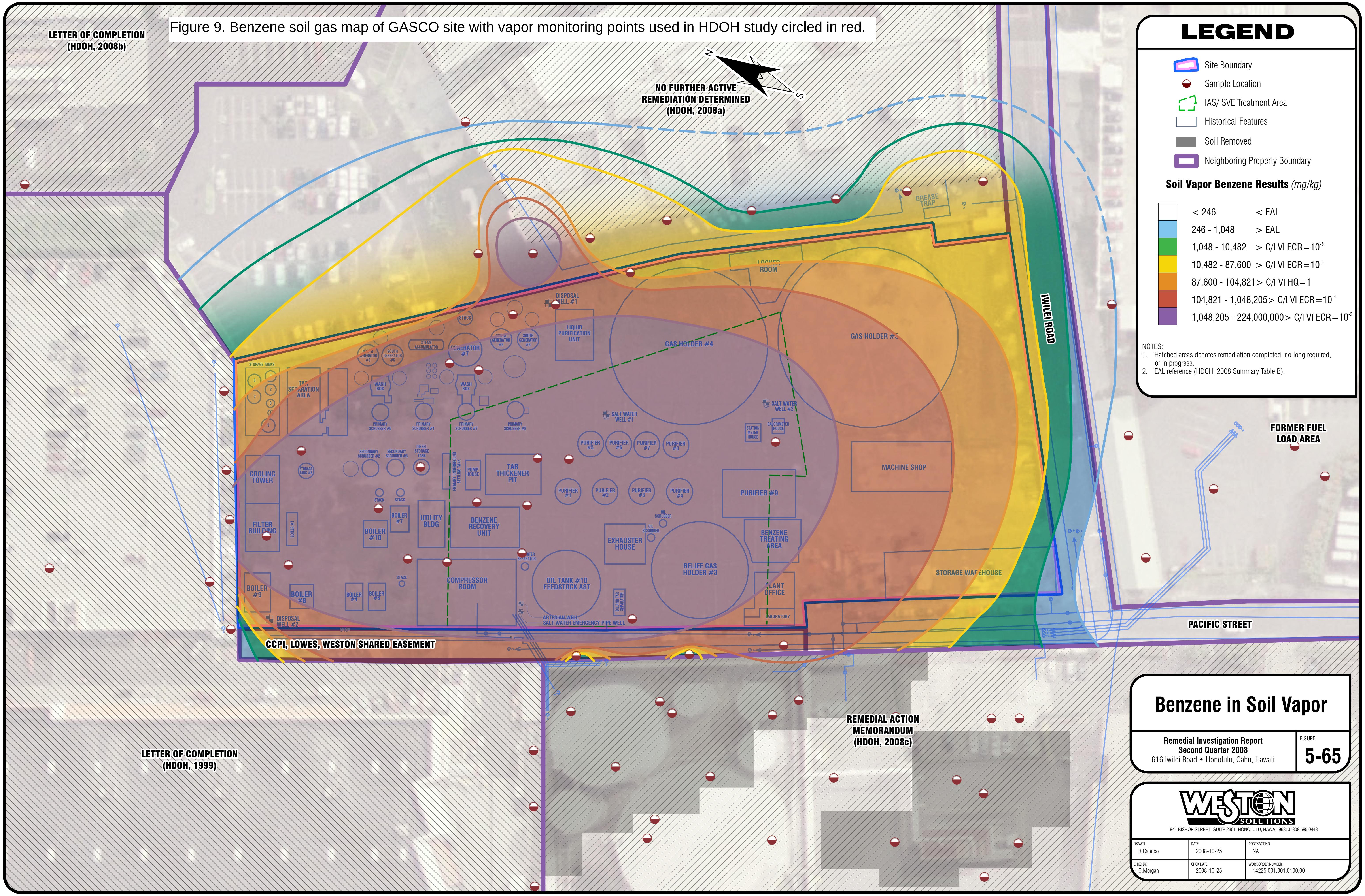
WESTON SOLUTIONS
841 BISHOP STREET SUITE 2301 HONOLULU, HAWAII 96813 808.275.2900

DRAWN S. Fallon	DATE 2010-12-23	CONTRACT NO.
CHKD BY: M. Ambler	CHCK DATE: 2010-12-23	WORK ORDER NUMBER:

SHEET
Figure 6-5

T:\Aloha Petroleum\1403 North School Street\18.1 Draft Summary Report\2010 Q3 GW Monitoring\Figures\Fig.6-01 thru 6-06 - Analytes in GW - RC 2010-12-23

Figure 9. Benzene soil gas map of GASCO site with vapor monitoring points used in HDOH study circled in red.



LEGEND

- Site Boundary
- Sample Location
- IAS/ SVE Treatment Area
- Historical Features
- Soil Removed
- Neighboring Property Boundary

Soil Vapor Benzene Results *(mg/kg)*

⬜	< 246	< EAL
🟦	246 - 1,048	> EAL
🟩	1,048 - 10,482	> C/I VI ECR=10^{-6}
🟨	10,482 - 87,600	> C/I VI ECR=10^{-5}
🟧	87,600 - 104,821	> C/I VI HQ=1
🟥	104,821 - 1,048,205	> C/I VI ECR=10^{-4}
🟪	1,048,205 - 224,000,000	> C/I VI ECR=10^{-3}

NOTES:
1. Hatched areas denotes remediation completed, no long required, or in progress.
2. EAL reference (HDOH, 2008 Summary Table B).

Benzene in Soil Vapor

Remedial Investigation Report
Second Quarter 2008
616 Iwilei Road • Honolulu, Oahu, Hawaii

FIGURE
5-65

841 BISHOP STREET SUITE 2301 HONOLULU, HAWAII 96813 808.585.0448

DRAWN R.Cabuco	DATE 2008-10-25	CONTRACT NO. NA
CHKD BY: C.Morgan	CHCK DATE: 2008-10-25	WORK ORDER NUMBER: 14225.001.001.0100.00

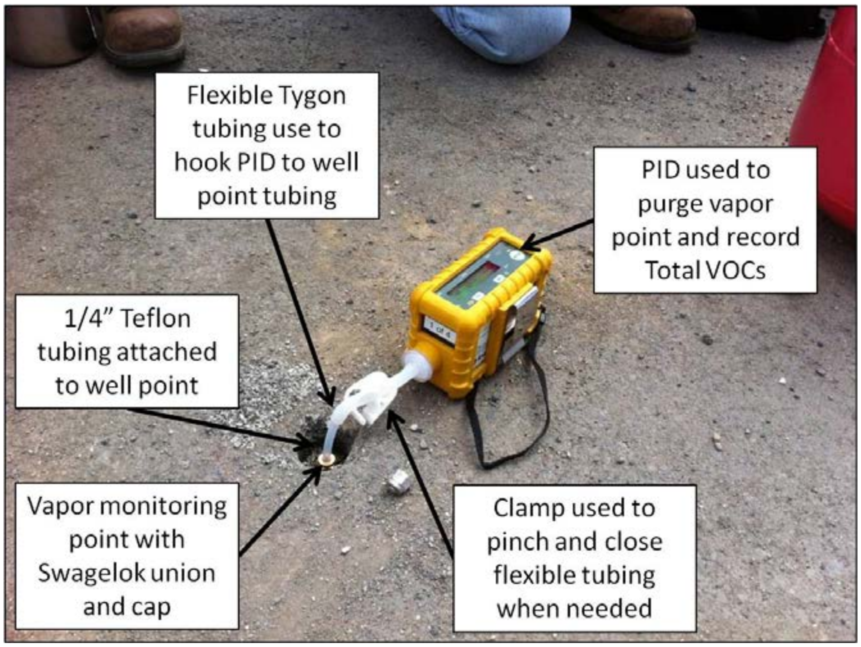


Figure 10. Purging of vapor monitoring points with a PID.

Figure 11. Connection of Summa and flow controller sampling train to vapor monitoring point.

Figure 12. Use of a plastic garbage bag as a helium shroud during Phase I of the study.

Figure 13. Five-gallon plastic bucket shroud with ports for sample collection and helium injection (not used due to height of the combined Summa canister and flow controller obtained from the lab for this study).

Figure 14. Use of a Tupperware container as a helium shroud during Phase II of the study (see also Attachment 4).

Figure 15. TO-17 sorbent tube sampling train using a 60ml syringe (50ml draw over thirty seconds for maximum 100 ml/minute flow rate; note use of second/upstream tube to check for breakthrough).

```
Data File: /chem/msd2.i/25oct11.b/2102512.d                                      Page 1
Date : 25-OCT-2011 13:45
Client ID:                                            Instrument: msd2.i
Sample Info: 6.0ml #12035
                                                      Operator: mtw
Column phase: RTx-624                                 Column diameter:  0.32
```

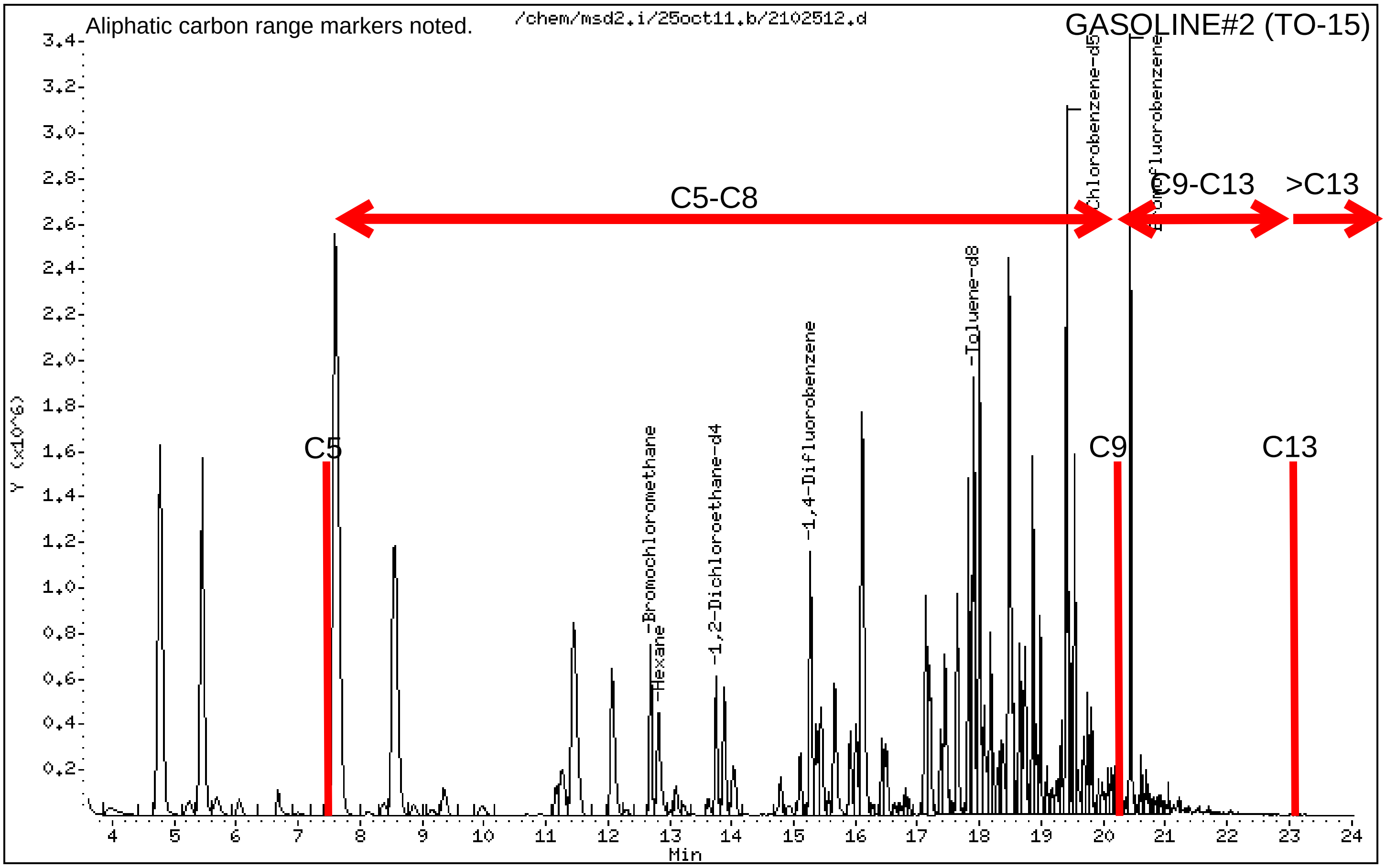
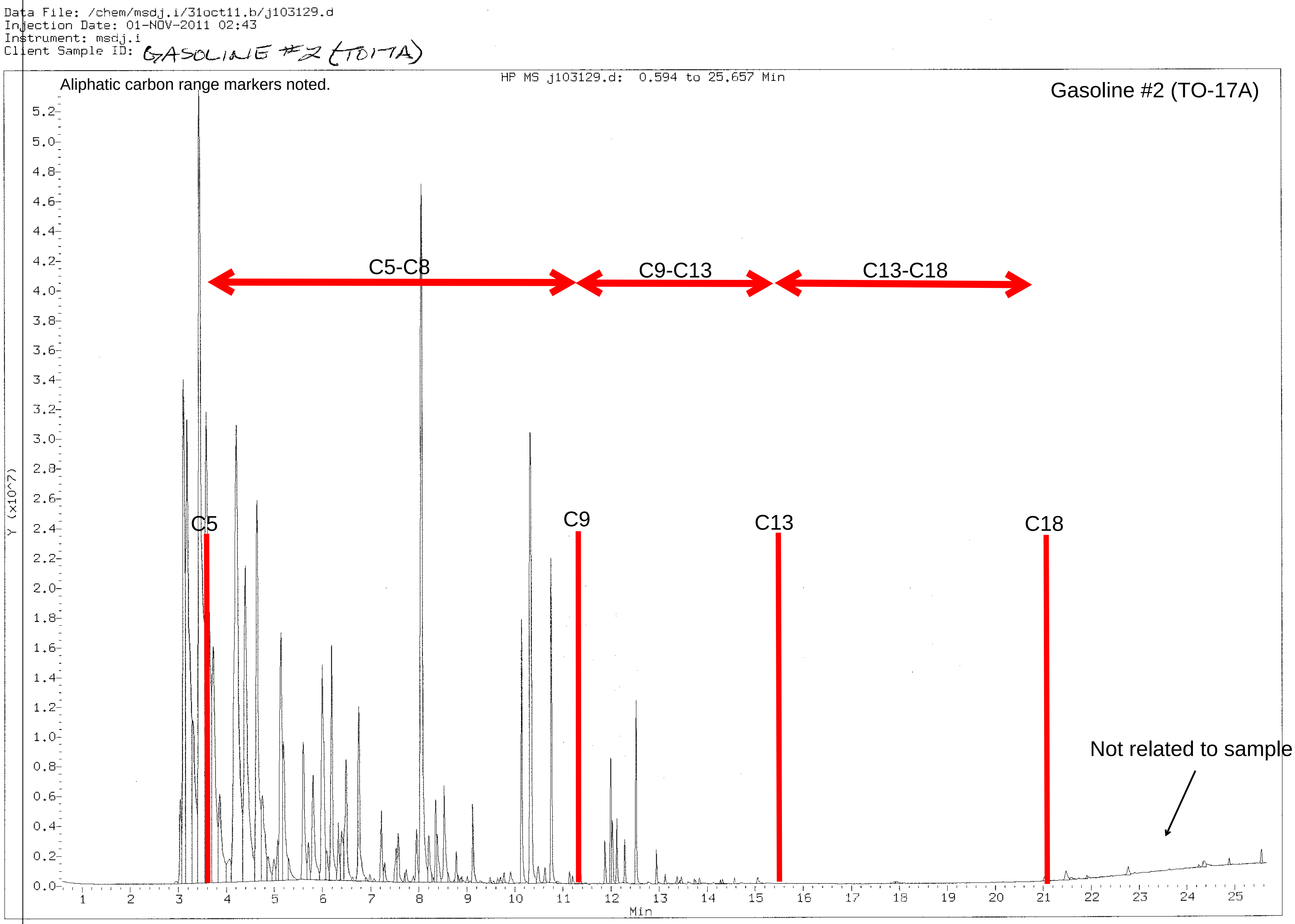


Figure 16a. Example gas chromatogram of vapors collected in summa canister from fresh gasoline fuel with key carbon range markers indicated.

Figure 16b. Example gas chromatogram of vapors collected with a sorbent tube from fresh gasoline fuel with key carbon range markers indicated.



Data File: /chem/msdj.i/31oct11.b/j103129.d
Injection Date: 01-NOV-2011 02:43
Instrument: msdj.i
Client Sample ID: GASOLINE #2 (TO17A)

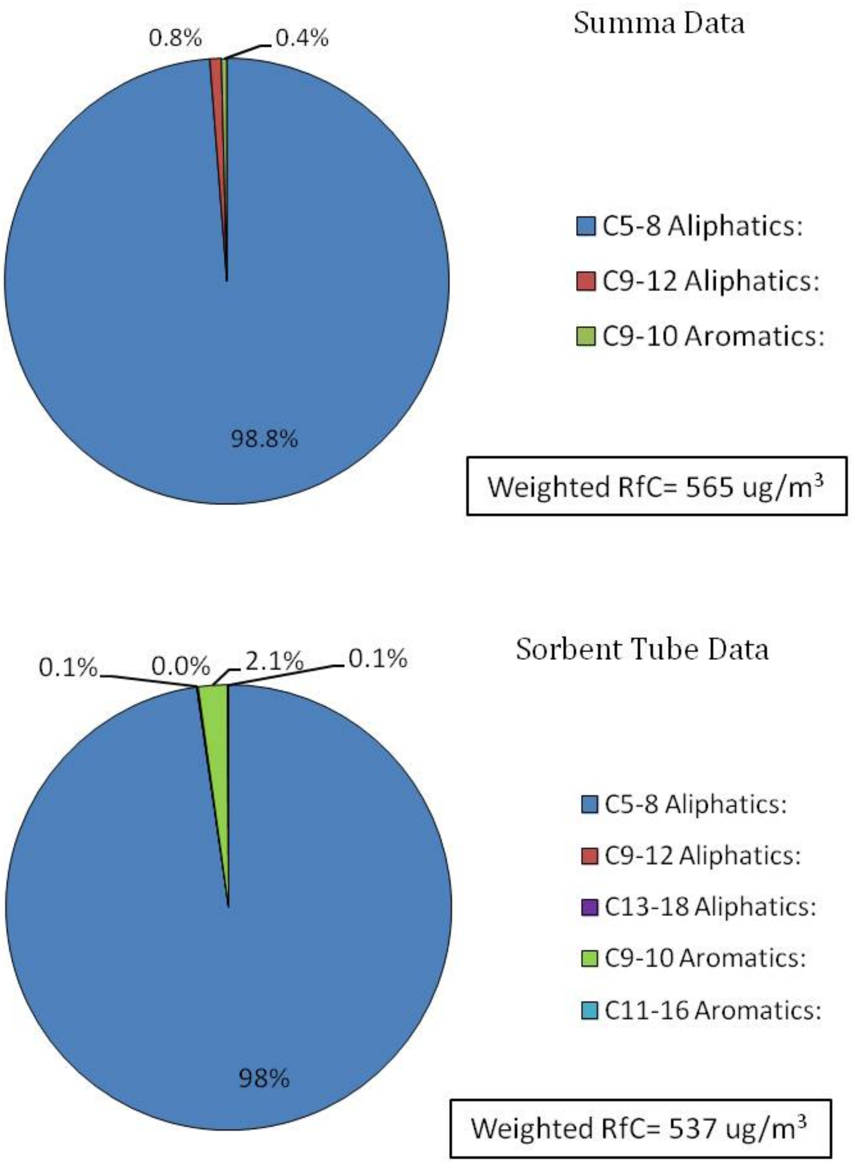


Figure 17. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples of vapors from fresh gasoline and correlative, weighted Reference Concentration for inhalation toxicity.

Data File: /chem/msd2.i/24oct11.b/2102412.d Page 1

Date : 24-OCT-2011 14:04

Client ID: Instrument: msd2.i

Sample Info: 30ml #37711

Operator: mtw

Column phase: RTx-624 Column diameter: 0.32

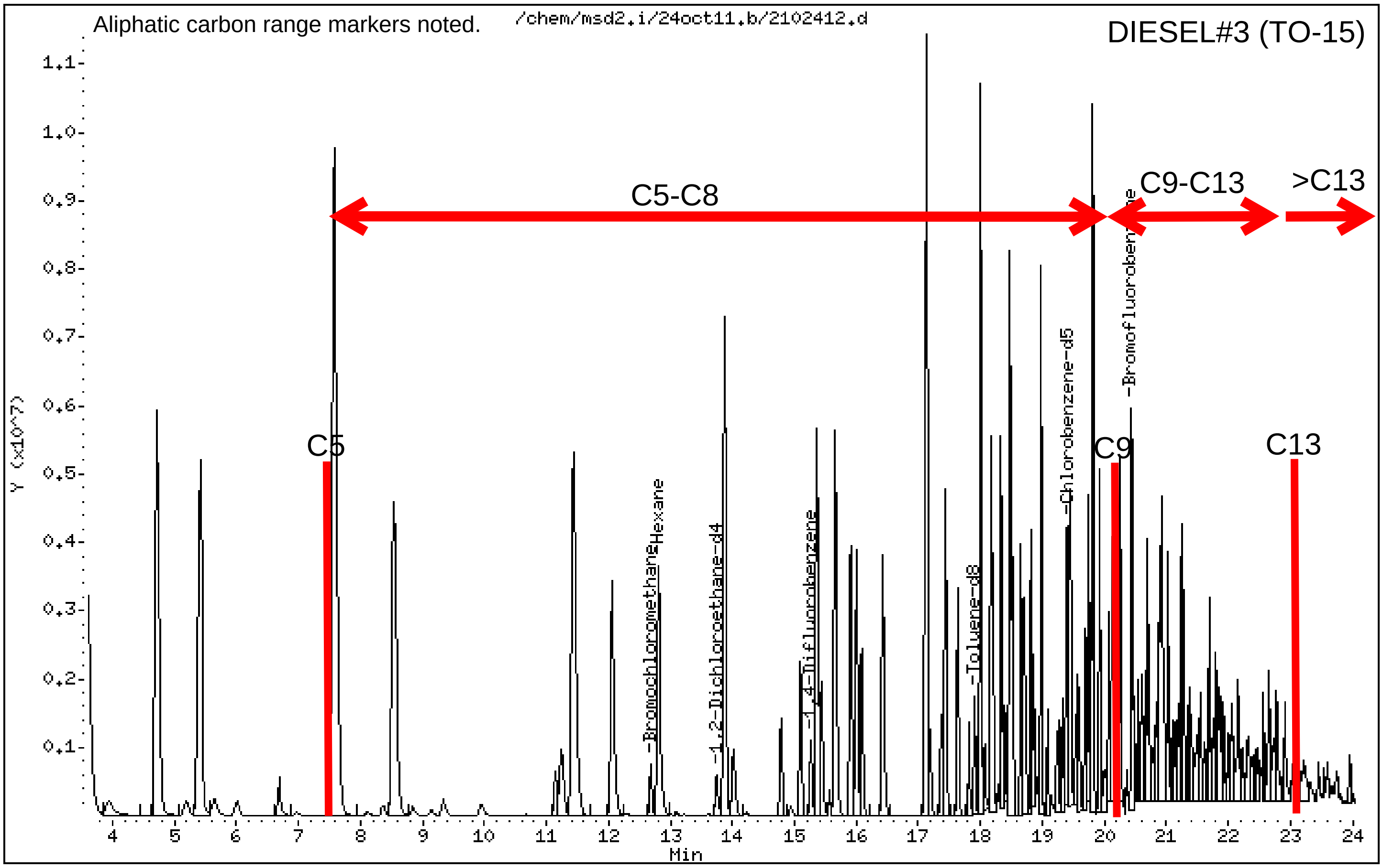
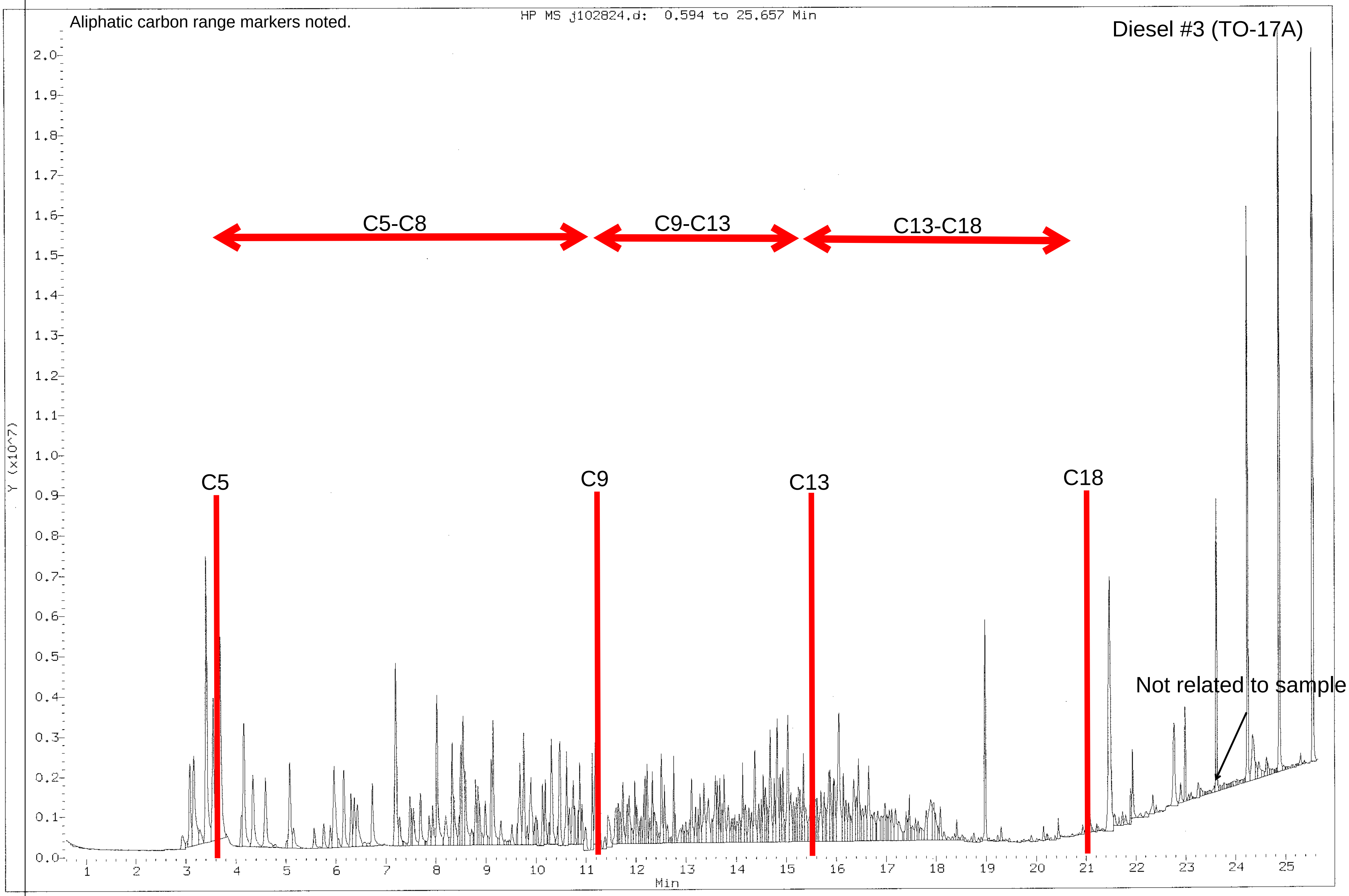
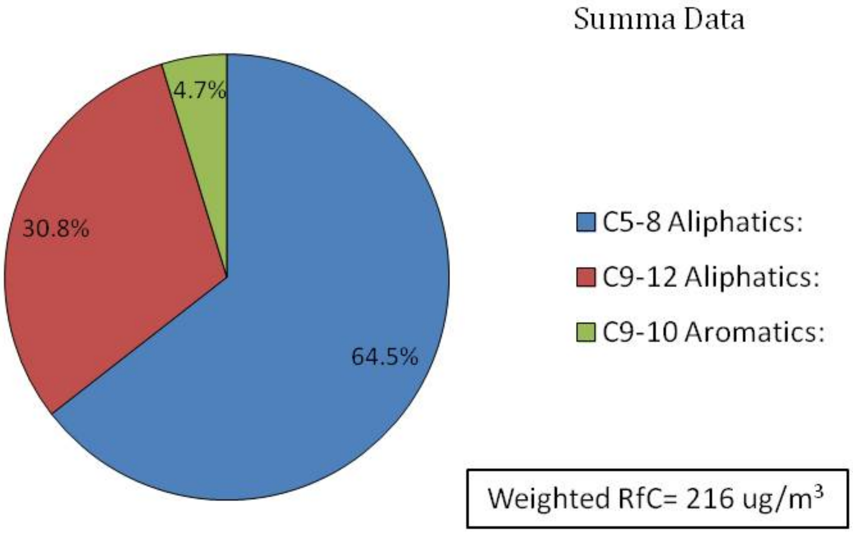


Figure 18a. Example gas chromatogram of vapors collected in summa canister from fresh diesel fuel with key carbon range markers indicated.

Figure 18b. Example gas chromatogram of vapors collected with a sorbent tube from fresh diesel fuel with key carbon range markers indicated.

Data File: /chem/msdj.i/28oct11.b/j102824.d
Injection Date: 28-OCT-2011 22:52
Instrument: msdj.i
Client Sample ID: DIESEL #3 (TO17A)





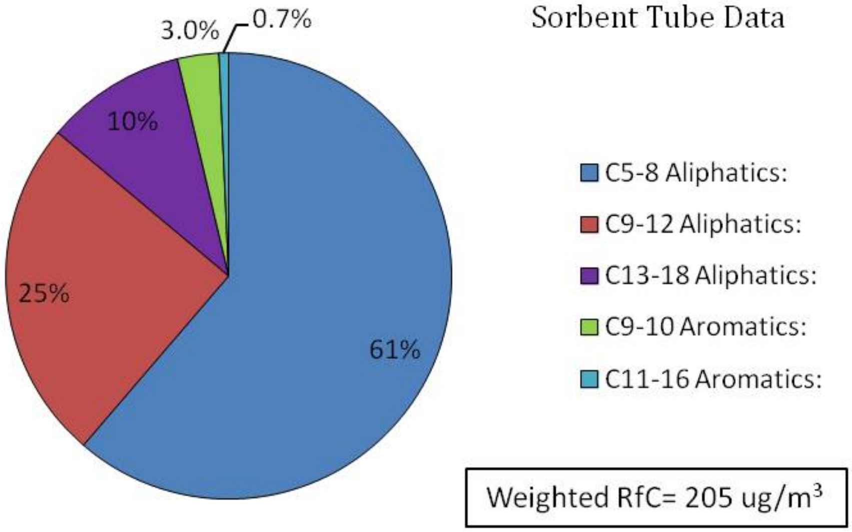


Figure 19. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples of vapors from fresh diesel and correlative, weighted Reference Concentration for inhalation toxicity.

Data File: /chem/msd2.i/12oct11.b/2101220.d Page 1

Date : 12-OCT-2011 18:55

Client ID: Instrument: msd2.i

Sample Info: 2.0ml #34656

Operator: EA

Column phase: RTx-624 Column diameter: 0.32

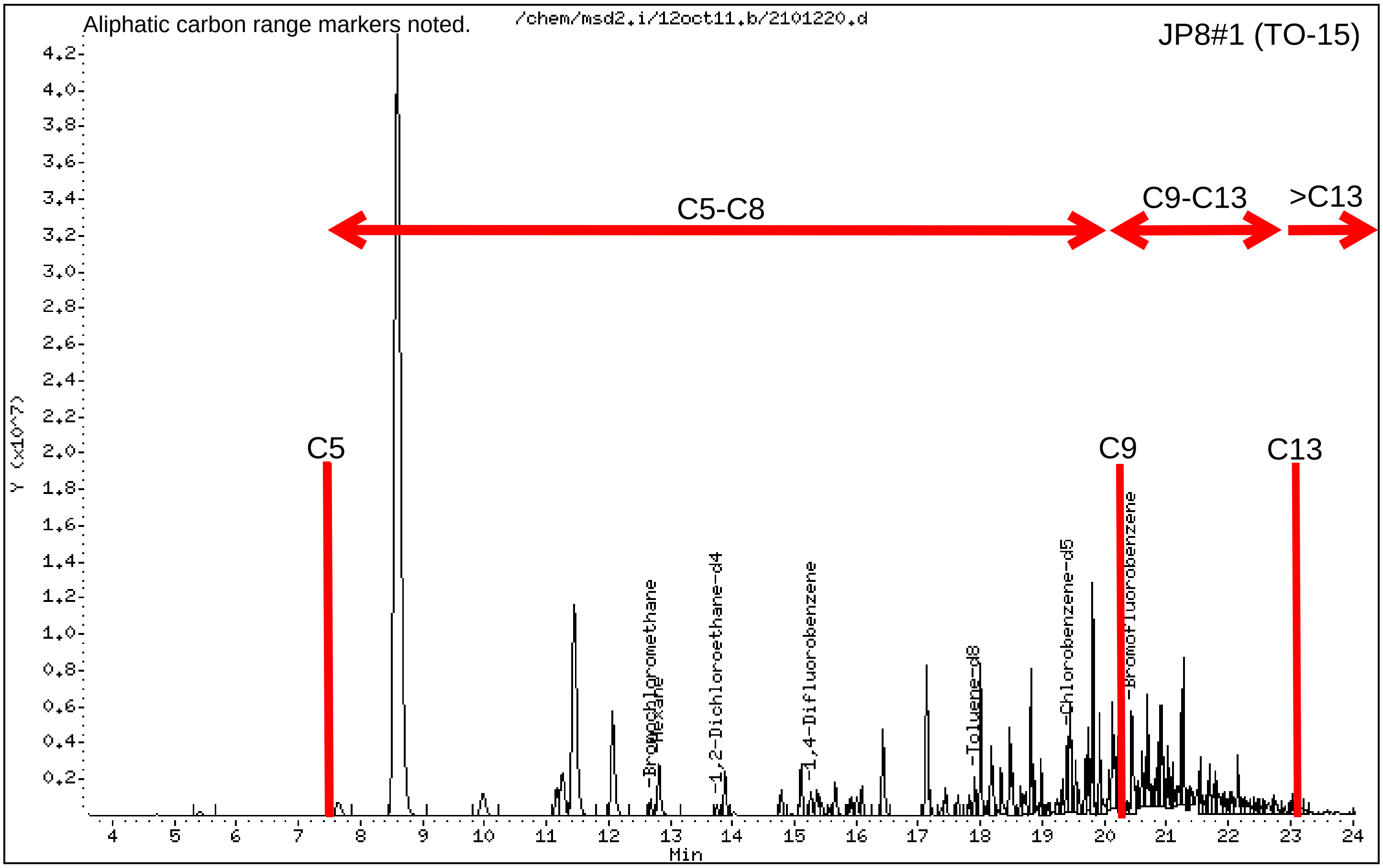
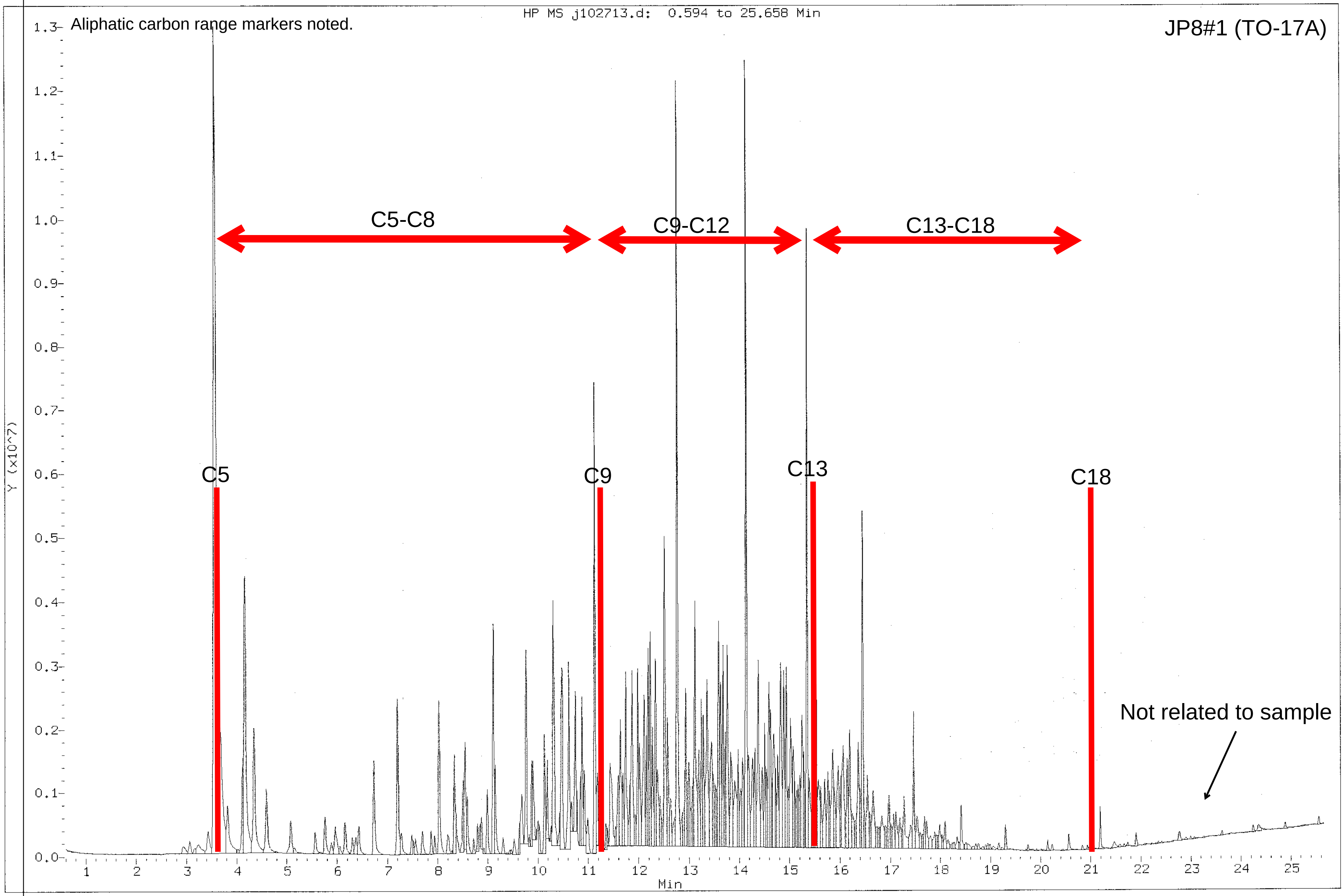
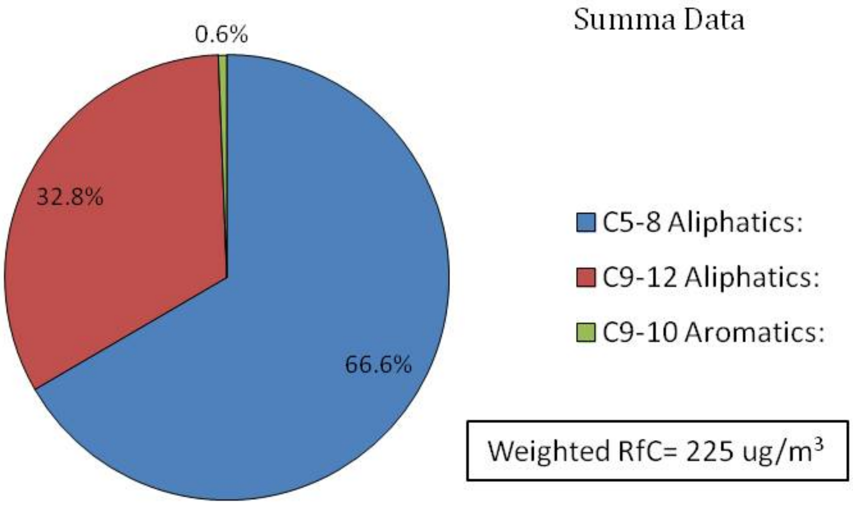


Figure 20a. Example gas chromatogram of vapors collected in summa canister from fresh JP-8 fuel with key carbon range markers indicated.

Figure 20b. Example gas chromatogram of vapors collected with a sorbent tube from fresh JP-8 fuel with key carbon range markers indicated.

```
Data File: /chem/msdj.i/27oct11.b/j102713.d
Injection Date: 27-OCT-2011 17:09
Instrument: msdj.i
Client Sample ID: JP8#1 (TO17A)
```





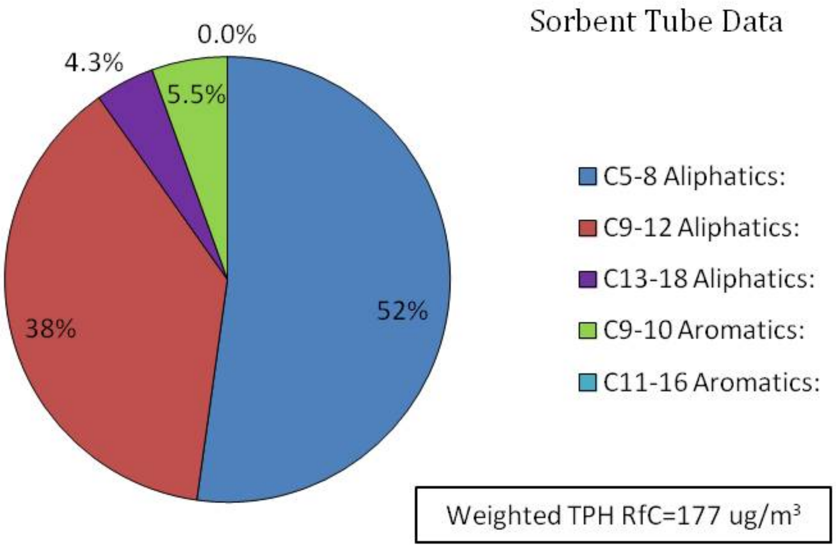


Figure 21. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples of vapors from fresh JP-8 and correlative, weighted Reference Concentration for inhalation toxicity.

Data File: /chem/msd2.i/24oct11.b/2102422.d

Page 1

Date : 24-OCT-2011 22:46

Client ID:

Instrument: msd2.i

Sample Info: 6.0ml #37684

Operator: srs

Column phase: RTx-624

Column diameter: 0.32

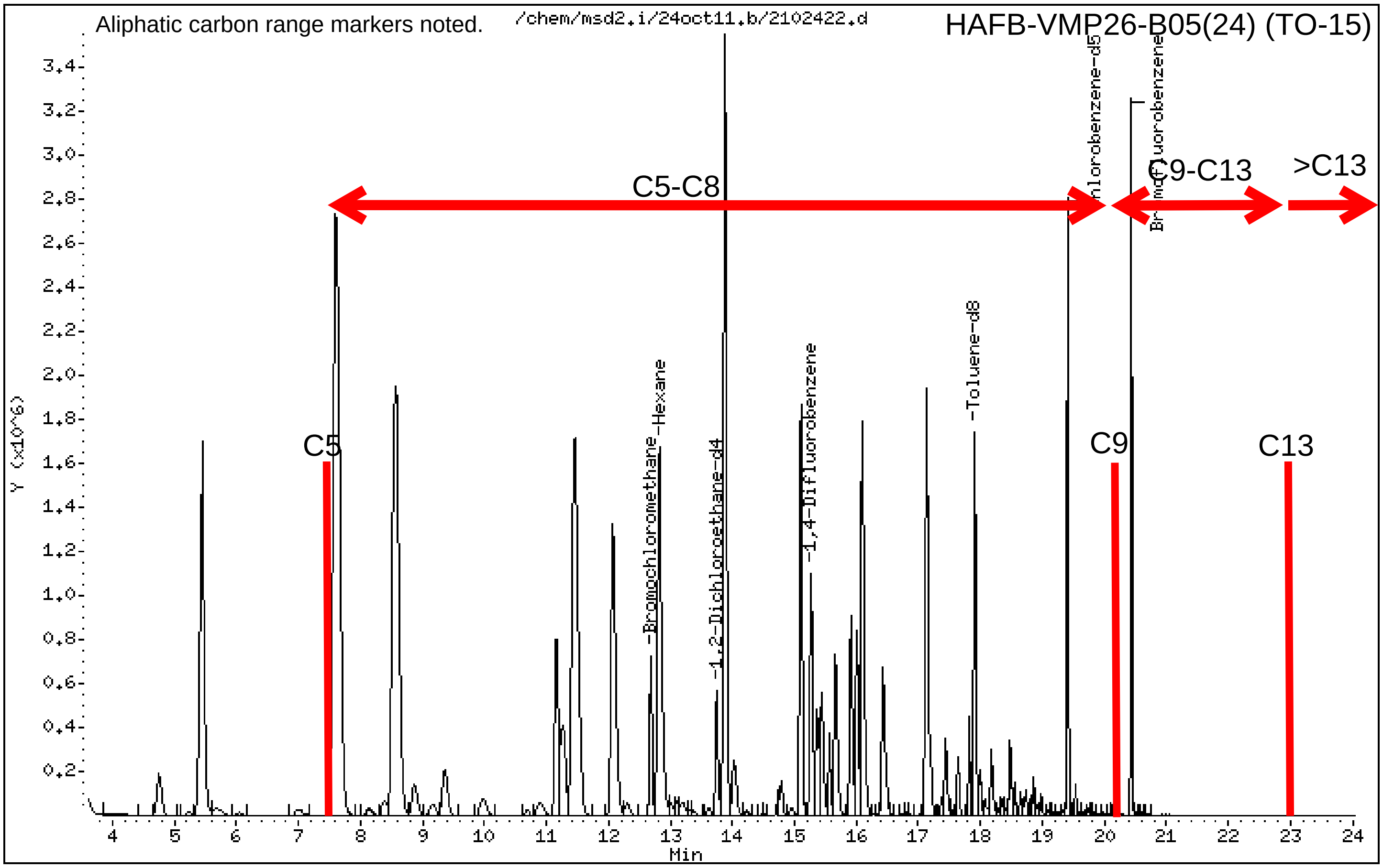
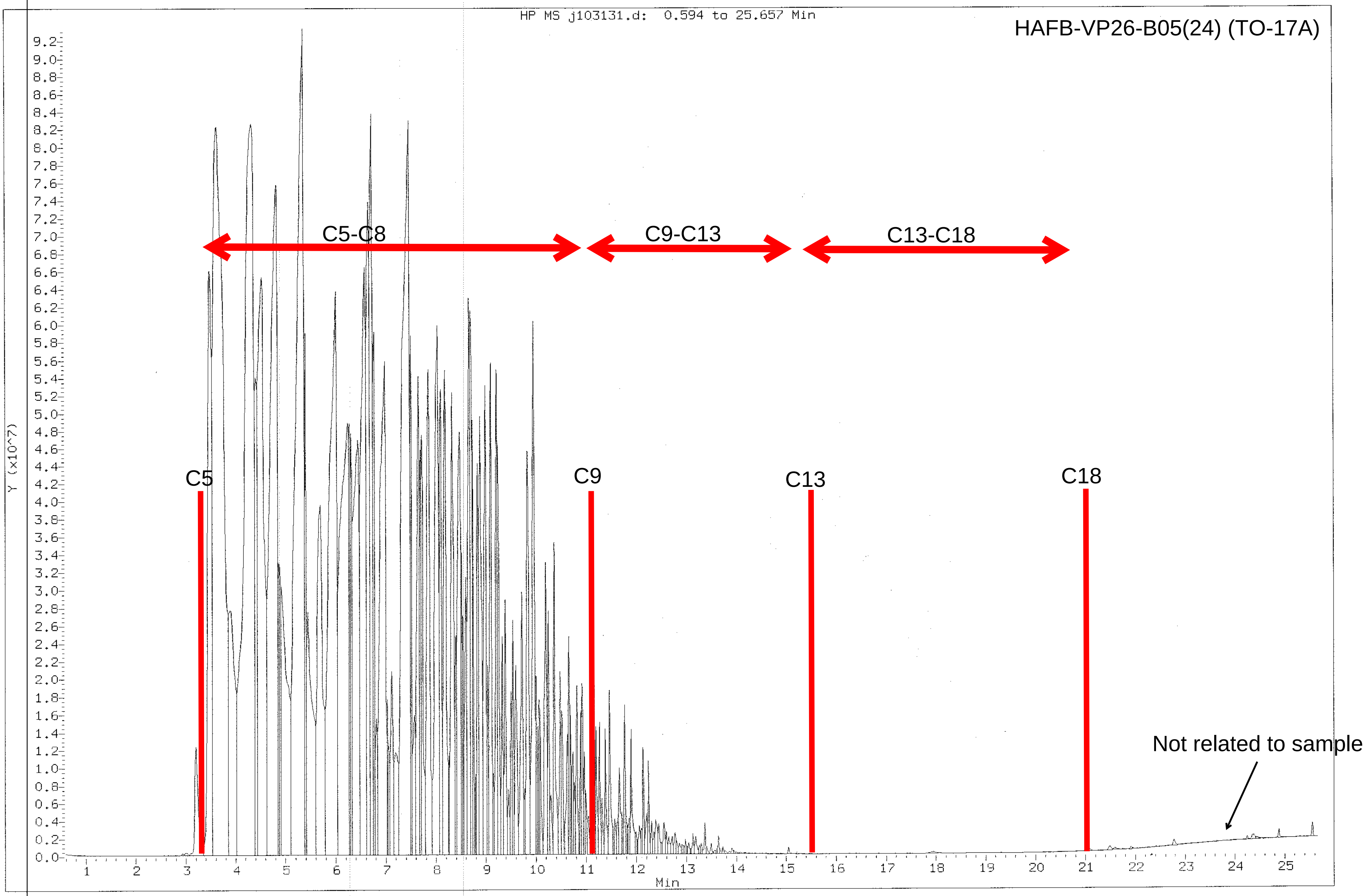


Figure 22a. Example gas chromatogram of vapors collected in summa canister from Site A (JP-4/AVGAS?) fuel with key carbon range markers indicated.

Figure 22b. Example gas chromatogram of vapors collected with a sorbent tube from Site A (JP-4/AVGAS?) fuel with key carbon range markers indicated.

Data File: /chem/msdj.i/31oct11.b/j103131.d
Injection Date: 01-NOV-2011 03:51
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B05(24)(TO17A)



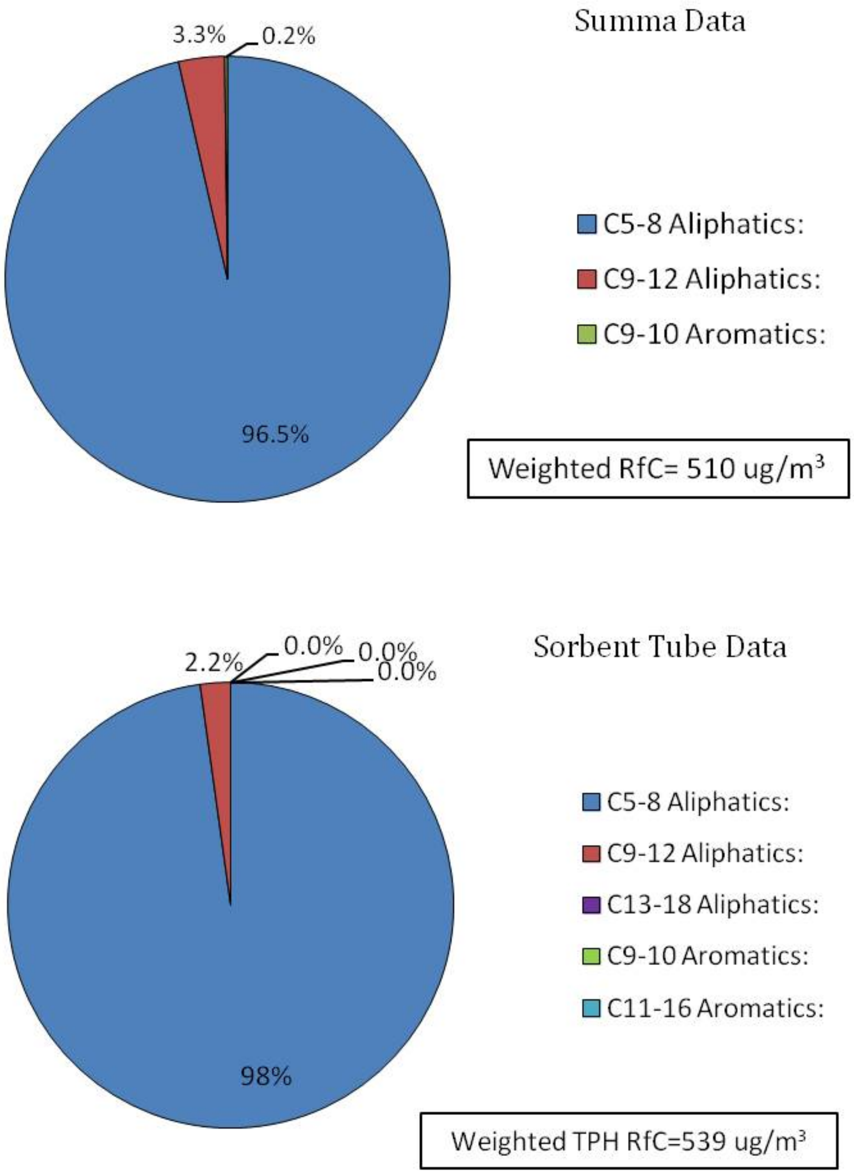


Figure 23. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples from Site A (JP-4/AVGAS) and correlative, weighted Reference Concentration for inhalation toxicity.

Data File: /chem/msd2.i/25oct11.b/2102510.d

Date : 25-OCT-2011 12:28

Client ID:

Sample Info: 2.0ml #34574

Column phase: RTx-624

Instrument: msd2.i

Operator: mtw

Column diameter: 0.32

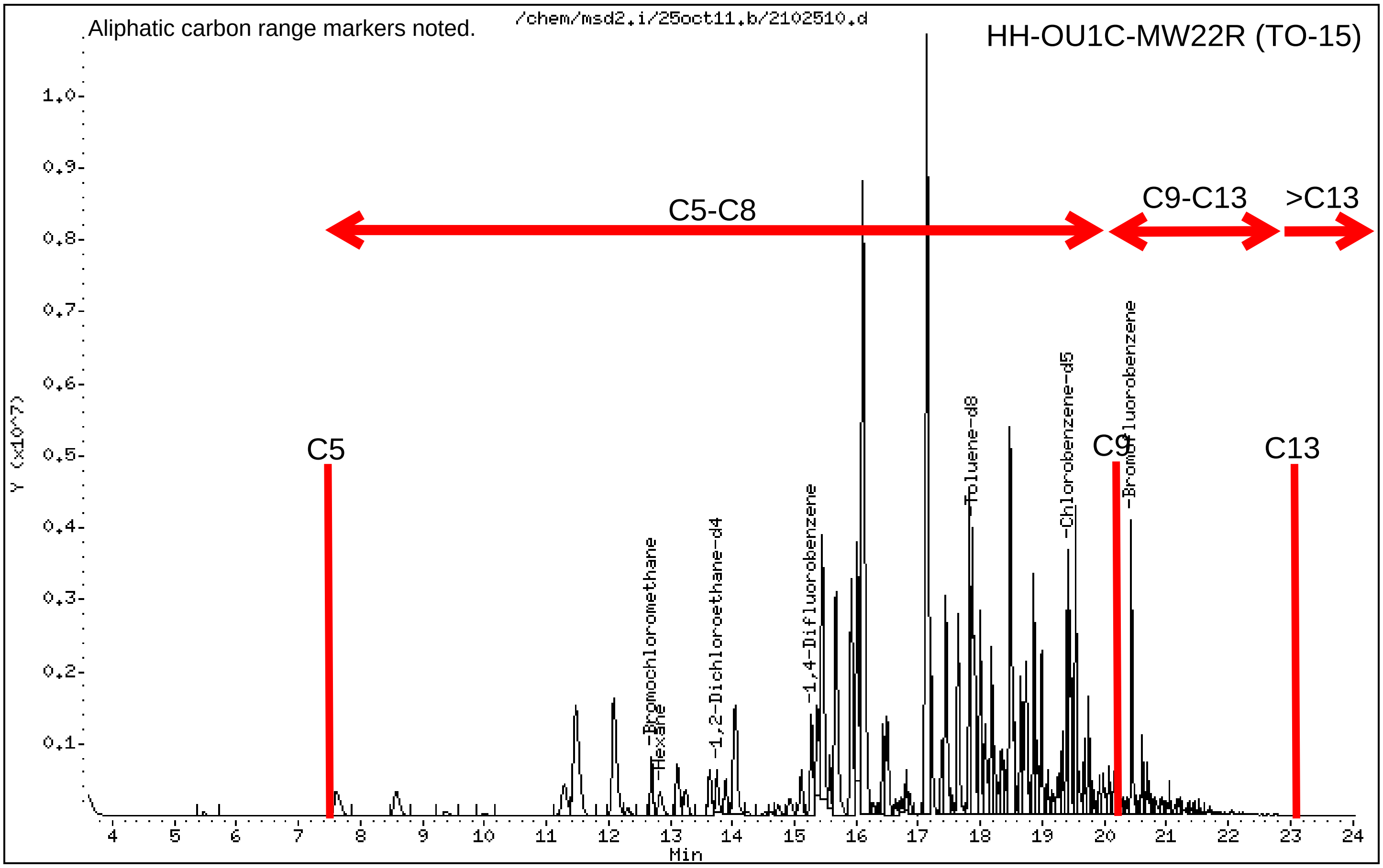
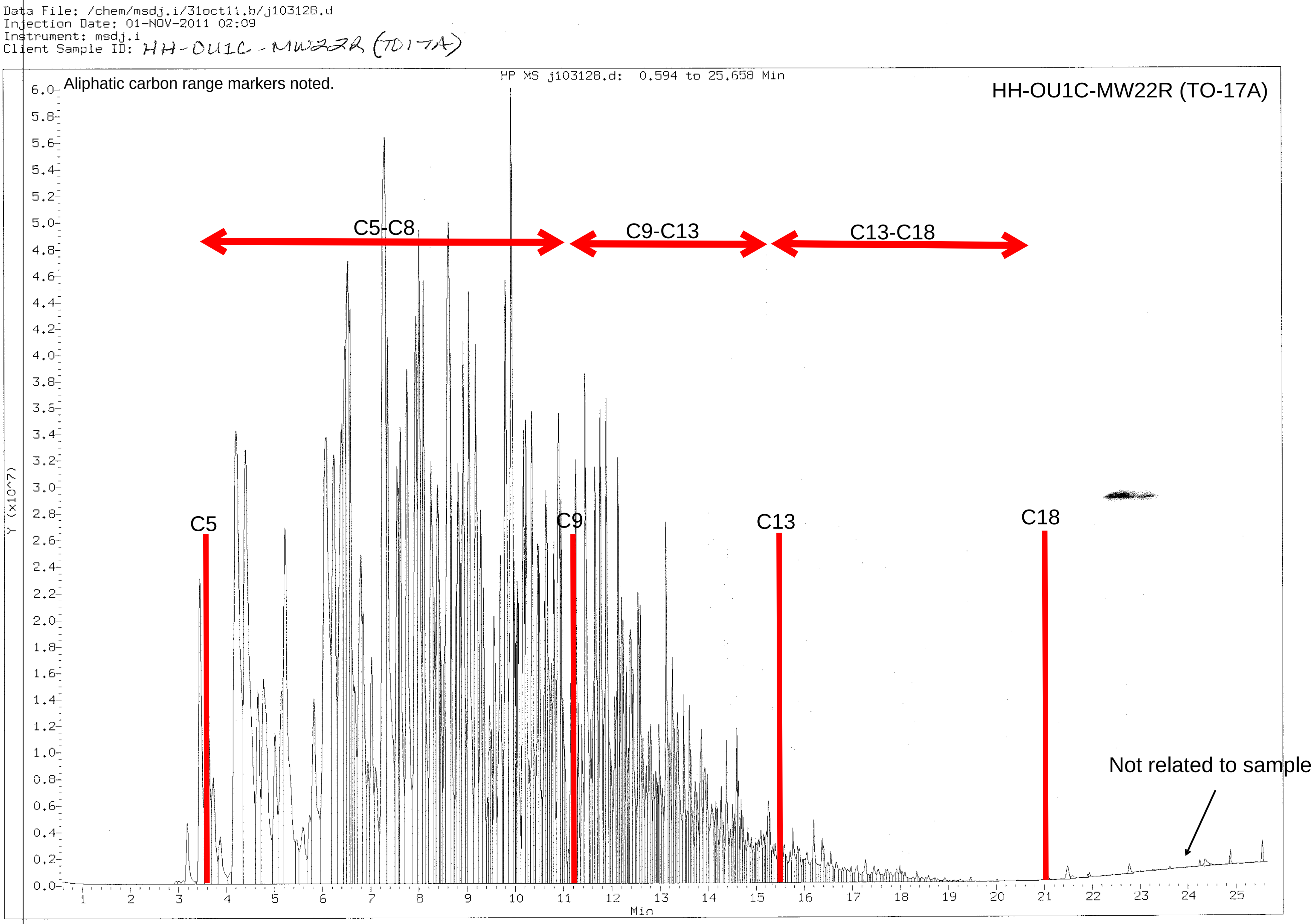


Figure 24a. Example gas chromatogram of vapors collected in summa canister from Site B (mixed fuels) with key carbon range markers indicated.

Figure 24b. Example gas chromatogram of vapors collected with a sorbent tube from Site B (mixed fuels) with key carbon range markers indicated.



Data File: /chem/msdj.i/31oct11.b/j103128.d
Injection Date: 01-NOV-2011 02:09
Instrument: msdj.i
Client Sample ID: HH-OU1C-MW22R (TO17A)

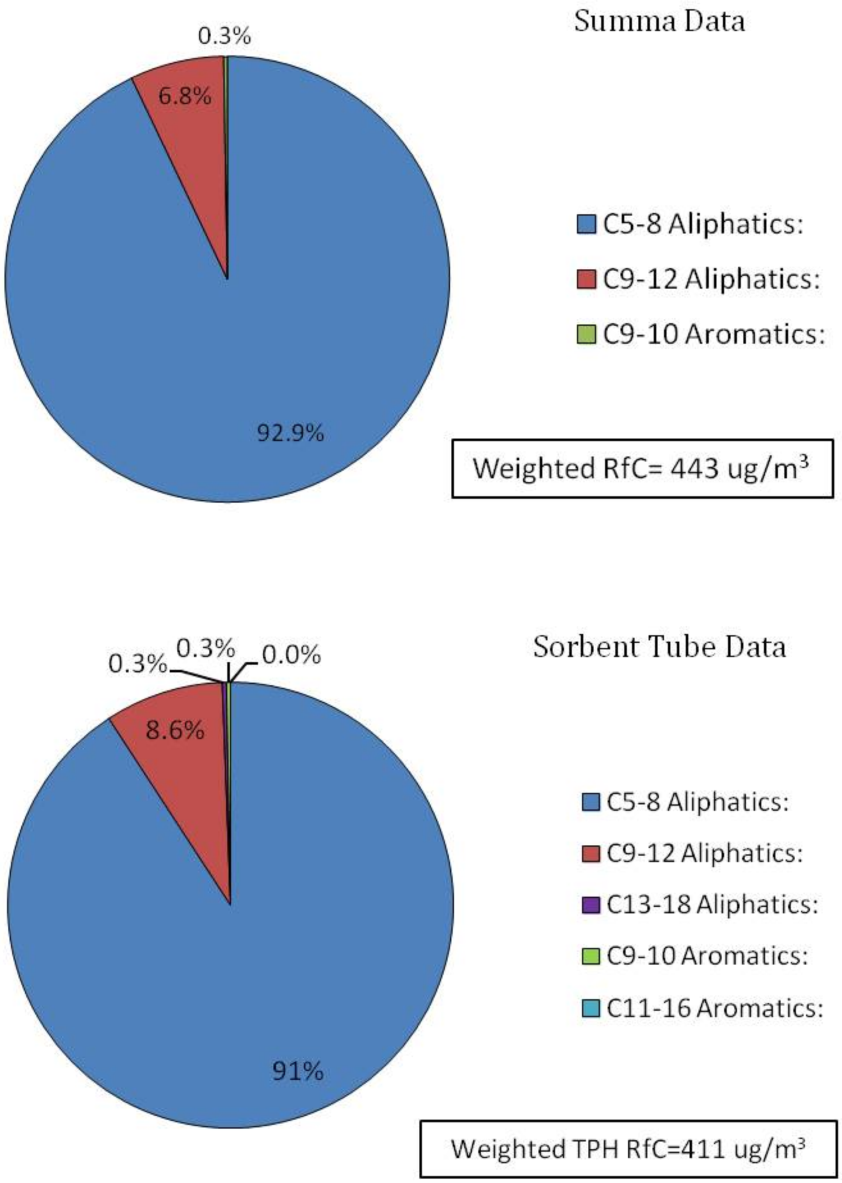


Figure 25. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples from Site B (mixed fuels) and correlative, weighted Reference Concentration for inhalation toxicity.

Data File: /chem/msd2.i/12oct11.b/2101218.d Page 1

Date : 12-OCT-2011 17:31

Client ID: Instrument: msd2.i

Sample Info: 2.0ml #36517

Operator: EA

Column phase: RTx-624 Column diameter: 0.32

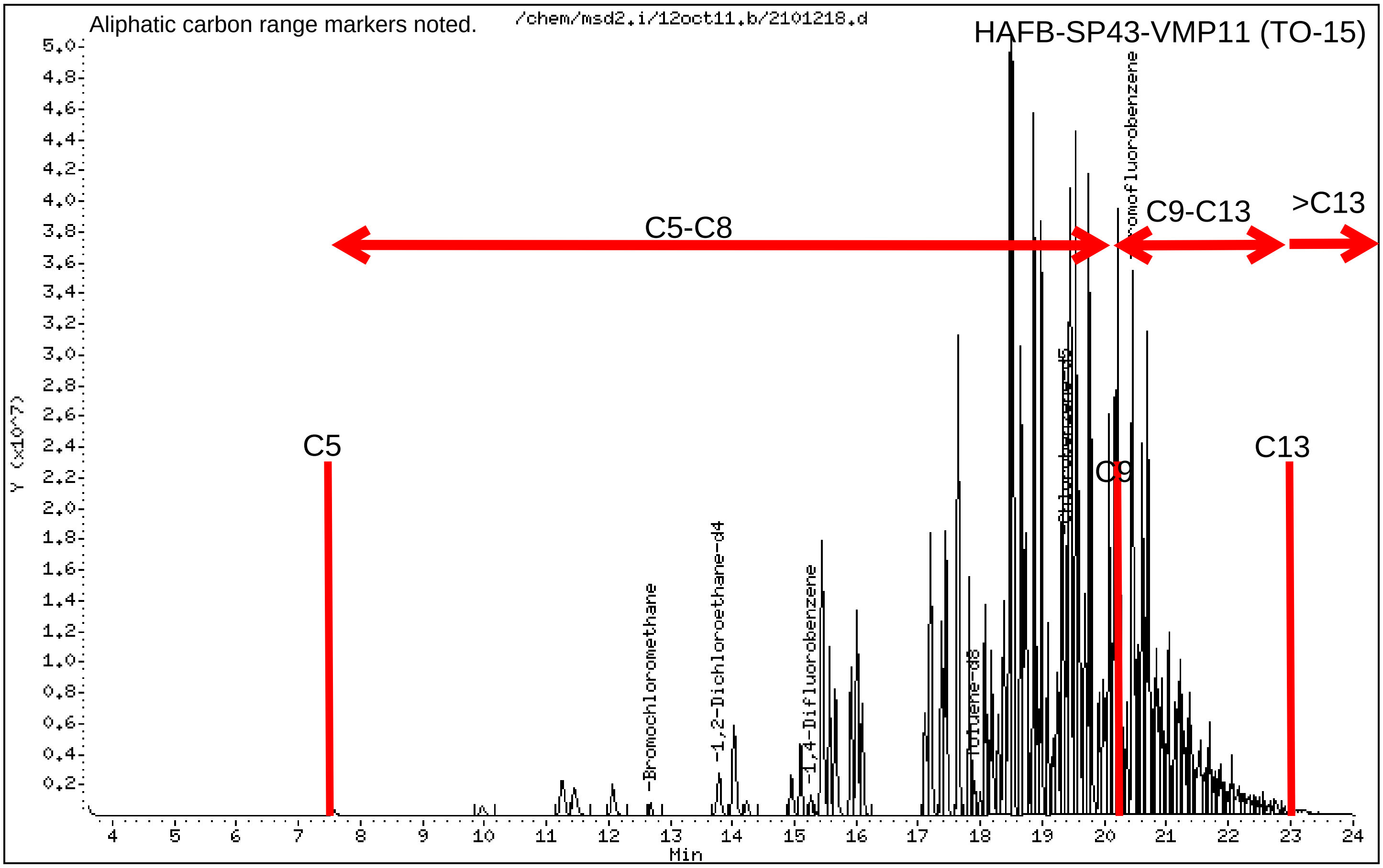
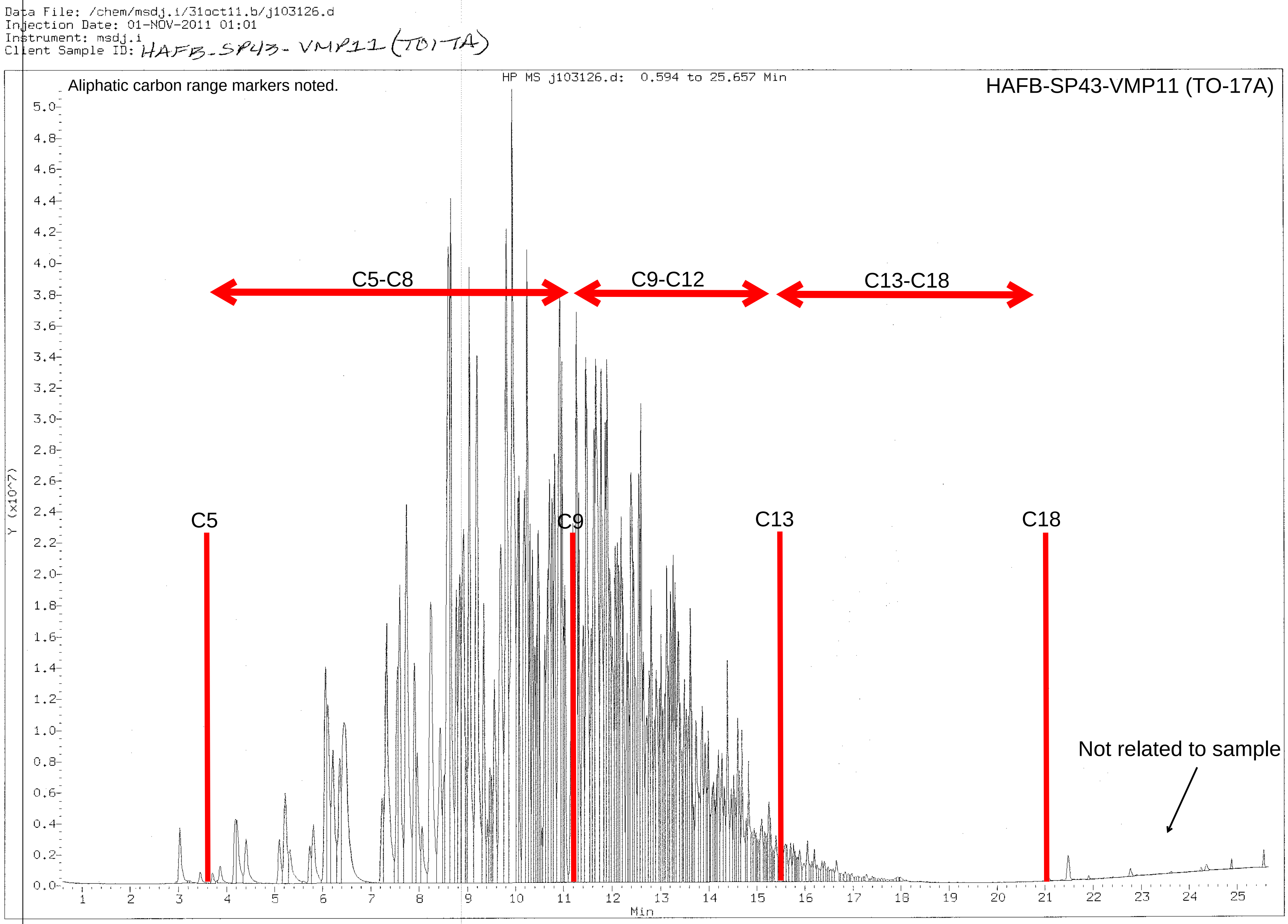


Figure 26a. Example gas chromatogram of vapors collected in summa canister from Site C (JP-8 +/- JP-4) with key carbon range markers indicated.

Figure 26b. Example gas chromatogram of vapors collected with a sorbent tube from Site C (JP-8 +/- JP-4) with key carbon range markers indicated.



Data File: /chem/msdj.i/31oct11.b/j103126.d
Injection Date: 01-NOV-2011 01:01
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP11 (TO17A)

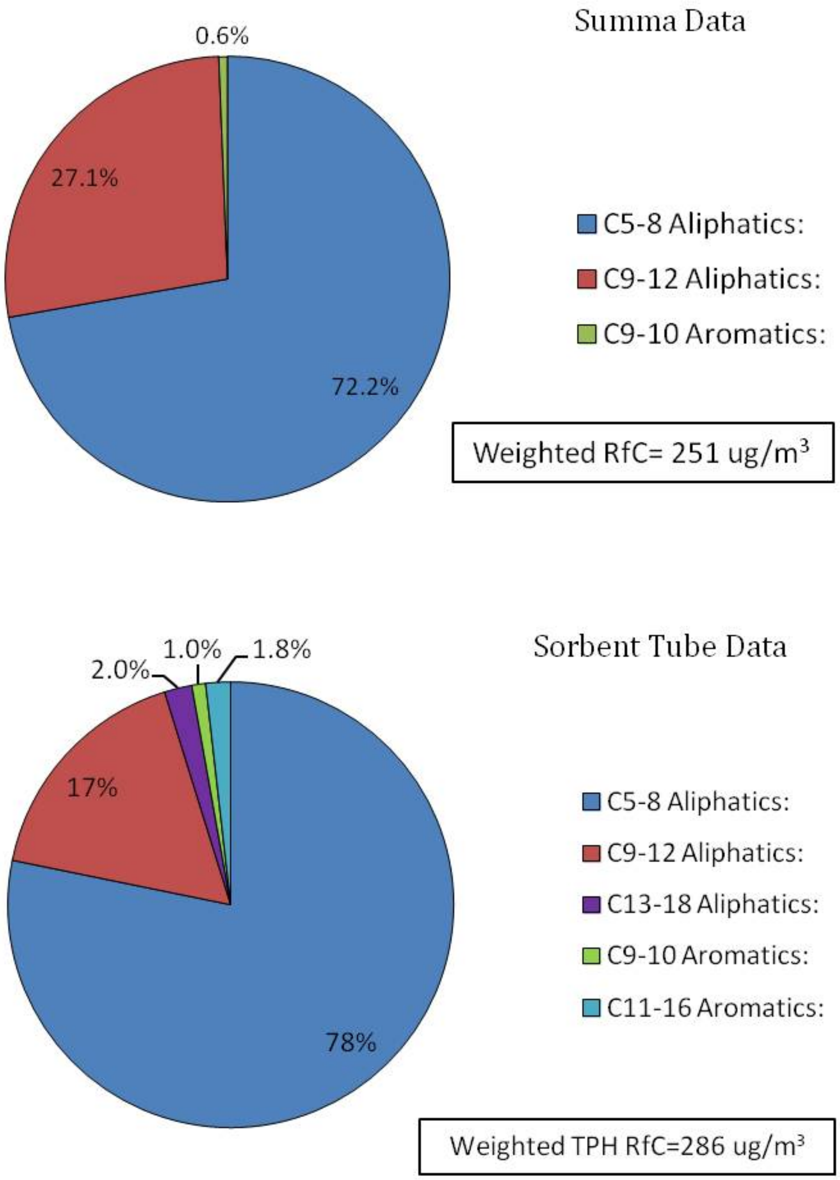


Figure 27. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples from Site C (JP-8 +/- JP-4) and correlative, weighted Reference Concentration for inhalation toxicity.

Data File: /chem/msd2.i/21oct11.b/2102115.d

Page 1

Date : 21-OCT-2011 18:08

Client ID:

Instrument: msd2.i

Sample Info: 15ml #3039

Operator: srs

Column phase: RTx-624

Column diameter: 0.32

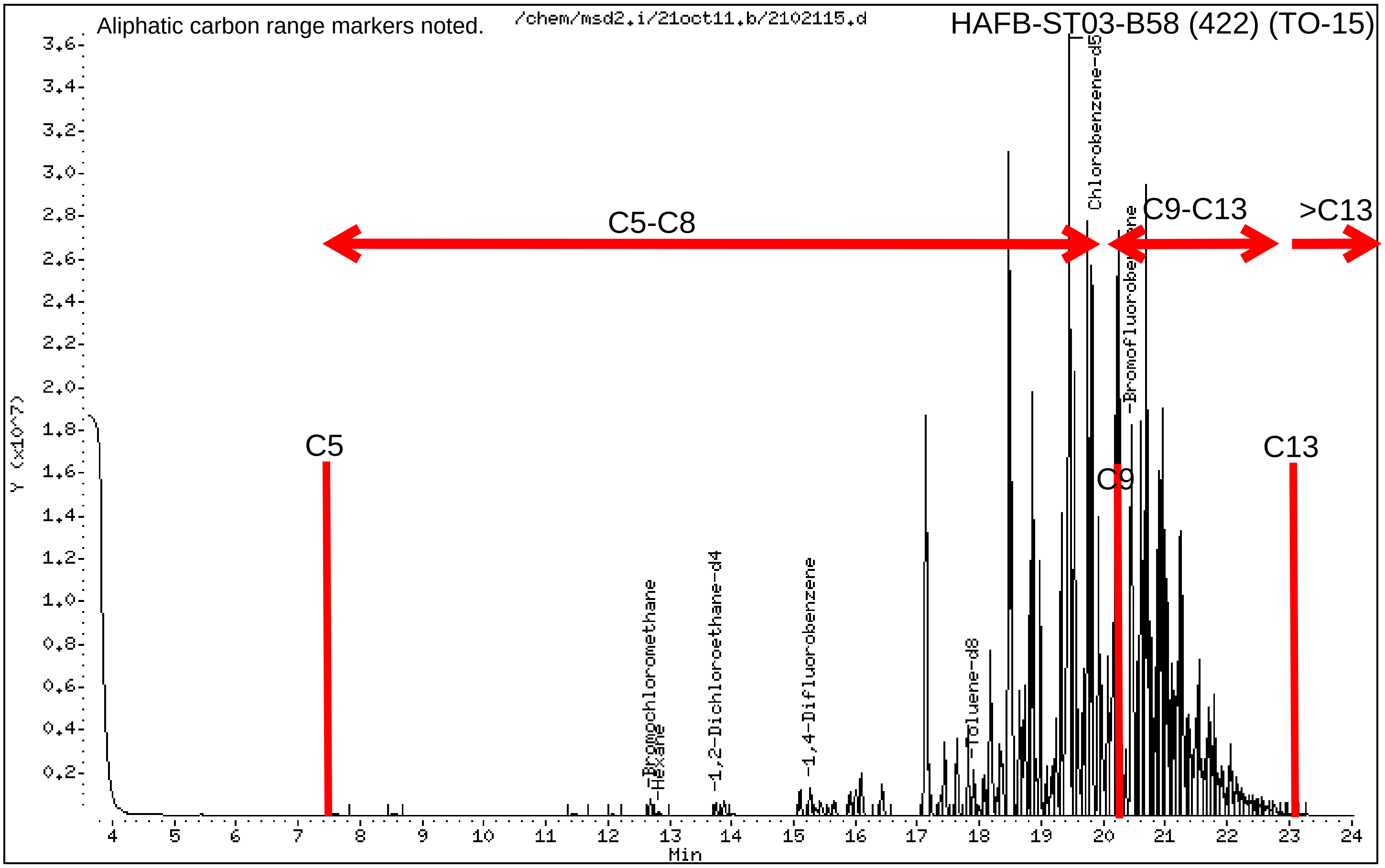
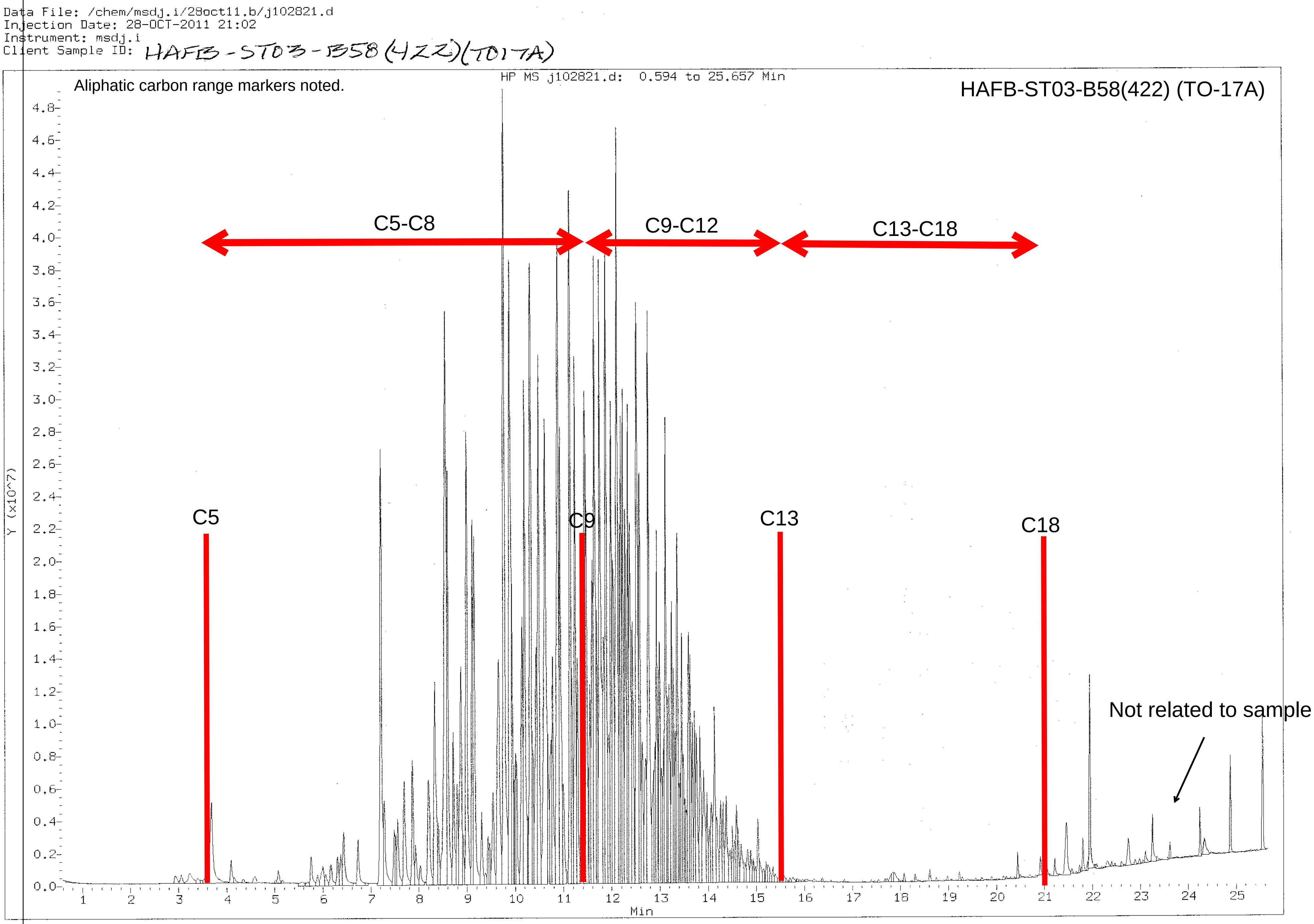


Figure 28a. Example gas chromatogram of vapors collected in summa canister from Site D (JP-4/AVGAS?) with key carbon range markers indicated.

Figure 28b. Example gas chromatogram of vapors collected with a sorbent tube from Site D (JP-4/AVGAS?) with key carbon range markers indicated.



Data File: /chem/msdj.i/28oct11.b/j102821.d
Injection Date: 28-OCT-2011 21:02
Instrument: msdj.i
Client Sample ID: HAFB-ST03-B58(422)(TO17A)

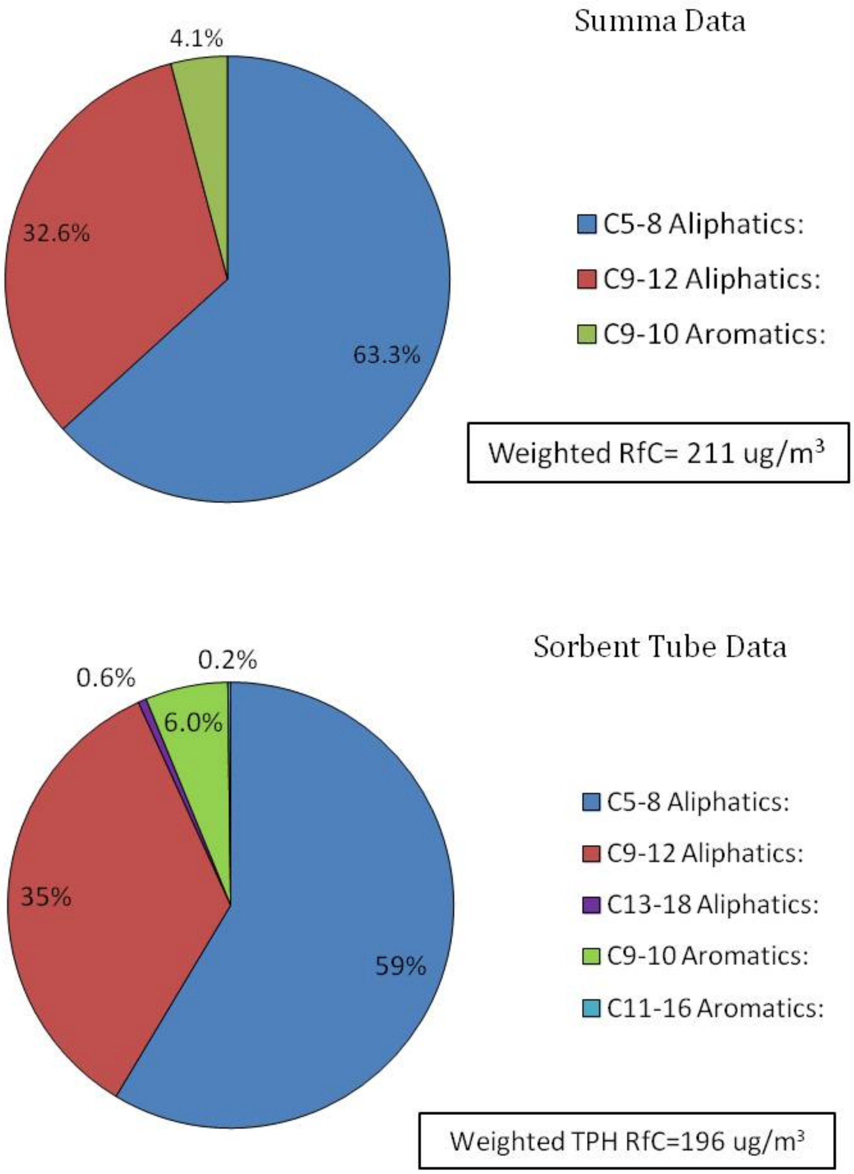


Figure 29. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples from Site D (JP-4/AVGAS) and correlative, weighted Reference Concentration for inhalation toxicity.

Data File: /chem/msd2.i/12oct11.b/2101224.d

Page 1

Date : 12-OCT-2011 21:52

Client ID:

Instrument: msd2.i

Sample Info: 2.0ml #37738

Operator: EA

Column phase: RTx-624

Column diameter: 0.32

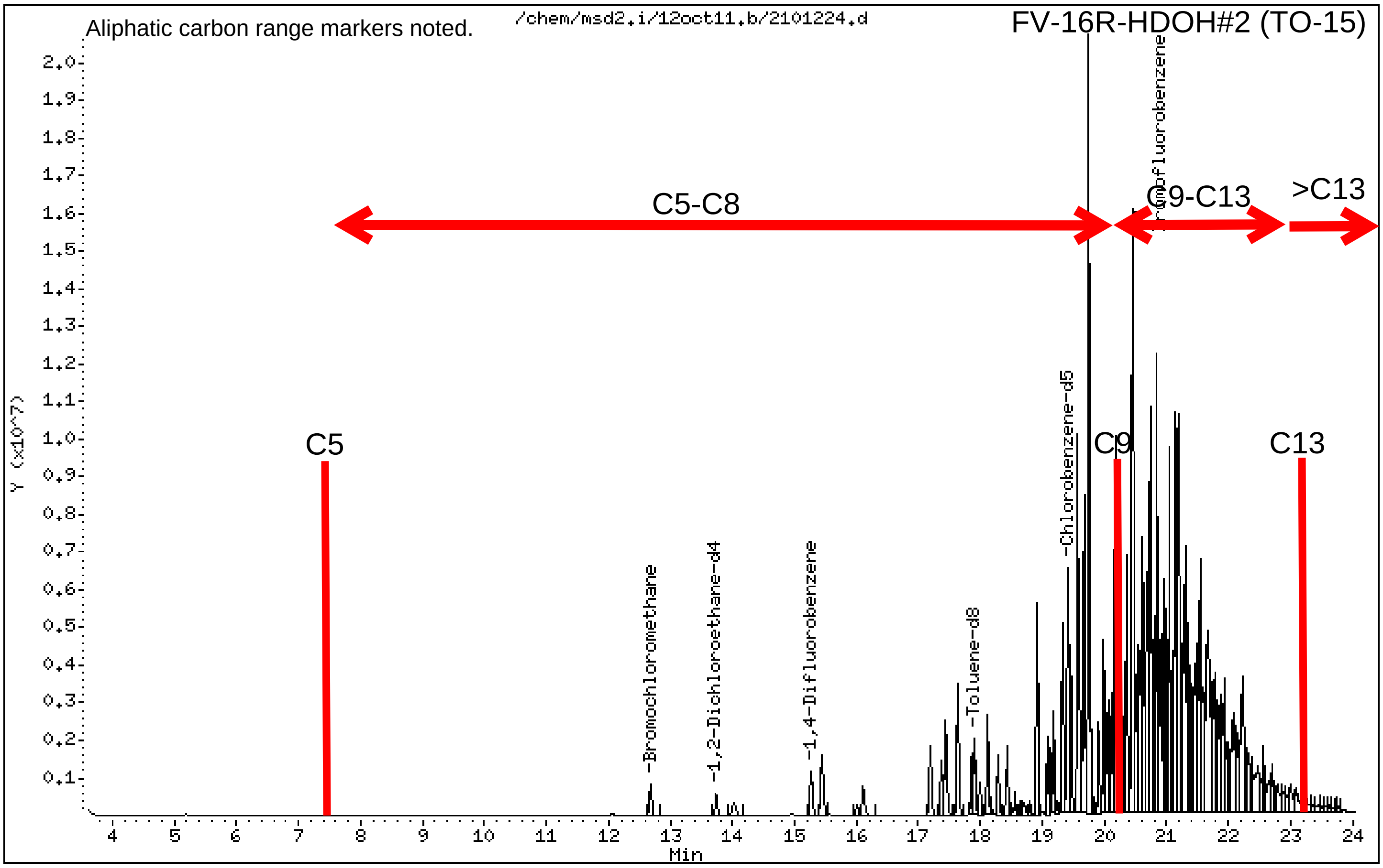
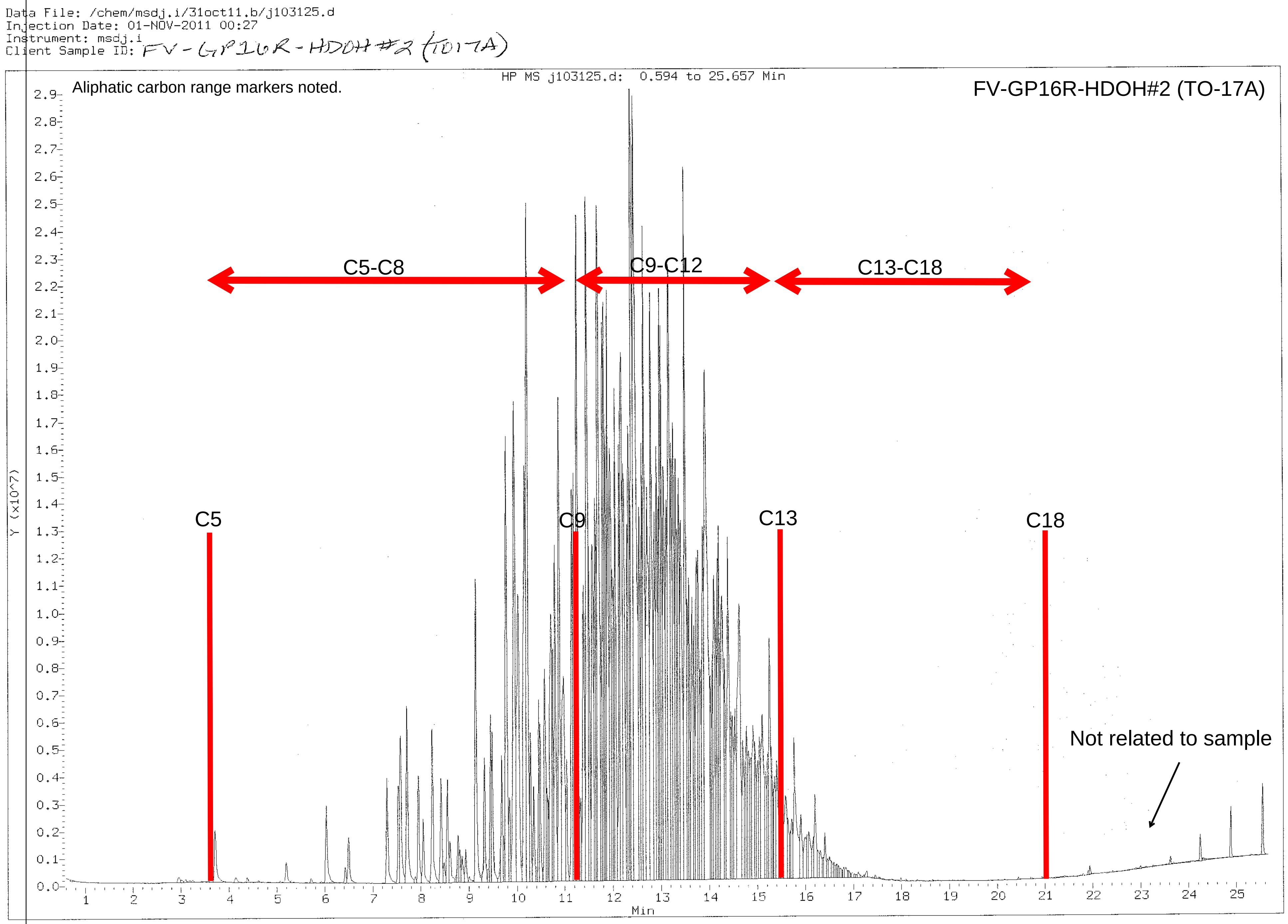


Figure 30a. Example gas chromatogram of vapors collected in summa canister from Site D (diesel) with key carbon range markers indicated.

Figure 30b. Example gas chromatogram of vapors collected with a sorbent tube from Site D (diesel) with key carbon range markers indicated.



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Data File: /chem/msdj.i/31oct11.b/j103125.d
Injection Date: 01-NOV-2011 00:27
Instrument: msdj.i
Client Sample ID: FV-GP16R-HDOH #2 (TO17A)
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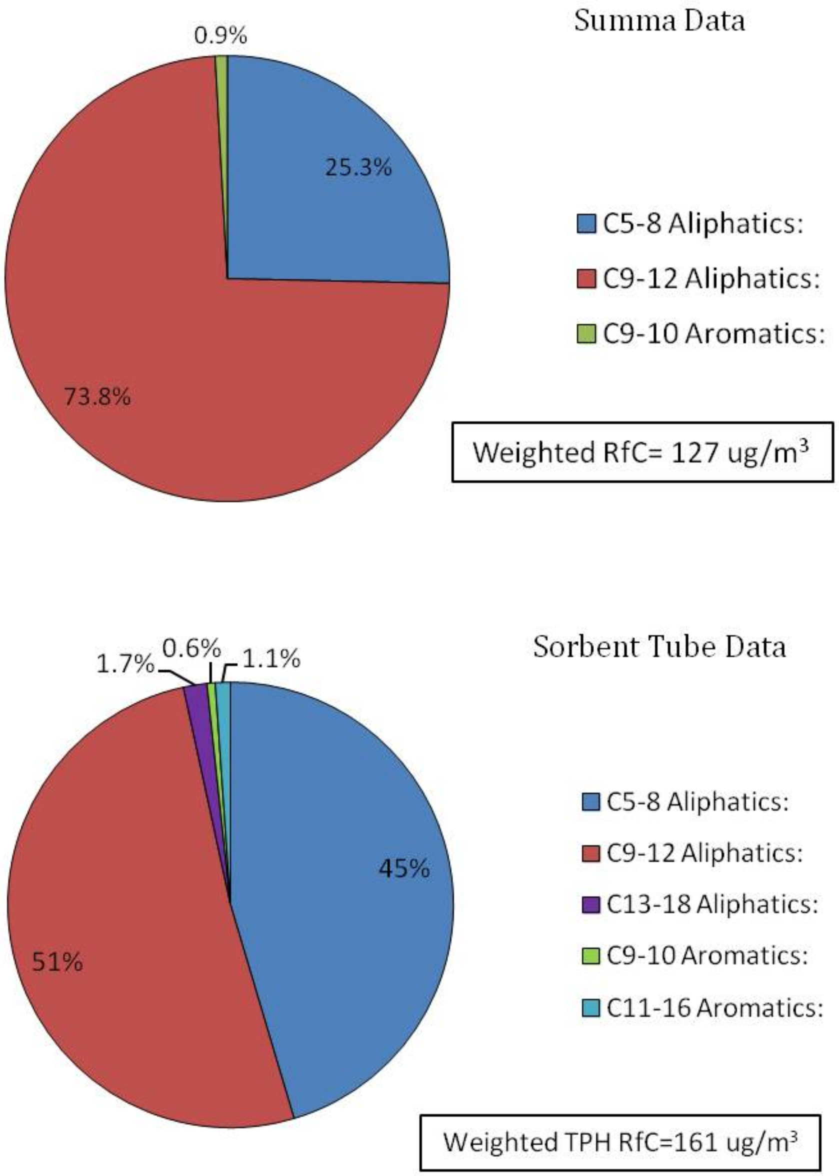
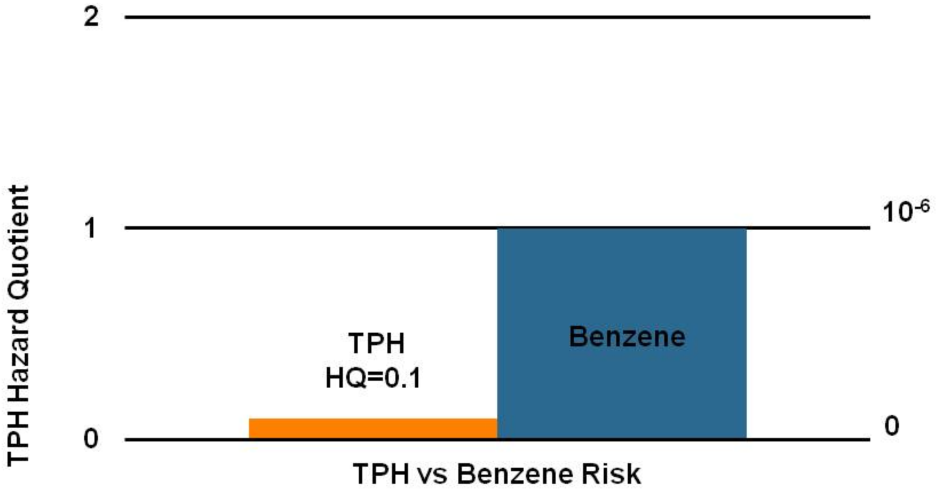
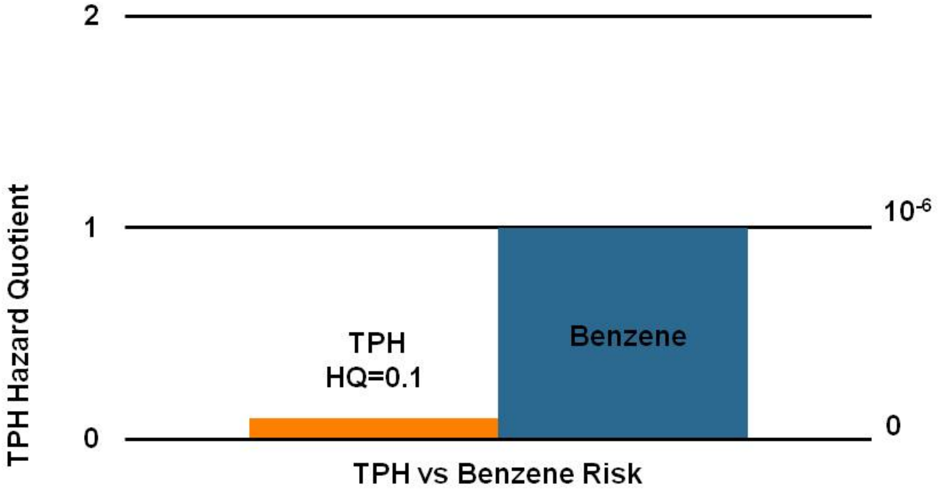


Figure 31. Pie chart of average TPH carbon range makeup of petroleum vapors based on Summa canister versus sorbent tube samples from Site E (diesel) and correlative, weighted Reference Concentration for inhalation toxicity.

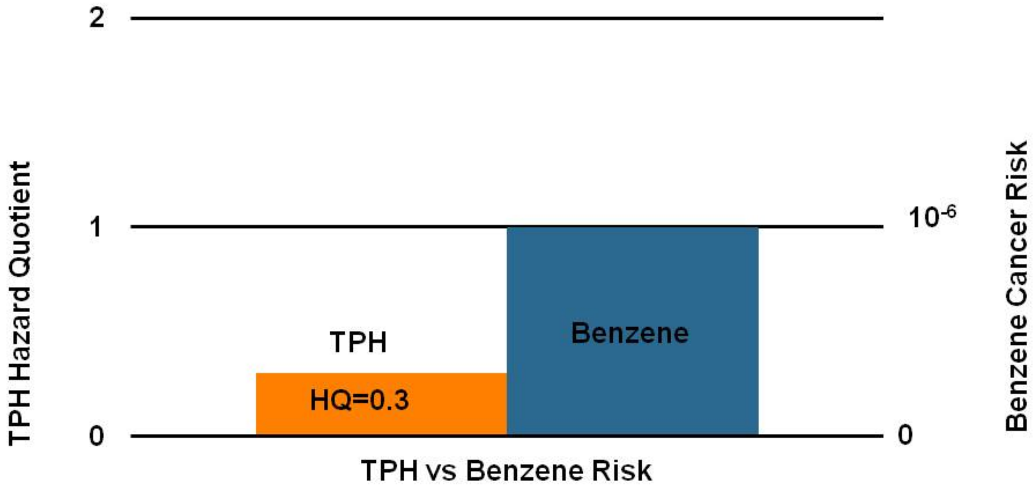


Summa Data



Sorbent Tube Data

Figure 32. TPH versus benzene as the risk driver for petroleum vapors collected over fresh gasoline based on Summa vs sorbent tube carbon range data. Benzene adequate to evaluate vapor intrusion hazards provided that a target 10^{-5} cancer risk is used (TPH noncancer HQ<1 when benzene risk 10^{-5}).



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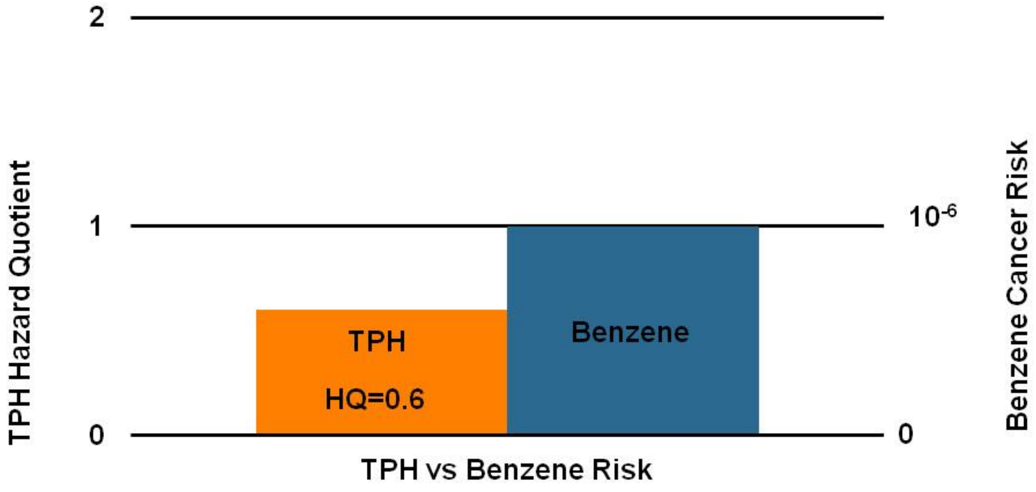
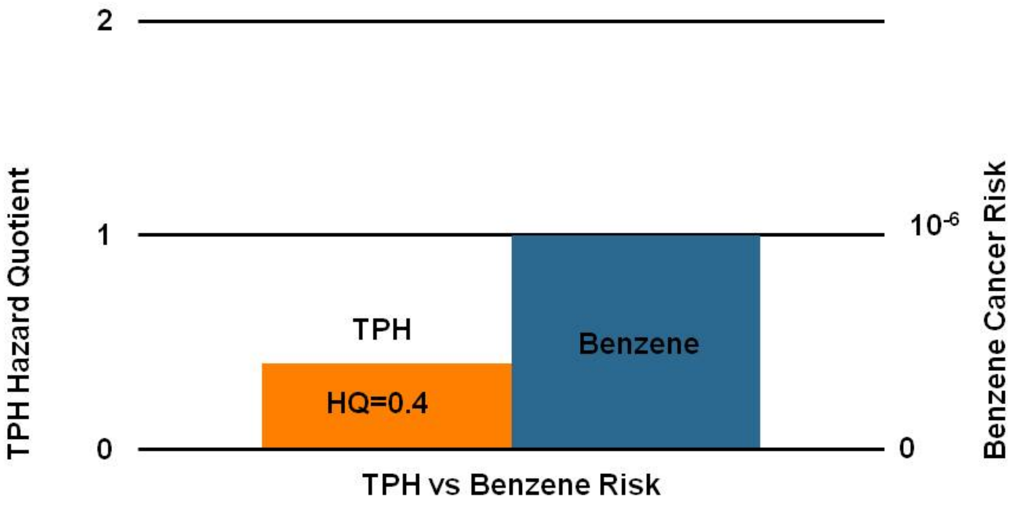


Sorbent Tube Data

Figure 33. TPH versus benzene as the risk driver for petroleum vapors collected over fresh diesel based on Summa vs sorbent tube carbon range data. Benzene adequate to evaluate vapor intrusion hazards (TPH noncancer HQ<1 when benzene risk 10^{-6}).



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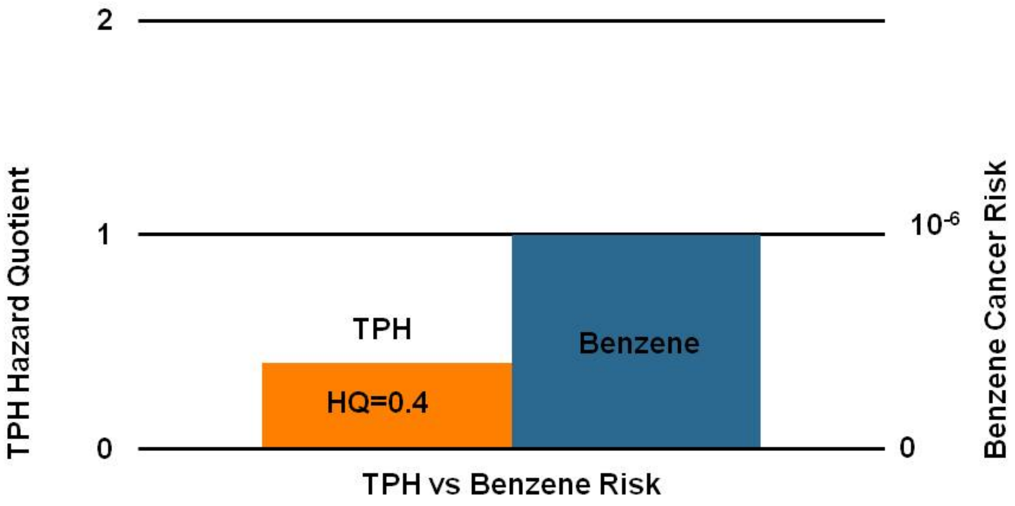
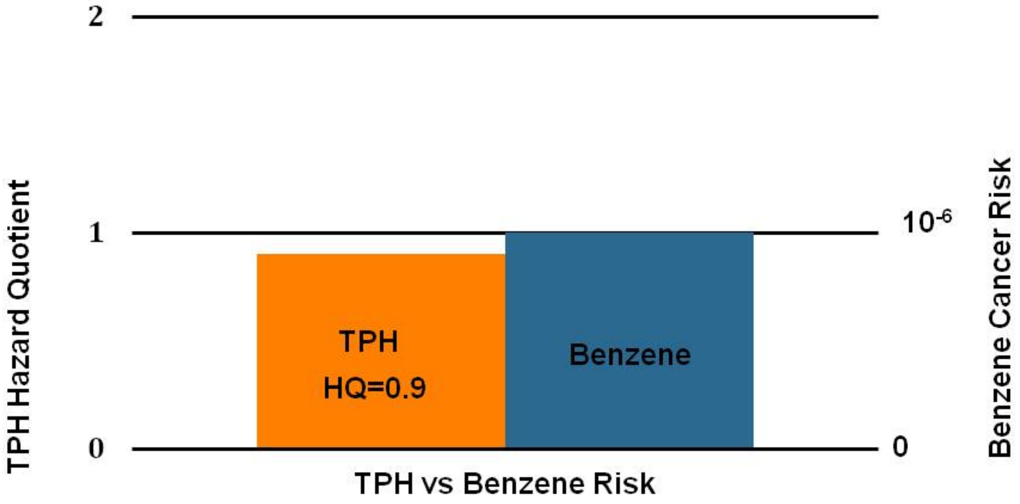


Sorbent Tube Data

Figure 34. TPH versus benzene as the risk driver for petroleum vapors collected over fresh JP-8 jet fuel based on Summa vs sorbent tube carbon range data. Benzene adequate to evaluate vapor intrusion hazards provided that a target 10^{-6} cancer risk is used (TPH noncancer $HQ<1$ when benzene risk 10^{-6}).



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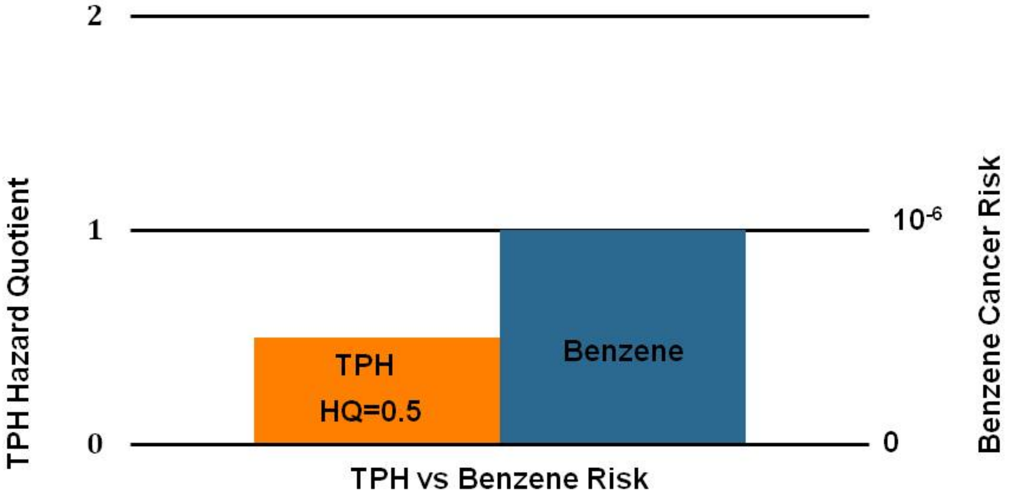
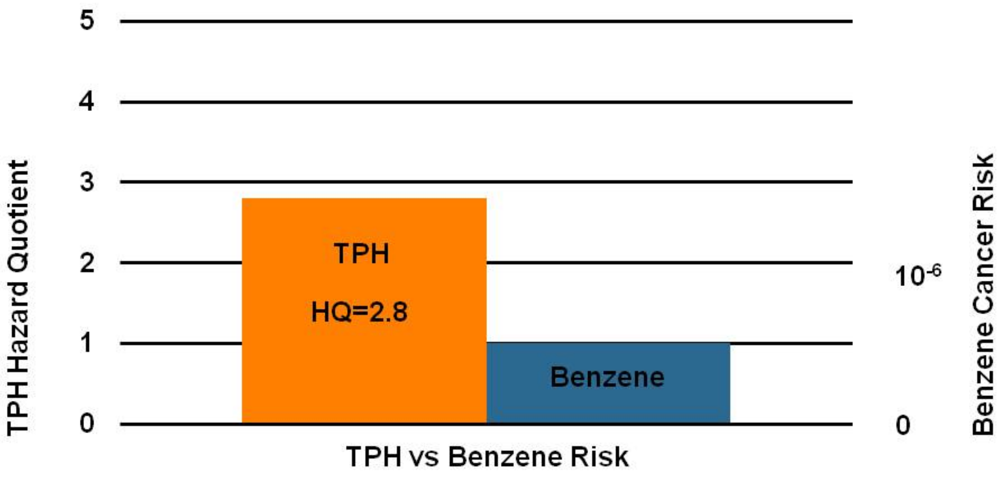


Sorbent Tube Data

Figure 35. TPH versus benzene as the risk driver for petroleum vapors in soil gas samples collected from Site A (JP-4/AVGAS) based on Summa vs sorbent tube carbon range data. Benzene adequate to evaluate vapor intrusion hazards provided that a target 10^{-6} cancer risk is used (TPH noncancer HQ<1 when benzene risk 10^{-6}).



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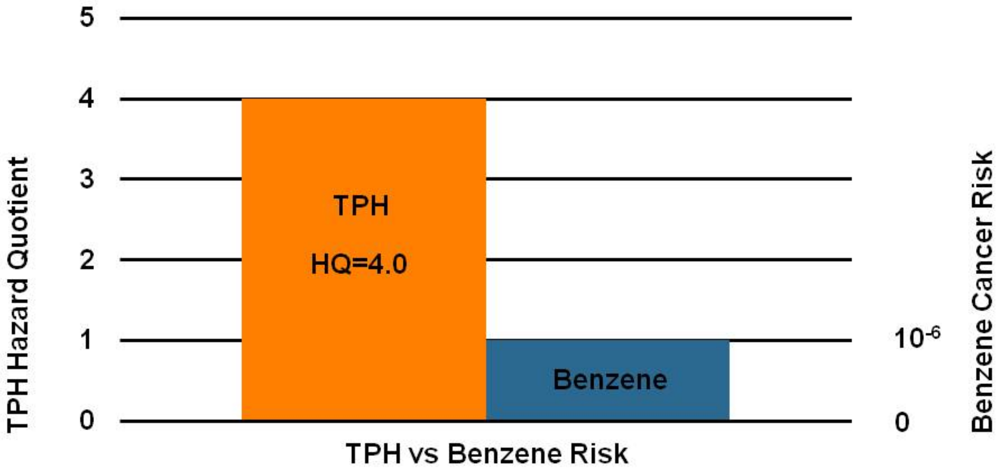
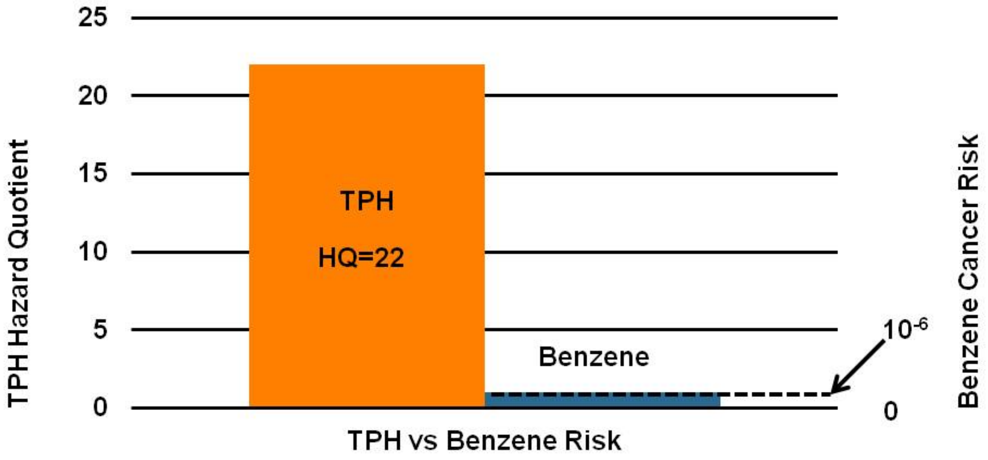


Sorbent Tube Data

Figure 36. TPH versus benzene as the risk driver for petroleum vapors in soil gas samples collected from Site B (mixed fuels) based on Summa vs sorbent tube carbon range data. TPH *always* drives potential vapor intrusion hazards (TPH noncancer HQ>1 even when benzene risk 10^{-6}).



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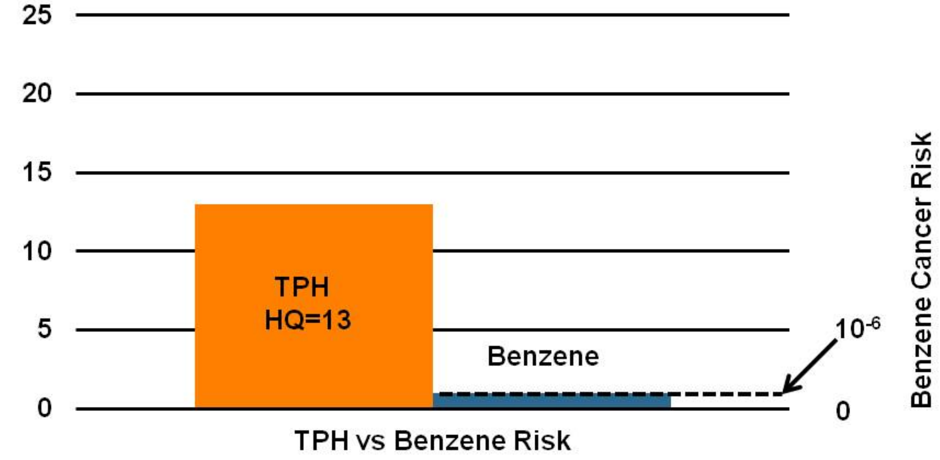
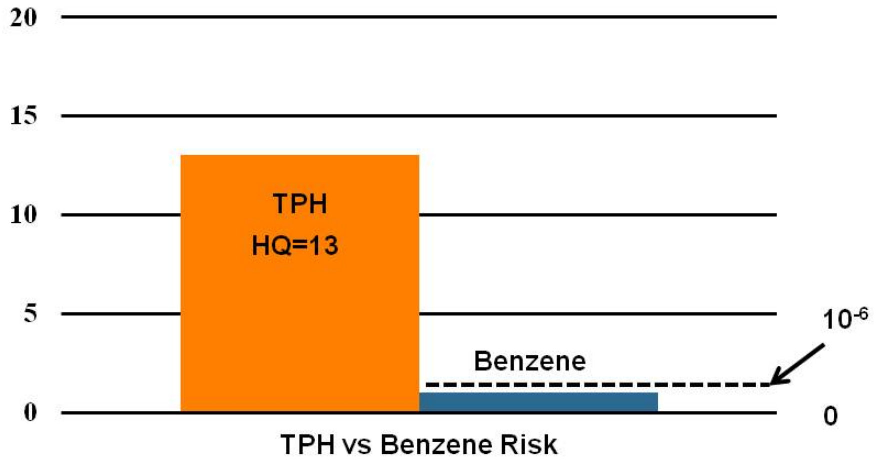


Sorbent Tube Data

Figure 37. TPH versus benzene as the risk driver for petroleum vapors in soil gas samples collected from Site C (JP-8 +/- JP-4) based on Summa vs sorbent tube carbon range data. TPH *always* drives potential vapor intrusion hazards (TPH noncancer HQ>1 even when benzene risk 10^{-6}).



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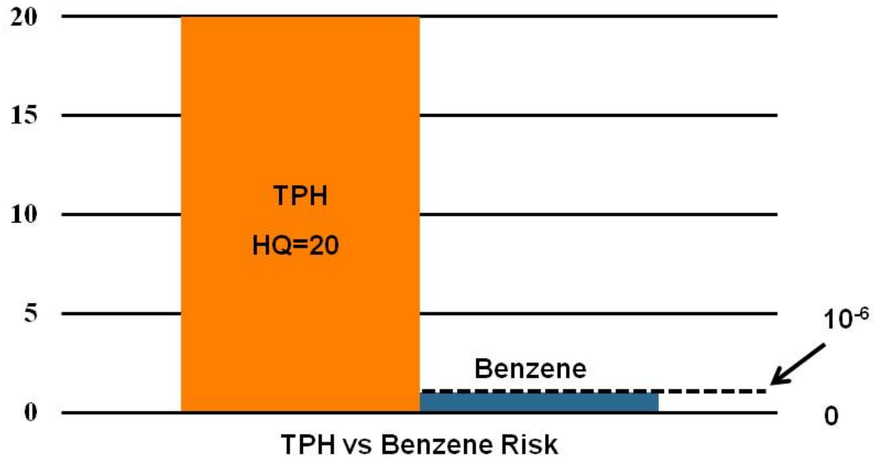
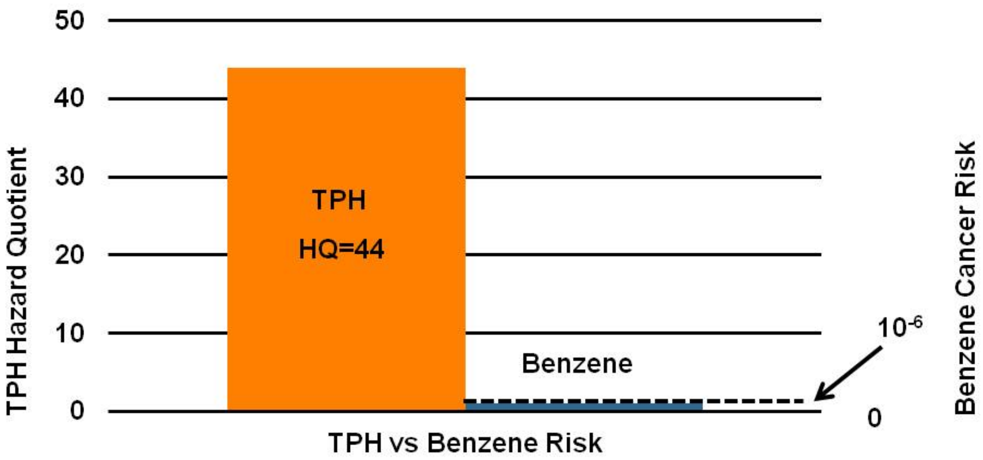
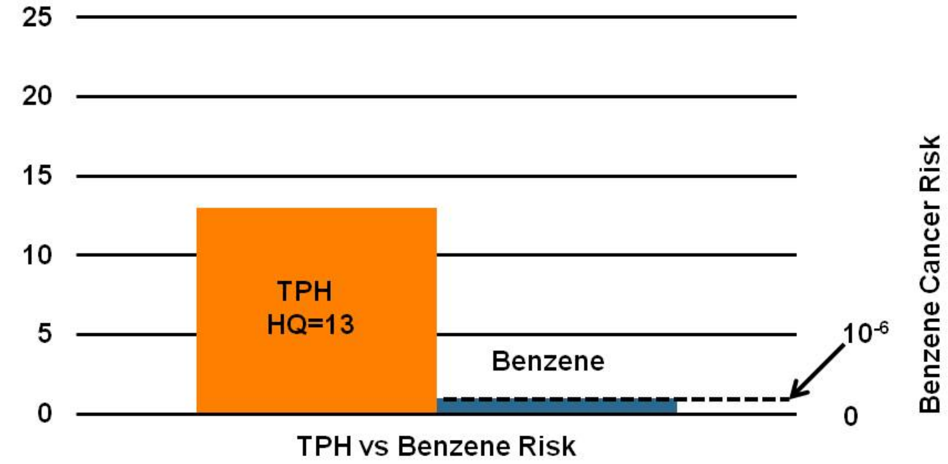


Sorbent Tube Data

Figure 38. TPH versus benzene as the risk driver for petroleum vapors in soil gas samples collected from Site D (JP-4/AVGAS) based on Summa vs sorbent tube carbon range data. TPH *always* drives potential vapor intrusion hazards (TPH noncancer HQ>1 even when benzene risk 10^{-6}).



Summa Data



Sorbent Tube Data

Figure 39. TPH versus benzene as the risk driver for petroleum vapors in soil gas samples collected from Site E (diesel) based on Summa vs sorbent tube carbon range data. TPH *always* drives potential vapor intrusion hazards (TPH noncancer HQ>1 even when benzene risk 10^{-6}).

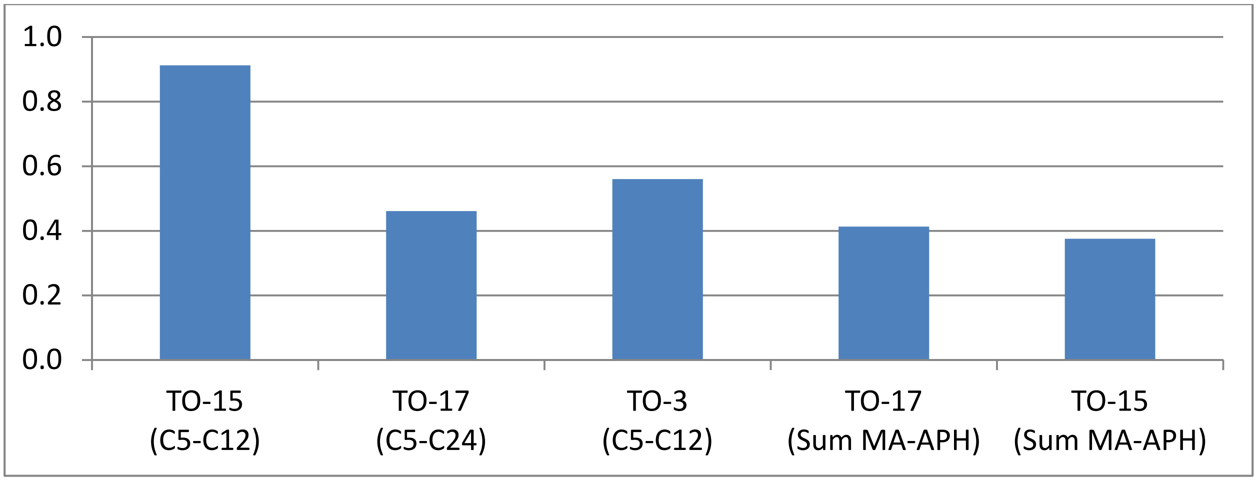


Figure 40. Comparison of average, relative TPHgasoline concentrations for individual samples tested using different laboratory methods during Phase II of the study (see Table 26a&b). TO-3 and TO-15 data reflect Summa canister samples. TO-17 data reflect sorbent tube samples collected immediately after corresponding Summa canister sample.

Attachment 1: Overview of Petroleum Chemistry from Appendix 1, Chapter 6 of the HEER EHE Guidance (HDOH 2011)

Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater

Volume 2: Background Documentation for the Development of Tier 1 Environmental Action Levels

Appendix 1: Detailed Lookup Tables

Hawai‘i Edition

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Fall 2011
(revised January 2012 to correct TPH toxicity factors; see Chapter 6)

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DISCLAIMER

This document, *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (Fall 2011), is a technical report prepared by staff of the Hawai’i Department of Health (HDOH), Environmental Management Division. The document updates and replaces the document *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater* (Interim Final, March 2009 and interim updates).

The document provides guidance for identification and evaluation of environmental hazards associated with contaminated soil and groundwater. The Environmental Action Levels (EALs) presented in this document and the accompanying text are specifically *not* intended to serve as: 1) a stand-alone decision making tool, 2) guidance for the preparation of baseline environmental risk assessments, 3) a rule to determine if a waste is hazardous under the state or federal regulations, or 4) a rule to determine when the release of hazardous substances must be reported to the HDOH.

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This document will be periodically updated. Please send comments, edits, etc. in writing to the above contact. This document is not copyrighted. Copies may be freely made and distributed. It is cautioned, however, that reference to the action levels presented in this document without adequate review of the accompanying narrative could result in misinterpretation and misuse of the information.

6

Soil, Soil Gas and Groundwater Action Levels for TPH

6.1 Introduction

Petroleum is a complex mixture of hundreds of different compounds composed of hydrogen and carbon (i.e., "hydrocarbon" compounds). The carbon range makeup of common petroleum fuels is noted in Figure 3. Non-specific, aliphatic and aromatic compounds collectively reported as Total Petroleum Hydrocarbons or “TPH” make up the overwhelming majority of the hydrocarbon mass in fuels and in vapors emitted from fuels (discussed below, see also Appendix 6). Individual, “indicator” compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) as well as naphthalene and other targeted polyaromatic hydrocarbons (PAHs) only make up a small percentage of the total mass in fuels and in vapors.

Testing and evaluation of the TPH component of petroleum-contaminated soil and groundwater and in associated soil gas in addition to targeted, individual compounds is therefore important. A summary of target analytes for petroleum in soil gas, soil and water in addition to TPH and with respect to different fuel types is provided in Table 6-1. In many cases the TPH component of the contamination will drive risk to human health and the environment over the minority fraction represented by individual BTEX and PAH compounds.

The development of risk-based action levels for Total Petroleum Hydrocarbons (TPH) in soil, soil gas and groundwater is described below. For the purposes of this document, petroleum mixtures are subdivided into "gasolines", "middles distillates" and "residual fuels", following the methodology used by the American Petroleum Institute (API 1994). Middle distillates include common diesel fuel, kerosene and jet fuels such as JP-8. The action levels are based on the assumed carbon range makeup of fuel types and associated vapors in conjunction with carbon range-specific toxicity factors published by USEPA and Massachusetts, among other agencies.

Several published documents were available to select a default, carbon range makeup of different fuel types (e.g., TPHWG 1998, MADEP 1997, 2003). Published data on the carbon range makeup and toxicity of vapors associated with petroleum fuels are limited. In 2011, the HEER office carried out a soil gas study of key, petroleum-contaminated sites in Hawaiʻi to help fill this data gap and update the EHE guidance and associated TPH EALs. The results of that study are summarized below and presented in Appendix 6.

Not surprisingly, and as described below and in Appendix 6, vapors are strongly biased toward lighter-end aliphatic compounds in comparison to the parent fuel type. Significant vapors were identified at both gasoline and middle distillate release sites. Gasoline is routinely considered to be "volatile" and a potential vapor intrusion hazard. As is obvious by their distinctive smell, middle distillates such as diesel fuel are also volatile and can pose vapor intrusion hazards if present at high enough concentrations and mass in soil and groundwater.

Sections 7 and 9 of the HEER office *Technical Guidance Manual* describes laboratory methods for testing of TPH in soil, water and soil gas contaminated with petroleum fuels. Detailed carbon range analysis of the aliphatic and aromatic makeup of the TPH component of the petroleum and development of site-specific, TPH action levels can be carried out as needed as an alternative to the action levels published in this guidance (see Volume 1). This is not anticipated to be necessary or cost-beneficial at most sites, however. An exception might be the need for more detailed carbon range data for soil gas at sites where reported concentrations of TPH exceed the Tier 1 action levels be less than a factor of three, the approximate magnitude that site-specific action levels might be increased over the default action level.

As discussed in the Volume 1, the use of EALs as final "cleanup levels" for petroleum-related compounds that are known to be highly biodegradable may be unnecessarily conservative. This is especially true TPH and petroleum-related compounds. Final cleanup levels should be evaluated on a site-specific basis and in conjunction with guidance from the overseeing regulatory agency (e.g., refer to HDOH 2007).

6.2 TPH Carbon Range Makeup of Fuels and Fuel Vapors

A summary of the selected, default carbon range TPH makeup of fuels and fuel vapors is provided in Table 6-2. This was used in combination with carbon range toxicity factors published by USEPA and other agencies to developed risk-based action levels for TPH in indoor air, soil gas, soil and groundwater. A detailed summary of data collected as part of the HEER office 2011 soil vapor study is provided in Appendix 6.

A detailed review of the chemistry and carbon range makeup of different petroleum fuel types is presented in guidance published by the Total Petroleum Hydrocarbon working Group (TPHWG 1998). Summaries have also been published by several states, including Massachusetts (MADEP 1997, 2003) and Indiana (IDEM 2010). A brief overview is provided below, with a focus on gasoline, #2 diesel fuel and residual fuels such as motor oil.

6.2.1 Gasolines

Gasolines are defined as petroleum mixtures characterized by a predominance of branched alkanes and aromatic hydrocarbons with carbon ranges of C6 to C12 and lesser amounts of straight-chain alkanes, alkenes and cycloalkanes of the same carbon range (TPHWG 1998). Based on information published by the State of Indiana, a relative TPH carbon range makeup of gasoline fuels (not including BTEX, naphthalene and other individual, targeted compounds) of 45% C5-C8 aliphatics, 12% C9-C12 aliphatics and 43% C9-C12 aromatics was selected for development of TPHgasoline action levels for soil and groundwater (see Table 6-2a). Separately targeted, individual such as BTEX and naphthalene generally do not make up more than 5% of gasoline fuels in Hawai‘i. Other compounds such as MTBE are not added in significant quantities.

An assumed TPH carbon range makeup of vapors associated with gasolines of 99% C5-C8 aliphatics, 0.5% C9-C12 aliphatics and 0.5% C9-C10 aromatics was selected for development of TPHgasoline soil gas action levels (see Table 6-2b). This was based on vapor data for locally purchased gasoline tested by HDOH, published information (e.g., BioVapor 2010) and site-specific data collected during the 2011 HEER office study (see Appendix 6). Vapors associated with fresh gasoline are dominated by C2-C4 aliphatics and C5-C8 aliphatics, with only a minor component (<5%) of BTEX and non-specific aromatic compounds (see Appendix 6). Vapors associated with weathered fuel, as is the case at most gasoline-release sites, are dominated by C5-C8 aliphatics with little to no C2-C4 aliphatics remaining and again a relatively minor component of BTEX and non-specific aromatic compounds (see Appendix 6; may differ on the mainland due to local gasoline formulations). The C2-C4 aliphatics primarily pose explosion hazards. Chronic toxicity factors have not been developed for these compounds.

The ratio of TPH to benzene in soil gas at gasoline-contaminated sites is typically less than 500:1, with the ratio lower ratio (i.e., increased proportion of benzene) at fresh release sites and higher ratio at more weathered sites (i.e., preferential loss of benzene).

6.2.2 Middle Distillates

Middle distillates (e.g., kerosene, diesel fuel, home heating fuel, JP-8 jet fuel, etc.) are characterized by a wider variety of straight, branched and cyclic alkanes, polynuclear aromatic hydrocarbons (PAHs, especially naphthalene an methylnaphthalenes) and heterocyclic compounds with carbon ranges of approximately C9 to C25. A small component of C5-C8 aliphatics and BTEX aromatics is also present.

Diesel #2 was selected as the most representative fuel for this petroleum type due to its more widespread use in comparison to other fuels. (JP-8 jet fuel is essentially diesel fuel with an increased component of lighter-end compounds.) Based on guidance published by the State of Indiana (IDEM 2010), an assumed, carbon range makeup for Diesel #2 fuel of 0.4% C5-C8 aliphatics, 35.2% C9-C12 aliphatics, 42.5% C19 and greater aliphatics, 14.2% C9-C12 aromatics and 7.7% C13 and higher aromatics was selected for development of soil and groundwater TPH action levels (see Table 6-2a). This is in line with the carbon range makeup of individual chemicals in diesel fuel published by the TPH Working Group (TPHWG 1998).

Selection of a default, carbon range makeup of vapors associated with middle distillates is less straight forward than for gasolines. Published data regarding the specific, carbon range makeup of vapors associated with diesel fuel and other middle distillates is lacking. Vapor headspace chromatograms have been published by a few private entities, however (e.g. Hayes 2007, NCFS 2011). Not surprising given the chemical makeup of middle distillate fuels, the chromatograms suggest a dominance of C12 and greater aliphatic compounds in vapors associated with these fuels, with an accompanying significant amount of C5-C8 aliphatics. The increased presence of the latter in vapor in part reflects the preferential release of lighter-end and more volatile aliphatic compounds from the fuels. Elevated C5-C8 aliphatics in the vapor could also reflect degradation of longer-chain compounds. The USGS has documented the latter in groundwater for a diesel release site they have been monitoring since the 1980s (Chaplain et al, 2002). Aromatic compounds, including BTEX and naphthalene make up only a small amount of the total mass of vapor-phase compounds.

Commercial laboratories are only able to reliably report up to C12 aliphatics and C10 aromatics in soil gas samples collected in summa canisters (e.g., see Hayes 2007). This is because longer-chain vapor compounds tend to condense on the inside of the canisters stick and are not extracted when a aliquot is removed for testing. This in turn means that the soil gas samples collected in summa canisters at middle distillate release sites could significantly under report the total concentration of TPH present in the soil gas and subsequently under represent the potential vapor intrusion hazard posed by the contamination.

In order to address this potential concern HDOH collected TO-17 sorbent tube soil gas samples at five key petroleum sites as part of its 2011 study. The TO-17 samples allowed full capture and extraction of the full range of petroleum compounds present in the soil gas. The samples were collected by drawing a fixed volume of soil gas (e.g., 50ml) through a narrow tube filed with a carbon-based sorbent material (see Appendix 6). Summa canister samples were also collected at the sites for comparison. The laboratory extracts and measures the mass of targeted VOCs captured by the sorbent material. Dividing this by the volume of soil gas (or air) drawn through the tube yields the original concentration of the individual VOC in the soil gas.

Soil gas data collected by HDOH at several middle distillate release sites in Hawai‘i revealed wide variations in the ratio of C5-C8 and C9-C12+ aliphatic compounds between and even within sites (see Appendix 6). In some cases C9-C12+ aliphatics dominated, in agreement with published chromatograms for headspace samples over diesel fuel (e.g. Hayes 2007, NCFS 2011). In other cases C5-C8 aliphatics dominated. This may have been in part due to mixing of vapors with nearby gasoline releases and/or the breakdown of longer-chain aliphatics into shorter chain aliphatics at more weather sites. Vapor samples collected over fresh fuels were likewise mixed (see Appendix 6), although it is suspected that the fuel associated with the sample that reported a higher proportion of C5-C8 aliphatics may have been excessively warmed in the sun prior to collection of the vapor sample. The distinct presence of C9-C12+ aliphatics in the soil gas samples, however, clearly distinguishes sites with middle distillate contamination from gasoline-release sites.

Based on the results of the HEER office study, an assumed TPH carbon range makeup of vapors associated with middle distillate fuels of 25% C5-C8 aliphatics, 75% C9-C12+ aliphatics and 0% C9-C10 aromatics was selected for development of TPH soil gas action levels (see Table 6-2b and Appendix 6). This reflects the worst-case sample collected at diesel-release site and is considered to be conservative, given that the toxicity of longer-chain aliphatics is assumed to be six times greater than shorter-chain aliphatics (see Table 6-3). An assumed dominance of C9-C12+ aliphatic compounds in middle distillate vapors is consistent with published chromatograms for headspace samples over diesel fuel noted above (e.g. Hayes 2007, NCFS 2011). A high percentage of C12+ aliphatics and C10+ aromatics was not, however, identified in the middle distillate sites investigated even this was predicted by the published chromatograms (maximum 13%, see Appendix 6). This may reflect the fact that the chromatograms reflect vapors collected over fresh fuels.

Small amounts of BTEX and naphthalene were reported in vapor samples collected over fresh fuel. Benzene, naphthalene and other aromatic compounds were present in only trace amounts in soil gas samples collected at targeted middle distillate release sites, however (generally <0.1%). The ratio of TPH to benzene was typically greater than

1,000:1 and in some cases over 10,000:1. Non-specific aliphatics clearly drove vapor intrusion risks at these sites over individual compounds such as benzene and naphthalene. Testing for only the latter in the soil gas samples would have significantly underestimated the vapor intrusion risk.

6.2.3 Residual Fuels Distillates

Residual fuels (e.g., Fuel Oil Nos. 4, 5, and 6, lubricating oils, "waste oils", “oil and grease,” asphalts, etc.) are characterized complex, polar PAHs, naphthenoaromatics, asphaltenes and other high-molecular-weight, saturated hydrocarbon compounds with carbon ranges that in general fall between C24 and C40. Published data on the specific, aliphatic and aromatic makeup of the TPH fraction of residual fuels after subtracting individual, targeted PAH compounds was not identified for use in this guidance but is expected to vary widely between different products and wastes.

For the purposes of this guidance, and as a conservative measure for risk-based action levels, a TPH carbon range composition of 75% C19+ aliphatics and 25% C17+ aromatics was assumed for estimation of a TPH reference dose for residual fuels and subsequent calculation of risk-based action levels (see Table 6-2a). This is based on the aliphatic-aromatic makeup of lubricating and motor oil presented in Table 13 of the TPH Working group guidance (TPHWG 1998). Testing for targeted, individual PAHs in addition to TPH at residual fuel release sits is critical. Motor oil that has been heated to high temperatures can, however, contain a significant proportion of carcinogenic, PAH compounds. Significant amounts of PAHs (e.g., naphthalene) could also be present at former gas manufacturing plants, asphalt production facilities, other sites where PAHs made up a significant proportion of the petroleum product released.

For the purposes of this guidance the makeup of vapors associated with heavy fuels was assumed to be identical to middle distillate vapors, with 25% C5-C8 aliphatics, 75% C9-C12 aliphatics and 0% C9-C10 aromatics (see Table 6-2b). The HEER office study did not include the review or collection of soil gas samples at sites contaminated with heavy petroleum fuels or products (e.g., Bunker C fuel oil). Vapor-phase compounds are expected to be dominated by C9-C12+ aliphatics, with little to no BTEX. As is suspected for some middle distillates sites, C5-C8 and even C9-C12 aliphatics could be present as breakdown products of longer-chain hydrocarbon compounds. Naphthalene may be a concern at manufacture gas plant (MGP) sites. The TPH fraction of soil and groundwater contaminated with residual fuels is only likely to pose significant vapor intrusion hazards if gross contamination is situated immediately beneath building floors, especially in comparison to gasoline- and even diesel-contaminated sites (with the exception of MGP site). Methane buildup may also be a concern at heavy fuel release sites.

Mineral oils used in electrical transformers are highly refined, fractions of crude oil with little to no chemical additives (EPRI 1998). The oils are dominated by C9-C30 aliphatics (approximately 85%) with a less amount of non-specific, aromatic compounds (approximately 15%) and overlap the carbon ranges discussed for middle distillates and residual fuels (see Figure 3). The volatile component of mineral oils is significantly lower than that found in middle distillates. The viscosity of the oils is also significantly greater. Carcinogenic PAHs such as benzo(a)pyrene are not present in detectable amounts. Releases of mineral oils from electrical transformers are relatively small in comparison to releases of diesel fuels and contamination is generally limited.

6.3 Carbon Range TPH Toxicity Factors and Physiochemical Constants

Carbon range toxicity factors published by Massachusetts (MADEP 2003) and more recently by the USEPA (USEPA 2009) were used to calculate weighted inhalation and oral toxicity factors for each of the three noted TPH categories, based on the assumed aliphatic and aromatic makeup of each category. A summary of toxicity factors selected for the each of the targeted carbon ranges is provided in Table 6.3. The following equations were used to calculate weighted Reference Concentrations and Reference Doses (see ODEQ 2003):

Weighted RfC (ug/m^3) =

$$\frac{\mathbf{1}}{\left[\left(\frac{\mathbf{(FractionC5 \cdot 8aliphatics)}}{\mathbf{C5 \cdot 8aliphaticsRfC}}\right)+\left(\frac{\mathbf{FractionC9 \cdot 12+aliphatics}}{\mathbf{C9 \cdot 12+aliphaticsRfC}}\right)+\left(\frac{\mathbf{FractionC9 \cdot 10+aromatics}}{\mathbf{C9 \cdot 10aromatics+RfC}}\right)\right]}$$

Weighted RfD (mg/kg-day) =

$$\frac{\mathbf{1}}{\left[\left(\frac{\mathbf{(FractionC5 \cdot 8aliphatics)}}{\mathbf{C5 \cdot 8aliphaticsRfD}}\right)+\left(\frac{\mathbf{FractionC9 \cdot 12+aliphatics}}{\mathbf{C9 \cdot 12+aliphaticsRfD}}\right)+\left(\frac{\mathbf{FractionC19+aliphatics}}{\mathbf{C19+aliphaticsRfD}}\right)+\left(\frac{\mathbf{FractionC9 \cdot 10+aromatics}}{\mathbf{C9 \cdot 10aromatics+RfD}}\right)\right]}$$

As noted in Table 6-4, weighted, oral Reference Doses of 0.03, 0.02 and 0.12 mg/kg-day were calculated for TPHgasolines, TPHmiddle distillates and TPHresidual fuels, respectively, based on the assumed carbon range makeup of the petroleum products. Weighted, inhalation Reference Concentrations of 571 ug/m^3 and 126 ug/m^3 were calculated for TPHgasolines and TPHmiddle distillates, respectively.

Default physiochemical constant values for TPH categories used in previous editions of the guidance were retained for use in the action level models (see Table H). The constants are based primarily on guidance published by Massachusetts DEP (MADEP 1997, 2002). As summarized below and in Appendix 1, these toxicity factors and physiochemical constants were used to develop soil gas, soil and groundwater TPH action levels. Risk-based action levels for TPH are based on a target, noncancer hazard quotient of 1.0. This is based on an assumption that TPH represents the primary noncancer risk posed by petroleum-contaminated soil, soil gas and groundwater due to the overwhelming mass of hydrocarbon compounds included in the analysis (see Section 1.4 and Appendix 6).

6.4 TPH Action Levels for Indoor Air and Soil Gas

Preliminary, risk-based action levels for TPHgasolines and TPH middle distillates in indoor air and soil gas as were calculated in the same manner as done for other volatile chemicals but with the use of a target, noncancer Hazard Quotient of 1.0 (see above and equations in Appendix 2). An indoor action level of 600 ug/m^3 was calculated for TPHgasolines. An indoor action level of 130 ug/m^3 was calculated for TPHmiddle distillates. Soil gas action levels were calculated using the default, Indoor Air:Soil Gas attenuation factors discussed in Section 2 (Residential: 1/1,000, Commercial/Industrial: 1/2,000). This generates residential soil gas action levels of 600,000 ug/m^3 for TPHgasolines and 130,000 ug/m^3 for TPHmiddle distillates (Table 6-5; soil gas action levels for carbon ranges also provided).

Petroleum release sites often contain a mix of fuels. Vapors in soil gas could likewise be a mix of several fuel types. Applying soil gas (and indoor air) action levels for gasolines versus middle distillate fuels is therefore not straightforward. *For the purposes of this guidance and for initial screening of petroleum-contaminated sites, the more conservative indoor air and soil gas action levels calculated for TPHmiddle distillates were selected for inclusion in the lookup tables for TPHgasolines (see Tables C-2 and C-3)*. The same action levels should be applied to petroleum vapors associated with residual fuels. This can be re-evaluated on a site-specific basis as needed by the collection of carbon range data for soil gas and calculation of site-specific action levels, or use of the TPHg soil gas action levels noted in Table 5b if laboratory data confirm that the carbon range makeup of the vapors is similar to that presented in Table 6-2b for gasolines. Note also that the TPH indoor air action levels could be below ambient background levels for indoor and outdoor air, due to the use of petroleum-based cleaners, auto exhaust, etc.

The soil gas action levels likewise do not take into account an expected reduction in concentration and associated risk over time due to biodegradation. This is also true for risk-based, TPH soil action levels presented in the Table I series. This can be evaluated on a site-specific basis as needed.

The collection and evaluation of soil gas samples at sites impacted with impacted with residual fuels is warranted where heavy contamination is to be left in place (see HDOH 2007). Soil gas action levels for vapors associated with TPHmiddle distillates should be applied in the absence of soil gas carbon range data. This will help to rule out potential vapor intrusion hazards and ensure that other sources of petroleum contamination were not missed.

6.5 TPH Action levels for Soil

6.5.1 TPH (gasolines, middle distillates)

Risk-based, direct-exposure action levels for TPHgasolines and TPHmiddle distillates in soil can be calculated in the same manner as done for individual chemicals, using the toxicity factors noted above and physiochemical constants noted in Table H (see Chapter 4). The model calculated residential direct-exposure soil action levels of 250 mg/kg and 210 mg/kg using this approach. These action levels are excessively conservative, in that they do not address biodegradation of TPH in soil over time, especially soil exposed at the surface. In order to address this issue upfront and for the purpose of this guidance, the final, residential direct-exposure soil action level for both TPHg and TPHmd was set to 500 mg/kg, similar to action levels in past editions of this guidance (see Table I-1).

As discussed in Chapter 4, maximum, direct-exposure action levels for volatile liquids in soil are normally set equal to the contaminants theoretical soil saturation level or Csat. This represents the concentration above which the contaminant can no longer be sorbed to soil particles (e.g., organic carbon or clay) or dissolved into the soil moisture (e.g., solubility limits reached). Above this concentration, free product will be present in the soil. This is important because the USEPA model used to calculate action levels for direct-exposure hazards is not valid above the Csat concentration for volatile chemicals (refer to Section 4.2.5). Maximum, direct-exposure action levels for volatile liquids in soil are therefore in general set to the chemical Csat concentration (e.g., refer to xylene action levels in Table I series).

This approach was used to establish Csat and maximum direct-exposure action levels for TPHgasolines (4,500 mg/kg; e.g., refer to Table I series). For TPH as middle distillates (e.g., diesel) the theoretical Csat concentration is much lower – 150mg/kg. This is due to the assumed, lower solubility of diesel and related middle distillate fuels (5 mg/L vs 150 mg/L for TPHg, refer to Table H). Confidence in the Csat value of 150 mg/kg is low, however, and this value is considered to be excessively conservative for use as a maximum, direct exposure action level. The use of alternative approaches to evaluate direct-exposure hazards posed by TPHmd and other volatile contaminants in soil is currently being evaluated (e.g., using soil gas rather than soil data). For the purposes of this document, it is assumed that the gross contamination action level for TPHmd of 500 mg/kg is adequate for protection of direct-exposure hazards posed by TPHmd. This value was used as an alternative Csat action level for TPHmd in the Table I series. Residual fuels are not considered to pose significant vapor emission hazards other than the potential generation of methane and related explosion hazards (refer to Volume 1).

Massachusetts developed generic physio-chemical constants for the C11-C22 aromatics carbon range fraction based on a review of compounds included within this fraction. These constants were adopted in this document to develop a soil leaching action level for TPH as gasolines and middle distillates (see Tables E and H). The soil action level calculated for leaching of TPH from soil and protection of groundwater that is a source of drinking water (rounded to 100 mg/kg) is coincidental with action levels presented in other technical documents prepared by local regulatory agencies in California (e.g., RWQCBSF 1990; RWQCBLA 1996). Similarly, the soil action level calculated for leaching of TPH from soil and protection of groundwater that could discharge into a body of surface water (rounded to 400 mg/kg (gasolines) and 500 mg/kg (middle distillates)) is coincidental with the action level developed for use in the CalEPA Board Order for the San Francisco Airport (RWQCB SF 1999a).

Ceiling levels for nuisance and other gross contamination concerns developed by Massachusetts for TPH as gasoline and diesel (latter included under "middle distillates") were modified for use in this document (MADEP 1997a,b, refer to Table F series). Based on calculated “odor indexes”, a shallow soil ceiling level of 100 mg/kg was selected for unrestricted (“residential”) land-use scenarios and a ceiling level of 500 mg/kg was selected for commercial/industrial land-use (both categories of TPH). For deep soils, a ceiling level of 5,000 mg/kg was retained (primarily intended to prevent the presence of potentially mobile free product in soil).

6.5.2 TPH (residual fuels)

Risk-based, direct-exposure action levels for TPH as residual fuels were calculated in the same manner as done for individual chemicals, using the toxicity factors and physiochemical constants noted earlier. The action levels developed incorporate the Particulate Emission Factor used by USEPA to calculate RSLs for nonvolatile contaminants (USEPA 2011, refer to Appendix 2). Risk-based action levels for TPHrf in drinking water and soil were then developed in the same manner as done for other chemicals (Table D-3 and Table I series, respectively). As discussed in Volume 1, testing for individual, target indicator compounds is also recommended for soil and groundwater contaminated by heavy fuels (e.g., PAHs, heavy metals, etc.).

Individual PAHs are likely to drive health risks posed by soils contaminated with residual fuels. The non-specific, TPH fraction of the petroleum may, however, pose gross contamination concerns even in the absence of significant PAHs. Following Massachusetts DEP guidance (MADEP 1997a,b), ceiling levels for gross contamination concerns of 500 mg/kg and 2,500 mg/kg were selected for exposed or potentially exposed soils in unrestricted ("residential") and commercial/industrial land use scenarios, respectively (see Table F series). The MADEP ceiling level of 5,000 mg/kg was selected for isolated or otherwise deep soils.

The Massachusetts DEP did not develop specific action levels for leaching of heavy hydrocarbons from soil (refer to C19-C36 carbon range summary in Appendix 6). Residual fuels are by definition characterized by a predominance hydrocarbon compounds with carbon ranges greater than C24. These compounds are considered to be substantially less mobile in the subsurface that hydrocarbon compounds that make up the lighter-weight petroleum mixtures. For TPH that is characterized by a predominance of C23-C32 carbon range compounds, the California EPA Los Angeles Regional Water Board proposes a action level of 1,000 mg/kg for protection of drinking water resources (RWQCBLA 1996). This action level was adopted for use in this document (refer to Table E). The target TPH action level for groundwater was not specifically stated but is presumably 100 ug/L or less.

The Los Angeles Regional Water Board did not present a similar action level for potential leaching of TPH from soil and subsequent discharge of impacted groundwater to a body of surface water. Although conservative, the Los Angeles TPH soil leaching action level 1,000 mg/kg was retained for this purpose (see Table E, refer also to Section 4.4).

The toxicity of mineral oils is relatively low and much less than that assumed for middle distillates. The volatile component of mineral oils is significantly lower than that found in middle distillates. The viscosity of the oils is significantly greater. Significant vapor emissions from soil and groundwater contaminated with mineral oil are not anticipated. For the purpose of this guidance and in order to address potential gross contamination concerns, a mineral oil TPH action level of 5,000 mg/kg is recommended for exposed soils or soils within three feet of the ground surface. For deeper soils an action level of 25,000 mg/kg is recommended. Refer also to the HEER office 2007 guidance for the long-term management of petroleum-contaminated sites (HDOH 2007). These action levels are not specifically called out in the EAL lookup tables.

6.6 TPH Action levels For Groundwater

Regulatory drinking water standards for TPH and petroleum in general have not been developed. Toxicity-based drinking water goals of 100 ug/L for gasoline, 460 ug/L for diesel and 84,000 ug/L for residual fuels were developed using on the USEPA RSL tapwater model and the above-noted toxicity factors (refer to Table F-3). (Note that the action level for residual fuels is likely to exceed the solubility in water, generally <5 mg/L) Action levels for benzene and related light-weight hydrocarbon compounds are considered to provide adequate additional protection of drinking water concerns for gasoline-impacted groundwater when used in conjunction with the TPH action level of 100 ug/L. A TPH-diesel taste and odor threshold of 100 ug/L referenced in the technical document *A Compilation of Water Quality Goals* (RWQCBCV 2007) was referred to as a substitute secondary MCL for all categories of TPH (see Table G-1). This takes precedence over the toxicity-based action level for selection of a final drinking water action level (see Tables D-1a and D-1b).

For the protection of aquatic life, an action level of 500 ug/L was selected for TPH-gasoline in freshwater and 3,700 ug/L in saltwater (see Table D-4b). A single action level of 640 ug/L was selected for TPH-diesel and TPH-residual fuels in both freshwater and saltwater. The freshwater action level for TPH-gasoline is based on a summary of available eco-toxicity data compiled for use at the Presidio of San Francisco under Regional Water Board Order 96-070 (RWQCBSF 1998b, Montgomery Watson 1999). The TPH-gasoline criteria for saltwater and the TPH criteria for diesel and residual fuels in general are based on action levels developed for use at the San Francisco Airport under Regional Water Board Order No. 99-045 (RWQCBSF 1999a).

The groundwater nuisance and odor concerns action level of 5,000 ug/L for TPH (all categories) noted in the Table G series for nondrinking water was taken directly from Massachusetts DEP risk assessment guidance (MADEP 1997a,b). This also corresponds with the approximate solubility of diesel fuel and light motor oil in fresh water (ATSDR 2001) and is intended to address potential nuisance issues (odors, etc.) if discharged to surface water. The TPH ceiling levels for gross contamination concerns are based on 1/2 the solubility of the respective TPH categories (refer to Table G series). The solubility of gasoline in freshwater is approximately 150,000 ug/L. The solubility of diesel range and heavier fuels is assumed to be approximately 5,000 ug/L. These action levels are intended to highlight the potential presence of free product on groundwater.

6.7 Additional Target Indicator Compounds

Laboratory measurement and assessment of each individual compound within a petroleum mixture is technically complex and generally not feasible or appropriate under most circumstances. More importantly, data regarding the physio-chemical and toxicity characteristics of the majority of petroleum compounds are lacking. Impacts to soil and water from petroleum mixtures are instead evaluated in terms of both TPH and well characterized "indicator chemicals" (e.g., benzene, toluene, ethylbenzene, xylenes and targeted PAHs). Indicator chemicals typically recommended for petroleum mixtures include (after CalEPA 1996):

Monocyclic Aromatic Compounds (primarily gasolines and middle distillates)

- benzene
- ethylbenzene
- toluene
- xylene

Fuel additives (primarily gasolines)

- MTBE
- other oxygenates as necessary

Polycyclic Aromatic Compounds (primarily middle distillates and residual fuels)

- methylnaphthalene (1- and 2-)
- acenaphthene
- acenaphthylene
- anthracene
- benzo(a)anthracene
- benzo(b)fluoranthene
- benzo(g,h,i)perylene
- benzo(a)pyrene
- benzo(k)fluoranthene
- chrysene
- dibenzo(a,h)anthracene
- fluoranthene
- fluorene
- indeno(1,2,3)pyrene
- naphthalene
- phenanthrene
- pyrene.

The TPH EALs should be used in conjunction with EALs for these chemicals. Note that volatile chemicals such as butylbenzene, isopropyl benzene, isopropyl toluene and trimethylbenzenes are often reported in analyses of gasoline and other light-end petroleum products. These chemicals are collectively addressed under action levels for "TPH" and generally do not need to be evaluated separately.

Soil and groundwater impacted by releases of waste oil may also require testing for heavy metals and chemicals such as chlorinated solvents and PCBs. Action levels for these chemicals are included in the lookup tables.

6.8 Ethanol

Gasoline formulations are anticipated to include an increasing proportion of ethanol in the near future. Soil, soil gas, indoor air and groundwater action levels for ethanol have therefore been added to the EAL document. Human-health, chronic toxicity factors for ethanol have not been developed. Ethanol is not considered to pose chronic health risks at the low doses posed by exposure to contaminated soil and groundwater. The action levels are therefore based only on nuisance and gross contamination concerns. “Ceiling Levels” for these concerns are presented in Tables F (soil and indoor air) and I (groundwater and surface water). The final action level for each of the groundwater categories is based on an “Upper Limit” of 50 mg/L (Table G series, see also Tables D-1a and F-1b). The final soil action level presented in each of the soil categories of 45 mg/kg is based on the protection of groundwater to the noted target groundwater action level (Table E, see also Table A and B series). The leaching based action level was adjusted upwards by a factor of ten to take into account the high, anticipated biodegradation rate of ethanol in the environment. The adequacy of this action level should be further evaluated in the field as appropriate (e.g., sites near producing water wells or bodies of surface water). The indoor air action level of 19,200 ug/m^3 (10 ppmv) is based on the published odor threshold potential for ethanol (Table F series, see also Table C-3). This concentration is well below the OSHA Permissible Exposure Limit of 1,000 ppmv for workers.

Although highly mobile in the environment, ethanol is also highly biodegradable, not significantly toxic in low dose, and is likely to only persist in the presence of other, more toxic components of gasoline, including benzene (Ulrich 1999). An assessment and cleanup of contaminated soil and groundwater to address health threats posed by associated compounds is expected to address any potential health concerns posed by exposure to residual ethanol in soil, air or water.

Table 6-1. Target analytes for petroleum contaminated media (see also Section 9 of the HEER office Technical Guidance Manual; HDOH 2009).

Petroleum Product	Media	Recommended Target Analytes
Gasolines	Soil	TPH, BTEX, naphthalene, MTBE and appropriate additives and breakdown products (e.g., DBA, TBA, lead, ethanol, etc.)
	Soil Vapor	Same as soil plus volatile additives and methane
	Groundwater	Same as soil
Middle Distillates (diesel, kerosene, Stoddard solvent, heating fuels, jet fuel, etc.)	Soil	TPH, BTEX, naphthalene, and methylnaphthalenes (1- and 2-)
	Soil Vapor	TPH, BTEX, naphthalene, and methane
	Groundwater	Same as soil
Residual Fuels (lube oils, hydraulic oils, transformer oils, Fuel Oil #6/Bunker C, waste oil, etc.)	Soil	TPH, *VOCs, naphthalene, methylnaphthalenes (1- and 2-), the remaining 16 priority pollutant PAHs, PCBs, and heavy metals unless otherwise justified
	Soil Vapor	TPH, BTEX, naphthalene, and methane
	Groundwater	same as soil

*VOCs include BTEX and chlorinated solvent compounds

Table 6-2a. Default carbon range makeup of TPH in petroleum fuels (after IDEM 2010).

Carbon Range	[1]$TPH_{gasoline}$	[1]TPH_{diesel}	[2]$TPH_{resfuels}$
C5-C8 aliphatics	45%	0.4%	0%
C9-C18 aliphatics	12%	35.2%	0%
C19+ aliphatics	0%	42.6%	75%
C9-C16 aromatics	43%	21.8%	25%

1. Indiana Department of Environmental management (IDEM 2010).
2. Massachusetts DEP (MADEP 1997).

Table 6-2b. Default carbon range makeup of TPH in petroleum fuel vapors.

Carbon Range	[1]$TPH_{gasoline}$	[1]TPH_{diesel}
C5-C8 aliphatics	99%	25%
C9-C18 aliphatics	0.5%	75%
C9-C16 aromatics	0.5%	0%

1. Based on HDOH soil as study and published information (see Appendix 6).

Table 6-3. Selected toxicity factors of for individual carbon range fractions.

Carbon Range	RfD_{0ral} (mg/kg-day)	RfC (ug/m^3)
C5-C8 aliphatics	[b]0.04	[a]600
C9-C18 aliphatics	[a]0.01	[a]100
C19+ aliphatics	[a]3.0	[c]nv
C9+ aromatics	[a]0.03	[a]100

a. USEPA 2009; b. MADEP 2003; c. Not significantly volatile. C17+ aromatics not considered separately.

Table 6-4. Weighted TPH toxicity factors for fuels and fuel vapors.

Carbon Range	RfD_{0ral} (mg/kg-day)	RfC (ug/m^3)
$TPH_{gasolines}$	0.03	571
$TPH_{middle\ distillates}$	0.02	126
$TPH_{residual\ fuels}$	0.12	-

Table 6-5a. Indoor Air and Soil Gas Carbon Range action levels.

	[1]Indoor Air		[1]Subslab Soil Gas	
Carbon Range	**Residential (ug/m^3)**	**Commercial/ Industrial (ug/m^3)**	**Residential (ug/m^3)**	**Commercial/ Industrial (ug/m^3)**
C5-C8 aliphatics	630	880	630,000	1,800,000
C9-C18 aliphatics	100	150	100,000	290,000
C19+ aliphatics	-	-	-	-
C9+ aromatics	100	150	100,000	290,000

1. Based on a noncancer Hazard Quotient of 1.0. Calculate cumulative risk if used to evaluate site-specific carbon range data for soil gas.

Table 6-5b Indoor Air and Soil Gas TPH action levels.

	Indoor Air		Subslab Soil Gas	
Carbon Range	**Residential (ug/m^3)**	**Commercial/ Industrial (ug/m^3)**	**Residential (ug/m^3)**	**Commercial/ Industrial (ug/m^3)**
$TPH_{gasolines}$	600	870	600,000	1,700,000
[1]$TPH_{middle\ distillates}$	130	330	130,000	370,000
[2]$TPH_{residual\ fuels}$	-	-	-	-

1. TPHmiddle distillate indoor air and soil gas action levels used as Tier 1 TPHgasoline action levels in final EAL tables due to potential for mixed fuel releases at sites. See Section 6.4.

2. Use TPHmiddle distillate indoor air and soil gas action levels sites contaminated with residual fuels.

Attachment 2: Massachusetts DEP overview of TPH Carbon Range Fraction Approach (MADEP 2002)

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Characterizing Risks Posed by Petroleum Contaminated Sites:

Implementation of the MADEP VPH/EPH Approach

FINAL POLICY

October 31, 2002

Policy #WSC-02-411

This Policy provides guidance for parties conducting response actions under the Massachusetts Contingency Plan (MCP) on the use and application of the Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH) methods to characterize risks posed by releases of petroleum products to the environment. This Policy updates and replaces draft documents that were issued on October 31, 1997 and June 2001. Parties who are currently using criteria and guidance contained in the June 2001 draft document may do so until May 1, 2003. A summary of significant changes between these earlier drafts and this Final Policy is provided in Appendix 6.

The information contained in this document is intended solely as guidance. This Policy does not create any substantive or procedural rights, and is not enforceable by any party in any administrative proceeding with the Commonwealth. This Policy provides recommendations and guidance on approaches the Department considers acceptable for meeting the performance standards set forth in the MCP and discussed in this document. These performance standards include, but are not limited to, the Response Action Performance Standards of section 310 CMR 40.0191 of the MCP. Parties using this guidance should be aware that there may be other acceptable alternatives for achieving and documenting compliance with the general regulatory requirements and performance standards of the MCP, including those of 310 CMR 40.0191. The regulatory citations in this document should not be relied upon as a complete list of the applicable regulatory requirements.

This Policy and further information on the development and application of the aliphatic/aromatic hydrocarbon evaluative technique employed by the Department, referred to as the "VPH/EPH" approach, may be obtained at http://www.state.ma.us/dep/bwsc/vph_eph.htm

10/31/02
Date

Signature on Original
Deirdre C. Menoyo
Assistant Commissioner
Bureau of Waste Site Cleanup

This information is available in alternate format. Call Aprel McCabe, ADA Coordinator at 1

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LIST OF ACRONYMS

AAS	Atomic Absorption Spectroscopy
APH	Air-Phase Petroleum Hydrocarbons
AQWC	Ambient Water Quality Criteria
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CEP	Critical Exposure Pathway
EDB	Ethylene Dibromide
EPA	Environmental Protection Agency
EPC	Exposure Point Concentration
EPH	Extractable Petroleum Hydrocarbons
eV	Electron Volt
FID	Flame Ionization Detector
GC	Gas Chromatography or Gas Chromatograph
GC/FID	Gas Chromatograph/Flame Ionization Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GRO	Gasoline Range Organics
GW	Groundwater
HVAC	Heating, Ventilation, Air-conditioning
ICP-AES	Inductively coupled plasma atomic emissions spectroscopy
IR	Infra-red
LNAPL	Light Non-Aqueous Phase Liquids
LSP	Licensed Site Professional
MADEP	Massachusetts Department of Environmental Protection
MCP	Massachusetts Contingency Plan
MtBE	Methyl tertiary butylether
NAPL	Non-Aqueous Phase Liquids
NRS	Numerical Ranking System
OTP	Ortho-terphenyl
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PID	Photoionization Detector
ppbV	Parts-per-billion by volume
ppmV	Parts-per-million by volume
QA/QC	Quality Assurance/Quality Control
RAF	Relative Absorption Factor
RAO	Response Action Outcome
RfC	Reference Concentration
RfD	Reference Dose
RL	Reporting Limit
SIM	Selective Ion Monitoring
SW	Surface Water
TIC	Tentatively Identified Compound
TOV	Total Organic Vapor
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UCL	Upper Concentration Limit
UCM	Unresolved Complex Mixture
UST	Underground Storage Tank
UV	Ultra-violet
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons
WSC	Waste Site Cleanup

1.0 INTRODUCTION

1.1 Background

Spills and releases of petroleum fuels are the leading source of environmental contamination in Massachusetts. Because petroleum products are a complex and highly variable mixture of hundreds of individual hydrocarbon compounds, however, characterizing the risks posed by petroleum-contaminated soil and water has proven to be difficult and inexact.

Traditional approaches have focused on the identification and evaluation of specific indicator compounds, like benzene, and/or the quantitation of a "Total Petroleum Hydrocarbon" (TPH) value. The limitations of an "indicator only" approach have long been recognized, especially at gasoline-contaminated sites, and it is clear that focusing on a select few compounds cannot adequately characterize the risks posed by all hydrocarbons present. While the quantitation of a TPH value is a step in the right direction, in that an attempt is being made to account for all compounds present, traditional TPH methods and approaches provide little or no information on the composition or toxicity of generated data.

In response to these shortcomings, the Massachusetts Department of Environmental Protection (MADEP) published a document in August 1994 entitled *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*. This document presented a new toxicological approach to characterize and evaluate risks posed by petroleum-contaminated sites, by breaking down TPH into collective aliphatic and aromatic fractions.

To support and implement this new toxicological approach, MADEP developed two analytical methods that differentiate and quantitate collective concentrations of aliphatic and aromatic hydrocarbons in soil and water. These methods, for *Volatile Petroleum Hydrocarbons* (VPH) and *Extractable Petroleum Hydrocarbons* (EPH), were issued in draft form in August 1995, and as final procedures in January 1998. At present, MADEP is in the process of finalizing a method for *Air-Phase Petroleum Hydrocarbons* (APH), which will allow for the collective quantitation of aliphatic and aromatic hydrocarbons in air. A draft APH method was issued by the agency in February 2000.

MADEP has integrated this new approach into the Massachusetts Contingency Plan (MCP), by developing and promulgating soil and groundwater cleanup standards for the aliphatic and aromatic ranges of interest. These standards became effective on October 31, 1997. Parties undertaking cleanup actions at petroleum-contaminated sites in Massachusetts now have the means to quickly and easily address risks posed by these complex mixtures, by the optional use of the generic *Method 1* cleanup standards. Conversely, such parties may elect to develop site-specific cleanup standards via use of a *Method 2* or *Method 3* risk assessment process.

1.2 Purpose and Scope

The purpose of this document is to (1) provide a succinct summary of key provisions of the "VPH/EPH" approach, (2) provide greater detail and specificity on important elements of this new approach, and (3) provide technical and regulatory insight, guidance, and ***Rules of Thumb*** to assist Licensed Site Professionals and others in understanding and applying this approach in a practical and cost-effective manner.

Rules of Thumb are suggestions and recommendations on how to approach, evaluate, and resolve investigatory, assessment, and remedial issues. In most cases, they are based upon reasonably conservative or "worst case" assumptions and considerations, and are intended to assist competent professionals in "ruling out" items of concern, or affirming a need to proceed to a more comprehensive level of evaluation. These rules are based upon current information, and are designed to be protective at most, but not all sites. Derivation details are provided in "Background/Support Documentation for the Development of Publication Guidelines and Rules of Thumb", available at: http://www.state.ma.us/dep/bwsc/vph_eph.htm.

***Rules of Thumb* may only be applied to the specific situations described in this document, as such guidelines are predicated upon a designated scenario and are reflective of the totality of conservative assumptions incorporated into that scenario. Changing any developmental element of these guidelines and/or applying them to situations not detailed in this document may not be sufficiently protective. Moreover, the use of these rules may not be appropriate at sites with complex or highly heterogeneous contaminant conditions or migration pathways, or at sites or portions of sites with highly sensitive receptors (e.g., drinking water wells).**

While striving to be as useful and complete as possible, nothing in this document should be viewed as limiting or obviating the need for the exercise of good professional judgment.

1.3 Applicability

The provisions of this document are applicable at sites contaminated by releases of one or more petroleum fuels and/or lubricating oils. The guidance contained in this policy is designed to help Licensed Site Professionals (LSPs) and others comply with the risk-based/performance-based requirements of the MCP to adequately investigate and assess releases of oil and waste oil to the environment.

The MCP – since 1988 – has required that parties conducting response actions at disposal sites document or achieve a level of no significant risk of harm to human health, safety, public welfare, and the environment. Because the MCP is performance-based, it does not dictate the specific means by which one demonstrates compliance with these standards. From a practical point of view, however, most parties did not have ready access to the tools and procedures needed to adequately characterize the total risks posed by petroleum contamination – until promulgation of the VPH/EPH approach, analytical methodologies, and Method 1 cleanup standards in 1997. For this reason, MADEP has adopted a prospective and retrospective position on the application of the VPH/EPH approach:

1.3.1 Site Closure on or after October 31, 1997

Since October 31, 1997, MADEP has provided parties conducting response actions a means to easily and adequately assess risks posed by petroleum contaminants. Therefore, all sites closed on or after this date (e.g., by filing of a Response Action Outcome Statement) must demonstrate compliance with this standard, by use of the VPH/EPH approach, or by use of another scientifically valid and health-protective approach. In these cases, the use of an “indicator only” approach is NOT acceptable.

There are no “grand fathering” provisions for sites that were not closed out prior to October 31, 1997. However, this document provides guidance on how one might utilize and/or “convert” old data obtained prior to this date, to more fully assess risks pursuant to the VPH/EPH approach, and support a post-1997 closure submittal.

Notwithstanding the implementation of this new approach, it should be noted that the MCP retains a cleanup standard for Total Petroleum Hydrocarbons (TPH), which is set conservatively at the lowest EPH fractional cleanup standard (typically C_{11}-C_{22} Aromatic Hydrocarbons). Parties may continue to use a TPH approach to characterize heavier petroleum products (i.e., $>C_9$), using the EPH method (in the TPH screening mode) or other scientifically valid and defensible method (See Section 3.7.1).

1.3.2 Site Closure Prior to October 31, 1997

In general, MADEP will not require reevaluation of petroleum-contaminated sites properly closed prior to October 31, 1997. Nonetheless, the agency reserves the right to do so, in cases where direct and compelling exposure concerns are believed to be present, and where human health is being directly threatened. Such concerns may exist at sites where (1) a release of gasoline has impacted a drinking water well, or (2) a release of gasoline has resulted in persistent, long-term odors or vapors within an occupied structure.

In cases where parties voluntarily conduct VPH/EPH testing at sites closed prior to October 31, 1997 (e.g., pursuant to a property transfer evaluation), the applicable “re-opener” language is contained at 310 CMR 40.0317(17). Under the provisions of this section of the MCP, a notification obligation would exist for this newly obtained VPH/EPH data if such information would change or negate the findings of the closure document (e.g., RAO, LSP Evaluation Opinion).

2.0 SUMMARY OF VPH/EPH APPROACH

2.1 The Concept

Petroleum is a mixture of hundreds of hydrocarbon compounds. Industry specifications for refined products, such as gasoline and diesel fuel, are based upon physical and performance-based criteria, not upon a specific chemical formulation. As such, the composition of petroleum products released to the environment are complex and variable, and are a function of (1) the origin and chemistry of the parent crude oil, (2) refining and blending processes, and (3) the use of performance-enhancing additives. Once released to the environment, the chemistry of a petroleum product is further altered by contaminant fate and transport processes, such as leaching, volatilization, and biodegradation.

It would be extremely difficult and expensive to identify and quantitate every single hydrocarbon compound present in petroleum-contaminated media. Even if this activity was accomplished, there is little toxicological data available for the vast majority of petroleum constituents. While there are limited data available on the toxicity of some petroleum fuels, the chemistry of weathered products typically encountered at contaminated sites may be quite different from the chemistry of the fresh product that was the subject of toxicological evaluation.

Based upon an evaluation of information and data available on the chemistry and toxicity of petroleum products, however, it is possible to make some broad observations and conclusions:

- ◊ petroleum products are comprised mainly of aliphatic/alicyclic and aromatic hydrocarbon compounds;
- ◊ aromatic hydrocarbons appear to be more toxic than aliphatic compounds; and
- ◊ the toxicity of aliphatic compounds appears to be related to their carbon number/molecular weights.

These three precepts are the foundation of the VPH/EPH approach. Specifically, under this approach, the **non-cancer** toxicity of petroleum-contaminated media is established by (1) determining the collective concentrations of specified ranges of aliphatic and aromatic hydrocarbons, and (2) assigning a toxicity value (e.g., Reference Dose) to each range. Toxicity values are determined on the basis of a review and/or extrapolation of available toxicological data on hydrocarbon mixtures and specific hydrocarbon compounds. The complete breakdown for all ranges of interest is summarized in Table 2-1.

Table 2-1: Toxicological Approach for Non-Cancer Health Effects

Hydrocarbon Fraction	Reference Dose (mg/kg/day)
C5-C8 Aliphatic Hydrocarbons	0.04[a]
C9-C18 Aliphatic Hydrocarbons	0.1[a]
C19-C36 Aliphatic Hydrocarbons	2.0[a]
C9-C22 Aromatic Hydrocarbons	0.03

[a] updated values (2002)

Cancer effects are evaluated separately, by the identification and quantitation of those specific hydrocarbon compounds, like benzene and certain polycyclic aromatic hydrocarbons (PAHs), which are designated carcinogens. Additional information and details on this approach are provided in the MADEP publication *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*, August, 1994, and as amended, available at http://www.state.ma.us/dep/bwsc/vph_eph.htm.

2.2 Hydrocarbon Fractions of Interest

Although the non-cancer toxicity of petroleum-contaminated media can be adequately described by division into the four hydrocarbon fractions listed above, MADEP has chosen to designate six hydrocarbon fractions of interest, because of the following analytical and program considerations:

- ◊ EPA analytical methods have traditionally used one approach for the analysis of volatile organics (i.e., purge and trap), and another for the analysis of semi-volatile/extractable organics (i.e., solvent extraction). To facilitate use by commercial laboratories accustomed to such division, the VPH and EPH methods developed by MADEP maintain this distinction. Moreover, because of the large carbon range covered by the new approach (i.e., C5 to C36), it would be difficult to detect all fractions using just one method: the volatile/purgeable methods can adequately cover the lighter hydrocarbons, but not the heavier fractions (>C12), while, due to losses of low molecular weight hydrocarbons that occur during the sample preparation process, extractable methods are generally unable to reliably detect lighter fractions (<C9).

- ◊ Given the need for two analytical methods, and a desire to minimize use of both methods on all samples, a decision was made to break up the C9-C18 Aliphatic range, to enable detection of all gasoline-range hydrocarbons in the VPH method. In this manner, it would only be necessary to use the VPH procedure to characterize gasoline releases.

For these reasons, it was necessary and desirable to divide the aliphatic and aromatic hydrocarbon ranges of interest into six separate entities; three detected by the VPH method, and three detected by the EPH Method, as listed in Table 2-2.

Table 2-2: Hydrocarbon Fractions of Interest

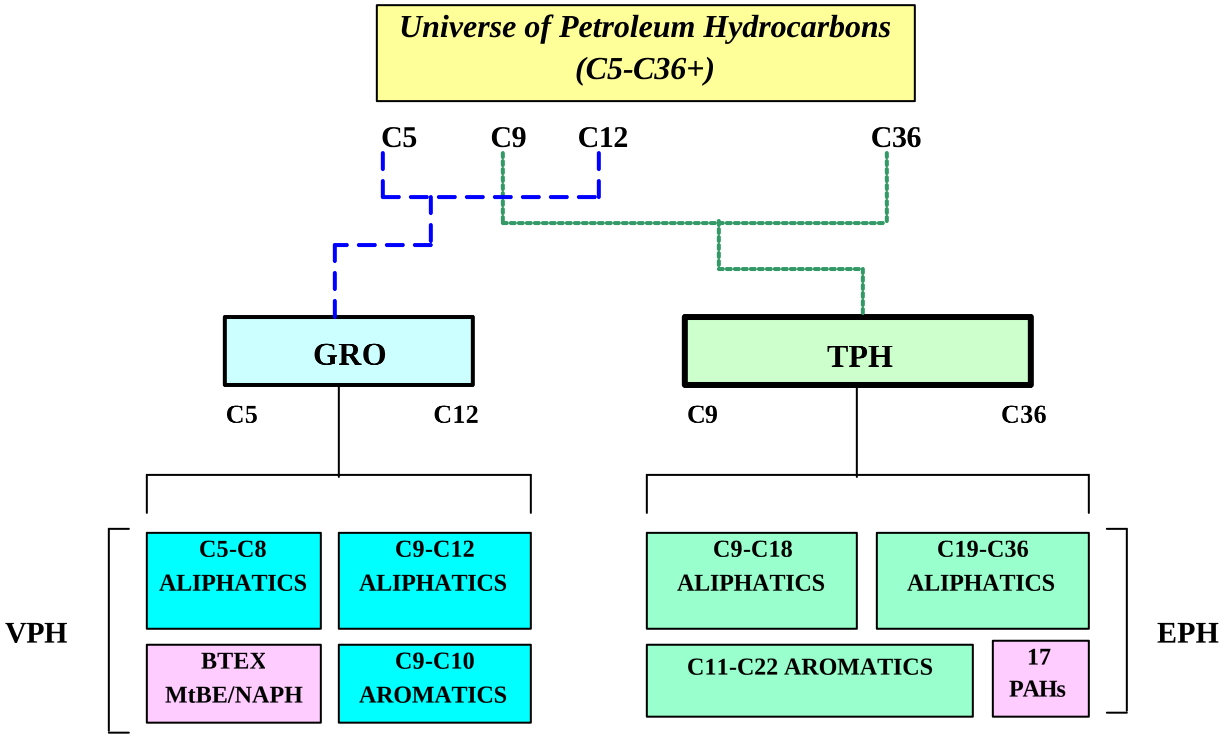
Toxicologically Defined Hydrocarbon Fraction	Analytical/Program Defined Hydrocarbon Fraction	Analytical Method	Reference Dose (mg/kg/day)
C5-C8 Aliphatics	C5-C8 Aliphatics	VPH	0.04[a]
C9-C18 Aliphatics	C9-C12 Aliphatics	VPH	0.1[a]
	C9-C18 Aliphatics	EPH	0.1[a]
C19-C36 Aliphatics	C19-C36 Aliphatics	EPH	2.0[a]
C9-C22 Aromatics	C9-C10 Aromatics	VPH	0.03
	C11-C22 Aromatics	EPH	0.03

[a] updated value (2002)

2.3 Relationship of VPH/EPH to TPH and Gasoline Range Organics (GRO)

The relationship between TPH, GRO, VPH and EPH is graphically displayed in Figure 2-1.

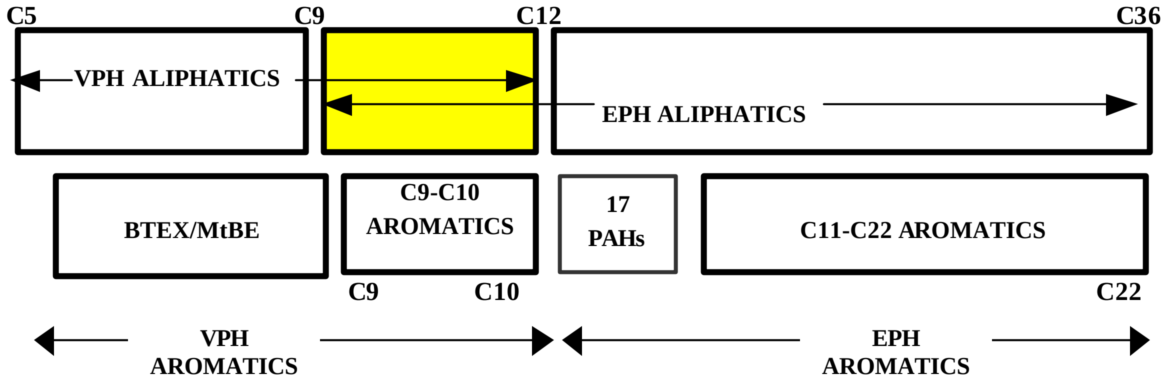
Figure 2-1: Relationship of GRO, TPH, VPH, and EPH



As can be seen in Figure 2-1, if the concentrations of the three EPH fractions and target PAH analytes were added together, it would be equal to a traditional "TPH" value. Similarly, if the three VPH fractions and BTEX/MtBE/naphthalene concentrations were added together, it would equal a GRO value.

It may also be noted that an overlap exists between the VPH and EPH methods, in that C9-C12 aliphatic hydrocarbons are quantitated by both methods. This overlap, further discussed in Section 4.2.3, is graphically illustrated in Figure 2-2.

Figure 2-2: Overlap of VPH and EPH Test Methods



Note that there is no overlap in the aromatic fractions: the C9-C10 Aromatic fraction from the VPH method ends just before naphthalene, and the C11-C22 Aromatic fraction from the EPH method starts just after naphthalene.

2.4 Additional Research and Data Needs

MADEP continues to gather and review information and data on petroleum hydrocarbon chemistry and toxicity. Recent efforts have focused on the review and evaluation of previously unavailable oral and inhalation toxicological data, which has lead to some revisions to the recommended RfD and RfC values for hydrocarbon fractions of interest (see Table 4-13). Additional study is also needed to better evaluate ecological risks posed by aliphatic and aromatic hydrocarbons.

On a national level, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) has published a number of documents relating to this subject. TPHCWG is comprised of representatives from the oil industry, Department of Defense, EPA, state agencies, environmental consulting firms, and academia. This group has recommended an aliphatic/aromatic fractional approach similar to the MADEP approach. Additional information and recommendations have also been provided on petroleum chemistry, hydrocarbon fate and transport, and analytical methodologies.

A number of TPHCWG publications are available on the World Wide Web at http://www.aehs.com/

3.0 ANALYTICAL METHODS

In order to use the VPH/EPH toxicological approach, it is necessary to be able to measure the collective concentrations of aliphatic and aromatic hydrocarbons in impacted media. Because conventional TPH and EPA test methods cannot produce this type of data, MADEP has developed and published two detailed analytical methods for Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH). Both methods are gas chromatography (GC) techniques, and are modifications of traditional EPA procedures contained in SW-846. As such, most laboratories that have conducted volatile and extractable organic analyses in the past should be able to perform these techniques.

3.1 Gas Chromatography

Chromatography is the separation of compounds or groups of compounds in a complex mixture. In gas chromatography, hydrocarbons in a sample are transferred to the vapor phase by purging (VPH) or heating (EPH). The gaseous sample then flows through a (100 meter long +/-) *capillary column* to a detector. A chemical coating on the walls of the column first sorbs, and then desorbs each compound in the sample, with the heavier molecular weight compounds being "detained" longer than the lighter compounds. In this manner, analytes exit or *elute* from the column in a predictable and reproducible manner, based upon the structure, molecular weight, and boiling point of the compound.

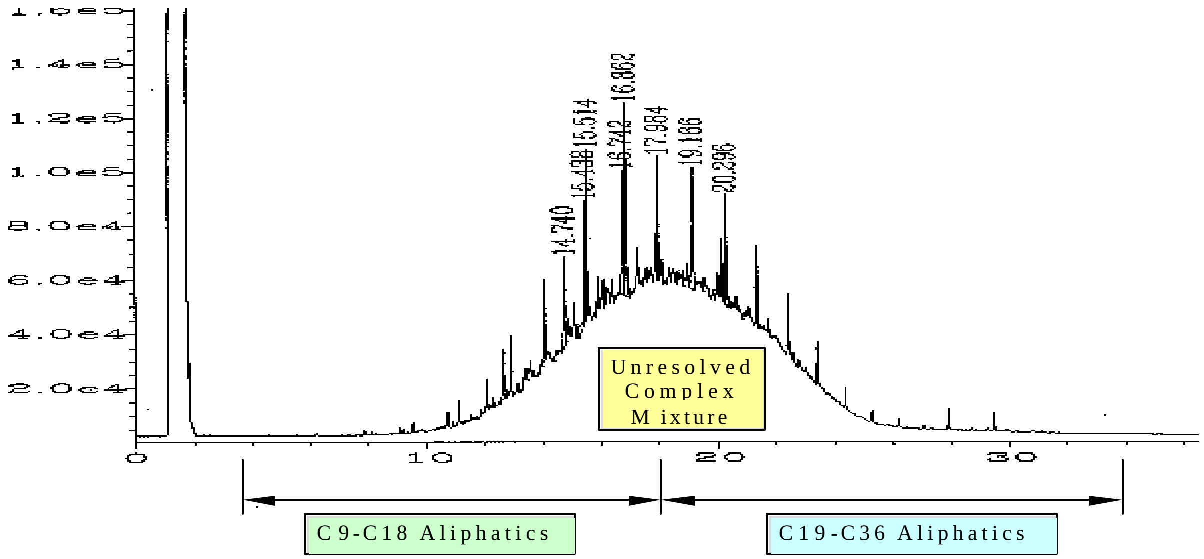
Once they elute from the column, analytes pass through a detector, where the presence of each compound produces a small electrical current, proportional to its mass. This current is then amplified and used to produce a chromatogram, which is simply a plot of electrical (detector) response over time. Each peak on a chromatogram represents one or more individual compounds. Compounds are identified based upon their *retention times*, which is the time (in minutes) it takes the compound to travel through the column. Compounds or ranges of interest are quantitated by an *integration* process that calculates the area beneath the chromatographic peak(s), for comparison to mass/area ratios derived from the injection of *calibration standards* of known mass or concentration.

To transfer the hydrocarbons within a sample medium into a gas chromatograph, and into a gaseous phase, various sample preparation techniques may be used. Volatiles within water samples are generally *purged* with an inert gas, which strips the dissolved volatile compounds from the aqueous phase into the gaseous phase, where they are initially retained on a *trap* containing an appropriate sorbent. This trap is then rapidly heated to desorb the analytes, and load them onto a chromatographic column. Volatiles within soils are first extracted with a solvent (e.g., methanol), then mixed with water and purged. Heavier non-volatile hydrocarbons in both water and soil samples are generally extracted with a solvent (e.g., methylene chloride); the extract is then injected into a gas chromatograph, where it is heated and vaporized into a gaseous state.

A key and novel requirement of the VPH/EPH approach is the need to separate or *fractionate* hydrocarbon mixtures into collective groupings of aliphatic and aromatic hydrocarbons. This fractionation is something that is not done in conventional TPH or Gasoline Range Organic analyses, or the EPA volatile/extractable methodologies detailed in SW-846. There are several different ways to accomplish this task, each with advantages and disadvantages. The recommended MADEP analytical methods use detector selectivity and a chemical exchange process to fractionate samples, but other techniques may also be acceptable and cost-effective.

An example of an EPH (GC/FID) chromatogram of the aliphatic portion of a weathered #2 Fuel Oil soil sample is provided in Figure 3-1.

Figure 3-1: Sample Chromatogram - #2 Fuel Oil



Note that the "x" axis is the retention time, in minutes, and the "y" axis is the detector signal strength. The retention time of some of the individual peaks are printed above those peaks. Note also the presence of a large chromatographic "hump" between 10 and 26 minutes, indicating the presence of an *Unresolved Complex Mixture (UCM);* this feature is an important issue discussed in more detail below.

3.2 MADEP Analytical Methodologies

MADEP has developed and published two analytical methodologies for the detection of Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH) in soil and water. Both methods separate complex hydrocarbon mixtures into collective fractions of aliphatic and aromatic hydrocarbons, and produce data that can be directly compared to MCP *Method 1* cleanup standards. MADEP has also issued a draft methodology for the detection of Air-Phase Petroleum Hydrocarbons (APH), to identify and quantitate collective ranges of aliphatic and aromatic hydrocarbons in air and soil gas.

The VPH, EPH, and APH methods were developed to allow a meaningful evaluation of the risks posed by hydrocarbon mixtures. Other procedures may also be available to fulfill this objective, or, perhaps more importantly, other data quality objectives. For example, it may be more cost-effective to use (or initially use) EPA Method TO-14 to evaluate indoor air quality, and establish whether a subsurface hydrocarbon transport pathway is present at a disposal site; if there is no pathway, there is no need to evaluate risks via the APH procedure.

3.2.1 Volatile Petroleum Hydrocarbons (VPH)

The MADEP VPH Method (1998) is a *Purge and Trap, GC/PID/FID* procedure. Using this method, the collective concentrations of C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C10 Aromatic Hydrocarbons can be quantitated in soil or water matrices. In addition to these fractional ranges, the VPH method may also be used to concurrently identify and quantitate individual concentrations of the *Target VPH Analytes* benzene, toluene, ethylbenzene, and xylenes (BTEX); Methyl-tertiary-butylether (MtBE); and naphthalene.

Samples are analyzed using a *purge-and-trap* sample preparation/concentration procedure. The gas chromatograph is temperature-programmed to facilitate separation of hydrocarbon compounds. Detection is achieved by a photoionization detector (PID) and flame ionization detector (FID) in series. The PID chromatogram is used to determine the individual concentrations of Target Analytes and the collective fractional concentration of aromatic hydrocarbons in the C9 through C10 range. The FID chromatogram is used to determine the collective fractional concentrations of aliphatic hydrocarbons within the C5 through C8 and C9 through C12 ranges. Individual “marker” compounds are used to establish the beginning and end of the hydrocarbon ranges of interest.

The MADEP VPH method relies upon the selectivity of the PID detector to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. Specifically, the PID will preferentially respond to hydrocarbon compounds with *pi* or double carbon (C=C) bonds, but will not respond well to hydrocarbon compounds with single carbon (C-C) *sigma* bonds. Because aromatic compounds have at least one benzene ring with three double bonds, they respond well to a PID; straight, branched, and cyclic aliphatic compounds with single carbon bonds respond poorly. Conversely, the FID is more of a universal detector, and will respond equally well to both aliphatic and aromatic hydrocarbons.

Because the PID can detect sample analytes without destroying them, compounds eluting from the chromatographic column are first passed through the PID, and then through the FID, where they are combusted in a hydrogen flame. In theory, the FID will detect the total concentrations of all petroleum hydrocarbons in the sample, and the PID will detect only (or mostly) aromatic compounds. By subtracting the PID from the FID response, it would be possible to quantitate just the aliphatic compounds. However, reality deviates from this theoretical ideal in the following ways:

- *Pi* bonds are present in hydrocarbon compounds other than aromatics - most notably alkenes, which are present in gasoline. Therefore, alkenes will be quantitated as aromatics. However, this bias is not deemed to be a major methodological limitation, due to the fact that (a) alkenes are typically not found in high concentrations in most petroleum products, and (b) alkenes may be more toxicologically similar to aromatics than to aliphatics.

- A more problematic issue is the fact that aliphatic compounds will produce some measurable response on a PID, especially heavier-molecular-weight branched and cyclic alkanes. Collectively, this response can become significant if there are a lot of these types of aliphatic compounds present, and will result in a falsely inflated quantitation of aromatics. Since a good portion of the hydrocarbons in the C9-C12 range of gasoline are in fact substituted aromatic compounds, this analytical overquantitation is not a major problem. However, other products, like kerosene and Jet A fuel, contain predominately aliphatic compounds within this range, and therefore use of the PID/FID approach can lead to significant overquantitation of the aromatic fraction.

Steps can be taken to minimize overquantitation of the aromatic fraction. Using a low energy PID lamp (e.g., 9.5 eV) will further diminish aliphatic response. Where essential, other techniques, such as chemical fractionation and/or use of a GC/MS approach, may be used to ensure more accurate data in this regard.

3.2.2 Extractable Petroleum Hydrocarbons (EPH)

The MADEP EPH Method (1998) is a *solvent extraction/fractionation GC/FID* procedure. Using this method, the collective concentrations of C9-C18 Aliphatic, C19-C36 Aliphatic, and C11-C22 Aromatic Hydrocarbons can be quantitated in soil or water matrices. In addition to these fractional ranges, the EPH method may also be used to concurrently identify and quantitate individual concentrations of the 17 Polycyclic Aromatic Hydrocarbon (PAH) *Target EPH Analytes*.

Soil and water samples are extracted with methylene chloride, solvent exchanged into hexane, and loaded onto a silica gel cartridge or column. The silica gel cartridge/column is rinsed with hexane to strip aliphatic compounds, and the resultant extract is collected and labeled. The silica gel cartridge/column is then rinsed with methylene chloride, to strip aromatic compounds, and the resultant extract is collected and labeled. The two extracts are then analyzed separately by direct injection into a temperature-programmed GC/FID. Individual target PAH compounds are identified by GC/FID analysis of the aromatic extract.

There are two important methodological elements that should be considered when reviewing EPH data:

- The MADEP EPH method relies upon a solvent-exchange/silica-gel-fractionation process to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. This fractionation process is a sensitive yet critical element of the analytical approach; small errors at this stage can result in significant over or underquantitation of aromatic and aliphatic ranges. For this reason, the method specifies use of *Fractionation Surrogates* to verify proper separation of the aliphatic and aromatic fractions.

- Like any GC/FID procedure, an *unresolved complex mixture (UCM) or "hump"* will typically be observed on the chromatogram of a heavier molecular weight petroleum product, particularly weathered products. (See Figure 3-1). A UCM is produced when many individual hydrocarbon compounds are eluting from the capillary column at the same time, overwhelming and preventing the detector signal from returning to baseline. Nevertheless, it is important that these compounds are included in the sample quantitation calculation, and for that reason the EPH method specifies the use of a *forced or projected baseline* when integrating chromatographic areas of fractional ranges. **If a laboratory does not takes steps to ensure this integration technique, resultant fractional range data may significantly under-report true hydrocarbon concentrations.**

The EPH method also contains an option to forego the solvent-exchange/silica-gel-fractionation process, to obtain a Total Petroleum Hydrocarbon (TPH) concentration. While this data will provide little information on the chemistry or toxicity of the petroleum mixture, it can provide a cost-effective analytical screening value, for comparison with TPH reporting and cleanup standards.

3.2.3 Air-Phase Petroleum Hydrocarbons (APH)

The draft MADEP APH method (2000) *is a GC/MS procedure*. Using this method, the collective concentrations of C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C10 Aromatic Hydrocarbons can be quantitated in air or soil gas matrices. In addition to these fractional ranges, the APH method may also be used to concurrently identify and quantitate individual vapor-phase concentrations of the *Target APH Analytes* 1,3-butadiene, benzene, toluene, ethylbenzene, and xylenes (BTEX); Methyl-tertiary-butylether (MtBE), naphthalene, and 2-methylnaphthalene.

Samples are collected in SUMMA ® passivated stainless steel canisters (other collection techniques are permissible and may be more appropriate for certain data quality objectives). A specified volume of sample is withdrawn from the canister through a mass flow controller using a vacuum pump. The sample is cryogenically concentrated to a volume of less than one mL in a nickel trap filled with nonsilanized glass beads. Following preconcentration, the sample is refocused at the head of a capillary column on a gas chromatograph using a cryofocusing accessory. This step further reduces the sample volume to less than one microliter for injection.

The sample is then injected into a gas chromatograph, which is used to separate the compounds and hydrocarbon fractions of interest. All compounds are detected using a mass spectrometer. Target APH Analytes are identified and quantitated using characteristic ions. Collective concentrations of C_9-C_{10} Aromatic Hydrocarbons are quantitated using extracted ions. Collective concentrations of aliphatic hydrocarbon fractions are quantitated using a total ion chromatogram, subtracting out Target APH Analytes and C_9-C_{10} Aromatic Hydrocarbons. It is important to note that the final APH method may contain modifications of the above procedures.

Air testing, whether by the APH procedure or other methodologies, is a specialty service that is not as widely available as soil and water analytical services. However, unlike the VPH and EPH methods, MADEP does not expect use of the APH method will be required at most petroleum contaminated sites, for the reasons listed below:

- Most releases of petroleum products do not result in an indoor air impact;
- For those sites where an indoor air impact is a potential concern, it is usually possible to evaluate and/or rule-out indoor air contamination problems using low-cost soil gas analytical screening techniques, as further detailed in Section 4.3.1; and
- Where indoor air sampling is required to evaluate a potential subsurface vapor transport pathway, traditional EPA procedures (e.g., EPA Method TO-14) may be used to determine if an impact is likely (based upon concentration of target analytes and qualitative presence of hydrocarbon peaks). The use of the APH (or similar) procedure would only be necessary if contamination is confirmed, and a quantitative risk assessment is required.

3.3 VPH/EPH Target Analytes

Although both the VPH and the EPH methods are capable of providing quantitation of Target Analytes (concurrent with the quantitation of aliphatic and aromatic ranges), because they are GC methods which identify analytes solely on the basis of retention times, they can produce "false positive" or over-inflated concentration data for these individual compounds. For example, the large peak eluting at 14.740 minutes in Figure 3-1 may be identified by the EPH method as hexadecane, because a hexadecane standard run as part of the calibration procedures eluted at this retention time. However, it is possible that hexadecane is not present in this sample at all, and some other (unknown) hydrocarbon compound is present which elutes at precisely this same time; or it is possible that hexadecane is indeed present, but that 2 or 3 other hydrocarbon compounds are *co-eluting* with hexadecane at precisely this time, which will lead to an overquantitation of the hexadecane concentration.

Although the sample-extract cleanup and fractionation procedures specified in the EPH method will tend to minimize interferences of this nature (by removing aliphatic compounds that may co-elute with the PAH Target Analytes), the only way to get positive identification and quantitation of these Target Analytes is to use a GC/MS analytical technique, like EPA Method 8270 for the PAHs, and EPA Method 8260 for BTEX/MtBE. For this reason, a laboratory may advise a client to use the VPH and EPH methods to quantitate the aliphatic/aromatic fractional ranges, but a GC/MS method to quantitate individual (Target) analytes. This approach is acceptable, although it may increase analytical costs.

To save money, it may be a worthwhile gamble to quantitate Target Analytes using the VPH/EPH Methods for samples that are believed to be relatively free from contamination - for example, when trying to confirm a "clean closure" at a tank removal site. If significant concentrations of Target Analytes are in fact found to be present, a re-analysis can be done using GC/MS, to provide a definitive determination in this regard (if the laboratory was instructed to retain the sample extract from the VPH/EPH samples, the cost for this re-analysis would be reduced).

3.4 Sampling Procedures and Requirements for the VPH/EPH Methods

Sample collection and preservation are critical elements in the VPH and EPH methodologies. A summary of requirements in this regard is provided in Table 3-1; detailed step-by-step sampling recommendations are provided in Appendix 1.

Sample preservation is essential. **VPH and EPH aqueous samples must be preserved in a manner that prevents biodegradation of hydrocarbons**. ***Simply cooling these samples is not sufficient.*** Biodegradation can be prevented by addition of acids (e.g., HCl to pH <2) or by the addition of bases (e.g., Trisodium Phosphate Dodecahydrate to pH > 11). *Note that acid preservation can significantly degrade levels of MtBE in aqueous samples (see Appendix 1).*

VPH soil samples must be preserved in a manner that (1) prevents sample losses due to volatilization, and (2) prevents sample losses due to biodegradation. There is now considerable evidence and data demonstrating substantial losses of volatile petroleum hydrocarbons from unpreserved sampling containers. The recommended preservation technique is to immerse VPH soil samples in methanol *at the time of collection*. Alternative techniques will be considered only if sufficient data are available to demonstrate the efficacy of sample preservation. Currently, only one alternative has been shown to provide acceptable preservation: the use of specially designed sealed-tube devices that obtain an air-tight soil sample.

Table 3-1: Sample Collection, Preservation, and Holding Times

Method	Matrix	Container	Preservation	Holding Time
VPH	Aqueous	40 mL VOC vial w/Teflon-lined septa screw caps; fill completely to zero headspace	pH <2 (add 3-4 drops of 1:1 HCl); cool to 4°C. Where MtBE is of concern, use 0.40– 0.44 grams TSP to raise pH > 11 (see Appendix 1)	14 days
	Soil	VOC vial or container; add 15g to 40mL vial; 25g to 60 mL vial	1 mL methanol per 1g soil (+/- 25%); cool to 4°C	28 days
EPH	Aqueous	1-Liter amber glass bottle with Teflon-lined screw cap	pH<2 (add 5 mL of 1:1 HCl); cool to 4°C	Extract within 14 days; analyze extract within 40 days
	Soil	4-oz (120 mL) +/- widemouth amber glass jar with Teflon-lined screw cap	cool to 4°C	Extract within 7 days; analyze extract within 40 days

Such devices have been shown to maintain sample integrity for 48 hours, by which time the sample must be extruded and preserved in methanol. Additional detail on the preservation of VPH aqueous and soil samples is provided in Appendix 1. Information and guidance on shipping methanol-preserved samples is contained in Appendix 2.

3.5 Modifications of the VPH/EPH/APH Methods

The MADEP VPH, EPH, and APH analytical techniques are "performance-based" methods, which means that modifications to specified procedures are allowable, as long as acceptable performance is demonstrated and documented.

The most common modification of the VPH and EPH methods involves the use of a GC/MS technique to identify and quantitate collective ranges of aliphatic and/or aromatic hydrocarbons. Under this approach, a mass spectrometer is used to break up the hydrocarbon molecules in a sample into fragments with certain masses and charges. A computer program is then used to search for specified fragments that are indicative of an aliphatic and/or aromatic hydrocarbon structure. Quantitation of a collective hydrocarbon range is accomplished by comparing the total mass of these selected fragments with the mass of fragments produced by calibration standards.

While MADEP believes that a GC/MS approach has promise, it has not yet issued guidelines or recommendations in this regard. Until such time as this occurs, all laboratories conducting such modifications must be able to provide complete documentation on their procedures, and must be able to demonstrate that their methodology is capable of generating data of a known level of accuracy and precision. Specific questions that a data user might want to address to laboratories include:

- ♦ *What "ions" (fragments) were used to quantitate specific aliphatic and/or aromatic hydrocarbon ranges? How were these ions chosen? Because hydrocarbon molecules fragment in different manners and proportions, how do the fragmentation patterns of the calibration standards correlate to the fragmentation patterns of the hydrocarbons likely contained in the sample?*

- ♦ *What studies did the laboratory do to validate the method? Were "neat" petroleum products analyzed? Fresh and/or "weathered"?*

- ♦ *Based upon the choice of quantitating ions and the results of the validation studies, under what (sample chemistry) conditions would a positive or negative identification and/or quantitating bias be expected?*

While MADEP encourages laboratories to develop "better mouse traps", ultimately, it is the responsibility of the data user to determine the validity and application of data obtained from modified methods. Parties unfamiliar with analytical chemistry and/or laboratory operations are advised to seek expert advice in such matters, and understand the nature, extent, and implication of all method modifications.

3.6 Data Quality and Report Content

Because the VPH and EPH methods are performance-based, and because MADEP does not (at this time) have a laboratory certification program for non-drinking/non-wastewater matrices, it is incumbent upon the laboratory and data users to take steps to ensure and document the quality of analytical data, consistent with the provisions and requirements of 310 CMR 40.0017.

The VPH and EPH methods have detailed and specific Quality Assurance and Quality Control (QA/QC) requirements, and a required data reporting content, which is provided in Appendix 3. The reporting content is designed to ensure that data users can easily ascertain (1) what is being reported, (2) basic sample and QA/QC information, (3) whether significant modifications were made to the recommended methods, (4) whether all recommended QA/QC steps were taken, and (5) whether all specified QA/QC and performance standards were met. *While it is not necessary to obtain and provide data in exactly the same form and order detailed on the reporting sheets provided in Appendix 3, data users should insist that all indicated information and statements be provided.*

Although a comprehensive review of all QA/QC information and data is beyond the ability and/or resources of most data users, there are several quick and easy steps that can and should be taken to help ensure the accuracy and reliability of VPH/EPH/APH data, by simply reviewing the information and data required in the data report:

◊ ***All sample information specified in Appendix 3 should be provided, describing the sample matrix, condition of containers, and sample preservation***. VPH samples that were not preserved in the field with methanol (or sampled/preserved in an acceptable alternative manner) are highly suspect.

◊ ***The dates of sample collection, receipt by laboratory, extraction (EPH) and analyses should be provided.*** Samples held beyond the recommended holding times are suspect, especially EPH soil samples that are preserved only by refrigeration.

◊ ***A percent moisture value should be reported for all soil samples***, to ensure that such data have been adjusted to a “dry weight” reporting basis.

◊ ***The analytical units must be clearly indicated,*** and should be appropriate for the matrix under evaluation (i.e., µg/g, mg/kg, or µg/kg for soil; µg/L or mg/L for water; µg/m^3 or ppbv for air).

◊ ***Reporting Limits (RLs) should be specified for each aliphatic and aromatic range and each Target Analyte***. The VPH, EPH, and APH methods contain specific procedures and requirements on how to establish Reporting Limits, which are the minimum concentration values that a laboratory can discern and report with sufficient confidence. These values must be experimentally determined by each laboratory. Note that expected RLs for the aliphatic and aromatic ranges in water are between 50 and 100µg/L; expected RLs for the aliphatic and aromatic ranges in soil are between 2 and 10 mg/kg; expected RLs for the aliphatic and aromatic fractions in air are between 25 and 100 µg/m^3.

◊ ***The percent recovery of sample surrogates should be provided, along with the acceptable range***. A surrogate is a (non-petroleum) chemical compound added (“spiked”) into each VPH and EPH water and soil sample prior to extraction and analyses. The purpose of surrogate spiking is to determine the efficiency and accuracy of sample extraction (EPH), sample purging (VPH), and instrument analyses. Surrogate recovery is expressed in terms of percent recovery; for example, if 1000 µg of the surrogate compound ortho-terphenyl (OTP) is spiked onto a 10 gram soil sample that is to be analyzed by the EPH method (yielding a theoretical concentration of 100 µg/g), and the resultant analysis quantified OTP at 70 µg/g, the percent recovery would be 70%. Although sample data with surrogate recoveries outside of the stated acceptance range should be carefully evaluated, they need not be summarily dismissed or considered categorically unusable. For example, data associated with a surrogate recovery greater than specified limits may be appropriate to use as an “upper limit” value; data associated with a surrogate recovery lower than specified limits may be appropriate to use as a “lower limit”, and would constitute knowledge of a release if exceeding Reportable Concentrations. Note that low recoveries are not uncommon (or unexpected) in clay/organic soil matrices. Also, low recoveries of sample surrogates may be observed in VPH soil samples with high moisture content.

◊ ***For the EPH Method, the percent recovery of Fractionation Surrogates should be provided, along with the acceptable range***. In the EPH method, a sample extract is loaded onto silica gel, followed by a hexane rinse, to remove and collect aliphatics, and a methylene chloride rinse, to remove and collect aromatics. However, because of the weakly polar nature of naphthalene and substituted naphthalenes, they are easily "stripped" into the aliphatic fraction - an especially problematic occurrence in water samples, as the naphthalenes constitute a large percentage of the water-soluble fraction of fuel oils. To monitor whether this action is occurring, Fractionation Surrogates are added directly to the sample extract just prior to the silica gel fractionation step (as opposed to the sample surrogates, which are added to the soil and water samples prior to extraction, to evaluate extraction efficiency). The currently recommended Fractionation Surrogates are 2-Fluorobiphenyl and 2-Bromonaphthalene - two compounds that are not normally present in petroleum, and that have polarities similar to naphthalene. Both compounds should be detected in the aromatic fraction within the specified acceptable percent recovery ranges.

Note: Changes and refinements to the EPH Method may affect the use and selection of Fractionation Surrogates.

◊ ***The laboratory should clearly indicate whether the reported VPH/EPH/APH fractional range concentrations include or do not include the concentration of Target Analytes, and the range(s) in which the Target Analytes elute.*** By definition, these ranges exclude Target Analytes, which are evaluated separately. (Absent this exclusion, Target Analytes like BTEX and PAHs would be "double counted" - once in the collective range concentrations, and once in a separate Target Analyte evaluation). If the laboratory did not subtract out the concentrations of these Target Analytes (perhaps they only provided range data), the data user may make this adjustment. It is also permissible for a data user to adjust a range concentration value by excluding the concentration(s) of non-petroleum analytes eluting within that hydrocarbon range (e.g., TCE eluting within a C5-C8 Aliphatic Hydrocarbon range). Note that unadjusted data are also acceptable to MADEP - they are just overly conservative.

◊ ***The laboratory must clearly indicate whether significant modifications were made to MADEP VPH/EPH/APH methods, and if so, should detail the nature and extent of these modifications***. Examples of "significant modifications" are specifically listed in Section 11 of each method. Note that MADEP encourages innovation, where appropriate.

◊ ***The laboratory should clearly indicate whether it has followed and met the QA/QC program and performance standards specified by the MADEP VPH/EPH/APH Methods.*** Such an affirmation is contained in the required laboratory report content. Note that on some samples, it will not be possible to meet all QA/QC specifications, and that such data need not be summarily dismissed as unacceptable, as long as an appropriate explanation is provided, and as long as limitations inherent in the data are acceptable for the given application and use of the data.

◊ ***A report narrative should be provided, if necessary, to document and explain any deviations from the method, analytical problems, and/or QA/QC issues.*** Laboratories using modifications of the method should have on file a written Standard Operating Procedure, which should be referenced or provided as appropriate. While a failure to perform or meet the data reporting and performance standards specified above does not necessarily mean that the provided data are not of sufficient quality, it does place the burden on the data user to make this determination.

◊ ***The laboratory should certify under the pains and penalties of perjury that the information contained in the data report form is accurate and complete.*** This attestation should be done via the signature of a responsible laboratory representative.

While minimum standards are specified in the methods, to ensure a minimum level of quality for all data, there is an expectation that laboratories should be able to achieve better results on most samples. In selecting a laboratory, a data user should make sufficient inquiry into the experience of the laboratory performing these (and any other) analytical methods, and on the QA/QC program in operation to monitor, document, and improve analytical quality. In addition, the scope of laboratory services should be negotiated and clearly articulated "up front", to ensure that the data user is procuring (and the laboratory is receiving compensation for) all desired information and data (e.g., QA/QC data, narrative reports, data usability discussions, etc.).

Additional guidance and recommendations on data quality issues for the VPH/EPH methods (as wells as most other common EPA methods) can be downloaded from MADEP at: http://www.state.ma.us/dep/bwsc/files/data/QAQCDocs.htm

Analytical data and testing should not be viewed as a commodity, but as a highly technical and sophisticated professional service, requiring the same level of scrutiny and oversight as any other professional service that will be relied upon by a Licensed Site Professional in rendering a waste site cleanup opinion.

3.7 Other Hydrocarbon Testing Methods

The VPH and EPH methods were developed to provide data on the chemistry and toxicity of complex hydrocarbon mixtures, to facilitate risk evaluations and to complement MADEP Method 1 cleanup standards. However, in cases where the total concentrations of hydrocarbons are relatively low, use of these fractionation procedures may be "overkill", and a "total petroleum hydrocarbon" (and Target Analyte) evaluation may suffice. Moreover, risk characterization is not the only site assessment objective or concern at disposal sites; other characterization needs may include: petroleum product identification, petroleum source identification, and/or Remediation Waste characterization. In these cases, other analytical procedures may be more appropriate and cost-effective.

A summary of other possible analytical approaches and methodologies in this regard is provided in Table 3-2.

Table 3-2: Other Analytical Approaches

Objective	Analytical Approach	Conditions/Caveats/Comments
Characterization of Remediation Wastes	TPH, VOCs, and/or jar headspace screening. Metals, PCBs and/or TCLP often required	Need to check with disposal or recycling facility for requirements
Risk Assessment & Compliance with Cleanup Standards	TPH via an appropriate methodology. Characterize Target Analytes as needed with EPA SW-846 methodologies	Applicable for low levels of C9 and heavier hydrocarbons (i.e., when TPH concentrations will likely < TPH cleanup standards)
Determining Type of Petroleum Product	High resolution GC/FID; advanced GC/MS chemical fingerprinting	Also recommended to differentiate petrogenic vs. pryrogenic PAHs
Determining Source of Petroleum Product	High resolution GC/FID; advanced GC/MS chemical fingerprinting; quantitation of biomarkers	Not always definitive; requires interpretative expertise

3.7.1 Total Petroleum Hydrocarbons (TPH)

Though a widely used and conceptually-simple testing parameter, there is no universal definition of TPH, and the term is essentially defined by the analytical method chosen by the laboratory. To further complicate this matter, many laboratories use undefined and inconsistent "modifications" of published methodologies to detect and quantitate TPH concentration values (e.g., Modified EPA Method 8100). This situation has lead to a significant degree of confusion over the application, comparability, and quality of TPH data.

The MCP provides a definition of TPH at 310 CMR 40.0006:

> *Total Petroleum Hydrocarbons and TPH each mean the total or cumulative concentration of hydrocarbons with boiling points equal to or greater than 150°C [C_9] and associated with a petroleum product, as measured by standard analytical techniques and/or by procedures approved by the Department, excluding the individual compounds listed at 310 CMR 40.0974(2).*

This definition reflects the fact that the vast majority of "TPH" analyses traditionally conducted in Massachusetts involved the use of an extraction solvent (e.g., Method 418.1), which leads to the loss of lighter hydrocarbons (<C9) present in the sample. Based upon this definition, the following rules and recommendations would apply to parties electing to use a TPH analytical method to support a risk assessment or document compliance with an MCP Method 1 TPH cleanup standard:

- ➢ The TPH method and resultant data may only be used to characterize releases of petroleum products that consist of hydrocarbons primarily in the C9 to C36 range. In other words, it may only be used in lieu of an EPH procedure, not a VPH procedure. Guidance on when an EPH procedure is appropriate is contained in Table 4-6.

- ➢ In addition to the TPH analysis, all appropriate Target Analytes must also be addressed. Guidance in this regard is contained in Tables 4-3 and 4-5.

- ➢ For analytical procedures that utilize a GC/FID technique, the TPH quantitation value must be based upon the integration to baseline of all peak areas from n-Nonane (C9) to n-Hexatriacontane (C36).

- ➢ As the MCP specifically excludes "individual compounds listed at 310 CMR 40.0974(2)" from its definition of TPH, it is acceptable to adjust gross TPH values by subtracting out the collective concentrations of these individual compounds. Note that, for all intents and purposes, the "individual compounds listed at 310 CMR 40.0974(2)" are synonymous with the EPH Target Analytes listed in Tables 4-3 and 4-5.

While the MCP defines TPH to be C9 and heavier hydrocarbons, there are some TPH and/or "Gasoline Range Organics" methodologies that may collectively quantitate lighter hydrocarbons in the range of C5-C12. Typically, these methods involve the use of a purge-and-trap or headspace development technique, followed by a GC/FID analytical procedure. While these procedures may NOT be used to obtain TPH data for comparison to the MCP Method 1 cleanup standards (because of the definition of TPH at 40.0006), they can be used as a screening tool for VPH range contaminants. Specifically, if the TOTAL concentration of hydrocarbons within the C5-C12 range (excluding VPH Target Analytes) is less than the lowest VPH Method 1 standard (usually C9-C10 Aromatic Hydrocarbons), it would be safe to assume that hydrocarbon levels are within all fractional standards.

While use of TPH methods may offer certain advantages, it is the responsibility of the party using and submitting such data to ensure that the specific technique and procedure(s) used is appropriate for the disposal site in question, and that appropriate Quality Assurance and Quality Control (QA/QC) measures are taken to monitor and document the quality and usability of the generated data. In general, MADEP expects all such methods to achieve a level of QA/QC consistent with the VPH and EPH methods.

A tabulation of commonly and/or historically available TPH analytical techniques is provided in Table 3-3.

Table 3-3: Common/Available TPH Testing Methods

Method	Technique	Comments
MADEP EPH	Extraction with methylene chloride & GC/FID analysis	Use in the "TPH" screening mode by eliminating the fractionation step per Section 1.5 of EPH Method
EPA Method 1664	Extraction with n-hexane & gravimetric analyses	New method (1999) to replace Method 418.1 (Freon extraction with IR analyses)
Modified EPA Method 8100	Extraction with appropriate solvent & GC/FID analysis	Must ensure quantitation in C9-C36 range with forced baseline integration if data is used to support MCP TPH cleanup standard
Modified EPA Method 8015	Purge-and-trap or headspace sample preparation & GC/FID analysis	Must ensure quantitation in the C5-C12 range with forced baseline integration if data is to be used to screen samples for compliance with MCP VPH cleanup standards

3.7.2 Environmental Forensic Techniques

In conducting a characterization of a petroleum-contaminated site, it may be necessary and/or desirable to identify the types of petroleum product present and/or the source of their release to the environment. In recent years, new analytical testing techniques have evolved to facilitate evaluations of this nature, and support an evolving specialization known as "environmental forensics".

In order to identify the types and/or source of petroleum products that were detected at a site, (up to) a three-step analytical regiment is recommended:

- Initially, samples should be analyzed by a high-resolution gas chromatography/flame ionization detection (GC/FID) methodology. Such techniques have been utilized for many years, and are a useful "first cut" to help identify the boiling-point range of the hydrocarbon mixtures present in the sample, which can then be used to make judgments on the type(s) of petroleum product(s) released at the site (e.g., #2 fuel oil vs. #6 fuel oil). In some cases, the data obtained in this manner is sufficiently conclusive to satisfy site characterization objectives.

In other cases, however, the contamination is highly weathered, and/or intermingled with hydrocarbons of pyrogenic origin (e.g., coal ash, soot, engine emissions).

- In situations where a GC/FID evaluation is inconclusive, additional analytical characterization by a gas chromatography/mass spectrometry (GC/MS) "advanced chemical fingerprinting" technique may be advisable. These methodologies focus on the identification and quantitation of polycyclic aromatic hydrocarbons (PAHs). Although most people are familiar with the 17 priority pollutant PAH compounds quantitated by the MADEP EPH method and EPA Method 8270, there are in fact many more PAH compounds present in petroleum products. Using a GC/MS technique and sophisticated quantitation algorithm, it is possible to identify and quantitate collective groupings of these PAH compounds based upon their structure, e.g., naphthalene with a side chain containing 1 carbon atom; naphthalene with a side chain containing 2 carbon atoms, etc. The presence and distribution of these side chains can then be used to help establish the type of petroleum product(s) present at the site. Moreover, this same information – often plotted as histograms – may also be used to differentiate petroleum-derived (petrogenic) hydrocarbons from combustion-derived (pyrogenic) hydrocarbons (given that the latter are predominated by the parent PAH compound, while the former are predominated by the alkylated side chain PAH compounds).

- Data on the distribution of alkylated PAHs can often provide definitive information on the type(s) of petroleum products present at a site, and even some evidence on the specific source(s) of release. However, in order to obtain more definitive proof of the source of a petroleum release, one additional analytical tool should be considered: the identification and quantitation of biomarkers. Biomarkers are chemical compounds present in petroleum products that are the remnants of the biological life (e.g., algae, plants, bacteria) that help create the parent crude oil. While certain biomarkers are identifiable using a GC/FID methodology (e.g., pristane and phytane), the most useful compounds in this regard (e.g., terpanes and steranes) are identified using a GC/MS technique in a selected ion monitoring (SIM) mode. Because each crude oil source has a distinct "fingerprint" of biomarkers, it is often possible to identify the specific source of a release of petroleum at a site using this approach (e.g., using a statistical/multivariate component analyses), though weathering processes may sometimes decrease confidence in such conclusions.

At the present time, advanced chemical fingerprinting is an innovative technology used by only a small number of laboratories. Given this status, and given the sophistication, complexity, and professional judgment inherent in these approaches, it is essential that data users seek out facilities and personnel with the appropriate expertise and experience.

3.8 Analytical Screening Techniques

The use of analytical screening techniques is encouraged, to provide timely and cost-effective data. As the sophistication and reliability of so-called "field" methods continue to increase, the distinction between conventional laboratory and analytical screening techniques becomes less defined, and less important. However, with this increased capability and performance comes an increased need to demonstrate and document a commensurate level of quality assurance/quality control (QA/QC), consistent with the provisions and requirements of 310 CMR 40.0017.

Various levels/approaches are possible:

◊ Screening techniques may be used solely to direct remedial actions and/or sampling programs for conventional VPH/EPH testing. Because such screening data will not be used in a "stand alone" capacity, QA/QC requirements are not as critical.

◊ Screening techniques may also be employed to obtain data that will be used, in whole or in part, to assess risks and/or determine compliance with cleanup standards, and/or to support the representativeness of ("lab") data used in the risk assessment process. While it is understood that such screening methodologies may lack the qualitative or quantitative accuracy of conventional VPH/EPH testing, *the same level of QA/QC will be expected, within the limits and bounds of the stated application of the data*.

The use of screening techniques depends upon, or may be enhanced by, the use of assumptions and conditions. This approach is acceptable, as long as conservative assumptions are made, and the use of such methods and assumptions are appropriate, given contaminant chemistry, site conditions, and area receptors. A tabulation of commonly used screening techniques, and recommended applications and *Rules of Thumb*, are provided in Table 3-4.

Table 3-4
VPH/EPH Analytical Screening Techniques

Technique	Description	Range	Applications	Limitations	Recommendations
PID/FID Headspace	Soil or water sample is placed in sealed container & headspace is allowed to develop. PID and/or FID meter is then used to test the headspace for total volatile organic compounds (VOCs). Reference: Recommended DEP jar headspace procedure	VPH	Excellent screening tool for gasoline; good tool for kerosene, jet fuel and fresh fuel oil. Best used to direct remedial operations, and provide first-cut site characterization data. PID preferentially responds to the more toxic aromatic compounds.	Not appropriate for heavy mineral/ lube/fuel oils or weathered diesel/#2 fuel oil. PID can be non-linear and/or erratic for gasoline headspace vapors > 150 ppmv. PID response lessened by high humidity/ moisture (instrument dependent). Additional confirmatory analyses usually required.	For gasoline, excluding clays & organic soils, headspace readings less than 100 ppmv usually means that all VPH fractions are below 100 µg/g. Confirmatory analyses needed.
PID/FID Soil Gas	Soil gas is extracted from a probe and analyzed with a PID and/or FID meter. Reference: see Section 4.3.1.1	VPH & EPH	Use to investigate soil gas/indoor air pathways, and evaluate sites with g.w. concentrations > GW-2 Method 1 standards. PID preferentially responds to the more toxic aromatic compounds.	Instrument response is flow-dependent; must ensure adequate flow rates. PID response affected by high moisture & high petroleum vapor concentrations (>150 ppmv). FID will respond to pipeline/naturally-occurring methane.	See recommendations in Section 4.3.1.1 and Table 4-9.
UV Fluorescence & Absorbance	The absorbance or fluorescence of a UV light source is used to directly quantitate the aromatic content of soil sample. Extraction solvent, such as methanol or Isopropyl alcohol, must be used. Reference: ASTM 5831-95	VPH & EPH	Good screening tool for petroleum products with significant aromatic content (e.g., diesel/#2 fuel oil and gasoline). UV Fluorescence has lower detection limits than absorbance, but is not as linear. UV methods target the more toxic aromatic fractions.	Does not respond to aliphatics; not appropriate for petroleum products that are primarily aliphatics (mineral oils or dielectric fluids). May pick up naturally occurring humic acids - calcium oxide can be used to decrease interference.	Calibrate with aromatic standard, like C11-C22 EPH standard, for direct measurement of aromatic hydrocarbons. For diesel/#2 fuel oil, assume aliphatic content is twice aromatic. This approach may significantly over-predict aliphatic content of highly weathered diesel/#2 fuel oil. Confirmatory analysis recommended for representative/worst-case samples.
Emulsion-Based TPH Methods	Hydrocarbons are extracted from a soil sample with a solvent (e.g. methanol), and a surfactant is added to create an emulsion. Optical sensor is used to measure extract turbidity	EPH	Gives "TPH" screening values, quantitating both aromatic and aliphatic hydrocarbons. Best correlation shown with diesel/#2 fuel oil.	Does not discriminate between aliphatics and aromatics. Interference possible in organic-rich and clay soils. Not recommend for gasoline.	For diesel/#2 fuel oil, assume 60% C11-C22 Aromatics and 40% C9-C18 Aliphatics.
Immunoassay Test Kits	Soil or water samples analyzed by antibody-antigen reaction. Enzyme conjugates used to allow colorimetric analysis of antigen (contaminant) conc. Soil extraction with methanol. Reference: EPA 4030/4035	VPH & EPH	Can be used to detect specific compounds or groups of compounds (e.g., BTEX and PAHs). "TPH" methods usually target naphthalene, and assume correlation to TPH.	Because antibodies bind with specific antigens (contaminants), cannot directly quantitate collective aliphatic/aromatic fractions or total hydrocarbons. Not effective for lube/hydraulic oils.	No general assumptions can be made. Each kit and application has to be individually evaluated.
Fiber-Optic Chemical Sensors	Probe with hydrophobic/organo-phyllic optical fiber is lowered into a well. Change in refraction index used to est. hydrocarbon conc. in groundwater	VPH & EPH	Allows in-situ measurements of volatile and semi-volatile dissolved hydrocarbons. Results calibrated to a p-xylene response. In-situ vapor measurement also possible.	Response decreases with increasing solubility; response to benzene 10 times less than p-xylene. Significant calibration/cleaning requirements between uses.	Insufficient information available to offer general recommendations.

3.8.1 Principles of Operation, Biases, and Calibration

All screening techniques and instruments are predicated upon certain principles of operation, detection, and calibration. Many have limitations and biases that need to be understood and accommodated. For example, an immunoassay “TPH” test method may be designed to detect the presence of naphthalene, and then extrapolate a TPH concentration based upon an assumption on the percentage of naphthalene in fresh fuel oil. Thus, two important assumptions and biases are present: (a) the concentration of a single compound (naphthalene) can be used to determine the concentration of a product which is made up of numerous (perhaps hundreds of) hydrocarbon compounds, and (b) the chemistry of a fresh fuel oil standard can be used to estimate the chemistry of a field sample. As such, a highly weathered fuel oil sample, or a fuel product low in naphthalene (e.g., mineral oils) may not yield reliable results.

To effectively use analytical/screening techniques, especially for risk and cleanup decisions, it is incumbent upon the data user to:

1. understand the application and limitations of the screening method(s) of interest;

2. consider site-specific contaminant/mixture chemistry and fate/transport processes; and

3. determine the precision and accuracy boundaries of the generated data, to see if they meet the desired data quality objectives and site characterization needs (e.g., if data can be considered accurate at 100 μg/g +/- 300%, and the cleanup standard is 500 μg/g, it may be acceptable).

In general, the following recommendations are offered:

◊ Techniques that detect a structural class and/or range of compounds are preferred, as opposed to methods that rely upon one specific indicator compound. Techniques that detect a range of compounds include PID/FID headspace techniques, UV absorbance/fluorescence, and emulsion-based TPH techniques. Procedures that target a single indicator compound require sufficient site-specific correlative and confirmatory data.

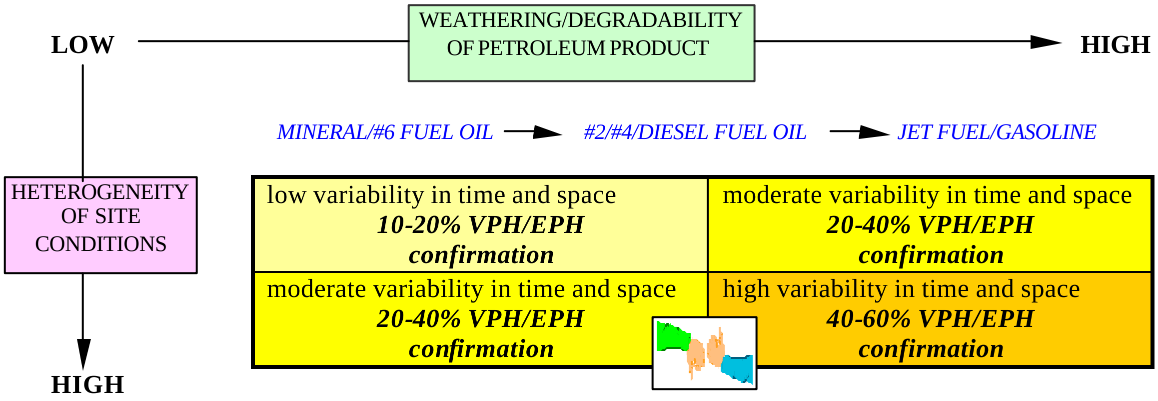
◊ Techniques that target aromatic hydrocarbons are preferred, as opposed to methods that target aliphatic compounds, due to the fact that aromatic hydrocarbons are, as a class, more toxic and mobile than aliphatic hydrocarbons. *On the whole, it is better to be able to accurately quantitate collective aromatic hydrocarbons, and estimate aliphatics, than to accurately quantitate collective aliphatic hydrocarbons, and estimate aromatics*. Techniques that target aromatics include PID headspace and UV absorbance/fluorescence.

◊ Techniques that involve a quick “shake out” extraction technique for soil analyses may not be sufficient for clay or organic-rich soils, due to partitioning efficiencies.

3.8.2 Recommended Approach

For small sites, such as residential underground storage tank (UST) excavations, screening techniques are perhaps best used to direct soil removal operations, identify areas for assessment and/or confirmatory VPH/EPH laboratory analysis, and/or provide a database to support the representativeness of decision-quality data. For larger sites, the use of screening data as a substitute and complement for VPH/EPH laboratory data may provide a better and less expensive approach to site characterization. For example, for the price of a single EPH test (approximately $200), it may be possible to perform 4 to 10 field screening analyses. So, for a sampling and analytical budget of $2000, it may make sense to take 8 EPH samples, and 8 to 20 field-screening samples, rather than (just) 10 EPH samples. The minimum number of VPH/EPH laboratory samples needed to understand contaminant chemistry, and provide confidence in screening data, is necessarily site-specific. The key variables are the heterogeneity of site conditions (stratigraphic/microbiological), source vs. migration areas, and the degradability of the petroleum product(s). Generalized *Rules of Thumb* in this regard are provided in Table 3-5. Note that additional confirmatory sampling would be indicated if sufficient correlation could not be established between the VPH/EPH values and screening/TPH values.

Table 3-5: Recommended Minimum VPH/EPH Laboratory Confirmation Data Needed to Support Analytical Screening



LOW → WEATHERING/DEGRADABILITY OF PETROLEUM PRODUCT → HIGH

MINERAL/#6 FUEL OIL → #2/#4/DIESEL FUEL OIL → JET FUEL/GASOLINE

LOW ↓ HETEROGENEITY OF SITE CONDITIONS ↓ HIGH

low variability in time and space ***10-20% VPH/EPH confirmation***	moderate variability in time and space ***20-40% VPH/EPH confirmation***
moderate variability in time and space ***20-40% VPH/EPH confirmation***	high variability in time and space ***40-60% VPH/EPH confirmation***

3.9 Drinking Water Testing Methods

When testing a potable drinking water supply, the use of the VPH/EPH analytical methods should be limited to quantitation of hydrocarbon ranges of interest; specific analytes of interest should be quantitated using the appropriate EPA “500” series drinking water methods.

4.0 CLEANUP STANDARDS

The Massachusetts Contingency Plan (MCP) provides three methods to assess risks and determine *how clean is clean enough*:

- ◊ Method 1 - generic cleanup standards in soil and groundwater
- ◊ Method 2 - site-specific modification of generic cleanup standards
- ◊ Method 3 - completely site-specific risk assessment

The easiest approach is Method 1, in that cleanup standards have already been established by MADEP. In support of the VPH/EPH approach, 6 generic standards have been developed and promulgated for the aliphatic and aromatic fractions of interest. A conservative TPH standard has also been retained, to allow continued use of such methods. *Note that it is not necessary to meet a TPH cleanup standard (or Reportable Concentration) if all 3 EPH fractional standards are achieved [see 310 CMR 40.0973(7) and 40.0360(2)].*

Because the Method 1 standards are generic, and were calculated assuming conservative site conditions, they can overestimate risk at some sites. In such cases, use of a Method 2 or 3 alternative approach may be advisable and cost effective. Guidance and recommendations in this regard are provided in Table 4-1.

For complete information and guidance on the use of the MCP risk assessment methods, consult the Massachusetts Contingency Plan at 310 CMR 40.0900, and MADEP’s *Guidance for Disposal Site Risk Characterization in Support of the Massachusetts Contingency Plan,* available at http://www.state.ma.us/dep/ors/orspubs.htm .

Attachment 3: Summary of Air Toxics MA-APH carbon range analysis method for soil gas and air samples.

15.0 AIR PHASE PETROLEUM HYDROCARBONS (MA APH)

The MADEP APH method describes techniques for the analysis of air-phase petroleum hydrocarbons (APH) collected as whole air samples in stainless steel canisters. Up to 0.5 Liters of air is withdrawn from the canister through a mass flow controller and is concentrated using a multisorbent trap which also serves as a hydrophobic dryer for moisture removal. The focused air sample is then flash heated through the hydrophobic drying system which removes the water from the sample stream prior to analysis by full scan GC/MS. Air Toxics Ltd. performs this analysis without taking modifications to the MADEP APH method. The standard target analyte list, Limit of Quantitation, QC criteria, and QC summary can be found in the following tables.

Table 15.1 APH Target Compound List

Analyte	Reporting Limit (ug/m3)	*Acceptance Criteria*	
		Accuracy Limits (%R)	**Precision Limits (RPD)**
1,3-Butadiene*	2.0	70 - 130	± 25
Methyl-tert-butyl ether (MTBE)*	2.0	70 - 130	± 25
Benzene*	2.0	70 - 130	± 25
Toluene*	2.0	70 - 130	± 25
Ethyl benzene*	2.0	70 - 130	± 25
m/p-Xylene*	2.0	70 - 130	± 25
o-Xylene*	2.0	70 - 130	± 25
Naphthalene	2.0	60 - 140	± 25

*Compounds comprise the LCS/2nd Source Standard.

Table 15.2 Aliphatics & Aromatics Hydrocarbon Ranges

Analyte	Reporting Limit ($\mu g/m^3$)	*Acceptance Criteria*	
		Accuracy Limits (%R)	**Precision Limits (RPD)**
C_5-C_8 Aliphatics	12	70 - 130	± 25
C_9-C_{12} Aliphatics	12	70 - 130	± 25
C_9-C_{10} Aromatics	10	70 - 130	± 25

Table 15.3 Internal Standards

Analyte	Accuracy Limits (%)
Bromochloromethane	50 to 200
1,4-Difluorobenzene	50 to 200
Chlorobenzene-d_5	50 to 200

Table 15.4 Surrogates

Analyte	Accuracy Limits (%R)
1,2-Dichloroethane-d_4	70 – 130
Toluene-d_8	70 – 130
4-Bromofluorobenzene	70 – 130

Table 15.5 Summary of Calibration and QC Procedures

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Tuning Criteria	Every 24 hours.	Compendium of Methods for Toxic Organic Air Pollutants, Method TO-14A, January 1999.	Correct problem then repeat tune.
5 Point Calibration	Prior to sample Analysis.	%RSD ≤30% for APH Target Analyte or hydrocarbon range. Naphthalene is ≤40%.	Correct problem then repeat initial calibration curve.
LCS (Subset of Target Compounds)	After each initial calibration curve, daily prior to sample analysis.	Recoveries for the APH target compounds and hydrocarbon ranges must be ±30%. If recovery of any compound is above 130%. Analyze samples as long as compound is not detected.	Check the system and re-analyze the standard. Re-prepare the standard if necessary. Re-calibrate the instrument if the criteria cannot be met.
Continuing Calibration Verification (CCV)	At the beginning of each day.	%D ≤ 30% for APH target compounds and hydrocarbon ranges. One compound is allowed to be out as long as it is ≤ 50%D. Target compound Naphthalene allowed %D ≤ 40%. If recovery of any compound is above 150%. Instrument must be re-calibrated.	Perform maintenance and repeat test. If the CCV still fails, perform maintenance and a new 5-7 point calibration curve.
Laboratory Blank	After the CCV/LCS.	Results less than the laboratory RL (Tables 15.1 and 15.2). Naphthalene and C12 are allowed to be 2X the RL.	Inspect the system and re-analyze the blank.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Internal Standard (IS)	As each standard, Blank, and sample is being loaded.	Retention time (RT) for the blanks and samples must be within ±0.33 min of the RT in the CCV. The IS area must be within -50 to 200% of the CCV's IS area for the blanks and samples.	**For blanks:** inspect the system and re-analyze the blank; **For samples:** If there is not obvious interference with the internal standard, re-analyze the sample. If the ISs are within limits in the re-analysis, report the second analysis. Dilution of the sample to get IS areas within limits may be used if the RL is being obtained.
Surrogates	As each standard, blank, and sample is being loaded.	70 – 130% R.	**For blanks:** inspect the system and re-analyze the blank; **For samples:** re-analyze sample unless obvious matrix interference is documented. If the %R is within limits in the re-analysis, report the 2nd analysis. If %R is out-of-limits a 2nd time, report data from 1st analysis and narrate.
Laboratory Control SpikeDuplicate (LCSD)	i 1 dup/analytical batch.	RPD ≤ 30% .	Inspect the system and re-analyze; if out again, narrate.

Table Elution/retention times for targeted VOCs and chemical markers use to define carbon ranges.

Target Chemical/ Carbon Range	Marker Chemical(s) on Chromatogram	Elution/Retention Time (minutes)	
		TO-15	**TO-17**
C5 aliphatics	Isopentane	7.445	3.302
C9 aliphatics	Nonane	20.240	11.121
C13 aliphatics	Dodecane	23.134	15.457
C18 aliphatics	Octadecane	NA	21.037
C24 aliphatics	Tetracosane	NA	24.991
C9 aromatics	o-Xylene	20.238	10.844
C11 aromatics	Naphthalene	23.060	14.978
C16 aromatics	Octadecane	NA	21.037
Benzene	“”	14.779	5.565
Ethylbenzene	“”	19.704	10.128
Toluene	“”	17.997	8.022
Xylenes	“”	M/P :19.816 O :20.138	M/P :10.321 O :10.744
Naphthalene	“”	23.160	15.078
1-Methylnaphthalene	“”	NA	16.549
2-Methylnaphthalene	“”	NA	16.370
TPHg (C5-C12)	Isopentane & Nonane	7.445 to 23.134	3.302 to 11.121
TPHg (C5-C24)	Isopentane & Tetracosane	NA	3.302 to 24.991
[1]TPHd (C5-C24)	Isopentane & Tetracosane	NA	3.302 to 24.991
[2]TPHd (C10-C24)	Nonane & Tetracosane	NA	12.671 to 24.991

1. Request lab to report TPHd as C5 to C24 to ensure inclusion of C5-C8 aliphatics.

2. Not recommended, excludes potential C5-C8 aliphatics in diesel and other middle distillate vapors.

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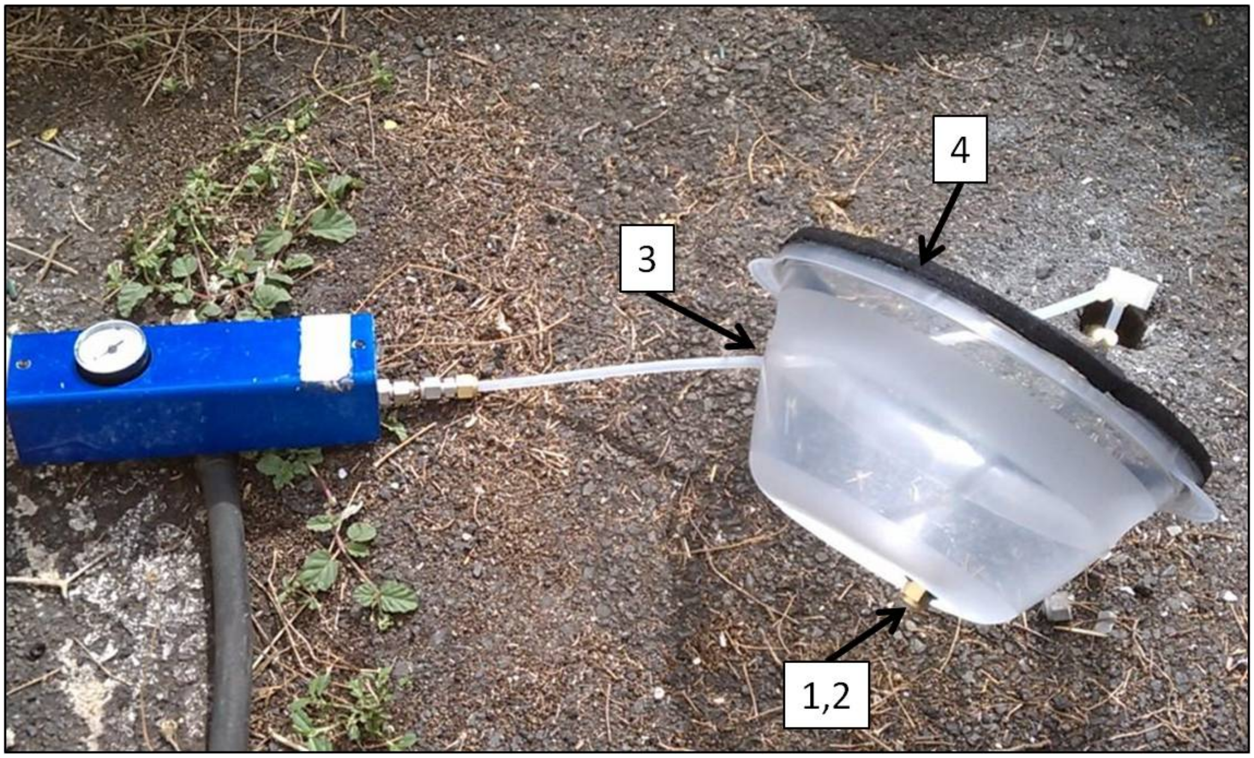
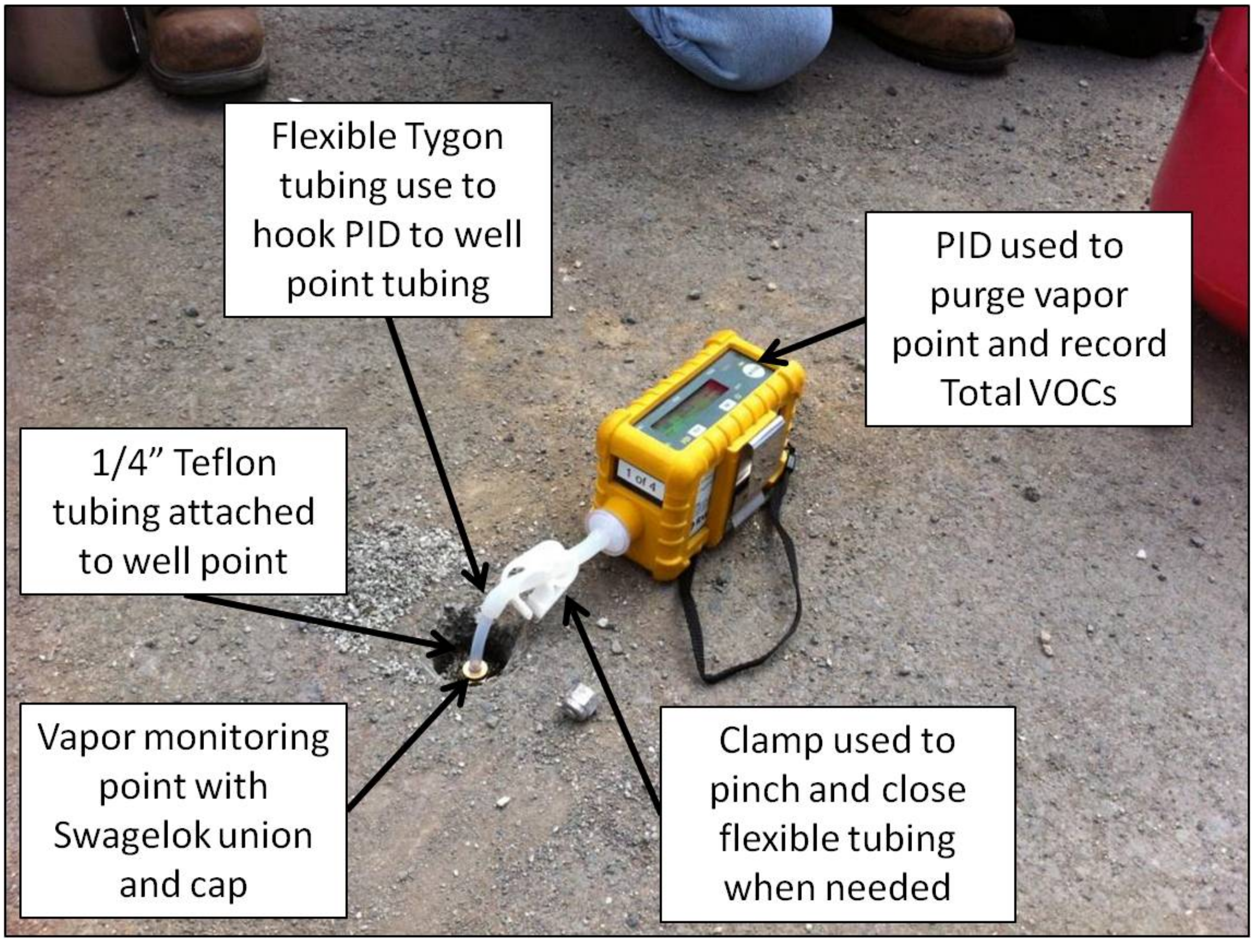
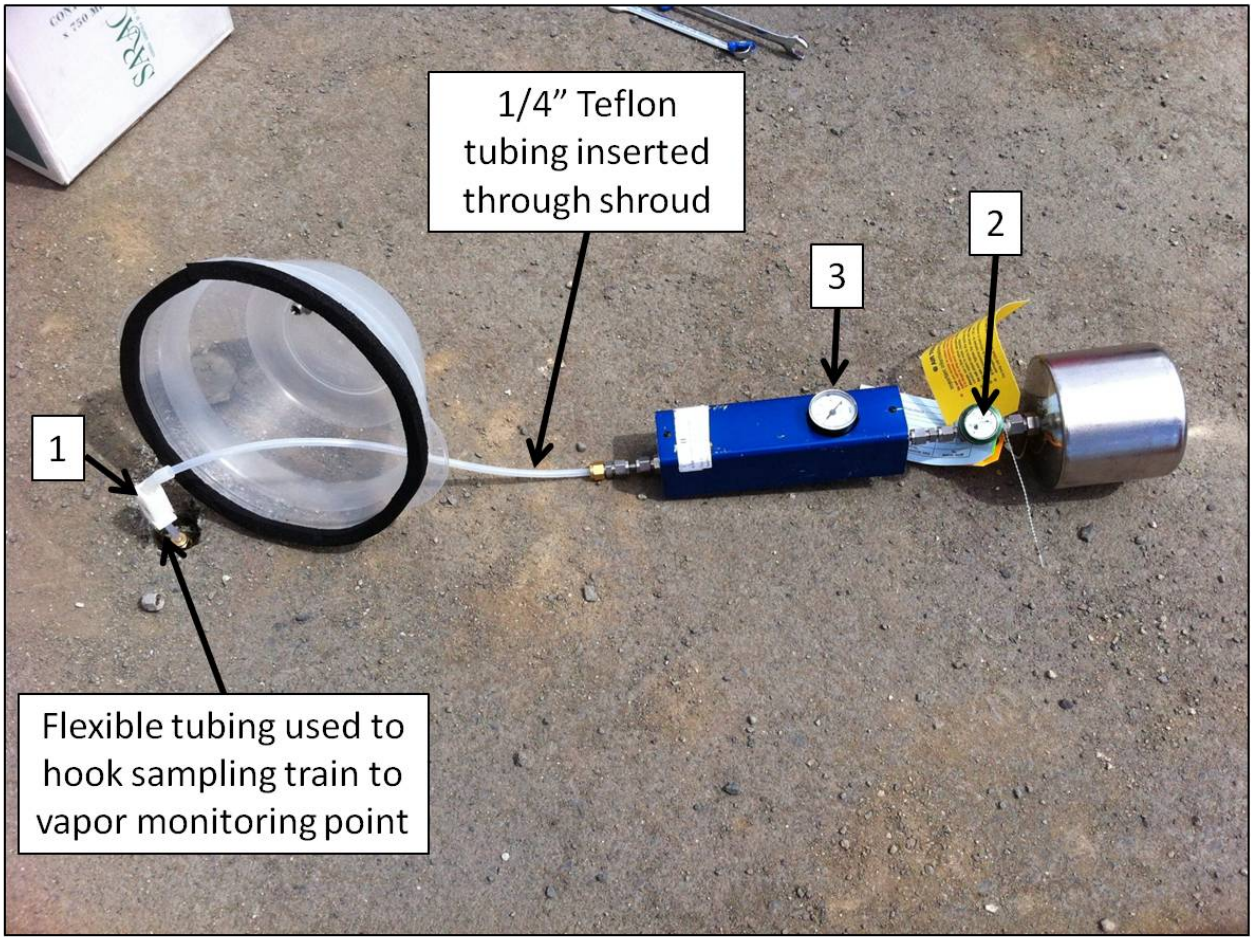
Attachment 4: Soil Gas Leak Detection Using a Tupperware Shroud



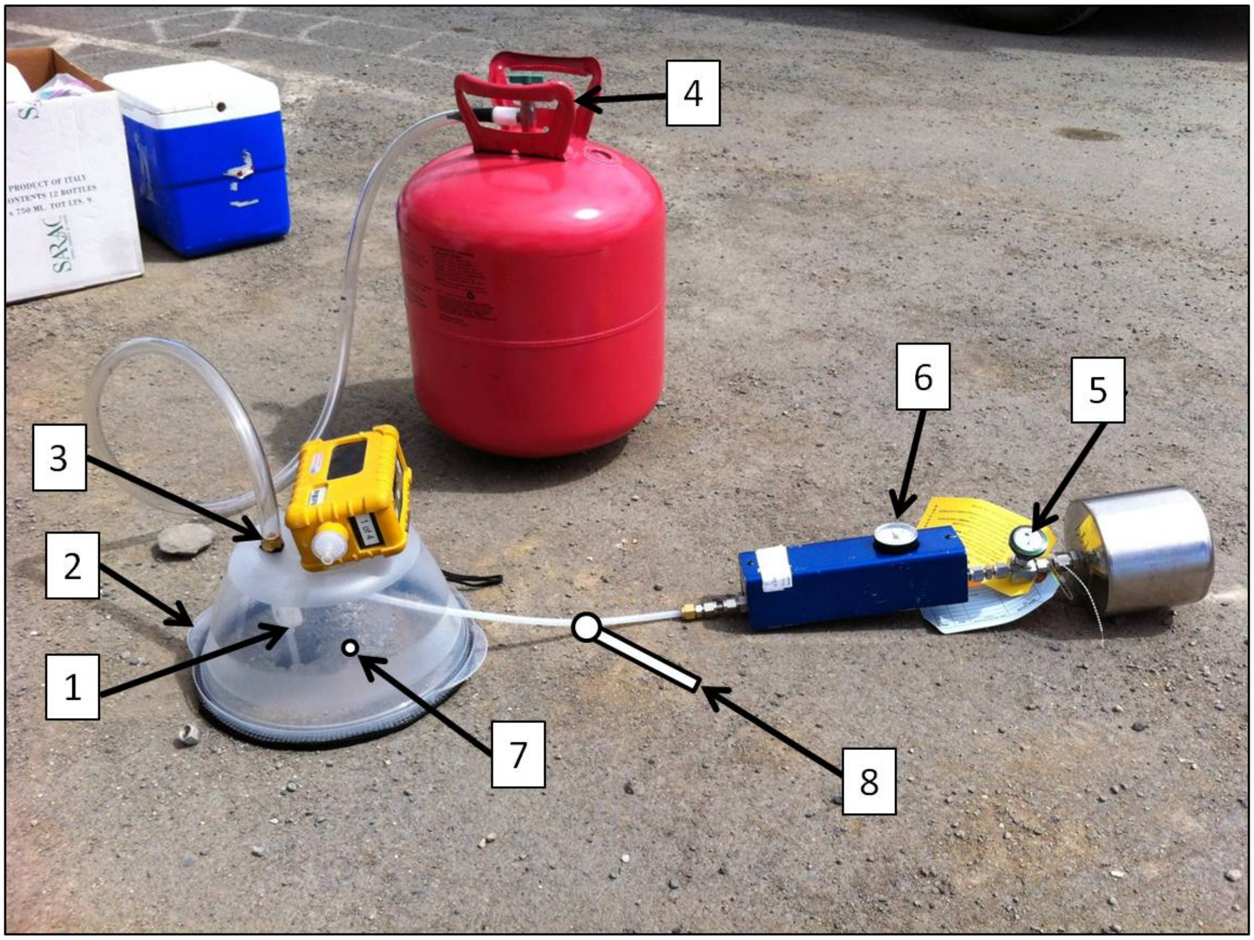
Step 1. To prepare shroud: A) Cut ½” hole on top for helium port; B) Insert Swagelok union into helium port from inside and fasten to Tupperware from the outside with a Swagelok on the top (or something similar, see Step 4); C) Cut ¼” hole on side for tubing from vapor point to flow controller; and D) Place door weather stripping around base.



Step 2. Purge vapor monitoring point and record PID reading for total VOCs and other parameters as needed. PID readings can also be recorded after sample collection.



Step 3. Prepare Summa canister sampling train. Insert tubing from flow controller through shroud and hook to well point. Include short length of flexible, Tygon (or similar) tubing at well point. Tygon tubing can absorb VOCs and its use should be minimized. For initial leak test: 1) Pinch flexible tubing shut (or close well point valve, if installed), 2) Open valve on Summa canister, and 3) Monitor vacuum gauge on flow controller for 60 seconds. If the vacuum does not drop over 60 seconds then it can be safely assumed that the sampling train is not leaking up to the well point itself.



Step 4. Test for leaks at vapor monitoring point hookup using helium, while soil gas sample is being collected: 1) Open clamp on flexible tubing; 2) Place shroud around vapor point (PID used to add weight for better seal in photo); 3) Hook tubing from helium tank to shroud, 4) Fill shroud with helium; 5) Open valve on Summa canister; 6) Monitor vacuum gauge and close valve at target vacuum level (usually around -5mm Hg); 7) Optional third port added to the shroud to monitor helium levels in the field (not shown); and 8) Optional bypass connector added to test for helium in the field and check for leaks around the vapor point annulus (not shown) . Target for a minimum of 20-30+% helium (usually accomplished with a 10-15 second burst of helium). Request that lab test for helium in sample (e.g., using ASTM-D 1945). If helium is identified in the sample then this suggests that the well point was leaking and the data should be flagged. Attempting to quantify the exact volume of ambient air that leaked into the Summa canister and adjust soil gas data accordingly is usually not practical.

Attachment 5: TO-15 and TO-17 Chromatograms for Key Samples.

TO-15 Chromatograms for Key Samples (carbon ranges marked)

Data File: /chem/msd2.i/30aug11.b/2083020.d

Date : 30-AUG-2011 21:37

Client ID:

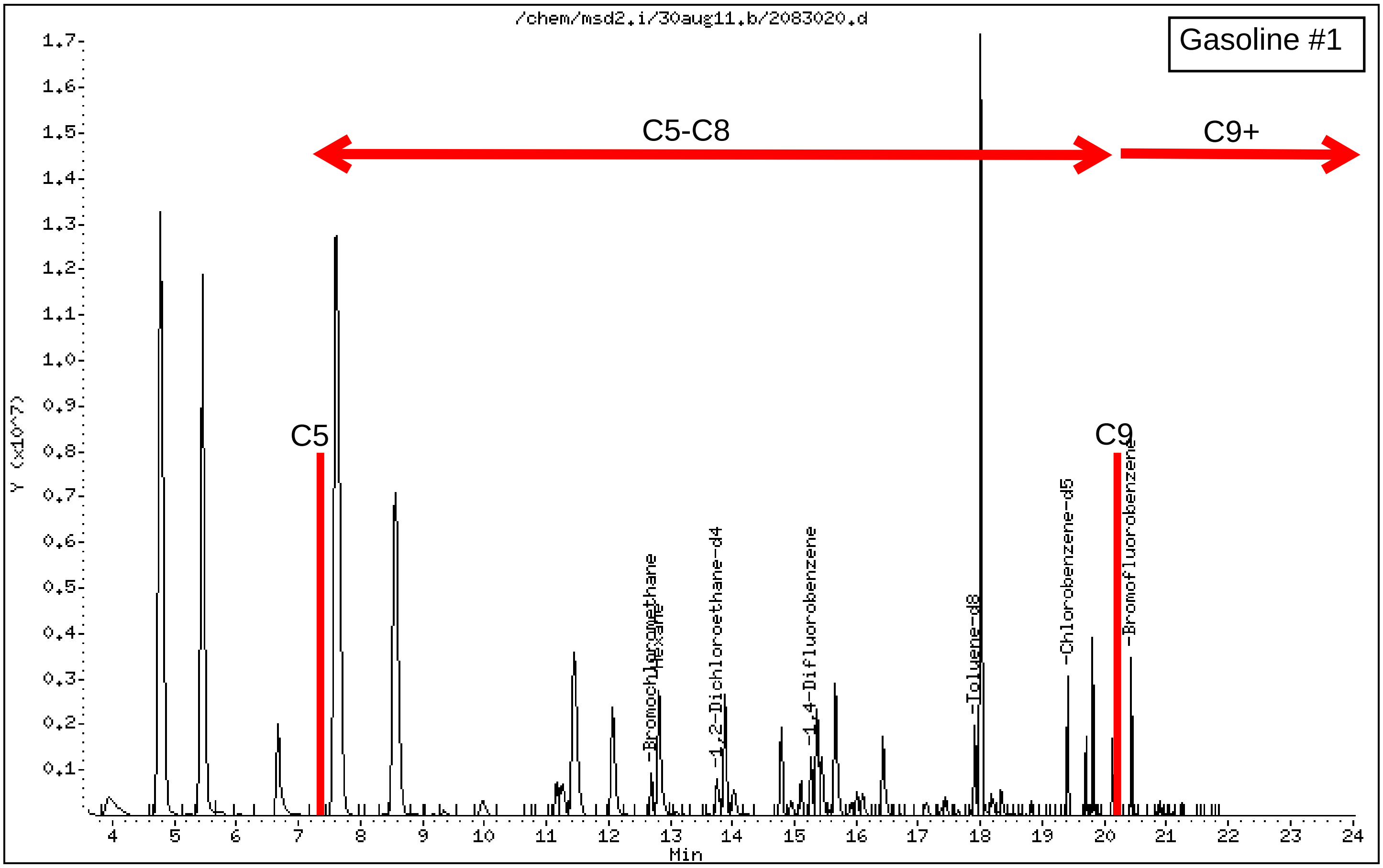
Instrument: msd2.i

Sample Info: 5.0ml #20777

Operator: srs

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/25oct11.b/2102512.d

Date : 25-OCT-2011 13:45

Client ID:

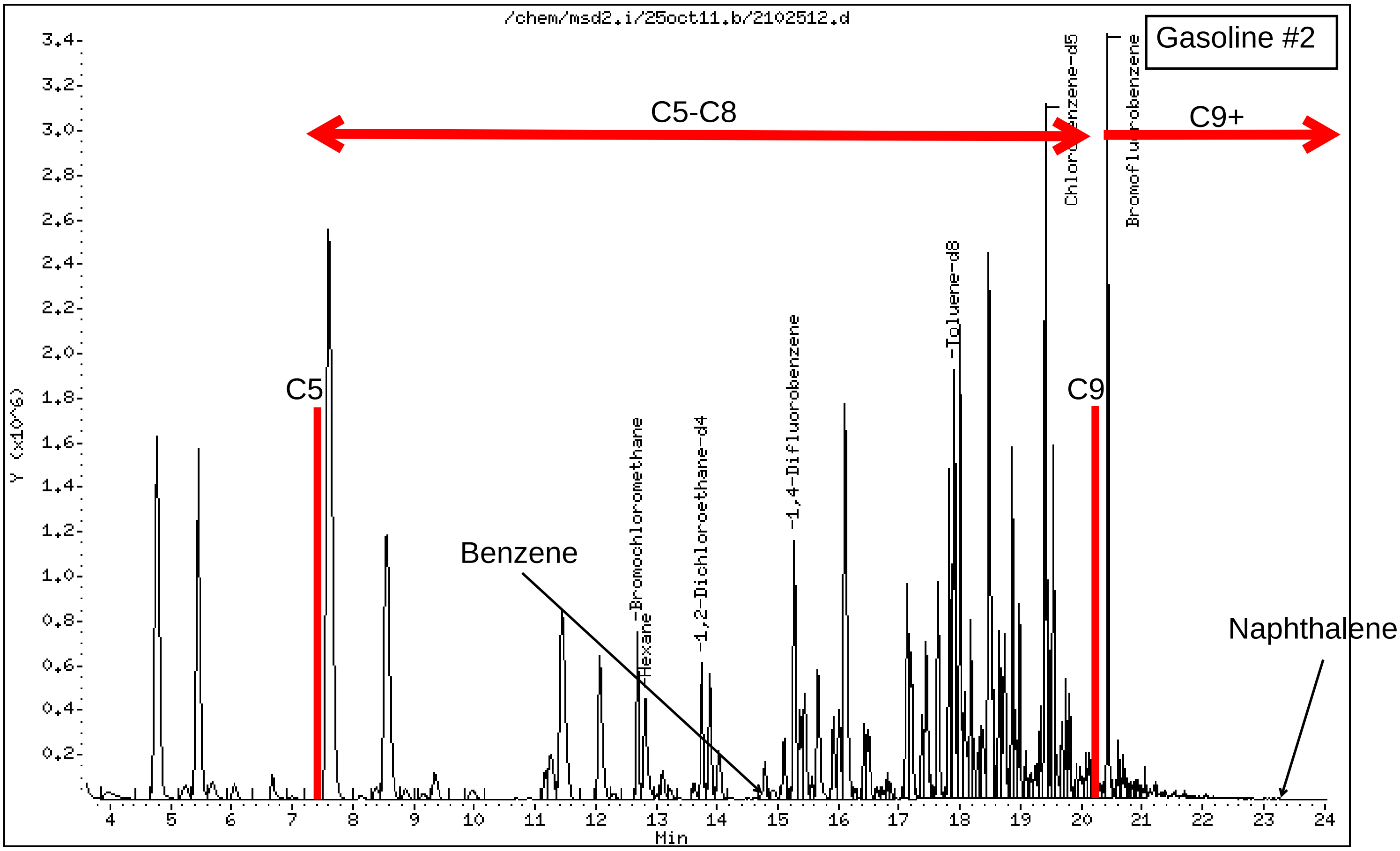
Instrument: msd2.i

Sample Info: 6.0ml #12035

Operator: mtw

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/15jun11.b/2061512.d

Date : 15-JUN-2011 15:12

Client ID:

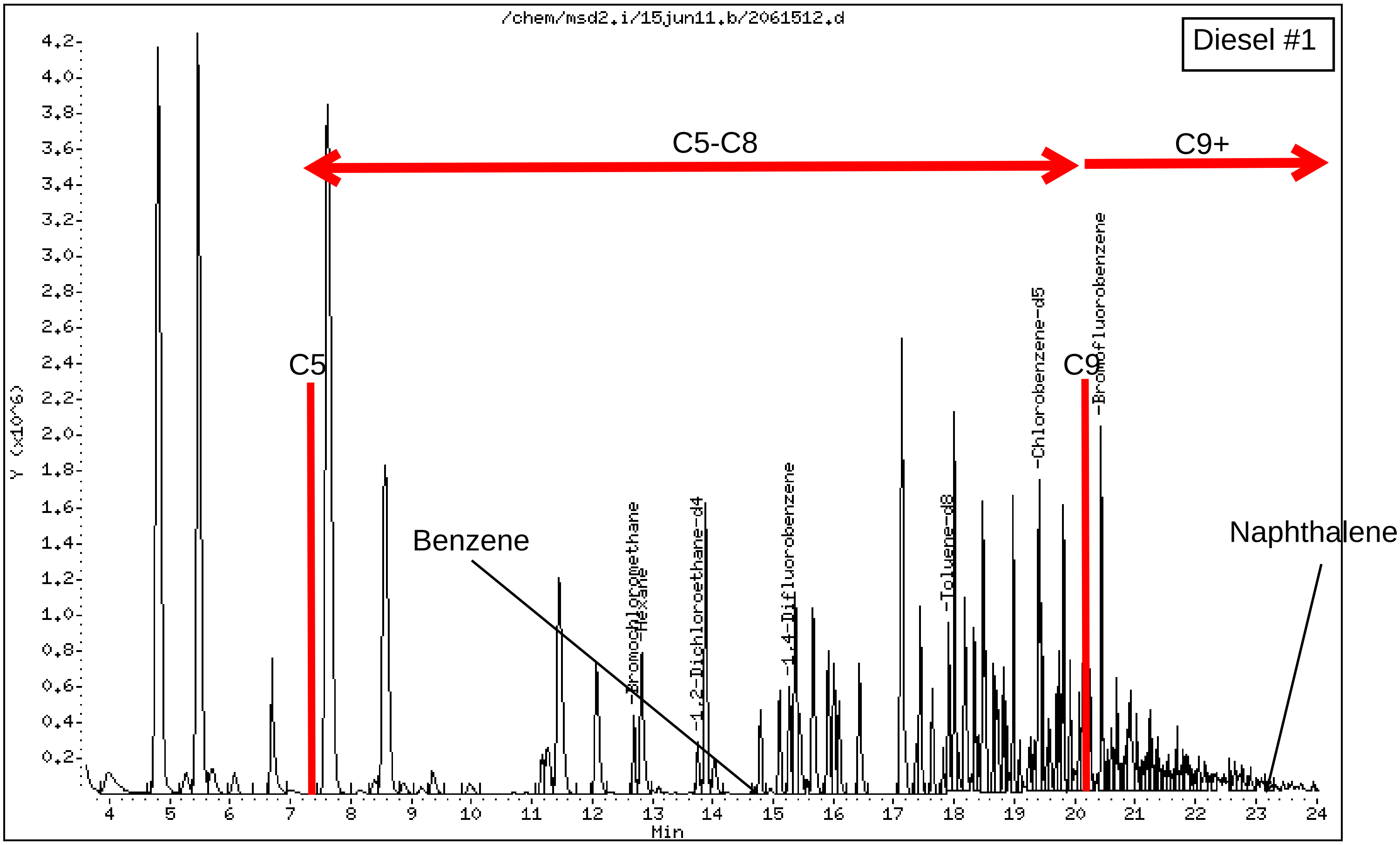
Instrument: msd2.i

Sample Info: 2.0ml #36491

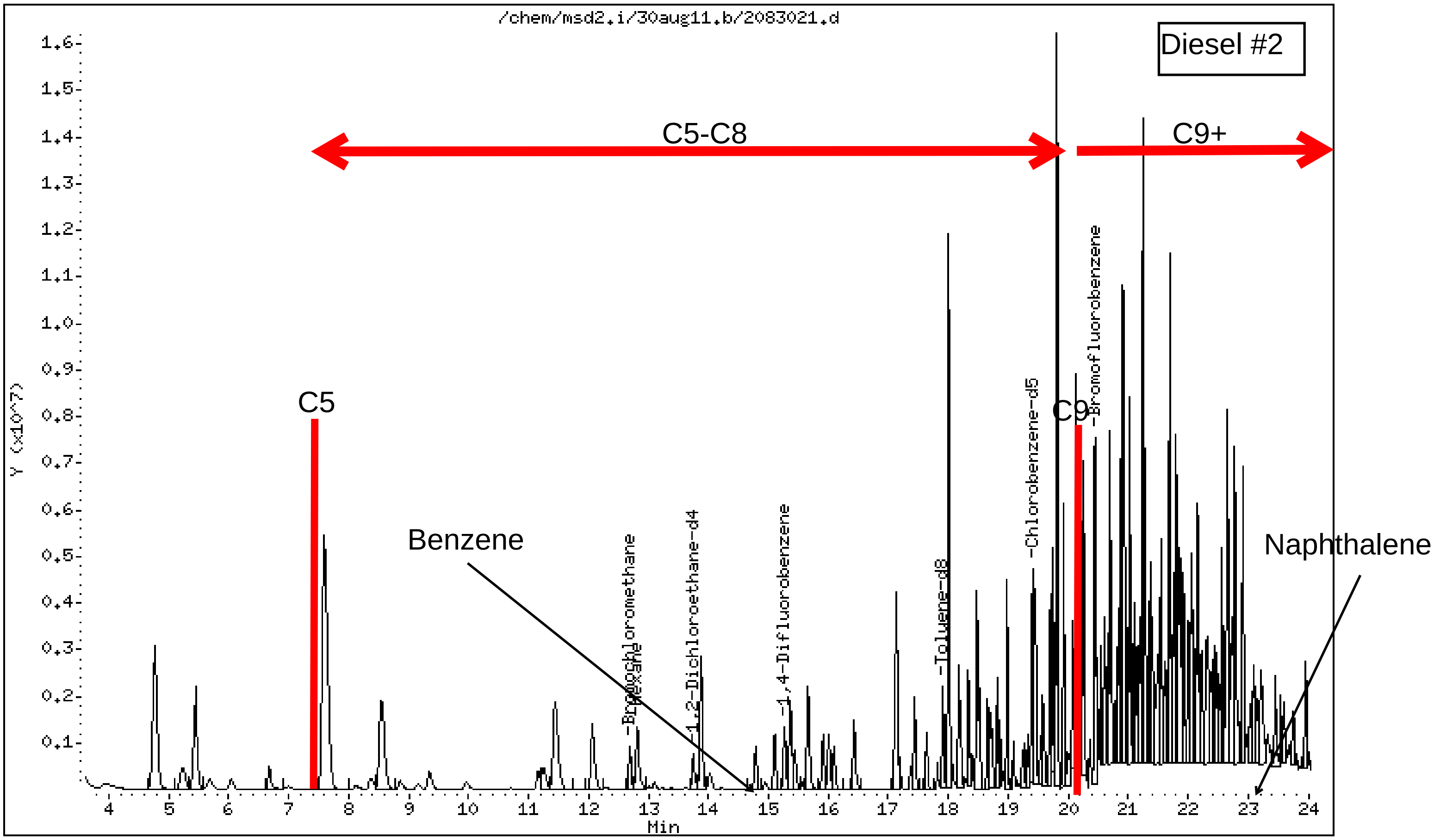
Operator: JP

Column phase: RTx-624

Column diameter: 0.32



```
Data File: /chem/msd2.i/30aug11.b/2083021.d                                                                   Page 1

Date : 30-AUG-2011 23:16

Client ID:                                                 Instrument: msd2.i

Sample Info: 8.0ml #36432

                                                           Operator: srs

Column phase: RTx-624                                      Column diameter:  0.32
```



Data File: /chem/msd2.i/24oct11.b/2102412.d

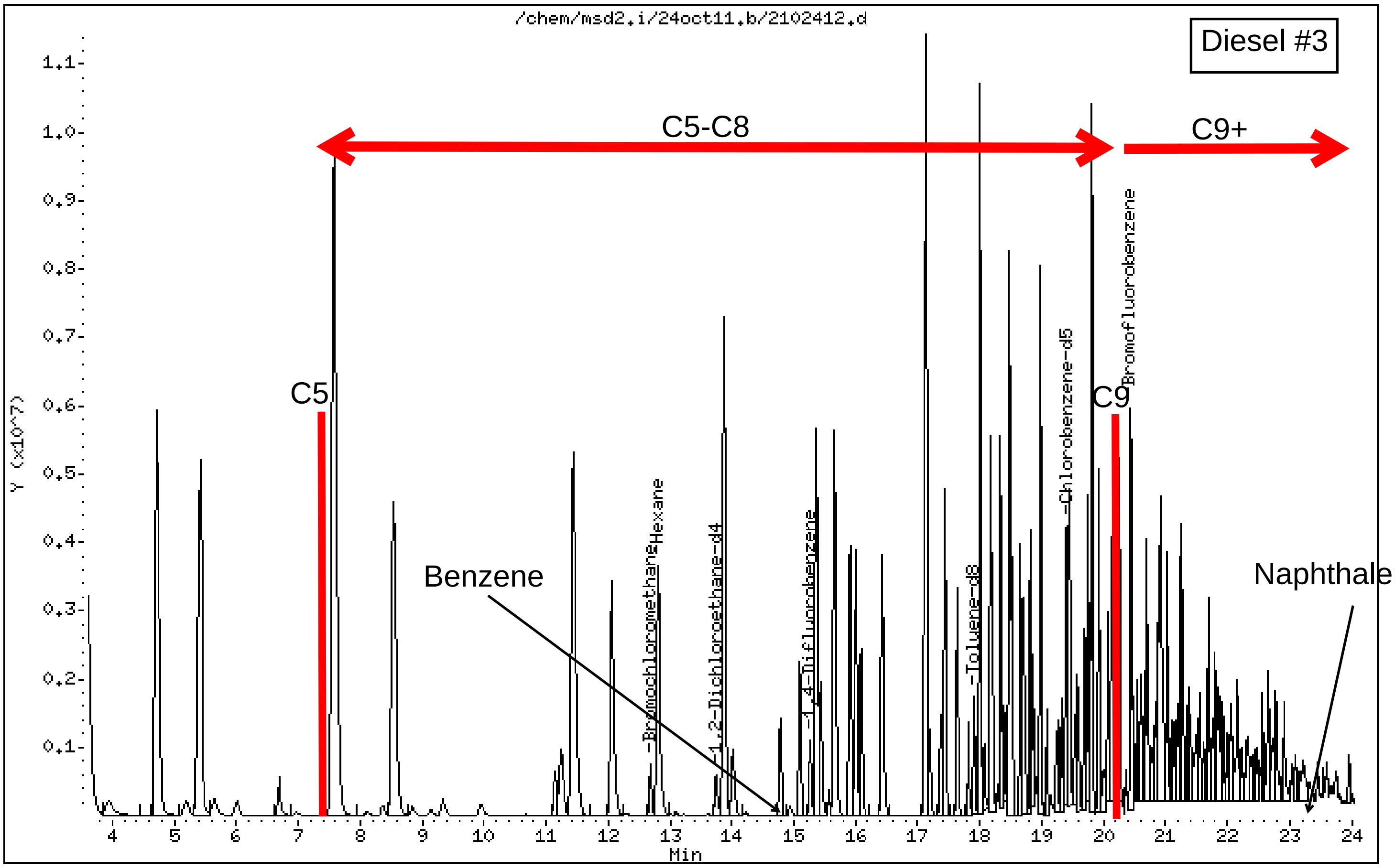
Date : 24-OCT-2011 14:04

Client ID: Instrument: msd2.i

Sample Info: 30ml #37711

Operator: mtw

Column phase: RTx-624 Column diameter: 0.32



Data File: /chem/msd2.i/12oct11.b/2101220.d

Date : 12-OCT-2011 18:55

Client ID:

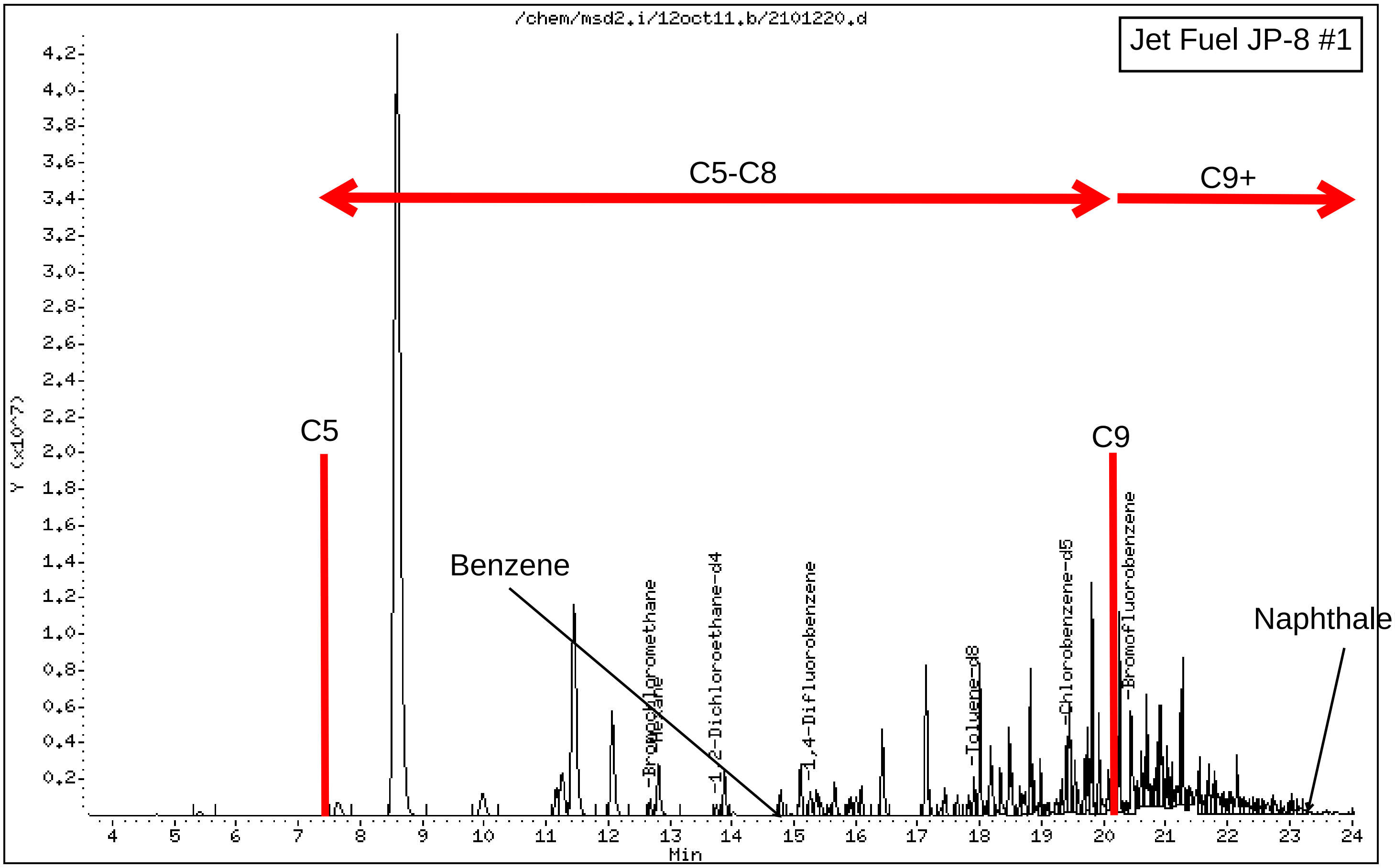
Instrument: msd2.i

Sample Info: 2.0ml #34656

Operator: EA

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/28jun11.b/2062817.d

Page 1

Date : 29-JUN-2011 06:53

Client ID:

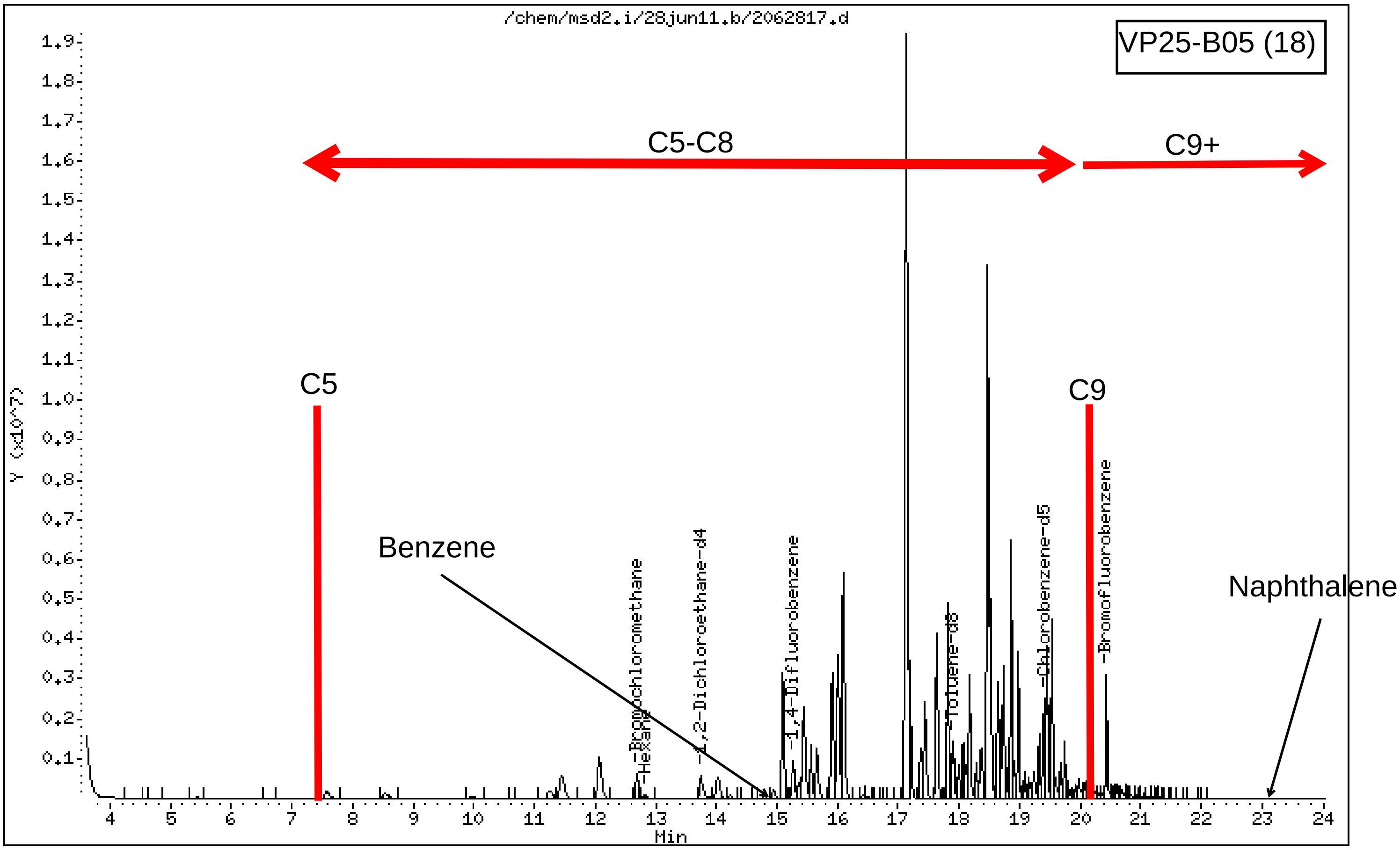
Instrument: msd2.i

Sample Info: 100mL #36428

Operator: mtw

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/28jun11.b/2062820.d

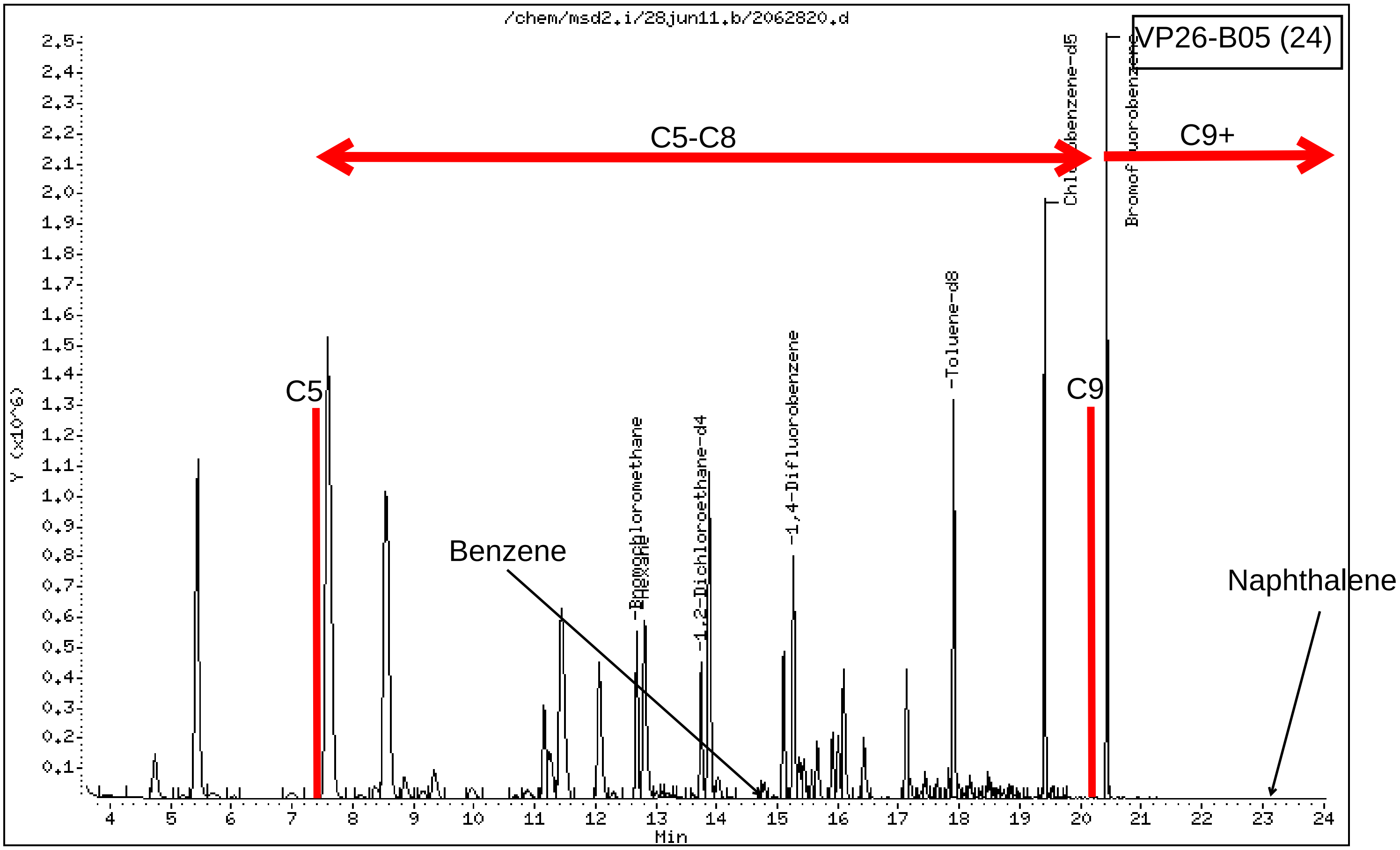
Date : 29-JUN-2011 09:09

Client ID: Instrument: msd2.i

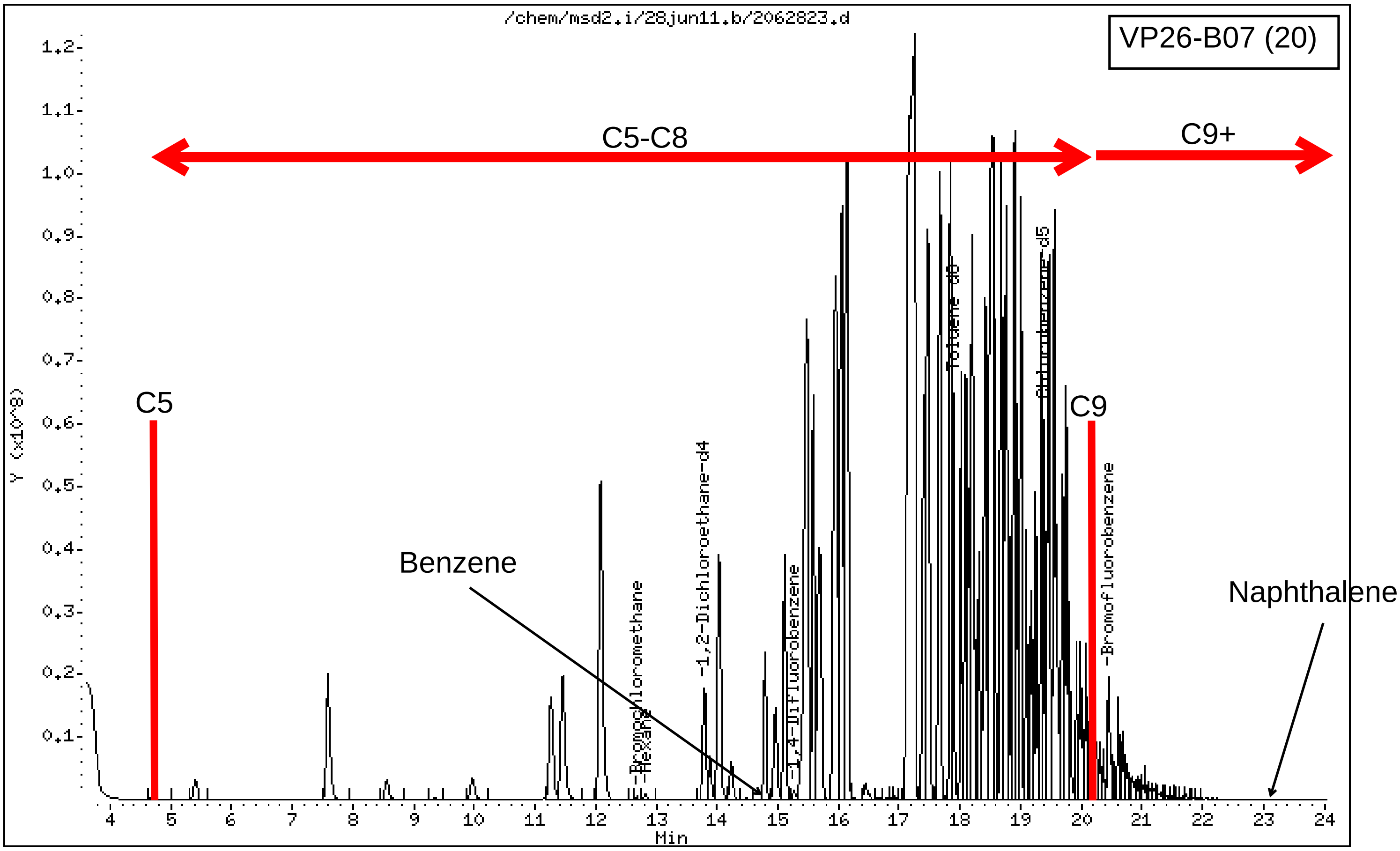
Sample Info: 2.0mL #35610

Operator: mtw

Column phase: RTx-624 Column diameter: 0.32



```
Data File: /chem/msd2.i/28jun11.b/2062823.d                                                    Page 1

Date : 29-JUN-2011 10:46

Client ID:                                              Instrument: msd2.i

Sample Info: 15mL #34177

                                                        Operator: mtw

Column phase: RTx-624                                   Column diameter:  0.32
```



Data File: /chem/msd2.i/28jun11.b/2062822.d

Date : 29-JUN-2011 10:17

Client ID:

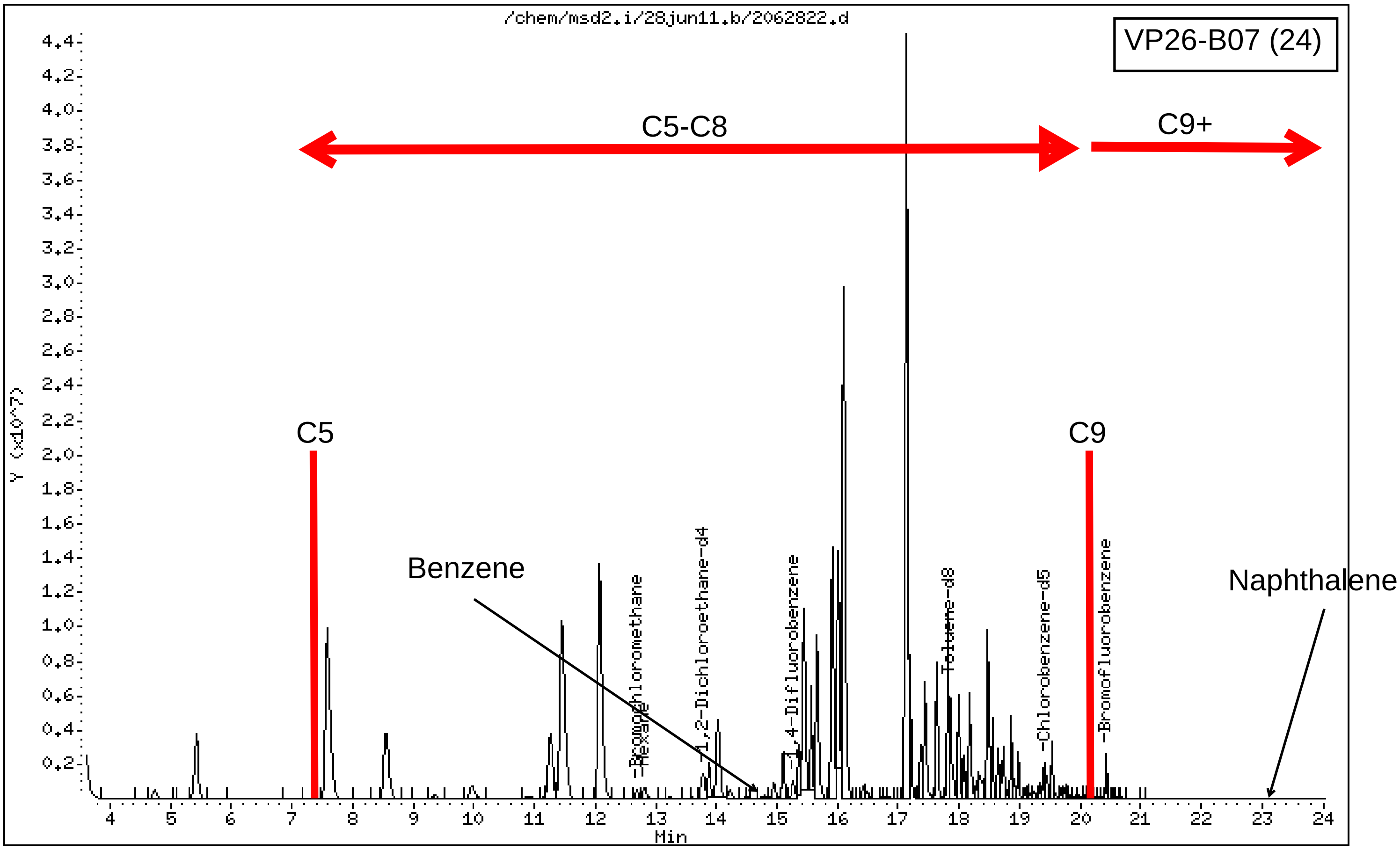
Instrument: msd2.i

Sample Info: 100mL #35682

Operator: mtw

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/19aug11.b/2081916.d

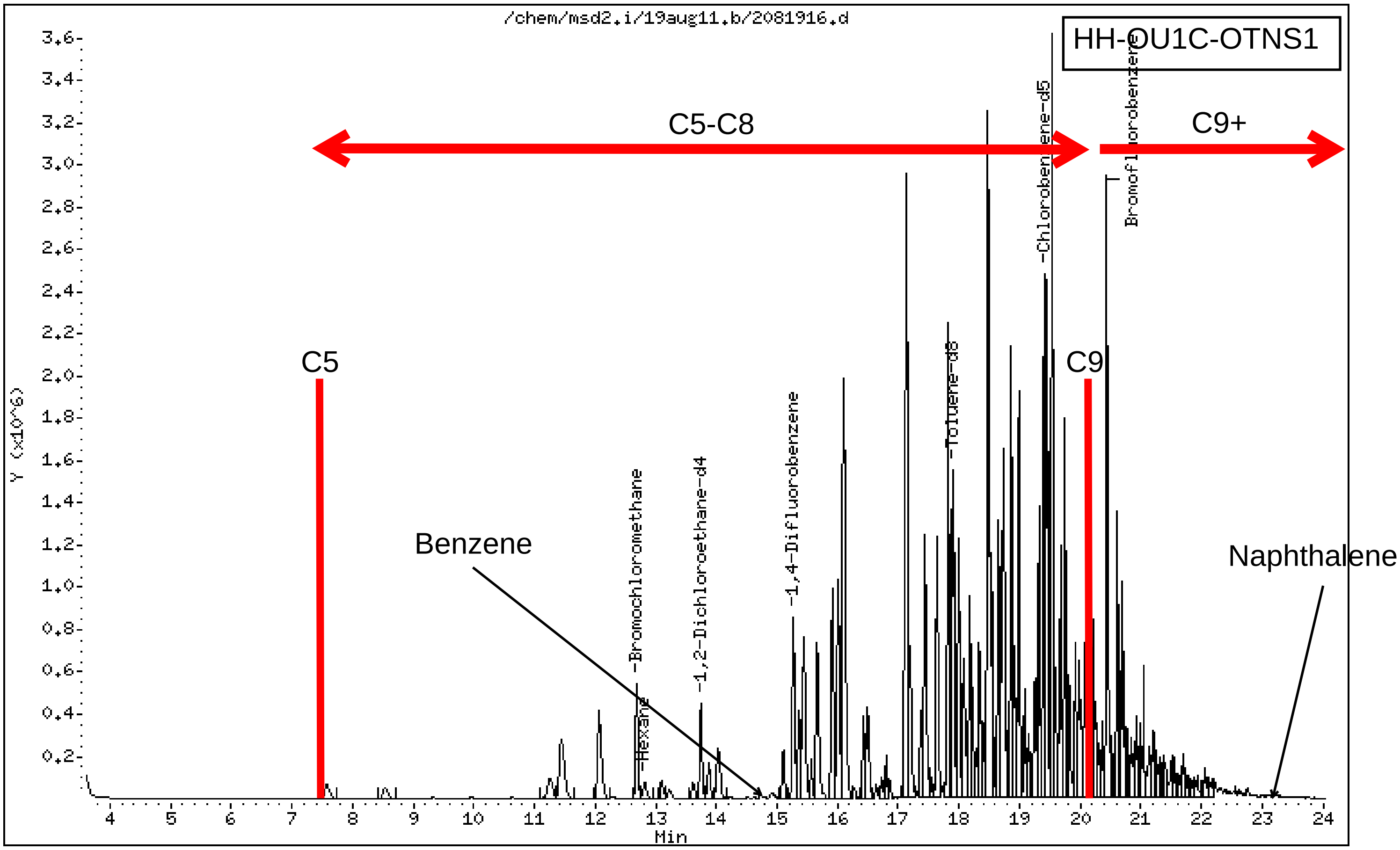
Date : 19-AUG-2011 14:38

Client ID: Instrument: msd2.i

Sample Info: 3.0mL #34117

Operator: JP

Column phase: RTx-624 Column diameter: 0.32



Data File: /chem/msd2.i/19aug11.b/2081927.d

Date : 19-AUG-2011 23:20

Client ID:

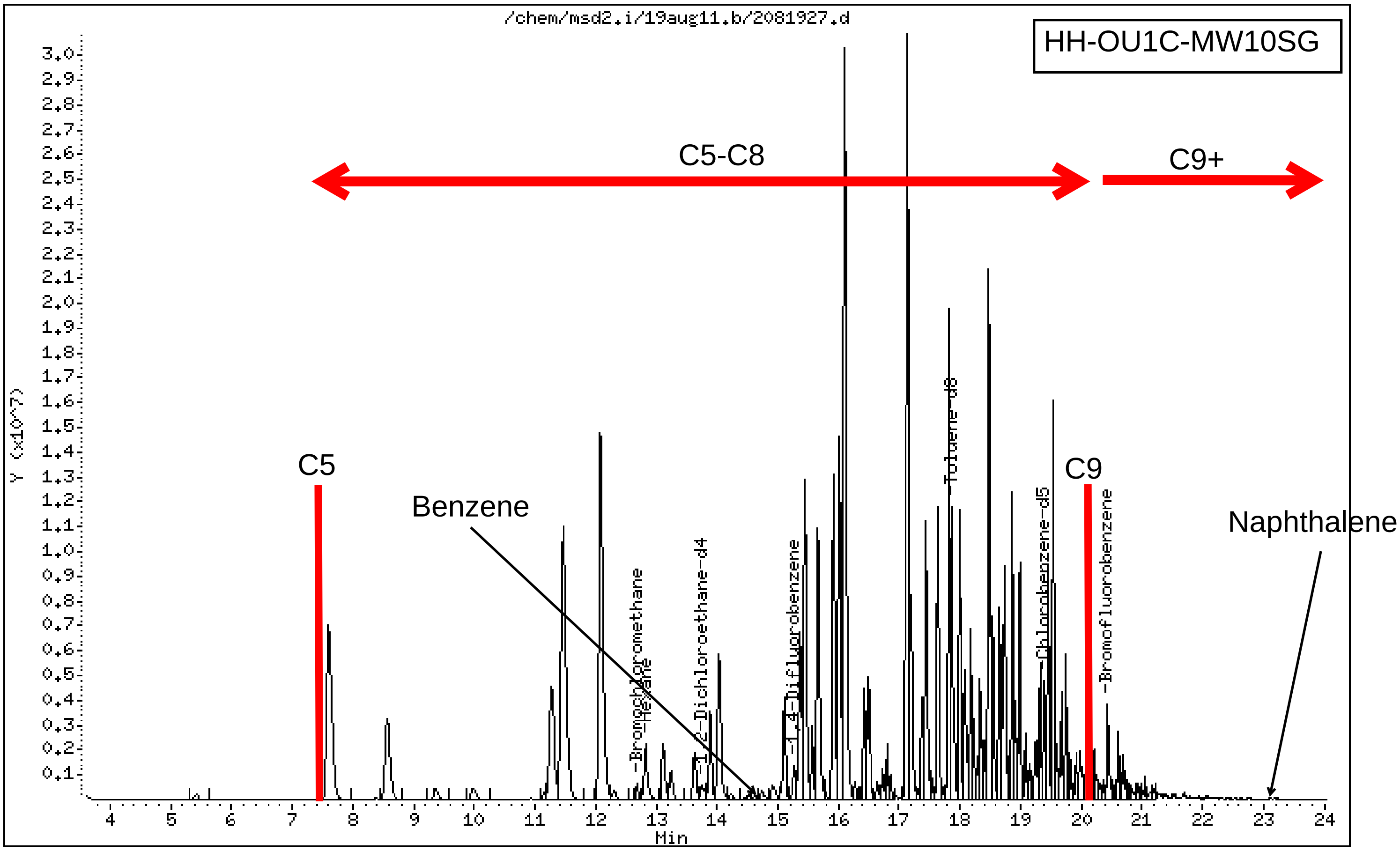
Instrument: msd2.i

Sample Info: 0.3mL #31790

Operator: srs

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/19aug11.b/2081917.d	Page 1

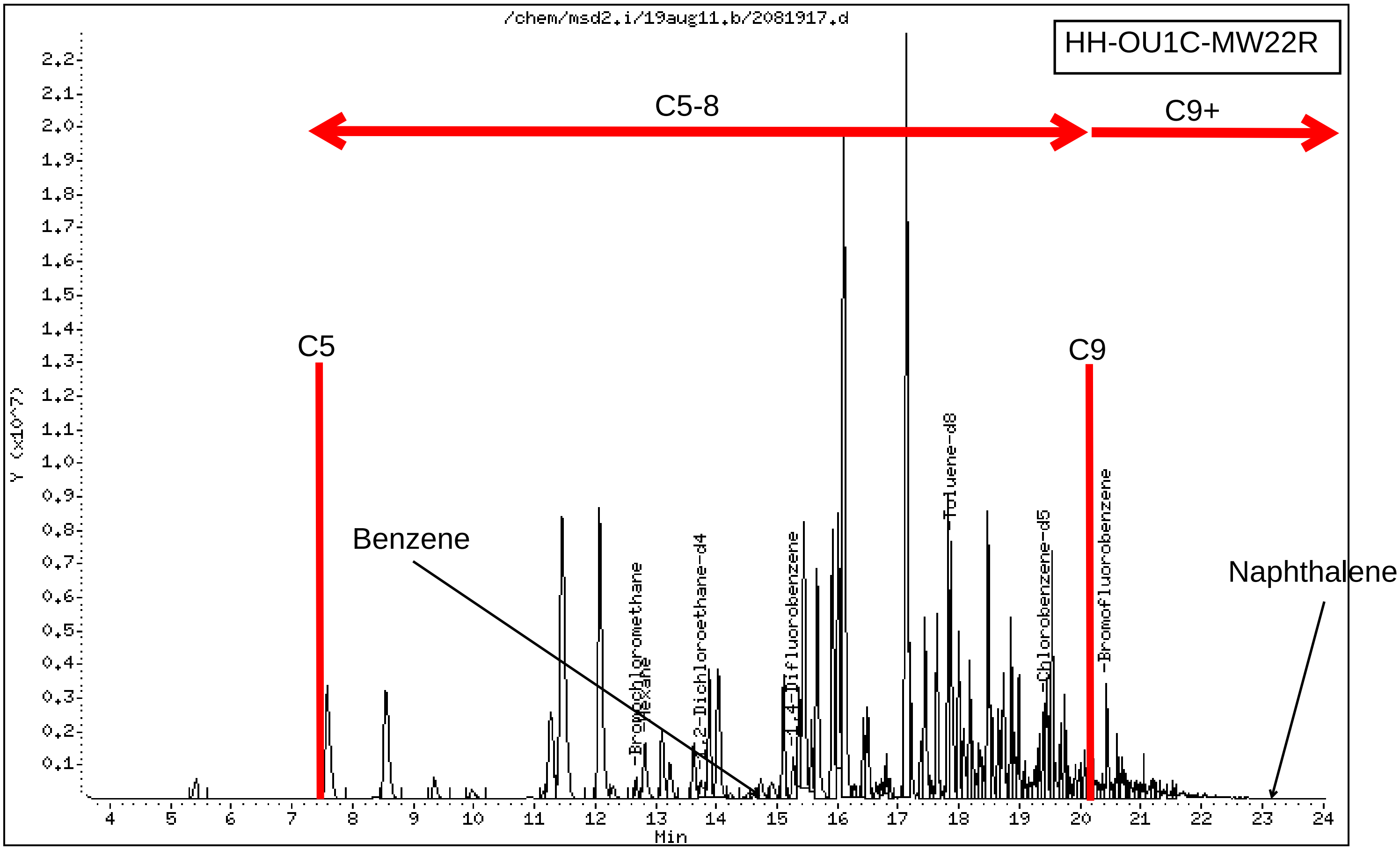
Date : 19-AUG-2011 15:18

Client ID:	Instrument: msd2.i

Sample Info: 0.5mL #2133

Operator: JP

Column phase: RTx-624	Column diameter: 0.32



Data File: /chem/msd2.i/12oct11.b/2101216.d

Date : 12-OCT-2011 16:09

Client ID:

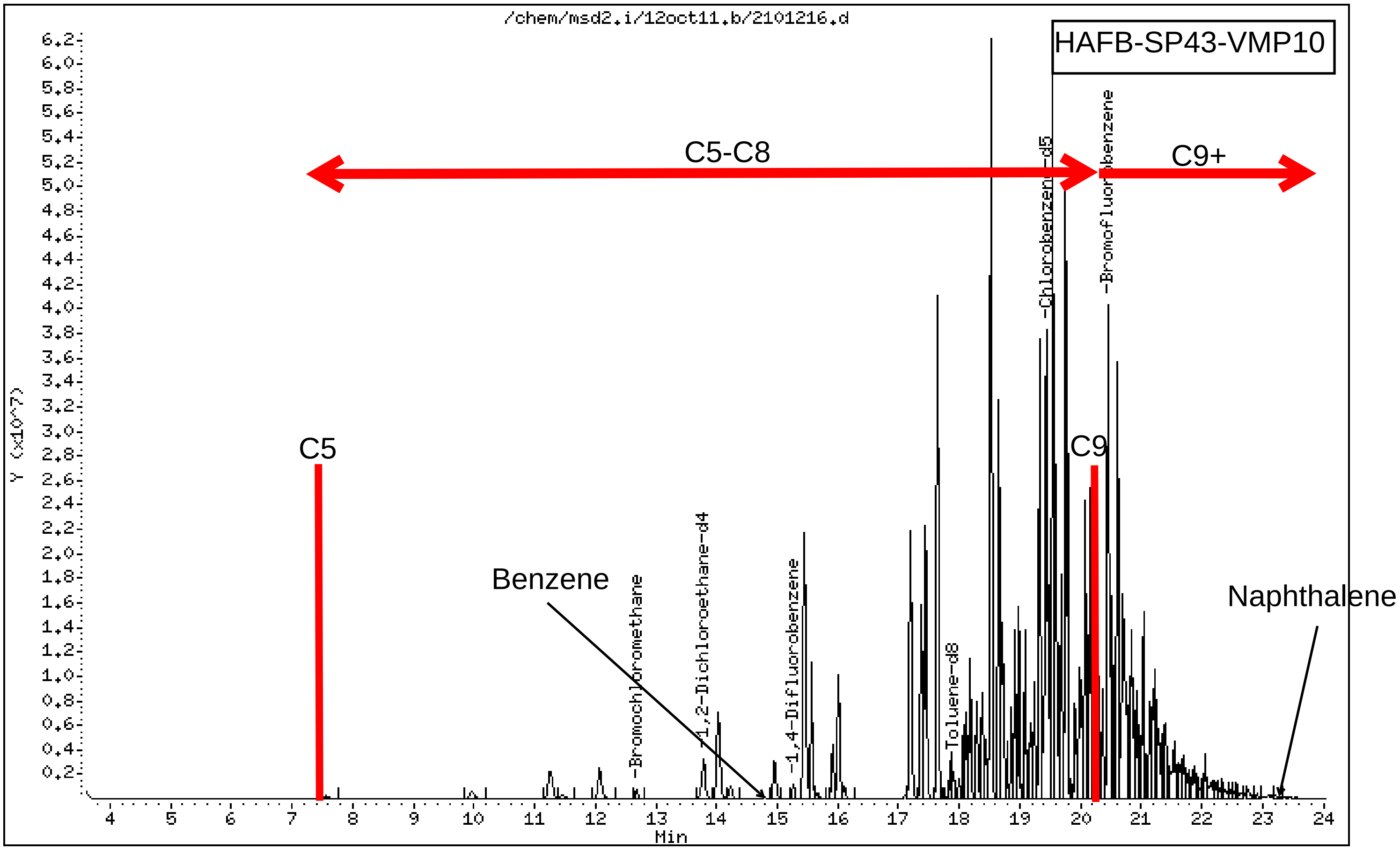
Instrument: msd2.i

Sample Info: 2.0ml #37672

Operator: dfm

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/12oct11.b/2101218.d

Date : 12-OCT-2011 17:31

Client ID:

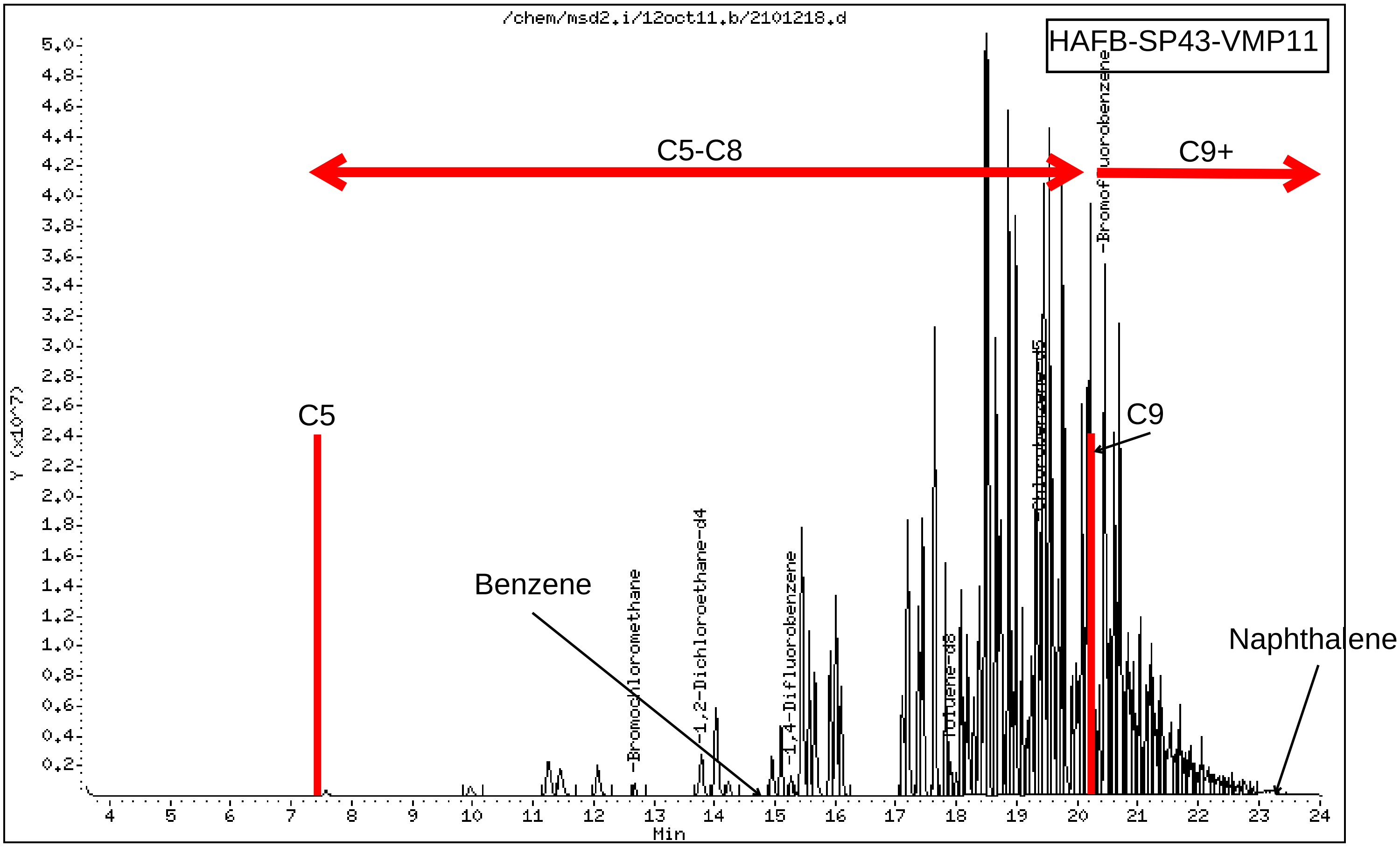
Instrument: msd2.i

Sample Info: 2.0ml #36517

Operator: EA

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/12oct11.b/2101222.d

Page 1

Date : 12-OCT-2011 20:39

Client ID:

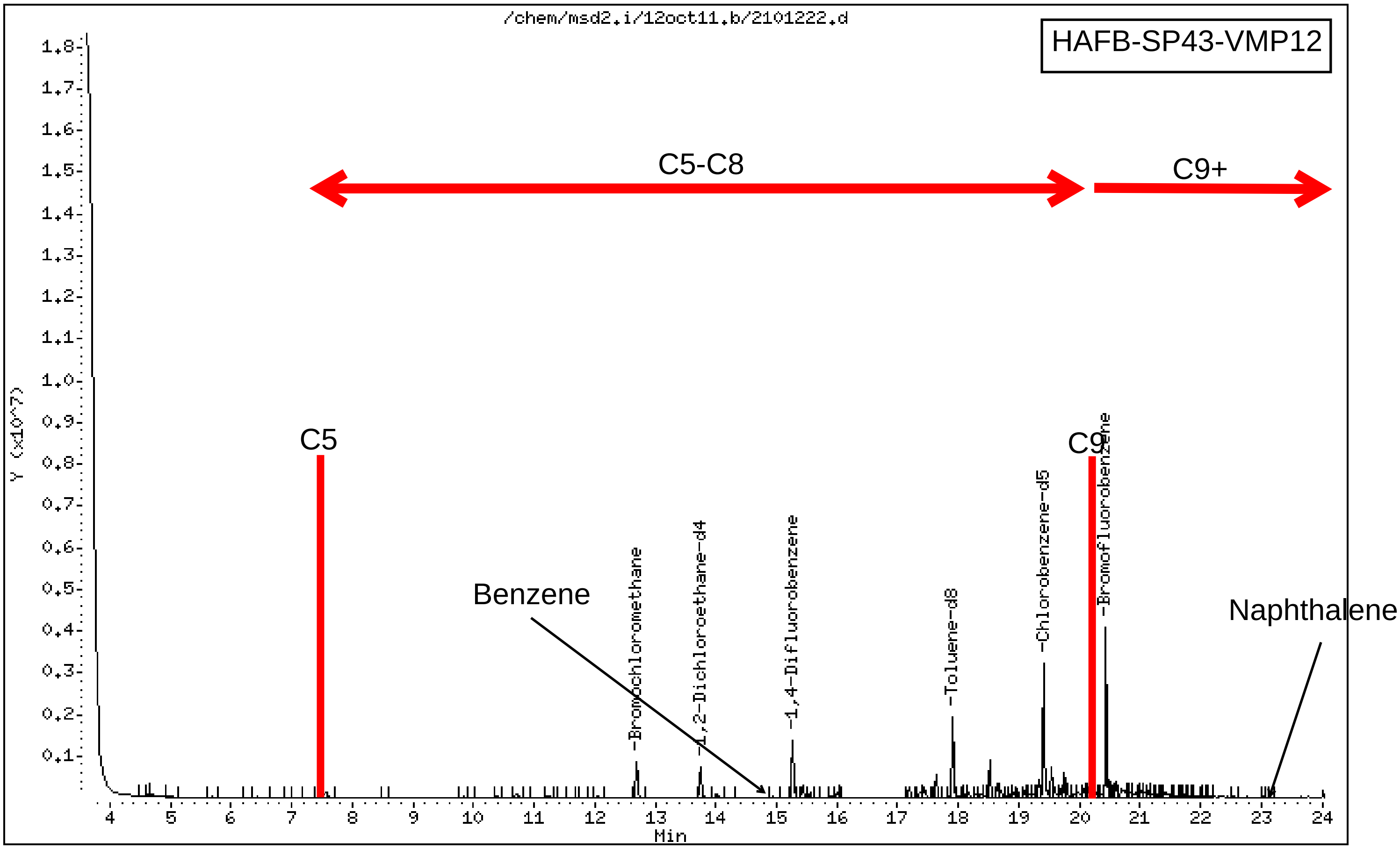
Instrument: msd2.i

Sample Info: 200ML #34179

Operator: EA

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/12oct11.b/2101219.d

Date : 12-OCT-2011 18:13

Client ID:

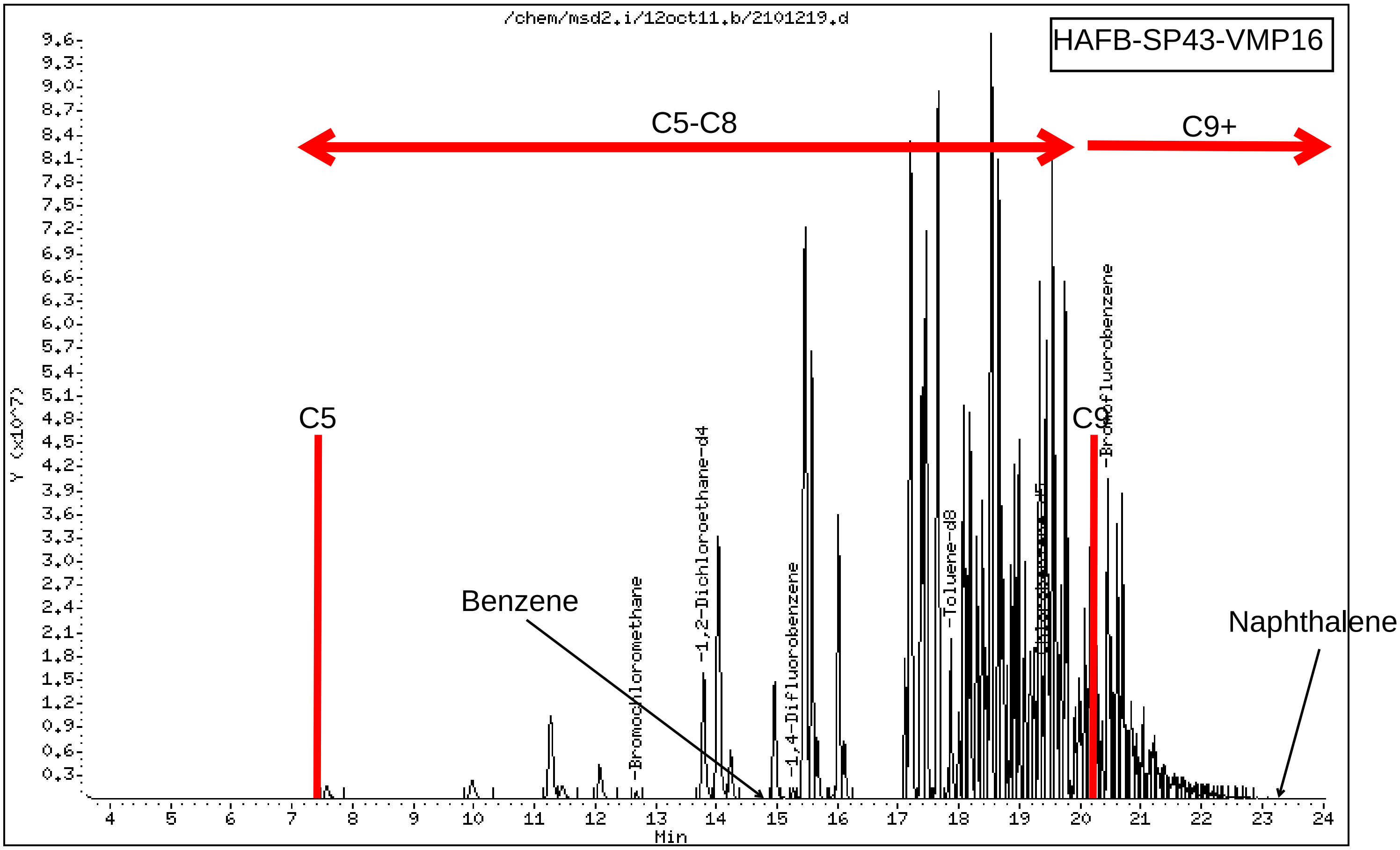
Instrument: msd2.i

Sample Info: 2.0ml #3011

Operator: EA

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/12oct11.b/2101214.d

Date : 12-OCT-2011 13:43

Client ID:

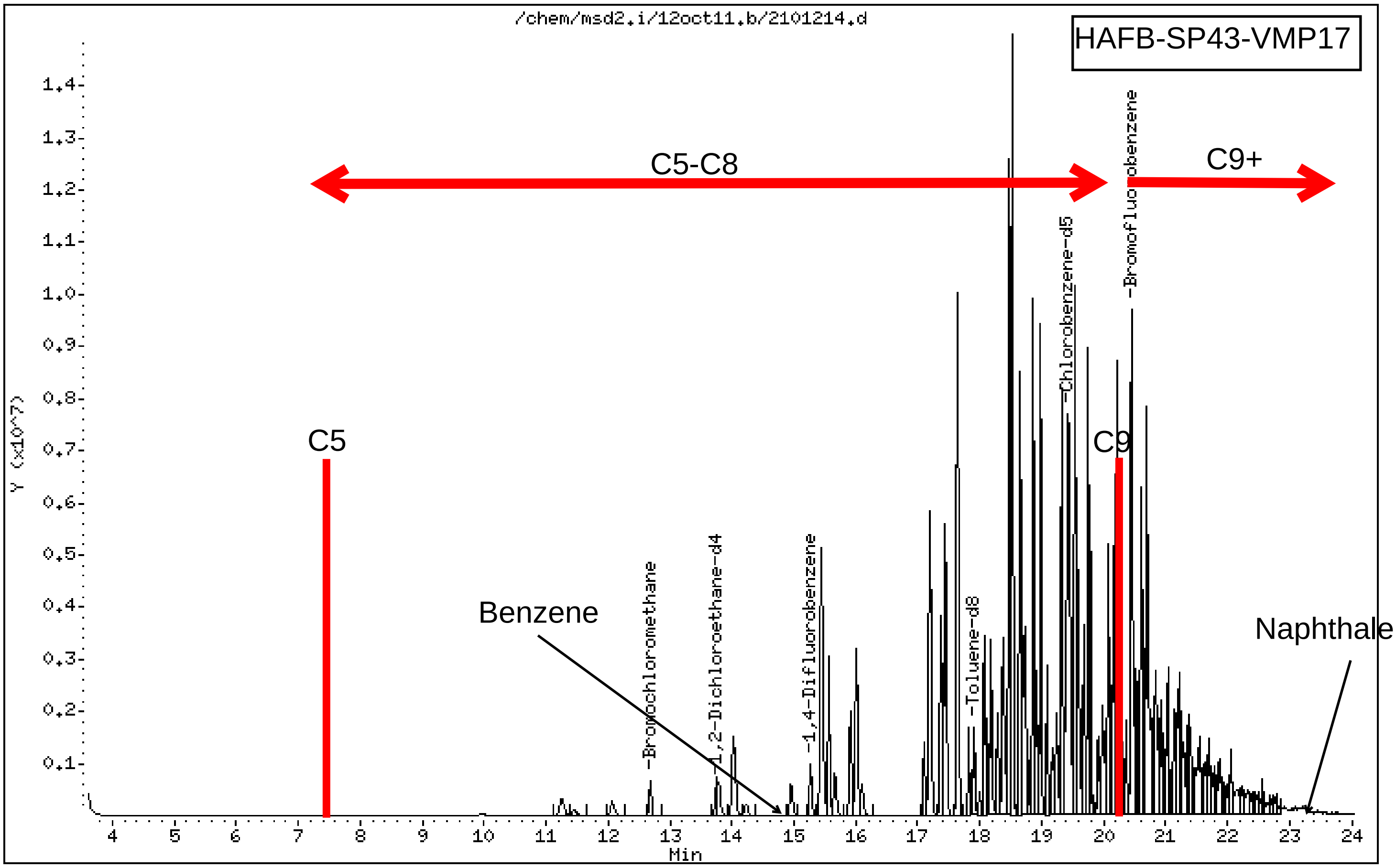
Instrument: msd2.i

Sample Info: 2.0ml #31799

Operator: dfm

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/21jul11.b/2072127.d

Date : 21-JUL-2011 21:52

Client ID:

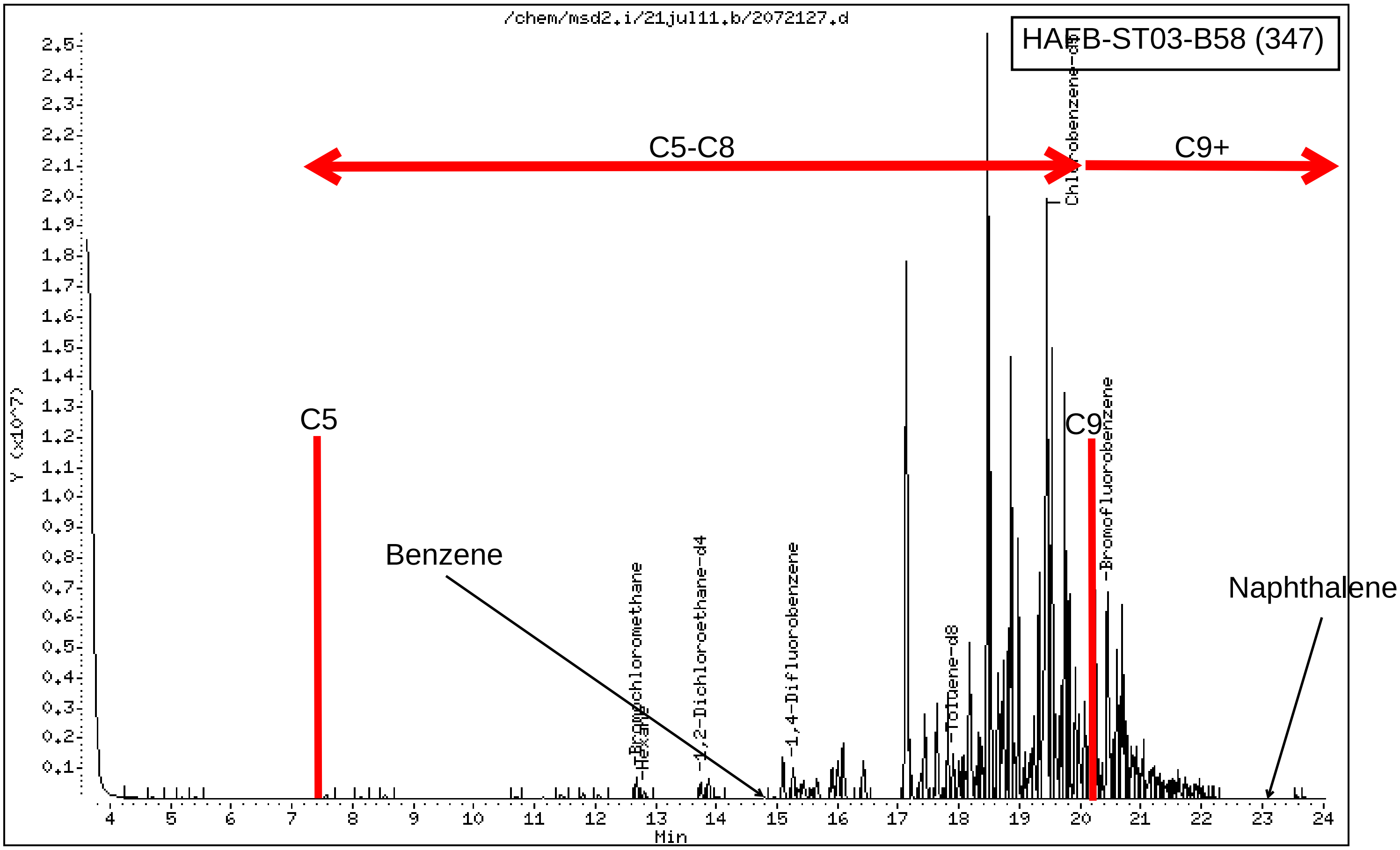
Instrument: msd2.i

Sample Info: 50mL #1354

Operator: dfm

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/21jul11.b/2072128.d

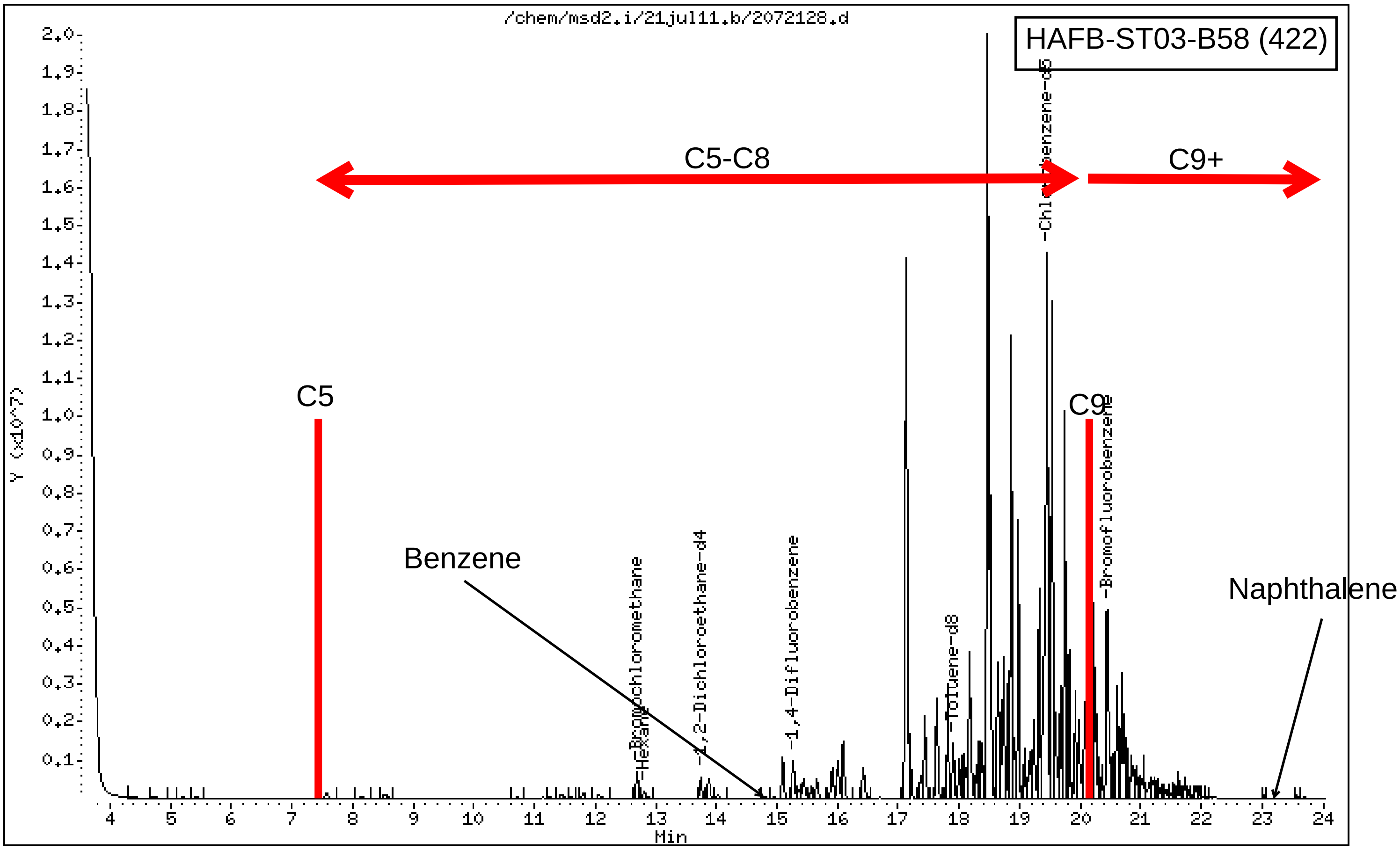
Date : 21-JUL-2011 22:21

Client ID: Instrument: msd2.i

Sample Info: 75mL #3036

Operator: dfm

Column phase: RTx-624 Column diameter: 0.32



Data File: /chem/msd2.i/21jul11.b/2072125.d

Date : 21-JUL-2011 20:53

Client ID:

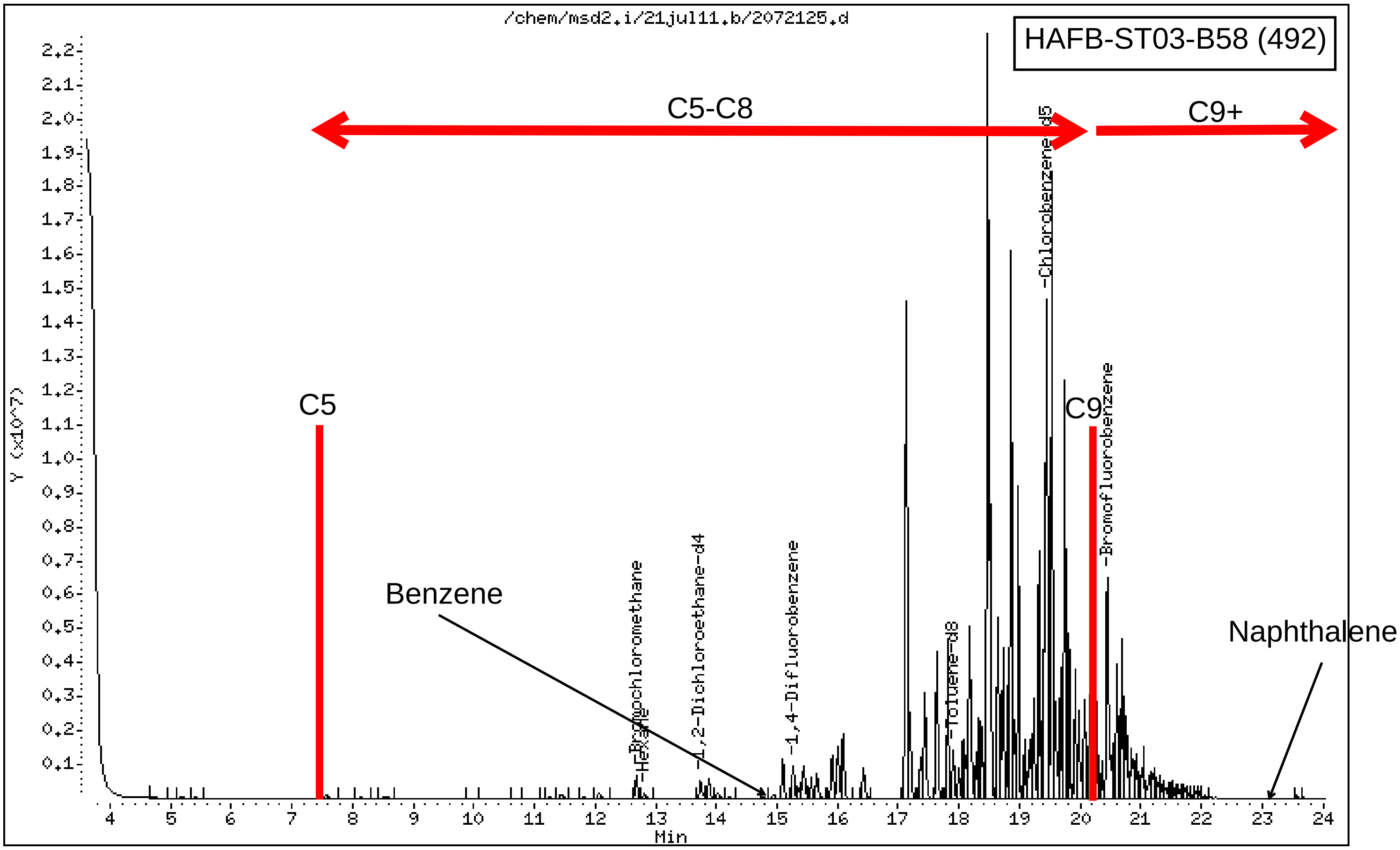
Instrument: msd2.i

Sample Info: 15mL #35667

Operator: dfm

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/21jul11.b/2072126.d

Date : 21-JUL-2011 21:21

Client ID:

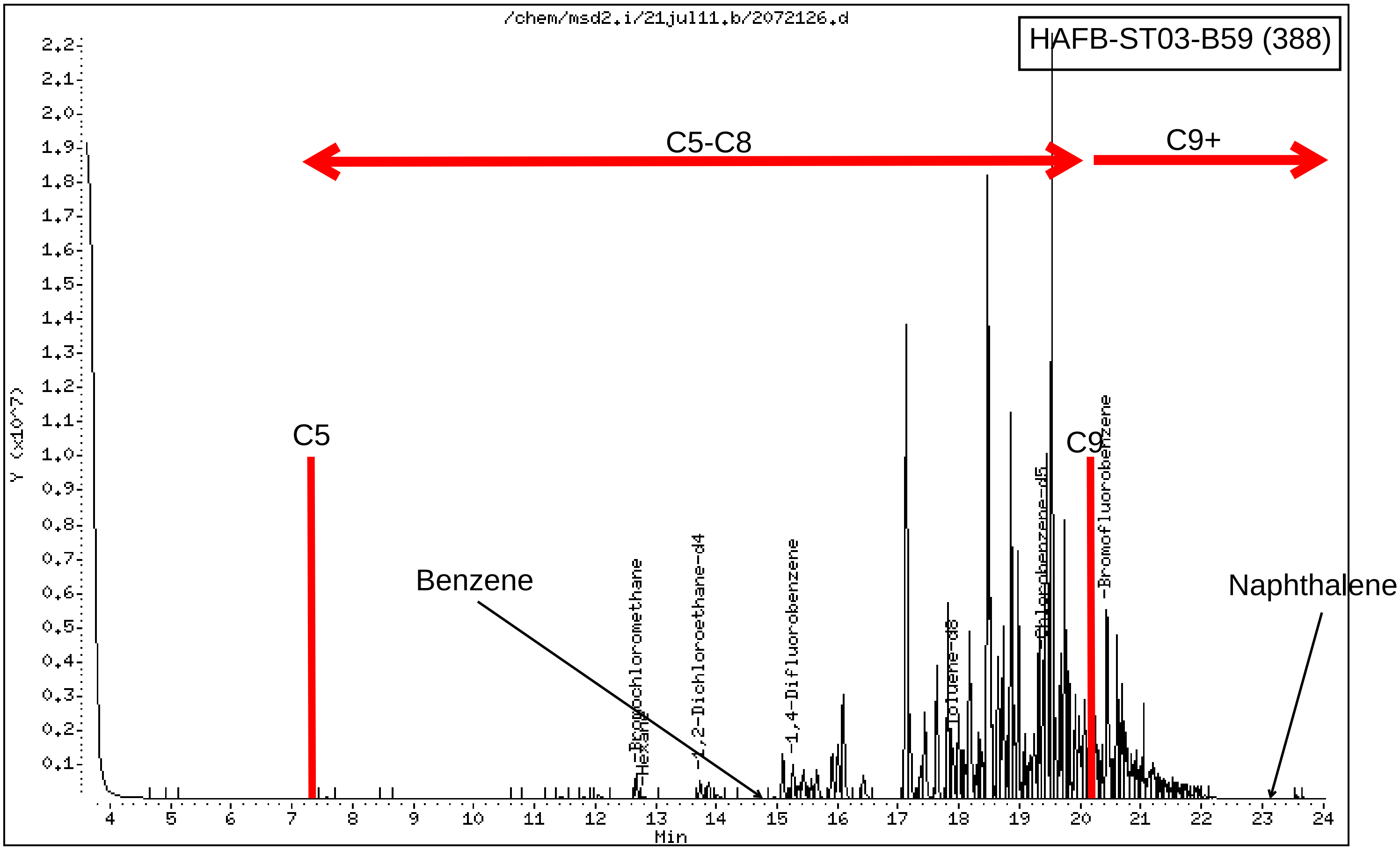
Instrument: msd2.i

Sample Info: 15mL #34669

Operator: dfm

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/02jun11.b/2060214.d

Date : 02-JUN-2011 14:42

Client ID:

Sample Info: 35ml #34100

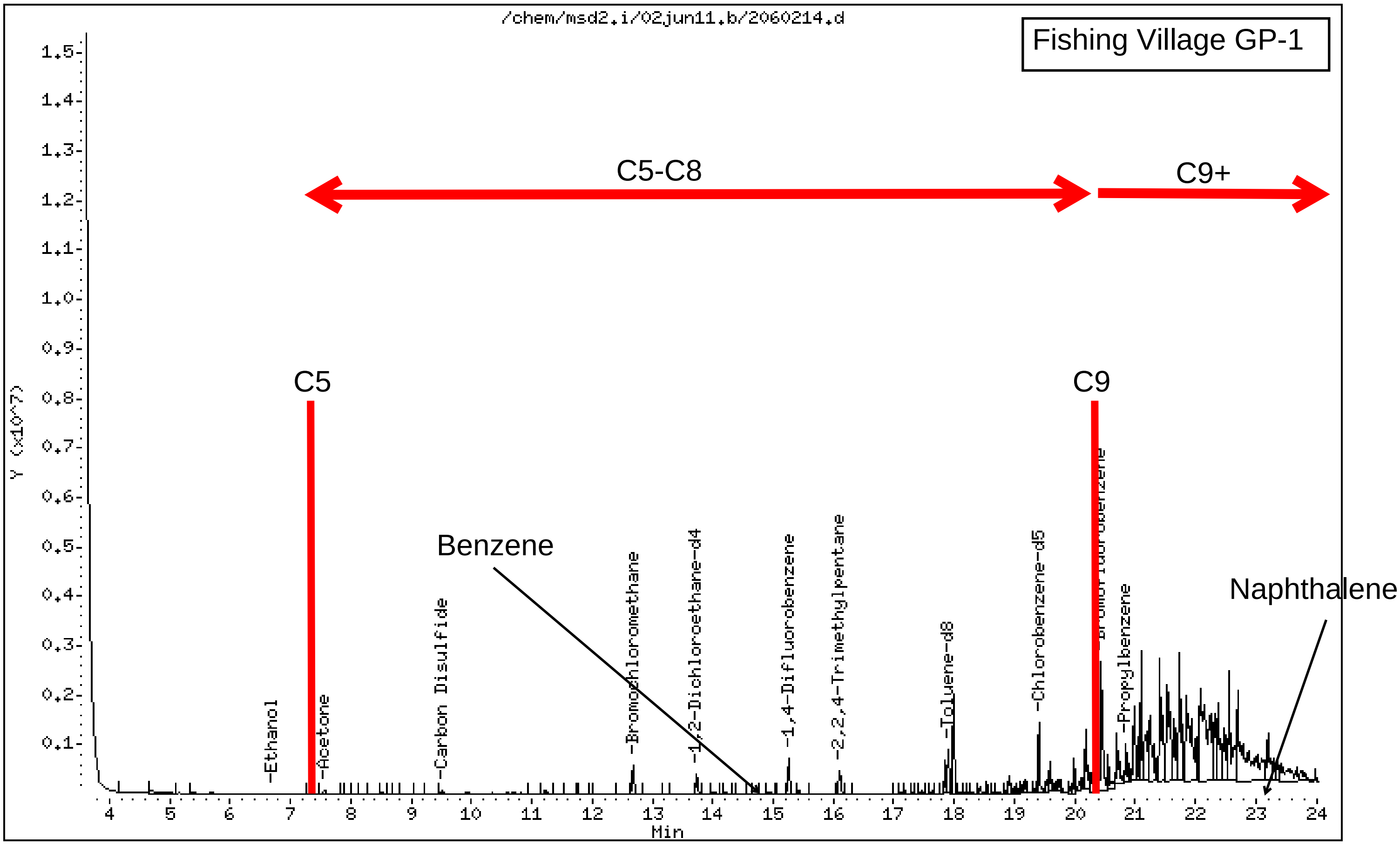
Column phase: RTx-624

Page 1

Instrument: msd2.i

Operator: JP

Column diameter: 0.32



Data File: /chem/msd2.i/02jun11.b/2060217.d

Date : 02-JUN-2011 16:25

Client ID:

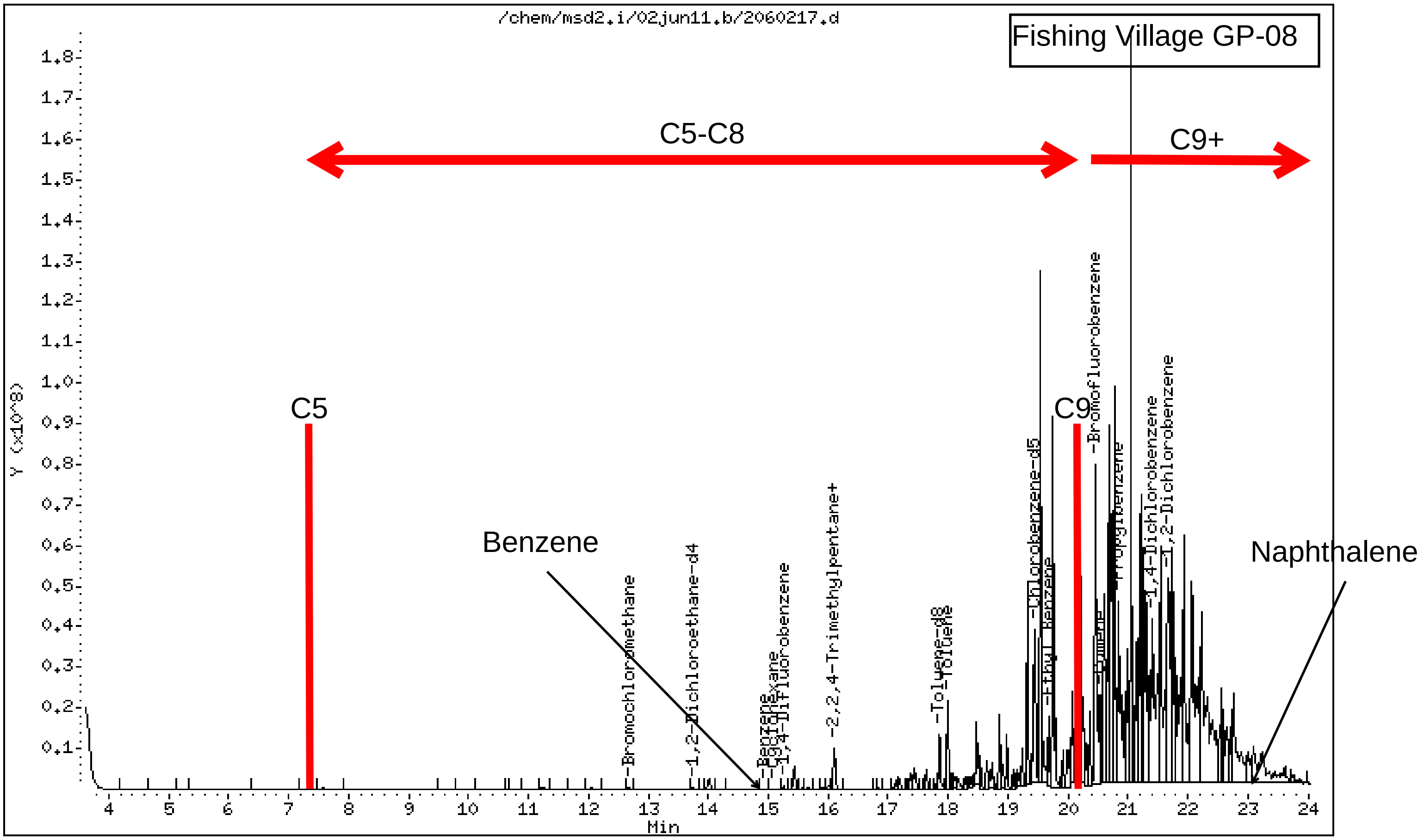
Instrument: msd2.i

Sample Info: 23ml #23832

Operator: JP

Column phase: RTx-624

Column diameter: 0.32



Data File: /chem/msd2.i/02jun11.b/2060219.d

Date : 02-JUN-2011 17:45

Client ID:

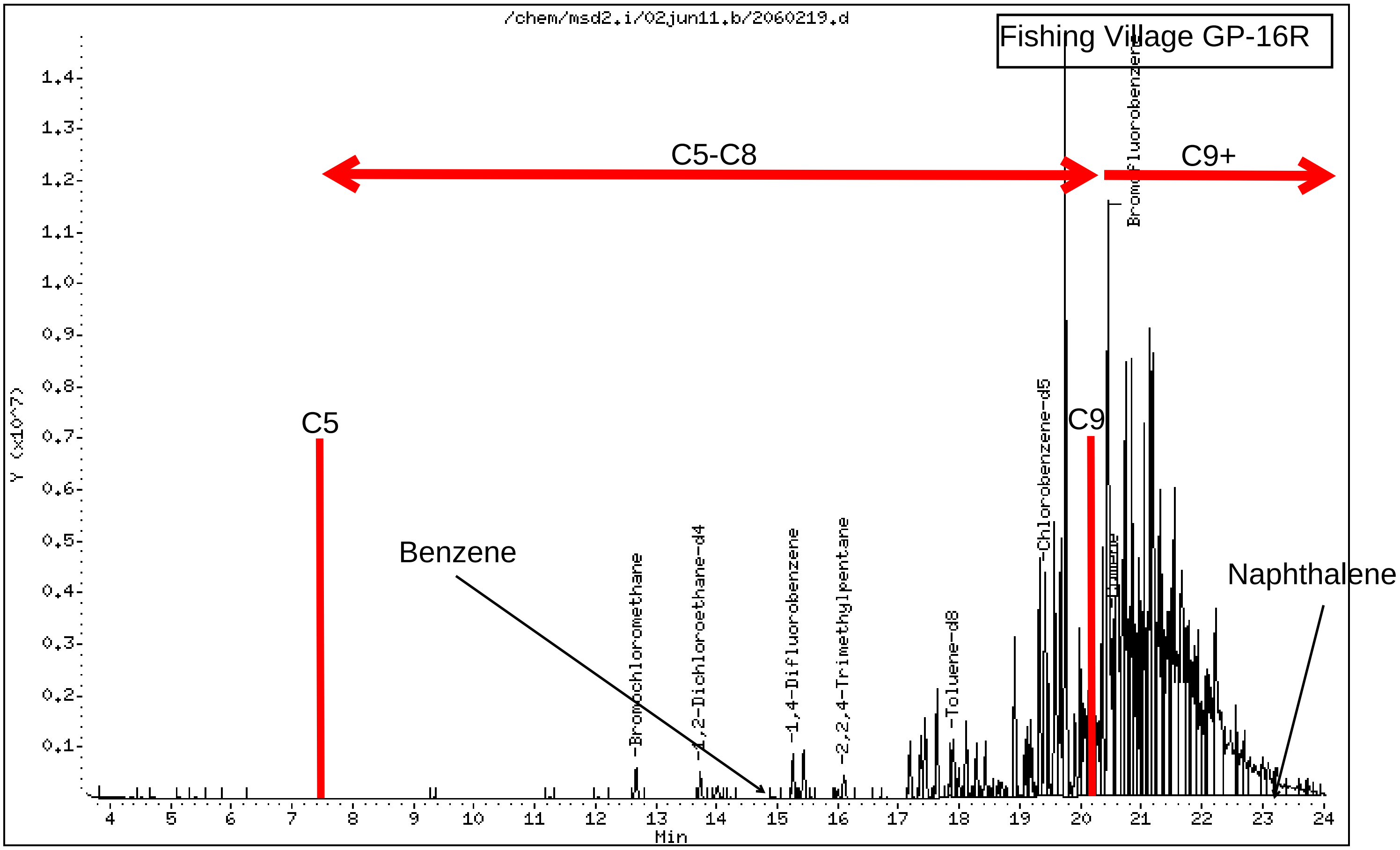
Instrument: msd2.i

Sample Info: 2.0ml #33710

Operator: ea

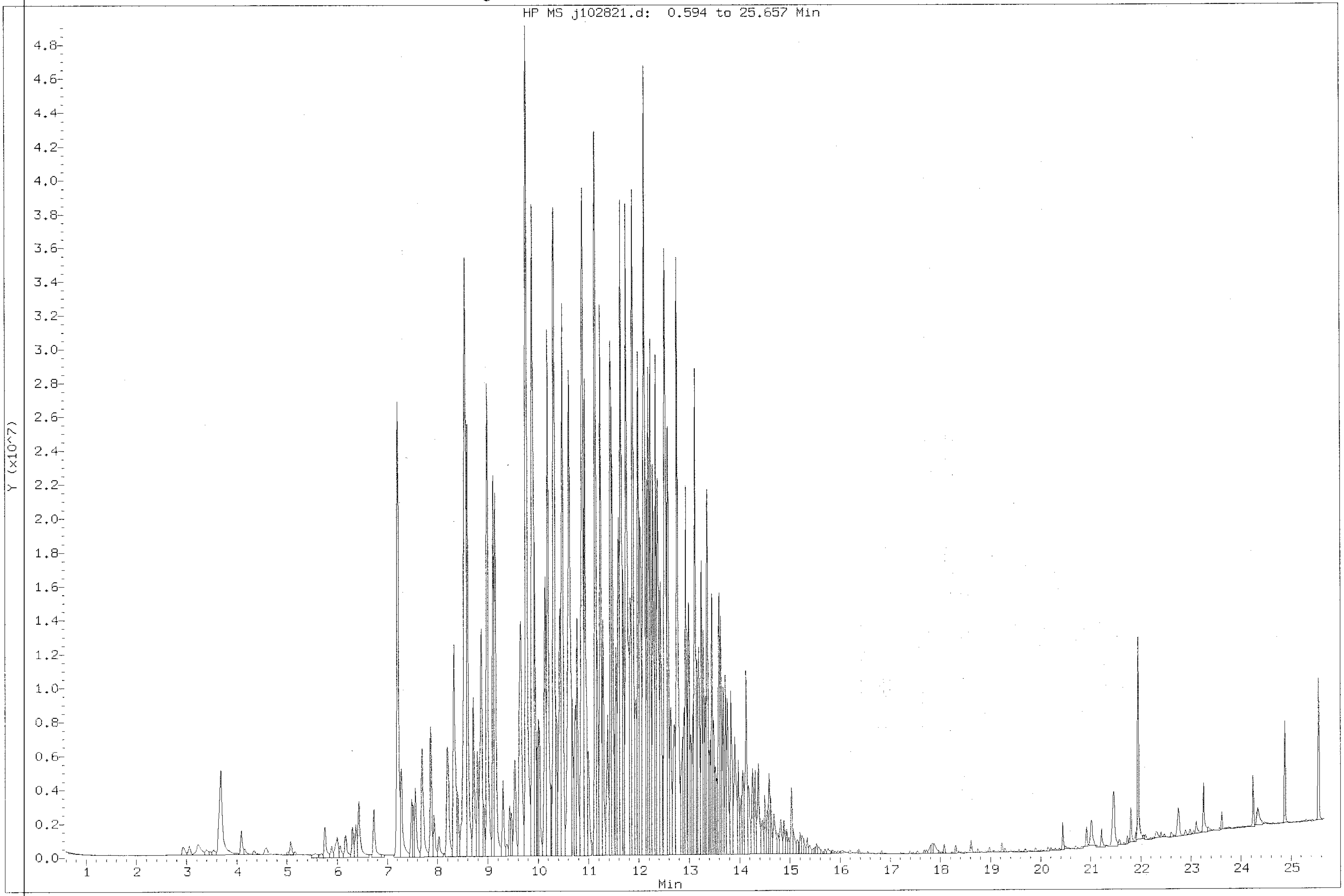
Column phase: RTx-624

Column diameter: 0.32

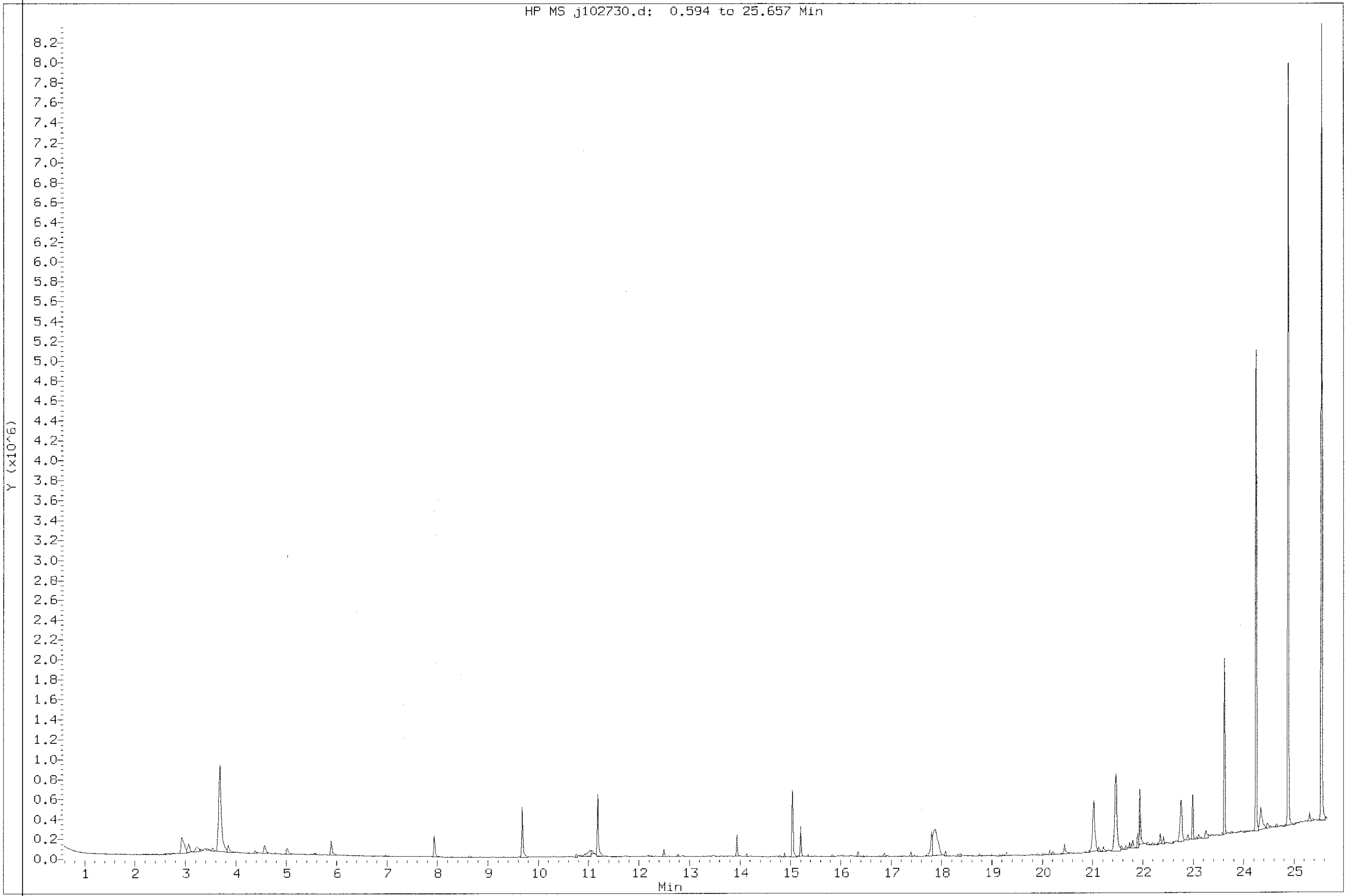


TO-17 Chromatograms for Key Samples (carbon ranges not marked)

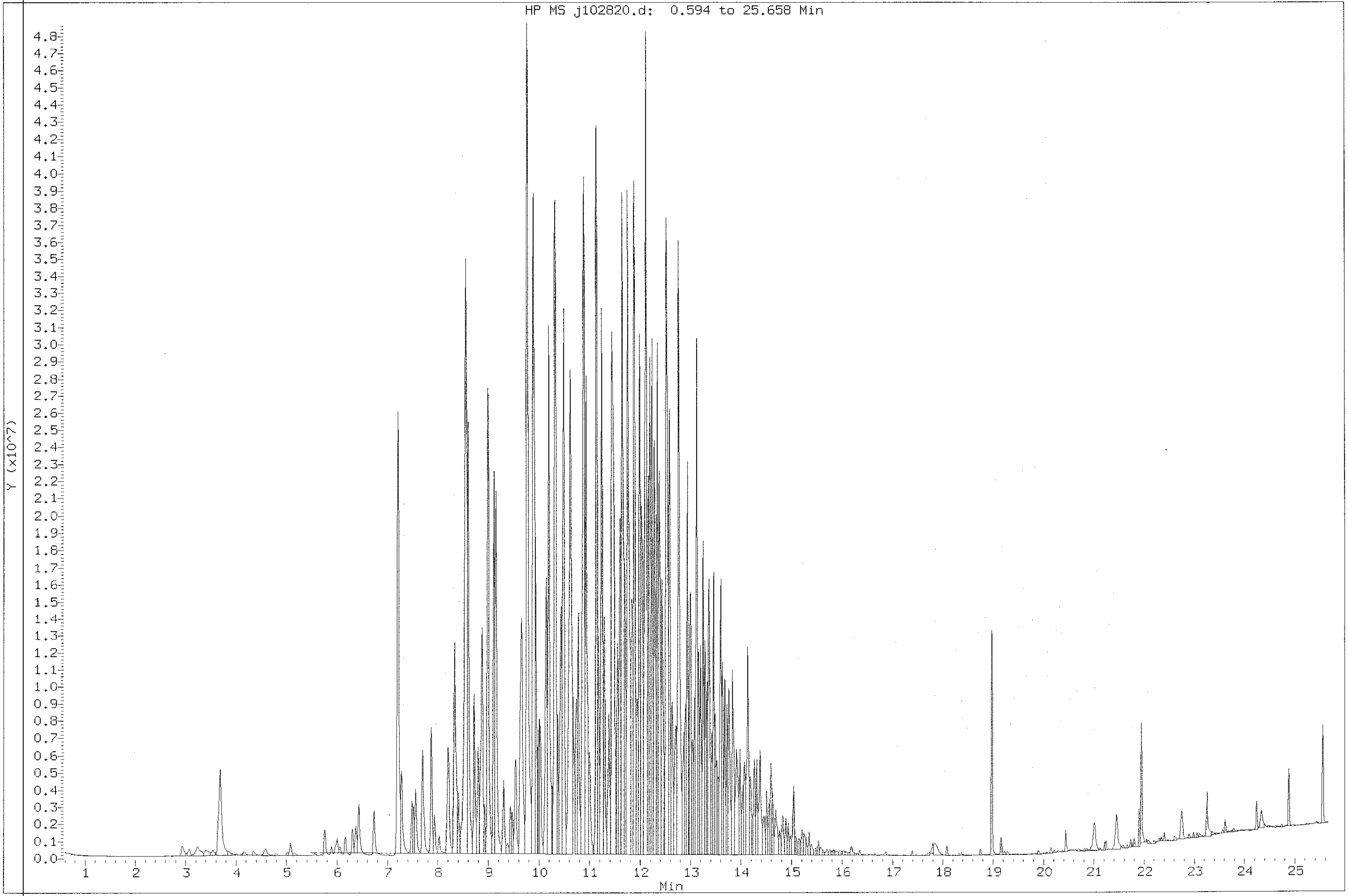
Data File: /chem/msdj.i/28oct11.b/j102821.d
Injection Date: 28-OCT-2011 21:02
Instrument: msdj.i
Client Sample ID: HAFB-ST03-B58(4ZZ)(T017A)



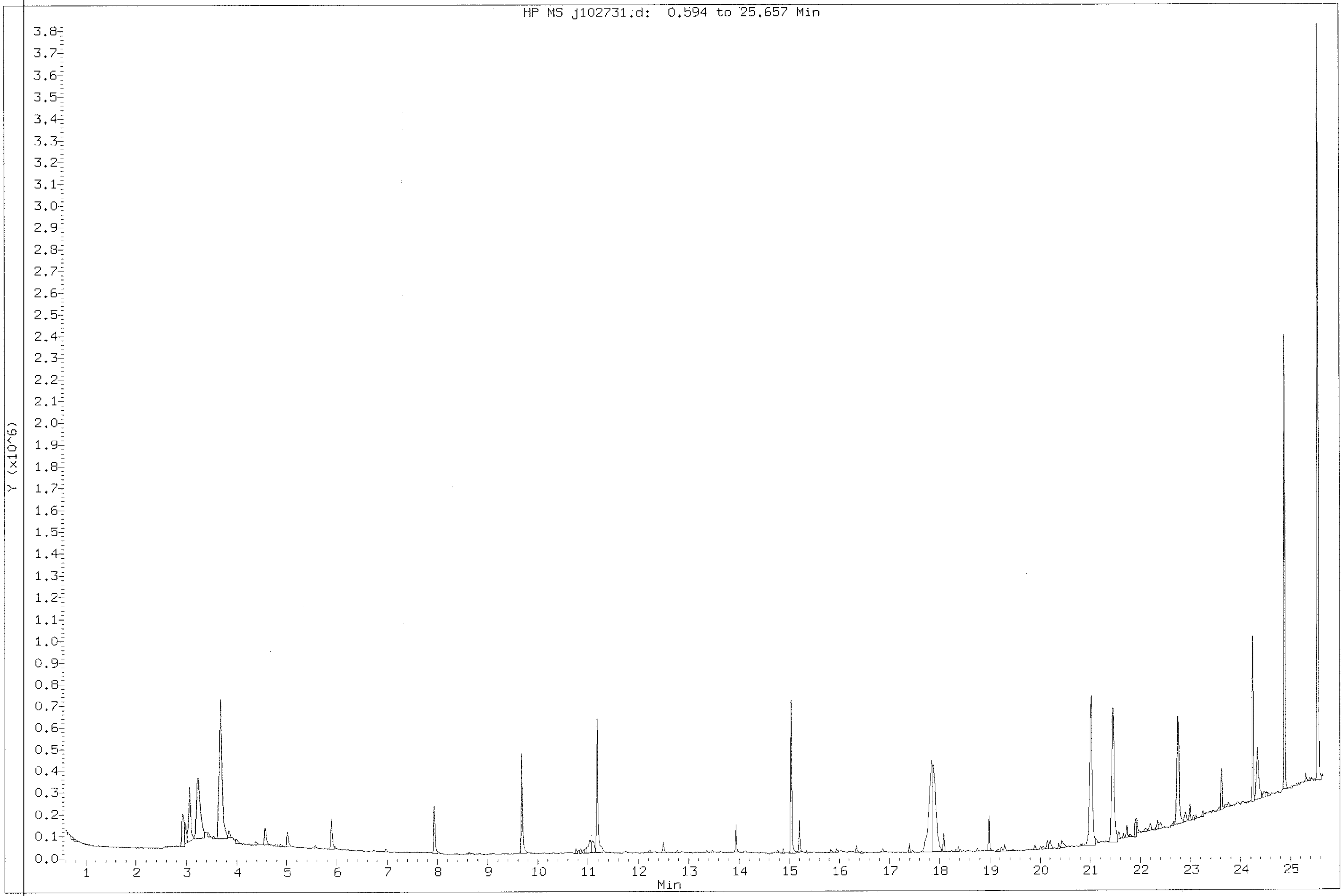
Data File: /chem/msdj.i/27oct11.b/j102730.d
Injection Date: 28-OCT-2011 03:23
Instrument: msdj.i
Client Sample ID: HAFB-ST03-B58 (422)(T017B)



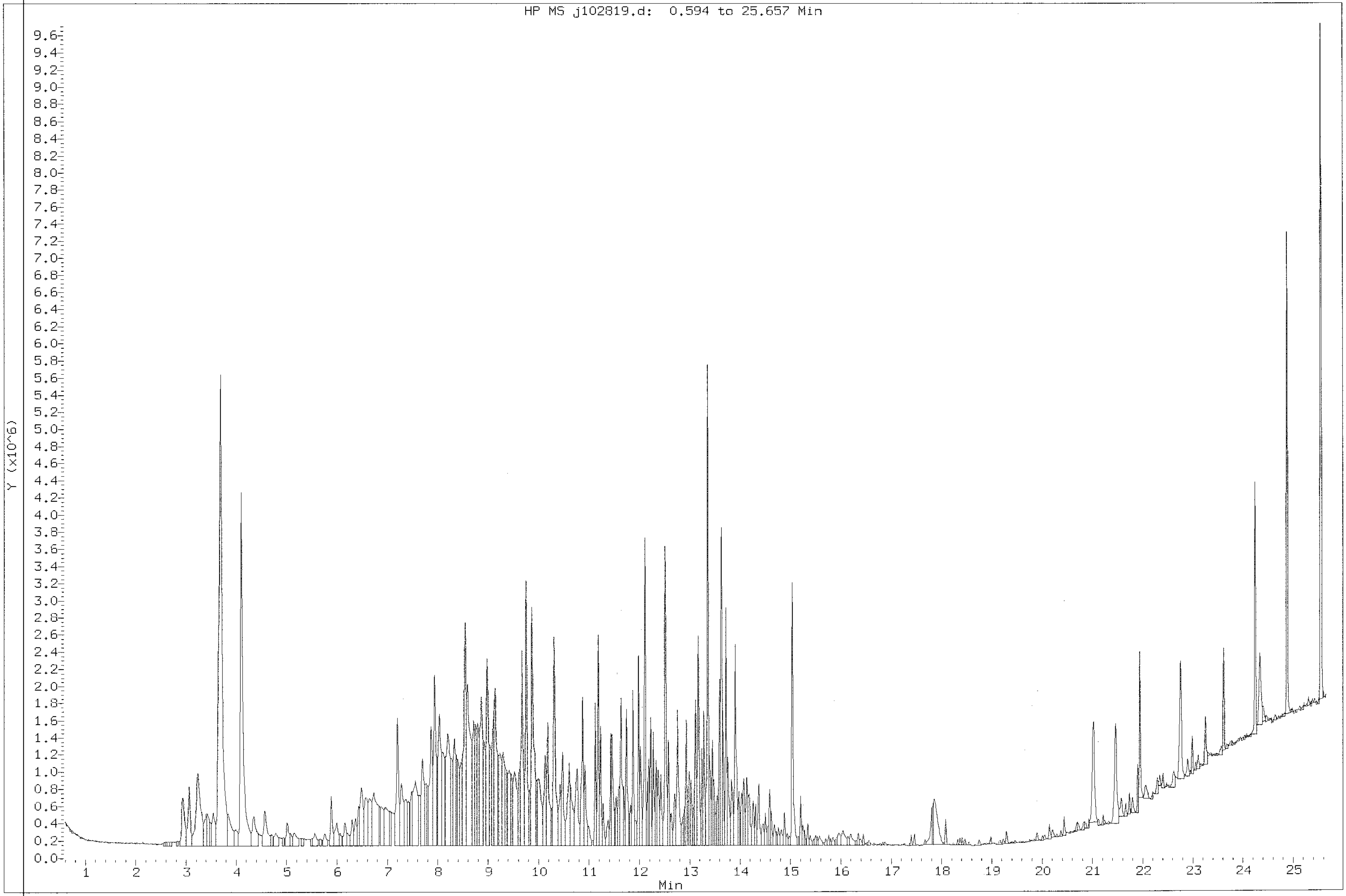
Data File: /chem/msdj.i/28oct11.b/j102820.d
Injection Date: 28-OCT-2011 20:26
Instrument: msdj.i
Client Sample ID: HAFB-ST03-B58 (402) (T017A)


HP MS j102820.d: 0.594 to 25.658 Min

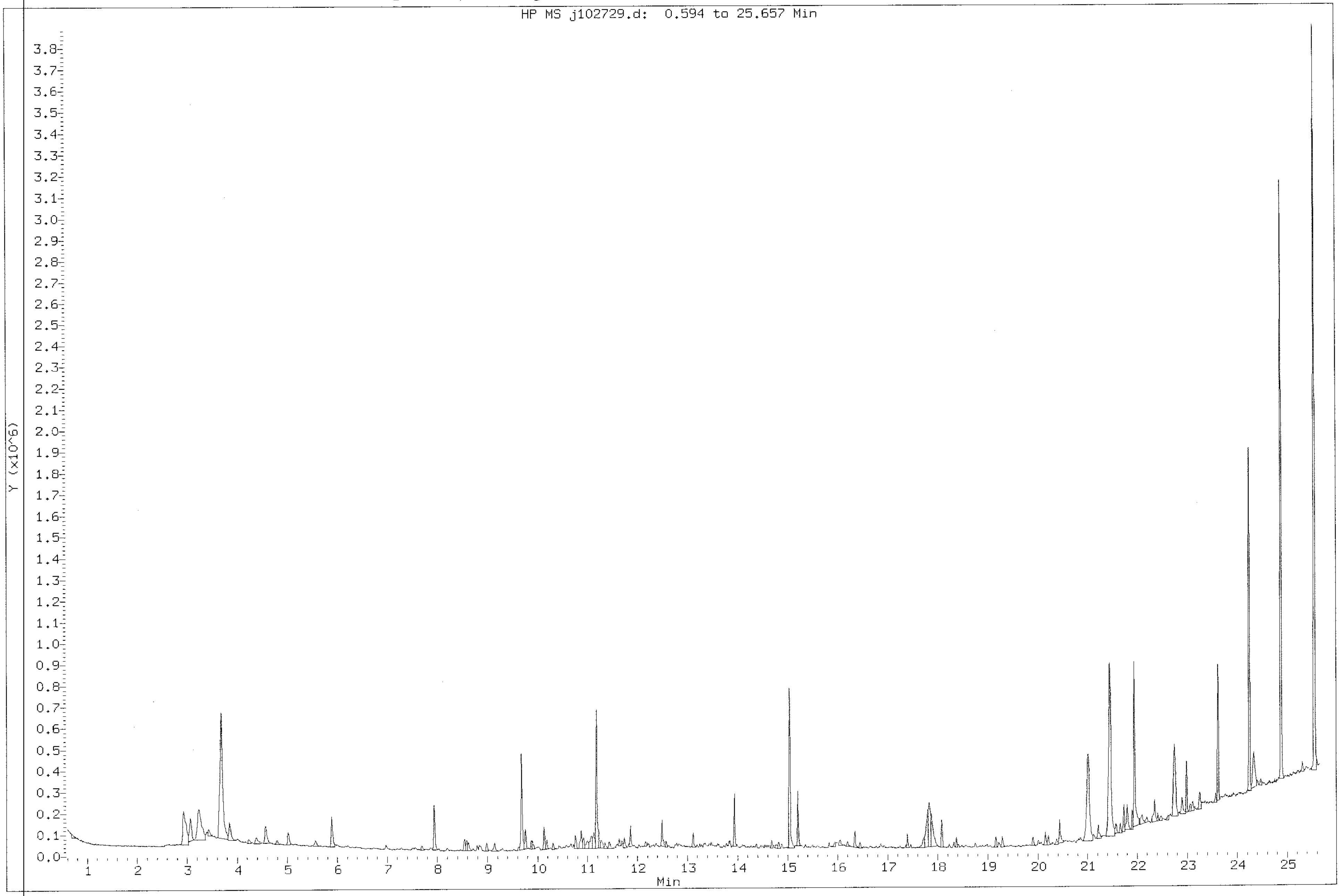
Data File: /chem/msdj.i/27oct11.b/j102731.d
Injection Date: 28-OCT-2011 03:59
Instrument: msdj.i
Client Sample ID: HAFB-ST03-B58 (492) (TO17B)



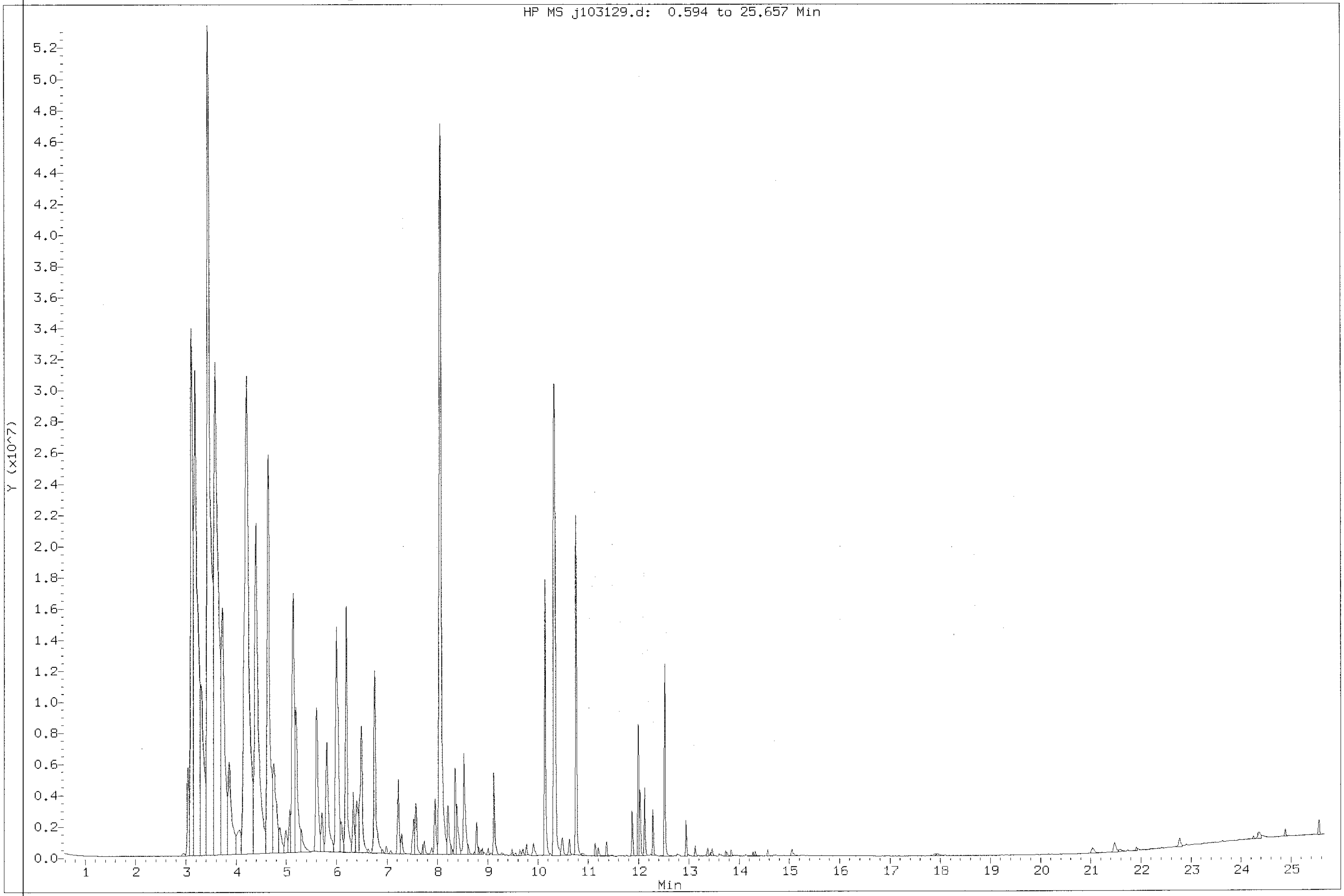
Data File: /chem/msdj.i/28oct11.b/j102819.d
Injection Date: 28-OCT-2011 19:49
Instrument: msdj.i
Client Sample ID: HAFB-ST03-B59(388)(T017A)



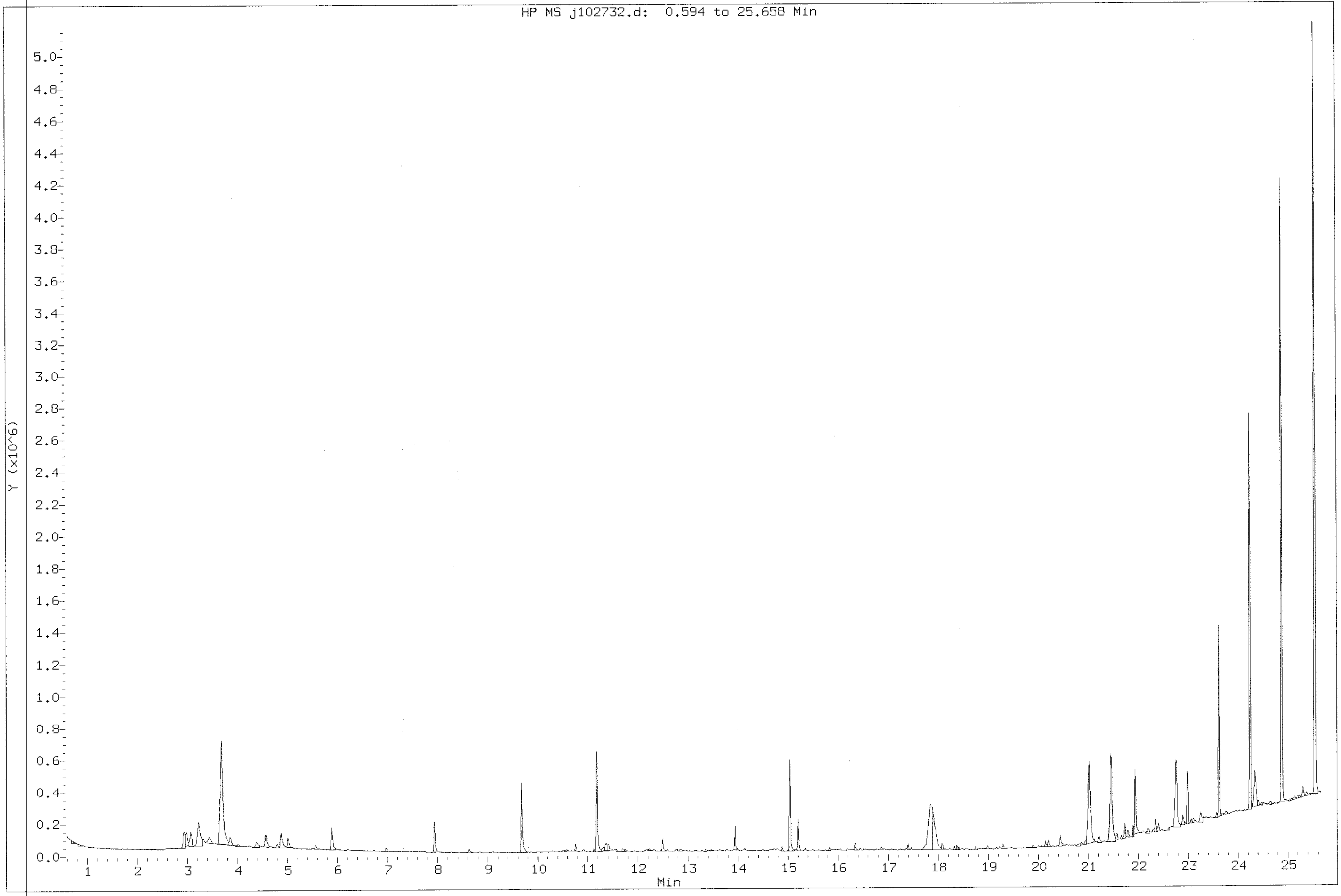
Data File: /chem/msdj.i/27oct11.b/j102729.d
Injection Date: 28-OCT-2011 02:46
Instrument: msdj.i
Client Sample ID: HAFB- ST03 - B59 (B88)(T01 TB)



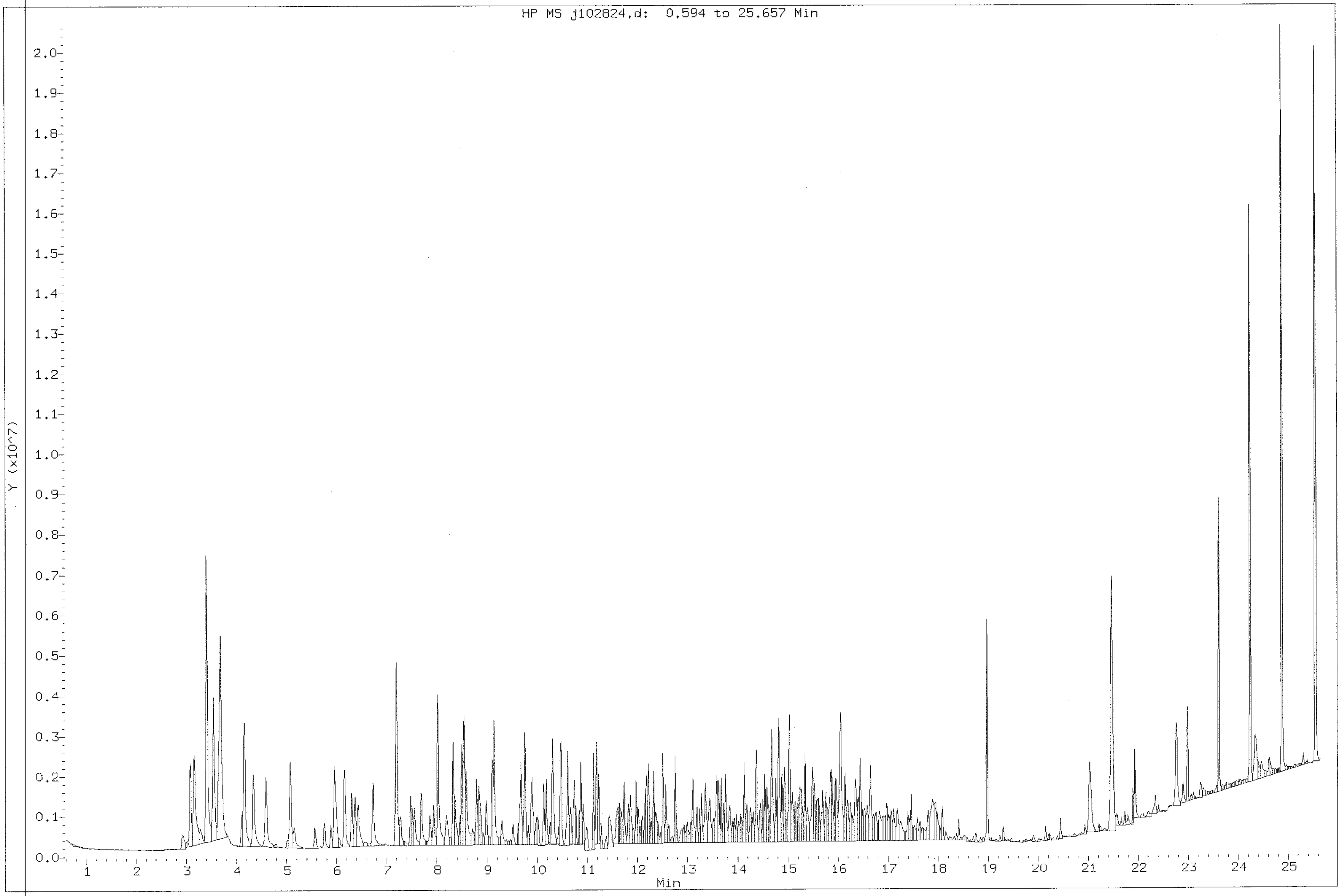
Data File: /chem/msdj.i/31oct11.b/j103129.d
Injection Date: 01-NOV-2011 02:43
Instrument: msdj.i
Client Sample ID: GASOLINE #2 (TD1-7A)



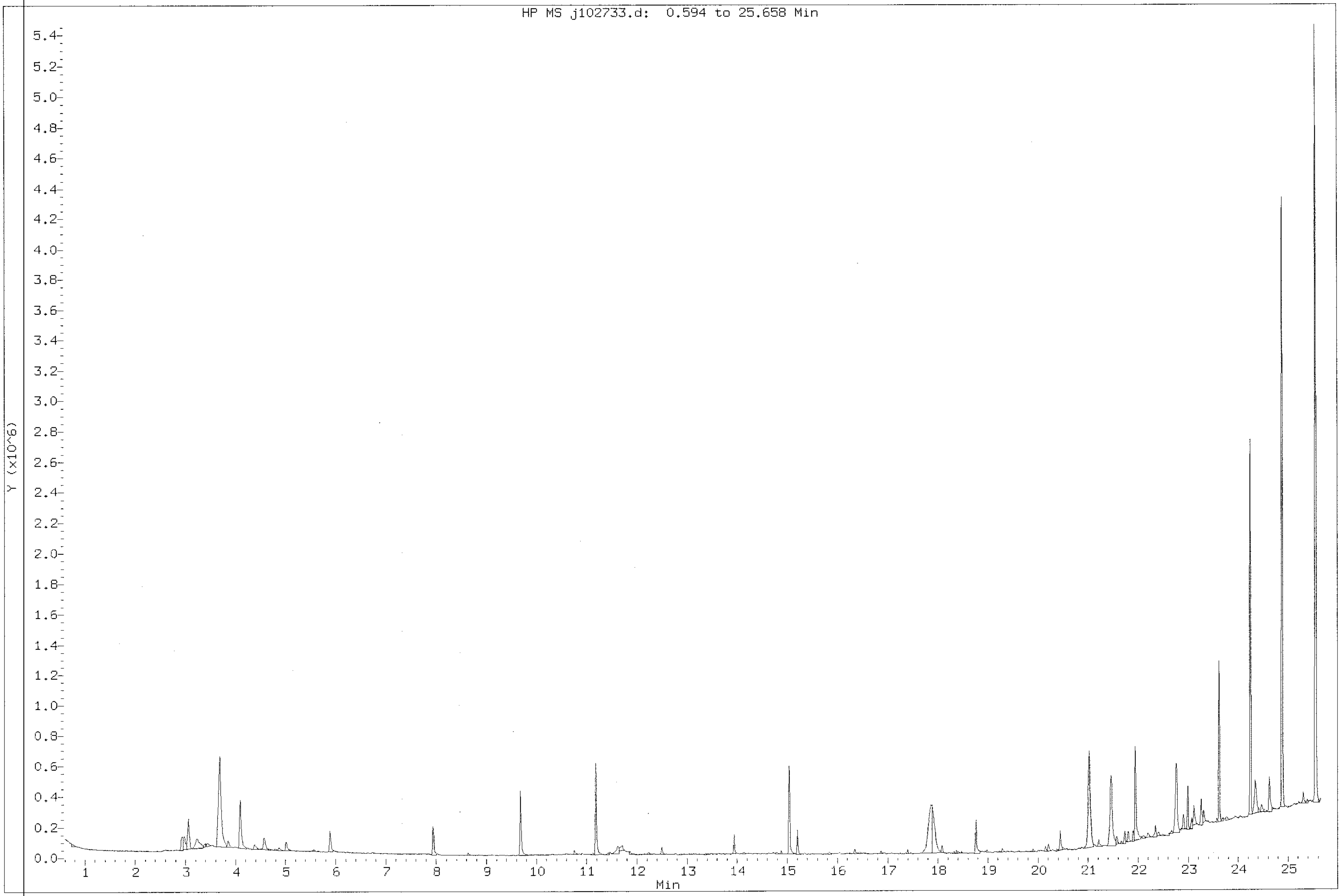
Data File: /chem/msdj.i/27oct11.b/j102732.d
Injection Date: 28-OCT-2011 04:36
Instrument: msdj.i
Client Sample ID: GASOLINE #2 (TD17B)



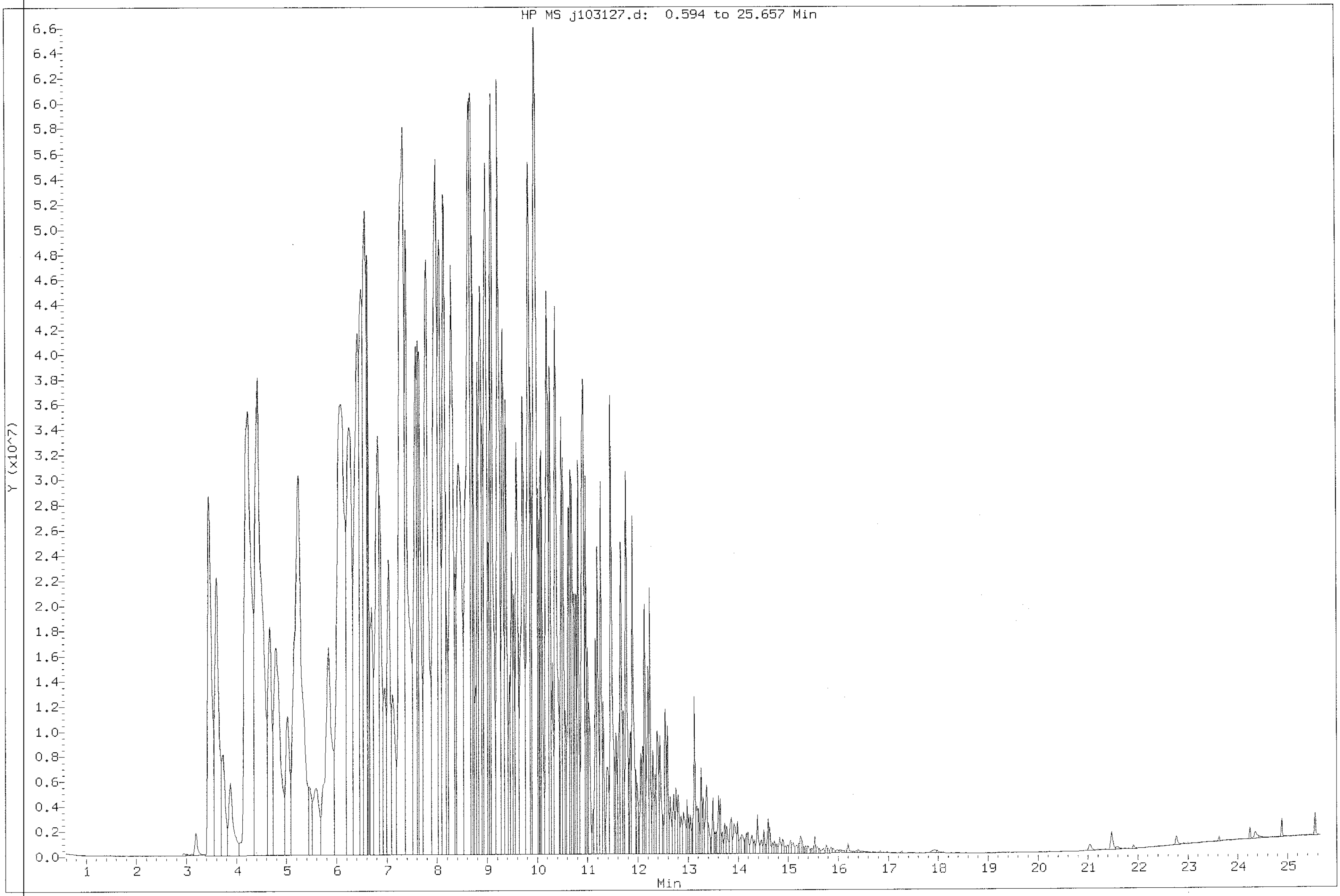
Data File: /chem/msdj.i/28oct11.b/j102824.d
Injection Date: 28-OCT-2011 22:52
Instrument: msdj.i
Client Sample ID: DIESEL #3 (T017A)



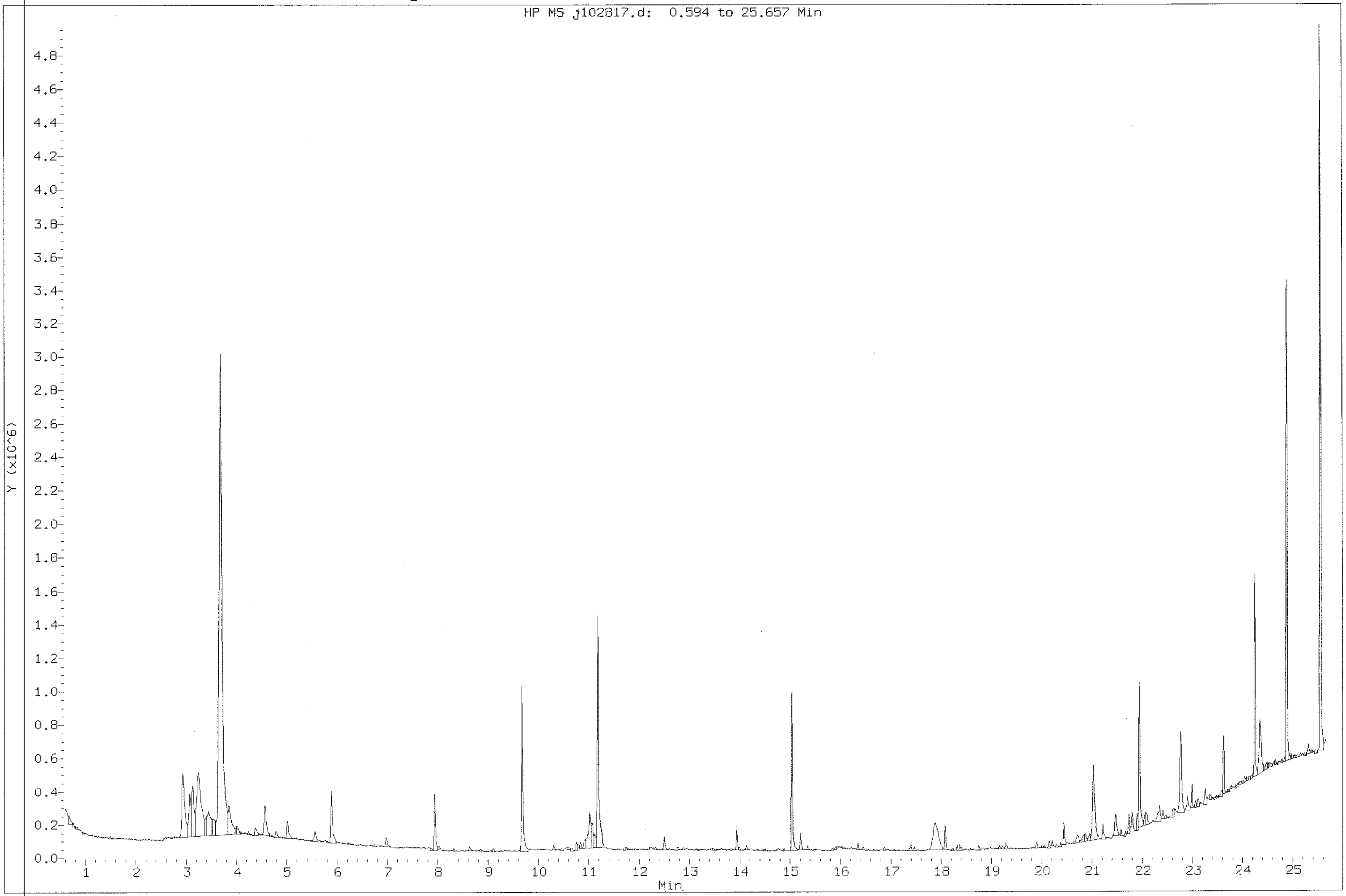
Data File: /chem/msdj.i/27oct11.b/j102733.d
Injection Date: 28-OCT-2011 05:13
Instrument: msdj.i
Client Sample ID: DIESEL#3 (TO17B)


HP MS j102733.d: 0.594 to 25.658 Min

Data File: /chem/msdj.i/31oct11.b/j103127.d
Injection Date: 01-NOV-2011 01:35
Instrument: msdj.i
Client Sample ID: HH - OU1C - MW105G (T01 TA)

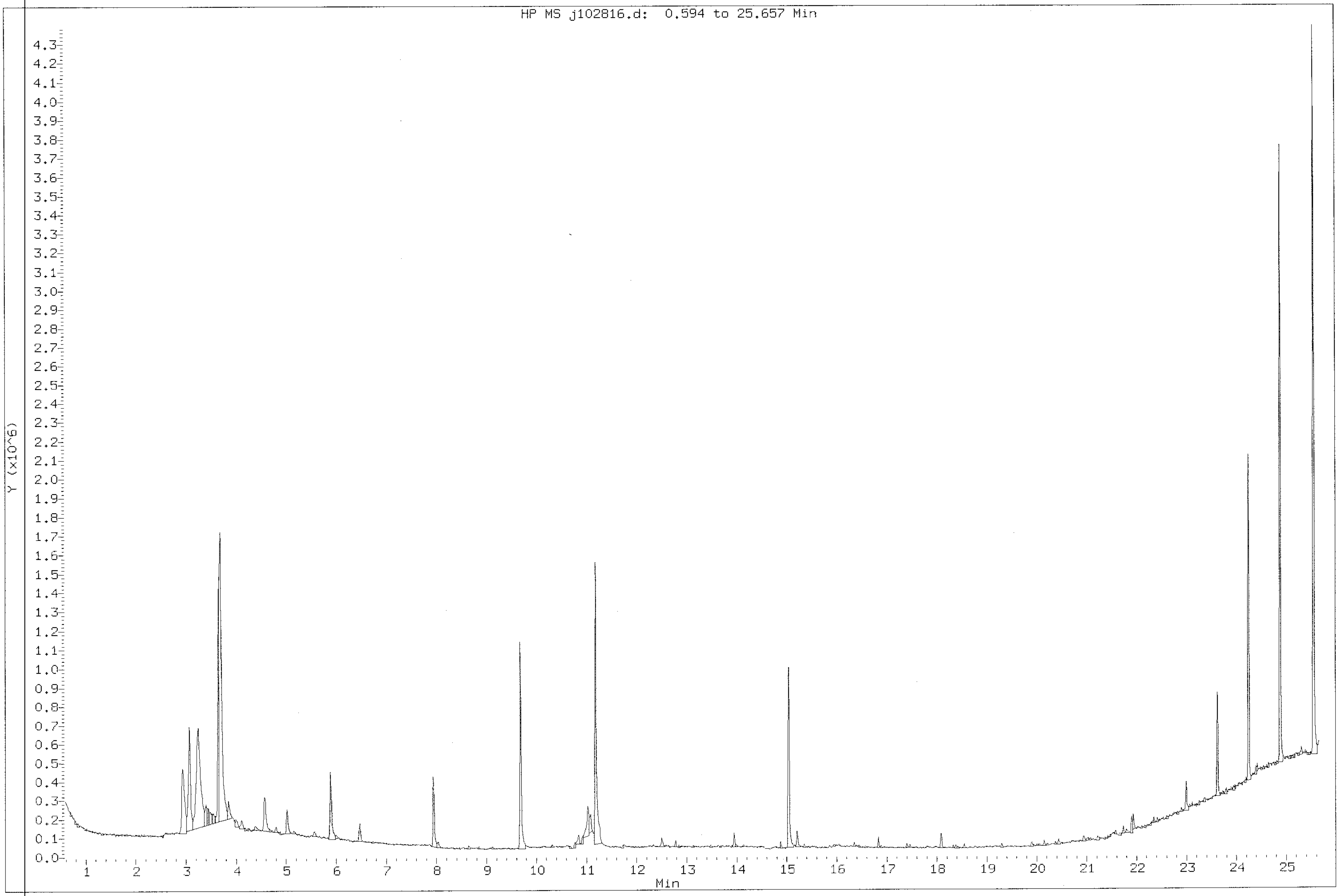


Data File: /chem/msdj.i/28oct11.b/j102817.d
Injection Date: 28-OCT-2011 18:36
Instrument: msdj.i
Client Sample ID: HH-OU1C-MW10SG(T01TB)

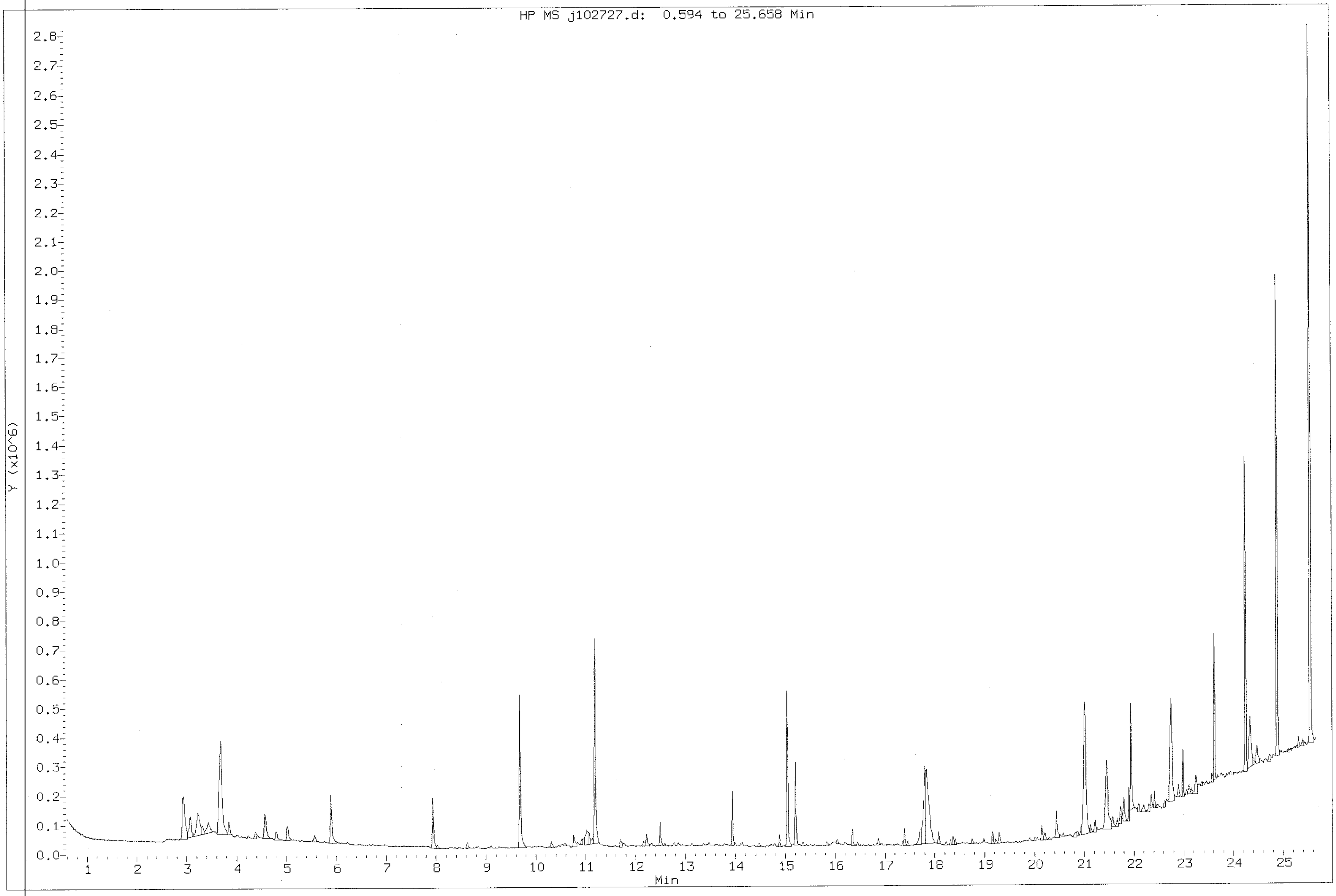


Data File: /chem/msdj.i/28oct11.b/j102816.d
Injection Date: 28-OCT-2011 17:59
Instrument: msdj.i
Client Sample ID: HH-OU1C-OTNS1 (TO17A)

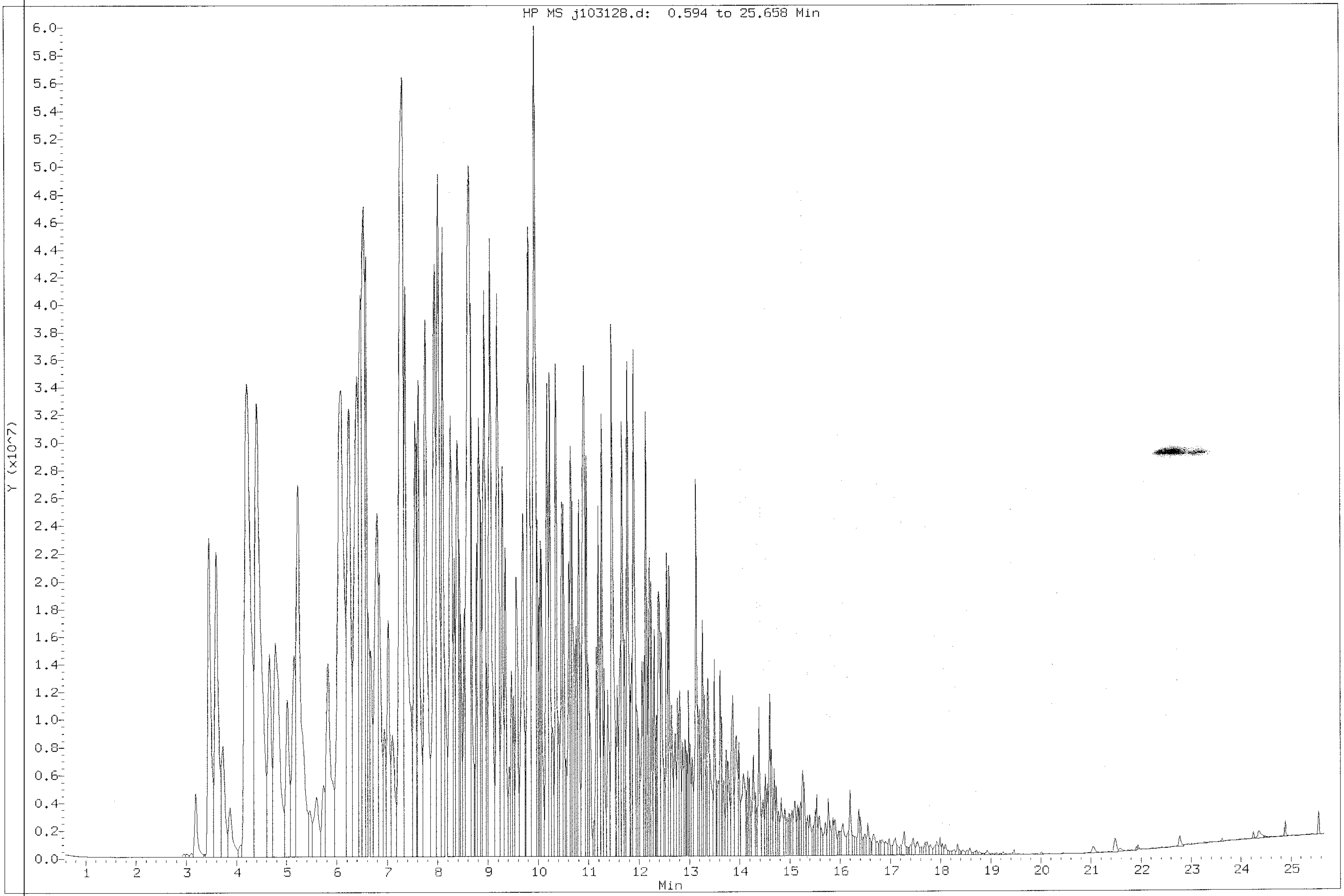
HP MS j102816.d: 0.594 to 25.657 Min



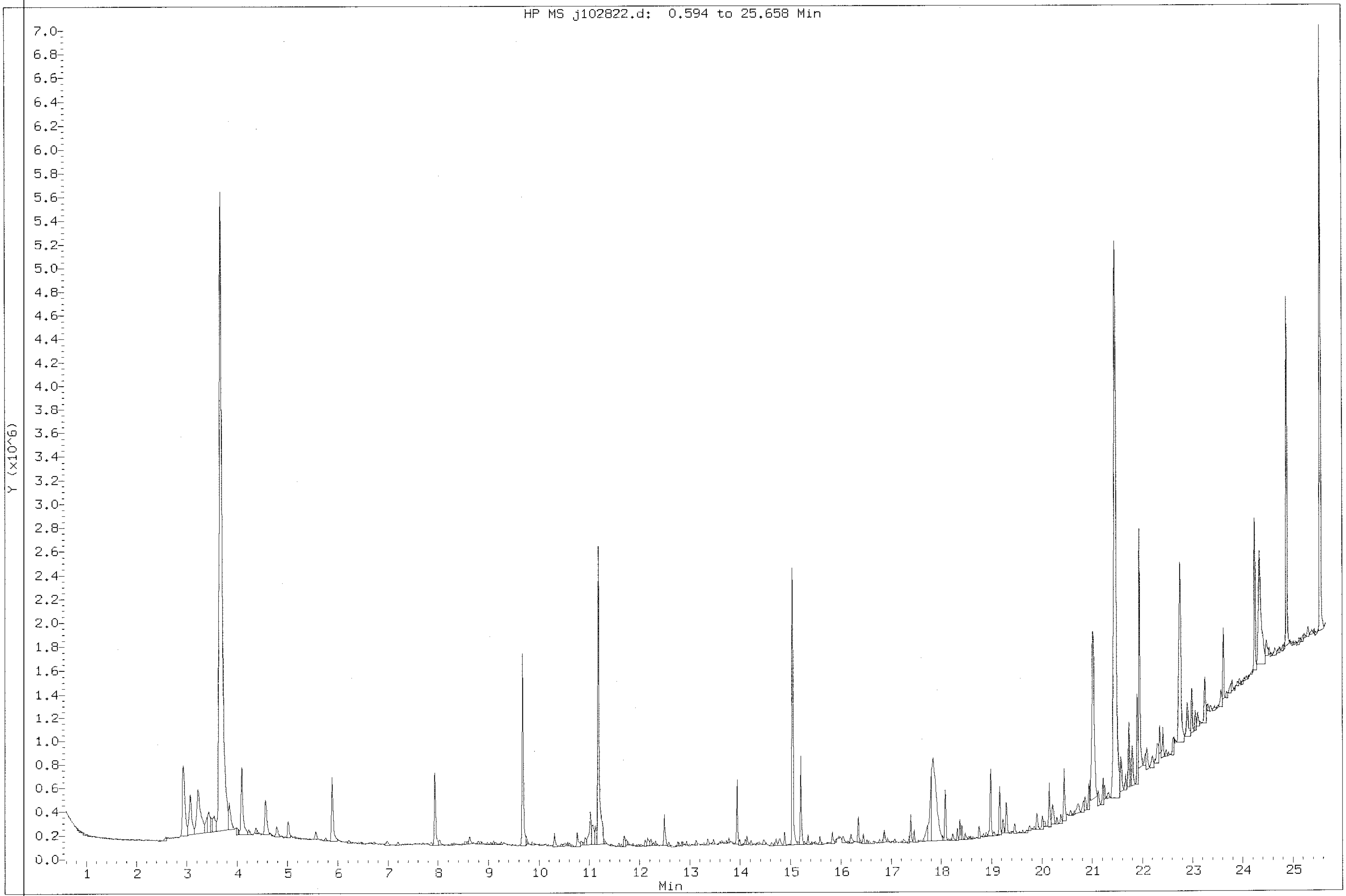
Data File: /chem/msdj.i/27oct11.b/j102727.d
Injection Date: 28-OCT-2011 01:32
Instrument: msdj.i
Client Sample ID: HH-OU1C-OTNS1 (TD17B)



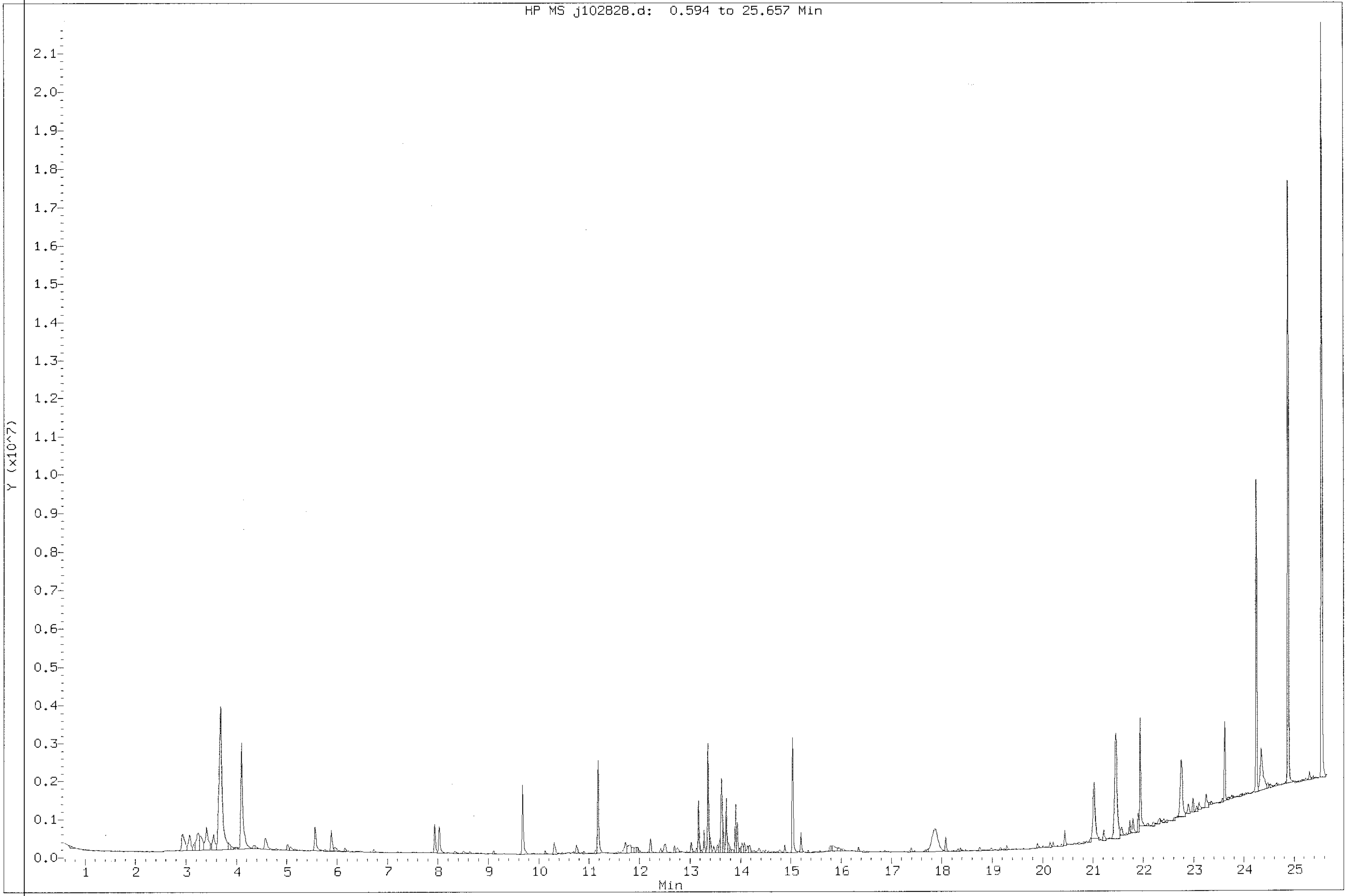
Data File: /chem/msdj.i/31oct11.b/j103128.d
Injection Date: 01-NOV-2011 02:09
Instrument: msdj.i
Client Sample ID: HH-OU1C-MW22R (TD17A)



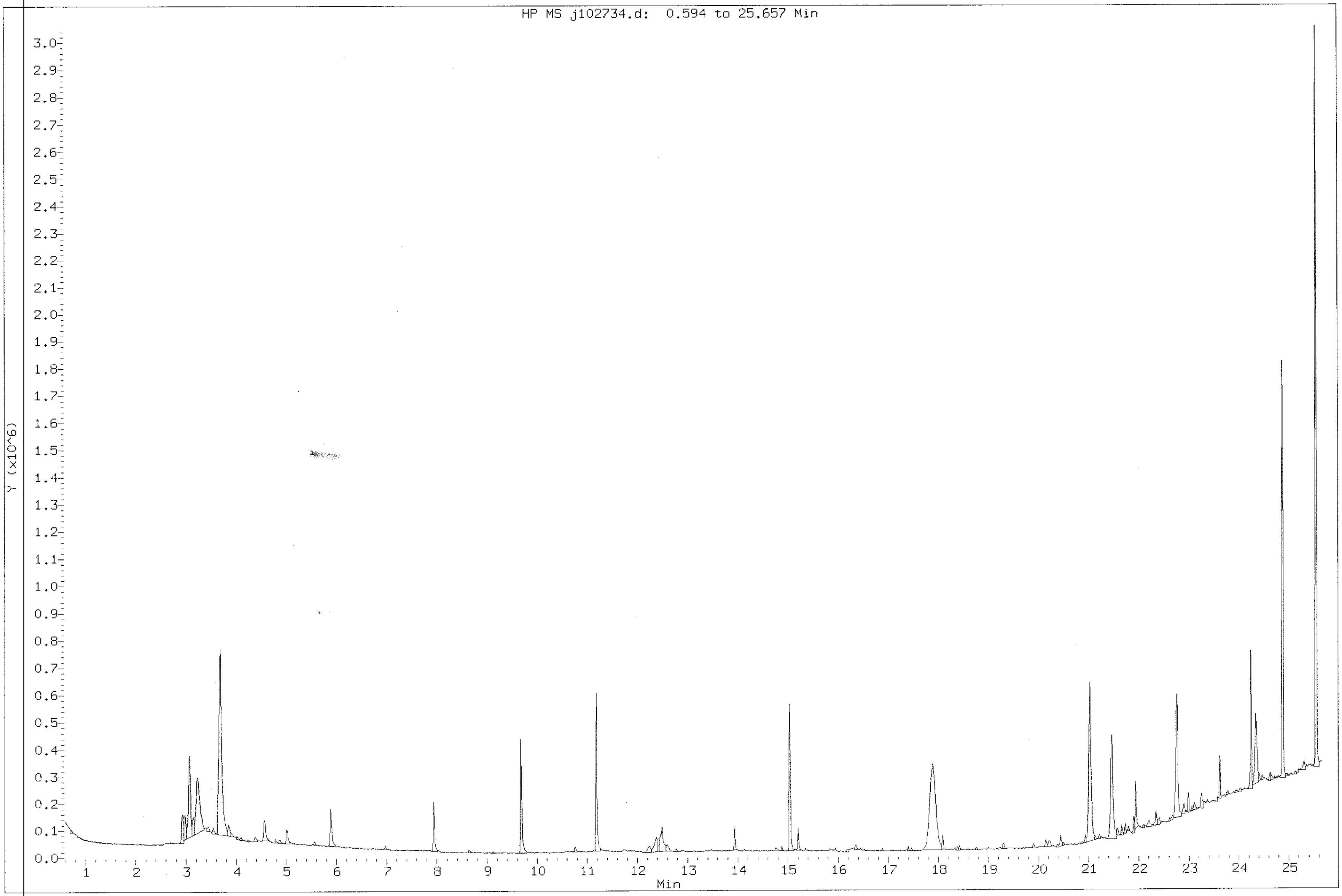
Data File: /chem/msdj.i/28oct11.b/j102822.d
Injection Date: 28-OCT-2011 21:39
Instrument: msdj.i
Client Sample ID: HH-OU1C-MW22R (TO17B)



Data File: /chem/msdj.i/28oct11.b/j102828.d
Injection Date: 29-OCT-2011 01:18
Instrument: msdj.i
Client Sample ID: GASOLINE-EXHAUST (TO17A)

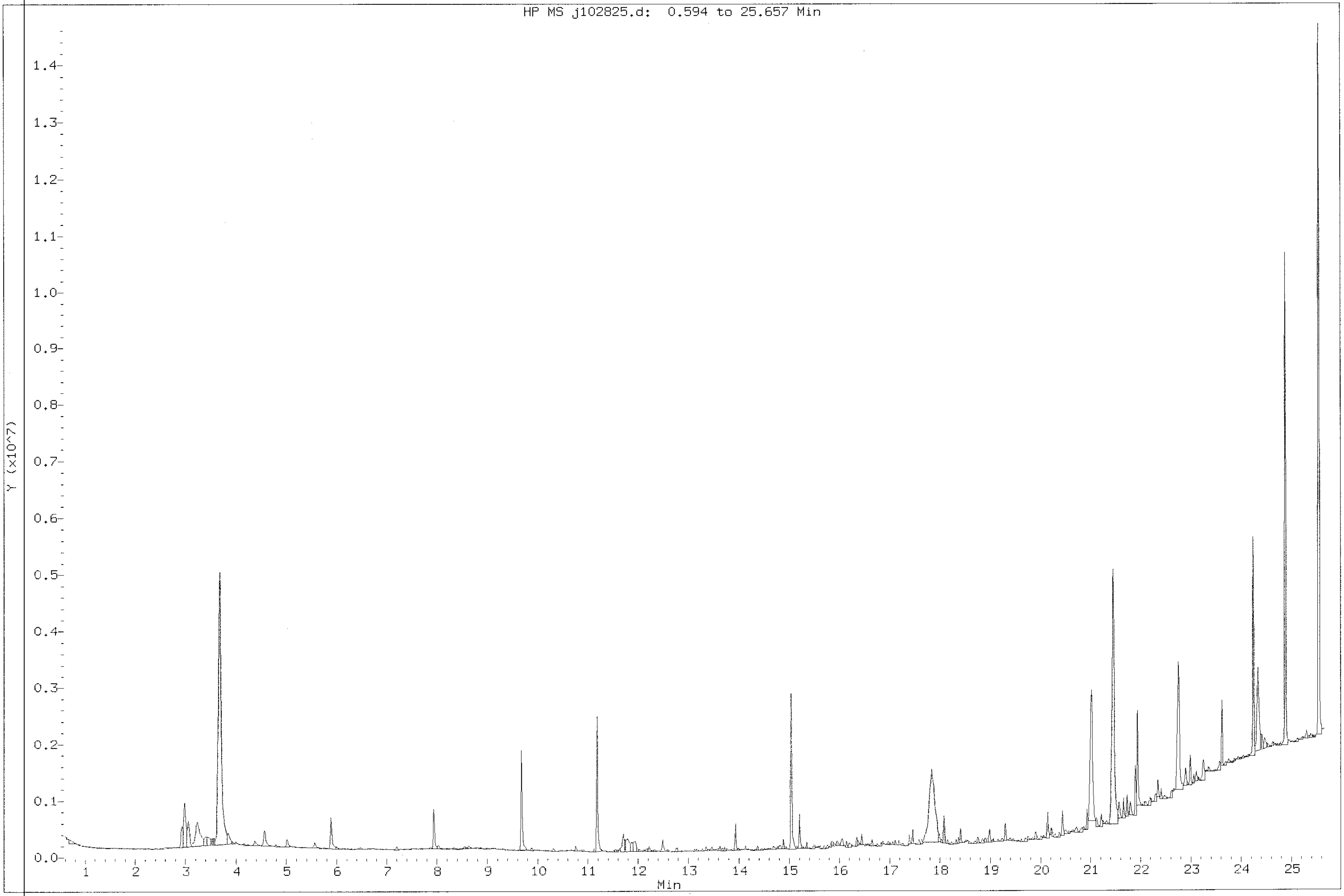


Data File: /chem/msdj.i/27oct11.b/j102734.d
Injection Date: 28-OCT-2011 05:50
Instrument: msdj.i
Client Sample ID: GASOLINE-EXHAUST (TO17B)

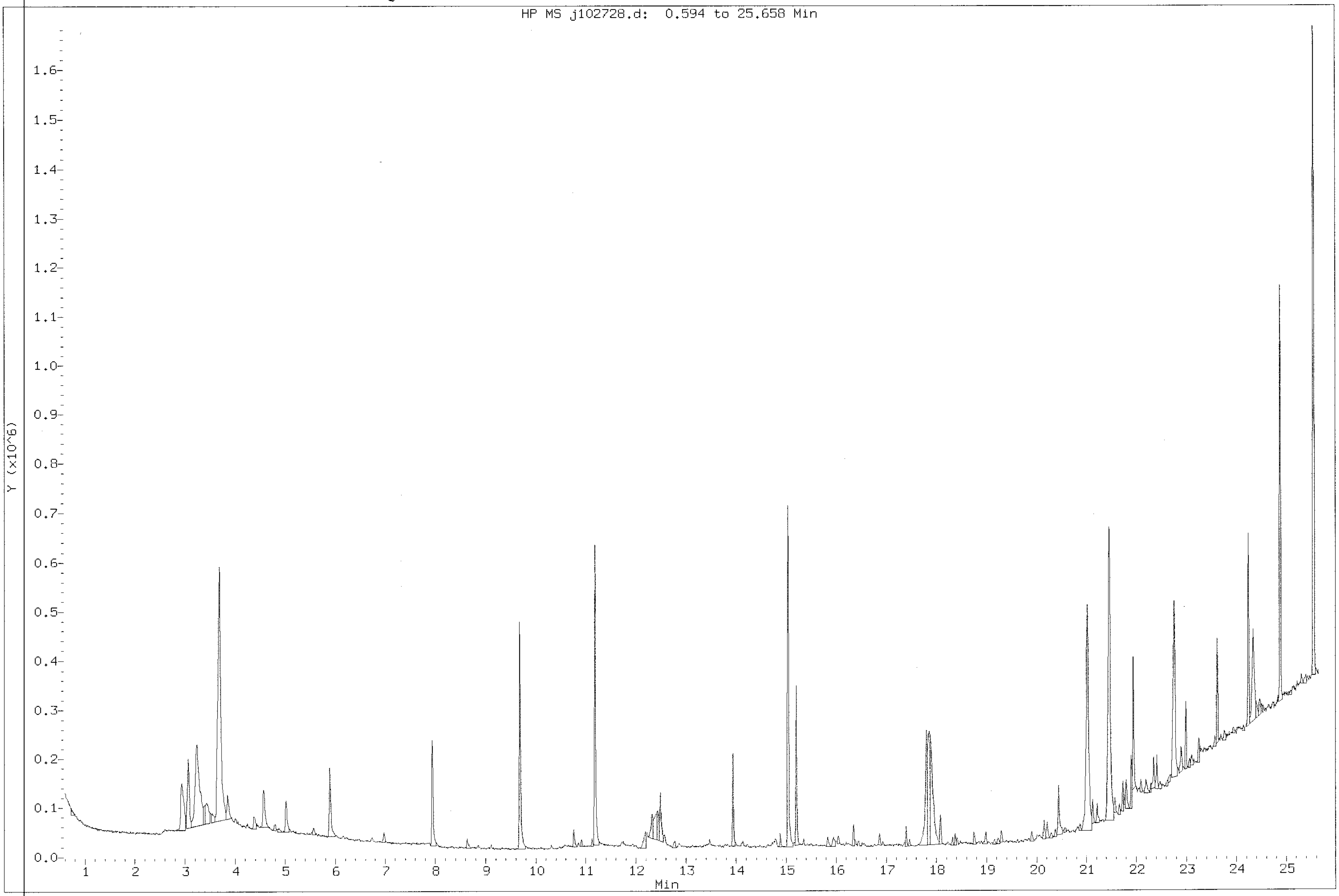


Data File: /chem/msdj.i/28oct11.b/j102825.d
Injection Date: 28-OCT-2011 23:29
Instrument: msdj.i
Client Sample ID: DIESEL- EXHAUST (TO17A)

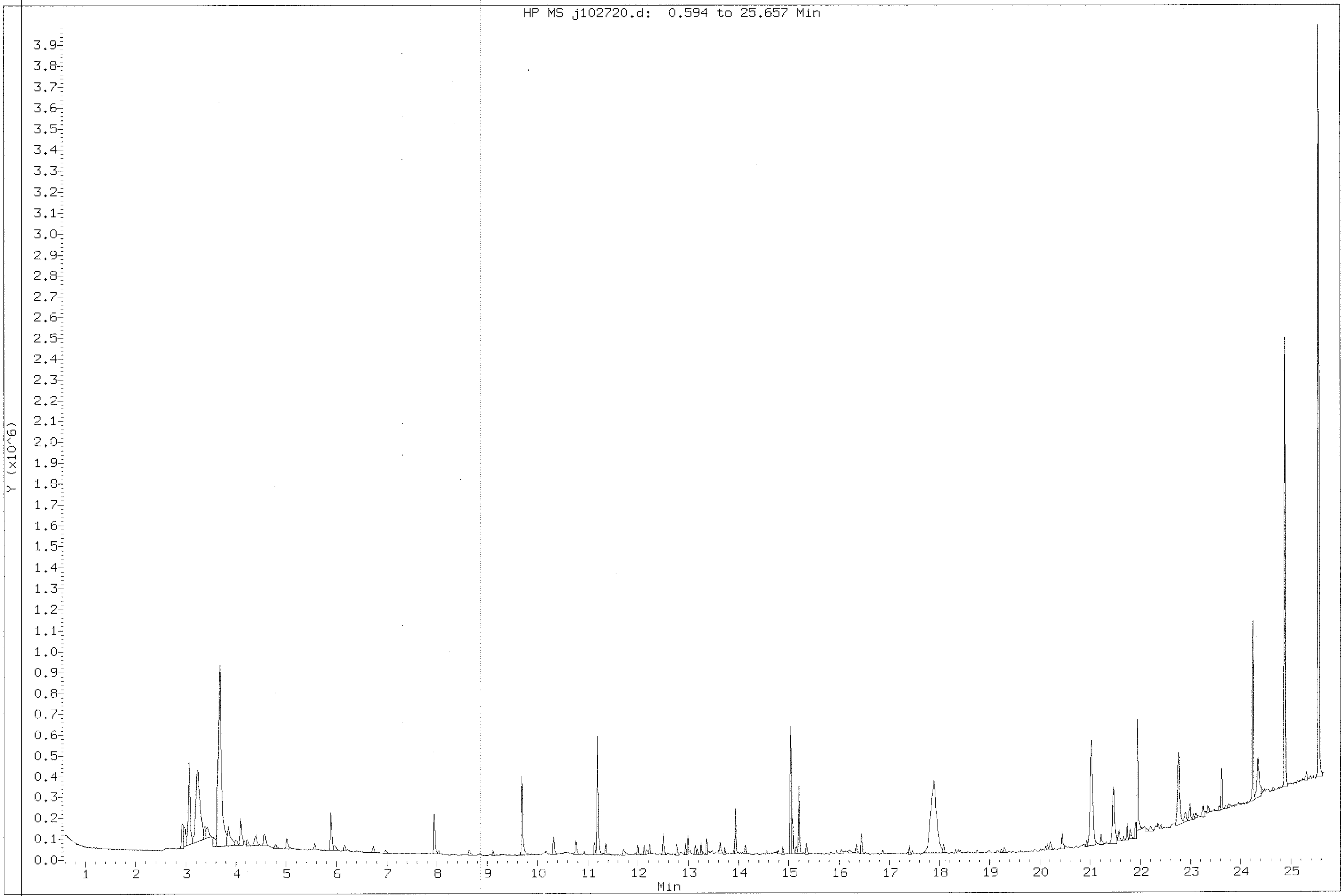
HP MS j102825.d: 0.594 to 25.657 Min



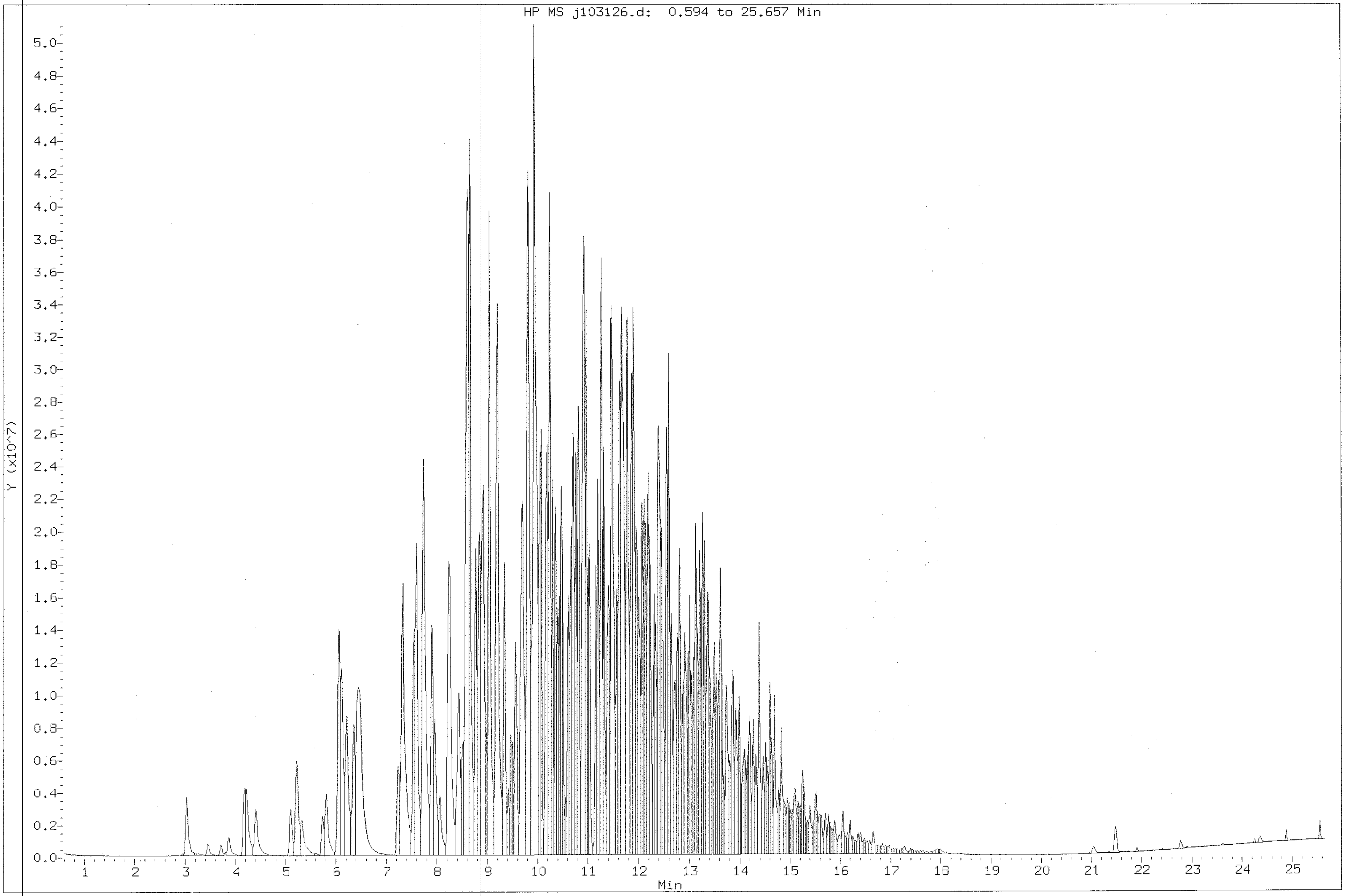
Data File: /chem/msdj.i/27oct11.b/j102728.d
Injection Date: 28-OCT-2011 02:08
Instrument: msdj.i
Client Sample ID: DIESEL-EXHAUST (TO17B)



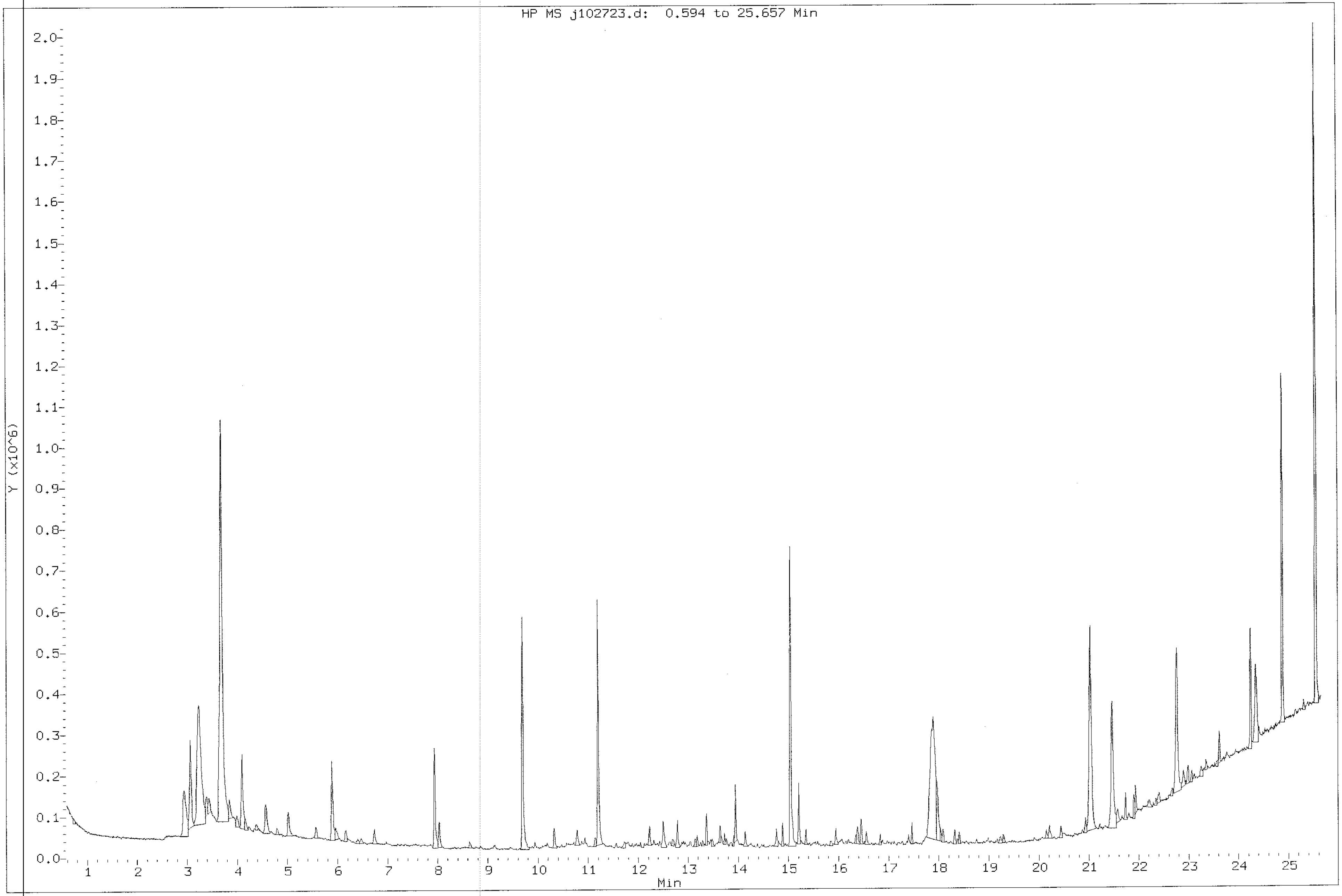
Data File: /chem/msdj.i/27oct11.b/j102720.d
Injection Date: 27-OCT-2011 21:19
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP10 (TO MB)



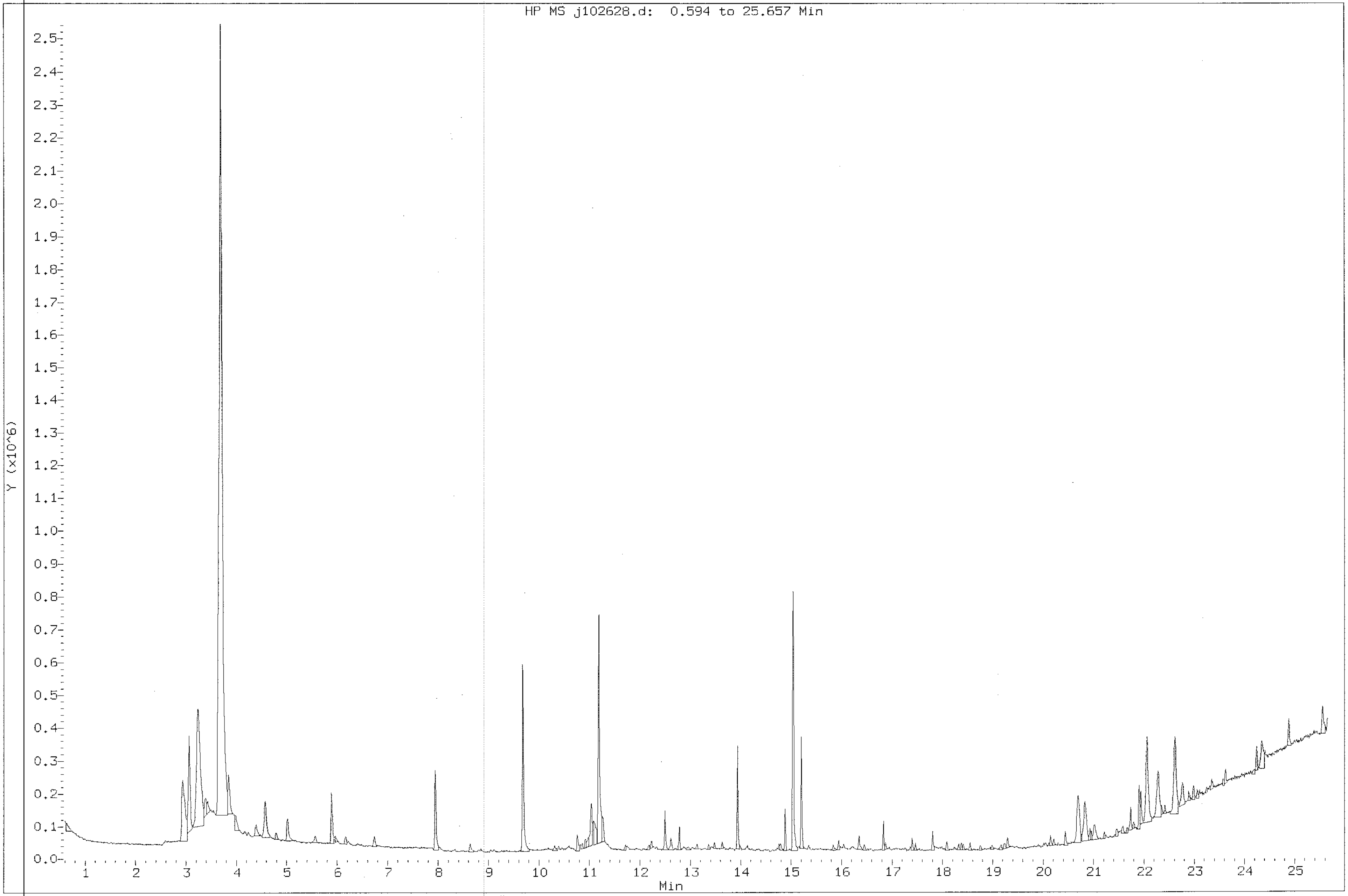
Data File: /chem/msdj.i/31oct11.b/j103126.d
Injection Date: 01-NOV-2011 01:01
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP11 (T01-TA)



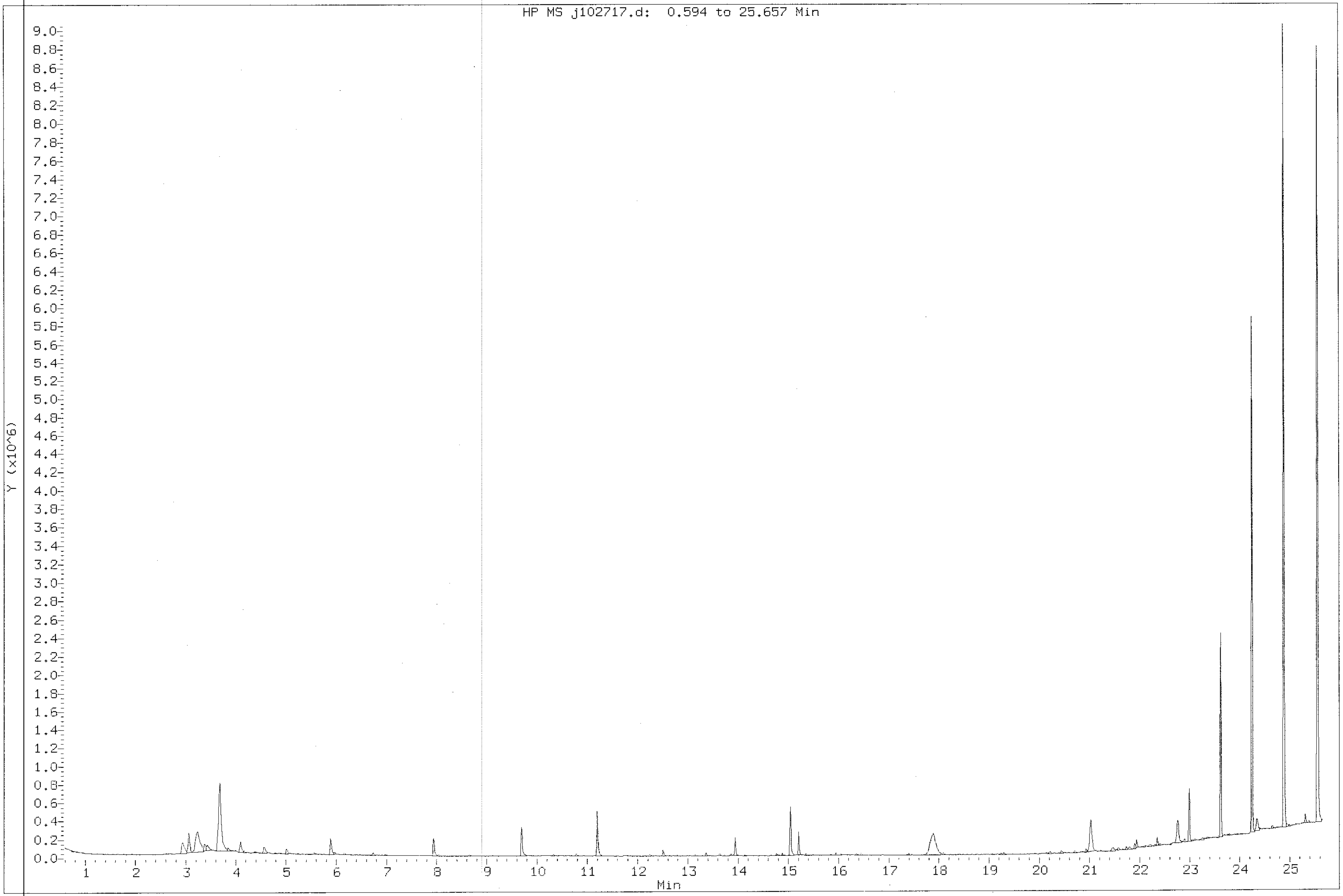
Data File: /chem/msdj.i/27oct11.b/j102723.d
Injection Date: 27-OCT-2011 23:07
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP11 (T017B)



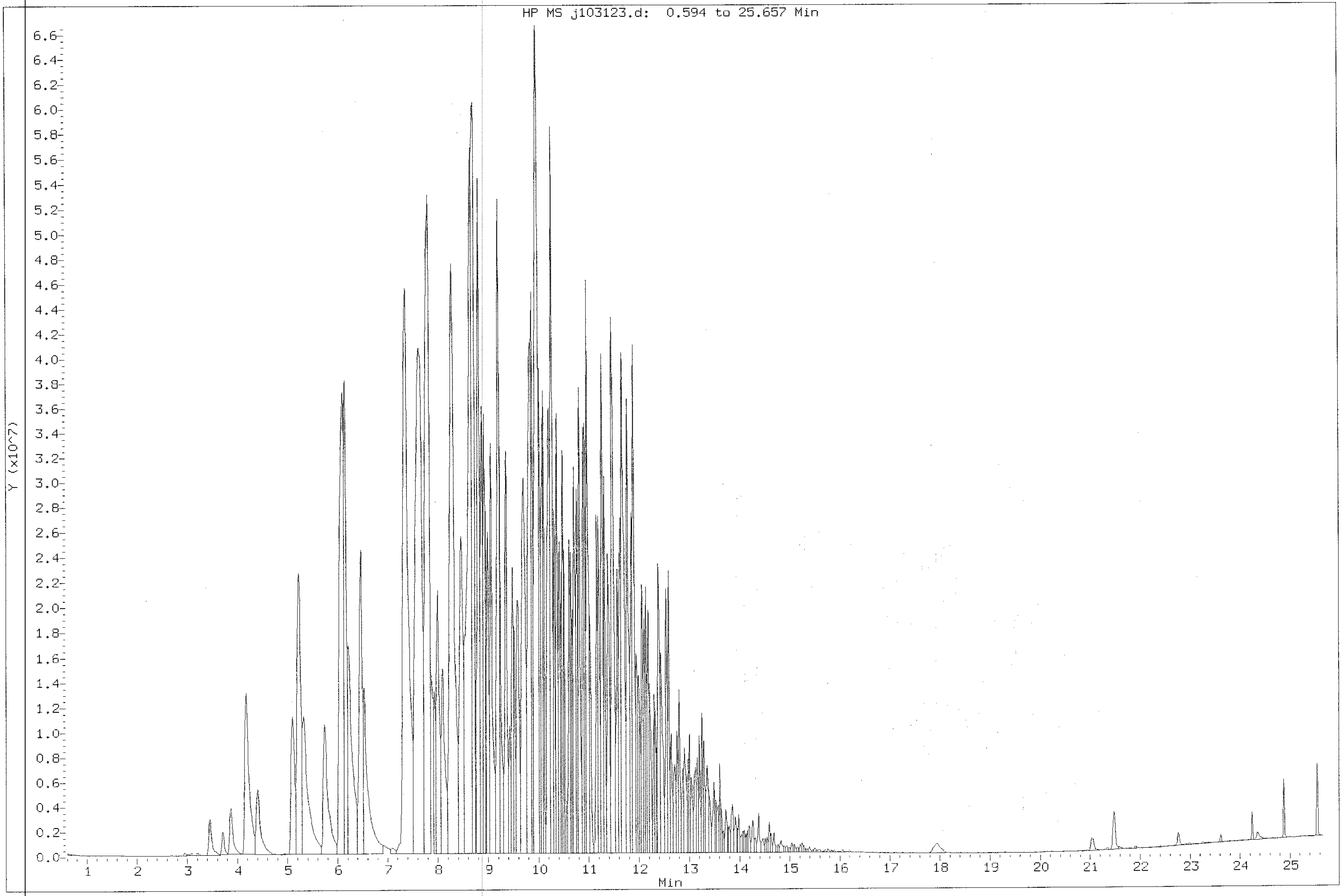
Data File: /chem/msdj.i/26oct11.b/j102628.d
Injection Date: 27-OCT-2011 02:53
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP12 (T017A)



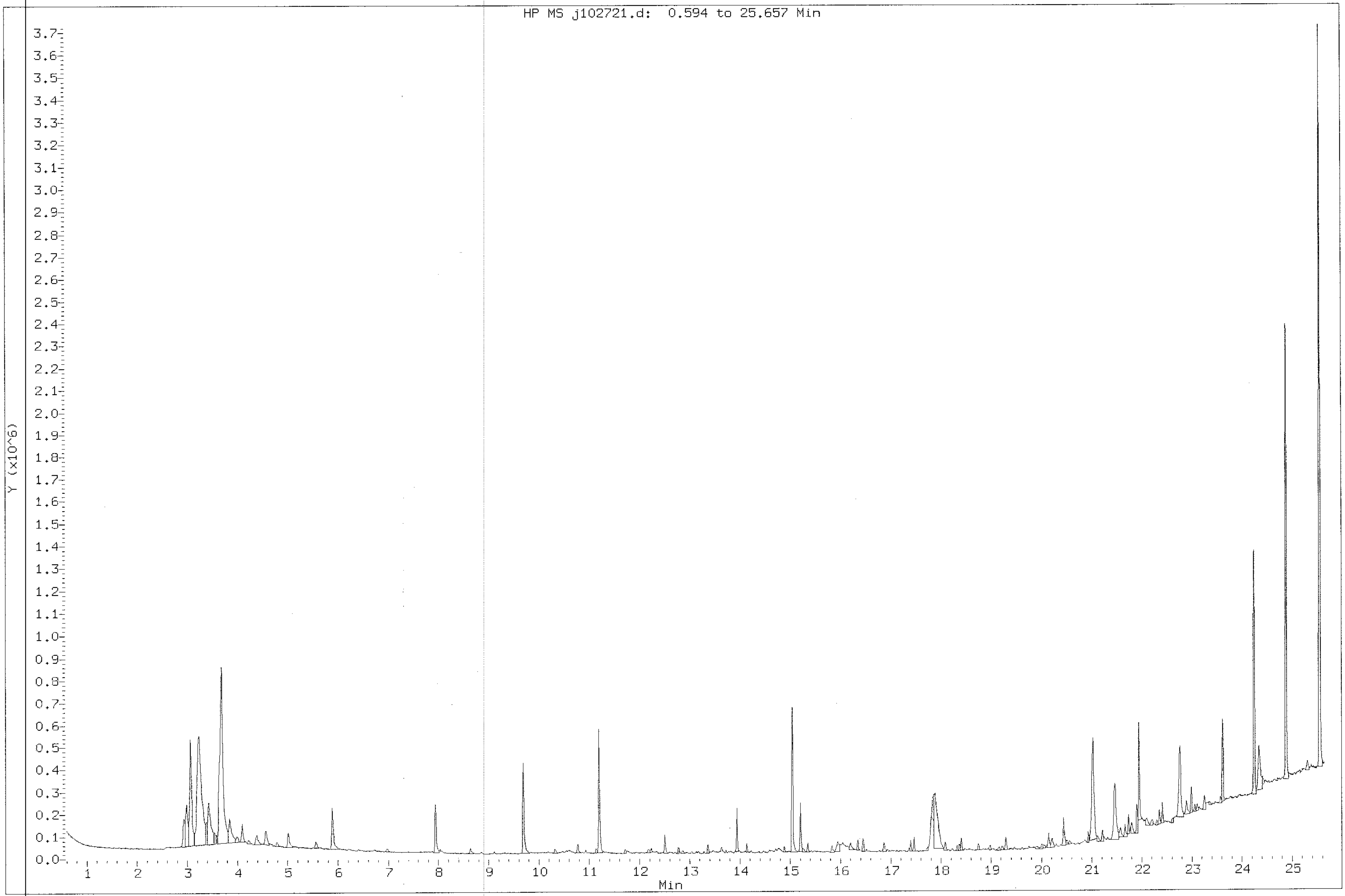
Data File: /chem/msdj.i/27oct11.b/j102717.d
Injection Date: 27-OCT-2011 19:31
Instrument: msdj.i
Client Sample ID: HAF13-SPL13-VMP22 (TO17B)



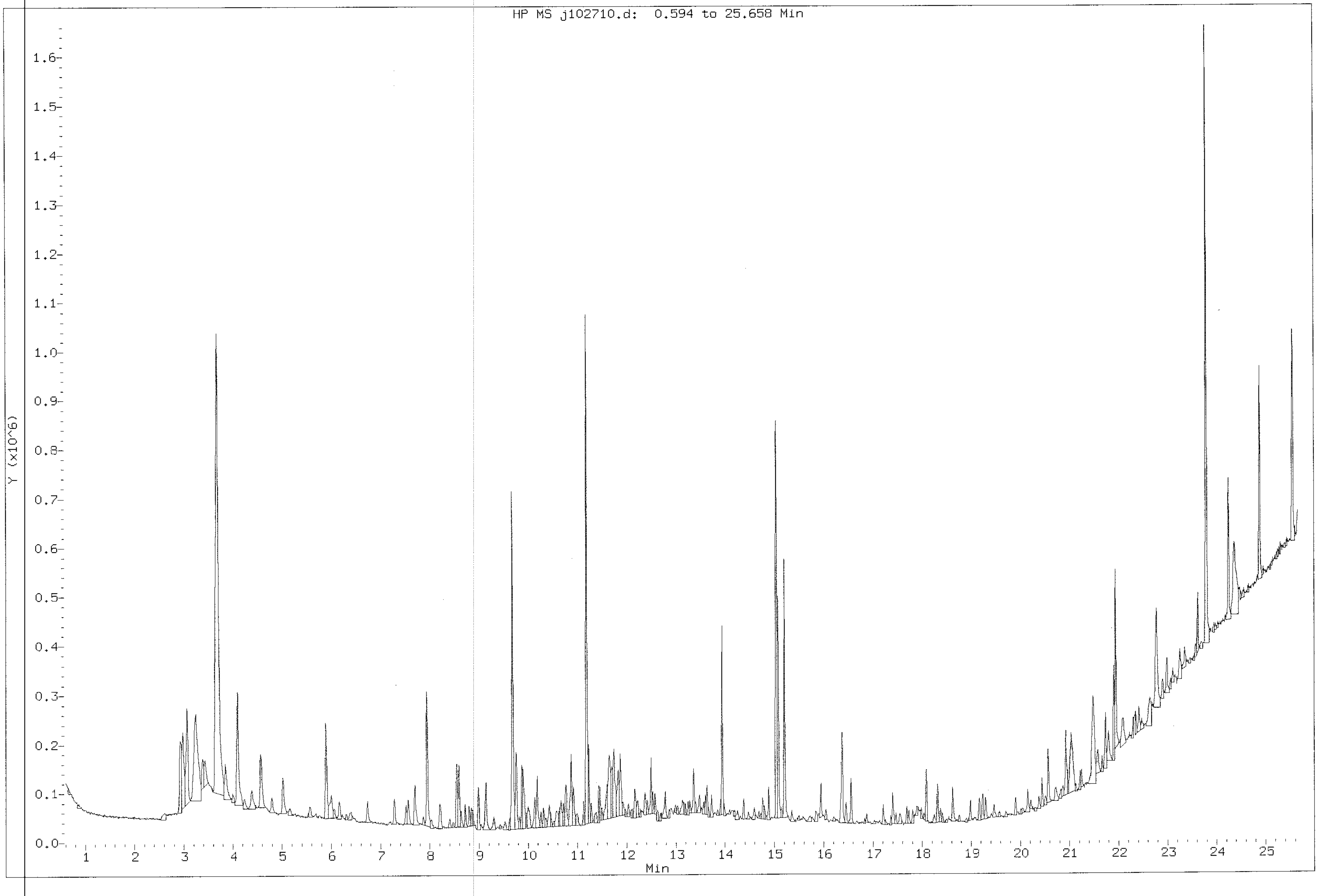
Data File: /chem/msdj.i/31oct11.b/j103123.d
Injection Date: 31-OCT-2011 23:20
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP16 (T017A)



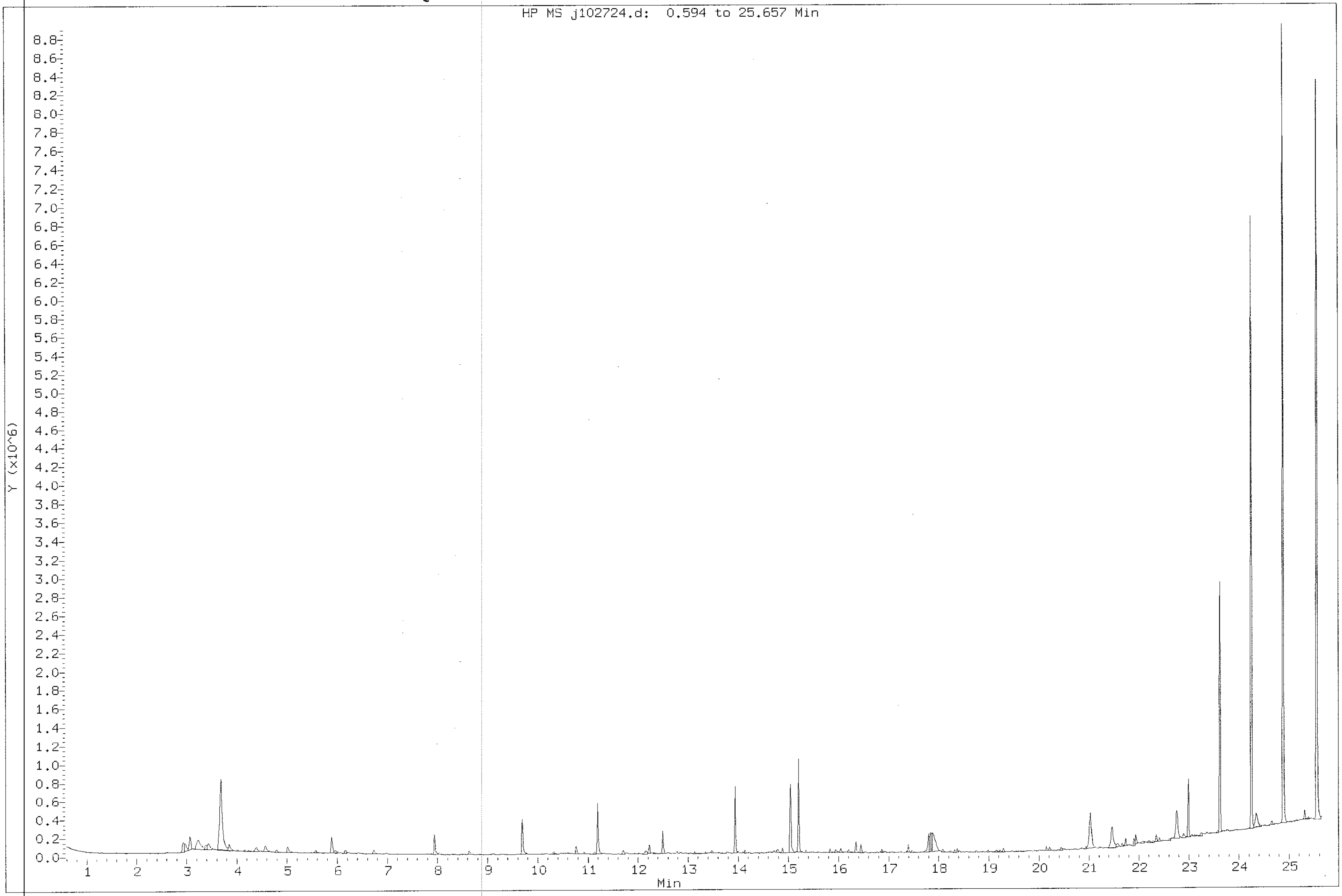
Data File: /chem/msdj.i/27oct11.b/j102721.d
Injection Date: 27-OCT-2011 21:55
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP16 (TO17B)



Data File: /chem/msdj.i/27oct11.b/j102710.d
Injection Date: 27-OCT-2011 15:11
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP17 (TO17A)

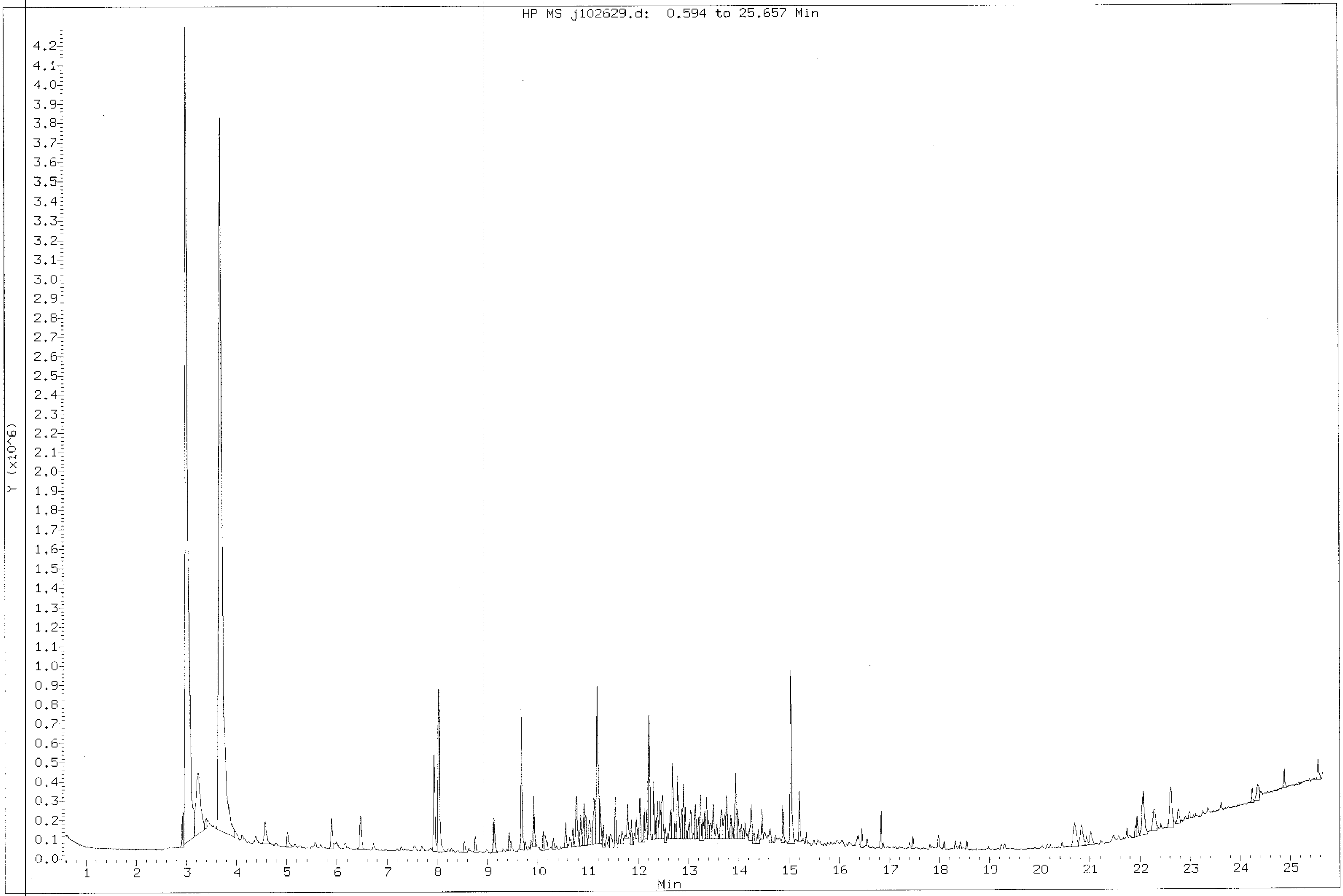


Data File: /chem/msdj.i/27oct11.b/j102724.d
Injection Date: 27-OCT-2011 23:43
Instrument: msdj.i
Client Sample ID: HAFB-SP43-VMP17 (T017B)

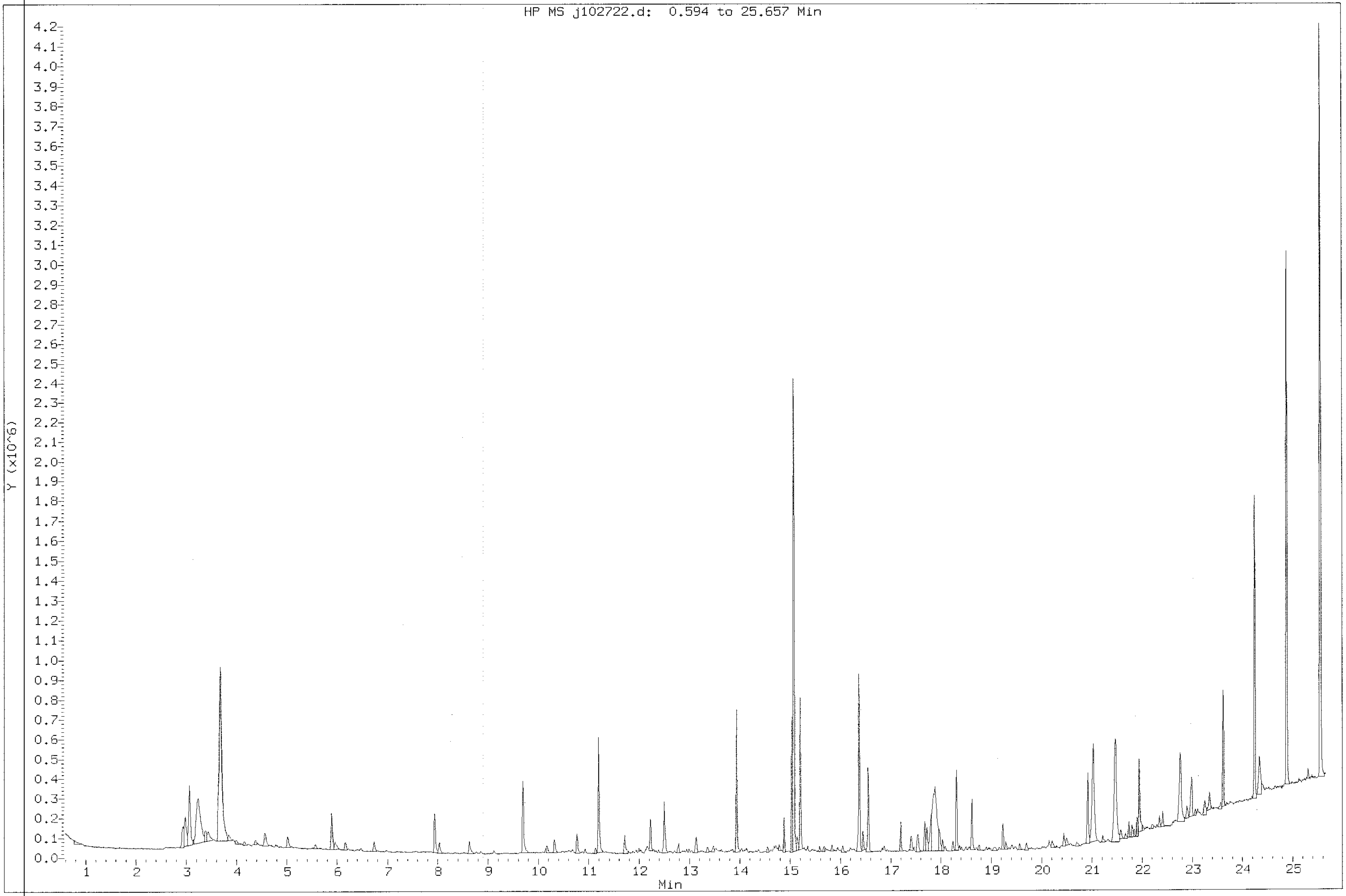


HP MS j102724.d: 0.594 to 25.657 Min

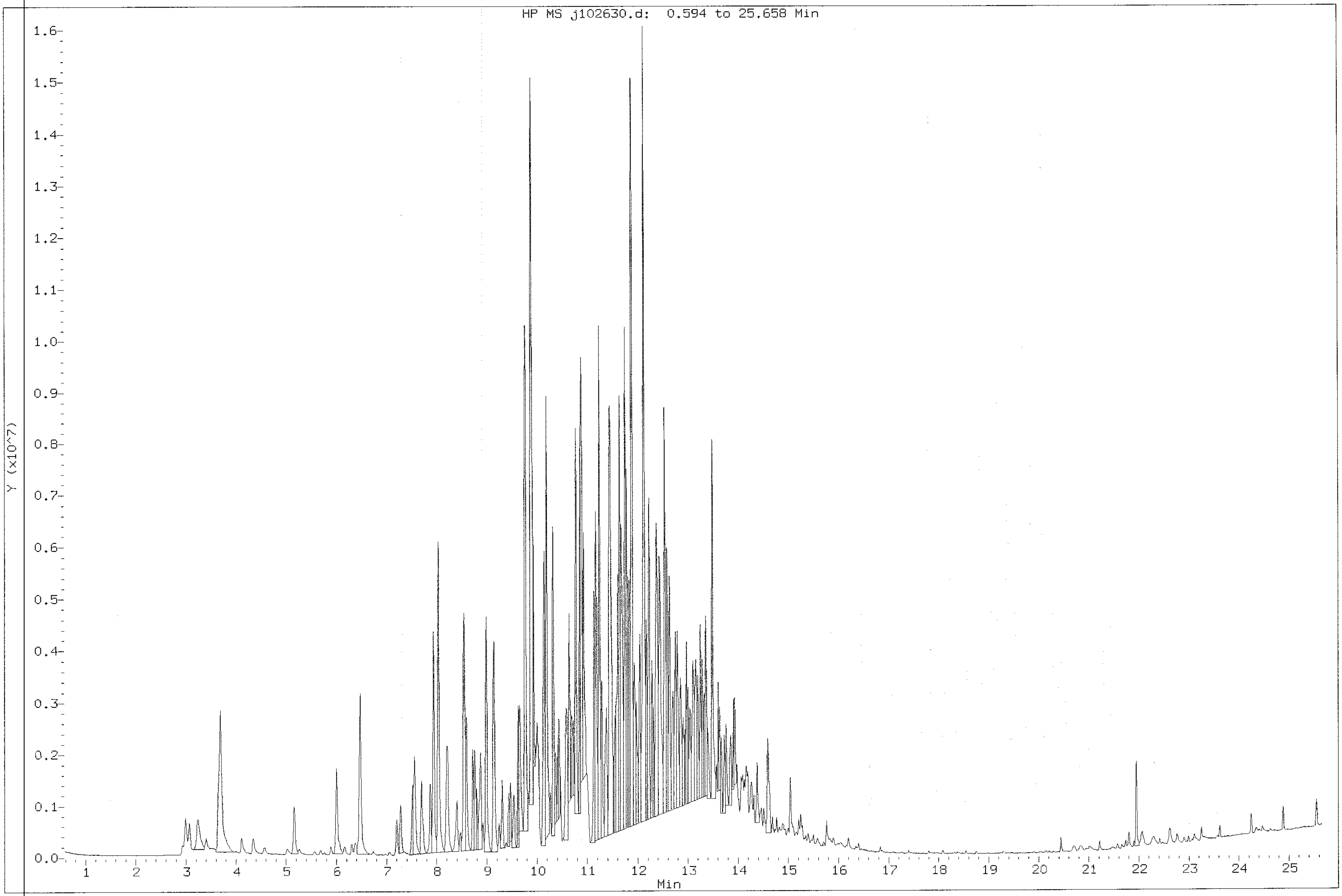
Data File: /chem/msdj.i/26oct11.b/j102629.d
Injection Date: 27-OCT-2011 03:29
Instrument: msdj.i
Client Sample ID: FV-GP01-HDOH#2 (TO17A)



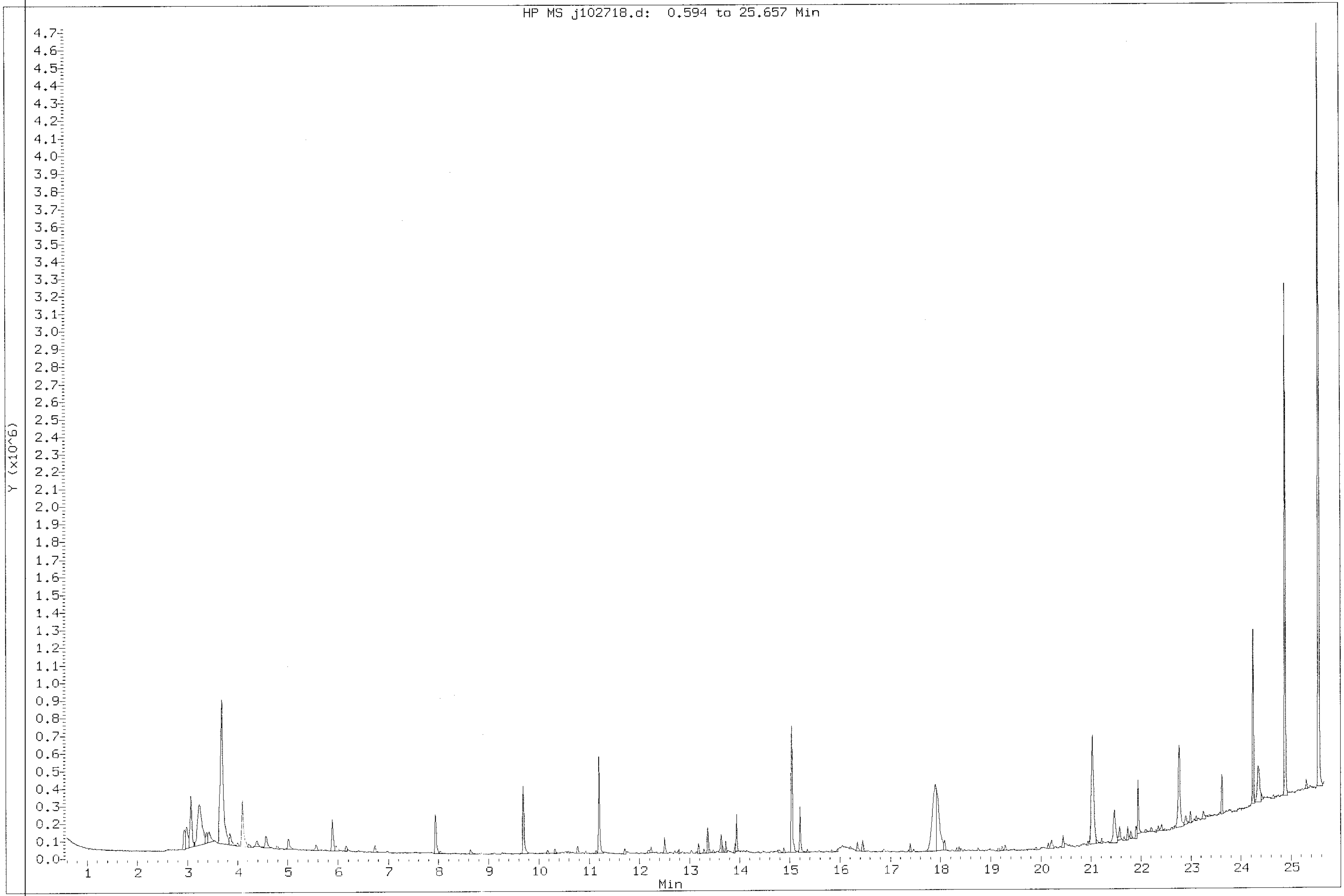
Data File: /chem/msdj.i/27oct11.b/j102722.d
Injection Date: 27-OCT-2011 22:31
Instrument: msdj.i
Client Sample ID: FV-GP01-HDOH #2 (TDMB)



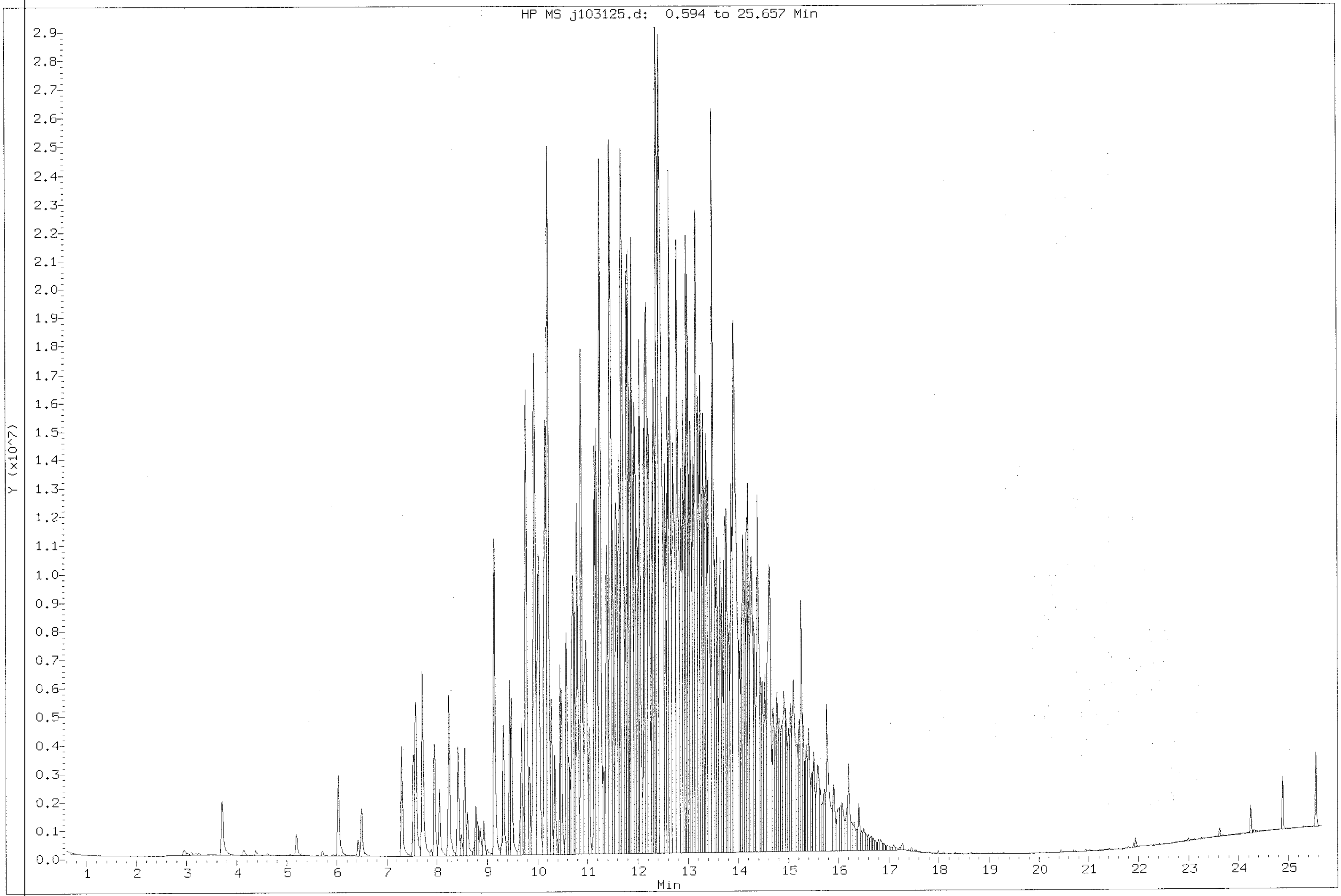
Data File: /chem/msdj.i/26oct11.b/j102630.d
Injection Date: 27-OCT-2011 04:06
Instrument: msdj.i
Client Sample ID: jFV-GP08-HDOH #2 (TO17A)



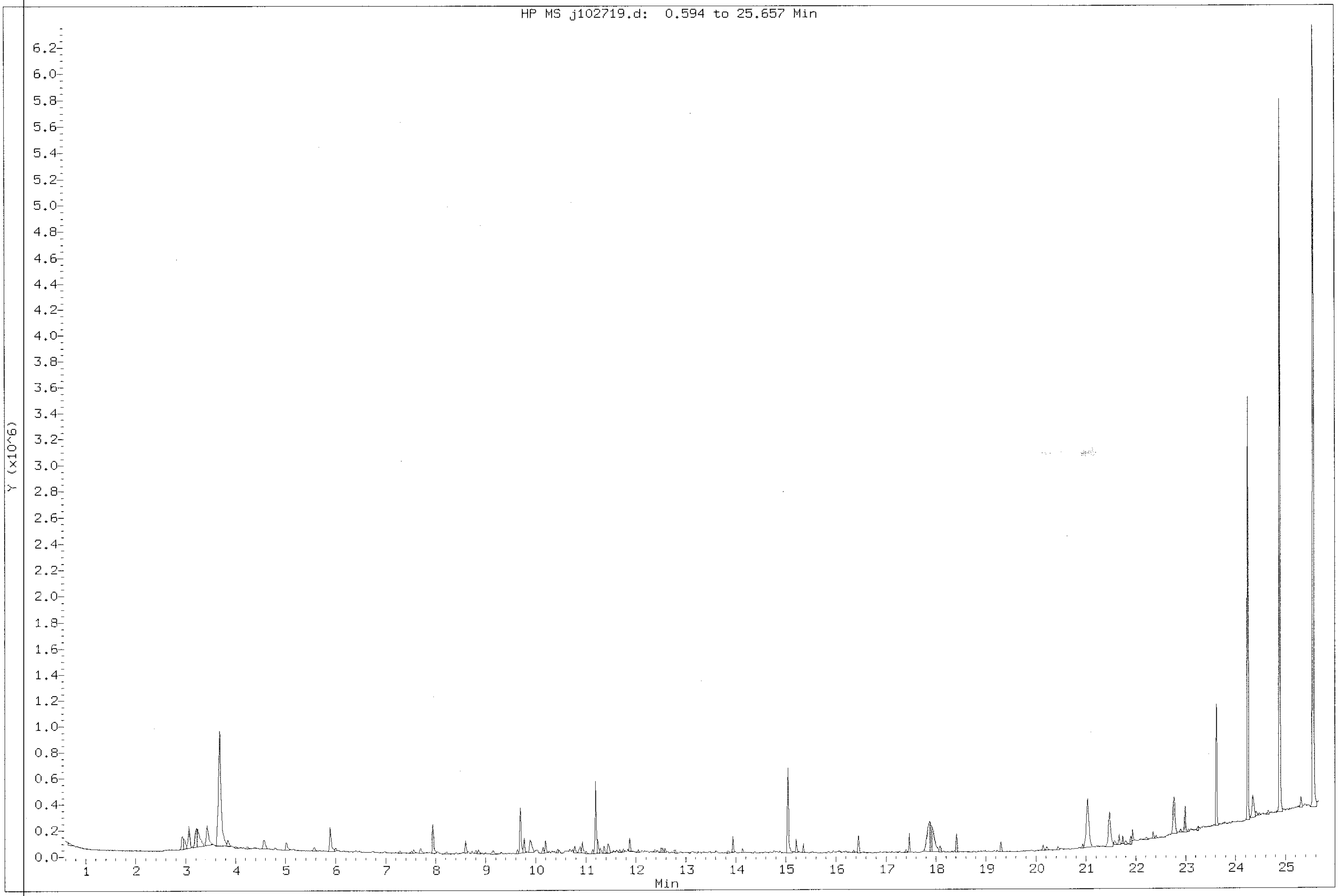
Data File: /chem/msdj.i/27oct11.b/j102718.d
Injection Date: 27-OCT-2011 20:07
Instrument: msdj.i
Client Sample ID: FV-GP08-HDOH #2 (T017B)



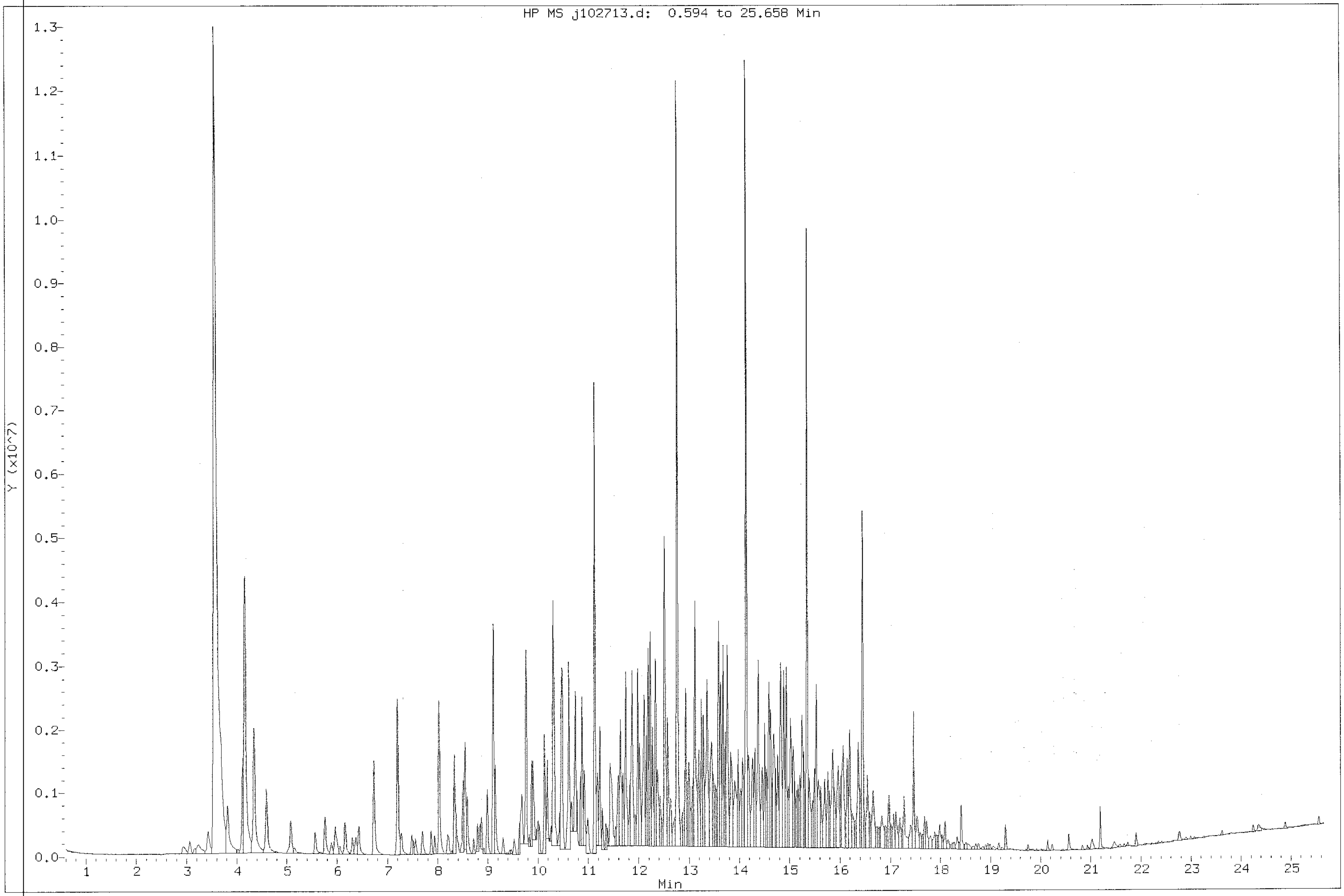
Data File: /chem/msdj.i/31oct11.b/j103125.d
Injection Date: 01-NOV-2011 00:27
Instrument: msdj.i
Client Sample ID: FV-GP16R-HDOH #2 (TD17A)



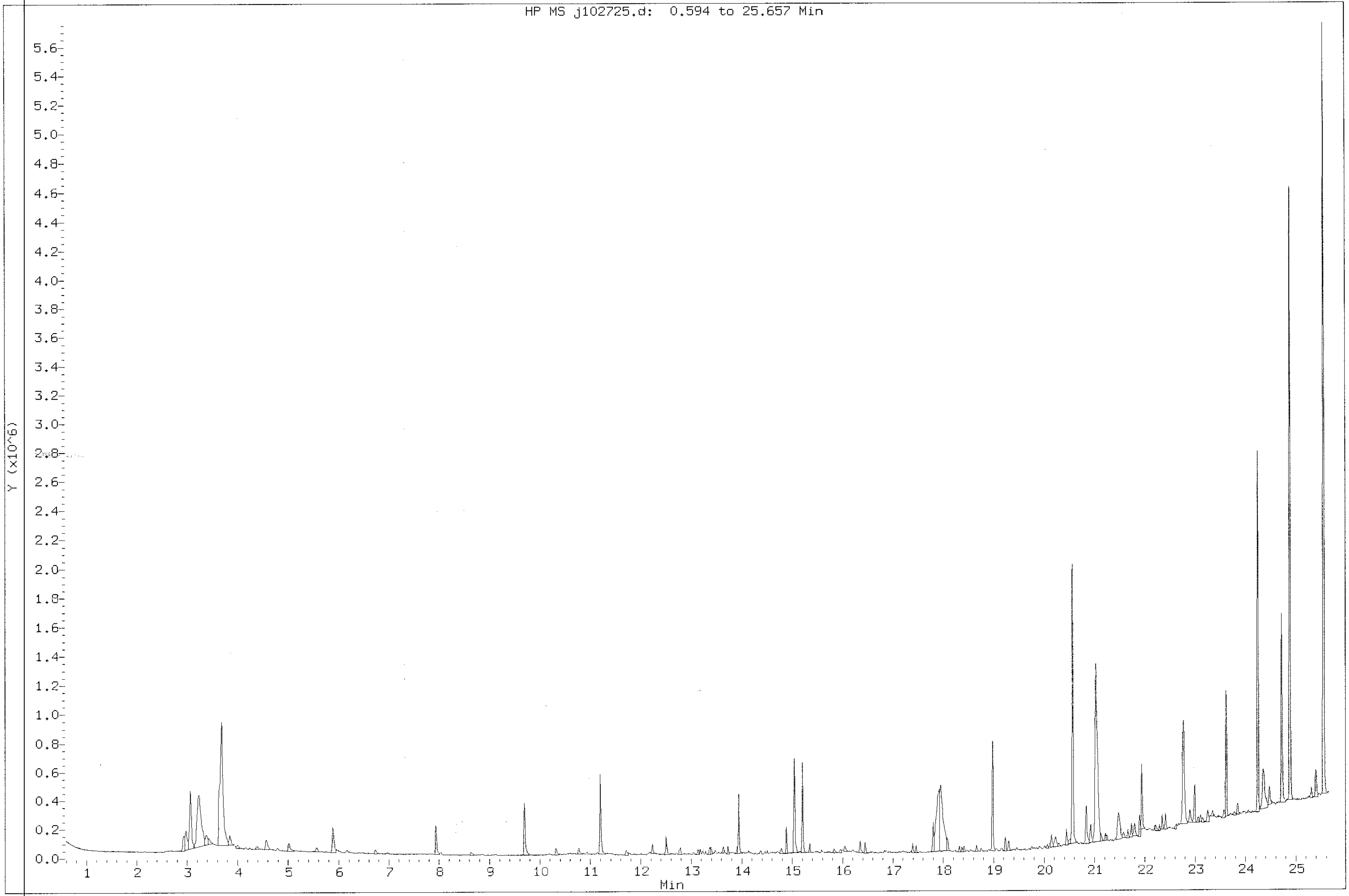
Data File: /chem/msdj.i/27oct11.b/j102719.d
Injection Date: 27-OCT-2011 20:43
Instrument: msdj.i
Client Sample ID: FV-GA6R-HDOH #2 (TO17B)



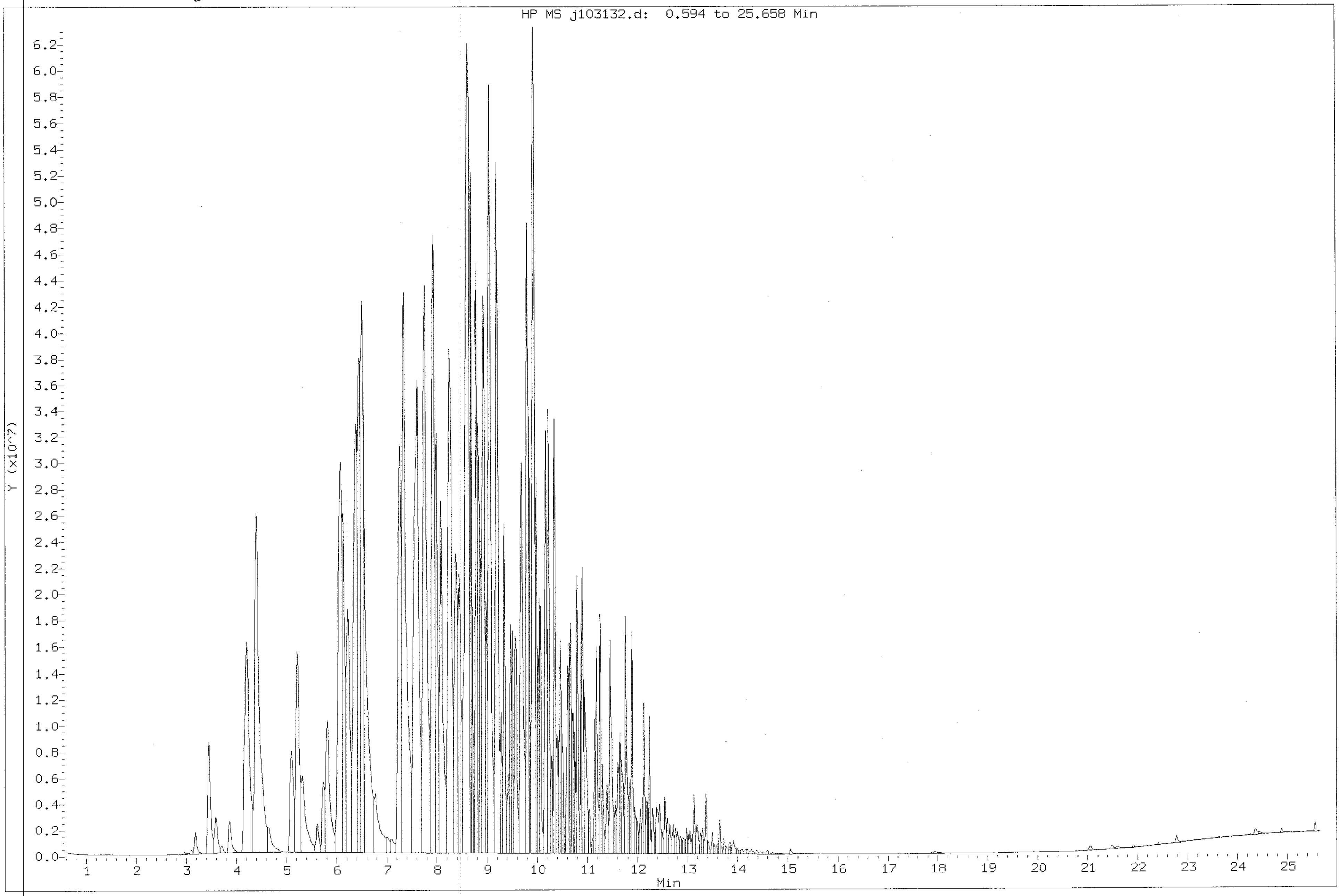
Data File: /chem/msdj.i/27oct11.b/j102713.d
Injection Date: 27-OCT-2011 17:09
Instrument: msdj.i
Client Sample ID: JP8 #1 (T017A)



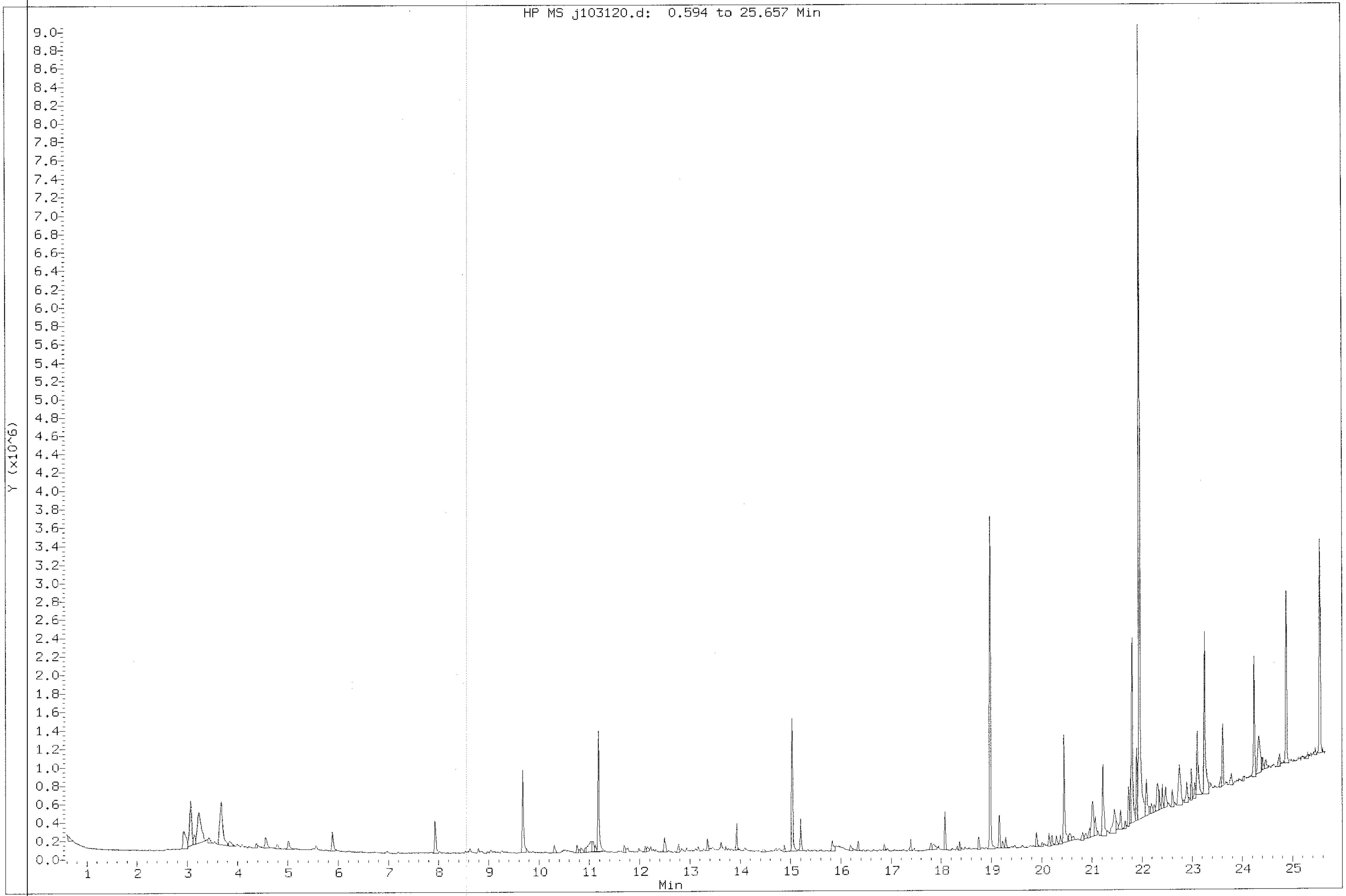
Data File: /chem/msdj.i/27oct11.b/j102725.d
Injection Date: 28-OCT-2011 00:19
Instrument: msdj.i
Client Sample ID: JP8#1 (TO17B)


HP MS j102725.d: 0.594 to 25.657 Min

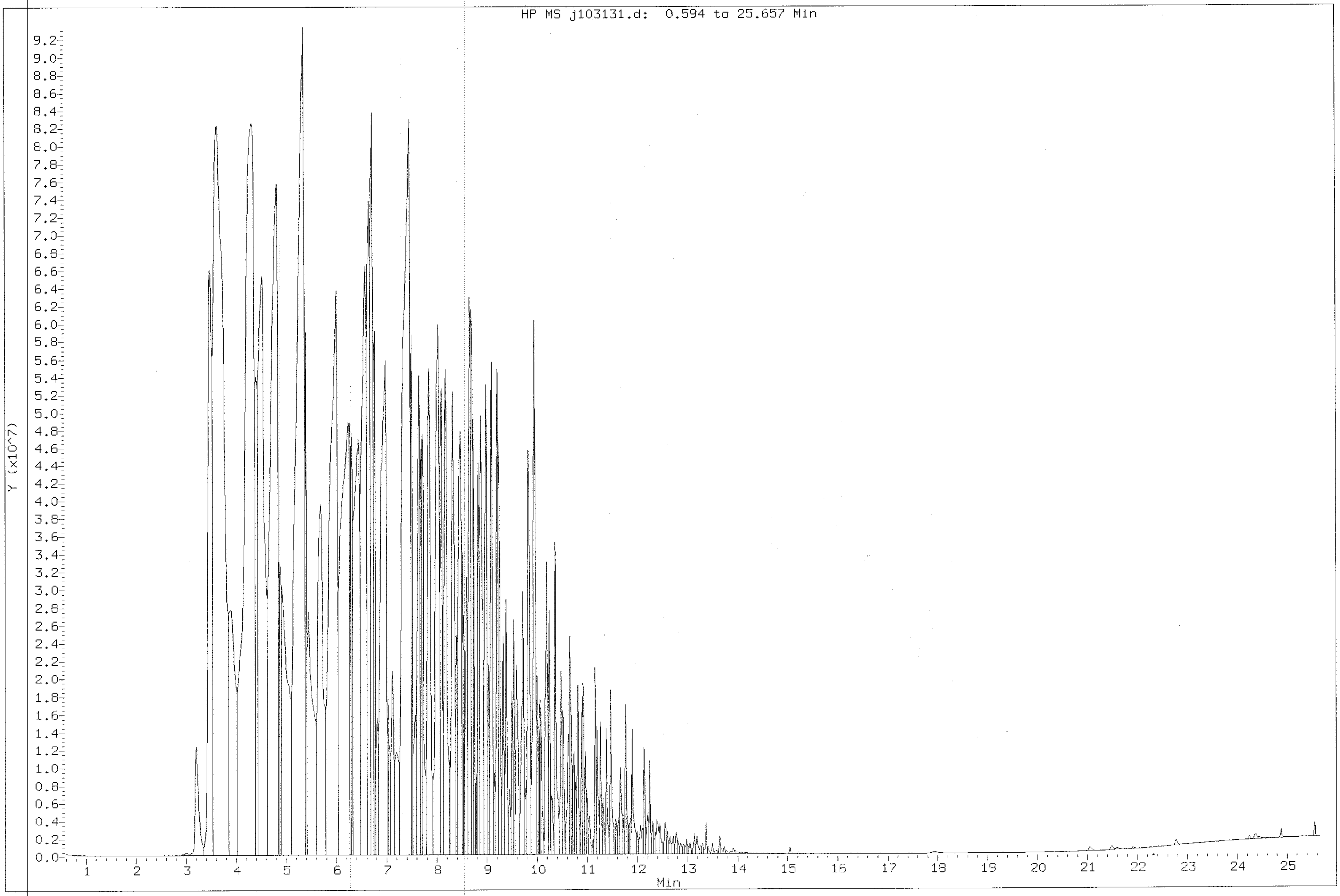
Data File: /chem/msdj.i/31oct11.b/j103132.d
Injection Date: 01-NOV-2011 04:25
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B05(18)(T017A)



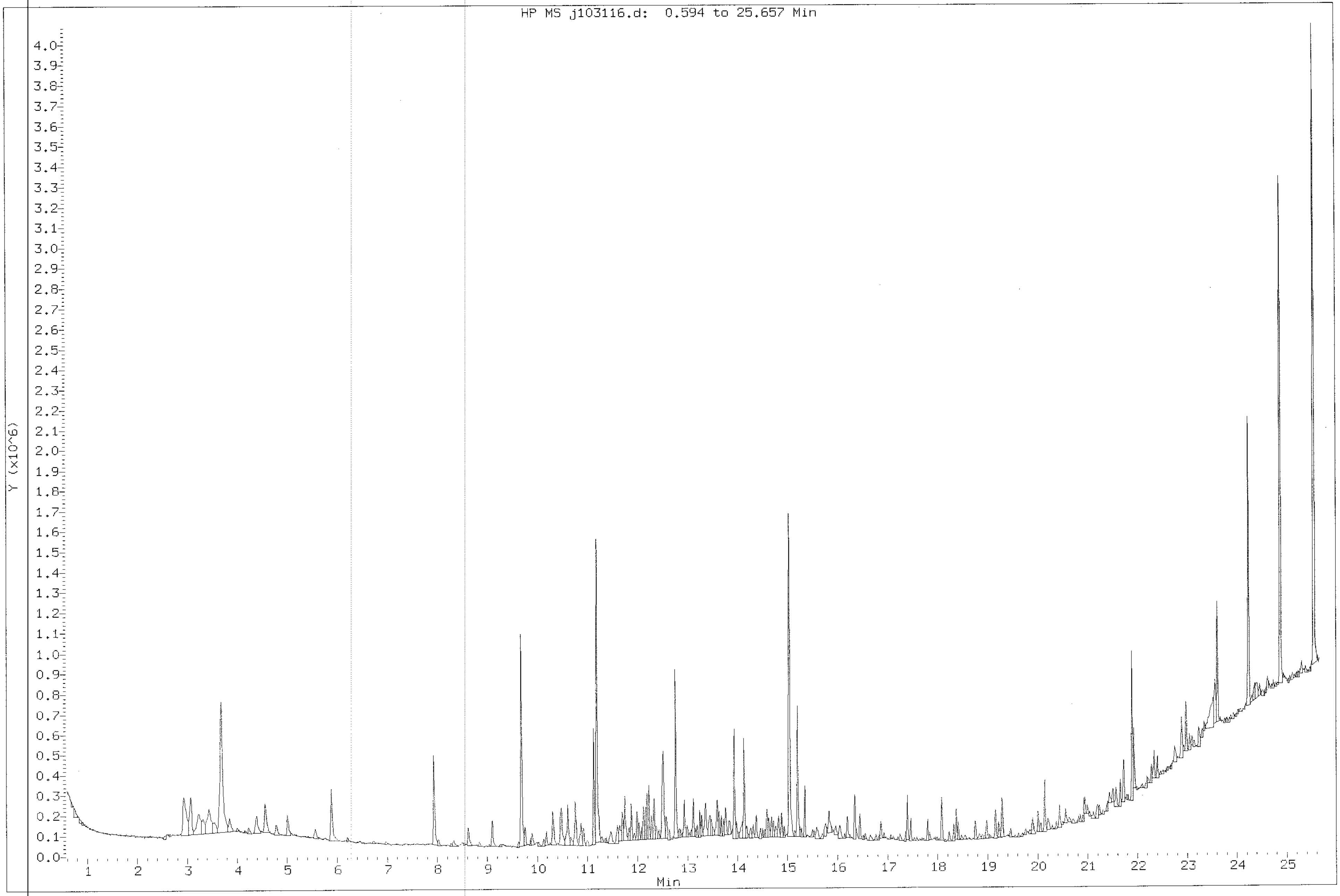
Data File: /chem/msdj.i/31oct11.b/j103120.d
Injection Date: 31-OCT-2011 21:34
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B05(18)(TO17B)



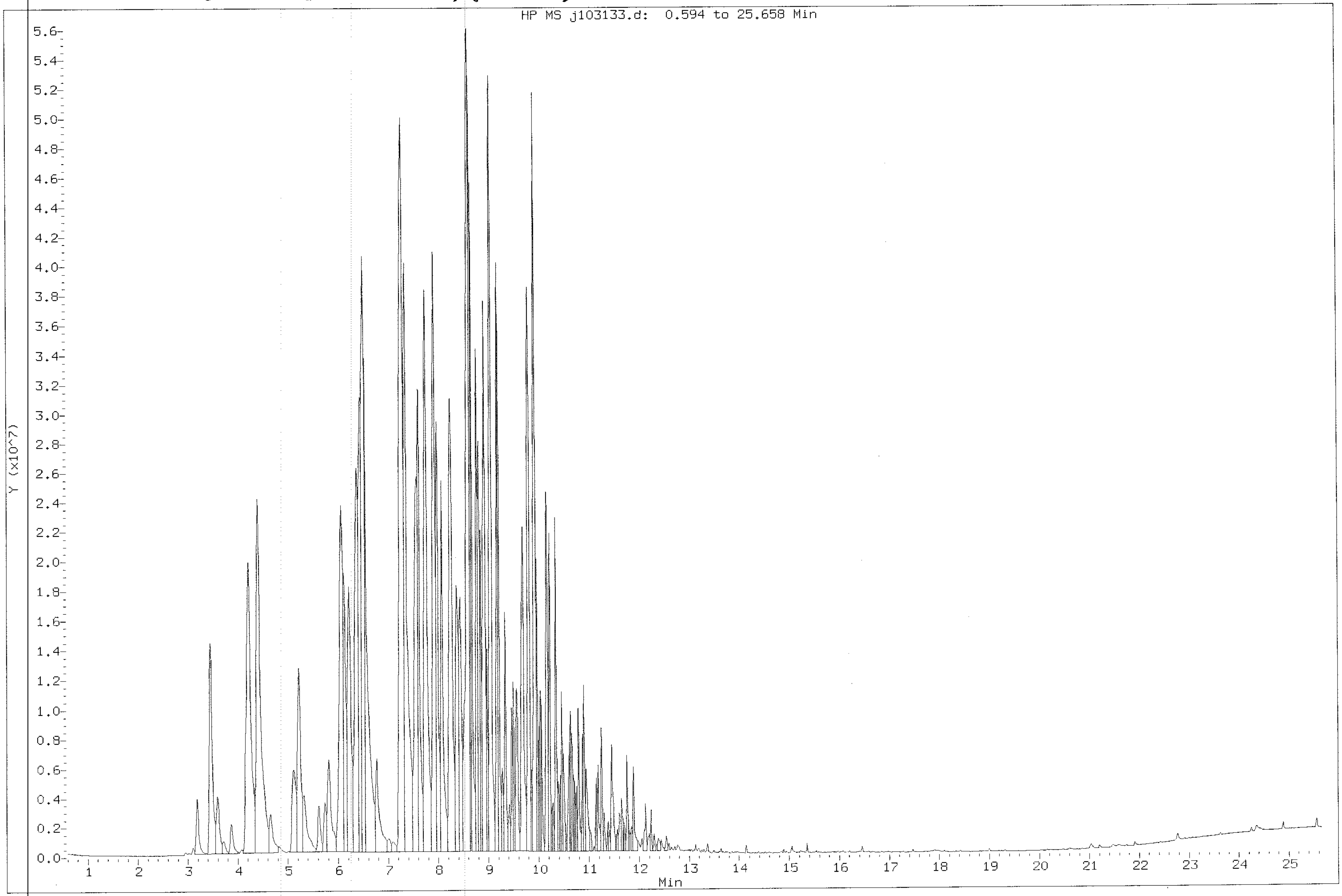
Data File: /chem/msdj.i/31oct11.b/j103131.d
Injection Date: 01-NOV-2011 03:51
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B05(24)(T017A)



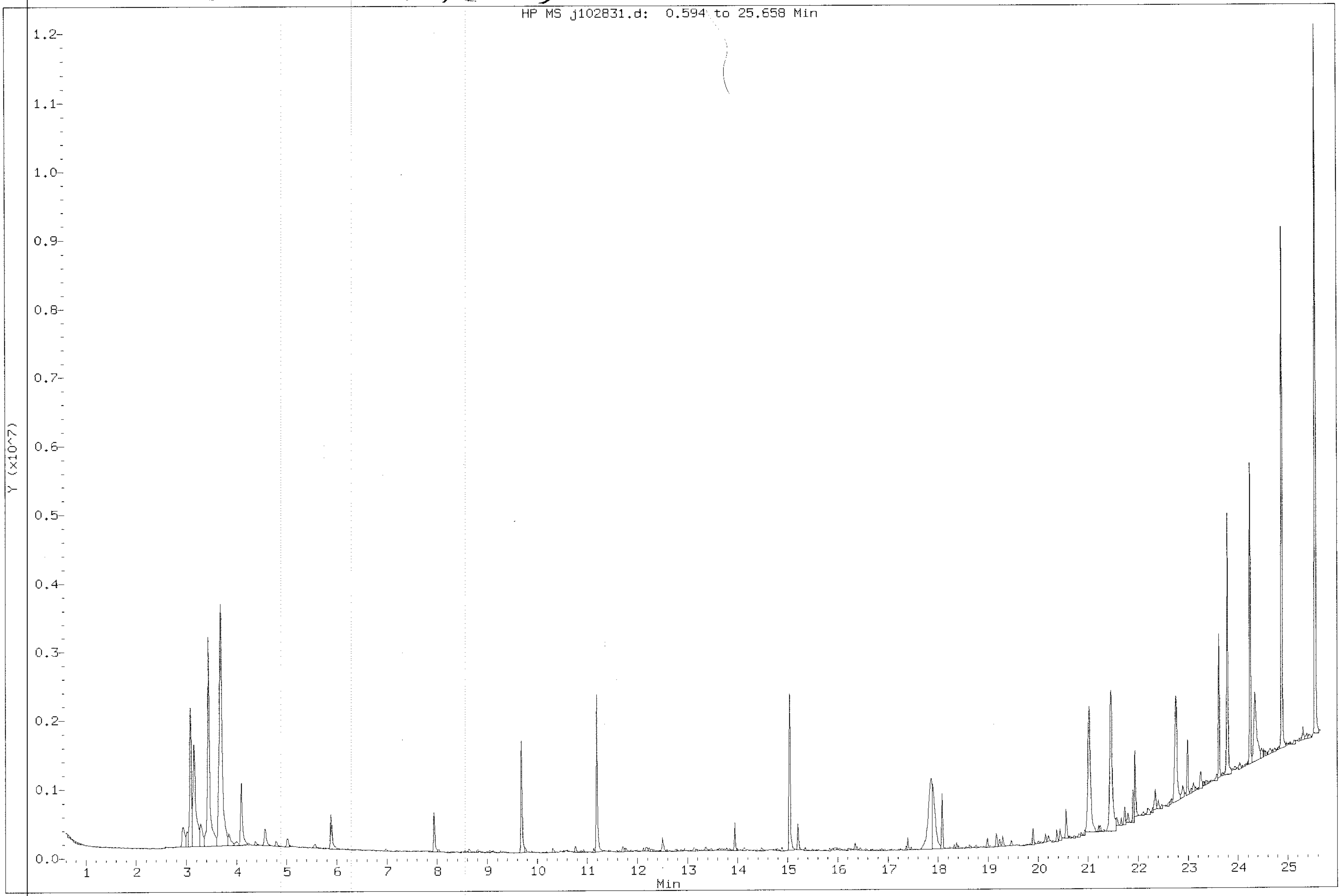
Data File: /chem/msdj.i/31oct11.b/j103116.d
Injection Date: 31-OCT-2011 18:59
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B05(24)(T017B)



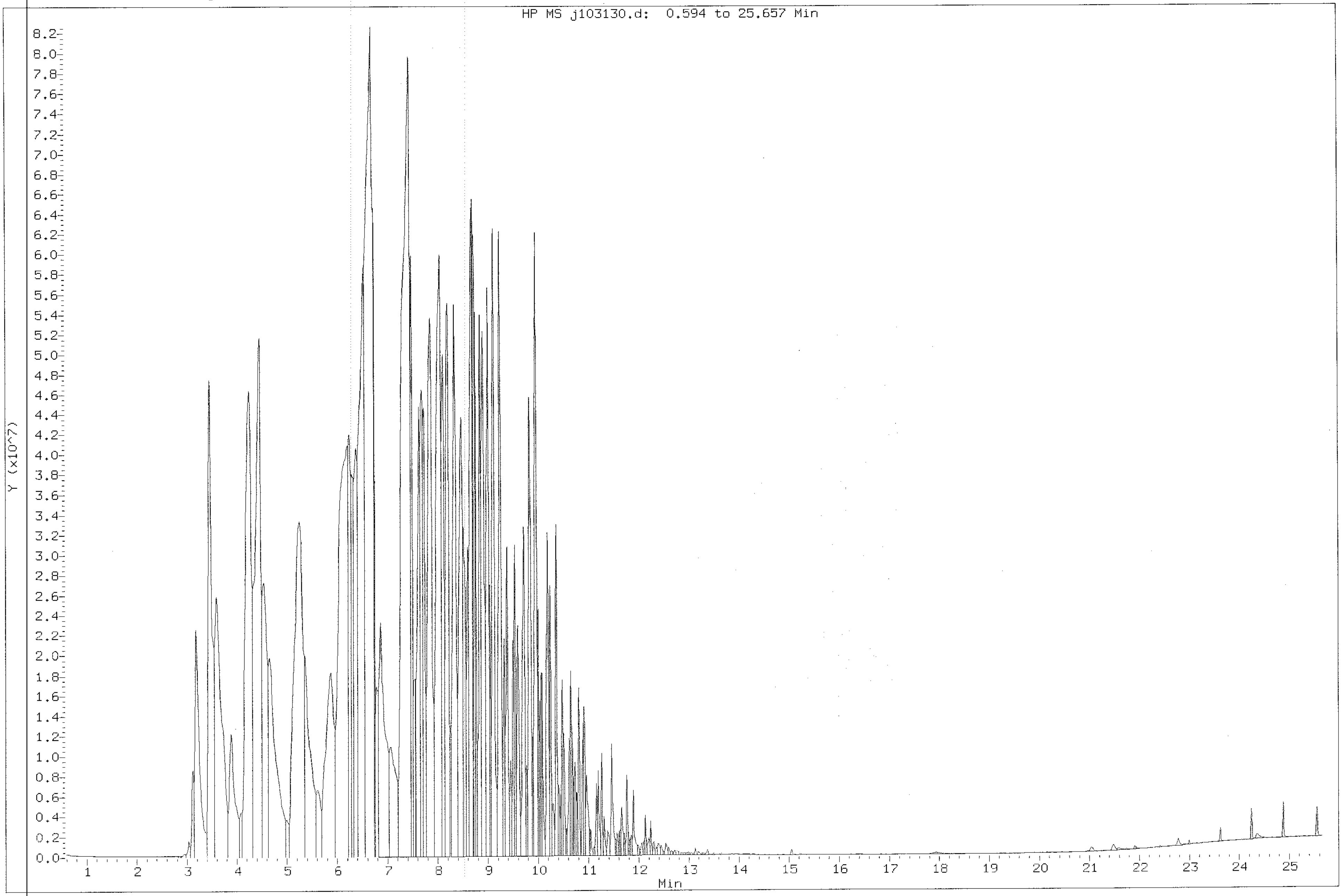
Data File: /chem/msdj.i/31oct11.b/j103133.d
Injection Date: 01-NOV-2011 04:59
Instrument: msdj.i
Client Sample ID: HAFB-VPZ6-B07(20)(T017A)



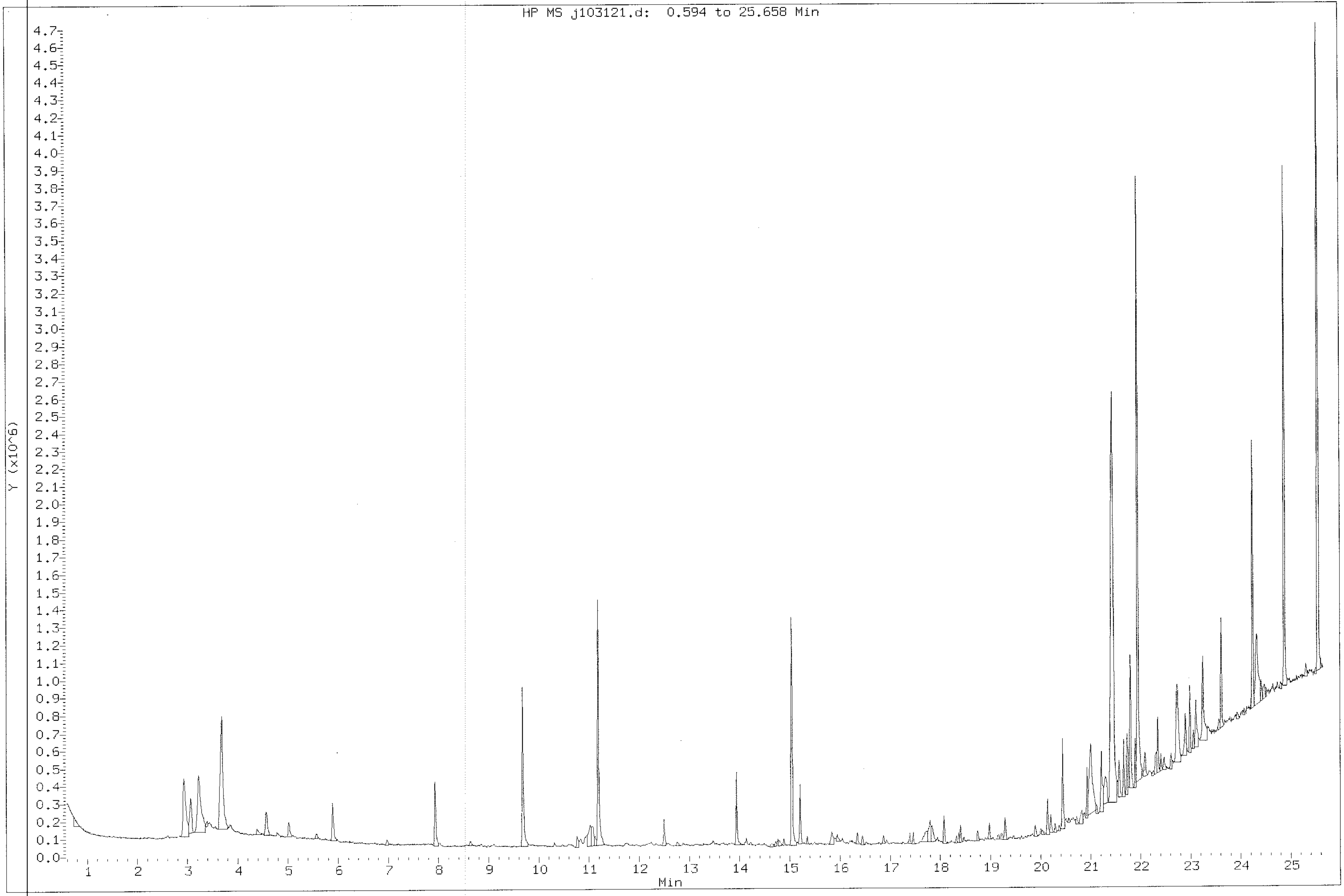
Data File: /chem/msdj.i/28oct11.b/j102831.d
Injection Date: 29-OCT-2011 03:07
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B07(20)(J017B)



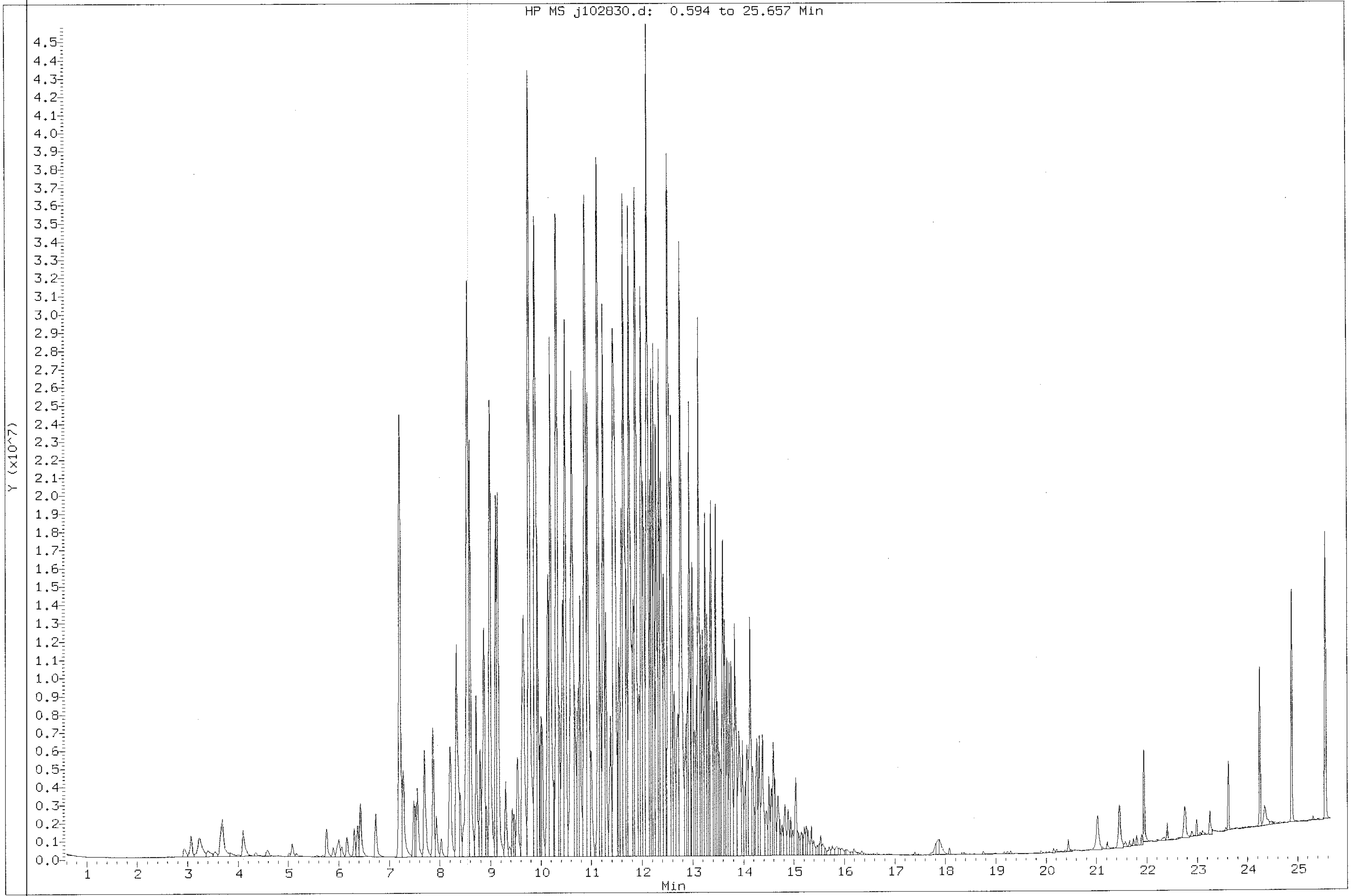
Data File: /chem/msdj.i/31oct11.b/j103130.d
Injection Date: 01-NOV-2011 03:17
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B07(25)(T017A)



Data File: /chem/msdj.i/31oct11.b/j103121.d
Injection Date: 31-OCT-2011 22:10
Instrument: msdj.i
Client Sample ID: HAFB-VP26-B07(25)(TO17B)



Data File: /chem/msdj.i/28oct11.b/j102830.d
Injection Date: 29-OCT-2011 02:31
Instrument: msdj.i
Client Sample ID: HAFB-ST03-B58 (347)(T017A)



Data File: /chem/msdj.i/31oct11.b/j103122.d
Injection Date: 31-OCT-2011 22:47
Instrument: msdj.i
Client Sample ID: HAFB-ST03-BS8(347)(TO17B)