

Strategies for Assessing Human Health Impacts of Crude Oil Releases

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ABSTRACT 300271:

Oil spills create unique challenges in regards to the assessment of potential exposures to response workers and members of the public, and in assessing the potential environmental impacts of the release. This presentation discusses the use of breathing zone air samples taken above or in the direct vicinity of freshly released product for the establishment of air (personal and ambient) monitoring strategies. Air samples collected directly in the vicinity of freshly released and weathered product can provide critical information regarding the potential for work-site and off-site community exposure monitoring. The relative levels in air of volatile organics emitted from fresh product can be used to focus analytical sampling efforts on those constituents with the greatest potential for exceeding occupational exposure levels and community exposure guidelines, and which have the potential for impacts on human health. Finally, analytical methods for evaluation of air samples should include reporting of tentatively identified compounds (TICs), as the primary constituents of crude oil are often not included as target analytes in commonly-employed analytical methods and will likely vary based on the type of crude oil released.

INTRODUCTION:

Crude oil is a complex mixture of hydrocarbons whose chemical constituents can vary depending upon the geographical areas from which the oil is extracted (Wang et al., 2003). While there are commonalities in the identity of chemicals found in different crude oil types, there can be marked heterogeneity in the percent mass of constituent chemicals across crude oil types. For example, analyses of different solid phase crude oils performed by Environment Canada and the U.S. Environmental Protection Agency (US EPA) demonstrated the concentration of total BTEX compounds (i.e. benzene, toluene, ethylbenzene, and xylene) varied by as much as 200% from one crude oil type to another (Wang et al., 2003). In particular, benzene levels in West Texas Intermediate Crude Oil were greater than 400% higher than that found in Arabian Light crude oil (Wang et al., 2003). Similar heterogeneities were observed in analyses of other US EPA priority hazardous air pollutants (HAPs), such as pyrenes and perylene. Some of the chemical constituents of crude oils, such as BTEX compounds, are classified as volatile organic compounds (VOCs) which can enter the air surrounding crude oil during weathering processes. The volatile component of crude oils include some chemicals which are considered HAPs and other chemicals which are not considered HAPs, but for which occupational and community health standards and/or guidelines for air quality exist. In the event of a crude oil release it is critical to identify what chemicals may have been released into the air and determine which chemicals should be considered target analytes with respect to the

protection of worker health during remediation activities as well as community health with regard to releases in proximity to populated areas.

One approach for identifying potential target analytes associated with crude oil releases is sampling and rapid analysis of breathing zone air captured above or in the direct vicinity of freshly released crude oil during the initial phase of a response. Collection and analysis of such samples in proximity to freshly released product allows for the identification and quantification of VOCs released into the air. The US EPA has established standardized analytical methods for profiling air samples for VOC content using gas chromatography / mass spectrometry (GC/MS) technology. Although these methods are designed to measure a set of chemicals designated as HAPs, they are also appropriate for use in profiling VOCs released from crude oil. Given the turn-around time needed to obtain results from GC/MS analysis of field samples, it is often not practical to wait for the return of analytical data before implementing air monitoring and worker / community health protection plans during a crude oil release event. Retrospective analysis of analytical air sampling data from previous events may be used to reasonably predict the variety of VOCs that would be released during a crude oil spill and provide initial guidance on potential target analytes to be monitored during release remediation activities. The list of potential target analytes could then be refined as analytical results become available. The analysis of airborne VOC levels in the context of worker and community health protective standards and guidelines provides a means to prioritize chemicals during crude oil releases.

The Emergency Management Issues Special Interest Group (EMI SIG) is sponsored by the US Department of Energy (US DOE) and functions to coordinate the open exchange of information and resources amongst US DOE and emergency management contractors and organizations. EMI SIG publishes chemical specific Protective Action Criteria (i.e. PAC values) designed to serve as guidance in situations involving the release of hazardous chemicals (DOE/SCAPA, 2012). A series of PAC values are established (i.e. PAC-1, PAC-2, PAC-3) which correspond to airborne concentrations of chemicals above which increasingly severe adverse effects on human health are expected to occur after 60 minutes of exposure. PAC-1 values correspond to a threshold for mild, transient health effects. PAC-2 values correspond to a threshold for serious or irreversible health effects, or effects that could impair the ability of a person to take protective action. PAC-3 values correspond to a threshold for life-threatening health effects. The EMI SIG PAC program integrates information from secondary sources to establish PAC values. Secondary sources include: Acute Exposure Guideline Levels (AEGL) published by the US Environmental Protection Agency (USEPA, 2013), Emergency Response Planning Guidelines (ERPG) published by the American Industrial Hygiene Association (AIHA, 2013) and Temporary Emergency Exposure Limits (TEEL) published by the US DOE Subcommittee on Consequence Assessment and Protective Actions (SCAPA). EMI SIG policy specifies a hierarchy of secondary sources for establishing PAC values with AEGL values preferred over ERPG and TEEL values, followed by ERPG, and then TEELs when neither AEGL or ERPG values are available (DOE/SCAPA, 2012). Each PAC level is evaluated independently; thus, PAC-1, PAC-2, and PAC-3 values for a particular chemical may be derived from a different secondary source. The US EPA AEGL program develops a time table for exposure thresholds spanning from ten minutes to eight hours. However, one hour values are selected from the AEGL tables when this secondary source is used to establish PAC values. Here, the PAC value database was used to analyze VOCs detected in breathing zone air above or

in the direct vicinity of freshly released crude oil to prioritize potential target analytes for use in community air monitoring strategies during an emergency response situation. In this analysis, both mild and intermediate health effect thresholds are considered through the independent analysis of PAC-1 and PAC-2 values.

Likewise, it is critical to identify target analytes with respect to the protection of worker health during the remediation of a crude oil release. Government organizations such as the Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Health and Safety (NIOSH) publish occupational exposure regulations and guidelines, known as OSHA Permissible Exposure Limits (PELs) (29 CFR 1910.1000) and NIOSH Recommended Exposure Limits (RELs) (NIOSH, 2005) respectively, for worker exposure to various chemicals. These limits are calculated as time weighted averages (TWA) over either an eight or ten hour workday. The American Conference of Governmental Industrial Hygienists (ACGIH) is a non-governmental organization which also publishes worker exposure guidelines in the form of eight hour TWAs, known as Threshold Limit Values (TLVs) (ACGIH, 2013). These values correspond to thresholds where persistent exposure of the majority of workers over the course of their work life is not expected to result in adverse health effects. Similar to the approach taken by the EMI SIG program, a critical health protective value (CHPV) was established for crude oil release emergency response workers by integrating information from the OSHA, NIOSH and ACGIH databases. The CHPV was then used to prioritize potential target analytes for use in air monitoring in the work zone surrounding a crude oil release.

METHODS:

VOC air concentrations analyzed in this work are derived from samples of ambient air taken in the breathing zone above or in the direct vicinity of released crude oil. Samples were taken during the initial phase of an emergency response operation relating to the release, prior to extensive weathering of the released product. Samples were collected in stainless steel canisters prepared by Galson laboratories in accordance with standards outlined in US EPA Compendium Method TO-15 "Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed by Gas Chromatography / Mass Spectrometry (GC/MS)" (US EPA, 1999). A description of the emergency response scenarios used in this analysis is given in Table 1. Note that Event 1A and Event 1B are samples taken during the initial phase of the same event in two geographically distinct locations. To maintain anonymity, the identity of the responsible party and location of the releases have been withheld from this report.

After air sampling for 24 h, the stainless steel canisters were shipped to Galson laboratories for GC/MS analysis using US EPA Method TO-15. VOCs identified during GC/MS analysis were designated as either a target compound or a tentatively identified compound (TIC). Target compounds are those for which standard curves have been measured by the analytical laboratory for use in quantifying a chemical concentration. TICs are chemicals which can be identified and whose quantity can be estimated using an analytical method, but for which a standard curve has not been established. A subset of the target compounds specified for the Galson TO-15 method are also found on the list of HAPs specified in Title III of the Clean Air

Act Amendments of 1990. A summary of the VOC concentrations for target and TIC compounds detected in crude oil air samples are listed in Table 2.

Table 3 lists PAC-1 and PAC-2 values as well as the worker critical health protective value (CHPV) for VOCs detected in crude oil air samples. The CHPV was defined as the minimum amongst the OSHA PEL-TWA, NIOSH REL-TWA and ACGIH TLV-TWA values. Ratios were calculated by dividing the mean VOC concentration detected in crude oil air samples by either the PAC-1, PAC-2 or CHPV values. PAC-1, PAC-2, or CHPV Ratios higher than 1 would indicate that concentrations of chemicals in the air in the vicinity of released crude oil exceed these exposure values. VOCs were then ranked according to the respective PAC-1, PAC-2 or worker CHPV Ratios in order to prioritize which VOCs may represent potential target analytes for community and worker exposure during an oil release response.

For Event 1A and Event 1B, air samples were taken in the same locations of the response over a period of three consecutive days. These data were used to examine the time course for air concentrations of VOCs in terms of community and worker health protective criteria.

RESULTS:

Table 2 summarizes the VOCs detected in crude oil air samples from three separate crude oil release events. Detections include aromatic hydrocarbons (including BTEX compounds), sixteen cyclic hydrocarbons with varying degrees of ethyl and methyl substitutions, eight aliphatic straight chain hydrocarbons three to ten carbons in length and twelve different aliphatic branched chain hydrocarbons. The frequency of detection across samples varied for different VOCs. Benzene, toluene, hexane, heptane, octane, cyclohexane, methylcyclohexane, trans-1,2-dimethylcyclopentane, 2-methylpentane, 2-methylhexane and 2-methylheptane were identified in all samples. The mean concentration of a majority of VOCs was below 1 ppm. The highest concentrations observed were for isobutane, hexane, pentane and 2-methylbutane at concentrations of 1.10, 1.15, 2.30 and 3.40 ppm, respectively.

PAC-1 and PAC-2 and worker CHPV values as well as PAC-1, PAC-2, and CHPV Ratios for VOCs detected in crude oil air samples are summarized in Table 3. In total, 23 of the 42 VOCs detected in crude oil air samples have associated PAC values including all aromatic hydrocarbon and straight chain aliphatic hydrocarbon species identified. In this analysis, isomers of xylene and trimethylbenzene were aggregated within each sample in order to obtain total xylene and total trimethylbenzene concentrations for comparison to health protective values. A smaller sub-set of cyclic and aliphatic branched chained hydrocarbons had PAC values. The lowest PAC-1 values were for decane and methylcyclopentane at levels of 1.9 and 0.77 ppm, respectively. The lowest PAC-2 values were also for decane and methylcyclopentane at levels of 20 and 8.5 ppm, respectively. VOCs were ranked according to the PAC-1 and PAC-2 Ratios to prioritize the potential target analytes for community air monitoring. Results of these rankings are visualized in Figure 1A and 1B, respectively. None of the VOCs detected in crude oil air samples exceeded the PAC-1 or PAC-2 health protective criteria. However, in air monitoring practices designed to protect a community (or a worker population), it is important to detect airborne VOCs prior to the point at which concentrations would exceed a health protective value. Thus, for the current analyses a lower boundary ratio of 0.01 (i.e. 100-fold below health

protective value) was considered for prioritization of VOCs as target analytes. This “safety factor” approach takes into account inherent uncertainty associated with the limited number of samples and events (four samples from three events) included in this analysis and the fact that uncertainty factors are not always applied in derivations of PAC or worker health protective values. Methylcyclopentane, decane and pentane had PAC-1 Ratios which exceeded the 0.01 safety factor threshold. Only methylcyclopentane had a PAC-2 ratio which exceeded the 0.01 safety factor threshold. Each of these VOCs are reported as TICs using the TO-15 GC/MS analytical method. Gray triangles in Figures 1A and 1B represent the average concentration of VOCs (in ppm, right y-axis) present in the crude oil air samples. Note that the chemicals with the highest airborne concentrations are not necessarily those that rank at the top of priority rankings when health protective values are taken into account.

Table 3 also summarizes worker CHPV values for VOCs detected in crude oil air samples. In total, 15 of the 42 VOCs detected in crude oil air samples have associated worker health protective values. These include all straight chain aliphatic hydrocarbons except for decane, a majority of aromatic hydrocarbons and relatively few cyclic and branched chain aliphatic hydrocarbons. The chemical with the lowest CHPV was benzene at a concentration of 0.1 ppm. Toluene and trimethylbenzenes had the next lowest CHPV at concentrations of 20 and 25 ppm, respectively. VOCs were ranked according to the CHPV Ratio to prioritize potential target analytes for worker air monitoring (Figure 1C). The same safety factor ratio threshold of 0.01 used in community air monitoring prioritization was used for worker air monitoring prioritization. Benzene was detected at levels approximately 1.5 times greater than the CHPV value of 0.1 ppm. Benzene is a target analyte in the TO-15 analytical method. Hexane and pentane were present at levels exceeding the 0.01 CHPV safety factor threshold. Hexane is a target analyte and pentane is a TIC in the TO-15 analytical method. Gray triangles in Figure 1C represent the average concentration of VOCs (in ppm, right y-axis) present in the crude oil air samples. Note that the chemicals with the highest airborne concentrations are not necessarily those that rank at the top of the priority ranking when worker health protective values are taken into account.

In the case of Event 1A and Event 1B, air samples were available for the same geographical location across the first three days of an oil release response. Data from these samples was used to characterize the time course of VOC air concentrations in terms of PAC-1 and PAC-2 Ratios (Figure 2A,B) as well as the worker CHPV Ratio (Figure 2C,D). Overall, data in Figure 2 demonstrate that airborne concentrations of VOCs in breathing zone air near crude oil decline rapidly during the initial days of a release. In analysis of PAC-1 ratios, concentrations of methylcyclopentane and pentane were detected at levels exceeding the 0.01 safety factor ratio threshold (Figure 2A-B, open symbols with solid lines). The concentrations of methylcyclopentane and pentane dropped below the 0.01 safety factor threshold by days three and two of the event, respectively. In analysis of PAC-2 Ratios, only concentrations of methylcyclopentane were detected at levels exceeding the 0.01 safety factor ratio threshold (Figure 2A-B, closed symbols with dotted lines). Concentrations of methylcyclopentane dropped below the 0.01 safety factor threshold by day two of the event.

In analysis of worker CHPV Ratios over time, benzene concentrations were detected at a concentration which exceeded a CHPV Ratio value of 1 during day one of the event (Figure 2C-

D). That is, benzene was detected at a concentration which exceeded the CHPV of 0.1 ppm, which is the NIOSH recommended exposure limit (REL) for benzene. Hexane was detected at concentrations exceeding the 0.01 safety factor ratio threshold, also on day one of the event. Concentrations of benzene dropped below the worker CHPV by day two of the event and were undetectable by day three of the event. Concentrations of hexane dropped below the 0.01 safety factor ratio threshold by day two of the event.

DISCUSSION:

This analysis presents an approach to prioritizing VOCs as target analytes at a crude oil release for the purpose of evaluating risks posed to response workers and the general public. It is based on the premise that the risk posed to individuals following a release is determined by the concentration of chemicals present in the air together with the inherent toxicity of the chemical as expressed by its worker or community health protective value. By determining a simple ratio of the air concentration of a specific chemical obtained near released crude oil divided by its health protective value, one can determine which chemicals to prioritize for evaluation of exposures to workers and members of the public. It is important to note that this evaluation for the general public is based exclusively on short-term (acute) exposure guidelines developed under the assumption that such exposures are not routinely experienced and, that they will end quickly either through evacuation of communities, or through mitigation/remediation efforts instituted following the release. A similar approach could be taken using guidelines that target slightly longer exposure durations, such as the Agency for Toxic Substance and Disease Registry (ATSDR) acute minimal risk levels (MRLs), which are intended to address exposures of up to 14 days in duration (ATSDR, 2013). In contrast, the evaluation for workers is based on workplace exposure guidelines or standards that presuppose a repeated, working lifetime, exposure.

A summary of the rank order prioritization using PAC Ratios (i.e., community evaluation) or worker CHPV Ratios is shown in Table 4. Rank order prioritization using PAC Ratios or worker CHPV Ratios yields disparate results in terms of prioritizing potential target analytes. For instance, benzene is the top ranked potential target analyte using the worker CHPV ratio, but is 9th or 18th in the PAC-1 or PAC-2 priority list, respectively. Similarly, methylcyclopentane and decane are the two top ranked potential target analytes using the PAC-1 or PAC-2 ranking system. However, worker health protective values for these two chemicals are not available. Overall, these data indicate that the prioritization of potential target analytes will vary depending upon the population under consideration for implementation of health protective air monitoring plans and what protective standards or guidelines are considered. There is some overlap, however, in the ranking of chemicals for worker and community exposure evaluations. For example, pentane, xylenes and cyclohexane are ranked in the top ten using the CHPV Ratio and are also ranked in the top ten using the PAC-1 or PAC-2 Ratio (Tables 4).

For the purpose of developing a strategy for assessing potential human health impacts of chemicals volatilized from crude oil following a release, the chemicals listed in Table 4 were further evaluated to determine if the CHPV or PAC Ratios were greater than the safety factor ratio threshold of 0.01. Chemicals meeting this criterion were selected to develop a proposed analyte list for use in analysis of time-integrated air samples collected during crude oil release incidents (Table 5). It is important to note that in these analyses, there were no airborne VOC

concentrations which exceeded community health protective levels and only benzene exceeded a worker health protective level. However, as stated above, a ratio of 0.01 was selected as the cut-off for inclusion in the proposed analyte list given: 1) a need to detect airborne VOCs before concentrations reach health protective levels, 2) the fact that uncertainty factors are not always used in the derivation of PAC or CHPV values, and 3) the limited number of air samples considered in the present analyses. While the data listed in Table 2 were collected in the breathing zone in the vicinity of released crude oil in actual emergency response situations, no two releases are identical and there is the potential that VOC concentrations at other spills may be present at higher levels than those reported here. However, these data do provide insight on which chemicals should be considered in air monitoring practices implemented in release scenarios. Some of the chemicals in the proposed analyte list (Table 5) are target analytes for the TO-15 method (i.e. benzene, toluene, and hexane). Others are TICs according to the TO-15 method (i.e. methylcyclopentane, pentane, and decane). In analyses using the current TO-15 method, a request can be made to the analytical laboratory to specifically report on these compounds as TICs. Alternatively, a refined analytical chemistry method can be developed which includes the TIC chemicals on the list of target analytes to be measured. This would provide more reliable and accurate quantification of these chemicals. Ranking of the proposed analyte list demonstrates that benzene has a CHPV Ratio that is substantially higher than any other chemical detected during a crude oil release (Table 6). This is due to its very low worker CHPV corresponding to a NIOSH REL of 0.1 ppm designed to protect workers from the carcinogenic effects of benzene.

The chemicals methylcyclopentane and decane have a comparatively high PAC-1 and PAC-2 ratios according to the present analysis (Tables 3 and 4). This is due to the comparatively low PAC-1 and PAC-2 values for methylcyclopentane (0.77 and 8.5 ppm, respectively) and decane (1.9 and 20 ppm, respectively). The PAC values for methylcyclopentane and decane are TEELs, which are designed to be temporary emergency response guidelines. TEELs are developed by US DOE for chemicals which do not have established AEGL or ERPG values and that typically have little or no available toxicity data. Once AEGL or ERPG values for a chemical are developed, the TEEL values are replaced in the PAC value database. For chemicals with little or no toxicity data, TEEL value development guidance specifies the use of LC₅₀ (i.e. the concentration of chemical needed to produce 50% lethality in test animals) or LC_{LO} (i.e. the lowest concentration in which lethality was observed) for calculation of a TEEL-3 value and subsequent extrapolation to lower TEEL-2 and TEEL-1 values (DOE, 2008). In the case of methylcyclopentane, no sub-lethal toxicity data were available at the time of the latest PAC values released to the public (Rev. 27, February 2012); therefore, lethal dose extrapolations were performed to arrive at the current PAC-1 and PAC-2 values of 0.77 and 8.5 ppm, respectively. However, a recent inhalation toxicity study demonstrates that methylcyclopentane does not cause any adverse health effects in rodents exposed 6 hours / day, 5 days / week, for 13 weeks at concentrations up to and including 1,300 ppm (Yang et al. 2014). In addition, the PAC-1 and PAC-2 values for decane are relatively low, particularly in comparison with other straight-chain aliphatic hydrocarbons. A toxicity study in rodents demonstrated that an eight hour inhalation exposure to 1369 ± 19 ppm of decane (a saturated vapor; i.e. the maximum concentration of decane vapor achievable in the air at 20 °C) did not cause any adverse health effects in rodents during a 14 day post-exposure observation period (Nilsen et al. 1988). Other inhalation toxicity studies of decane have also demonstrated no adverse effect levels at concentrations in the

hundreds of ppm (Lammers et al. 2011; reviewed in Amoruso et al. 2008). These data indicate that the PAC values currently specified for methylcyclopentane and decane may not be an accurate estimation of the toxicity of this chemical and further review is warranted.

Real-time air monitoring information regarding the concentrations of chemicals following a crude oil release can play a critical role in making informed decisions during the response. The target analytes listed in Table 5 and 6 were evaluated to determine which of these chemicals can be detected using available “real-time” monitoring methods. This evaluation is presented in Table 7. As illustrated therein, all of the chemicals on the proposed analyte list can be rapidly detected using non-specific photoionization (PID) instrumentation which allows detection of a wide variety of VOCs. Five chemicals can be detected using chemical-specific colorimetric detection tubes (i.e. Gastec tubes). Four chemicals can be detected specifically using infrared spectroscopy (i.e. MIRAN SapphIRE). In addition, benzene can be detected in real-time with an UltraRAE PID instrument equipped with a chemical specific separation tube.

A real-time air monitoring strategy would involve monitoring for total VOCs using a PID instrument and confirming the presence of particular VOCs with secondary methods if an action level is exceeded. Site management and workers could then be informed to take appropriate protective actions. The PID instrumentation is non-specific and will detect mixtures of VOCs present in air around the crude oil release. Therefore, confirmation of the presence of target analytes through secondary instrumentation may be required. For a work zone or community around a crude oil release, action levels would correspond to the CHPV or PAC values, respectively, (or some fraction thereof) for the target analytes listed in Table 3. Confirmatory sampling for the presence of these analytes would be initiated following any PID readings above the CHPV or PAC, taking into consideration the correction factor for the instrument being used for VOC analysis. There are currently no real-time methods for specific detection of methylcyclopentane or decane. However, as previously discussed, available toxicity data indicate that the PAC values for these chemicals are inaccurate and may not be appropriate for use in determining air monitoring action levels.

Analysis of time course data from Event 1 demonstrate that VOCs released from crude oil can dissipate over a period of a few days (Figure 2). However, this may not always be the case particularly in scenarios where fresh oil continues to be released throughout and beyond the initial phase of the response, and/or during remediation when un-weathered reservoirs such as sub-surface deposits are accessed for removal.

In conclusion, following the collection of analytical air samples during a crude oil release, it is important to report the presence and estimated concentrations of TICS. It is also important to continue to expand and refine the analyses presented here as additional data from crude oil releases or additional toxicity data for crude oil VOCs becomes available.

FIGURE CAPTIONS:

Figure 1. Prolife of crude oil VOCs in relation to PAC and worker health protective values
VOCs detected in crude oil were ranked based upon either a PAC-1 Ratio (panel A), PAC-2 Ratio (panel B) or worker CHPV Ratio (panel C). Ratios were calculated by dividing the

mean concentration of the specific VOC detected in crude oil air samples by the respective PAC-1, PAC-2 value or worker CHPV. Open blue circles correspond to target VOCs for the TO-15 GC/MS method used to analyze the samples. Open red squares are TICs from the TO-15 GC/MS method. Blue and red symbols correspond to the left y-axes. Horizontal dotted lines corresponds to ratios of 0.01 and 1, respectively. Gray triangles are the mean concentrations of VOCs (in ppm) detected in the air and correspond to the right y-axes.

Figure 2. Time course analysis of crude oil VOCs in relation to PAC Ratios and worker CHPV Ratios

Air samples were taken in the breathing zone in proximity to crude oil released during Event 1A (panels A and C) and 1B (panels B and D) during days 1, 2 and 3 of the response. Numbers 1, 2 and 3 correspond to the first, second and third day of the event, respectively. The time course for target VOCs (blue circles) and TICs (red squares) detected in the air samples is shown in terms of their respective PAC-1 (open symbols, solid lines) or PAC-2 ratios (closed symbols, dotted lines) in panels A and B and in terms of their CHPV for panels C and D. For some chemicals, the PAC-1 and PAC-2 values are the same; therefore, the time course for only the PAC-1 values is shown in Panels A and B. The horizontal dotted lines correspond to ratios of 0.1 and 1, respectively.

TABLES:

| Table 1. Descriptions of crude oil release events. | | | |
|---|------------------------|-----------------------------|----------------------|
| | Event 1A and 1B | Event 2 | Event 3 |
| Event Type | Pipeline Release | Pipeline Release | Railcar release |
| Type of Oil Released | Heavy crude oil | Crude petroleum oil | High sweet crude oil |
| Flash Point | < 21 °C | < 23 °C | < 40 °C |
| Shipping Name | Petroleum Sour Crude | Petroleum crude oil (sweet) | Petroleum crude oil |
| Hazard Class and Division | 3 | 3 | 3 |
| Packing Group | II | NA | II |
| Sulfur Content | > 1 % | < 1 % | < 1 % |
| Boiling Point / Range | > 35 °C | > 38 °C | > 35 °C |
| Average Temperature | 53.6 °F | 53.8 °F | 48 °F |
| Average Humidity | 90 | 88 | 66 |
| Average Atmospheric Pressure at Sea Level | 30.2 mmHg | 30.1 mmHg | 30.2 mmHg |

| Table 2. Air concentrations (ppm) of VOCs and TICs detected in air sampled in proximity to released crude oil. | | | | | | | | |
|---|--------------------------------|------------|-----------------------------|-------|------|------|------|------------------|
| | Analyte | CAS | Classification ^a | Event | | | | Mean Conc. (ppm) |
| | | | | 1A | 1B | 2 | 3 | |
| Aromatic hydrocarbons | | | | | | | | |
| | Benzene | 71-43-2 | Target / HAP | 0.04 | 0.11 | 0.29 | 0.18 | 0.16 |
| | Toluene | 108-88-3 | Target / HAP | 0.05 | 0.11 | 0.58 | 0.12 | 0.21 |
| | Ethylbenzene | 100-41-4 | Target / HAP | - | - | 0.10 | - | 0.10 |
| | Xylenes ^b | Multiple | Target / HAP | - | - | 0.54 | - | 0.54 |
| | Trimethylbenzene ^c | Multiple | Target | - | - | 0.18 | - | 0.18 |
| | 4-Ethyltoluene | 622-96-8 | Target | - | - | 0.03 | - | 0.03 |
| Cyclic hydrocarbons | | | | | | | | |
| | Methylcyclobutane | 598-61-8 | TIC | 0.15 | 0.47 | - | - | 0.31 |
| | Cyclohexane | 110-82-7 | Target | 0.09 | 0.27 | 0.73 | 0.35 | 0.36 |
| | Methylcyclohexane | 108-87-2 | TIC | 0.15 | 0.40 | 0.98 | 0.16 | 0.42 |
| | Ethylcyclohexane | 1678-91-7 | TIC | - | - | 0.13 | - | 0.13 |
| | 1,3-Dimethylcyclohexane | 591-21-9 | TIC | - | - | 0.14 | - | 0.14 |
| | cis-1,3-Dimethylcyclohexane | 638-04-0 | TIC | 0.03 | 0.06 | - | 0.06 | 0.05 |
| | 1,1,3-Trimethylcyclohexane | 3073-66-3 | TIC | - | - | 0.08 | - | 0.08 |
| | Methylcyclopentane | 96-37-7 | TIC | 0.24 | 0.73 | 0.07 | - | 0.35 |
| | Ethylcyclopentane | 1640-89-7 | TIC | - | - | 0.20 | - | 0.20 |
| | 1,1-Dimethylcyclopentane | 1638-26-2 | TIC | - | - | 0.10 | - | 0.10 |
| | cis-1,2-Dimethylcyclopentane | 1192-18-3 | TIC | 0.03 | 0.08 | - | 0.06 | 0.06 |
| | trans-1,2-Dimethylcyclopentane | 822-50-4 | TIC | 0.04 | 0.10 | 0.27 | 0.09 | 0.12 |
| | 1,3-Dimethylcyclopentane | 2453-00-1 | TIC | 0.03 | 0.08 | - | 0.06 | 0.05 |
| | cis-1,3-Dimethylcyclopentane | 1759-58-6 | TIC | - | - | 0.18 | - | 0.18 |
| | 1,2,3-Trimethylcyclopentane | 15890-40-1 | TIC | - | - | - | 0.03 | 0.03 |
| | 1,2,4-Trimethylcyclopentane | 4850-28-6 | TIC | - | - | - | 0.03 | 0.03 |

| Table 2 (continued). Air concentrations (ppm) of VOCs and TICs detected in air sampled in proximity to released crude oil. | | | | | | | | |
|---|-----------------------|-----------|--------------|------|------|------|------|------|
| Aliphatic straight chain hydrocarbons | | | | | | | | |
| | Propane | 74-98-6 | TIC | 0.04 | 0.12 | - | - | 0.08 |
| | Butane | 106-97-8 | TIC | 0.72 | 2.10 | - | 0.08 | 0.97 |
| | Pentane | 109-66-0 | TIC | 1.10 | 3.50 | - | - | 2.30 |
| | Hexane | 110-54-3 | Target / HAP | 0.30 | 1.10 | 1.30 | 1.90 | 1.15 |
| | Heptane | 142-82-5 | Target | 0.10 | 0.24 | 0.84 | 0.49 | 0.42 |
| | Octane | 111-65-9 | TIC | 0.04 | 0.10 | 0.28 | 0.06 | 0.12 |
| | Nonane | 111-84-2 | TIC | - | - | 0.17 | 0.03 | 0.10 |
| | Decane | 124-18-5 | TIC | - | - | 0.12 | - | 0.12 |
| Aliphatic branched chain hydrocarbons | | | | | | | | |
| | 2-Methylbutane | 78-78-4 | TIC | - | 3.40 | - | - | 3.40 |
| | 2,2-Dimethylbutane | 75-83-2 | TIC | 0.04 | 0.12 | - | - | 0.08 |
| | Isobutane | 75-28-5 | TIC | - | 1.10 | - | - | 1.10 |
| | 2-Methylpentane | 107-83-5 | TIC | 0.46 | 1.40 | 0.08 | 0.13 | 0.52 |
| | 3-Methylpentane | 96-14-0 | TIC | 0.25 | 0.74 | - | 0.08 | 0.36 |
| | 2,3-Dimethylpentane | 565-59-3 | TIC | - | - | 0.16 | 0.03 | 0.09 |
| | 2-Methylhexane | 591-76-4 | TIC | 0.07 | 0.16 | 0.44 | 0.07 | 0.18 |
| | 3-Methylhexane | 589-34-4 | TIC | 0.07 | 0.17 | 0.48 | - | 0.24 |
| | 2-Methylheptane | 592-27-8 | TIC | 0.04 | 0.09 | 0.22 | 0.07 | 0.10 |
| | 3-Methylheptane | 589-81-1 | TIC | - | - | 0.12 | - | 0.12 |
| | 2,6-Dimethyl-2-octene | 2216-33-3 | TIC | - | - | 0.10 | - | 0.10 |
| | 2,3-Dimethylnonane | 4057-42-5 | TIC | - | - | 0.07 | - | 0.07 |
| <p>^a Target = target compounds for US EPA TO-15 GC/MS method for profiling of VOCs in air samples. TIC = Tentatively identified compound for US EPA TO-15 GC/MS method for profiling of VOCs in air samples. HAP = hazardous air pollutants included in the Clean Air Act Amendments of 1990. ^b There are three isomers of xylene including <i>m</i>-, <i>p</i>-, and <i>o</i>-xylene (CAS #: 103-38-3, 106-42-3 and 108-38-3, respectively). In the PAC database, CAS# 1330-20-7 refers to total xylene isomers. Here all xylene isomers detected were summed within each event and averaged to obtain the mean concentration. ^c There are three isomers of trimethylbenzene including 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene (CAS #: 526-73-8, 95-63-6, 108-67-8, respectively). In the PAC database, each isomer is individually indexed. In this analysis, all trimethylbenzene isomers detected were summed within each event and averaged to obtain the mean concentration.</p> | | | | | | | | |

Table 3. PAC and CHPV values for VOCs detected in air samples collected in the vicinity of released crude oil.

| Analyte | PAC-1 Value | | PAC-2 Value | | Worker CHPV ^h | | PAC-1 Ratio | PAC-2 Ratio | CHPV Ratio |
|---------------------------------|-------------|--------|-------------|--------|--------------------------|----------------------|-------------|-------------|------------|
| | ppm | Source | ppm | Source | ppm | Source | | | |
| Benzene ^{a,c} | 52 | AEGL | 800 | AEGL | 0.1 | NIOSH | 0.0030 | 0.0002 | 1.5500 |
| Toluene ^{a,c} | 200 | AEGL | 1200 | AEGL | 20 | ACGIH | 0.0011 | 0.0002 | 0.0107 |
| Ethylbenzene ^{a,c} | 33 | AEGL | 1100 | AEGL | 100 | OSHA / NIOSH / ACGIH | 0.0030 | 0.0001 | 0.0010 |
| Xylenes ^{a,c} | 130 | AEGL | 920 | AEGL | 100 | OSHA / NIOSH / ACGIH | 0.0042 | 0.0006 | 0.0054 |
| Trimethylbenzenes ^a | 140 | AEGL | 360 | AEGL | 25 | NIOSH / ACGIH | 0.0013 | 0.0005 | 0.0070 |
| 4-Ethyltoluene ^a | 12 | TEEL | 130 | TEEL | - | - | 0.0028 | 0.0003 | - |
| Cyclohexane ^a | 100 | TEEL | 100 | TEEL | 100 | ACGIH | 0.0036 | 0.0036 | 0.0036 |
| Methylcyclohexane ^b | 400 | TEEL | 400 | TEEL | 400 | NIOSH / ACGIH | 0.0011 | 0.0011 | 0.0011 |
| Methylcyclopentane ^b | 0.77 | TEEL | 8.5 | TEEL | - | - | 0.4489 | 0.0407 | - |
| Propane ^b | 5500 | AEGL | 17000 | AEGL | 1000 | OSHA / NIOSH / ACGIH | >0.0001 | >0.0001 | 0.0001 |
| Butane ^b | 5500 | AEGL | 17000 | AEGL | 800 | NIOSH | 0.0002 | 0.0001 | 0.0012 |
| Pentane ^b | 120 | TEEL | 610 | TEEL | 120 | NIOSH | 0.0192 | 0.0038 | 0.0192 |
| Hexane ^{a,c} | 300 | TEEL | 3300 | AEGL | 50 | NIOSH / ACGIH | 0.0038 | 0.0003 | 0.0230 |
| Heptane ^a | 440 | TEEL | 440 | TEEL | 85 | NIOSH | 0.0009 | 0.0009 | 0.0049 |
| Octane ^b | 300 | TEEL | 385 | TEEL | 75 | NIOSH | 0.0004 | 0.0003 | 0.0016 |
| Nonane ^b | 200 | TEEL | 200 | TEEL | 200 | NIOSH / ACGIH | 0.0005 | 0.0005 | 0.0005 |
| Decane ^b | 1.9 | TEEL | 20 | TEEL | - | - | 0.0632 | 0.0060 | - |
| 2-Methylbutane ^b | 600 | TEEL | 610 | TEEL | - | - | 0.0057 | 0.0056 | - |
| 2,2-Dimethylbutane ^b | 510 | TEEL | 510 | TEEL | - | - | 0.0002 | 0.0002 | - |
| Isobutane ^b | 800 | TEEL | 800 | TEEL | 800 | NIOSH | 0.0014 | 0.0014 | 0.0014 |
| 2-Methylpentane ^b | 510 | TEEL | 510 | TEEL | - | - | 0.0010 | 0.0010 | - |
| 3-Methylpentane ^b | 510 | TEEL | 510 | TEEL | - | - | 0.0007 | 0.0007 | - |
| 2-Methylheptane ^b | 300 | TEEL | 385 | TEEL | - | - | 0.0003 | 0.0003 | - |

^a Target, USEPA TO-15 Method ^b TIC, USEPA TO-15 Method. ^c HAP. ^h The worker critical health protective value (CHPV) is the minimum value amongst OSHA, NIOSH and ACGIH TWA values. Where multiple sources are listed, values are the same from each source.

Table 4. Comparative ranking of VOCs using worker or community health criteria.

| Analyte | Worker CHPV Ratio Rank | PAC-1 Ratio Rank | PAC-2 Ratio Rank |
|--------------------|------------------------|------------------|------------------|
| Benzene | 1 | 9 | 18 |
| Hexane | 2 | 6 | 14 |
| Pentane | 3 | 3 | 4 |
| Toluene | 4 | 13 | 19 |
| Trimethylbenzenes | 5 | 12 | 13 |
| Xylenes | 6 | 5 | 11 |
| Heptane | 7 | 16 | 9 |
| Cyclohexane | 8 | 7 | 5 |
| Octane | 9 | 19 | 15 |
| Isobutane | 10 | 11 | 6 |
| Butane | 11 | 21 | 22 |
| Methylcyclohexane | 12 | 14 | 7 |
| Ethylbenzene | 13 | 8 | 21 |
| Nonane | 14 | 18 | 12 |
| Propane | 15 | 23 | 23 |
| 4-Ethyltoluene | - | 10 | 17 |
| 2,2-Dimethylbutane | - | 22 | 20 |
| 2-Methylbutane | - | 4 | 3 |
| Methylcyclopentane | - | 1 | 1 |
| Decane | - | 2 | 2 |
| 2-Methylheptane | - | 20 | 16 |
| 2-Methylpentane | - | 15 | 8 |
| 3-Methylpentane | - | 17 | 10 |

Table 5. Proposed analyte list for laboratory analysis of air samples collected during a crude oil release.

| Aromatic hydrocarbons | |
|--|-----------------------------------|
| | Benzene ^{b,e} |
| | Toluene ^{b,e} |
| Cyclic hydrocarbons | |
| | Methylcyclopentane ^{c,d} |
| Aliphatic straight chain hydrocarbons | |
| | Pentane ^{c,d,e} |
| | Hexane ^{b,e} |
| | Decane ^{c,d} |

^aThe proposed analyte list includes chemicals with a PAC or worker CHPV ratio greater than 0.01. ^bTarget. ^cTIC. ^dSelected from analysis of PAC ratios. ^eSelected from analysis of worker CHPV ratios.

Table 6. Combined ranking of chemicals on proposed crude oil analyte list.

| Analyte | PAC-1 or CHPV Ratio |
|--------------------|---------------------|
| Benzene | 1.5500 ^b |
| Methylcyclopentane | 0.4489 ^a |
| Decane | 0.0632 ^a |
| Hexane | 0.0230 ^b |
| Pentane | 0.0192 ^b |
| Toluene | 0.0107 ^b |

^aValue corresponds to PAC-1 ratio. ^bValue corresponds to worker CHPV ratio.

Table 7. Real-time air monitoring methods for crude oil VOCs.

| Analyte | MultiRAE/ AreaRAE ^a | ppbRAE ^a | Gastec ^b | MIRAN SapphIRe ^c |
|--------------------|--|---|------------------------------------|--------------------------------|
| Benzene | 0.1-2000 ppm [0.53] | 0.001-200 ppm [0.53] | 121 L, 0.1-65 ppm | 2-200 ppm |
| Methylcyclopentane | 0.1-2000 ppm [1.5±0.5] ^d | 0.001-200 ppm [1.5±0.5] ^d | - | - |
| Decane | 0.1-2000 ppm [1.4] | 0.001-200 ppm [1.4] | 105 ^e , 200-6000 ppm | - |
| Hexane | 0.1-2000 ppm [4.3] | 0.001-200 ppm [4.3] | 102 L, 10-1200 ppm [0.08] | 0.25-500 ppm |
| Pentane | 0.1-2000 ppm [8.4] | 0.001-200 ppm [8.4] | 104, 30-1680 ppm [1.2] | 6-2000 ppm |
| Toluene | 0.1-2000 ppm [0.50] | 0.001-200 ppm [0.5] | 122 L, 1-100 ppm | 1-1000 ppm |

^a Photoionization detection methods. Values are the instrument detection range [correction factor for 10.6 eV lamp] ^b Colormetric tube method. Values are the tube manufacturer's part number, detection range, [correction factor if specified]. ^c Infrared spectroscopy method. Values are the measuring range. ^dValue estimated by RAE Technologies (personal communication).

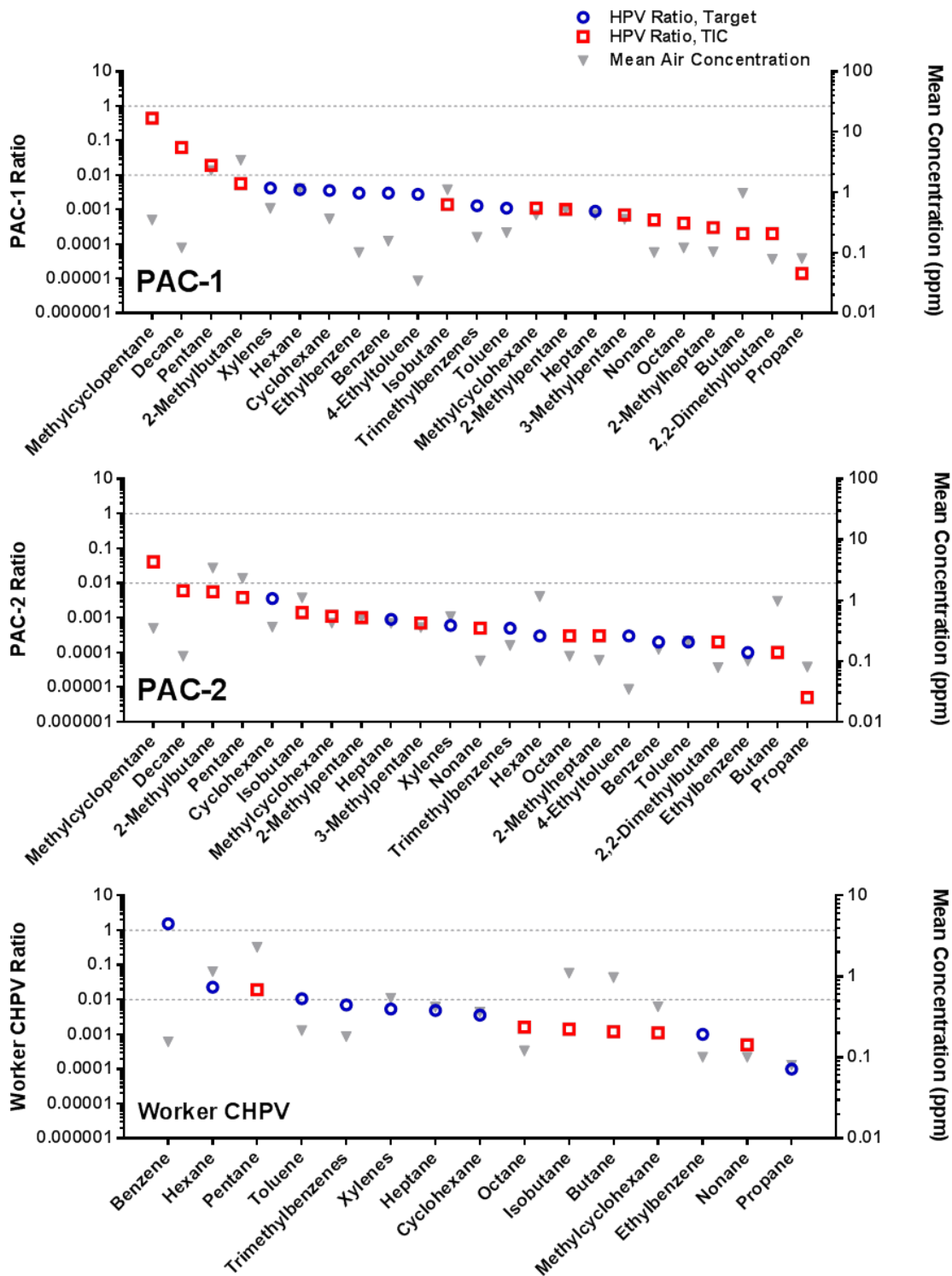


Figure 1.

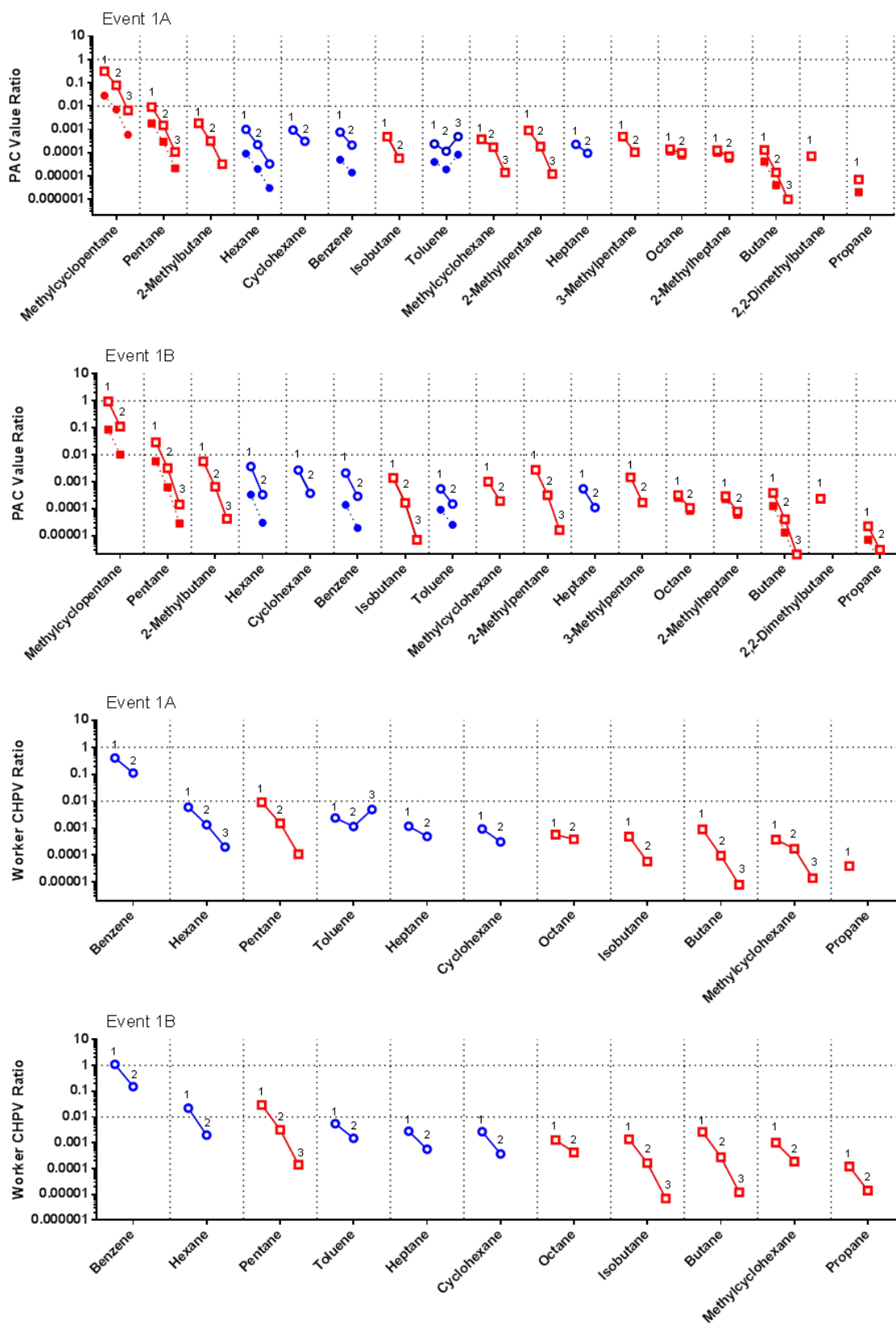


Figure 2.

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