



THE SCIENCE OF READYSM

TECHNICAL GUIDANCE
SUPPORTING THE ESTABLISHMENT OF A
VOLATILE ORGANIC COMPOUND ACTION LEVEL
FOR GOM CRUDE OIL INCIDENTS

EXECUTIVE SUMMARY

In the event of a seafloor Gulf of Mexico (GoM) Crude Oil Well Blowout, rig personnel, emergency responders, and remediation engineers and scientists may be in the vicinity of, or develop the need to operate adjacent to, surfaced crude oil. Oil released from the seafloor travels upwards through the seawater – often thousands of feet – subsequently surfacing and releasing a fraction of its remaining mass into the air, termed ‘Crude Oil Volatile Compounds’. While some light end hydrocarbons (i.e., benzene) may be scrubbed from the oil during its transition from the seafloor to the surface, the remaining volatiles are often dispersed via volatilization and wind dispersion. It is these surfaced Crude Oil Volatile Compounds that may pose a hazard to those attempting to control and remediate the well in the Source Control Area. This report was prepared for the purposes of determining if a total volatile organic compound (VOC) action level could be developed for these Crude Oil Volatile Compounds and, if so, identify what this action level – and associated action(s) – may be. Subsequently, this report highlights the use of readily available instruments and their role in detecting Crude Oil Volatile Compounds.

The first challenge in establishing a Crude Oil Volatile Compound Action Level (AL) value is to benchmark the toxicity of the chemical, agent or mixture against reliable dose-response data that describe the advance of symptoms of interest with increasing exposure. Various organizations, agencies and institutions have established exposure levels that were considered; however, only the Emergency Response Planning Guideline (ERPG) values established by the American Industrial Hygiene Association provided a set of exposure values for Crude Oil or Crude Oil Volatile Compounds. A review of the ERPG Guidance Documents identified the most sensitive endpoint for exposure to light end hydrocarbon mixtures as ocular irritation, identifying a Lowest Observable Adverse Effects Level (LOAEL) at 160 ppm. Because the purpose of an action level is to identify ambient concentrations of a compound prior to the development of adverse effects, a recommended AL of 100 ppm Crude Oil Volatile Compounds (or $\frac{1}{2}$ of the ERPG-1 value of 200 ppm) is suggested for durations of up to 24 hours. Because environmental and sample variables may impact benzene concentrations, because benzene concentrations do vary among petroleum samples, and because of the recognized health hazard of benzene, benzene-specific monitoring should be undertaken. Additional monitoring for other BTEX components and for naphthalene should be undertaken.

The next challenge is establishing or validating a method to rapidly and efficiently detect and quantify Crude Oil Volatile Compounds with the instrumentation readily available in an offshore environment or during an emergency incident. Photoionization Detectors (PID) – often found on hand-held multi-gas meters – can fulfill this role as they offer real time evaluation of atmospheric contaminants; however, the sensors record general airborne volatile compounds and require the application of a scientifically developed chemical-specific or mixtures correction factor (CF) to accurately quantify the analyte or

mixture of interest. A review of the scientific literature did not identify a CF for Crude Oil Volatile Compounds. Because such a CF is a necessity when utilizing a PID for comparison of results to an AL, this report highlights several approaches to PID CF development for Crude Oil Volatile Compounds including both a literature-based mathematical approach and an empirical laboratory-based derivation.

A mathematical component-based approach was undertaken utilizing the molar composition of identified components and CF values for individual components, if available. Airborne chemical mixture data were obtained from a variety of crude oil incidents as available in the published literature, including a seafloor release with exposure measured on a working platform. Estimates based on these published data yielded CF that ranged from 1.2 – 2.54, slightly higher than those published for other hydrocarbon mixtures. Simultaneously, a Chevron-supplied GoM Crude Oil sample was sent to a National Institutes of Occupational Safety and Health (NIOSH) laboratory, where VOCs were analyzed for application in the empirical derivation of a PID correction factor. The NIOSH evaluation of vapor generated from the supplied crude oil yielded a PID CF value of 1.33.

Taken collectively, a PID CF (10.6 eV Lamp) correction factor of 1.3 is recommended for crude oil vapor, pertinent to the exposure scenario here considered. Application of this correction factor to the 100 ppm Crude Oil Volatile Compounds AL indicates that such a concentration is achieved when the PID reads 77 ppm when calibrated with isobutylene gas.

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1.0 Background and Introduction

In the event of a sub-sea well blowout in the GoM, rig personnel and emergency responders may be exposed to Crude Oil Volatile Compounds following their release at the seafloor and migration through the water column to the ocean surface. While readily available hand-held instruments are capable of measuring general VOCs (in isobutylene units, if isobutylene is used as a calibration gas), there is currently no available general VOC action level (AL) for crude oil vapors nor is there a developed correction factor (CF) for which to extrapolate the concentration of general VOCs (in isobutylene units) to the concentration of Crude Oil Volatile Compounds in the air. This document will seek to provide solutions to both of these questions with the overall goal of providing a recommendation for an acute Crude Oil Volatile Compound Action Level which may be utilized in for both initial health and safety decision making immediately following the emergency event and for an acute time frame during oil spill remediation.

Crude oil contains myriad components, and the composition and ratio of components varies by deposit, depth of well and geographic location. These components are separated and blended to best match their intrinsic properties for specified uses. For example, less volatile, higher molecular weight components are used in products like greases and lubricants, while more volatile lighter molecular weight components are used in products like fuels and solvents. Lighter components having higher vapor pressures are more likely to volatilize from crude oil than heavier molecular weight components with lower vapor pressures. In addition, the release of crude oil during a well blowout results in an uncontrolled release of pressure, and pressurized gaseous components (like methane) may exit the crude oil based primarily on the pressure gradient.

The release of crude oil below a column of sea water imposes another consideration – that of water solubility of component chemicals. While many components of crude oil are not water soluble, there is a gradient of solubilities among the components, such that some components may be fairly effectively “scrubbed” from surfacing crude oil (Ryerson et al., 2011), resulting in a preferential removal and dilution of these components into sea water. These and other factors impacting the concentration of VOC components in crude oil following an unanticipated release need to be considered when assessing the exposure and risks resulting from inhalation exposure to crude oil vapors.

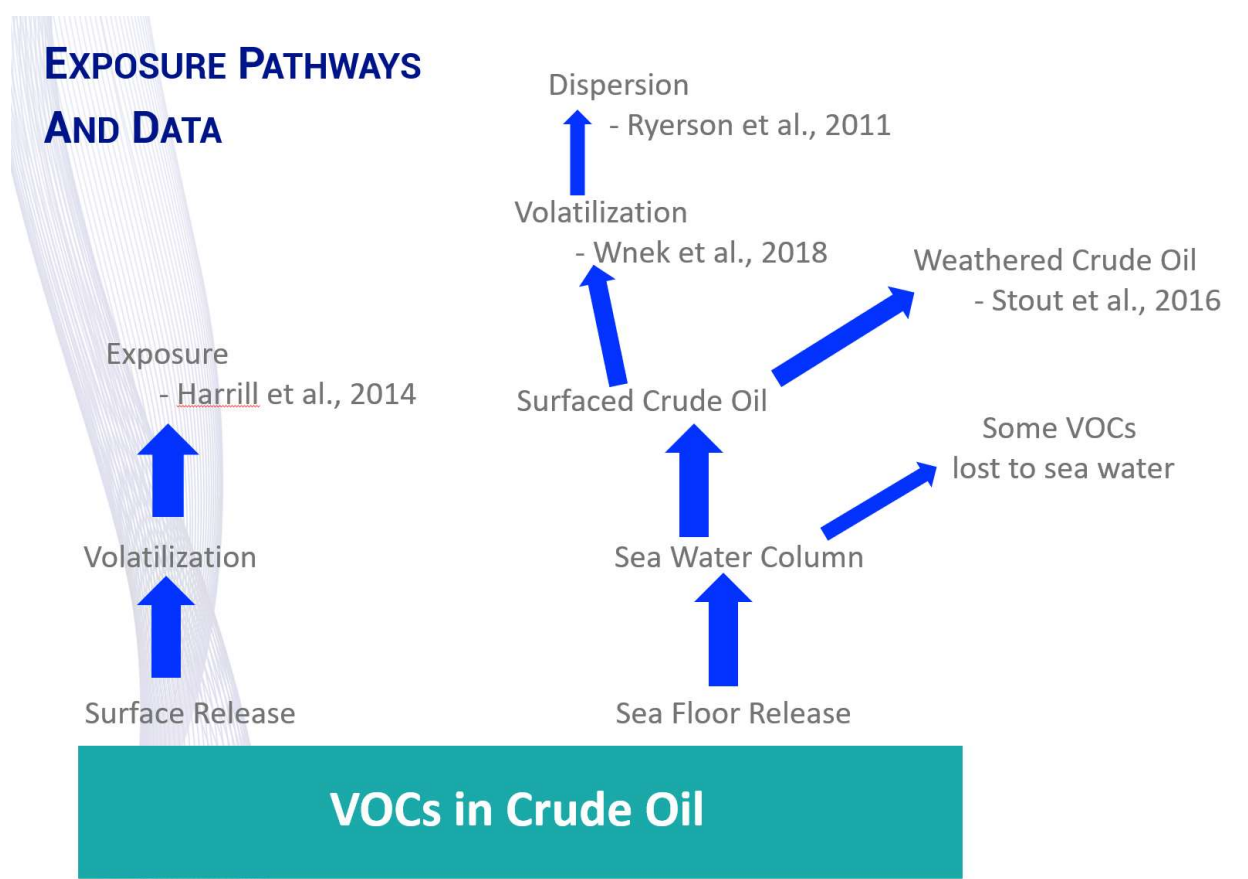
2.0 Identifying the Exposure Scenario

The exposure scenario presented here considers an individual in the Oil and Gas Industry located within the Source Control Area of a damaged GoM oil platform or vessel as a result of, or in response to, a well blowout. The worker is assumed to be present during the first 24 hours of a blowout and exposed via inhalation only. The crude oil involved will have been released at the seafloor and will have surfaced through perhaps thousands of feet of seawater. The surfaced oil will be fresh, not weathered, and the VOCs released will be those immediately released, or released during the initial minutes or hours of

surfacing, with released crude oil continuing to surface, thus “replenishing” the VOCs which may have dissipated due to wind drift or rising through the atmosphere.

Thus, the mixture of VOC components to which workers are expected to be exposed will be a subset of the components present in crude oil, reduced by considerations of pressure-based off-gassing and solubilization in seawater, and a low vapor pressure of some remaining (surfacing) components. . The exposure pathway is demonstrated in **Figure 1**.

Figure 1. Exposure Pathway for Crude Oil Volatile Compounds



Exposure Pathway for Crude Oil Volatile Compounds. For this scenario, crude oil is released at the seafloor, rises through the sea water column with loss of some components, reaches the surface and volatile components are released from surfacing crude oil. Volatilizing components enter the atmosphere and reach the breathing zone of workers, while other components remain in surfaced crude oil and are subjected to weathering. This figure identifies some studies which have characterized the VOC composition of vapors originating in crude oil. These data are more fully presented and evaluated later in this report.

3.0 Development of a Conceptual Site Model

The conceptual model comprises problem formulation, a description of the conceptual model and an analysis plan. The conceptual model for this analysis addresses the exposure, risk and need for detection of contaminant concentrations which have been associated with a predetermined level of a specified effect.

3.1 Problem Formulation

Scenario: Accidental release of crude oil from a GoM sea floor drilling operation resulting in crude oil surfacing and subsequent volatilization of VOCs in the absence of fire. Irritant endpoints (i.e., ocular irritation) have been identified as the most sensitive endpoint for acute exposure. As exposure increases, central nervous system effects may become evident.

Objectives:

- (1) Determine an Action Level for Crude Oil Volatile Compounds (as VOCs) based on toxicological endpoints for acute exposure in an emergency scenario.
- (2) Validate a correction factor to quantify exposure to Crude Oil Volatile Compounds using hand-held PID instrument.

Perhaps the single greatest benefit of documenting Problem Formulation considerations is its use in guiding an assessment that can be used to support a risk management decision (NRC, 2009). One goal of Problem Formulation is to lay out the technical aspects of the assessment consistent with the decision context. This is accomplished via development of a Conceptual Model and an Analysis Plan. In this case, the decision context might be most concisely established as,

What level of Crude Oil Volatile Compounds inhalation exposure measured as total VOCs resulting from crude oil released at the sea floor is associated with the development of irritant effects and how can this level of exposure be quickly measured?

3.2 Conceptual Model

Stressor: Crude Oil Volatile Compounds (as VOCs)

This exercise focuses on the volatile constituents of source crude oil (SCO). The constituents, especially the volatile constituents, have been characterized in some SCO samples. The VOC content of crude oil types found in the Gulf of Mexico will be targeted for this analysis.

Source: Surfaced, non-burning Crude Oil

The exposure scenario includes accidental release of crude oil from sea floor drilling operations. The source of the exposure is crude oil released at the sea floor and surfaced by moving upward through the water column.

Exposure Media: Air

This exposure is characterized by the volatilization of Crude Oil Volatiles in the ambient air. Furthermore, it is assumed that individuals working in the Source Control Area may experience an inhalation exposure as part of their occupational work adjacent to surfaced oil.

Receptors: Humans (Occupational)

For the purposes of this risk assessment, the target receptor is a human. Furthermore, due to the job description and location, this population likely represents ‘healthy workers’, thus minimizing the potential for exposure to sensitive sub-populations. Humans exposed via inhalation to elevated levels of released VOCs in an acute scenario may experience symptoms of irritation and at higher levels, intoxication.

Attribute Change: Irritation

While exposure to Crude Oil Volatiles can result in several types of acutely manifested as well as delayed (chronic) effects, this exercise will focus on the irritation as the initial sign of exposure and potential intoxication. Reliance on irritation as the sentinel effect will be protective against more serious effects which occur with increasing concentration.

3.3 Analysis Plan

Approach: This assessment will identify an Action Level for Crude Oil Volatile Compounds through efforts aimed at examining the volatile components of crude oil vapor and applying a component-based mixtures toxicity approach to estimate the risk of each mixture, as well as examining exposure guidance values for

similar mixtures. The approach to VOC quantitation will involve developing a mixtures CF¹ for use in a PID Instrument, based on information available for components of several pertinent VOC mixtures, as well empirically determining the correction factor for a pertinent crude oil sample.

To enable PID quantitation of Crude Oil Volatile Compound-containing atmospheres, CF values will be identified for components and applied in a mixture-based approach to estimate the CF for the identified, characterized mixtures. A separate analysis will identify the VOC components released from a Chevron-supplied GoM crude oil sample, and a correction factor will be developed for the crude oil sample provided.

Scope: The evaluation will center on the volatiles released from surfaced crude oil, exposed immediately to humans via inhalation of contaminated air in the immediate vicinity of the surfaced oil. It will not evaluate exposures to or risks from exposures to VOCs resulting from subsequent proximity to crude oil surfaced and further dispersed or weathered. The analysis will focus on irritant effects.

Agent: The assessment will focus on volatile components of crude oil, characterized as “total VOC” to enable a comparison of direct-read, PID instrumentation readings to risk values.

Exposure Route: It is anticipated that occupational exposure to Crude Oil Volatile Compounds would most likely occur via the inhalation route. It is anticipated that Crude Oil Volatile Compounds may emanate from crude oil released at the sea floor and surfaced through sea water as a result of natural buoyancy (density). Volatilization of Crude Oil Volatile Compounds from surfaced oil into the air in the breathing zone of workers in the vicinity will result in inhalation exposure. Neither oxidation, reduction, degradation nor metabolism is expected to influence the type of composition of volatiles derived from released crude oil. However, some evidence may indicate that lower molecular weight VOCs maybe “scrubbed” from surfacing oil due to solubilization in sea water.

Absorbed Dose: Because the irritancy of VOCs results with direct contact with sensitive tissues like eyes and mucus membranes of the respiratory tract, no evaluation of absorption into blood or tissues will be examined.

Effects: This evaluation will focus on irritant effects for an acute exposure time frame. For the purposes of this report, the acute time frame is 24 hours. It is anticipated that characterization and assessment of the atmosphere surrounding a well blowout at time points beyond 24 hours would be performed using chemical specific monitoring or analytical air sampling.

¹ PIDs are not chemical-specific and the instrument reading must be “corrected” for detection of the compound or the mixture of interest when calibrated with a specific calibration gas (i.e., isobutylene). CFs for some mixtures are available. CF values for mixtures are determined by the composition of the mixture and the CF values for the chemicals comprising the mixture. Compilation of CF values are available, and many of the chemical components of the VOC mixtures here evaluated have CF values developed for them.

Data Sources: Reliable sources of information from the peer reviewed literature or from other authoritative sources will be used to determine or estimate the volatile content of crude oil and atmospheric concentrations of VOCs associated with a crude oil release. Where necessary and appropriately justified, data from a studied crude oil type may be used to estimate content and exposure values for an unstudied crude oil type.

Quantitative Approaches: Routinely applied risk methods including the hazard index (HI)-based dose additive models will be employed. Hazard quotient (HQ) values for some unstudied chemicals may be accomplished by developing and including estimates of potency developed through grouping efforts, which may include the Reciprocal Calculation Method used by ACGIH®, based on Group Guidance Values previously established. HQ values for other, specifically characterized components, may be developed through chemical-specific, rather than grouped, information. The application of the Hazard Index approach is consistent with dose addition models for mixtures risk, because the expected mode of action to produce irritant effects is expected to be similar (or the same) for these components.

Uncertainties/Assumptions: Because risk is a function of hazard and exposure, it will be important to separate the uncertainties and assumptions according to their impact. For example, grouping approaches applied to crude oil volatile risk (e.g., McKee et al., 2005) assign potency values (guidance values) to groups of chemicals, often based on reliable information which may be available for one or only a few components of the group. Whether the potency of unstudied chemicals in the group is higher or lower than the “index” chemical for the group cannot be known. Lumping exposures to individual chemicals by group ignores the impact of within-group variability in the VOC content of source crude oil specimens.

A key uncertainty may be the relative composition of the crude oil source. Variations in VOC composition have been characterized for some sources, but the extent to which the composition of these sources relates to MC252 (or pertinent GOM source crude oil) has not been completely established. An uncertainty exists as to whether lower molecular weight VOCs may be removed from crude oil prior to surfacing. Whether or not this occurs can impact HI values combined in the estimation of risk. To address the impact of this uncertainty, risk estimates will be completed using the VOC content of subject crude oil and estimates of VOC exposures developed from site monitoring data. Both risk estimates will be converted to “total VOC” content for comparison.

Assuming that some low molecular weight components might not contribute to inhalation exposure will remove their contribution to the toxicity and HI value for the mixture. Because these lower molecular weight compounds may more efficiently move from air to blood and thence to brain, the impact of removing them is that the estimates of potency for the mixture may be underestimated.

Using ACGIH’s Reciprocal method to estimate risk through a HI approach imposes some uncertainty in translating risk from HI to actual exposure (ppm). Uncertainty is a result of the method treating the HI

contribution from each group equally, without regard to its contribution to the overall VOC exposure burden.

The development of a prototype VOC mixture *to develop a benchmark (guidance) exposure limit* may represent a defensible approach, but it also embodies uncertainty as to whether the prototype mixture actually represents the VOC content of the study (subject) sample. Using the VOC content of a “pure” (not previously released and surfaced) crude oil sample to determine the VOC content will provide valuable information. However, because the approach involves developing an Action Level based on total VOC content, and because not only the composition but also the ratios of components vary among sources of crude oil, there will be some uncertainty in extrapolating the level of risk at a given total VOC exposure from one sample of crude oil to another. Using VOC composition and risk data from an unreleased sample ignores the possibility that some components may be scrubbed by seawater during ascent, and the uncertainty associated with that proposition has been identified previously. Using a VOC sample that contains different, more, and potentially more (or less) potent VOC components will likely overestimate the risk from exposure to a VOC mixture containing components of a lesser toxic potency, and will likely underestimate the risk from exposure to a VOC mixture containing components of a higher toxicity.

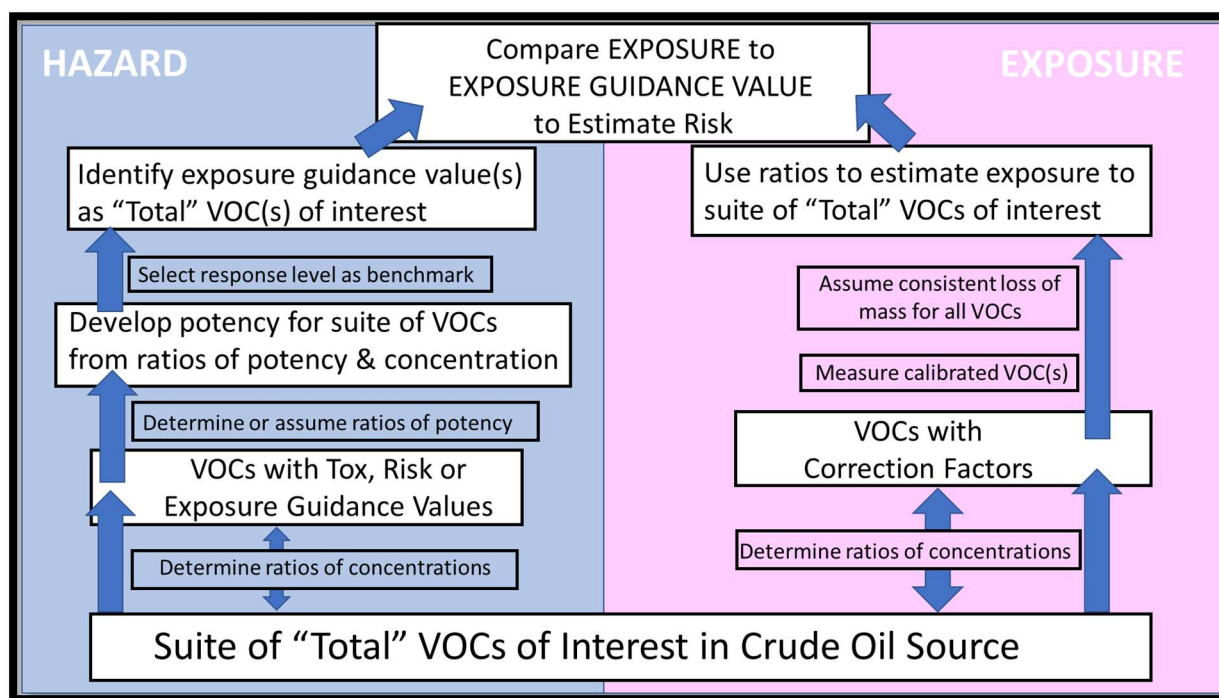
Many of these uncertainties could be reduced if the VOC content could be determined for immediately surfaced crude oil, or crude oil captured during surfacing but below the surface. Likewise, the laboratory-based determination of a correction factor for VOCs released from such a sample would also reduce an appreciable amount of uncertainty.

Figure 2 demonstrates the approaches used to estimate exposure to the Crude Oil Volatile Compounds of concern from SCO, and to estimate the hazard potential from VOCs of concern from SCO. Both approaches use information describing the ratios of VOCs within the SCO as the basis for estimation. A hazard estimate for the suite of VOCs in SCO is determined based on available estimates of toxic potency for VOC components, and potency estimates developed for unstudied components, combined with information describing the ratio of VOC components in SCO. An exposure estimate for the suite of VOCs in SCO is determined based on measured concentrations of VOCs for which correction factors are available, with adjustments made for unmeasured VOC components based on the ratio of VOC components in SCO. Risk estimates are developed by comparing the exposure concentration (“Exposure”) to the guidance value (“Hazard”).

Hazard and exposure will be addressed by component-based approaches shown in **Figure 2**. After identifying and determining the fractional composition of VOCs of interest in SCO, the hazard of the VOC mixture will be estimated using a relative potency factor-based approach where the potency of an unstudied component is scaled to the potency of the selected index chemical; the hazard contribution of all components to the mixture of concern (the suite of VOCs targeted in this analysis) will be scaled based on fractional composition. Risk at a preselected level of severity will be determined and expressed as

exposure to the mixture of concern. Exposure will be estimated based on fractional composition of the VOC mixture of concern in SCO, based on measured atmospheric concentrations of components for which correction factors are available. Adjustment of the concentration of measured components to concentration of all components of the mixture of interest will be accomplished through adjustments made on the basis for fractional composition of the mixture accounted for by the measured components. A comparison of the estimated exposure to the developed hazard (potency, risk toxicity) value will determine risk.

Figure 2. Estimating Hazard, Exposure and Risk from VOCs in Source Crude Oil



4.0 Chemical Mixtures Risk Assessment

Assessing the risks associated with exposure to a chemical mixture, such as Crude Oil Volatile Compounds, can be accomplished via whole mixtures approaches using data from the mixture of interest or a mixture deemed sufficiently similar on the basis of its constituents. Data from one mixture can be generalized to another, once the composition of each has been characterized (and an acceptable degree of similarity exists). For the purposes of this assessment, $\frac{1}{2}$ of the ERPG-1 value for Crude Oil Volatile Compounds will be considered as the basis for Action Level determination (discussed in section 5). In that, this paper adapts an existing exposure guideline level developed on the basis of underlying toxicity data developed

for another mixture and developed for an exposure duration appreciably shorter than the targeted 24-hour duration. A separate mixture, component-based evaluation will be conducted to “ground-truth” the Action Level value proposed (see Component Based Risk Estimates, below).

Component-based approaches utilize chemical (component)-specific data describing exposure to – and toxicity of – the individual identified components. This includes data on the ratio of their contribution to the mixture as a whole. Regardless of the approach to mixtures risk assessment, performing a dose-response assessment for a mixture (or to its components) requires data on both exposure and hazard. Hazard (dose-response) data for the whole mixture could be developed by conducting studies with laboratory animals exposed to controlled and well characterized vapors from materials of interest. Exposure should be quantified by a laboratory method (i.e., gas chromatography-mass spectrometry) to characterize the chemical composition of the whole mixture (a requirement to generalize findings to other mixtures) once they are characterized. When the total concentration of the whole mixture’s volatile components have been characterized to determine its concentration (units of mg/m^3), then a PID calibrated with isobutylene may be used to determine a CF) for the mixture – a necessary and presently absent variable required to enable PID-characterization of exposure. Coupling whole mixture-specific animal response data (e.g., for irritation) with exposure allows completion of the dose-response evaluation, and identification of exposures (exposure guidance values) specific to the exposure duration and severity of responses of interest.

The whole-mixture approach, in this case as applied to Crude Oil Volatile Compounds emanating from released and surfaced GoM Crude Oil, requires resources presently unavailable. An actual sample of the crude oil, untreated and released, and subjected to the scrubbing effect of seawater is required, as is access to an approved animal testing facility with inhalation exposure capability, and access to analytical chemistry support sufficient to identify and quantify VOC vapors both crudely and at a component level. This approach may be considered in the future.

4.1 Crude Oil Mixtures Exposure Data

A component-based approach requires information on both the exposure and hazard for individual components. Special care should be applied to examine data sources and to identify a source of exposure (and toxicity) data pertinent to the exposure of concern. The ideal data set would be one that characterizes Crude Oil Volatile Compound concentrations in air in those areas where workers are present at times that correlate with the surfacing of oil during an on-going response. This may represent a worst-case scenario. Thus, the most rapidly and effectively volatilizing of the VOCs are continually renewed, with concentrations diminished only by atmospheric dispersion.

Several publications (referenced in **Figure 1**) report on the characterization of chemical composition of crude oil or its volatilized components. Each reference is of differing relevance to the present analysis of inhalation exposure to released VOCs from freshly surfaced crude oil. The GoM well-blowout scenario is

one of a deep-water release and depressurization of untreated GoM Crude Oil with subsequent rising through the sea water column. Human exposures at working locations are anticipated to comprise volatile components; some “scrubbing” of more water-soluble compounds by sea water should be anticipated (Stout et al., 2016). Consideration of this scenario was used to evaluate the applicability of four VOC data sets, described below. Technical evaluations of these mixtures are discussed later.

Stout et al., (2016)

These authors examined the VOC content remaining in surfaced and weathered crude oil (even washed up onshore) following the Deep Water Horizon release. The samples analyzed were from the subject well, but the impact of appreciable weathering (wave action, sunlight, air) is expected to have caused an unquantified, but potentially nearly complete removal of the more volatile components – the exact type of component to which Source Control workers may be exposed-to while working in and around surfacing crude oil. For this reason, this characterization of components remaining in weathered crude oil was not deemed appropriate for this exercise.

During and following the DHW blowout, samples of floating and stranded (“beached”) crude oil were analyzed for chemical content and the results reported by Stout et al., (2016). These authors analyzed samples that had immediately surfaced, as well as samples that had been subjected to weathering, perhaps for as long as 7 weeks. The objective of the study was *“to reveal the composition of the surface oil, particularly PAHs, ranging from the time when oil first reached the sea surface to when it was found stranded over approximately 800 km of northern GoM shorelines within about seven weeks after the spill ended.”* No analysis of airborne materials was conducted. Data may imply inhalation exposures to at least the components remaining in surfaced oil. Because the analysis focuses on collected oil samples and not atmospheric concentrations, these data may underestimate the number of contaminants in an inhalation exposure, because the possibility of volatilization of some components of surfaced oil cannot be ruled out.

Stout et al., (2016) reported that *“Oil collected immediately upon reaching the sea surface had already lost most mass below n-C8, from dissolution of soluble aliphatics, monoaromatics, and naphthalene during the oil’s ascent with further reductions extending up to n-C13 due to the onset of evaporation.”* These findings indicate that exposure to the mixture of Crude Oil Volatile Compounds emanating from weathered crude oil (oil that has been surfaced for days or perhaps even hours), may not represent exposure to the mixture of VOCs released from freshly surfaced (or continually surfacing) crude oil. For this reason, attention should be preferentially given to data from Stout et al., (2016) pertinent to the most freshly surfaced of the samples taken (JF3-2km-onet-20100616-surf-N143; Table 2) crude oil, and to the extent possible with respect to volatilized, atmospheric concentrations. It must be recognized that data from this sample represent a conservative estimate of the number of components to which inhalation exposure may occur.

The analysis of oil content of components was reported for “*fresh*” Macondo oil, (apparently not surfaced), for “*floating*” Macondo oil (apparently the JF3 sample collected “*within seconds*” of surfacing, and stranded Macondo oil collected from shorelines. Data presented in **Table 2** show the concentrations of analytes in the oil samples, presented as microgram per gram of oil (not atmospheric, volatilized compound). In general, with increased duration and weathering, the content (micrograms per gram oil) of lighter compounds decreased with time (implied by fresh versus surfaced versus stranded characterizations), while the concentrations of heavier components increased with time. This is expected given the preferential volatilization of lighter compounds, leaving heavier compounds to make up a higher fraction of the remaining oil mass.

Relative to their goal of characterizing oil components following surfacing and weathering, and consistent with some findings indicative of dissolution of some oil components in seawater, Stout et al. apparently did not fully incorporate post-surfacing volatility (which may occur immediately) as a possibility when attributing differences between the components of surfaced oil versus fresh oil solely to dissolution in sea water. While the assumptions embedded in this approach have little bearing on the interpretations of the impact of weathering on crude oil composition, in failing to directly address volatilization, it substantially complicates the interpretation of these data relative to an inhalation exposure. For example, through a comparison of components between fresh and surfaced oil samples, Stout et al. demonstrate² the dissolution of a number of crude oil components in sea water, accounting for as much as 100% of some components. These findings demonstrate the impact of sea water-dissolution during surfacing, and underscore the conservatively-biased uncertainty in using data (A) describing the composition of liquid crude oil (versus headspace analysis) or (B) describing the vapor concentrations of components from releases from locations other than seafloor when estimating the type, number and concentration of crude oil components to which humans may be occupationally exposed to in environments containing freshly-surfaced crude oil.

Findings from Ryerson et al., (2011; discussed in more detail below) provide additional context (in the form of complete or near-complete volatilization of some VOC components) for the interpretation of the data from Stout et al., (2016) relative to exposure. Stout et al. reported appreciable differences between the VOC content of immediately surfaced versus fresh (not surfaced) Macondo oil. Such differences demonstrate a complete absence of some components in surfaced versus fresh oil. These authors interpreted the findings as representing a complete removal or dissolution of these components during surfacing, without considering post-surfacing volatilization.

It is important to consider the goal of the Stout et al. investigation which was to consider the impact of weathering on the content of oil. In that context, whether the components were removed through the impact of seawater or the impact of volatilization (which may be immediate) has no impact on findings

² See Stout et al. Supplemental Table S-5, Panel A

interpreted in the context of this investigation. Indeed, atmospheric samples were not taken, and so no analysis of components volatilized from this sampling was undertaken. Differences in some components, interpreted in the context of other studies, are informative.

Harrill et al., (2014)

Harrill et al., (2014) reported airborne VOCs following the surface release of various crude oil types from pipeline and rail car spills. None involved interaction with seawater, and so these data do not characterize the impact of seawater “scrubbing” of VOC chemicals. As such, these data may indicate a ‘worst case’ exposure scenario in terms of the number of components. None of the samples are of Macondo crude oil. Because the chemical composition of crude oil varies by geographic region and because the inherent toxicity of the components whose content may differ between this exposure scenario and that involving a seafloor release is unknown, these data are not directly applicable to the exposure scenario pertinent to this this assessment. Nonetheless, these data are of utility for review as they represent a potential inhalation exposure to VOC components volatilized from released crude oil.

Data presented by Harrill et al., (2014) demonstrate VOCs characterized according to USEPA Method TO-15. The samples were reportedly taken from pipeline and rail spills of crude oil samples characterized as “*heavy crude oil (petroleum sour crude)*”, “*crude petroleum oil (petroleum crude oil)*”, and “*high sweet crude oil (petroleum crude oil)*”. It is possible that these oils had been subjected to chemical treatment prior to transportation, and none of these samples of crude oil were subjected to “*extraction*” of components by seawater (as evaluated Stout et al., 2016). Thus, reliance on qualitative and quantitative characterizations of volatilized components of these samples as surrogates for crude oil VOC components to which humans are exposed following a deep-water blowout presents both complications and uncertainties. These are conservatively biased toward a potential qualitative and quantitative over estimation of the type and number of components comprising the exposure relative to that expected to occur following a release of crude oil from the seafloor and freshly surfaced. Additional uncertainties surround the uncharacterized geographical impact of the samples.

Nonetheless, the data for the “*high sweet crude oil*” rail car spill sample from Harrill et al. and associated interpretations provided important context for this investigation. These data will be discussed later, relative to developing a correction factor for crude oil VOCs.

Ryerson et al., (2011)

Ryerson et al., (2011) presents findings from an aerial collection and analysis of crude oil volatile compounds taken from flyovers of the Deep Water Horizon rig during the release. These data potentially underestimate exposure in that they identify chemicals that have been released from surfaced Macondo crude oil but were taken potentially hundreds of feet above the location in which workers may be exposed. This difference may be accompanied by further dispersion and potential loss of some

components, or their dilutions to concentrations below limits of detection. However, it may be assumed that the components identified by Ryerson et al., (2011) represent at least some of the components to which an individual in the Source Control Area may be exposed during a seafloor well blowout.

An analysis of atmospheric concentrations of VOCs over the DWH spill was also reported by Ryerson et al., (2011). Citing the separate impact of water dissolution and atmospheric evaporation, these authors present and interpret data on atmospheric concentrations of VOCs to evaluate the extent of a crude oil release, not to estimate worker exposure or assess risk/safety. These authors estimate that 33% of the mass of released crude oil dissolved in the water column, and that 14% of the mass that surfaces *“evaporates promptly after surfacing”*. Data were collected by an instrumented P3 aircraft flying above the Deep Water Horizon platform during initial containment and cleanup operations several days after a cap had been loosely secured. These data were used to quantify atmospheric emissions from surfaced oil escaping the cap and from flaring of natural gas recovered via the cap. Emissions from deliberately burned surface oil *“were measured but are not presented”*. By determining differences in their content in reservoir fluid oil and the atmosphere, these authors concluded that data for ethane and benzene *“demonstrates nearly complete dissolution of these VOCs in the water column prior to surfacing”*. Further comparisons (see Figure 2 of Ryerson et al.) of atmospheric concentrations, normalized to atmospheric n-hexane concentrations; to reservoir fluid concentrations, also normalized to fluid reservoir n-hexane concentrations demonstrated a decreased normalized ratio (atmosphere to reservoir) decreasing with increasing water solubility, demonstrating the impact of dissolution in seawater in decreasing the potential for atmospheric release and subsequent human exposure to some VOC components of released crude oil.

Ryerson et al. quantified atmospheric concentrations of 38 VOC components of Macondo crude oil; these data will be discussed later, relative to their value in determining a PID correction factor value for VOC exposures resulting from surfaced Macondo crude oil.

Wnek et al., (2018)

Wnek et al., (2018) report findings from air samples taken at various locations relative to surfacing Macondo crude oil during the Deep Water Horizon (DWH) well blowout. The report includes data describing atmospheric VOC concentrations collected by 6-liter canister ranging from locations three feet above the water’s surface to working locations on the platform of a rig drilling a relief well. Among these, *“Sample 4”*, taken from the work platform of the relief well drilling was prioritized for analysis. Among the samples evaluated in this exercise, those evaluated by Wnek et al. are the most well-associated with the worker exposure scenario under investigation.

Based on samples collected by the authors, Wnek et al., (2018) present an analysis of atmospheric samples taken close to (some within three feet of) the sea surface, and within, near or above surfacing Macondo Crude Oil from the DWH platform blowout. Evacuated canisters (6L) collected samples from locations

including 3 feet above the water from the Skandi Neptune construction vessel (Samples 1, 2). Additional samples were taken from approximately 3 feet above the water from the Q4000 (Sample 3) and immediately above the water's surface from the vessel BOA SUB C (Sample 5). Sample 4 was taken from the deck of the Q4000, and Sample 6 was taken from the deck of the BOA SUB C, also comprising emissions from combustion engines. There were both qualitative and quantitative differences noted among the samples analyzed. For example, in Samples 1 through 6, propyl benzene was only detected in Sample 6 (950 ppb); and pentanycyclohexane was detected only in Sample 3 (85.3 ppb) and Sample 4 (5.38 ppb). Decane was detected in Samples 1 through 6 at concentrations of 47.4, 118, 191, 22.5, 11.2 and 704 ppb, respectively; n-heptane was detected in Samples 1 through 6 at concentrations of 143, 302, 52, 10, 19.7 and 237 ppb, respectively. Sample 4 (this analysis) was collected from the deck of the Q4000 and so is thought to be representative of subject working locations; data from Sample 4 were preferred for analysis, as discussed below. Very low, if any concentrations of benzene and naphthalene were detected. For Sample 4, 23 components were identified and quantified, with concentrations ranging from 1.08 ppm (methylcyclohexane, 1,2,3-trimethylcyclopentane) to 22.5 ppb (decane). These data will be discussed later, relative to developing a correction factor value for crude oil VOCs and to provide context for characterizing the level of protection offered by the AL proposed.

5.0 Toxicity Data and Action Level Development

The Action Level recommended for atmospheres containing Crude Oil Volatile Compounds is 100 ppm. This represents one-half the ERPG-1 established for crude oil volatiles. AIHA based this EPRG value on gasoline vapors, noting the expected similarity between volatiles from gasoline and from crude oil. Like AEGL values, EPRG values are developed for application in emergency response, setting them apart in applicability versus other health-conservative values like RfC. The rationale for this value is described in this section.

Dose-response data are evaluated to develop applicable exposure values including, but not limited to, Acute Exposure Guideline Level (AEGL) values, Emergency Response Planning Guideline (ERPG) values, Provisional Peer Reviewed Toxicity Values (PPRTV), and inhalation Reference Concentration (RfC) values. These values differ with regards to the exposure duration in which they apply, with ERPG values applying to one hour duration, AEGL values applying to durations from 10 minutes to 8 hours, PPRTVs applying to subchronic or chronic durations, and RfC values applying to lifetime exposure durations. Also, these value systems are developed for purposes that differ in the level of health protection, in that ERPG and AEGL values address effects from mild and reversible to lethal, while PPRTV and RfC values only address mild, sometimes indicator effects, through extrapolation procedures than for ERPG and AEGL values that are less health conservative than PPRTV or RfC values.

The intent of this assessment is to develop guidance values for a 24-hour acute exposure duration for Crude Oil Volatile Compounds resulting from surfaced of GoM crude oil releases. Available 8-hour AEGL values (for irritation as a Tier 1 effect, and CNS alterations for a Tier 2 effect) can ideally address

component-specific exposure guidance for 8 hours. Available underlying dose-response data for inhalation exposures can be extrapolated to 8 and 24 hours, when the difference between the experimental exposure duration and the 8 or 24 hour duration is not too high. Extrapolation will be accomplished via the ten Berge approach where response $k = c^{-n} \times t$, where n is the Toxic Load Exponent (TLE). The assumption for irritant effects is that they will not accumulate with time, and so no temporal extrapolation will be performed for irritant effects unless chemical-specific data warrant such.

For chemicals with underlying inhalation dose-response data for CNS effects, but for which a TLE for CNS alterations has not been developed, the AEGL database will be evaluated to determine the TLE assigned for CNS effects for various generally structurally related chemicals. These TLE values will be used to justify a TLE assigned to temporally extrapolate the POD derived from the existing dose response data. For chemicals which lack CNS dose response data, the AEGL database will be evaluated to identify POD values for CNS effects for generally structurally similar compounds, and these POD values will be converted to molar units. Data describing POD values in units of molar concentration will be used to estimate a molar POD value for the unstudied chemical, which will then be converted to units of ppm and mg/m³ for further dose response analysis. For extrapolations where a chemical- and effect-specific TLE has not been determined, and in accord with AEGL guidance, a TLE of 1 will be used to extrapolate to longer durations (except for irritant effects), and a TLE of 3 will be used to extrapolate to shorter durations.

ERPG values (ERPG-1, ERPG-2, ERPG-3) have been established for Crude Oil Volatile Compounds for the one hour duration at levels of 200 ppm (654 mg/m³), 1,000 ppm (3,272 mg/m³) and 4,000 ppm (13,088 mg/m³), respectively. The ERPG-1 value for Crude Oil Volatile Compounds is based on eye irritation observed in humans exposed to gasoline vapors (see **Appendix A** for ERPG Report). The American Conference of Governmental Industrial Hygienists (ACGIH) developed an 8-hour occupational exposure value (Threshold Limit Value Time-Weighted Average; TLV-TWA) of 300 ppm or 890 mg/m³ and a Threshold Limit Value-Short Term Exposure Limit (TLV-STEL; 15-minute) of 500 ppm or 1480 mg/m³ for gasoline vapors. The ACGIH stated, “A TLV-TWA of 300 ppm to minimize the potential for ocular and upper respiratory tract irritation is recommended for bulk handling of gasoline, based on Runion’s calculations on hydrocarbon content of gasoline vapor.” What was shown in data collected by Runion, (1975) from multiple samples of gasoline from several countries was that saturated compounds accounted, consistently, for approximately 90% by mass of vapor phase components from gasoline.

The most sensitive endpoint associated with acute exposure to light-to-mid range hydrocarbon (i.e., gasoline) volatiles is ocular irritation (Davis et al., 1960); however, other effects, such as upper respiratory irritation (e.g. cough, throat irritation) and central nervous system (CNS) effects (dizziness, feeling of inebriation, headache, nausea) are also known to occur (Cairney et al., 2002; Maruff et al., 1998). The ERPG documentation indicates that volunteers reported various symptoms of irritation and CNS depression following 30-minute exposures to several types of unleaded gasoline (0, 200, 500, or 1000 ppm), but the reference cited indicates that the only significant effect was ocular irritation (Davis et al.,

1960). In that study, gasoline vapor exposure at a concentration of 200 ppm for 10 minutes caused mild tearing of the eyes in some individuals (3% response rate). Therefore, this may be considered near a threshold concentration for this effect. The ATSDR Medical Management Guideline for gasoline agrees regarding ocular irritation, indicating that *“Eye irritation from gasoline vapors begins at about 200 ppm. Inflammation is generally slight.”* As such, 200 ppm became the basis for the ERPG-1 (AIHA, 2017). As expected, duration did not significantly impact irritation in a study of volunteers exposed to gasoline vapors for 8 hours (Drinker et al., 1943). In this study, men exposed to 270 ppm and women exposed to 160 ppm reported ocular itching and/or irritation. Drinker et al. also reported that, at 1,000 ppm, CNS symptoms including nausea, headache, and slight dizziness were reported, while dizziness or inebriation occurred with 5 minutes of exposure to 10,000 ppm. Slight dizziness, irritation of eyes, nose, and throat have been reported at 900 ppm by Davis et al., (1960) and Runion, (1975) reported that prompt dizziness and headaches occur with brief (few minutes) exposures in excess of 1,000 ppm.

The concentration chosen as an AL for crude oil volatiles should provide sufficient warning to protect against eye irritation. Since CNS effects generally occur at higher concentrations, the level chosen should be protective for CNS effects as well. Whereas 200 ppm (ERPG-1) caused mild, transient ocular irritation in 1 hour in 3% of those tested, 1000 ppm (ERPG-2) caused mild, transient CNS effects in 30 min (500-900 ppm in 1 hour also reported). For the gasoline 8-hr TLV, 300 ppm was chosen to protect against irritation, whereas 500 ppm for the 15 min STEL was chosen to protect against irritation and CNS effects. The OSHA PEL and STEL are also 300 ppm and 500 ppm.

ALs have been historically set at 10-50% of the PEL or other OEL, values that are set to allow for no effects in the majority of the working population. As such, 50% of the ERPG-1 are conservatively recommended as the basis of the AL. The 60-min ERPG-1 for crude oil volatiles is 200 ppm. Thus, 50% of the ERPG-1 (100 ppm) is designated as the ‘Action Level’ to provide adequate warning against mild, transient effects which may be experienced at the ERPG-1 concentration. Increasing duration from 1 hour (as in the ERPG) to 24 hours should not require lowering the AL since it has been suggested that the concentration of petroleum vapor is the primary determinant of acute toxicity rather than duration of exposure (Wang and Irons, 1961, as cited by UKHPA, 2007). In support of this rationale, the proposed Acute Exposure Guideline-1 (AEG-1) values for gasoline are the same concentration (~250 ppm) for all durations ranging from 10 min – 8 hr. (USEPA, 2016). Since some of the most hazardous components in gasoline are expected to either not be present in a subsea scenario or be present in a greatly reduced amount (e.g. BTEX, naphthalene, other smaller hydrocarbons) (Wnek et al., 2018; Stout et al., 2016), 100 ppm should be an adequately protective, if not a conservative, concentration. It is notable that exceedance of this recommended 100 ppm action level does not mean that an adverse effect has or will occur. Nonetheless, it is recommended that should this action level be approached or exceeded for a specified time period in the absence of immediate remedial action, workers should attempt to don respiratory protection (i.e., air purifying respirators) or attempt to egress (or move upwind or crosswind) from their current location.

With respect to the hazards of benzene, Runion, (1975) indicated, *“Benzene exposures in excess of the [existing] 10 ppm TLV [for benzene] would with Gulf U.S. gasolines (and probably most U.S. gasolines), require sustained 8-hour gasoline vapor level exposures far in excess of 1400 ppm. Such exposures would be intolerable for much more than a few minutes.”* Runion further indicated that if gasoline vapor exposure were kept within the TLV, it would be impossible to exceed the TLV for benzene. While these comments were made within the context of existing (1975) TLVs, the ratio of gasoline components (approximately 1% benzene) is such that, with respect to TLV values for gasoline (TLV-TWA of 300 ppm; 890 mg/m³), calculations shown by Runion (demonstrating a 240 ppm concentration of VOCs from gasoline containing 5.18% benzene would produce a vapor containing 5% benzene) would result in 0.96 ppm benzene in a vapor concentration of 240 ppm resulting from gasoline containing 1% benzene.

However, two atmospheric samples of volatilized VOCs taken from DWH may indicate the effect of seawater scrubbing on some volatile components, including benzene. Data reported by Wnek et al. (as described in Section 4.0) demonstrated crude oil volatile components in vapors immediately above surfacing GoM (MC252) Crude Oil from the DWH blowout. This data demonstrated non-detectable levels of benzene in 4 out of 6 samples, with the highest measured benzene concentration of 6.4 parts per billion (ppb). In addition, Ryerson et al., (2011) presented results from an airborne sampling of the atmosphere above the DWH blowout, also demonstrating no detectible amounts of benzene. These data indicate that the toxic contributions of benzene from a seafloor blowout of crude may be negligible, especially at the VOC concentrations proposed as ALs in this report. Given the correction factor for benzene (0.47) and its very low anticipated mass contribution to vaporized VOC compounds, its contribution to the overall correction factor is also expected to be minimal.

While 100 ppm is suggested as an action level for crude oil VOCs, derived from the ocular irritation-based gasoline ERPG-1 value, action levels prompting lower levels of concern and action are also possible. Table 1, below places the 100 ppm action level in this context.

Table 1. Action Levels for Crude Oil VOC

Sustained Readings of VOC Action Level (ppm)*	Action
10	<ul style="list-style-type: none"> • notify industrial hygienist, • increase vigilance around controlling exposures (like work upwind where possible), • collect a whole air sample in common work areas for lab analysis
50	<ul style="list-style-type: none"> • take early mitigative actions including positioning upwind, • application of localized chemical dispersants or scavengers, • physical dispersing and additional focus on oil removal, • pre-planning for respiratory protection, communications of risk and personal work habits to reduce exposures, • full shift and STEL exposure monitoring for benzene with evaluation by industrial hygienist
100	<ul style="list-style-type: none"> • respiratory protection air purifying OV filter change daily, • initiation of advanced dispersion techniques such as SSDI to control the risk of exposure and PPE burden on workers, • collect a whole air sample in common work areas for lab analysis, • increase air sampling capabilities to establish safe work zones < 100 ppm

*As explained in Section 7.5, a reading of 77 ppm on an isobutylene calibrated PID = 100 ppm crude oil VOC; this number might change due to different types of crude slates.

6.0 Component-Based Risk Estimates

Short of empirical evidence from the whole mixture of interest, a component-based approach to estimating the acceptability of a given exposure is required. Here, the proposed Crude Oil Volatile Compounds AL (100 ppm) is parsed among components identified in several studies, based on mass (not molar) fraction in characterized atmospheres, and a hazard index-based approach is applied to estimate risk of the Wnek et al. atmosphere, at 100 ppm, for comparison. Atmospheric characterizations taken from reliable reports were selected based on similarity to the anticipated seafloor release of crude oil.

For this analysis, Sample 4, as described by Wnek et al., (2018) was selected due to the authors' reporting that it represented exposure in an occupationally relevant location, without complications from running internal combustion engines. The reported concentrations (ppb) of the 22 individual components (o-, m- and p-xylenes combined) was summed. The combined mass (0.1877 ppm) was extrapolated to 100 ppm and parsed by ratio among the identified components. For example, the characterized atmosphere amounted to 0.1877 ppm, and cyclohexane accounted for 0.0059 ppm of the total. If the exposure had been to the same mixture, but at a concentration of 100 ppm (the proposed Action Level), then cyclohexane would have been present at 3.14 ppm. The extrapolated component concentrations (e.g., 3.14 ppm cyclohexane) was used in subsequent hazard index-based risk estimates.

Based on the approach taken by Harrill et al., (2014) the ratio of anticipated component-specific concentrations (within a total concentration of 100 ppm) to critical health protective values (CHPV) was developed, and summed to estimate overall impact, according to the hazard index approach, where

$$HI = \sum (E / CHPV)$$

Where HI is Hazard Index of the mixture, E is exposure concentration of a given component, and CHPV is the critical public health value for the same given component. The term, “E/CHPV” is essentially the hazard quotient (HQ) for any given component, where exposure is divided by an acceptable limit for exposure (“E/AL”).

Within Sample 4, CHPVs were available for 8 components. The HI developed from hazard quotient values for these 8 components was 0.53. Where no CHPV was available, alternate, conservative approaches were taken to develop the HI for irritation for this mixture. First, the mean CHP value (85 ppm) for the components for which a CHPV was available was assigned to components for which a CHPV was not available. This method developed a mixtures HI value of 1.2. Next, the lowest value of any CHPV identified for any component (25 ppm, trimethylbenzenes) was assigned to components for which no CHPV was available. This method resulted in a mixtures HI value of 2.8. To evaluate the level of conservatism in these approaches, TLV values for irritant substances, categorized by the National Toxicology Program were identified for structurally similar chemicals (NTP, 2021). They were: methylcyclohexane, 400ppm; cyclopentane, 600 ppm; cyclopentadiene, 75 ppm; cyclohexene, 300 ppm; methylcyclohexanol, 50 ppm; and naphthalene, 10 ppm. Thus, even under these conservative approaches, the possible HI for the mixture does not exceed a value of 3, which is a benchmark used by some to offset conservative assumptions made in calculating HQ and HI values.

Table 2. Hazard Index Approach Applied to the Wnek et al. Sample 4 Mixture

Component	Actual Conc (ppm)	Extrapolated Conc (ppm)	CHPV	E/CHPV	E/CHPV*	E/CHPV**
Cyclohexane	0.0059	3.14	100	0.031	0.031	0.031
n- Heptane	0.01	5.33	85	0.063	0.063	0.063
1,2,4-Trimethylbenzene	0.0047	2.50	25	0.100	0.100	0.100
1,3,5-Trimethylbenzene	0.0019	1.01	25	0.040	0.040	0.040
m&p-Xylene	0.0037	1.97	--	--	--	--
o-Xylene	0.0015	0.80	--	--	--	--
Xylenes ***	0.0052	2.77	100	0.028	0.028	0.028
n-Hexane	0.0102	5.43	50	0.109	0.109	0.109
pentane, 2-methyl	0.00551	2.94	NA	--	0.035	0.117
cyclohexane, methyl	0.00108	0.58	NA	--	0.007	0.023
octane	0.0137	7.30	75	0.097	0.097	0.097
nonane	0.0221	11.77	200	0.059	0.059	0.059
cyclohexane, propyl	0.0124	6.61	NA	--	0.078	0.264
decane	0.0225	11.99	NA	--	0.141	0.479
undecane	0.0182	9.70	NA	--	0.114	0.388
cyclohexane, 1-methyl-2-	0.00595	3.17	NA	--	0.037	0.127
cyclohexane, butyl-	0.00725	3.86	NA	--	0.045	0.155
cyclohexane, pentanyl	0.00538	2.87	NA	--	0.034	0.115
Naphthalene, decahydro-2-	0.00612	3.26	NA	--	0.038	0.130
cyclopentane, 1,2,3-	0.00108	0.58	NA	--	0.007	0.023
heptane, 2-methyl-	0.00553	2.95	NA	--	0.035	0.118
cyclohexane, 1,4-dimethyl	0.00652	3.47	NA	--	0.041	0.139
nonane, 2-methyl	0.0059	3.14	NA	--	0.037	0.126
benzene, 1-methyl-2-propyl	0.00538	2.87	NA	--	0.034	0.115
Sum	0.1877	100	HI	0.53	1.2	2.8

* When no CHPV available, a value of 85 (the average of available CHPVs) was assigned.

** When no CHPV available, a value of 25 (the lowest of available CHPVs) was assigned.

*** The concentrations of o-, m- and p-xylenes were combined

7.0 Photoionization Detector Correction Factors

Correction Factors (CF) are used to adjust the resultant PID reading from units (i.e., ppm) of a calibration gas such as isobutylene to a particular gas of interest (i.e., crude oil volatiles). CF values can be determined at several different PID lamp voltages, the most common and readily available being a lamp energy of 10.6 eV. Thus, references made to PID correction factors within this document will refer to readings recorded using a 10.6 eV lamp. Technically, CF values are determined via PID readings according to the following equation.

$$CF = \frac{\text{Instrument Isobutylene Response} \times \text{Gas Y Conc. in ppmv}}{\text{Isobutylene Conc. in ppmv} \times \text{Gas Y Instrument Response}}$$

Correction factors are used (as multipliers) to adjust PID instrument readings (in ppm) to concentration of the gas (in ppm). The instrument reading is multiplied by the relevant correction factor to yield the actual concentration of the gas (or mixture of gases) to which the correction factor applies. Correction factors can range from ≤ 1 for some gases to ≥ 10 for others.

Table 3. Hypothetical Application of Correction Factors to a 100 ppm Action Level

Crude Oil Volatiles Action Level	Hypothetical Correction Factor	Reading on PID Instrument
100 ppm	2.0	50
100 ppm	1.3	77
100 ppm	1.2	83
100 ppm	1.0	100
100 ppm	0.50	200

In order of preference, for a given mixture, first preference is given to the CF value developed for the mixture of interest (here, VOCs from crude oil released from the seafloor and surfaced through seawater – which is not available). Second preference is given to CF values developed for similar mixtures, and there are several to evaluate. Values for these mixtures being unavailable (or deemed inapplicable), an approach to develop a CF for the mixture based on its components should be undertaken.

7.1 CF Values for Similar Mixtures

CF values are available for vapors of some common, reasonably similar, petroleum hydrocarbon mixtures. Given the relative volatility (vapor pressure) of crude oil components and the refined composition of these mixtures, CF values for related mixtures may be considered when estimating the CF value for surfaced crude oil.

Table 4. PID CF for Some Similar Petroleum Vapors

ANALYTE	CORRECTION FACTOR (10.6 eV PID)
Gasoline (No. 2; 92 Octane)	1.0
Gasoline (No 1; automotive)	0.9
Diesel Fuel (Automotive)	0.7
Mineral Spirits	0.7
Diesel Fuel	0.9
Jet Fuel / Kerosene	0.6 - 1
VM&P Naphtha	0.97

7.2 CF Values Estimated from Mixture Components

CF values can be identified using a mixtures approach, and will be determined based on the chemical composition and CF values available for components of several crude oil-derived VOC mixtures. CF for chemical mixtures are estimated using data describing the molar composition and CF values for identified components. The mixture CF (CF_{mix}) is determined according to the following equation:

$$CF(mix) = \frac{1}{\frac{MFA}{CFA} + \frac{MFB}{CFB} + \frac{MFC}{CFC} \dots}$$

where MF is molar fraction, CF is correction factor, and components A, B, C, etc. Table 5 presents the results of an exercise to estimate the CF value for a hypothetical five component mixture.

Table 5. Development of a PID CF for a Hypothetical Five-Component Mixture

CHEMICAL	MOLAR FRACTION	CORRECTION FACTOR	MF/CF
A	0.10	4.2	0.024
B	0.35	4.2	0.083
C	0.35	0.8	0.438
D	0.35	1.3	0.269
E	0.15	8.1	0.019
SUM	1.0	SUM	0.833
		CF Mix = 1/Sum:	1.20

Developing a mixture CF via a component-based approach allows for tailoring the CF value to the mixture of interest, when CF values are available for component chemicals. The developed mixture CF values might be applied to other mixtures, so long as their components and ratios of their concentrations are characterized and can be justified as being sufficiently similar.

At the present time, no CF value is available for Crude Oil Volatile Compounds. CF values for several VOC component chemicals are available for application in a component-based approach to develop CF values for Crude Oil Volatile Compounds.

The component-based approach to develop a mixture correction factor for crude oil, illustrated above, requires data describing the compositional fraction of the mixture contributed by each identified component and its unique correction factor. Honeywell documentation (Technical Note 106) is a primary source for CF data, augmented where necessary by data from other sources. The molar composition of vapors reported by Harrill et al., (2014), Ryerson et al., (2011) and Wnek et al., (2018) were determined and CF values sought for individual components and a mixtures-based CF Developed (see **Table 6**). Stout et al., (2016) evaluated the VOC composition of weathered crude oil, but did not characterize atmospheric VOC concentrations, and so was not further considered in this analysis. Mixtures, component-based CF values derived from these data sets are shown in **Appendices B-D** and are described more fully below. Among the atmospheres sampled by these investigators, that from Wnek et al., (2108) described as “Sample 4” taken from the work platform of the Q4000 repair rig stationed at the Deep Water Horizon location was considered the most relevant to this evaluation.

Table 6. Calculated Mixtures-Based CF for Crude Oil Volatiles

Source	Describing	Percentage of Mixture Components with Available CF	Calculated CF Value
Ryerson et al., 2011	Atmospheric VOCs from surfaced crude oil	69%	1.96
Harrill et al., 2014	Airborne concentrations of VOCs from railcar spill	68%	2.54
Wnek et al., 2018	Airborne concentrations of VOCs from deck of repair platform	54%	1.20

Ryerson et al. (2011)

The authors of Ryerson et al., (2011) present an analysis of MC252 crude oil spilled from the DWH blowout, taken via aircraft at an unspecified altitude. These investigators demonstrated the molar relationship of VOC components relative to n-heptane. These data can be considered to represent the vapor phase of components to which humans may be exposed; the components measured range from C₁ through C₁₁, not inclusive. Thirty-nine (39) components were measured (3 were not detected: methane, ethane, benzene); m- and p-xylene contents were summed. Methane, ethane and benzene were not measurable (were “off scale”) due to “negligible or zero atmospheric flux”, (per Ryerson). The molar ratios of components relative to n-hexane were presented graphically and were digitized and numerically captured for this analysis. Ryerson assigned the molar ratio of 1.0 to n-heptane for display. Using the Digitizit software for this analysis, a value of 0.998 was determined for n-heptane, comparing favorably with Ryerson’s assigned value of 1.0 and adding confidence to molar ratios determined for this mixture, by this method. Thirty-six compounds were detected with a non-zero concentration with molar ratios ranging from 0.2% (toluene) to 9.8% (n-pentane). The analysis reported combined “m- and p-xylene”; the total molar fraction was divided evenly between the two isomers for this analysis. For this sample, CF values were not available for nine components, comprising 13% of the molar mass. These include: propane (0.5%), 2,3-dimethylbenzene (0.6%), 1-methyl-4-ethylbenzene (2.6%), 1-methyl-3-ethylbenzene (0.7%), 2,2-dimethylbutane (0.2%), 2,3-dimethylpentane (1.0%), 2-methylhexane (2.9%), 3-methylhexane (3.3%), and 2-methylheptane (3.2%).

Nine additional chemicals (accounting for 57% of the VOC mass) have PID correction factors but lack available acute exposure guideline values (n-pentane, n-heptane, n-nonane, n-octane, n-decane, isopentane, cyclohexane and methylcyclopentane, 2-methylpentane). Developing exposure guidance values for these chemicals would significantly add to the confidence placed in any component-based approach (to the risk assessment of any mixture containing these components).

In total, CF values were available for 27 components (accounting for 87% of the molar fraction). The mixture-based CF based on 87% of the molar fraction of this mixture was calculated to be 1.96. This characterization is shown in **Appendix B**.

Harrill et al. (2014)

The authors in Harrill et al., (2014) present a volatiles analysis conducted according to USEPA Method TO-15 for a rail car spill of high-sweet crude oil. Nineteen components were identified, with molar ratios ranging from 0.15% (n-hexane) to 14% (n-nonane). For this sample, six components did not have CF values available comprising 50% of the molar mass. These include: Cis-1,3-dimethylcyclohexane (6%), Trans-1,1-dimethylcyclopentane (3.5%), 1,3-dimethylcyclopentane (5.3%), 1,2,3-trimethylpentane (12%), 1,2,4-trimethylpentane (12%), and 1,2-dimethylpentane (11%).

Individual CF values were available for 13 components, accounting for 50% of the molar fraction. The CF based on 50% of the molar fraction of this mixture is 2.54. This characterization is shown in **Appendix C**.

Wnek et al. (2018)

The authors on Wnek et al., (2018) present an analysis of MC252 crude oil, based on ambient air samples taken during a surfacing event, from working locations, including the platform of the repair platform (Q4000). This sample is uncomplicated by internal combustion engine emissions, is temporally relevant as well as directly relevant to surfaced crude oil vapors. A sample from this location demonstrated 24 components, with molar ratios ranging from 0.9% (nonane) to 15.9% (1,2,3-trimethylcyclopentane). Correction factor values were available for 13 components, comprising 51% of the molar fraction. The analysis reported combined "*m- and p-xylene*"; the total molar fraction was divided evenly between the two isomers for this analysis. For this sample, correction factor values were not available for 11 components, comprising 49% of the molar mass. These include: 1,2,4-trimethylbenzene (3.9%), propylcyclohexane (1.6%), 1-methyl-2-propylcyclohexane (3.6%), butylcyclohexane (3%), pentanycyclohexane (4.4%), Decahydro-2-methylnaphthalene (3.8%), 1,2,3-trimethylcyclopentane (15.9%), 2-methylheptane (3.2%), 1,4-dimethylcyclohexane (2.6%), 2-methylnonane (3.7%), 1-methyl-2-propylbenzene (3.8%).

Correction factor values were available for 13 components, accounting for 51% of the molar fraction. The CF based on 51% of the molar fraction of this mixture is 1.20. This characterization is shown in **Appendix D**.

7.3 Common Crude Oil Volatile Compounds

The identification of components common to these aforementioned references in Section 7.2 can identify potential chemical markers of exposure for further application. While not necessary for the present evaluation, an approach using these commonly identified chemicals as *'the backbone'* for exposure reconstruction may be valuable. Such an analysis might consider the molar ratio of these components and make adjustment to include ratios expected for other components, identified in other analyses.

Table 7 compares components detected among the data sets of Ryerson (R; MC252; 39 components), Harrill (H; high sweet crude oil; 19 components) and Wnek (W; MC252, Sample 4; 24 components) revealed that there were 49 components detected overall, with 10 common to all sets. There were 21 components unique to the Ryerson data set, two components unique to the Wnek data set and no components unique to the Harrill data set. Thirteen components were found in at least two data sets.

Table 7. Comparison of Components among Three Crude Oil Vapor Samples

COMPONENT	CASRN	SAMPLE
ethylbenzene	100-41-4	R,H
n-propylbenzene	103-65-1	R,H
p xylene	106-42-3	R,H
n-butane	106-97-8	R,H
2-methylpentane	107-83-5	R,H,W
benzene, 1-methyl-2-propyl	1074-17-5	W
1,3,5-Trimethylbenzene	108-67-8	W
2,4-dimethylpentane	108-08-7	R
m- xylene	108-38-3	R
m + p xylene	108-38-3; 106-42-3	R,W
1,3,5-trimethylbenzene	108-67-8	R
methylcyclohexane	108-87-2	R,H
toluene	108-88-3	R,H
n-pentane	109-66-0	R,H
n-hexane	110-54-3	R,H,W
cyclohexane	110-82-7	R,H,W
n-octane	111-65-2	R,H,W
n-undecane	1120-21-4	R,H,W
n-decane	124-18-5	R,H,W
o-xylene	1330-20-7	R,H,W
n-heptane	142-82-5	R,H,W

COMPONENT	CASRN	SAMPLE
cyclohexane, propyl	1678-92-8	H,W
cyclohexane, butyl-	1678-93-9	H,W
cyclopentane, 1,2,3-trimethyl	2815-57-8	H,W
cyclopentane	287-92-3	R,W
Naphthalene, decahydro-2-methyl	2958-76-1	H,W
cyclohexane, 1-methyl-2-propyl	4291-79-6	H,W
cyclohexane, pentanyl	4292-92-6	H,W
1,2,3-trimethylbenzene	526-73-8	R
n-nonane	556-67-2	R,H,W
2,3-dimethylpentane	565-59-3	R
3-methylhexane	589-34--4	R
cyclohexane, 1,4-dimethyl	589-90-2	H,W
2-methylhexane	591-76-4	R
2-methylheptane	592-27-8	R,H,W
1-methyl-3-ethylbenzene	611-14-3	R
1-methyl-4-ethylbenzene	622-96-8	R
benzene	71-43-2	R
methane	74-82-8	R
ethane	74-84-0	R
propane	74-98-6	R
2,2-dimethylbutane	75-83-2	R
isobutane	78-28-5	R
isopentane	78-78-4	R
2,3-dimethylbutane	79-29-8	R
nonane, 2-methyl	871-83-2	H,W
naphthalene	91-20-3	R
1,2,4-trimethylbenzene	95-63-6	R,H,W
3-methylpentane	96-14-0	R
methylcyclopentane	96-37-7	R

7.4 Laboratory-Derived CF For Crude Oil Volatiles

Because of the uncertainties highlighted in the aforementioned sections describing the development of a PID CF using a mixtures-based approach, a sample of GoM Oil was provided and supplied to a laboratory at the National Institutes of Occupational Safety and Health (NIOSH) in order to empirically determine a CF for the volatile compounds emanating from a native (but not release and/or surfaced) crude oil sample. It is notable that this sample has not been subjected to the effects of *'seawater scrubbing'* of the more water-soluble components. For these reasons, the spectrum of volatile compounds from this sample should not be expected to be an exact replication of those volatiles to which humans are exposed in GoM subsea well-blowout situations. Because of the chemical (mixture component)-specific nature of CF values, and because of the uncharacterized relationship of components in this sample to components of surfaced crude oil, it is not possible to determine whether the CF developed for this sample is higher than or lower than the CF value which could be determined for surfaced crude oil. However, given the range of CF values available for several other related mixtures (e.g., kerosene, diesel fuel), it is possible that the difference is relatively small.

The NIOSH-derived PID CF for this GoM Crude Oil Sample was 1.33 and a detailed analysis is provided in **Appendix E**. Briefly, an aliquot of crude oil was subjected to environmentally-relevant temperature in a closed vessel to volatilize VOCs. Generated atmosphere was analytically characterized and the fractions and individual components in the range of C6 to C14 were quantified, and their fractional contribution to the total VOC was determined. Next, correction factor values available for individual component chemicals were combined with corresponding fractional composition to develop a correction factor for the specific VOC mixture resulting from GoM crude oil. This analysis did not specifically target naphthalene for quantification.

Table E-2. Determination of Crude Oil Vapor Correction Factor

Component	Mole fraction	Correction Factor CF)	X/CF
Hexane	0.086	5.10	0.017
Heptane	0.190	2.80	0.068
Octane	0.095	1.80	0.053
Nonane	0.022	1.40	0.016
Decane	0.003	1.40	0.002
Composite C6-C14	0.280	2.50	0.112
Benzene	0.008	0.47	0.017
Toluene	0.043	0.47	0.091
Ethylbenzene	0.022	0.45	0.050
Xylenes	0.043	0.43	0.100
C6-C12 Composite	0.100	0.45	0.222
		Total CFMix	1/0.748 = 1.33

7.5 Recommended CF Values for Crude Oil Volatiles

This evaluation presents the technical basis for derivation and estimation of a CF value for Crude Oil Volatile Compounds. CF values were identified for several similar mixtures, and a CF value for crude oil from the geographic region of interest was determined, although this GoM sample did not reflect the impact of seawater extraction. Component-based mixture CF values were developed for several VOC samples taken from accidentally released crude oil, including crude oil released from a seafloor blowout. Values previously determined for other lighter-end hydrocarbon mixtures ranged from approximately 0.6 to 1, with most values approximating 1. Estimated and Calculated CF values were 1.96 for the atmospheric sample, 2.54 for the rail car spill sample and 1.20 for the repair rig platform sample. The CF value which was empirically determined for unreleased crude oil was 1.33

Based on these data, a correction factor value of 1.3 is recommended for Crude Oil Volatile Compounds based upon the use of 10.6 eV lamp and an isobutylene calibration. A concentration of 100 ppm crude oil volatiles would be demonstrated by a PID reading of 77 ppm: $77 \text{ ppm} \times 1.3 = 100 \text{ ppm}$.

8.0 Additional Air Monitoring and Sampling Recommendations

The AL presented here is based on air monitoring utilizing a PID instrument. While this assessment may provide basic protection during an event, it is recommended that additional monitoring (i.e., lower explosive limit, hydrogen sulfide, etc.) be conducted basic on the known or intrinsic properties of the source oil. For example, lower explosive limit (LEL) monitoring should be carried out separately since many of the light hydrocarbon gases that contribute to the flammability of crude oil vapors are not detectable via a 10.6 eV PID.

As soon as possible (or when available) chemical specific monitoring be conducted for individual compounds (i.e., benzene, toluene, ethyl benzene, xylene, n-hexane, naphthalene) to ensure that site-specific VOC composition is adequately covered by this correction factor. This is because there may be other sources of these compounds in the source control area (i.e., exhaust). It is notable that longer-term decision making will likely be influenced by the concertation of these individual chemicals as measured on chemical-specific real-time equipment (i.e., Drager X-PID or UltraRAE 3000 or similar) or through the use of analytical sampling. As soon as possible consult with the appropriate USCG Contingency Plan for any additional recommendations, such as monitoring for volatile PAHs (e.g., naphthalene), which may or may not be present in the subject crude.

9.0 Conclusions

This report presents the estimation of an Action Level for Crude Oil Volatile Compounds. Using the proposed action level of 100 ppm for up to 24 hours of exposure is expected to be protective against mild, irritant effects. Based on the dose-response relationship established in the EPRG values, this value (100 ppm) is ten-fold lower than the ERPG value established for more severe effects, which included dizziness. The PID correction factor of 1.3 recommended for crude oil vapors can be used in rapid-reading instrumentation to effectively quantify the action level concentration. As soon as possible, monitor also for BTEX and naphthalene to ensure site-specific VOC composition is adequately covered by this adjustment factor, and consult with the appropriate USCG Contingency Plan for any additional recommendations, such as monitoring for volatile PAHs (e.g., naphthalene), which may or may not be present in the subject crude.

While monitoring for VOCs from crude oil, also:

- Monitor also for BTEX and naphthalene,
- Conduct additional monitoring (i.e., lower explosive limit, hydrogen sulfide, etc.) based on the properties of the source oil,

- Monitor specifically for individual compounds (i.e., benzene, toluene, ethyl benzene, xylene, n-hexane, naphthalene) because there may be other sources of these compounds and these chemicals may influence longer-term decision making, and
- Consult with the appropriate USCG Contingency Plan for any additional recommendations.

9.1 Technical Approach

The approach to estimate an action level incorporates a level of protectiveness and is based on an effect that is expected to be mild and reversible. This action level is independent of instrument reading, but the efforts to develop a PID correction factor enable rapid detection of this concentration, using basic industrial hygiene equipment, typically widely available and expected to be available during the initial phase of accidents. Using a calibrated PID device, like a RAE systems PID, the action level concentration of 100 ppm would be reflected by a PID reading of 77 ppm; $77 \text{ ppm} \times 1.3 = 100 \text{ ppm}$.

9.2 Applicability and Generalizability

The AL value is independent of the means of detection. The 100 ppm concentration should be considered a guideline value for exposure to VOC-containing vapors originating from crude oil. Workers exposed to this concentration for up to 24 hours are not expected to experience irritation from VOC vapors. However, other components in crude oil vapors (e.g., hydrogen sulfide) should be considered and separately monitored. The intrinsic nature of the sample and circumstances of the exposure scenario are impactful; for example, benzene has been reported in some studies of crude oil volatiles, but not others. Monitoring for BTEX and naphthalene should begin as soon as possible to ensure site-specific VOC composition is adequately covered by this adjustment factor. Specific monitoring to characterize the LEL and specific vapor composition of toxic chemicals such as hydrogen sulfide. Consult with the appropriate USCG Contingency Plan for any additional recommendations, such as monitoring for volatile PAHs (e.g., naphthalene), which may or may not be present in the subject crude.

9.3 Uncertainties

The action level recommended in this report has been benchmarked against irritation effects observed following exposure to gasoline vapors, which provided the dose response basis for development of the ERPG-1 value of 200 ppm, for a one-hour exposure. Because of the yet-unstudied differences between the individual VOC components of the gasoline sample(s) used to develop the dose response data and the

individual VOC components released from surfaced crude oil have not been characterized, there is some uncertainty in applying the dose-response data for gasoline to crude oil vapors. However, that level of uncertainty was not sufficient to dissuade the ERPG committee from using those data as the basis upon which to establish exposure guideline values for crude oil.

While exposure to the recommended 100 ppm action level for 24 hours is not expected to result in irritation, it may produce irritation in some sensitive individuals. Further, there may be additional components (e.g., hydrogen sulfide) in vapors from crude oil that may produce additional effects. Some effects may be predicated based on odors. When there is a concern for these contaminants, additional monitoring and/or sampling efforts should be undertaken. While 100 ppm is recommended as a time weighted concentration, the influence of intermittent fluctuations (peaks) in exposure concentrations have not been accounted-for in this analysis.

The PID correction factor is recommended based on multiple independent data streams. The empirically measured value of 1.33 reported by NIOSH was determined for VOCs released from supplied GoM Crude Oil, but which had not been subjected to surfacing through a seawater environment. For these reasons, the VOC components of this sample may not exactly mirror those expected to be released from untreated crude oil which has surfaced through thousands of feet of seawater. However, the CF value of 1.33 is markedly similar to the estimated CF value of 1.36 estimated based on 46% of the molar fraction reported by Wnek et al., (2018). Uncertainty is the result of potential differences in the VOC content of the sample used for empirical CF determination versus the subject exposure mixture, and the incomplete CF characterization of all components analyzed from the Wnek exposure mixture

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Appendix A

ERPG Documentation

APPENDIX A. DOCUMENTATION OF CRUDE OIL VAPOR ERPG VALUE DETERMINATION
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EMERGENCY RESPONSE PLANNING GUIDELINE

TECHNICAL SUPPORTING DOCUMENTATION

CRUDE OIL HYDROCARBON VOLATILES

ERPG-3: 4000 ppm (13,088 mg/m³)

The maximum airborne concentration below which nearly all individuals could be exposed to for up to one hour without experiencing or developing life-threatening health effects.

ERPG-2: 1000 ppm (3,272 mg/m³)

The maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.

ERPG-1: 200 ppm (654 mg/m³)

The maximum airborne concentration below which nearly all individuals could be exposed to for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.

EMERGENCY RESPONSE PLANNING GUIDLINE

TECHNICAL SUPPORTING DOCUMENTATION

CRUDE OIL HYDROCARBON VOLATILES

Author: John Kind (2019)

ERPG-3: 4000 ppm (13,088 mg/m³)

ERPG-2: 1000 ppm (3,272 mg/m³)

ERPG-1: 200 ppm (654 mg/m³)

I. Identification

Chemical Name: Crude Oil

Synonyms : Petroleum

CAS Number : 8002-05-9

Molecular/Structural Formula: Mixture of paraffins (C_nH_{2n+2}), naphthenes (C_nH_{2(n+1-g)}, g = number of rings), and aromatic hydrocarbons (C_nH_{2n-6}, monocyclic). Composition and relative fractions of hydrocarbons (by weight) can vary greatly depending on oil source.

II. Chemical and Physical Properties (NIOSH) (API 2011)(USEPA 2011)

Physical State: Light, mobile, straw-colored liquid to highly viscous, semi-solid black substance.(American Petroleum Institute 2011)

Odor Description: Aromatic (odor characteristic of aromatic hydrocarbons), rotten egg odor (sour crudes).(American Petroleum Institute 2011)

Molecular Weight and Components: Varies with composition. The Volatile Organic Compounds (VOCs) emitted from crude oil are similar to those emitted from gasoline and gasoline blending streams (American Petroleum Institute 2011). Predominant volatile hydrocarbons (the crude oil fraction most likely to present risk of inhalation exposure) reported for light, medium, and heavy crude oils aromatic hydrocarbons such as the BTEX (benzene, toluene, ethylbenzene and xylene) compounds, cyclic hydrocarbons (*i.e.*, substituted cyclohexanes and

cyclopentanes), C₃-C₁₀ straight chain aliphatic hydrocarbons, and branched chain aliphatic hydrocarbons such as methylated butanes, pentanes, hexanes, and heptanes (Wang, Geppert, and Fischer *et al* 2015) (Yang, Wang, and Li *et al* 2007) (Wnek, Kuhlman, and Harrill 2018). The average molecular weight of gasoline volatiles is approximately 80 g/mol. This average molecular weight is used as a surrogate molecular weight in deriving the crude oil ERPGs.

Conversion Factors: 1 ppm = 3.3 mg/m³ (Based on MW of 80)
1 mg/m³ = 0.33 ppm (Based on MW of 80)

Boiling Point: -1°C (30°F) to 720°C (1328°F)
(measured distillation range) at 760 mmHg (API 2011)

Vapor Pressure: 45 mmHg to 338 mmHg at 37.8°C (100°F) (API 2011)

Specific Gravity: 0.7 to 1.1

Vapor Density
(Air=1): 2.5 – 5.0

Flash Point
(Closed cup): -40°C (-40°F) to -65.5°C (-86°F)

Flammability Limits (NIOSH):

Lower Flammability Limit:	0.9%-1.6%
Upper Flammability Limit:	5.9%-8.4%

Autoignition
Temperature: >260°C (500°F)

Stability and
Reactivity: Reacts with strong oxidizers

Solubility: Slightly soluble in water, 10.42 mg/L to 58 mg/L at 22°C (71.6°F)
(API 2011)(Shiu, Bobra and Bobra *et al* 1990)

III. Animal Toxicity Data

A. Acute Toxicity

1. Oral Toxicity

Rats: LD₅₀ > 5000 mg/kg body weight

Groups of 10 rats (5 males and 5 females) were given light crude oil (Mobil 1984 No. 40951) or synthetic crude oil from oil sands (Stubblefield, McKee and Kapp *et al* 1989) in single oral doses of 5 g/kg and monitored for 14 days. There were no deaths following gavage. Post dosing lacrimation and a discharge covering the perineum were observed during the first week. At termination of the study all animals gained normal appearance. In other studies, oral LD₅₀ was greater than 5000 mg/kg for medium and heavy crudes. (Mobil 1984) (Mobil 1997).

2. *Eye Irritation*

In an eye irritation study, 0.1 mL of undiluted light crude oil was instilled into the conjunctival sac of one eye of each of six rabbits. Eyes were not washed and were examined for irritation at 1, 24, 48, and 72 hours. The test material was judged to be non-irritating. (Mobil 1984 No. 40953)

3. *Skin Irritation*

In a dermal irritation study, 0.5 mL of light crude oil was applied to the shaved skin in 6 areas on each of 6 rabbits. Three areas were left intact and the others abraded. One abraded and one intact site was covered with an occlusive dressing. After 4 hours the dressing was removed, and the dosed skin was wiped to remove residual test item. The skin sites were evaluated for irritation at 30 min, 24 hr, 48 hr, 72 hr, 7 days, and 10 days after the application. Mean erythema values (24, 48, and 72 hrs) were 1.69. Slight edema was present, but all evidence of skin irritation was resolved within 10 days. (Mobil 1990 No. 63830, 63831, 63832, 63833)

In similar dermal irritation studies with light and heavy crude, comparable levels of irritation were reported up to 48 hrs, but both erythema and edema were resolved within 72 hrs, with little difference in response between intact or abraded sites. (Mobil 1997) (Mobil 1985 No. 40964) The reported findings typically occur in contact with skin-dehydrating hydrocarbons.

4. *Inhalation Toxicity*

Inhalation exposure to crude oil volatiles is likely to involve low boiling point gases, including H₂S (from “sour” crude oils) and Volatile Organic Compounds (VOCs). H₂S-specific ERPG values have been derived previously. (AIHA 2014) No data are available for inhalation exposures in animals to airborne gases from unrefined crude oil. However, data are available for inhalation of gasoline and gasoline blending streams, representing the most likely group of compounds, other than H₂S, that would volatilize from crude oil shortly after an accidental release. (API 2008)

No lethality was observed in rats over a 14-day period following a single 6-hr inhalation exposure to 4000 mg/m³ of aerosolized synthetic Canadian-sands crude oil (Stubblefield, McKee and Kapp *et al* 1989). However, half of the mice (5/10) died

during the 14-day post-exposure period. These data are limited for use as a basis for ERPG derivation because of the aerosol nature of the exposure and because synthetic crude oil was used.

No lethality was observed in rats exposed for 4 hours to ≥ 5000 mg/m³ light alkylate naphtha (1235 ppm naphtha equivalents) of alkylate, sweetened, catalytic-cracked, or full catalytic reformed naphtha. (API 1984 Rpt. #31-30681) (API 1986 Rpt. #33-30594) (API 1986 Rpt. #33-32722) (API 1986 Rpt. #30-31990) (API 1986 Rpt. #33-30497) (API 1987 Rpt. #34-30636) (API 1987 Rpt. #34-32777) (API 1987 Rpt. #33-31827)

Numerous repeat exposure studies of rats to gasoline vapors at concentrations of up to 20 mg/l (6200 ppm) produced no more than minor effects. (Huntingdon Life Sciences 2001 No. 00-6125) (Huntingdon Life Sciences 2001)

5. *Respiratory Irritation*

No acute-duration data was available for respiratory irritation from crude oil or constituent vapors. However, mice exposed to 2056 ppm unleaded gasoline for 6 hours/day, 5 days/week, for two years exhibited no signs of respiratory irritation. Identically-exposed rats exhibited only mild pulmonary irritation at 2056 ppm. (MacFarland, Ulrich, Holdsworth *et al* 1984)

B. Subacute Toxicity

1. *Oral Toxicity*

Groups of ten mice (5 male and 5 female) were dosed with heavy or light crude oil by oral gavage at 0, 5, and 10 ml/kg daily for 5 days. The initial dosing was distasteful to the mice, and some died from inhalation of the liquid oil during dosing. None of the crude oils tested resulted in significant changes in packed cell volume, number of red blood cells or whole blood hemoglobin. The treatments resulted a significant reduction in body weight gain, a 74% increase in liver weight, and a 66% reduction in thymus weight. There were no gross abnormalities at necropsy besides the reduction in the size of thymus glands. (Leighton 1990)

2. *Inhalation Toxicity*

Mice (12 mice/sex/group) were exposed to 0, 100, 300, 500, or 3000 ppm heavy straight run naphtha generated by flash evaporation for 28 days. Decreased body weight and thyroid cellular enlargement was observed at 3000 ppm, but not at 500 ppm. No neurobehavioral effects were seen at 3000 ppm. (API 2008 No. DuPont-18331)

C. Subchronic Toxicity

1. *Dermal Toxicity*

Rats (10/sex/group) were administered 0, 30, 125, or 500 mg/kg/day Lost Hills Light or Belridge Heavy crude oil applied dermally to unoccluded skin for 13 weeks. No fatalities were reported. Skin irritation, including hyperplasia and hyperkeratosis was observed at the administration site for all treated groups. Decreased hemoglobin, hematocrit and red blood cell counts in male rats only were observed at 500 mg/kg/day for both oil types. Reduced weight gain was reported for Belridge Heavy 500 mg/kg/day group. (Feuston, Mackerer, Schreiner *et al* 1997) (Mobil 1992 No. 63846)

2. *Inhalation Toxicity*

Rats (10/sex/group) were exposed to 0, 147, 572, or 2136 ppm vaporized light catalytic-cracked naphtha for 6 hours/day, 5 days/week, for 13 weeks. The only observed effect was reduced number of sperm per gram caudal epididymis in males exposed to 2136 ppm, but not in males exposed to 572 ppm. (Dalbey, Feuston, Yang *et al* 1996)

Rats (15/sex/group) were exposed to 0, 96, 464, or 1894 ppm full range catalytic-reformed naphtha for 6 hours/day, 5 days/week, for 13 weeks. Increased liver and kidney weights were observed in males and decreased white blood cell counts were seen in females exposed to 1894 ppm, but not in the 464 ppm groups. (Dalbey and Feuston 1996)

Rats (16/sex/group) were exposed to 0, 750, 2500, or 7500 ppm for 6 hours/day, 5 days/week, for 13 weeks. Mild nasal epithelial changes were seen at 7500 ppm, but not at 2500 ppm. No neurobehavioral effects were seen in any group. (Lapin, Bui, Breglia *et al* 2001)

Rats (/sex/group) exposed to 0, 627, 3100, and 6210 ppm gasoline vapors for 6 hours/day, 5 days/week, for 13 weeks exhibited red nasal discharge in the 6210 ppm group. No other treatment-related adverse effects were reported. (Huntingdon Life Sciences 2001 No. 00-6125)

D. Chronic Toxicity/Carcinogenicity

1. *Dermal Toxicity*

Mice (50 males/group) were dermally dosed with 50 mg of undiluted naphthenic API crude oil C or paraffinic API crude oil D twice weekly for 18 months or until tumor formation was observed. Tumors developed in 33% of mice treated with crude oil C, with an average latency of 76 weeks. 56% of mice treated with crude oil D developed tumors, with an average latency of 64 weeks. (Lewis, King, Cragg *et al* 1984) Mice (25/sex/group) were dermally dosed with 25 mg San Joaquin Heavy crude oil applied dermally three times weekly for up to 105 weeks. There was no indication of toxic or oncogenic effects on internal organs. 84% of mice developed tumors, with an average latency of 62 weeks. (Clark, Walter, Ferguson *et al* 1988)

2. *Inhalation Toxicity*

Mice and rats (100 animals/sex/group) were exposed to 0, 67, 292, or 2056 ppm unleaded gasoline vapors (generated using a heated column) for 6 hours/day, 5 days/week, for 24 months. Renal disease was observed in the 292 and 2056 ppm and renal carcinomas or sarcomas were seen at all doses in male rats, while mouse liver tumor incidence was increased in the 2056 ppm group. (MacFarland, Ulrich, Holdsworth *et al* 1984)

E. Reproductive/Developmental Toxicity

1. *Oral Toxicity*

Pregnant rats (9, 10, or 11/group) were administered heavy crude oil via oral gavage, either 1) as a single dose (5 ml/kg) on either day 3, 6, 11, 15, or 17 of gestation, 2) daily from gestation days 6-17 at a dose level of 1.0 or 2.0 ml/kg, or 3) as a single dose on day six of gestation at either 2, 5, 7, or 10 ml/kg. There were no maternal deaths following oral administration. Fetal resorptions and deaths were increased in rats given heavy crude during the early days of pregnancy, whereas those dosed during the later stages of pregnancy were unaffected. Treatment was also associated with reduced fetal body weight. (Khan, Martin, Payne *et al* 1987)

2. *Dermal Toxicity*

Groups of twelve pregnant female Sprague Dawley rats were dosed dermally with heavy crude oil at 125, 500, or 2000 mg/kg/day from day 0 to day 19 of gestation. Both crude oils produced maternal and developmental toxicity. Reproductive effects were observed in all treated groups, which included an increase in the number of fetus resorptions, decrease in litter size, decrease in fetal body weight, and delayed ossification. (Feuston, Hamilton, Schreiner *et al* 1997)

3. *Inhalation Toxicity*

Male and female rats (10/sex/group) were exposed to 0, 750, 2500, or 7500 ppm vaporized light catalytic- reformed naphtha for 6 hours/day, 7 days/week, for 6 weeks 2 weeks prior to mating through gestational day 19 (females) or for 7 consecutive weeks beginning 2 weeks prior to mating (males). No effects on reproductive capability were observed at any exposure level. (Schreiner, Bui, Breglia *et al* 2000)

Pregnant mice and rats (10/sex/group) were exposed to 0, 597, or 2128 ppm vaporized light catalytic-cracked naphtha for 6 hours/day on gestation days 0-19. No treatment-related clinical abnormalities were noted in treated dams during exposure. An increased number of skeletal variations were observed in pups born to dams exposed to 2128 ppm. (Dalbey, Feuston, Yang *et al* 1996)

4. *Other Routes of Toxicity*

Male mice (10-12 weeks) were injected i.p. daily for 5 days with Wilmington crude at doses of 1.0 and 2.1 g/kg. After 35 days, examination of the mice's cauda epididymis did not reveal any treatment-associated effects on the animal's sperm. (Lockard, Prater, Viau *et al* 1982)

F. Genotoxicity/Mutagenicity

1. *In vitro*

Significant mutagenic activity was observed for Arab Light, Beryl, Mid-Continent, and Belridge Heavy, but not Lost Hills Light crude oil using the optimized Ames test. This test employs a DMSO extraction step and utilizes a hamster liver S-9 metabolic activation mixture.^{41, 42} One group of investigators have reported a strong correlation between polycyclic aromatic hydrocarbon content and mutagenicity potential as identified using the optimized Ames test. (Roy, Johnson, Blackburn *et al* 1985) (Roy, Johnson, Blackburn *et al* 1988)

2. *In vivo*

Rats (5/sex/group) were administered 0, 30, 125, or 500 mg/kg/day Lost Hills Light crude dermally for 13 weeks. Bone marrow from the rats were subjected to a bone marrow micronucleus assay. No cytogenetic damage was induced. (Mobil 1990 No. 63835) (Mobil 1991 No. 63847)

G. Metabolism/Pharmacokinetics

There are no relevant data available on the rates and extent of adsorption, distribution, metabolism, or excretion of crude oil in humans. Considerable data exists for individual chemical constituents of crude oil; however, the pharmacokinetics of the mixture as a whole has not been studied.

IV. Human Uses and Experience

A. Odor Threshold Data

The odor threshold for crude oil volatiles is dependent on the sulfur content. For “sour” crude oils possessing relatively high H₂S concentrations, the H₂S odor threshold may be as low as 0.5 parts per billion⁴⁷. “Sweet” crude oils, having a lower sulfur content, will have an odor threshold similar to gasoline: 0.5 parts per million (AIHA 2010).

B. Toxicity Data

The general public is unlikely to be exposed to crude oil volatiles, except in the event of an accidental release. In such an event, the acute human toxicity would be mediated by the

low boiling-point organic compounds that volatilize from the oil into the air. As such, acute crude oil volatile toxicity to humans would be similar, if not identical, to that of gasoline and gasoline blending streams (API 2011) (Wang, Geppert, Fischer *et al* 2015) (Yang, Wang, Li *et al* 2007) (Wnek, Kuhlman, Harrill *et al* 2018). For this reason, acute human toxicity to gasoline exposure (AIHA 2010) will be used as a surrogate for acute human crude oil volatile toxicity.

An oral dose of approximately 8 g/kg gasoline has resulted in death. (Machle 1941) CNS depression has been observed to occur within three to five minutes after intentional inhalation of high concentrations. CNS effects of acute intoxication may also include ataxia, double vision, euphoria, slurred speech, and encephalopathy. (Maruff, Burns, Tyler *et al* 1998) (Cairney, Maruff, Burns *et al* 2002)

For volunteers exposed for 8 hours to gasoline vapors, men exposed to 270 ppm and women exposed to 160 ppm reported itching and/or irritation of the eyes. Coughing and throat irritation were reported by female volunteers. All effects were reported by the volunteers as being mild. At 1000 ppm, nausea, headache, and slight dizziness were reported, while dizziness or drunkenness occurred with 5 minutes of exposure to 10,000 ppm. (Drinker, Yaglou, W.M. 1943)

Ten volunteers were exposed to 0, 200, 500, and 1000 ppm gasoline vapor for 30 minutes. Eye irritation incidence was reported as 5, 23, 60, and 73% for 0, 200, 500, and 1000 ppm exposures, respectively. Conjunctival blood vessel swelling/reddening was observed in 10, 23, 53, and 80% of subjects exposed to 0, 200, 500, and 1000 ppm, respectively. Tearing occurred at 10, 3, 10, and 27% of the time for respective exposures of 0, 200, 500, and 1000 ppm. Volunteers reported a number of other subjective symptoms, including upper respiratory irritation, dizziness, drowsiness, nausea, and headache. (Davis, Schafer, and Bell 1960)

C. Workplace Experience

D. Epidemiology

Investigators examined the occurrence of hematologic cancerous lesions in Norwegian upstream crude oil workers. The Norwegian Registry of Employees was used to identify 27,919 crude oil workers and 366,114 referents, matched by age, gender, and residential community. Smoking or tobacco use was not addressed as a possible confounder. The authors reported that offshore upstream operators had a rate ratio (RR) for blood and marrow tumors of 1.90 (95% CI: 1.19-3.02). This association was ascribed to increased risks in these workers for acute myelogenous leukemia (RR: 2.89, %CI: 1.25-6.67) and multiple myeloma (RR: 2.49, %CI: 1.21-5.13). (Kirkeleit, Riise, Bratveit *et al* 2008)

V. Current Occupational Exposure Guidelines

There occupational exposure guidelines exist for several of the individual constituents of crude oil, there are currently no occupational exposure limits for whole crude oil.

VI. Recommended ERPGs and Rationales

The ERPGs derived for crude oil volatiles are based on toxicity data from volatile crude oil components (C₄-C₁₂) found in crude oil headspace (Wang, Geppert, Fischer *et al* 2015) (Yang, Wang, Li *et al* 2007) (Wnek, Kuhlman, Harrill *et al*), and naphtha fractions of gasoline blending streams. (API 2011) These compounds are the most likely compounds to be found in air following an accidental release of crude oil. (API 2011)

As previously mentioned, crude oil is a complex mixture of organic and inorganic constituents, some of which can contribute significantly to the potential health risks associated with airborne exposure to crude oil vapors. These include the BTEX compounds and hydrogen sulfide. It is recommended that initial monitoring be conducted for these compounds in addition to VOCs to determine if they are present at levels of health concern. Refer to the applicable ERPG or AEGL values for these compounds for guidance on community exposure levels.

It is also recommended that responders conduct flammability (i.e. lower explosive limit or LEL) monitoring, as many of the light hydrocarbon gases that contribute to the flammable nature of crude oil vapors are not detectable on a standard photoionization detector (PID).

A. ERPG-3: 4000 ppm (13,088 mg/m³) as gasoline

4000 ppm of crude oil hydrocarbon volatiles is the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects. This level is below the lower flammability limit (9000 ppm) and is below the 10,000 ppm concentration of gasoline vapors that produced dizziness and intoxication within 5 minutes in human volunteers (Drinker, Yaglou, W.M. 1943). It is also below the 6200 ppm gasoline vapor exposure that was non-lethal to rats in a 6 hr exposure. (Huntingdon Life Sciences 2001 No. 00-6125) (Huntingdon Life Sciences 2001)

B. ERPG-2: 1000 ppm (3,272 mg/m³) as gasoline

1000 ppm of crude oil hydrocarbon volatiles is the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious adverse health effects or symptoms which could impair an individual's ability to take protective action. This is the same concentration that caused mild and transient dizziness in human volunteers exposed for 30 minutes (Drinker, Yaglou, W.M. 1943).

C. ERPG-1: 200 ppm (654 mg/m³) as gasoline

200 ppm of crude oil hydrocarbon volatiles is the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects. It is notable that, depending upon the type

of crude oil, an objectionable odor could be experienced below this concentration. Volunteers exposed to 200 ppm gasoline vapor for 10 minutes experience a 3% response rate for tearing of the eyes; a 500 ppm gasoline vapor exposure to the same volunteers resulted in a 10% response rate for tearing of the eyes. (Davis, Schafer, and Bell 1960)

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Appendix B

CF Derivation from Ryerson et al. Data

Table B-1. Data and Derivation of CF Value for Ryerson et al. (2011).

CHEMICAL	CASRN	CF	MF (-)	MF (+)	MF/CF
methane	74-82-8	NR		0.000	NA
ethane	74-84-0	NR		0.000	NA
propane	74-98-6	NR	0.0056		NA
benzene	71-43-2	0.47		0.000	NA
toluene	108-88-3	0.45		0.002	0.004699
isobutane	78-28-5	100		0.016	0.000162
n-butane	106-97-8	67		0.059	0.000879
cyclopentane	287-92-3	15		0.003	0.000196
n-propylbenzene	103-65-1	NR		0.003	NA
1,3,5-trimethylbenzene	108-67-8	0.35		0.006	0.016183
2,3-dimethylbutane	79-29-8	NR	0.0061		NA
m xylene	108-38-3	0.44		0.009	0.019739
p xylene	106-42-3	0.39		0.009	0.02227
ethylbenzene	100-41-4	0.65		0.004	0.006274
o-xylene	1330-20-7	0.45		0.005	0.010909
1-methyl-4-ethylbenzene	622-96-8	NR	0.0026		NA
cyclohexane	110-82-7	1.4		0.030	0.021362
n-pentane	109-66-0	8.4		0.098	0.011688
isopentane	78-78-4	8.2		0.083	0.010131
methylcyclopentane	96-37-7	1.5		0.035	0.02311
1,2,4-trimethylbenzene	95-63-6	0.3		0.015	0.050097
1-methyl-3-ethylbenzene	611-14-3	NR	0.0073		NA
1,2,3-trimethylbenzene	526-73-8	0.3		0.006	0.021398
n-hexane	110-54-3	4.3		0.085	0.019847
2,2-dimethylbutane	75-83-2	NR	0.0021		NA
2-methylpentane	107-83-5	1.5		0.049	0.032475
3-methylpentane	96-14-0	1.5		0.030	0.019686
n-heptane	142-82-5	2.8		0.075	0.026919
methylcyclohexane	108-87-2	0.97		0.085	0.087202
2,3-dimethylpentane	565-59-3	NR	0.0096		NA
2,4-dimethylpentane	108-08-7	1		0.005	0.004909
2-methylhexane	591-76-4	NR	0.0292		NA
3-methylhexane	589-34—4	NR	0.0327		NA

CHEMICAL	CASRN	CF	MF (-)	MF (+)	MF/CF
2-methylheptane	592-27-8	NR	0.0315		NA
n-octane	111-65-2	1.8		0.052	0.028615
n-nonane	556-67-2	1.4		0.044	0.03172
naphthalene	91-20-3	0.42		0.005	0.011688
n-decane	124-18-5	1.4		0.030	0.021686
n-undecane	1120-21-4	2		0.014	0.007137
		SUM	0.13	0.87	0.511
			Correction Factor		1.96

CF = correction factor; MF (-) = molar fraction for component lacking correction factor; MF (+) = molar fraction for component with correction factor available; NR = correction factor not reported; NA = MF/CF value not available due to unavailable CF.

Correction factor determined as reciprocal of sum of MF/CF values. Here, $CF = 1/0.511 = 1.96$; this value represents 87% of the molar mass of this mixture.

Appendix C

CF Derivation from Harrill et al. Data

Table C-1. Data and Derivation of CF Value for Harrill et al. (2014)

CHEMICAL	CASRN	CF	MF (-)	MF (+)	MF/CF
benzene	71-43-2	0.47		0.014	0.030
toluene	108-88-3	0.45		0.025	0.055
cyclohexane	110-82-7	1.4		0.008	0.006
methylcyclohexane	108-87-2	0.97		0.020	0.021
cis 1,3-dimethylcyclohexane	638-04-0	NR	0.061		NA
cis 1,2-dimethylcyclopentane	1192-18-3	1.2		0.053	0.044
trans 1,1-dimethylcyclopentane	822-50-4	NR	0.035		NA
1,3-dimethylcyclopentane	2453-00-1	NR	0.053		NA
1,2,3-trimethylcyclopentane	2815-57-8	NR	0.121		NA
1,2,4-trimethylcyclopentane	2815-58-9	NR	0.121		NA
n-butane	106-97-8	67		0.024	0.000
n-hexane	110-54-3	4.3		0.001	0.000
n-heptane	142-82-5	2.8		0.007	0.002
n-octane	111-65-2	1.8		0.107	0.060
n-nonane	556-67-2	1.4		0.139	0.099
2-methylpentane	107-83-5	1.5		0.021	0.014
3-methylpentane	96-14-0	1.5		0.035	0.023
2,3-dimethylpentane	565-59-3	NR	0.108		NA
2-methylhexane	591-76-4	1.2		0.046	0.039
		SUM	0.50	0.50	0.394
			Correction Factor		2.54

CF = correction factor; MF (-) = molar fraction for component lacking correction factor; MF (+) = molar fraction for component with correction factor available; NR = correction factor not reported; NA = MF/CF value not available due to unavailable CF.

Correction factor determined as reciprocal of sum of MF/CF values. Here, $CF = 1/0.394 = 2.54$; this value represents 50% of the molar mass of this mixture.

Appendix D

CF Derivation from Wnek et al. Data

Table D-1. Data and Derivation of CF Value for Wnek et al. (2018).

CHEMICAL	CASRN	CF	MF (-)	MF (+)	MF/CF
Cyclohexane	110-82-7	1.4		0.022	0.016
n- Heptane	142-82-5	2.8		0.015	0.005
1,2,4-Trimethylbenzene	95-63-6	ND	0.039		
1,3,5-Trimethylbenzene	108-67-8	0.35		0.097	0.276
m-xylene	108-38-3	0.44		0.022	0.050
p-xylene	106-42-3	0.39		0.022	0.056
o-Xylene	1330-20-7	0.45		0.108	0.240
n-Hexane	110-54-3	4.3		0.013	0.003
pentane, 2-methyl	107-83-5	1.4		0.024	0.017
cyclohexane, methyl	108-87-2	0.97		0.139	0.143
octane	111-65-2	1.8		0.013	0.007
nonane	556-67-2	1.4		0.009	0.006
cyclohexane, propyl	1678-92-8	ND	0.016		
decane	124.18.5	1.4		0.010	0.007
undecane	1120-21-4	2		0.013	0.007
cyclohexane, 1-methyl-2-propyl	4291-79-6	ND	0.036		
cyclohexane, butyl-	1678-93-9	ND	0.030		
cyclohexane, pentanyl	4292-92-6	ND	0.044		
Naphthalene, decahydro-2-methyl	2958-76-1	ND	0.038		
cyclopentane, 1,2,3-trimethyl	2815-57-8	ND	0.159		
heptane, 2-methyl	592-27-8		0.032		
cyclohexane, 1,4-dimethyl	589-90-2		0.026		
nonane, 2-methyl	871-83-0		0.037		
benzene, 1-methyl-2-propyl	1074-17-5	ND	0.038		
		SUM	0.49	0.51	0.834
			Correction Factor		1.20

CF = correction factor; MF (-) = molar fraction for component lacking correction factor; MF (+) = molar fraction for component with correction factor available; NR = correction factor not reported; NA = MF/CF value not available due to unavailable CF.

Correction factor determined as reciprocal of sum of MF/CF values. Here, $CF = 1/0.834 = 1.20$; this value represents 51% of the molar mass of this mixture.

Appendix E

NIOSH Laboratory Report

Empirical Determination of a Photoionization Detector Correction Factor for Crude Oil Vapor

Photoionization detectors (PIDs) are used for nonspecific detection of a variety of chemicals, particularly hydrocarbons and other volatile organic compounds (VOCs). PIDs typically measure VOCs from 0-1000s ppm (or mg/m³) and can identify contaminant sources or activities that present VOC exposure sources. Their very fast response time makes them able to detect rapidly changing concentration gradients in workplace air. PIDs, though very sensitive, cannot positively identify a single contaminant and where more than one airborne contaminant is present, the instrument may not distinguish one from the other.

PIDs use a high energy ultraviolet (UV) light source to ionize chemicals in an airstream. The ionized molecules collect on a charged surface that generates a current that is directly proportional to the concentration of the ionizable VOCs the air. The ionization potential (IP) defines the amount of energy needed to induce ionization in a specific chemical. If the energy of the UV lamp is greater than or equal to the IP of the chemical being sampled, then the chemical will be detected. The NIOSH Pocket Guide has IPs for many chemicals and Rae Systems Technical Note 106 *A Guideline for PID Instrument Response* lists specific IP values for several chemicals. Many PIDs are configured with 10.6 electron volts (eV) lamps. The 10.6 eV lamp energy is sufficient for most of the gases and vapors that we sample, and these lamps are rugged and have a very long service life.

The amount of electric current (signal response) generated in a PID varies with the chemical to be measured, along with the lamp energy. The detector response for a specific chemical relative to a reference gas, usually isobutylene, can be used to determine an instrument correction factor for a given chemical. The instrument reading is multiplied by the correction factor to determine the concentration of the contaminant of interest. Correction factors for many chemicals are pre-programmed into the instrument. For chemicals whose correction factors are not preprogrammed into the instrument, the correction factor may be determined by exposing the detector to a known concentration of the gas of interest and comparing the rereading to readings taken from known concentrations of isobutylene. Custom correction factors for mixtures such as a vapor from a crude oil sample may be calculated from the sum of the mole fractions X_i of each component divided by their respective correction factors CF_i : $CF_{mix} = 1 / (X_1/CF_1 + X_2/CF_2 + X_3/CF_3 + \dots X_i/CF_i)$. The procedure outlined in this document was developed for the Rae Systems by Honeywell MiniRae 3000 (Rae Systems by Honeywell *TN-106 A Guideline for PID Instrument Response*). For other PID instruments follow the process described in the instrument manual or consult the manufacturer.

Experimental Procedure

Calibration of the MiniRae 3000: The MiniRae 3000 was calibrated with 100 ppm isobutylene (PN 600-0002-001 from Rae Systems by Honeywell) each day. Manufacturer procedures were followed. Following calibration, the instrument was function or “bump” tested with certified standards at different concentrations (5, 10, 100 ppm isobutylene).

Generation of Crude oil vapor: Crude oil vapor was generated using a simplified diffusion apparatus. In short- a specified volume of crude was placed in a vessel and closed with a two hole stopper; the inlet air tube was adjusted so that it was $\frac{1}{4}$ the vessel height above the crude sample; the outlet air tube extended $\frac{1}{4}$ the vessel height into the headspace; ultra-high purity air was delivered into the inlet air tube at different flow rates and the air from the outlet tube was collected in FlexFoil® PLUS Air Sample Bag (SKC Inc. Eighty Four ,PA 15330). Different vessel sizes, volumes of crude oil, temperatures and flow rates were evaluated. Typically, composition of the vapor components was similar between each experiment. Concentrations were directly dependent on temperature and surface area of the vessel. Because the goal of the experiment was to replicate a vapor phase sample of a spilled product, conditions were optimized to generate head spaces that were no more than 1400 ppm by a flame ionization detector and produced a PID reading as calibrated to isobutylene of about 250 ppm. With this in mind, headspace vapors were generated using a 50 ml straight wall glass cylinder with a ground glass 2-hole stopper. One ml of crude oil was added, and the inlet and outlet lines connected. After 1 hour at 23° C, one ml/min high purity air was flowed through the inlet line and the outlet was connected to a 10 l FlexFoil® PLUS Air Sample bag.

Determination of components of crude oil vapor: Relative hydrocarbon composition of crude oil vapor was determined by gas chromatography using Baseline Series 9100 GC/FID and GC/PID analytical instruments. Three dedicated instruments used by the National Institute for Occupational Safety and Health Oil and Gas Research Program were used to characterize the relative composition of vapor from the crude oil samples. Methods developed using these instruments have been used to characterize vapor phase exposures for workers throughout upstream oil and gas activities both on and offshore, as well as research involving exposures in other workplaces including emergency response. Briefly, these instruments use techniques described in NIOSH Manual of Analytical Methods 3700-3704 which rely on collecting area or personal breathing zone samples in sample bags followed by injection of the sample into the gas chromatograph for analysis. The gas chromatographs are designed to measure concentrations of specific analytes in the present case: C1-C5 Hydrocarbons (0-100% by volume), C6-C12

Hydrocarbons (0-100 ppm) and aromatic hydrocarbons (i.e. BTEX 0-20 ppm). Because the samples collected and injected are whole-air samples they may be diluted with ultra-high purity air to conform with the analytical range of the instrument. The C1-C5 instrument was calibrated with a NIST-traceable standard containing 2500 ppm concentrations of methane, ethane, propane, iso-butane, n-butane, iso-pentane and n-pentane. The C6 to C14 instrument was calibrated with a NIST-traceable standard of 5 ppm each of n-hexane, n-heptane, n-octane, n-nonane and n-decane and 1 ppm each of n-undecane, n-dodecane, n-tridecane and n-tetradecane. The aromatic instrument was calibrated with 10 ppm each of benzene, toluene, ethylbenzene, m-xylene, p-benzene and o-benzene. Concentrations of hydrocarbons were automatically calculated by the instrument software for those hydrocarbons that had standards. Concentrations for unknown hydrocarbons were predicted based on area of the curve of unknowns and compared to the adjacent standard.

Results

MiniRae 3000: The MiniRae 3000 typically holds calibration for more than 30 days. Measurement of known standards were accurate and exceeded the NIOSH direct reading instrument acceptance criteria that the instrument provides results that were within $\pm 25\%$ of the (true) concentration 95% of the time.

Generation of crude oil vapor: Crude oil vapors were generated by diffusion of vapors from crude oil into vessel headspace that was collected over a defined period in a FlexFoil® PLUS Air Sample bag. The fractional composition of vapors generated at temperatures from 20° C to 30° C were comparable but, concentration was found to increase proportionally with increased temperature. Likewise, surface area of the crude oil sample was found to be positively correlated with concentration of vapor. To keep concentrations of small saturated alkanes (C1-C5) low and avoid PID interference by methane/ethane attenuation of photons from the light source, generation conditions that produced vapor concentrations near 250 ppm by PID/1500 ppm by FID were chosen. Use of a 50 ml cylindrical vessel, 1 ml crude oil and 1l/min air flow through the chamber would consistently produce samples that were 1300-1500 ppm by FID/230-255 ppm by PID (Table E-1, Figure E-1).

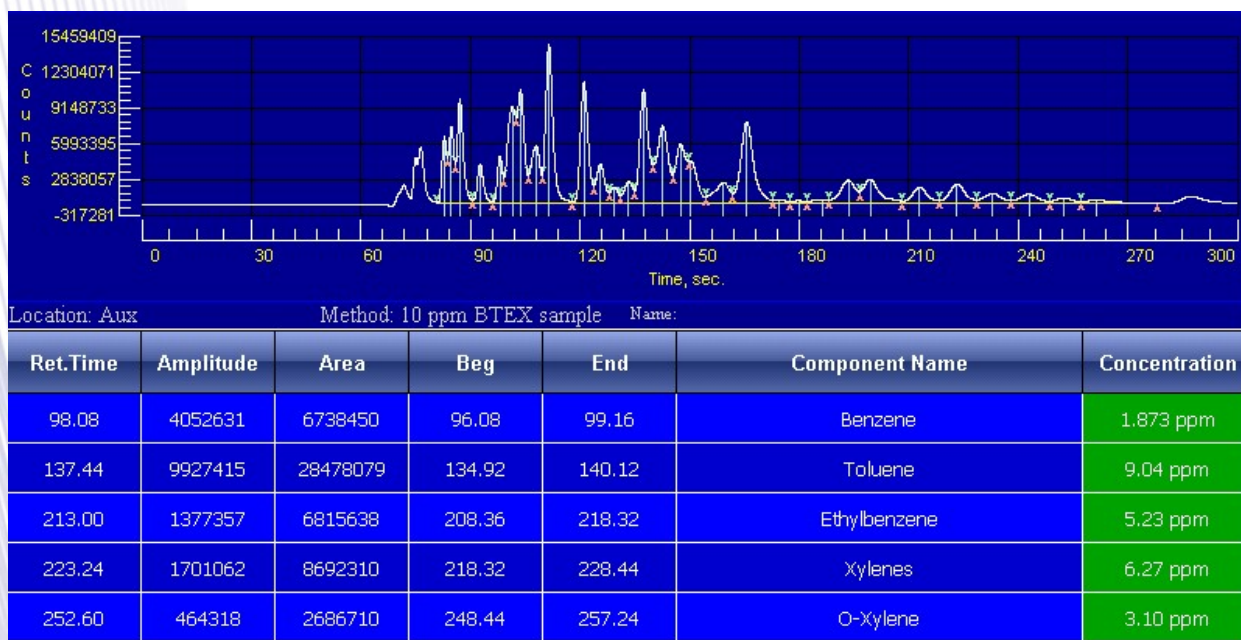
Table E-1. Headspace vapor phase hydrocarbons (ppm) from crude oil at 23° C

C1-C5	n-Hexane	n-Heptane	n-Octane	C6-C8 Composite	n-Nonane	n-Decane	C9-C14 Composite
40.3±0.47	21.1±0.7	45.0±0.8	22.7±1.2	45±0.8	5.1±1.1	0.7±0.2	25.0±4.3

Benzene	Toluene	Ethylbenzene	Total Xylenes	C6-C12 Composite
1.9±0.05	9.4±0.2	5.2±0.1	9.7±0.4	25.0±1.3

Figure E-1. Chromatogram of hydrocarbon vapor from each GC. A) C1-C5, B) C6-C14 and C. Aromatic hydrocarbons





C)

Calculation of custom PID (with a 10.6 eV lamp) correction factor for vapor mixture of the crude oil sample (Table E-2) was performed using the sum of the mole fractions (X) of each component and representative correction factors (CF) by the equation: $CF_{mix} = 1 / (X_1/CF_1 + X_2/CF_2 + X_3/CF_3 + \dots X_i/CF_i)$

Table E-2. Determination of Crude Oil Vapor Correction Factor

Component	Mole fraction	Correction Factor CF)	X/CF
Hexane	0.086	5.10	0.017
Heptane	0.190	2.80	0.068
Octane	0.095	1.80	0.053
Nonane	0.022	1.40	0.016
Decane	0.003	1.40	0.002
Composite C6-C14	0.280	2.50	0.112
Benzene	0.008	0.47	0.017
Toluene	0.043	0.47	0.091
Ethylbenzene	0.022	0.45	0.050
Xylenes	0.043	0.43	0.100
C6-C12 Composite	0.100	0.45	0.222
		Total CFMix	1/0.748 = 1.33

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