# CONSIDERATION OF TOTAL VOLATILE HYDROCARBON EXPOSURE DURING OIL SPILL RESPONSE[1]

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*Public perception and environmental awareness place increasing demands on the petroleum industry to facilitate fast and efficient oil spill containment and recovery to mitigate environmental damage. HSE legislation also places increasing demands on Oil Spill Response Organisations to ensure a safe working environment for responders. This paper looks at the trade-offs facing oil spill response planning from the perspective of occupational exposure to Total Volatile Hydrocarbons (TVH).*

*TVH is a term used to represent a large group consisting of hundreds of chemical compounds that derive from crude oil. Under certain circumstances, in-situ response measures represent a significant risk to local air quality and human health. Mechanical and manual oil spill recovery in close proximity with TVHs place spill responders and potentially the general public at an increased risk from fire/ explosions as well as acute and chronic health implications.*

*Over the course of a spill, physical and chemical processes are continuously changing TVH composition. This requires rapid on-scene monitoring and/ or predictive modelling to optimise spill countermeasures and responder safety. The use of personal and area TVH monitoring equipment is discussed in a practical spill recovery context, and an overview is provided of portable gaseous testing equipment with respect to key criteria such as; conformity, configuration, user-friendliness and robustness. Current developments in TVH monitoring models are reviewed and their contribution to future oil spill contingency planning assessed.*

*Consideration is given to hazardous vapour exposure and the resulting health and safety issues that were faced by OSRL during the Tasmin Spirit and an inland well-blow out in Georgia.*

## INTRODUCTION

Oil Spill Response Limited (OSRL) provide an international Tier 3 response service for its participants. Given prompt equipment mobilisation, visa applications and transit times, OSRL responders and equipment can be on the scene and deploying response equipment within 72 hours of an initial international call out. As well as responding to member and associate member call-outs, OSRL also respond to 3rd party spills. Under these circumstances, OSRL may be requested to mount a response operation where local incident management structure, oil response resources and trained personnel are compromised or absent.

In the past, when responding to Tier 3 incidents OSRL has required member oil companies or the clients to provide the necessary environmental and occupational air monitoring data in accordance with legislation. However, we shall look at two examples of Tier 3 spills that OSRL has recently responded to, to highlight the occupational health issues that faced OSRL responders, and which prompted a revision of OSRL's Occupational Health procedures.

On 27th July 2003 the 87,584 DWT crude oil tanker *Tasmin Spirit* ran aground whilst entering Karachi Harbour, Pakistan. The Global Alliance (OSRL/EARL) had been mobilised and was in-country when the vessel broke in half releasing an estimated 20,000 $m^3$ of crude oil. The HSE factors affecting this spill included; the possibility of hazardous vapours in close proximity to the local populous, and the safety of Alliance response personnel on the scene within hours of the major oil release. Acclimatising to the climate in Pakistan also posed considerable challenges to responders. Accurate and ongoing air monitoring, and the correct level of PPE was thus vital to the response planning phase. However, despite specific requests for such air monitoring data to be made available from in-country experts, the information was not forthcoming. This greatly hindered the speed of the response effort conducted by OSRL, and the decision to hold back response operations till a "worst case scenario" timeframe had passed, and not attempt any response clean-up operations in confined areas during the first phase of the clean-up.

On 13th September 2004 OSRL responded to a third party call from CanArgo-Georgia, following a 3 day well blow out which released 15-30,000bbl. of sweet crude, API 40°, down a hillside in the Caucasus mountain range. OSRL arrived in country the day after the well was capped (14/09/04), to establish the severity of the incident and to agree a response strategy. Concerns regarding the poorly ventilated forest area and well blow-out site, plus the possibility of residual atomised oil posed the biggest risks. The Georgian Ministry of the Environment undertook air monitoring at all the response sites. The findings suggested that 5 days after the wellhead had been capped, VOC levels were still three times over the TWA for an 8-hour working day at approximately 320ppm. Although the client arranged air monitoring, the subsequent validity and content of the data was called into question. The timeframe to organise the necessary air monitoring and the resulting dubious data compromised the response strategy employed by OSRL. These findings restricted the response operation at the wellhead to approximately to 2.5hr per day

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per person till the findings were shown to have decreased to 100ppm by the 20th September 2004.

As HSE legislation changes, and gas monitoring requirements come to the forefront of responder safety, Oil Spill Response Organisations (OSRO) are becoming increasingly concerned with the chronic affects of the many hazardous vapours and gases encountered during an oil spill (Wrenn, 2001). In line with these views, and following concerns raised following the aforementioned recent responses, OSRL is currently undertaking a comprehensive revision of its Air Monitoring and HSE Response Strategy. As part of this review it has been deemed necessary to revise our instrumentation and undertake a comprehensive training programme to enable response staff to assess hazardous vapour concentrations, and modify response strategies accordingly.

This paper does not attempt to embark on a full discussion of site characterisation and oil spill clean up procedures, nor does it aim to highlight the acute and chronic effects of the various VOC constituents; there is a wealth of information in literature on these topics (e.g. Park & Holliday, 1999). The purpose of this review was rather to highlight questions raised whilst reviewing international occupational health regulations, Occupational Exposure Limits (OEL), and the literature available on past spill air monitoring data and oil spill models relating to TVHs. The desired outcome of this paper, to call on the OSR community to assist in bridging these gaps to enhance future oil spill response planning.

## DISCUSSION

### Evaluating exposure limits during site characterisation

Oil spill recovery inevitably involves contact with hazardous compounds; when deploying, repositioning or trouble shooting recovery equipment, or during the various aspects of manual cleanup. Being in such close proximity to large volumes of oil released into the environment exposes responders to crude oil constituents through inhalation and dermal contact. The specific airborne hazards to the oil spill responder will depend on the chemical and physical nature of the crude oil, and the environmental factors acting upon it (Park & Holliday, 1999).

During the initial 72 hours of a large spill, approximately 30% to 45% of the crude oil and up to 75% of light oils can be evaporated into the atmosphere (Zhou & Wong, 1997). It is essential to understand the chemical composition of these gaseous releases in order to effect a safe response operation. The volatile components evaporated from oil spills can be categorised into three groups: aromatics, alkanes and non-hydrocarbon components. The majority of literature to date concentrates on the risks posed by single aromatic ring compounds (e.g. Benzene, Toluene, Xylene) and Hydrogen Sulphide due to their acute and chronic toxic and volatile nature. The acute and chronic health risks posed by these constituents can be reviewed in Park & Holliday (1999). The risks posed by Total Volatile Hydrocarbons (TVH) and oil mists have received little attention, a fact that we shall return to later on. The weight percentage of the volatile components varies with differing oil sources and degrees of refining, and is a major factor in determining the impact distance, Permissable Exposure Limit (PEL) and response strategy for each spill (Chang & Butler, 2002). During site characterisation it is essential to understand the product(s) involved and the respective risks involved. Accessibility to the relevant Material Safety Data Sheets (MSDS), current legislation and the Occupational Exposure Limits (OELs) for the relevant constituents avoid costly delays to the response operation.

### Crude oil information / conformation

On review of 8 crude oil product type MSDS, it became apparent that the use of generic descriptors of their chemical composition (e.g. Hydrocarbon mixtures (aromatics, naphthenics, and paraffinics) (ConocoPhilips, 2003)), gave no assistance when trying to formulate TVH exposure limits. Although the majority of MSDS sheets included individual exposure limits for hazardous compounds such as benzene and hydrogen sulphide, where applicable, the exposure standards do not reflect combined exposure standards. Often petroleum crude oil exposure limits are either 'not available', or defined using the exposure standards for refined mineral oil mist in MSDS's. Yet this standard is not adequate for unrefined oils and those containing contaminants or additives. Regulations (e.g. Australia and UK) state that a mixed compound formula should be used to derive mixed crude oil products (NOHSC, 2004; HSE, 2002). In a real-time spill situation, locating the accurate mixed exposure limits presents a very complex task.

MSDS sheets are traditionally classified with the petroleum refiner in mind. An example of the type of information provided can be seen in Park & Holliday (1999). Despite giving information regarding the products physical properties, health hazards and emergency and first aid procedures, more specific information is called for aimed at large oil spill response operations.

Various attempts have been made to classify crude oils. CONCAWE based a 5 group classification scheme on the physical 'spreading behaviour' and expected evaporation rates of 58 crude oil (CONCAWE, 1983). This classification scheme has a direct bearing on both oil spill clean up methods, and also inhalation exposures of spill responders (Park & Holliday, 1999). However, its occupational health limitations, and the difficulty in predicting the toxic properties of crude oil types still exists.

### When is oil mist not oil mist?

Although it is agreed that VOCs have usually evaporated within the first 72 hours of a spill, oil mists may be formed in all stages of the spill clean up operation (Park & Holliday, 1999). Anecdotal reports and papers published following the Braer, Exxon Valdez and Amoco Cadiz all reported hazardous levels of oil aerosols and mists during spill clean-up (NRC, 1985; Campbell et al., 1993; Reller, 1993). Responder exposure is particularly applicable when undertaking high pressure water and steam shoreline washing, or offshore oil recovery in rough sea conditions. On examination of the current legislation, there appears to be an anomaly in the TWA exposure limit of oil mists that needs highlighting.

In most countries the Time Weighted Average (TWA) exposure limit stated for oil mists is 5 $mg/m^3$ (e.g. ACGIH, OSHA, UK, Australia). However, this standard is only applicable for highly refined mineral oils, and does not apply to the petroleum oil aerosols or mists that may be encountered during a crude oil or unrefined oil spill. Despite warnings in 1980 by the American Conference of Governmental Industrial Hygienists (ACGIH) it has become common practice to apply the 5 $mg/m^3$ TWA to all varieties of oil mist without regard to the composition of the original oil type, as mentioned previously in regard to MSDS.

CONCAWE undertook a review to establish what types of oil a TWA of 5 $mg/m^3$ is applicable to. Their findings suggest that is it is not prudent to apply this TWA for all types of oil mist due to a lack of conclusive research. In particular, oils which contain significant concentrations of polycyclic aromatic hydrocarbons. Their recommendations were to use the more conservative ACGIH TLV-TWA of 0.2 mg/m3 (CONCAWE, 1986). These findings suggest that additional research is needed to establish a TWA that is relevant to heavier fractions of oil and crude oils readily encountered during a spill response operation.

### TVH research void

The complexities involved in assessing TVHs airborne hazards are reflected in the lack of available real spill data and modelling on the subject. There is evidence to support the chronic and acute health risks posed by the various components of crude oil (e.g.

MacFarland (1988), Mehlman (1994), Goldstein (1988)). But the inevitable difficulty in undertaking experiments on such a diverse and complex substance as crude oil has promoted little, if any, study of the health implications of TVHs (Park & Holliday, 1999). Some studies suggest that they may be able to predict the health effects of various types of crude oil from correlating the various individual constituents (Eide & Zahlsen, 1996). Even so, on the whole it can be concluded that a lack of data pertaining to oil spill responder exposure levels and the complexities surrounding crude oil chemistry have researchers on pause.

Various anecdotal reports and oil spill models focus on hazardous airborne crude oil constituents, with most research directed towards the evaporation rates of benzene and other single VOC constituent compounds (Thayer & Tell (1999), Hanna & Drivas (1993), Zhou & Wong (1997), Delikat et al., (1992), and Holliday & Park (1993). This research is in agreement that most volatile constituents are driven off from refined products within the first few hours of the spill, and from crude products within 8 hours or so. This timeframe may be extended in calm, cool conditions, and/or in confined environments such that the oil is unable to spread to a thin film. Even so evidence is available that most if not all, aromatic hydrocarbons will have been volatilised and lost within a 24 hour period. As a consequence inhalation risks in open environment responses are usually considered to be negligible after the first 24 hours or so.

Yet without sufficient investigation it cannot be ruled out that a mixture of these volatile components may present more chronic health risks than currently assumed (Zhou, 1997). Without extensive chemical information about the compositions of the commonly used oils, and further research into the toxicities of oil vapour mixtures and the field observations and measurements is necessary to support the findings, we could be overlooking a serious HSE issue.

Despite the high number of large oil spills globally, it is surprising to discover the lack of real-time spill VOC constituent or TVH data available in published data. A fact that can only highlight the need for governments and OSROs to make spill data more readily accessible to all interested parties. Without such data to compare/test predictive modelling tools, essential research cannot progress. On reviewing the models currently developed, the shared opinion is that the rate VOCs evaporation following a discharge of oil into the environment is a function of oil mass, thickness, surface area and containment; and environmental factors such as temperature, wind speed, sea state and precipitation. The role these variables play when modelling a spill scenario is still contested. However, temperature is accepted as the most significant factor in VOC evaporation. Accurate and detailed reporting of actual spill air monitoring data and the external environmental variables acting on the oil will enable researchers to clarify and strengthen available predictive oil spill models.

### Occupational gas monitors

Multi-gas or Toxic gas monitors make up the bulk of real-time gas monitoring in the response industry. Such monitors typically measure Oxygen ($O_2$), the Lower Explosive Limit (LEL) of combustible gases, Carbon Monoxide (CO) and Hydrogen Sulphide ($H_2S$). However, they are not suitable for detecting the many common gases and vapours that may make up major constituents or by-product of oil spills (e.g. TPH or benzene). Response organisations which rely solely on multi-gas monitors run the risk of being under-protected, with negative health results, or over-protected with loss of responder productivity due to excessive PPE or restricted response times (Wrenn, 2001).

In order to fully assess the acute and chronic effects of total volatile hydrocarbons, and comply with current occupational legislation it is essential to utilise instruments that can accurately measure in parts per million (ppm). Broadband scanning monitors are simple to operate, and provide such detection capabilities. When used in unison with a multi-gas or LEL detector during a site characterisation, and as personal or area monitoring equipment throughout the post emergency phase of a spill, a responder can establish if excessive TPH vapour levels are present. A more specific monitoring instrument can then be used, or electronic broadband instruments can be re-calibrated in the field to determine the hazardous gas or vapour levels, and the response strategy can be modified accordingly.

There are a variety of survey instruments available which are designed to respond to specific and/or broad spectrum contaminants e.g. TPH. When choosing the correct equipment best suited for oil spill monitoring, it is essential to fully understand the capabilities of the different categories of equipment on the market and its limitations in a spill environment. Published instrument data sheets and review studies, such as Wrenn (2001), have been summarised here to give an overview of the portable methods available to the oil spill responder and their effectiveness and practicalities in a spill environment.

Colorimetric tubes (often referred to as "Draeger" tubes) have been the "work horse" of early warning gas detection for years, enabling the measurement of specific individual toxic gases and vapours at sequential ppm levels. Draeger tubes themselves are inexpensive, but have a short shelf life and thus it may be expensive in the long run to maintain a comprehensive stock for sporadic spill response. In the field, Colorimetric tubes cannot provide continuous monitoring, there is no danger warning alarm, the results are only qualitative, the equipment is prone to operator error and can be very difficult and hazardous to use with level A or B hand protection.

Absorbent tubes followed by Gas Cromatography/Mass Spectroscopy (GC/MS) laboratory analysis can be used to provide continuous specific compound monitoring over an entire workday. Low flow pumps are used to pull a sample through an absorbent tube. These sample are then sent off for laboratory analysis to obtain an average concentration of chemical exposure for the responder that wore the pump. This method can be a very accurate and inexpensive way to gain ongoing air monitoring data throughout the spill for later interpretation of PEL. However, the delay in gaining the data from the laboratory requires another method to be used to determine real-time response decisions.

Portable GC/MS, although very accurate at snap-shot, specific compound monitoring. Such pieces of equipment tend to be prohibitively expensive for the returns possible compared to other methods of gas monitoring equipment.

Semiconductors or Metal Oxide Sensors (MOS) were the first true "broad-band" sensors and respond to a wide variety of compounds. They are very inexpensive, and are a good combined gauge of toxic gases. However, they are difficult to operate in full PPE, they are affected by temperature and moisture, and can be easily contaminated in spill work zones.

Organic Vapour Analysers, such as Flame Ionisation Detectors (FIDs) and Photo Ionisation Detectors (PIDs) are widely used to measure broad band VOCs and other toxic gases in low concentrations from ppb up to 10,000 ppm. Both are very sensitive broad spectrum monitors e.g. Total Petroleum Hydrocarbons (TPH), not unlike a "low-level LEL monitor. While FID's linearity is excellent, their use as an item of international oil spill response equipment is limited by their large size and weight, the high costs involved in purchasing and maintaining the detector, and the need to carry a hydrogen cylinder (Wrenn, 2001).

PID's efficiently provide the same function as FIDs. However, PIDs are smaller, easier to operate and significantly less expensive, so their usefulness in oil spill response is potentially greater than FIDs. PIDs are routinely used during site characterisations to ensure responder safety and prevent over exposure to airbourne VOCs. Whilst PIDs are not selective, it can provide continuous monitor and instantaneous feedback to responders, which is invaluable during the initial emergency phase and for the duration of the post emergency phase of a spill.

Budget, demand and ease of real time interpretation always factors heavily when investing in air monitoring instruments. On communication with other OSRO's the general consensus is that a continuous PID and a simple specific detector such as a multi-gas detector or colormetric ("Draegar") tubes would be most pertinent in the earliest stages of the spill response, or where elevated VOC levels may be suspected.

In addition to the wide range of monitoring methods available, the various makes and models of equipment available on the world market is extensive, and beyond the scope of this paper.

### What is valid data?

It should, however, be highlighted that data comparability is a major problem in occupational monitoring since laboratory and field methods are continually changing and in view of the fact that there are so many different "standard methods" published by various regulatory bodies. However, these are problems that must be overcome in order to further the development of oil spill response strategies, predictive spill modelling and safety contingency planning. In spite of the numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of conflicting research opinions and data rather than having a proportion of this information arbitrarily censored. It is more constructive to say " I knew about that data, assessed it based on the following quality assurance criteria and decided not to use it for this application" rather than not have access to the data at all.

## CONCLUSION

During the emergency and post-emergency phase of a spill, it is essential that the incident commander has a full understanding of the risks posed by hazardous vapours and can modify the response strategy accordingly. Time is critical in making these decisions, therefore OSROs have a vested interest in promoting research and development into updating the format of MSDS sheets, occupational health legislation and airborne volatile gas and vapour predictive modelling in order to base this process on fact rather than supposition.

This paper looked at the risks posed to responders when assessing total volatile hydrocarbon releases during an oil spill. This subject has received considerable interest recently, but the reoccurring theme in the literature is a general lack of real time oil spill air monitoring data; a lack of conformity regarding current international legislation and a need to agree on the cost-benefit of PPE specified for emergency response personnel.

Oil spill response organisations face very similar issues the world over. The need has never been greater to join forces in order to disseminate information and formulate a standardised international HSE response strategy through internationally agreed permissible exposure limits, a readily accessible oil spill air monitoring database, and total hydrocarbon monitoring model development.

## BIOGRAPHY

Alex holds a BSc in Marine Biology from Aberdeen University, Scotland and a MSc in Applied Marine Science from Plymouth University, UK. After working in the field of marine environmental management for the last 7 years, she joined Oil Spill Response Ltd, UK, as an oil spill technician.

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