

## Review of Emissions from Oil Fires

Merv Fingas  
Spill Science  
Edmonton, Alberta, Canada  
fingasmerv@shaw.ca

### ABSTRACT 285468:

The concern over emissions often dominates concerns regarding in-situ burning of oil spills. This paper reviews the results of emission measurement from both test fires and full-scale fires. More than 50 meso-scale burns of crude and diesel were conducted to study various aspects of diesel and crude oil burning in-situ. Extensive sampling and monitoring of these burns were conducted at downwind stations, and in the smoke plume. Later, the burning characteristics of heavy oils and emulsified heavy oils were studied. More than 15 meso-scale burns of these heavy oils were conducted. Measurements of the volatile components and particulates were made. Finally, some measurements were made on the in-situ burns carried out during the 2010 Deepwater Horizon spill.

In summary, these measurements found that PAHs were found to be lower in the soot than in the starting oil, although somewhat higher concentrations of the larger molecular PAHs were found in the soot and residue. Particulates in the air were measured by several methods and were only found to be greater than recommended exposure levels at ground level if an inversion was present. Combustion gases including carbon dioxide and carbon monoxide did not reach exposure level maximums. Volatile organic compound (VOCs) emissions were found to be extensive from fires, but the levels were lower than an evaporating crude oil spill. Carbonyls, including aldehydes and ketones, were found to be higher from diesel burns than from crude oil burns.

Measurement of the highly toxic compounds, dioxins and dibenzofurans, were made during the test fires. None were found. Similar results were found for the 2010 Deepwater Horizon burns.

Water under the burns was analysed in the case of some of the test fires; no compounds of concern could be found at the detection levels of the methods. The burn residue was analysed for the same compounds as the air particulate samples. The concentrations of PAHs were lower in the residue than in the original oil, although the concentrations of some higher molecular weight species increased slightly. Furthermore, in all burns it was found that emissions of any type, did not exceed that of health concerns at distances greater than about 1 km, if the smoke plume did not impact the ground.

### 1.0 INTRODUCTION:

The concern over atmospheric emissions remains the biggest barrier to the widespread use of insitu burning of oil (Fingas, 2011) and the burning of other combustible materials. And while analysis is difficult, extensive studies have been conducted and technology now permits an assessment of key compounds and comparison to ambient levels of pollution.

Emissions include the smoke plume, particulate matter precipitating from the smoke plume, combustion gases, unburned hydrocarbons, organic compounds produced during the burning process and the residue left at the burning pool site. Soot particles, although consisting largely of carbon particles, have a variety of chemicals absorbed and adsorbed. Complete analysis of the emissions from a burn involves measuring all of these components.

## 2.0 MEASUREMENT OF EMISSIONS:

### 2.1 Crude Oil and Diesel Fuel Burns

Extensive measurement of burn emissions began in 1991 with the instrumentation of several burns conducted at Mobile, Alabama, to measure various physical facets of oil burning (Fingas et al., 1993). Analysis of the data from these burns showed several interesting facts and several data gaps. Monitoring of burns continued for several years. In 1992, two further series of burns were monitored for emissions (Fingas et al., 1993; Booher and Janke, 1997). In 1993, two major burns were conducted at sea specifically to measure emissions and many other measurements (Fingas et al., 1994; 1995). During these offshore tests samples and measurements were taken on as many as 2000 different compounds or parameters. Further burn tests were conducted in 1994, 1997 and 1998 (Fingas et al., 1996; 1998, 1999, 2000). Detailed analytical methods are given in these papers. The measurement of these burns included as many as 18 emission measuring stations with as many as 15 instruments or samplers each. Figure 1 shows three downwind measuring stations set up for a burn test. Analysis of samples measured as many as 500 different compounds.

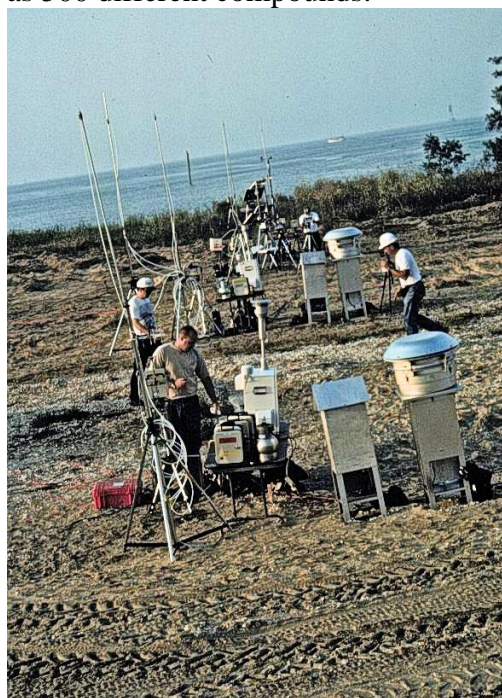


Figure 1 Three burn emission stations set up to measure emissions (Photo from Environment Canada).

The monitoring of emissions at these burns was intended to be comprehensive and used the best field samplers or instrumentation available at the time. Measurement techniques have progressed through the years and are now available to measure many suspected emissions with high accuracy.

The emphasis on sampling has been the air emissions at ground level. Such heights are usually 5 feet or 1.5 metre, the typical receptor heights for humans. This is the primary concern and also is the basis of the regulated value for human health purposes. This paper will focus on these receptor emission values.

Volatile Organic Compounds (VOCs) were sampled using 6 L pre-evacuated (to 0.05 mm Hg) stainless steel canisters (Summa canisters). Upwind and background samples were always taken. Analysis was by GC-MS. More than 150 compounds were measured and over 90 hydrocarbons identified in the vapours from an evaporating or burning slick.

Carbonyls were sampled by reacting them on a DNPH (2,4-dinitrophenylhydrazine)-silica cartridge through which air was pumped. The sample was subsequently analysed using HPLC.

Polycyclic Aromatic Hydrocarbons (PAHs) were sampled in air using filters and from particulates collected on high volume samplers. Analysis of PAHs was also conducted from various particulate sampling including fractionation samplers, PM-10, PM- 2.5 or cascade samplers, and filters from low and medium-volume pumps. Analysis was by standard methods using GC-MS.

Heavy metals on soot were collected using personal sampling pumps and filters. Analysis was by ICP, using standard techniques.

Polychlorinated dibenzo-p-dioxin/furan was measured on particulate samples. High volume samplers were employed to collect cumulative samples at upwind and downwind locations. Sampling media were glass-fibre filters followed by a polyurethane foam plug (PUF). These same samples were used to measure TSP, or Total Suspended Particulate levels and sometimes were analysed for PAHs, other organics or metals.

PM-10 particulate (PM-10 are particulates less than 10  $\mu\text{m}$  in size, a critical size below which human lungs are affected) air sampling was performed using a General Metal Works model PM-10 instrument. The sampling media consisted of a quartz fibre filter. Some of these filters were also analysed for PAHs.

PM-2.5 are particulates less than 2.5  $\mu\text{m}$  in diameter, and are particularly dangerous to

human lungs. PM-2.5 particulate air sampling was accomplished using a Partisol PM-2.5 sampler. A Teflon filter was placed in the apparatus and used to collect sample.

Real-time particulate measurements were taken with RAMs or DataRAMs. The Ram-1 instrument was used to perform real-time aerosol monitoring during the earlier burns and measure relative concentrations of airborne particulates. This instrument responds to a physical particle size of 0.1 to 30 microns. The DataRAM (MIE Inc, Bedford MA) is an updated version of the RAM. The apparatus is capable of employing several different sampling head configurations. These are total particulate, the 0 to 10  $\mu\text{m}$  particulate fractions or the 0 to 2.5  $\mu\text{m}$  particulate fractions.

Sulphur dioxide was measured using the Biosystems Cannonball. These data were logged electronically. Sulphur dioxide in acid form was measured using a Gilian pump and a sodium hydroxide-filled impinger. The impinger fluid is titrated to determine the amount of sulphuric acid/dioxide. Carbon Dioxide was measured using two electronic instruments, the Metrosonics AQ501 and the Armstrong CD-1 carbon dioxide analyser. Carbon dioxide was also measured in some Summa samples using gas chromatography. The Metrosonics instrument also measures carbon monoxide, moisture and temperature. Nitric oxides were measured using the Biosystems Cannonball.

## **2.2 Heavy Oil and Emulsion Burns**

Four oils were burned: Bitumen (Orimulsion settled), Orimulsion, Bunker C, and Heavy test oil (Fingas et al., 2003, 2004; 2005). Many small-scale burns were carried out in 2001 and 2002 (Fingas, 2002). Larger-scale experiments were carried out in both 2003 and 2004. Volatiles were measured using HNu instruments and the values recorded. Particulates were measured by a sample filter pump and glass filter media. The glass filter media were further analysed for PAHs.

## **3.0 RESULTS OF EMISSION MEASUREMENT:**

The following summarizes the basic results:

### **3.1 Particulates**

All burns, especially those of diesel fuel, produced an abundance of particulate matter. The concentrations of particulates from diesel at the same distances were approximately 4 times that for similar-sized crude oil burns. PM-10 concentrations were sometimes about 0.7 of the total particulate concentration (TSP), as would be expected, but sometimes were the same as the TSP. The PM-2.5 concentrations were sometimes 0.5 of the TSP, as would be expected, but sometimes were closer to the PM-10 values.

### **3.2 PAHs**

PAHs or Poly Aromatic Hydrocarbons are aromatic compounds found in crude oil and are often produced as a result of combustion. Many PAHs are toxic to man and the environment, particularly the larger PAHs. Crude oil burns result in PAH downwind of the fire, but the

concentration on the particulate matter is often an order-of-magnitude less than the concentration in the original oil and sometimes several orders-of-magnitude less. Diesel contains significant levels of PAHs of smaller molecular size, the 2- 3-ring PAHs predominating. Burning diesel results in more pyrogenic PAHs of larger molecular sizes. Larger PAHs are either created or concentrated by the fire. Larger PAHs, some of which are not even detectable in the Diesel fuel, are found both in the soot and in the residue. The concentrations of these larger PAHs are low and often just above detection limits. Overall, more PAHs are destroyed by the fires than are created.

### **3.3 VOCs**

VOCs or volatile organic compounds are hydrocarbons that have a significant concentration in the vapour phase. One-hundred and forty-eight volatile organic compounds were measured from samples taken in Summa canisters and some on carbon absorption tubes. The concentrations of VOCs are about the same in a crude or diesel burn. Concentrations appear to be under human health limits even at the closest monitoring station. VOC concentrations are about three times higher when the oil is not burning and is just evaporating. This is difficult to measure at many burns.

### **3.4 Dioxins and Dibenzofurans**

Dioxins and Dibenzofurans are toxic compounds sometimes produced from the combustion of organic materials containing chlorine. Particulates precipitated downwind and oil residue were analysed for dioxins and dibenzofurans. The levels of these toxic compounds were at background levels indicating no production by either crude or diesel fires. Similar studies were performed during the 2010 Gulf oil spill burns and no dioxins were found either (Aurell et al, 2010; Schaum et al., 2010)

### **3.5 Carbonyls**

Oil burns produce low amounts of the small aldehydes (formaldehyde, acetaldehyde, etc.) and ketones (acetone, etc.), collectively known as carbonyls. These would not be a health concern because of the low levels detected at distances from the source fire. Carbonyls from crude oil fires are found at very low concentrations and those from diesel fires are detected at slightly higher concentrations.

### **3.6 Carbon Dioxide**

Carbon dioxide is the end result of combustion and is found in increased concentrations around a burn. Normal atmospheric levels are about 300 ppm and levels near a burn can be around 500 to 800 ppm. There is no human danger in this level. Concentrations at ground level are as high as 10 times that of the plume. Distribution along the ground is broader than for particulates.

### **3.7 Carbon Monoxide**

Carbon monoxide levels are usually at or below the lowest detection levels of the instruments and thus do not pose any hazard to humans. The gas has only been measured when the burn appears to be inefficient, such as when water is sprayed into the fire. Carbon monoxide appears to be distributed in the same way as carbon dioxide.

### **3.8 Sulphur Dioxide**

Sulphur dioxide, per se, is usually not detected at significant levels or sometimes not even at measurable levels. Sulphuric acid, or sulphur dioxide that has reacted with water, is detected at fires. Sulphur dioxide must be measured using impingers rather than conventional gas detectors. The measured concentrations of sulphuric acid are below concern levels and appear to correspond to the sulphur contents of the oil.

### **3.9 Other Gases**

Attempts were made to measure oxides of nitrogen which might be the result of combustion. None were measured in 10 experiments.

### **3.10 Other Compounds**

A concern about burning crude oil lies with any "hidden" compounds that might be produced. One study was conducted several years ago in which soot and residue samples were extracted and "totally" analysed in various ways. The study was not conclusive, but no compounds of the several hundred identified, were of serious environmental concern. The soot analysis revealed that the bulk of the material was carbon and that all other detectable compounds were present on this carbon matrix in abundances of parts-per-million or less. The most frequent compounds identified were aldehydes, ketones, esters, acetates and acids. These are formed by incomplete combustion of the oil. Similar analysis of the residue shows that the same minority compounds are present at about the same levels. The bulk of the residue is unburned oil.

A preliminary study of nitro-PAHs showed that these may be present at the parts-per-billion level. Because of the difficulty of analysis of these, further work was not done.

### **3.11 Residue**

The residue from burning oil is largely unburned oil with some lighter or more volatile products removed. When the fire ceases, unburned oil is left that is simply too thin to sustain combustion. In addition to unburned oil, oil is also present that has been subjected to high heat and is thus weathered. Finally, heavier particles are re-precipitated from the smoke plume into the fire and thus become part of the residue. Highly efficient burns of some types of heavy crude oil may result in oil residue that sinks in sea water after cooling. Figure 2 shows a heavy oil residue that is quite solid.



Figure 2 - The residue of a heavy oil burn. This residue is so thick it can be picked up as one piece (Photo from Environment Canada).

#### 4.0 DATA SYNTHESIS AND CALCULATION:

Sufficient data are now available to correlate emission data results with spatial and burn parameters. The extensive work is described in the literature (Fingas 2011). Many correlations were tried, and it was found that atmospheric emissions correlated relatively well with distance from the fire and the area of the fire. This information was used to develop prediction equations for each pollutant, using the data gathered from the 50 test burns conducted (Fingas, 2011). Sufficient data are available to calculate prediction equations for more than 150 individual compounds and for all the major groups. The result of the correlation will significantly increase understanding of in-situ burning in the areas of assessing the importance of specific emissions and classes, predicting 'safe' distances, and predicting concentrations at a given point. These predictions are far more accurate than those obtained from models because they are based solely on actual data.

The emissions at a given downwind site are a function of various factors including wind direction and speed, atmospheric stability conditions, and the size of the fire. The data available correlate satisfactorily because they were obtained in about the same conditions, at wind speeds of about 10 km/h, and at standard daylight atmospheric stabilities. Previous workers have shown

that the area of the fire yields the burn rate (Fingas, 2011). Thus, the area correlates satisfactorily with the emissions produced. The data are subject to a variety of sources of noise, including patchiness of emissions caused by turbulence and wind anomalies in the field. In addition, some of the data sets are derived when the wind changed and emissions that are very dependant on wind direction, such as particulates, impact a different set of sensors. Based on these historical data on particulate emissions, safe distances have been calculated for a variety of fire sizes given the similar measurement conditions.

## 5.0 CONCLUSIONS:

The measurement of emissions and calculation using equations developed from emission data, have revealed several facts about the fate, behaviour and quantity of the basic emissions from burning.

*Particulate Matter/Soot* - Particulate matter at ground level is a matter of concern (greater than occupational health criteria maximum values) close to the fire and under the plume. The concentration of particulates under the smoke plume may not be a concern past about 1000 metres for typical crude oil burns. The level of respirable particulates, those which have a size less than 2.5  $\mu\text{m}$ , is the emission of concern. Diesel fuel burns result in significantly more soot production and safe distances are much farther.

*PAHs* - Oils contain significant quantities of PAHs. These are largely destroyed in combustion. The total amount of PAHs in the smoke, both in the plume and the particulate precipitation at ground level are much less than the starting oil. This also includes the multi-ringed PAHs that are often created in other combustion processes such as low-temperature incinerators and diesel engines. The burn residue does, however, show a slight increase in the concentration of multi-ringed PAHs. Burns of diesel fuel show an increase in the concentration of multi-ringed PAHs, but still a net destruction of the total PAHs is noted.

*Gases* - Combustion gases such as carbon dioxide and carbon monoxide are significantly under any concern level.

*VOCs* - Many volatile organic compounds are emitted by fires, but in lesser quantity than when the oil is not burning. VOCs are not a primary concern, but can rise to close to concern levels very near a fire (<100 m).

*Organic Compounds* - No exotic or highly-toxic compounds are thought to be generated as a result of the combustion process. Organic macro-molecules are in lesser concentration in the smoke and downwind than they are in the oil itself. Dioxins and dibenzofurans are not created by oil fires.



*Carbonyls* - Carbonyls such as aldehydes and ketones are created by oil fires, but do not exceed health exposure limits at reasonable distances from the fires.

Overall, emissions are now understood to the extent that fires of various sizes and types can be evaluated for emission levels and safe distances. A standard crude oil fire such as would be conducted in a full-boom tow, would not exceed exposure limits for emissions beyond about 1000 m.

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