

STUDIES OF EMISSIONS FROM OIL FIRES

Mervin F. Fingas, Patrick Lambert, Ken Li, Zhendi Wang, Francine Ackerman, Robert Nelson, and Mike Goldthorp
Emergencies Science Division, Environment Canada
3439 River Road
Ottawa, Ontario K1A 0H3, Canada

Joseph V. Mullin
U.S. Minerals Management Service
Herndon, Virginia

Rod Turpin, Royal Nadeau, and Phil Campagna
U.S. Environmental Protection Agency
Edison, New Jersey

Steve Schutz and Mike Morganti
Weston, REAC
Edison, New Jersey

Robert Hiltabrand
U.S. Coast Guard Research & Development Center
Groton, Connecticut

ABSTRACT: Over 35 meso-scale burns 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, upwind stations, and in the smoke plume.

Particulate samples were taken in air and analyzed for polycyclic aromatic hydrocarbons (PAHs). PAHs were found to be lower in the soot than in the starting oil, although higher concentrations of the larger molecular PAHs were found in the soot and residue, especially for diesel burns. Particulates in the air were measured by several means, and were found to be greater than recommended exposure levels up to 500 meters downwind at ground level, depending on the size and type of fire. Diesel fires emit much more particulate matter and have longer exposure zones. Combustion gases, including carbon dioxide and carbon monoxide, were below exposure level maximums. Volatile organic compound (VOCs) emissions were measured, but the levels were less than from an evaporating crude oil spill. Over 140 compounds were identified and quantified. Carbonyls, including aldehydes and ketones, were found to be below human health concern levels.

Emission data from over 30 experimental burns were used to develop prediction equations for over 150 specific compounds or emission categories. These were used to calculate safe distances and levels of concern for a standard burn size of 500 square meters, an amount that would typically be contained in a boom. The safe distance for a crude oil burn of this size is about 500 m and for a diesel burn, much farther.

data which should lead to broader acceptance of *in situ* burning as an acceptable spill countermeasures alternative.

Burning has distinct advantages over other countermeasures. First and foremost, it offers the potential to rapidly remove large quantities of oil. *In situ* burning has the potential to remove as much oil in one day as several mechanical devices could in one month. Application of *in situ* burning could prevent a large amount of shoreline contamination and damage to biota by removing oil before it spreads and moves to other areas. Secondly, *in situ* burning requires minimal equipment and much less labor than any other technique. It can be applied in areas where other methods cannot be used because of the remoteness of a spill and lack of support personnel and equipment. Thirdly, burning of oil is a complete solution compared to mechanical recovery. When oil is recovered mechanically it still has to be transported, stored and disposed of. Fourth and finally, burning may be the only option available in certain situations. Oil with ice and on ice are examples of situations where practical alternatives to burning rarely exist.

There are disadvantages to burning. The first and most visible disadvantage is the large black smoke plume that burning oil produces. The second disadvantage is that the oil must be a minimum thickness to burn. Thin slicks will not burn. Oil rapidly spreads, forming thinner and thinner slicks. Most oils will spread rapidly and in time will be far thinner than their minimum burning thickness. An approach to dealing with such oils is to concentrate them into thicker slicks using fire-resistant booms and then burn them. This has the obvious disadvantage of requiring boats, booms, people and time. It should be noted, however, that concentrating oil for burning requires less equipment than does collecting oil using skimmers. Third and finally, burning oil is not an appealing alternative to some individuals, compared to collecting and reusing the oil. In very few cases has the collected oil been recycled in this way. Most often collected oil is incinerated because it contains too many contaminants to economically reprocess it. Often, no reprocessing facilities are readily accessible.

The concern over atmospheric emissions remains the biggest barrier to the widespread use of burning. The burning of all kinds of materials is believed to be a questionable because of concern

Introduction

In situ burning of oil spills has been tried for more than thirty years with limited acceptance as an oil spill cleanup option in certain parts of the world. Such lack of acceptance is primarily because of the lack of understanding regarding combustion products and the issues involving the combustibility of oil-on-water. Extensive research is currently underway to understand the many facets of burning oil. A consortium of several agencies in the United States and Canada have joined forces to study burning and to conduct large scale experiments. This effort has resulted in

over combustion by-products. 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.

Measurement of emissions

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, but many other measurements were

taken as well (Fingas *et al.*, 1994a,b; 1995a,b). Further tests were conducted in 1994 and 1997 (Fingas *et al.*, 1996a,b, 1998; Lambert *et al.*, 1998). Detailed analytical methods are given in these papers. These tests and numbers of fires monitored are summarized in Table 1.

The monitoring of emissions at these burns were 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 sufficient accuracy. The summary of measurements taken is given in Table 2.

The emphasis on sampling has been the air emissions at ground level. Such heights are usually 5 feet or 1 meter and 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 the same measurements.

Volatile Organic Compounds (VOCs) were sampled using sorption tubes (in 1991 and 1992) and by taking whole air samples. Whole air samples were also taken 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. Over 150 compounds were measured by 1997 and over 90 hydrocarbons identified in the vapors from an evaporating or burning slick. The latter compounds are listed in Table 3.

Table 1. Summary of studies used to measure *in situ* burn emissions.

Location	Year	Number of burns	Number monitored	Oil type	Prime purpose	Burn area range (m ²)	Time of burns (min.)	Number of instruments	Number of target compounds
Mobile	1991	14	14	Louisiana crude	Physics	37 to 231	20 to 60	30	70
Mobile	1992	6	6	Louisiana crude	Physics	36 to 231	20 to 60	30	70
Calgary	1992	20	3	Crude, diesel	Emissions	37	20 to 70	25	40
Newfoundland	1993	2	2	Crude (ASMB)	Emissions	467 to 600	60 to 90	200	400
Mobile	1994	3	3	Diesel	Physics	199 to 231	60 to 80	95	400
Mobile	1997	9	8	Diesel	Boom tests	25	60	95	400

Note: Above values are approximate or rounded-off.

Table 2. Samples taken and target emission parameters.

Sample taken	Sampler	Measurement parameter	Secondary parameters	Additional parameters
Soot at ground level	High volume sampler	Dioxins and dibenzofurans	Particulates	PAHs
	High volume sampler	Sized particulates (PM-10, PM-2.5)		PAHs
	Sampling pump	PAHs	Particulates	
	RAM, dataram	Particulates		
	Cascade sampler	Particle size	PAHs	
Soot in smoke plume	Sampling pump - low volume	PAHs	Particulates	Metals
	Blimp, remote-controlled helicopter, research aircraft		Particulates	PAHs
Air at ground level	Summa canister	Volatile organic compounds	CO ₂ , CO, NO _x	
	Sampling pump- low volume	Volatile organic compounds		
	CO ₂ meter	Carbon dioxide		
	SO ₂ meter	Sulphur dioxide		
	NO ₂ meter	Nitrogen dioxide		
	CO meter	Carbon monoxide		
	SO ₂ impinger	Sulphur dioxide in acid form		
	DNPH cartridge	Carbonyls		
Oil		PAHs	Metals	Full analysis
Burn residue		PAHs	Metals, toxicity	Full analysis
Water under burn		PAHs	Organics	Toxicity

Table 3. Volatile organic compounds found from evaporating or burning oils.

Propene	c-2-Heptene
Propane	2,2-Dimethylhexane
Isobutane (2-Methylpropane)	Methylcyclohexane
1-Butene/2-Methylpropene	2,5-Dimethylhexane
1,3-Butadiene	2,4-Dimethylhexane
Butane	2,3,4-Trimethylpentane
t-2-Butene	Toluene
2,2-Dimethylpropane	2-Methylheptane
1-Butyne	4-Methylheptane
c-2-Butene	1-Methylcyclohexene
2-Methylbutane	3-Methylheptane
1-Pentene	c-1,3-Dimethylcyclohexane
2-Methyl-1-Butene	t-1,4-Dimethylcyclohexane
Pentane	2,2,5-Trimethylhexane
Isoprene (2-Methyl-1,3-Butadiene)	Octane
2-Methyl-2-Butene	t-1,2-Dimethylcyclohexane
2,2-Dimethylbutane	t-2-Octene
Cyclopentene	c-1,4/t-1,3-Dimethylcyclohexane
4-Methyl-1-Pentene	c-2-Octene
3-Methyl-1-Pentene	c-1,2-Dimethylcyclohexane
Cyclopentane	Ethylbenzene
2,3-Dimethylbutane	m/p-Xylene
t-4-Methyl-2-Pentene	o-Xylene
2-Methylpentane	Nonane
c-4-Methyl-2-Pentene	iso-Propylbenzene
3-Methylpentane	3,6-Dimethyloctane
1-Hexene/2-Methyl-1-Pentene	n-Propylbenzene
t-2-Hexene	3-Ethyltoluene
2-Ethyl-1-Butene	4-Ethyltoluene
t-3-Methyl-2-Pentene	1,3,5-Trimethylbenzene
c-2-Hexene	2-Ethyltoluene
c-3-Methyl-2-Pentene	tert-Butylbenzene
2,2-Dimethylpentane	1,2,4-Trimethylbenzene
Methylcyclopentane	Decane
2,4-Dimethylpentane	iso-Butylbenzene
2,2,3-Trimethylbutane	sec-Butylbenzene
1-Methylcyclopentene	1,2,3-Trimethylbenzene
Benzene	p-Cymene
Cyclohexane	Indane
2-Methylhexane	1,3-Diethylbenzene
2,3-Dimethylpentane	1,4-Diethylbenzene
Cyclohexene	n-Butylbenzene
3-Methylhexane	1,2-Diethylbenzene
2,2,4-Trimethylpentane	Undecane
t-3-Heptene	Naphthalene
Heptane	Dodecane
t-2-Heptene	Hexylbenzene

Carbonyls were sampled by reacting them on a DNPH (2,4-dinitrophenylhydrazine)-silica cartridge through which air was pumped. The sample was subsequently analyzed using HPLC. The carbonyl analytes are listed in Table 4.

Table 4. Carbonyl analytes.

Formaldehyde	Benzaldehyde
Acetaldehyde	2-Pentanone / Isovaleraldehyde
Acetone	Valeraldehyde
Acrolein	o-Tolualdehyde
Propionaldehyde	m / p-Tolualdehyde
Crotonaldehyde	Methyl isobutylketone
2-Butanone	Hexanal
Iso / n-Butylaldehyde	2,5-Dimethylbenzaldehyde

Polycyclic aromatic hydrocarbons (PAHs) were sampled in air using sorbent tubes initially, but later 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. PAH analytes are listed in Table 5.

Table 5. Poly aromatic hydrocarbon (PAH) analytes.

Oil characteristic alkylated PAH	Other EPA priority PAH pollutants
Naphthalenes	Biphenyl
C ₀ -naphthalene	Acenaphthylene
C ₁ -naphthalenes	Acenaphthene
C ₂ -naphthalenes	Anthracene
C ₃ -naphthalenes	Fluoranthene
C ₄ -naphthalenes	Pyrene
Phenanthrenes	Benz(a)anthracene
C ₀ -phenanthrene	Benzo(b)fluoranthene
C ₁ -phenanthrenes	Benzo(k)fluoranthene
C ₂ -phenanthrenes	Benzo(e)pyrene
C ₃ -phenanthrenes	Benzo(a)pyrene
C ₄ -phenanthrenes	Perylene
Dibenzothiophenes	Indeno(1,2,3cd)pyrene
C ₀ -dibenzothiophene	Dibenz(a,h)anthracene
C ₁ -dibenzothiophenes	Benzo(ghi)perylene
C ₂ -dibenzothiophenes	
C ₃ -dibenzothiophenes	
Fluorenes	Chrysenes
C ₀ -fluorene	C ₀ -chrysene
C ₁ -fluorenes	C ₁ -chrysenes
C ₂ -fluorenes	C ₂ -chrysenes
C ₃ -fluorenes	C ₃ -chrysenes

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

Polychlorinated dibenzo-p-dioxin/furan were measured on particulate samples. High volume samplers were employed to collect cumulative samples at upwind and downwind locations. Sampling media were glass-fiber filters followed by a polyurethane foam plug (PUF). These same samples were used to meas-

ure 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 μm in size, a critical size below which human lungs are affected) air sampling was performed using a General Metal Works model PS-1 instrument. The sampling media consisted of a quartz fiber filter and a polyurethane foam (PUF) filter. Some of these filters were also analyzed for PAHs.

PM-2.5 are particulates less than 2.5 μm 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 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 advantage of this unit over the RAM is its internal data logging and processing capabilities. The apparatus is capable of employing several different sampling head configurations. These are total particulate, the 0-10 μm particulate fractions or the 0-2.5 μm 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. After each burn 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. All these data were recorded at intervals of one minute averages of 10 second measurement intervals. Carbon dioxide was also measured in some Summa grab samples using gas chromatography. The Metrosonics instrument also measures carbon monoxide, moisture and temperature.

Nitric oxides were measured using the Biosystems Cannonball. Electronic output data was recorded in manner similar to the above.

Results

Summarized data appears in the references. These data are too extensive even to provide encapsulating summaries, but, qualitative statements will be made regarding these.

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 same is true of the PM-2.5 concentrations. This may be indicative that most material is of PM-2.5 category or that the sampling units break the particles into smaller ones. Further research is being done on this important aspect.

PAHs. PAHs 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 starting oil and sometimes several orders-of-magnitude less. Diesel contains low levels of PAHs with smaller molecular size, but results in more 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.

VOCs. VOCs are hydrocarbons having a significant concentration in the vapour phase. One-hundred 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. Unfortunately, this is difficult to measure at all burns.

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 analyzed for dioxins and dibenzofurans. The levels of these toxic compounds were at background levels indicating no production by either crude or diesel fires.

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, even close to 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.

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 ppm. There is no human danger in this level. The three-dimensional distributions of carbon dioxide around a burn have been measured. Concentrations of carbon dioxide are highest at the 1 m level and fall to background levels at the 4 m level. Concentrations at ground level are as high as 10 times that of the plume. Distribution along the ground is broader than for particulates.

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.

Sulphur dioxide. Sulphur dioxide 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. The measured concentrations of sulphuric acid are below concern levels and appear to correspond to the sulphur contents of the oil.

Other gases. Attempts were made to measure oxides of nitrogen and other fixed gases which might be the result of combustion. None were measured in about 10 experiments.

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" analyzed 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 oxygenation 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.

Data synthesis and calculation

Sufficient data are now available to correlate with spatial and burn parameters. The extensive work is described in the literature (Punt *et al.*, 1998). Although many correlations were tried, it was found that atmospheric emissions correlated relatively well with "distance from the fire" and the "area of the fire." This fact then was used to develop prediction equations for each pollutant, using the data gathered from the 30 experiments conducted to date. Sufficient data were available to calculate equations for over 150 individual compounds and for all the major groups. In some cases data were insufficient to yield high correlation coefficients and low errors. Continued data collection will improve this situation. The result of the correlation should provide several significant advances in the understanding of *in situ* burning: assessment of the importance of specific emissions and classes; capability of predicting a "safe" distance; and capability of predicting concentrations at a given point. Predictions from this type of empirical evaluation are far more accurate than that from models because they are based solely on experimental data.

The correlation procedure involved collecting all emission data from the studies and then finding the best correlation procedure and the best equation that fit most data. A simple equation was found to fit the data most universally using the software package, TableCurve 3D. This software calculates up to 2000 equations and sorts them in terms of best fit (best regression coefficient, r^2). This equation and parameters for the total of some groups of emissions and for some emissions is given in Table 6. This table also shows the regression coefficient for each equation and the error. The error given is the standard error from regression fitting and is roughly equivalent to standard deviation. As can be seen from this table, the 'quality' of fit as evidenced by the regression coefficient varies with emission type. The lower ones are generally associated with lesser amounts of data. The amount of data

available to calculate each compound or class varied from a low of 5 to a high of about 40 data points.

These data were then used to calculate the difference between the regulated level (typically the time weight average recommended exposure to a substance), and the calculated amount of the polluting substance for several burns. The 'safe' distance for a series of burns was also calculated. Results of a simple exercise of this type are shown in Table 7. The concern level noted in this table is the recommend health maximum exposure level. So if a pollutant emission from a burn is at the concentration of the maximum recommended health exposure level, then it is taken to be at 100% of the concern level. Table 7 shows that a 500 square meter continuous burn would exceed the TSP or PM-10 level by about 30% or 130% or the concern level and the PM-2.5 level by 200% or 300% of concern level. Table 7 shows that the concern over diesel emissions are significantly higher than with crude oil, as had been noted from several studies of particulate emissions (Fingas *et al.*, 1996a; 1996b). This is especially true of the particulate matter. The amount of other concerns are about similar for diesel and crude oil, although the PAHs are somewhat higher with diesel. This calculation confirms that the greatest concern lies with the particulate matter, secondly with the PAHs on the particulate matter and next with the total VOCs.

Manipulation of the VOCs shows these to be close to being a matter of concern, but it should be noted that the level of VOCs is much higher (as much as 3 times as measured in some tests) when oil is evaporating in the absence of burning than the level of VOCs emitted when burning. The next level of concern is with the carbonyls, but they are significantly under concern levels for the scenarios in Table 7. There is no concern for fixed gases such as carbon dioxide, carbon monoxide. A final point should be made that the level of PM-2.5 measured for diesel emissions is the same or exceeds the PM-10 level. This indicates that most of the matter consists of PM-2.5 or that the devices for measuring PM-2.5, fracture the particles during collection. Further work is needed on PM-2.5 measurements and emissions.

Table 6. Prediction equation parameters.

Crude Oil						Diesel					
Substance	a	b	c	r^2	Error	a	b	c	r^2	Error	Units
Total particulates	12.7		0.0347	4.79	0.69	2.6	2.65	0.00886	0.854	0.55	mg/m ³
PM-10	12.7		0.0347	4.79	0.69	1.8	1.49	0.00558	0.467	0.56	mg/m ³
PM-2.5	12.7		0.0347	4.79	0.69	1.5	1.34	0.00523	0.412	0.52	mg/m ³
Total VOCs	13450		24.02	4426	0.35	4700	203	2.1	4.77	0.36	99 µg/m ³
PAHs	16.2		0.0048	3.03	0.19	4.8	51.7	0.124	16.9	0.57	8.2 µg/m ³
Fixed gases											
Sulphur dioxide	19.4		0.0266	5.29	0.69	2.8	0.557	0.00114	0.183	0.54	ppm
Carbon dioxide	520		0.523	81.5	0.18	130	77	0.246	19.6	0.49	25 ppm
Carbon monoxide	7.72		0.0012	1.56	0.18	1.8	3.06	0.0237	1.935	0.63	0.67 ppm
Carbonyls											
Acetaldehyde	23.3		0.115	12.9	0.36	23	0.499	0.0325	18.4	0.81	7.8 µg/m ³
Acetone	11.3		0.0445	5.11	0.18	15	14.7	0.0573	3.84	0.73	3.8 µg/m ³
2-butanone							115.1	0.0407	3.64	0.52	4.4 µg/m ³
Butyraldehydes							22.5	0.0344	5.68	0.74	2.8 µg/m ³
Formaldehyde	58.4		0.103	20.1	0.39	17.4	35.4	0.107	9.18	0.77	6.5 µg/m ³
Propionaldehyde							19.6	0.0371	4.85	0.69	3.1 µg/m ³

Note: $y = a + b(\text{size of fire, } m) - c(\text{distance from fire, } m)$.

Table 7. Calculation of concern levels for emission groups.

Substance	Crude oil (500-square meter continuous burn)			Diesel (500-square meter continuous burn)		
	Percent of concern	Percent of concern	Distance to the safe health level (m)	Percent of concern	Percent of concern	Distance to the safe health level (m)
	Level at 500 m*	Level at 1500 m		Level at 500 m	Level at 1500 m	
Total particulates	130	0	510	1180	560	3340
PM-10	130	0	520	920	580	6930
PM-2.5	300	0	530	1910	1170	7340
Total VOCs	0	0	-	0	0	-
PAHS	0	0	-	4	0	-
Fixed gases	0	0	-	0	0	-
Carbonyls	0	0	-	0	0	-

* percent of concern level is percentage of calculated emission level versus the suggested maximum health exposure level

Conclusions

The measurement of emissions and calculation using equations developed from emission data have revealed several facts about the fate, behavior 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 in the smoke plume may not be a concern past about 500 meters for typical crude oil burns. The level of respirable particulates, those which have a size less than 10 μm , or 2.5 μm , is not understood well, but follows the trends noted for TSP. 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 PAH concentrations 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 concentration of 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. However, when considering the mass balance of the burn, most of the five and six-ringed PAHs are largely destroyed by the fire. Burns of diesel fuel show an increase in the concentration of multi-ringed PAHs, but still a net destruction of 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 concern, but can rise to close to concern levels very near a fire (<100 m).

Organic compounds. No exotic or highly-toxic compounds are 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 even very near 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 would not exceed exposure limits for emissions beyond about 500 m.

Biography

Merv Fingas is Chief of the Emergencies Science Division, in Environment Canada. Dr. Fingas' speciality is research in the analysis and behavior of oil spills in the environment. He manages 35 other scientists and staff studying various aspects of oil and chemical spills. He has devoted the last 25 years of his life to spill research and has over 350 papers and publications in the field.

References

1. Booher, L.E. and B. Janke, 1997. "Air Emissions from Petroleum Hydrocarbon Fires", *American Industrial Hygiene Association Journal*, Vol. 58: pp 359-365.
2. Fingas, M.F., K. Li, F. Ackerman, P.R. Campagna, R.D. Turpin, S.J. Getty, M.F. Soleki, M.J. Trespalacios, J.R.P. Paré, M.C. Bissonnette and E.J. Tennyson, 1993. "Emissions From Meso-scale *in situ* Oil Fires: The Mobile 1991 and 1992 Tests", in *Proceedings of The Sixteenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 749-821.
3. Fingas, M.F., F. Ackerman, K. Li, P. Lambert, Z. Wang, M.C. Bissonnette, P.R. Campagna, P. Boileau, N. Laroche, P. Jokuty, R. Nelson, R.D. Turpin, M.J. Trespalacios, G. Halley, J. Bélanger, J.R.J. Paré, N. Vanderkooy, E.J. Tennyson, D. Aurand and R. Hiltabrand, 1994a. "The Newfoundland Offshore Burn Experiment - Preliminary Results of Emission Measurement", in *Proceedings of The Seventeenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1099-1164.
4. Fingas, M.F., G. Halley, F. Ackerman, N. Vanderkooy, R. Nelson, M.C. Bissonnette, N. Laroche, P. Lambert, P. Jokuty, K. Li, W. Halley, G. Warbanski, P.R. Campagna, R.D. Turpin, M.J. Trespalacios, D. Dickins, E.J. Tennyson, D. Aurand and R. Hiltabrand, 1994b. "The Newfoundland Offshore Burn Experiment - NOBE Experimental Design and Overview", in *Proceedings of The Seventeenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1053-1061.
5. Fingas, M.F., G. Halley, F. Ackerman, R. Nelson, M.C. Bissonnette, N. Laroche, Z. Wang, P. Lambert, K. Li, P. Jokuty, G. Sergy, W. Halley, J. Latour, R. Galarneau, B. Ryan, P.R. Campagna, R.D. Turpin, E.J. Tennyson, J. Mullin, L. Hannon, D. Aurand and R. Hiltabrand, 1995a. "The Newfoundland Offshore Burn Experiment", in *Pro-*

- ceedings of the 1995 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 123–132.
6. Fingas, M.F., F. Ackerman, P. Lambert, K. Li, Z. Wang, J. Mullin, L. Hannon, D. Wang, A. Steenkammer, R. Hiltabrand, R.D. Turpin and P.R. Campagna, 1995b. “The Newfoundland Offshore Burn Experiment: Further Results of Emissions Measurement”, in *Proceedings of the Eighteenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 915–995.
 7. Fingas, M.F., F. Ackerman, P. Lambert, K. Li, Z. Wang, R. Nelson, M. Goldthorp, J. Mullin, L. Hannon, D. Wang, A. Steenkammer, S. Schuetz., R.D. Turpin, P.R. Campagna and R. Hiltabrand, 1996a. “Emissions from Mesoscale *In Situ* Oil (Diesel) Fires: The Mobile 1994 Experiments”, in *Proceedings of the Nineteenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 907–978.
 8. Fingas, M.F., K. Li, F. Ackerman, Z. Wang, P. Lambert, L. Gamble, M.J. Trespalacios, S. Schuetz., R.D. Turpin, and P.R. Campagna, 1996b. “Soot Production from *In Situ* Oil Fires: Review of the Literature, Measurement and Estimation Techniques and Calculation of Values from Experimental Spills”, in *Proceedings of the Nineteenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 999–1032.
 9. Fingas, M.F., P. Lambert, F. Ackerman, B. Fieldhouse, R. Nelson, M. Goldthorp, M. Punt, S. Whitarcar, P.R. Campagna, D. Mickunas, R.D. Turpin, R. Nadeau, S. Schuetz, M. Morganti, and R.A. Hiltabrand, 1998. “Particulate and Carbon Dioxide Emissions from Diesel Fires: The Mobile 1997 Experiments”, in *Proceedings of the Twenty-First Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 569–598.
 10. Lambert, P., F. Ackerman, M. Fingas, M. Goldthorp, B. Fieldhouse, R. Nelson, M. Punt, S. Whitarcar, S. Schuetz, A. Dubois, M. Morganti, K. Robbin, R. Magan, R. Pierson, R.D. Turpin, P.R. Campagna, D. Mickunas, R. Nadeau, and R.A. Hiltabrand, 1998. “Instrumentation and Techniques for Monitoring the Air Emissions During *In Situ* Oil/Fuel Burning Operations”, in *Proceedings of the Twenty-First Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 529–567.
 11. Punt, M., M. Fingas, J. Charles, P. Lambert, R. Hiltabrand and J. Mullin, 1998. *Manual for In Situ Burning, Procedures and Data*, Environment Canada and the United States Coast Guard, in preparation.

