

# Soot Production From In-Situ Oil Fires: Review of the Literature, Measurement and Estimation Techniques and Calculation of Values from Experimental Spills

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## Abstract

A review of the amount of soot produced by in-situ oil and fuel fires was conducted. The nature and behaviour of in-situ fires were reviewed noting that there is significant gas separation between the plume and the surface. Secondly, there is significant soot precipitation out of the plume near the fire. The difficulty of performing the soot production measurement and estimating the value is noted. A literature review of soot production shows values vary from 1% to as high as 16%. Methods to measure soot production were reviewed. Methods that capture the soot entirely are classed as the only true measurement technique whereas others are classed as estimation techniques. Values calculated from the method known as "carbon balance" assumes that all carbon resulting from the fire is in the plume. Data from many burns show that the CO<sub>2</sub> is often ten times lower in the plume than on the surface. The carbon balance method may be somewhat applicable for very small burns where sampling is performed directly in the chimney and where the gases do not have a chance to escape from the smoke. A recalculation of two large burns shows that a single carbon balance measurement in the plume over-estimates soot production by a factor of seven times. The most accurate method is that of direct soot collection, however to perform such, soot is usually collected directly over the flame. Significant amounts of soot are collected which might otherwise precipitate back into the fire. Although accurate, these measurements may over-estimate soot from a large fire by as much as double. A variant on the total soot capture method is to use a proportionate sampling system and calculate the proportion of the smoke taken and multiply this times the weight of the sample captured. This is, in theory, more accurate because one can measure farther away from the source of the flame, however, the inaccuracies in determining the proportion sampled can be large.

Two new methods of estimating soot production were demonstrated, integration of the soot concentration by volume under the plume and integration of soot deposition weight over the area under the plume. Extensive experimental data from burning shows that there exists a strong correlation between the product burned and the amount of soot deposited downwind. The Mobile and NOBE experimental burn data were used to estimate the soot production from the volume under the plume. For diesel, the value of soot production obtained was 8.6%. For crude a value of 1.7 % was obtained. Integration

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of the soot deposition on the area under the plume yielded soot production values of 4.3% for diesel and 1.7% for crude oil. These values are consistent with the primary soot-capture method values. Only the integration of the soot deposition by area offers potential for future application.

Most estimation methods would appear to over-estimate by as much as a factor of 10. It is concluded that the value of soot produced varies significantly down-plume because of precipitation of material. Downwind soot concentrations are likely to be as low as 0.5 % for crude oil and about 3% near the fire. For diesel, the downwind concentrations may be about 1% and about 6% near the source. There should be, however, significant variation for the type of material burned and also for some of the environmental conditions. Current measurement and estimation techniques are fraught with numerous difficulties. "True" values may not be forthcoming for a period of time. It is suggested that laser particle sizing and counting techniques may be a solution to the problem.

### Introduction

The amount of soot produced in an in-situ oil fire has been a matter of concern for some time. Over the years this information has been needed for several purposes:

1. To establish a mass balance of burning
2. To understand the air emissions of in-situ fires
3. To establish specific effects of fires such as the effects upon a community impacted by a fire
4. To establish guidelines for the burning of various fuels
5. To develop smoke and soot control products such as ferrocene
6. To provide input for smoke and particulate models and
7. To understand the combustion process in general.

Little scientific attention has been paid to the process in general. A few groups have published data in the literature, however, these data do not agree and often vary from each other by as much as an order of magnitude. Current emission data is often as variant as by an order-of-magnitude - even for the same experiment. Furthermore, there appears to be fundamental disagreement on the basic nature of fires. There are statements in the literature indicating that there is no precipitation of soot from a fire and that there is no separation of gases from the smoke plume. The basic nature of a fire had not been established until recent studies showed the nature and distribution of gases from in-situ fires. Furthermore, as will be pointed out later in this paper, much of the earlier data are very noisy, both because of instrumentation difficulties, but also because of the high variations in emissions from fires. This noisiness has led earlier researchers to conclude certain things about the nature of a fire, that was not consistent with recent data.

The nature of soot production itself is only partly understood but has some well-known facts (Calcote, 1981; Cofer et al., 1992; Lin et al., 1996; Olson and Calcote, 1981; Prado and Lahaye, 1981; Bittner and Howard, 1981; Wagner, 1981). Literature shows that three distinct steps are recognized:

1. Nucleation - the formation of a particle or 'embryo' around which other

molecules cling,

2. Growth to spherical particles of 10 to 50 nm diameter, and
3. Aggregation or agglomeration of the spherical units to form chains.

Further work by others confirms that soot always consists of these particles of size 10 to 50 nm in chains. It has also been noted through several references noted in this paper that the particle size can be changed by measurement techniques presumably because the chains are easy to rupture.

Ladommatos et al. (1996) reviewed the soot formation tendencies of various pure hydrocarbons. Literature data and new experimental data clearly showed the tendency for greater soot production with increasing molecular size along a homologous series of substances. The ring, either aromatic or not, is an important structure leading to soot production. Double bonds and triple bonds have similar effect. The length of chain is an important indicator of increasing soot formation.

It has been observed that in certain fires, fine droplets of the fuel itself can form the nucleation sites. This then would explain some of the anecdotes of fuel or crude oil being transported significant distances from the fire (Smith, 1981).

### **The Nature of Emissions from Fires**

A first approximation about the output of soot (smoke) and gaseous substances from a fire would be that they are emitted downwind and that there would be a separation of soot from the gases because of the differences in buoyancy of the substances. Work on laboratory fires in the mid-sixties indicated that there was not much of a separation in test systems (Mulholland et al., 1988). This was applied by the same group to larger fires over the past decade (Evans et al., 1990). The assumption was that there was no separation in little fires was also true in larger cases and cases where there was open burning. Little focus or effort was placed on measured emissions at various points around a fire.

The first large scale burns were conducted by a group consisting of the United States Minerals Management Service (MMS), National Institute for Standards and Technology (NIST), Environment Canada, the United States Coast Guard (USCG) and the United States Environmental Protection Agency (EPA). Samples of emissions were taken in the plume and at the standard receptor height (5 ft.) as specified in most standards. There was a surprising abundance of carbon dioxide and volatile organic compounds (VOCs) found at the surface during all 12 burns that were monitored (Fingas et al., 1993). The monitoring network was expanded in a series of burns in 1992 and again the same phenomenon was noted (Fingas et al., 1993). The data on carbon dioxide was not as clear as that for volatile organic compounds and many difficulties were noted with the instruments. During subsequent burns, better carbon dioxide measurement techniques were invoked to ensure that difficulties were eliminated. An extensive three-dimensional array of sensors was placed around a series of three fires in 1994 (Fingas, et. al, 1993, 1994, 1995, 1996). These show that the separation of carbon dioxide is very distinct and emanates in all directions from a burn in low wind conditions. This array technique also revealed that the highest carbon dioxide concentrations are closest to the ground. Concentrations even 3 metres above the surface are significantly lower than those at the one-metre mark. This is strongly indicative of a distinct separation of gases. Table 1 shows some of the carbon dioxide concentrations at the test sites. The plume

concentrations were not published by NIST and the researchers could not supply such upon request. Figure 1 shows the schematic of how gases may be distributed from an in-situ fire.

The question of why the carbon dioxide separates from the smoke plume can be answered very simply. Carbon dioxide gas is substantively heavier at all temperatures than is air. Figure 2 shows the densities of air and carbon dioxide at relevant temperatures (Boltz and Tuve, 1976; Braker and Mossman, 1980; Dean, 1979; Weast and Astle, 1982). This figure clearly shows that density of carbon dioxide is about 30-40% greater at all temperatures. This is far too great to permit a significant portion to be carried with the plume. There are some common everyday experiences that highlight the gas separation. First there is the fact, that one can smell fire wood burning, outside or even from a fire place. This shows that the volatile components are separating from the plume to an extent and are not totally carried up, even if there is a chimney. The second everyday illustration relates to the presence and use of carbon dioxide fire extinguishers. If carbon dioxide moved with the smoke plume, it would be useless as a fire extinguisher. Since thermal differences in density between it and the surrounding air also do not negate the separation effect, this is a powerful argument for gas separation.

The second factor of importance is that of soot precipitation. Table 1 illustrates some of the precipitation that occurs from soot and that it occurs exponentially from the fire source. This behaviour is illustrated in Figure 3. This is important because this means that the value of the soot produced changes downwind. Furthermore, it infers that a single value of soot production must consider the point at which this was measured. Obviously, the soot production factor approaches zero somewhere downwind.

#### **Literature Values of Soot Production**

An extensive literature search was conducted. Table 2 summarizes the values found and values calculated in this work. Values are divided into three categories based on the judgement of whether the values were primary, secondary or tertiary. Primary values were assigned to those methods where all soot was captured and weighed directly. Secondary values were assigned to those estimated from certain parameters or where soot was sampled from the total plume. Tertiary values are those assigned on the basis of a literature review or reported by others. As can be seen by the table, soot production values vary widely. Primary values for crude oil average about 2.5 % and for diesel, about 7%. It is the secondary and tertiary measurements that show higher values than these, especially those performed by carbon balance. It is important to note that many values are quoted repeatedly from one source to another, sometimes incorrectly. This variance in literature data also shows the need for a consistent understanding of soot emission rates.

Many precise soot production factors exist for controlled burn sources such as incinerators. Table 3 shows the most relevant ones applicable to this paper (EPA FIRE Database, 1995). These are for closed combustion sources for which there are no forms of pollution control. As can be seen these values are 1 to 2 orders-of-magnitude smaller than that from in-situ burns. Furthermore, the order of the sootiest products do not necessarily follow. Field experience has shown that in open combustion that diesel produces the most smoke and Bunker C the least. This is not necessarily so in enclosed systems.

Table 1 Summary Table of Tests Burns

Burn	Size (m <sup>3</sup> )	Carbon Dioxide (ppm above background)				Soot (µg/L)		Blimp	
		Downwind 1	Downwind 2	Downwind 3	Plume	Downwind 1	Downwind 2	Downwind 3	Plume Range Height
<b>Mobile 91 Louisiana Crude</b>		<b>33 m</b>	<b>60 m</b>			<b>33 m</b>	<b>60 m</b>		
1-Apr-16	3.36					0.1			61 128
2-Apr-17	1.6					0.2			61 56
3-May-16	1.3	159	67			0.5			56 44
4-May-17	2.25					1.1	1.5		106 100
5-May-22	3.37	40	26			3.9	0.4		83 38
6-May-23	3.31	62	51			0.1	0		48 30
7-May-24	5.56	35	31			0	0		
8-May-28	2.25	52	73			0.1	0		87 45
9-May-29	2.31		71			2.7	0.5		47 16
10-May-30	5.8	132	26			0.5	0.1		87 45
11-May-31	11.8	107	101			0.1	0		103 150
12-Jun-03	7.22	76	8			0.1	0		108 150
13-Jun-04	6.98	37	12			0.5	0.2		109 160
14-Jun-05	14.1	142	28			0.8	0.3		100 121
<b>Mobile 92 Louisiana Crude</b>		<b>75 m</b>	<b>100 m</b>	<b>150 m</b>		<b>75 m</b>	<b>100 m</b>	<b>150 m</b>	
1-Nov-03	2.26	127	59	23		7.44	4.1	0.5	70 30
		<b>100 m</b>	<b>150 m</b>	<b>250 m</b>		<b>100 m</b>	<b>150 m</b>	<b>250 m</b>	
2-Nov-05	13.1	93	74	49		5	3	1.3	90 90
3-Nov-06	12.9	96	73	36		3.4	2	1.6	90 80
4-Nov-07	12.6	60	59	46		1	2	2.1	80 140
5-Nov-09	12.5	238	173	111			0.5	0.2	40 220
6-Nov-10	12.7	152	90	132		3.5	0.3	0.1	80 110
<b>NOBE 93 Alberta</b>		<b>50 m</b>	<b>100 m</b>	<b>500 m</b>					
1-Aug-12		126	265	22		6.1	7.2	0.05	300 150
2-Aug-12		581	377	23		10.3	12.3	0.07	400 150
Analysis by GC from Summa Canister/bag									
1-Aug-12		199	452	71	26				
2-Aug-12		629	543	75	46				
<b>Mobile 94 Diesel</b>									helicopter
1	3	108	50			80	34	6	60 65
2	13.3	88	55	24		2754	1224	179	30 53
3	13.3	120	34	27		1958	885	357	23 23

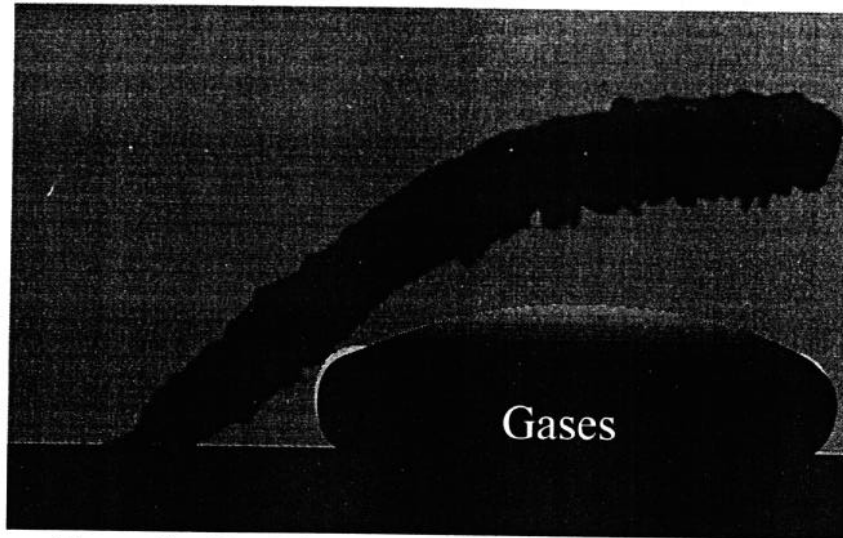


Figure 1 - Gas Distribution at a Burn

Figure 2 - Density of Carbon Dioxide and Air At Burn Temperatures

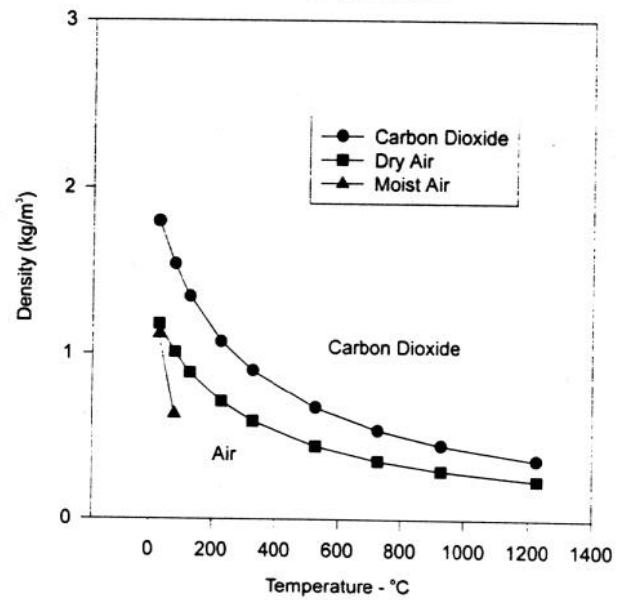


Table 2 Soot Production Data from the Literature

Product	Soot Production in Percent			Experiment or situation	Methodology	Literature Reference
	Primary Measurement	Secondary Measurement	Tertiary Reference			
Crude			<5%	Kuwait oil fires	estimation?	Bauer, 1991
	2.2% (2.8%)		2-6%	accepted value	literature review	Crutzen et al., 1984
				14 small fires	soot capture	Day et al., 1979
			0.90%	offical EPA value	series of lab tests	El-Shobokshy & Al-Saedi, 1993
		9.7% average		4 small fires	carbon and flux	Evans, 1988
		10% average		small fires	carbon balance	Evans, 1990
			2.2% average	Kuwait oil fires	carbon balance ?	Fendell & Mitchell, 1993 <small>reporting on Hobbs data</small>
		1%		20 mid-size fires	integration of soot	Fingas et al., 1996 (This Work)
		1.70%		20 mid-size fires	integration of soot	Fingas et al., 1996 (This Work)
		2.10%		2 large fires	carbon balance	Fingas et al., 1996 (This Work)
		1.6% (0.3%)		Kuwait oil fires	carbon balance	Hobbs & Radke, 1992
			2-9.8%	refer to lab data		Khordagui & Al-Ami, 1993
		10% average		7 small fires	carbon balance	Koseki et al., 1990
	3.3% average	2ml/15g		small fires	soot capture	Mitchell, 1985
			7.6% average	3 micro fires	soot capture	Mitchell, 1991a
Diesel	1.5% average			2 small fires	carbon balance	Mitchell, 1991a (reporting NIST data)
		7% volume		7 small fires	soot capture	Mitchell, 1991b
		26% more than JP4		mid-size fires	soot sample	Mitchell, 1992b
		9.0% average		mid-size fires	soot sample	Mitchell, 1993
		9% average		4-mid-size fires	carbon balance	Mulholland et al., 1987
		8.7% average		4 small fires	carbon balance	Mulholland et al., 1988
		2-6%		2 large fires	carbon balance	Mulholland et al., 1988
			3%	accepted value	literature survey	NRC, 1985
			7.30%	large fires	estimation	Penner et al., 1986
		8.7% average			average of literature	Ransonhoff, 1989
			5.70%	2 large fires	carbon balance	Rosa et al., 1996
			1.60%	Kuwait fires	estimation from literature	Smail, 1991
				Kuwait fires	used literature value	Smyth, 1993
		11.3% average		5 meso and 1 lab fire	carbon balance	Walton et al., 1993
		8.60%		3 mid-size fires	integration of soot	Fingas et al., 1996 (This Work)
Gasoline		4.30%		3 mid-size fires	integration of soot	Fingas et al., 1996 (This Work)
	11% average			5 small fires	soot capture, sampling	Fleishman et al., 1990
			1.60%		unknown	Mitchell, 1991a (reporting CRC data)
			16.5% average	2 small fires	carbon balance	Mitchell, 1991a (reporting NIST data)
			8.3% average	3 fires	unknown	Mitchell, 1991a (reporting U Cal data)
	<2.4 X amount of crude			small fires	soot capture	Mitchell, 1992a
		12% volume		mid-size fires	soot sample	Mitchell, 1992b
	3.3% average			small fires	soot sample	Patterson et al., 1991
			5%	mid-size fires	recommended	Rasbash and Pratt, 1980
Kerosene				small fire	soot capture	Mitchell, 1992a
	<3.4 X amount of crude			mid-size fires	soot sample	Mitchell, 1992b
		24% volume		mid-size fires	unknown	Mitchell, 1991a (reporting CRC data)
Other Fuels			0.22%	mid-size fires	recommended	Rasbash and Pratt, 1980
			3%			
All Fuels		6% volume		mid-size fires	soot sample	Mitchell, 1992b
	2.9% average			small fires	soot sample	Patterson et al., 1991
			5%	mid-size fires	recommended	Rasbash and Pratt, 1980
			3.7% average		average of literature	Ransonhoff, 1989
			2.3% average		average of literature	Ransonhoff, 1989
				mid-size fires	soot sample	Mitchell, 1993
		26% less than crude		mid-size fires	soot sample	Mitchell, 1994
		25% less than JP5		mid-size fires	soot sample	Mitchell, 1993
		35% more than JP4		mid-size fires	soot sample	Mitchell, 1994
		25% more than JP4		mid-size fires	soot sample	Mitchell, 1994
		1.3% avg. PM10		mid-size fires	carbon balance in chamber	Einfield and Momson, 1996
		26% more than JP4 same as crude		mid-size fires	soot sample	Mitchell, 1993
		35% more than JP4		mid-size fires	soot sample	Mitchell, 1994
All Refined Fuels		9% volume		mid-size fires	soot sample	Mitchell, 1992b
		10% volume		mid-size fires	soot sample	Mitchell, 1992b
		8% volume		mid-size fires	soot sample	Mitchell, 1992b
		16% volume		mid-size fires	soot sample	Mitchell, 1992b
		1.0% average		5-mid-size fires	carbon balance	Mulholland et al., 1987
		11.7% average		11 small and large fires	carbon balance	Mulholland et al., 1988
		1% average		2 small fires	carbon balance	Koseki et al., 1990
	5.3% average			small fires	soot sample	Patterson et al., 1991
		~10% average		19 small fires	light extinction	Wighus, 1991
			2-10%	nuclear winter	literature review	Penner, 1986
			1-1% urban, 3.3% suburbs	nuclear winter	literature review	Penner, 1986

Note: Amounts indicated as "volume" are based on volume where the density was not measured. A relative density of 1.000 was assumed. This may be conservative because the liter values were not backed and thus the percentage could be lower.

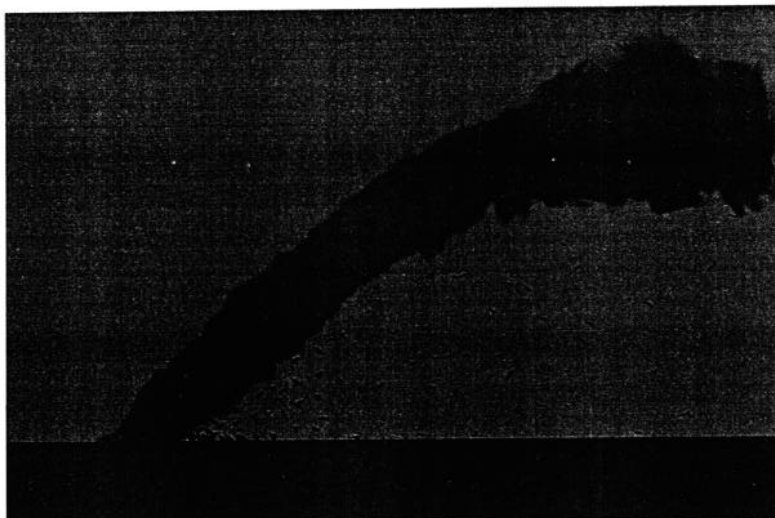


Figure 3 - Schematic of Soot Precipitation

Table 3  
Soot Emission Factors from Uncontrolled Burners and Furnaces

Fuel Type	Average Soot Emission Factor (%)	Range	Number of Studies (number of separate factors)
<b>Filterable Particulates (course)</b>			
Number 2 (diesel)	0.1	0.1-0.12	9
Number 4	0.05	.053-.056	2
Number 5	0.09	0.09	1
Number 6 (Bunker)	0.1	.1-.12	15
Crude Oil	0.11	0.11	2
Waste Oil	0.5	.5-.51	2
<b>Particulate Matter &lt;10<math>\mu</math> (or not specified)</b>			
Number 2 (diesel)	0.01	0.01	9
Number 4	0.06	.05-.06	8
Number 5	0.06	.07-.11	4
Number 6 (Bunker)	0.11	.06-.08	7
Waste Oil	0.5	0.5	4

All data are from the EPA database 'Fire'



## **Review of Measurement Techniques**

### **Total Soot Capture**

The most reliable means currently available is to capture all soot from a fire and compare the weight of the soot captured with the starting weight of the oil. This method has strict disadvantages; it is restricted to small fires; the soot amount is exaggerated because the capture methodology will often result in poor oxygenation; the soot amount is also exaggerated because particles that would normally be re-precipitated into the fire are captured and measured; and the necessity for enclosures dictated that only limited experimentation can be performed. Despite the possibility for exaggeration, the soot values by total soot capture are among the lowest noted in Table 2. One theory is that this relates to the size scale, and that large scale fires, because of poor oxygenation produce more soot. The relation between large and small scale fires in terms of soot production, is still an open question.

### **Soot Sampling**

Instead of capturing all the soot one can sample the soot and then extrapolate this sample weight to the total. The extrapolation is difficult and leads to great uncertainty. One method employed is to 'calibrate' the sample to a total soot capture experiment. The difficulty in calculating the percent of soot capture, has not made this a popular technique. Often the issue of sample ratio was avoided by giving the mass as a relative factor or as a percentage related to another fuel.

### **Light Blocking**

Another method employed is to calibrate a passage through a chimney and measure the light blockage, typically using a laser. Whitely (1994) prepared a note on the use of light blocking techniques noting additional problems such as the difference in extinction coefficients for different soot types. It is nearly impossible to 'calibrate' the system to yield an exact percentage of soot production. Some data were published with relative values.

## **Review of Estimation Methods**

### **Carbon Balance**

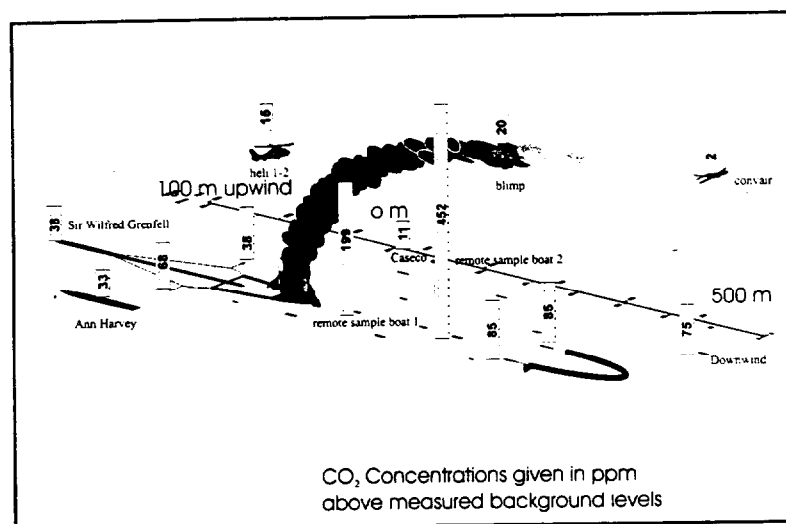
A very common approach has been to use the carbon balance method. This method tracks the carbon in the plume and then attempts to relate it to the percentage of soot. The carbon balance equation is simply: the percentage of soot is given by the percentage of carbon as soot in the plume. The carbon in the plume is given by the sum of the soot, carbon dioxide and carbon monoxide. The latter is often ignored because it is generally a very small percentage. The major assumption is that all the carbon is found in the smoke plume. The secondary assumption is that the soot does not precipitate. The latter assumption is not serious in terms of consequences because it only relates to the discrepancy in the observations that soot precipitates exponentially outwards from the fire and that the carbon balance method does not show a decrease in soot production as the sampling moves outward from the fire.

The problem lies with the assumption that most of the carbon dioxide (or all of it) is in the smoke plume. As noted above the density of carbon dioxide, even at

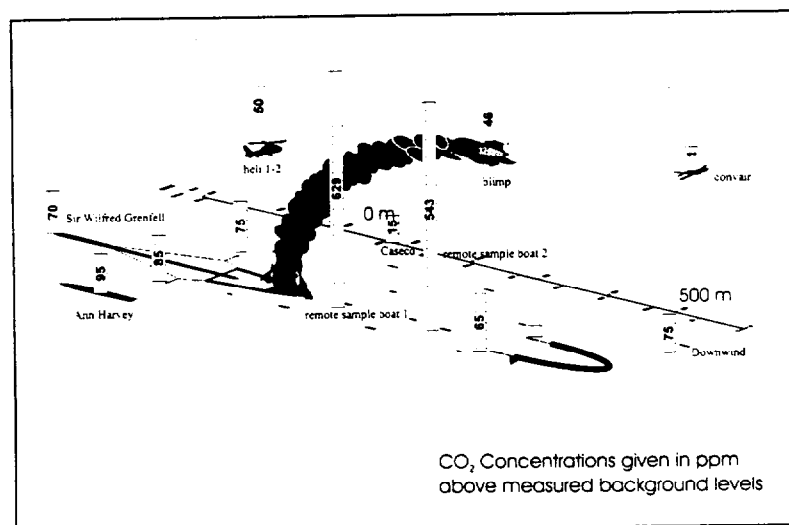
elevated temperatures is such that it will sink, until well-mixed with air. Observations at several burns show that the main flow of carbon dioxide is along the surface. Such observations are noted in Figure 4 and Figure 5 where the carbon dioxide concentrations measured at the Newfoundland Offshore Burn Experiment (NOBE) are summarized. It should be noted that the carbon dioxide concentration in this and subsequent diagrams are measured in ppm above normal background. This shows that the ground concentrations of carbon dioxide are often over an order-of-magnitude greater than those found in the air and in the smoke plume. Further it is noted that even the remote-controlled helicopter samples contained low amounts of carbon dioxide, at only about 20 m above the sea surface. These findings were further confirmed in the 1994 experiments conducted at Mobile, Alabama, on the burning of diesel. An extensive array of 21 carbon dioxide meters and 9 sampling stations were implemented. Nine of the sampling stations were at the 4-metre level and the remainder were at 1-metre height. The results for three burns is shown in Figures 6, 7 and 8. These clearly show an exponentially decreasing concentration outward from the fire, a high concentration at the 1 metre mark and low concentrations at the 4-metre level. Specific concentrations were not available for in the plume, however, they are believed to have been around 40 ppm above ambient. These data clearly show that the carbon dioxide does not reside with the smoke, and in fact is highest near the ground. This is exactly what would be expected from its density differential with air. Table 1 shows the concentrations of both carbon dioxide and soot at several burn experiments conducted over the past few years. Concentrations of the carbon dioxide in the smoke plumes are not generally available although carbon balance numbers for these same experiments have been published. They are understood to generally range around 40 ppm above background levels (background levels are generally around 300 ppm).

The question remains, of course, why would this method be used if it were so obviously wrong? The answer probably lies in the origins of the method. The method was first proposed for small scale experiments. Soot sampling methods were used to measure soot production and in enclosed systems, where the carbon dioxide is better mixed with the smoke, the two methods produce similar answers. As the scale of the fire increases and the carbon dioxide has the opportunity to separate, the method yields increasing variance from absolute methods. Finally, the separation of carbon dioxide is not a well-known phenomena and with the high variances and noise in measurements, may have not been noted. Another reason is the fact that only recently have larger-scale experiments been performed and instrumented to take measurements.

Proponents of the method, suggest that several phenomena they have observed show that the carbon dioxide does not separate. One such argument involved the results from carbon dioxide meters at ground level near the fire and correlation of this with soot data at the same location. The high correlation of soot and carbon dioxide concentration was interpreted as proof that soot and carbon dioxide are directly proportional. But this correlation does not extend downwind and thus the argument is not correct. Some workers have noted the correlation of soot and carbon dioxide in the plume itself. This may be due to many reasons. Concentrations of carbon dioxide will be given off by desorption from soot for some time after the combustion point. The correlation may also be an instrument error. Most carbon dioxide instruments are infrared based and will change signal with temperature, moisture and particulate matter. Furthermore, many of

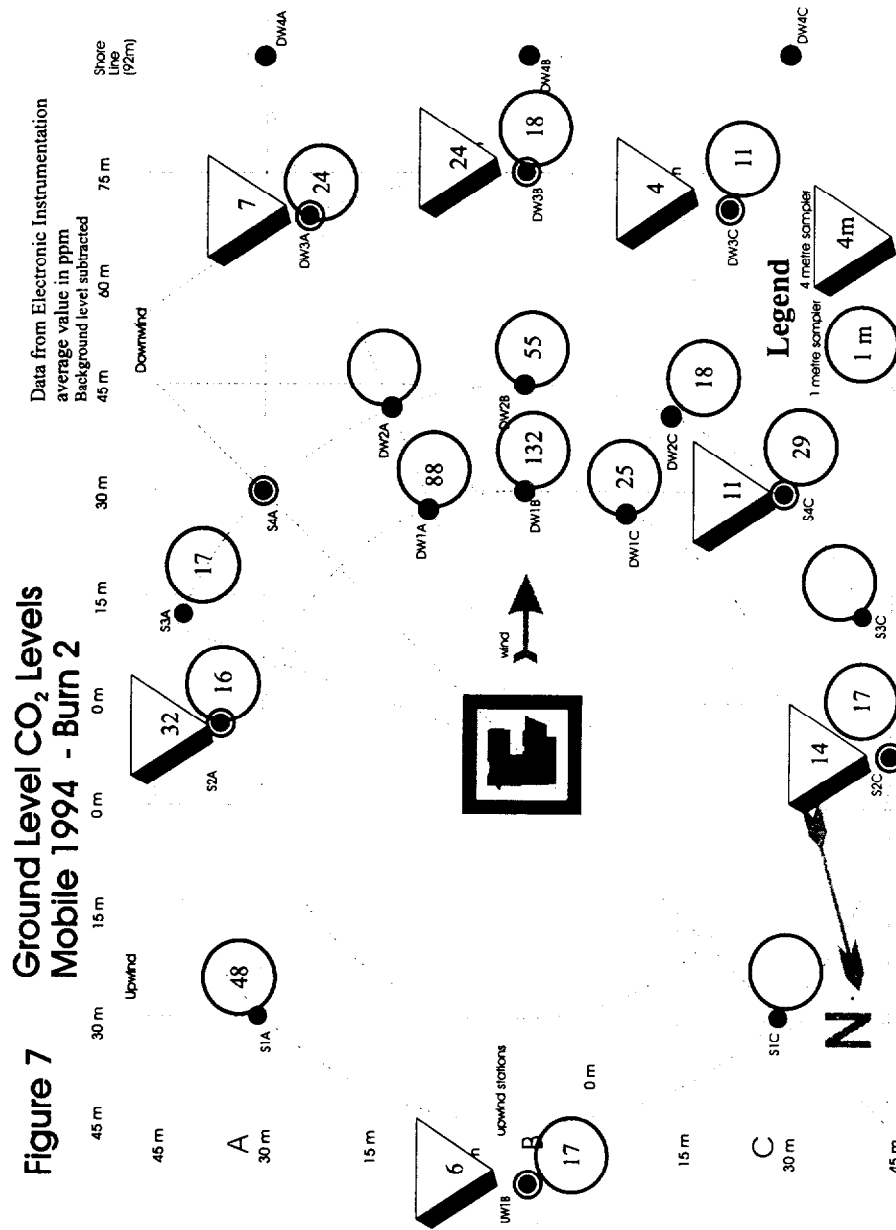


**Figure 4** Relative Concentrations of Carbon Dioxide  
at NOBE Burn 1

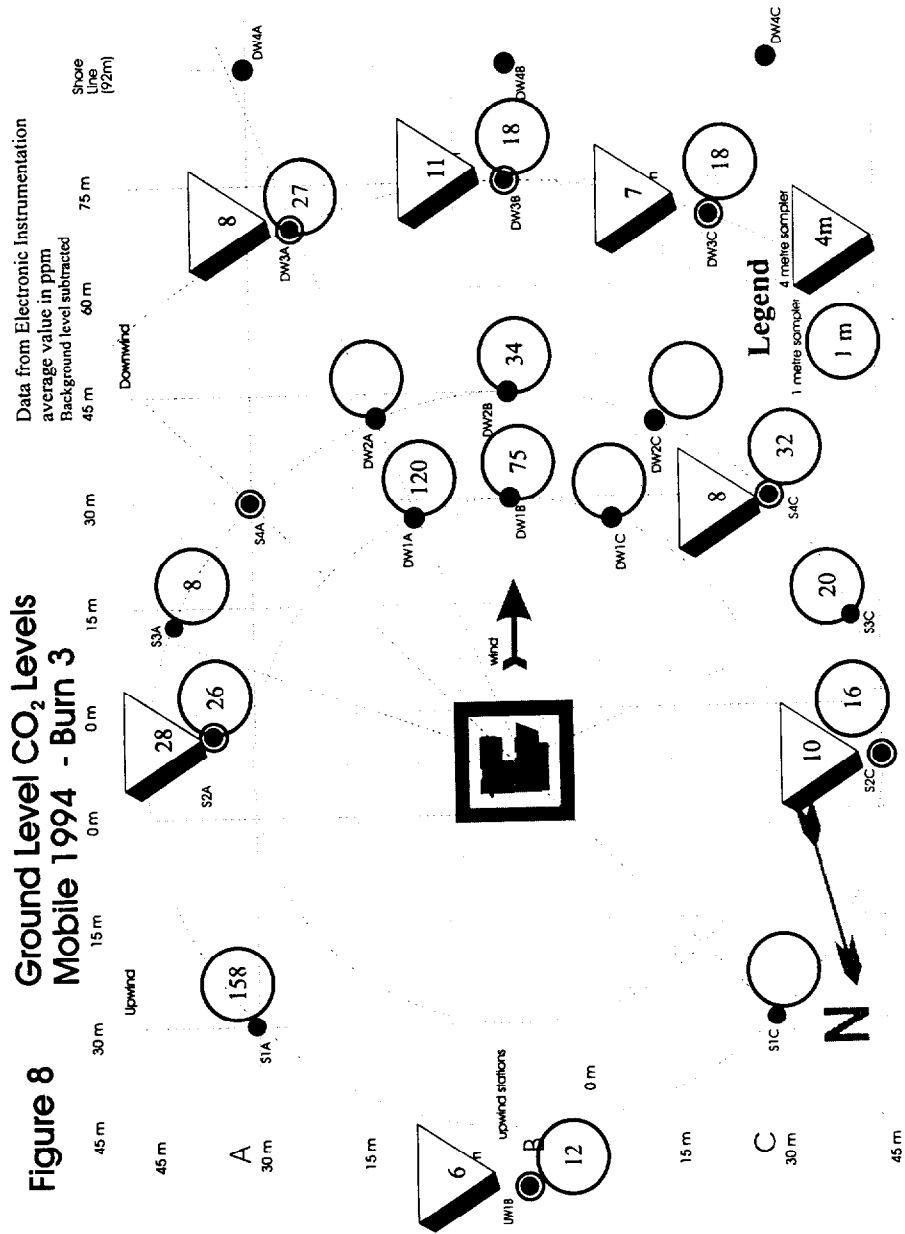


**Figure 5** Relative Concentrations of Carbon Dioxide  
at NOBE -Burn 2





**Figure 8**  
**Ground Level CO<sub>2</sub> Levels**  
**Mobile 1994 - Burn 3**



these meters are not able to handle the high carbon dioxide, moisture and temperature conditions in a plume. Finally, it should be noted that correlation of soot and carbon dioxide concentrations do not show that there is no carbon dioxide separation, especially when numerous measurements show that there is about one order-of-magnitude higher concentrations of carbon dioxide at ground level.

It should also be noted that there is strong motivation for adherence to the carbon balance method, even if it is wrong. First, it is the only method available at the moment. Second, because of eddy correlation and other environmental physics, such a coupled flow (carbon dioxide and soot) implies explicitly that many other correlations are possible (Monteith, 1990). Examples of this are that the correlation product of the particulate concentration and carbon dioxide would then yield turbulence levels. Unfortunately, the correlation between  $\text{CO}_2$  and soot does not exist and therefore further use of eddy correlation is not valid.

The effect of the separation of carbon dioxide implies that the carbon balance vastly overestimates soot production. In fact, it over-estimates soot production by roughly one-half of the  $\text{CO}_2$  concentration differences between the surface and the plume. A scan of Table 2 shows that the carbon balance values are all very much higher (generally a factor of 5) than those by other means. This can be better illustrated by taking a specific calculation. The NOBE burn soot percentage was calculated by one group as averaging 14% using the carbon balance method. This has been re-calculated in this paper as 2.1% by averaging the carbon balances in a block up to plume level. Data are taken from Fingas et al., 1994. The re-calculation is shown in Table 4.

#### **Soot Integration in the Plume**

It has been suggested that plume soot concentrations, particularly those gathered by aircraft could be used to integrate the amount of soot over the entire length. In particular, this could be done at the end of an experimental fire so that the entire soot plume was in the air at once. This has been proposed, but no results using this methodology could be found in the literature.

#### **Soot Integration Estimation Methodologies**

Two new methods will be demonstrated in this paper to assess soot methodologies further. These methods employ two types of data that are readily available from ground measurements, soot concentration levels and weights of soot deposition on filters. In the first case, one integrates the volume under the plume along with the soot concentration to yield a total volume of soot. This assumes that: the height of the plume is well-known, that the concentration of soot is constant from the surface to the plume in a vertical trajectory and most critically, that the fire is out and all the soot is now airborne (thus time is not a factor). The second calculation method will be described further below.

##### **Integration by Volume under Plume**

Extensive experimental data from burning shows that there exists a strong correlation between the product burned and the amount of soot deposited downwind. These data can then be used to estimate the total soot deposited and the near-field deposition. Far-field deposition can be estimated from this data using the distribution

curves developed from near-field data.

The data were taken from a series of burns conducted in Mobile, Alabama in 1991, 1992 and 1994. Fourteen burns using Louisiana crude were conducted in 1991. Six burns using a different blend of Louisiana crude were conducted in 1992. In 1992 more than 20 burns of an Alberta crude were conducted in Calgary, Alberta, although these were not as highly instrumented as other burns. In 1993, two major burns were conducted offshore Newfoundland with more than 2000 parameters or compounds measured. This burn will be referred to here as 'NOBE' for Newfoundland Offshore Burn Experiment. In 1994, three burns of diesel took place in Mobile, Alabama. The results of chemical and physical emissions were widely published (Fingas et al., 1993, 1994, 1995, 1996). Soot deposition concentrations were measured in all cases using calibrated 'RAMs' (Real-time Aerosol Monitors) as well as traditional high-volume and mid-volume samplers.

Analysis of data showed that the distribution of soot both along the x and y axis was nearly identical for all crudes, despite location, and for diesel runs in Mobile, Alabama. The data does not, except for NOBE, extend far downwind, however, from NOBE data it was noted that downwind data can be reliably estimated from near-wind data.

Since it is suspected that the soot concentrations are similarly distributed, given similar wind and weather conditions under which the experiments were conducted, one can estimate the total deposition of soot from a fire by integrating over the volume under the plume. Data are also available on the plume heights from these burns, and it has been noted that (under the conditions noted - generally winds from 2-8 m/s) the plume rises quickly to 20 m and then rises at a rate of 1.5 degrees thereafter (McGratten et al., 1993, 1994).

Centre-line and downwind concentrations can be estimated using a simple logarithmic formula. Data for soot concentrations are given in the Table 5. The curve fits to the logarithmic equation are listed in the Table 6. Data on distribution of soot perpendicular to the plume path are available from the 1994 diesel trials and the 1992 crude oil trials. These data were calculated to yield a formula to relate the perpendicular concentrations to the centre-line plume concentrations. The following formula is the average of the data from the Mobile 1994 trials:

$$\text{soot concentration at any point} = [\text{centre line concentration} \times 2] / \text{distance from centre line in m.}$$

For this type of calculation the height of the plume is critical. The wind conditions affect this, however, no relationships for this have been established. The consistency of the plumes at the Mobile experiments and at NOBE might be attributed to the similar wind conditions under which all these experiments were conducted, or about 2-8 m/s. Higher winds would distribute the soot much farther downwind, but quantitative information is not available to calculate this. All modelling here is for the relatively calm situations and would show deposition closer to the source than would be the case for higher winds.

The equations noted above were applied to the Mobile and NOBE data to estimate the soot deposition for each of the two oils. The model for diesel is shown in



Table 7. The spread sheet is used to calculate a concentration for each point on the ground under the smoke plume. The equations for the centre-line and perpendicular concentrations, as given above, were used to perform the calculations for each block. The near-field spreading of the plume complies to the experimental data measured at Mobile 1994. The shaded blocks show the inputs to the model. These are the centre-line concentrations and the plume starting height (always taken as 20 m). The concentrations in each cell are integrated with the area in each cell (varies across and along the matrix) to yield a total weight of soot in mg and then in kg. The model also shows the percentage deposited in each swath. It should be noted that the scale is not the same in the x and y directions. Furthermore, the x-scale increases along the centre-line. This is necessary to permit the entire model to fit on a page and to show the high soot levels in the near field close to the burn. The soot yield (the weight of soot produced compared with the weight of material burned) is calculated by taking the total soot deposited in the model versus the starting weight of material. For diesel, the value is 8.6%, which is between the literature values of 11% and 3.1%. The model for crude is shown in Table 8, this model yielded a soot production value of 1.7%, also very close to literature values.

Sensitivity tests were performed on the model. The model shows high sensitivity to plume height, some sensitivity to starting concentration and lesser sensitivity to distribution models. It is concluded that this model form is instructive but because of the potential variabilities and thus potential for inaccuracies does not have high potential for future use.

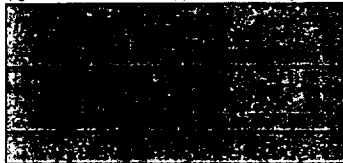
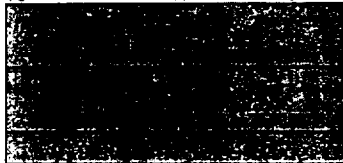
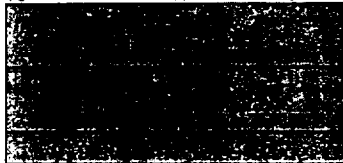
#### **Integration by Weight of Soot Deposition**

A second method that will be described and tested here is to test the use of the weight of soot precipitated onto filters. The precipitation is integrated over the area of the ground where soot deposition is thought to occur. This form of calculation, as above, ignores the particulate matter that is transported downwind in the plume. Aircraft measurements at two experimental spills show that the densities of the soot decreases faster downwind than does the area increase, showing that significant portion of the soot does precipitate (Ross et al., 1996). The other weakness of the method is that one must presume that the samplers do not draw more particulate matter than would be normally deposited on the ground. It is well known that this does indeed occur, so that the method should produce a high result. This may be counterbalanced, at least somewhat by the amount remaining in the plume that is ignored and by the measurement of soot over a smaller area than might be indeed the case.

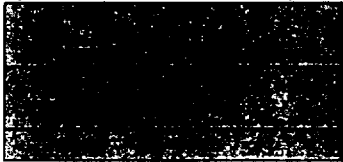
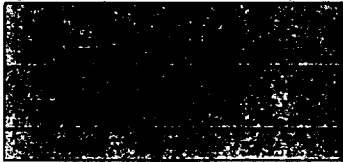
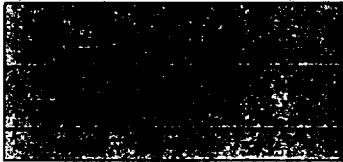
The mathematical methodology is similar to that above. Equations were fitted using data obtained from the Mobile 1994 data, then these equations used to calculate deposition amounts between measured stations. The depositions are then summed to yield a total soot amount and hence a soot production value. Table 9 shows the values of the deposition amounts for diesel in the Mobile 1994 trial. These data were averaged to yield one set. Equations were fitted to these data to yield a downwind distribution equation. As usual, the highest regression coefficient and simplest equation were chosen ( $r^2=0.999$ ). The equation result is:

Table 4 Recalculation of NOBE Carbon Balances Using Ground Concentrations

**Burn 1**

layer	location	Soot concentration $\mu\text{g}/\text{m}^3$	CO <sub>2</sub> Concentration ppm above background	CO <sub>2</sub> Concentration $\mu\text{g}/\text{m}^3$	carbon balance
plume				12220	0.0614
				12220	0.0614
above ground				11750	0.0042
				11750	0.0042
ground				212440	0.0004
				average	0.0263
each block represents a length of 50 metres				soot percentage	2.6

**Burn 2**

layer	location	Soot concentration $\mu\text{g}/\text{m}^3$	CO <sub>2</sub> Concentration ppm above background	CO <sub>2</sub> Concentration $\mu\text{g}/\text{m}^3$	carbon balance
plume				21620	0.0357
				21620	0.0357
above ground				11750	0.0042
				11750	0.0042
ground				255210	0.0002
				average	0.016
each block represents a length of 50 metres				soot percentage	1.6

<b>Average Soot Percentage</b>	<b>2.1</b>
--------------------------------	------------

Table 5  
Particulate Downwind Distributions

(soot concentrations in  $\mu\text{g}/\text{m}^3$ )

<b>Mobile 94 - diesel</b>			
Distance	average	second	third
15	2068	2180	1960
30	711	1224	884
75	180	180	360
92	149	69	229

<b>ASMB - NOBE</b>		
Distance	Burn 1	Burn 2
50	13	12.3
150	11	10.3
500	0.08	0.07

<b>Mobile 1991</b>	
Distance	Average
30	0.75
60	0.21

<b>Mobile 1992</b>		
Distance	Average	maximum
23	4.19	27
30	1.93	18
46	0.96	8

<b>Mobile 94 - diesel</b>				
Sideways		Sideways		
Distance	Conc.	Distance	Conc.	
1	2069	1	711	
15	1368	18	63	
30	108	36	34	

Sideways		Sideways	
Distance	Conc.	Distance	Conc.
1	180	1	596
31	12	38	0.01
62	6	76	0

Table 6

# Systematic Calculation of Downwind Soot Concentrations

## Calculation of Far-Field Concentrations

Experiment	Diesel	Concentration at 500 m	Concentration at 1000 m	Concentration at 5000 m	Concentration at 12200 m
	Equation (best-fit, declining equation)				
94- average	$1/y = a + bx \ln x$ ( $a = -8.06e-5$ , $b = 1.29e-5$ )	23.2	10.4	1.7	0.63
94-burn 2	$\ln Y = a + b \ln x$ ( $a = 8.057$ , $b = -0.00918$ )	1.295E-09	0	0	0
94-burn 3	$\ln Y = a + b \ln x$ ( $a = 10.6$ , $b = -1.12$ )	38.91	17.94	2.97	1.1
	average	20.7	9.45	1.56	0.58
	best log curve fit $y = a + b \ln x$ ( $a = 54.1$ , $b = -5.93$ )				
<b>Crude Oil</b>					
NOBE - burn 1	$y^{0.5} = a + bx^2$ ( $a = 3.63$ , $b = 11.38E-5$ )	0.039	0	0	0
NOBE - burn 2	$\ln Y = a + bx^3$ ( $a = 2.514$ , $b = -5.32E-08$ )	0.016	0	0	0
Louisiana 92	$1/y = a + bx^{2.5}$ ( $a = -1.72$ , $b = 0.408$ )	0.135	0.089	0.037	0
	average	0.06	0.03	0.012	0
	best log curve fit $y = a + b \ln x$ ( $a = 172$ , $b = -0.0191$ )				

## Near Field Concentrations

Experiment	a-parameter	b-parameter
<b>Diesel</b>		
94- average	log curve $y = a + b \ln x$	4551 -1010
94-burn 2		5304 -1174
94-burn 3		4245 -906.3
	average	4700 -1030
<b>Crude</b>		
NOBE - burn 1		36.6 -5.67
NOBE - burn 2		34.6 -5.36
Louisiana 92 - maximum/average (over-stated)		65.2 -7.1
Louisiana 92 - average		17.7 -4.45
average	average	38.5 -5.6

### Soot Production Model for Diesel

based on data from Module B4 burns - data fit to best mode

values are in grid are mg per individual cell

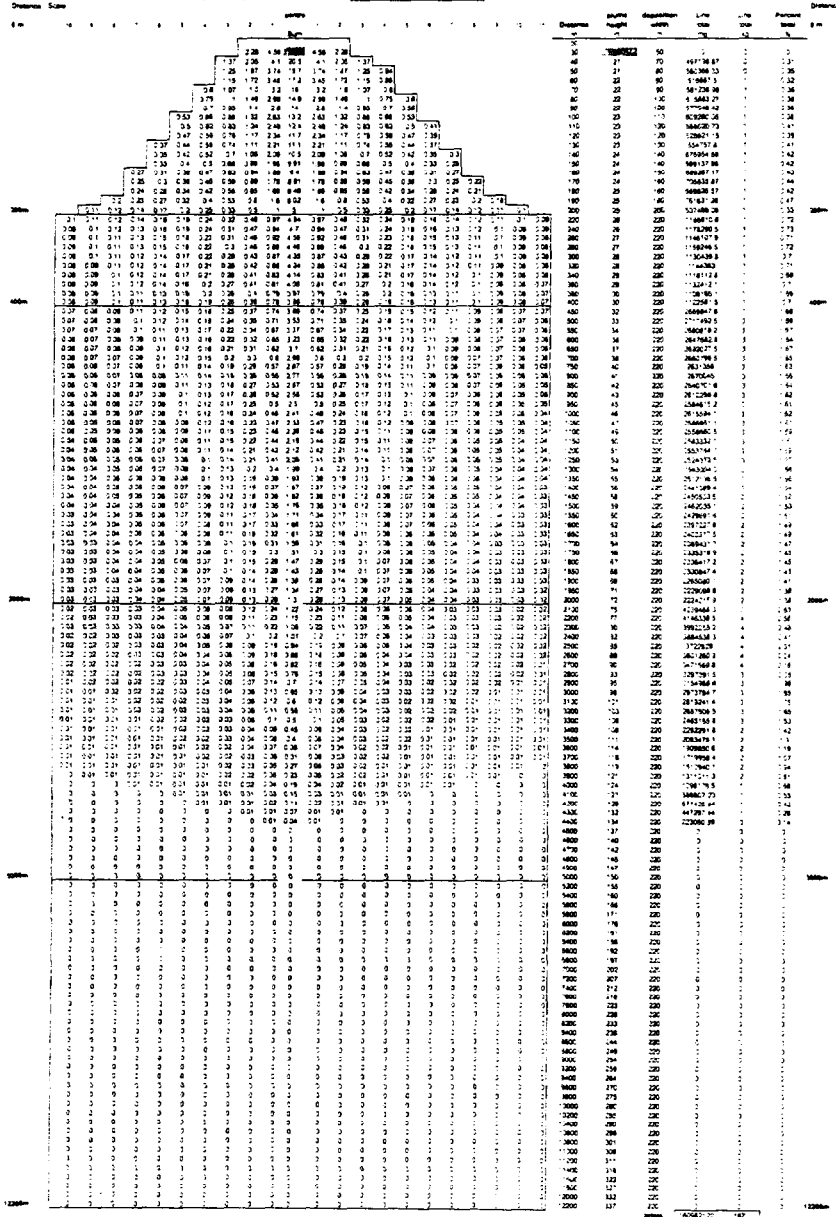
**Total cost year 4**      **8.6 %**

[illegible]

Table 3  
**Soot Generation Model for Crude Oil**  
based on data from Mobile #1, #2 and NOSE burns - data fit to best model

Values are in gnd are mg per individual cell

Total stock yield *	1.3 %
---------------------	-------



$$1/y = a + b/x^{0.5}$$

Where y is the soot deposition in  $\mu\text{g}/\text{m}^3$

$$a = 0.145$$

$$b = -.088$$

x is the downwind distance in metres

Sideways distributions were calculated using the equations as above for the integration by volume value. Table 10 shows the deposition model for diesel as calculated from the average of the Mobile 1994 data. This shows a soot production of 4.3% for diesel which agrees with some primary data (3.1 to 11%, see Table 1). Table 11 shows the deposition model for crude oil which shows a soot production value of 1.7% which is also in good agreement with the primary average of around 2.5%.

Sensitivity tests on this model show that it is much more stable than the previous model of integrating volume under the plume; yields reasonable results and is relatively simple to implement. The downfall is, of course, the lack of immediate confirmation by absolute values that it is correct. The assumption that the soot in the filters was not concentrated by the air flow, yield much higher values than true values, however, not all the area may be integrated and some soot still remains in the plume after deposition is not counted. This particular method may have potential for future work if more data on soot ground deposition can be obtained.

#### Other Possible Methods

It is obvious that no method currently exists to measure the soot production from large-scale oil fires. Small scale methods are not applicable. Two new methods, integration of the volume under the plume and integration of soot deposition under the plume were tried above. The latter method may have future potential. Future research might focus on absolute methods. One method that might have potential is the use of laser particle counters to count particles by size as they move overhead. This could only be done some distance downwind where particles in lower parts of the plume do not obscure other particles. Furthermore, current instruments are not fully capable of this method. Variations on this method, such as moving a laser instrument through the plume to catch very accurate "slices" could yield enough accurate data to extrapolate values to the entire plume.

#### Summary and Conclusions

Literature values for soot production vary considerably, from 1% to as high as 16%. The nature and behaviour of an in-situ fires were reviewed noting that there is significant gas separation between the plume and the surface. Secondly, there is significant soot precipitation out of the plume near the fire. The difficulty of performing the soot production measurement and estimating the value is noted.

In view of the behaviour of fires, methods that capture the soot entirely are classed as the only true measurement technique whereas others are classed as estimation techniques. Values calculated from the method known as "carbon balance" assumes that all carbon resulting from the fire is in the plume. Data from many burns show that the  $\text{CO}_2$  is often ten times lower in the plume than on the surface. The carbon balance

Table 9 Soot Deposition Amounts - Mobile 1994

sample number (6" x 10" filter)	POSITIONS	BURN #	soot per square metre in mg/m <sup>2</sup>	TSP PARTICULATES UNCORRECTED (g)
6261095	DW1A	1	0.31200	0.00600
6261098	DW1B	1	0.06760	0.00130
6261100	DW1C	1	0.63440	0.01220
6261094	DW2A	1	0.07020	0.00135
6261092	DW2B	1	0.00780	0.00015
6261089	DW2C	1	0.21840	0.00420
6261083	DW3A	1	0.08320	0.00160
6261086	DW3B	1	0.11440	0.00220
6261076	DW1A	2	2.43100	0.04675
6261078	DW1B	2	8.97000	0.17250
6261080	DW1C	2	1.12320	0.02160
6261069	DW2A	2	1.08420	0.02085
6261072	DW3A	2	0.26780	0.00515
6261074	UPWIND	2	0.00000	0.00000
6261060	DW1A	3	3.42160	0.06580
6261062	DW1B	3	5.73040	0.11020
6261061	DW1C	3	0.14040	0.00270
6261056	DW2A	3	1.07640	0.02070
6261058	DW3A	3	0.36400	0.00700



**Soot Deposition Model for Diesel**

Table 10

Based on data from 10 Mobile B4 burns - data fit to soot model

Using integration of filter values over time

Values are in and are mg per individual cell

Total soot yield = 4.3 g

Line	Lat	Long	Alt	Temp	Hum	Wind	Dir	Speed	Pressure	QNH	QFE	QFF	Time	Remarks
1	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
2	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
3	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
4	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
5	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
6	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
7	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
8	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
9	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
10	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
11	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
12	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
13	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
14	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
15	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
16	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
17	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
18	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
19	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
20	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
21	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
22	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
23	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
24	34 15 10	139 45 10	100	15.0	85	10	090	10	1013.5	1013.5	1013.5	1013.5	1000	1000
25	34 15 10	139 45 10												

Table 11 Soot Deposition Model for Crude Oil  
based on data from Mobile 92 burns - data fit to best model  
using integration of flow values over area

		values are in g/m <sup>2</sup> per individual cell																				Total soot yield = 1.7 %																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
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method may be accurate for very small burns where sampling is performed directly in the chimney and where the gases do not have a chance to escape from the smoke. The most accurate method is that of direct soot collection, however to perform such soot is usually collect directly over the flame. Significant amounts of soot are collected which might otherwise precipitate back into the fire. Although accurate, these measurements could over-estimate soot from a large fire. A variant on the theme is to use a proportionate sampling system and calculate the proportion of the smoke taken and multiply this times the weight of the sample captured. This is, in theory, more accurate because one can measure further away from the source of the flame, however, the inaccuracies in determining the proportion sampled can be large. Because of these accuracies, total soot captures are classified as "primary" and methods to estimate these such as carbon balance as "secondary". The separation of the plume relates to the measurement of carbon dioxide at a spill site. It is noted that the use of IR electronic meters at in-situ fires is difficult because of the high noise level and because of the interference of water vapour, high-volumes of combustion compounds, and the applicability of the technique at high levels - especially in the smoke plume.

Extensive experimental data from burning shows that there exists a strong correlation between the product burned and the amount of soot deposited downwind. These data can then be used to calculate the total soot deposited and the near-field deposition. Far-field deposition can be estimated from this data using the distribution curves developed from near-field data. The Mobile and NOBE experimental burn data were used to estimate the soot deposition. For diesel, the value of soot production obtained is 8.6%. For crude a value of 1.7 % is obtained. Another new method was proposed, that of integration of the soot deposition on the area under a plume. This method yielded soot production values of 4.3% for diesel and 1.7% for crude oil. This method may have future potential.

Most estimation methods would appear to over-estimate soot production by as much as a factor of 10. It is concluded that the value of soot produced varies significantly down-plume because of precipitation of material. Downwind (perhaps 5 km) soot emission values are likely to be as low as 0.5 % for crude oil and about 3% near the fire. For diesel, the downwind emissions may be about 1% and about 6% near the source. There should be, however, significant variation for the type of material burned and also for some of the environmental conditions. Current measurement and estimation techniques are fraught with numerous difficulties. "True" values may not be forthcoming for a period of time. It is suggested that laser particle sizing and counting techniques may be a solution to the problem.

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