Analysis of Emissions from Methods to Improve Combustion Efficiency of *In Situ* Oil Burns

Performance of an Emulsified Crude Oil Spray Burner

Final Report

June 19, 2020

Dr. Johanna Aurell
University of Dayton Research Institute, Power & Energy Division, Energy and Environmental Sciences

Dr. Brian Gullett
US EPA, Office of Research and Development, Center for Environmental Measurement and Modeling

ABSTRACT

The U.S. Department of the Interior's (DOI) Bureau of Safety and Environmental Enforcement (BSEE) enlisted U.S. EPA's Office of Research and Development (ORD) to characterize emissions from the Naval Research Laboratory's (NRL) novel crude oil spray burner design. This effort aimed to characterize emissions from the crude oil spray burner using two crude oils with different viscosities, comparing emulsified and non-emulsified crude oil, and with two different flow rates (11.8 L/min and 7.0 L/min) of the oil to the burner. EPA's ORD sampled emissions using a telescopic boom lift to bring ORD's customized instrument system termed the "Kolibri" into the plume. The Kolibri system consists of advanced, lightweight real time sensors and bulk samplers measuring $PM_{2.5}$ (particulate matter less than 2.5 micrometers), carbon monoxide (CO), carbon dioxide (CO_2), black carbon (BC) and UVPM, total carbon/organic carbon/elemental carbon (TC/OC/EC), volatile organic compounds (VOCs), and polyaromatic hydrocarbons (PAHs).

The crude oil spray burner emitted minimal levels of CO resulting in modified combustion efficiencies (MCEs) ($CO_2/(CO_2+CO)$) ranging from 0.998 to 0.999. Emulsified oil emitted ten times higher $PM_{2.5}$ emissions than non-emulsified oil and the higher oil flow rate resulted in a two-fold increase of $PM_{2.5}$ emissions compared to the lower flow rate. The 12-test, run-weighted average $PM_{2.5}$ emission factors were 4 and 5 times lower than *in situ* oil burn simulations and Deepwater Horizon measurements in the Gulf of Mexico, respectively.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

ACRONYMS

BC	Black carbon
BSEE	Bureau of Safety and Environmental Enforcement
CA	California
CO	Carbon monoxide
CO_2	Carbon dioxide
CRREL	US Army's Cold Regions Research Engineering Laboratory
DAS	Data acquisition system
DOI	Department of Interior
EC	Elemental carbon
FL	Florida
FR	Fast response
GC/MS	Gas chromatography/mass spectrometry
GPS	Global position system
HOOPS	Hoover offshore oil pipeline system
HRGC	High Resolution Gas Chromatography
IR	Infrared
ISB	In-situ burns
MCE	Modified combustion efficiency
MD	Maryland
MW	Middle weight
NDIR	Non-dispersive infrared
NIST	National Institute for Standards and Technology
NRL	Naval Research Laboratory
NSWC	US Navy Surface Warfare Center, Dahlgren
OC	Organic carbon
OCS	U.S. Outer Continental Shelf
OD	Outer diameter
ORD	Office of Research and Development

OSRR	Oil Spill Response Research
PAH	Polycyclic aromatic hydrocarbon
PEM	Personal environmental monitor
PM	Particulate matter
PMI	Personal modular impactor
ppm	parts per million
PUF	Polyurethane foam
QAPP	Quality assurance project plan
RH	Relative humidity
RPD	Relative percent difference
RSD	Relative standard deviation
SD	Secure digital
SIM	Selective ion monitoring
TC	Total carbon
TOA	Thermal optical analysis
UAS	Unmanned aircraft system
UDRI	University of Dayton Research Institute
USB	Universal serial bus
UV	Ultraviolet
VOCs	Volatile organic compounds
XAD-2	Brand name of sorbent Polymeric resin

1 INTRODUCTION

1.1 Background

In 2014 the U.S. Department of the Interior's (DOI) Bureau of Safety and Environmental Enforcement (BSEE) solicited proposals seeking testing in specific areas of interest to BSEE's Oil Spill Response Research (OSRR) Program on Oil Spill Response Operations on the U.S. Outer Continental Shelf (OCS). Responsive to this request, the Naval Research Laboratory (NRL) submitted and was awarded an effort to examine performance and engineering aspects of an emulsified crude oil spray burner. The purpose of these tests was to determine igniter operability and limits, to measure burner-specific heat transfer and temperature, and to measure emissions. The performance measures of interest included the operability of flame igniters and their performance limits, quantifying the amount of heat transfer from the burner to the deck, the temperature of the burner structure, and the measurement of the combustion emissions from the burner. During this testing BSEE enlisted EPA's Office of Research and Development (ORD) to conduct emission sampling and analysis of the plumes. ORD characterized and quantified the pollutants while NRL conducted the oil burning procedures.

ORD has considerable experience in sampling emissions from oil burns. A recent 1 m^2 pan study [1] with Bayou Sweet crude simulated the Deepwater Horizon burns, finding ~6% of the oil by mass became a particle emission of median diameter 1 µm and over 90% of which was light absorbing black carbon (BC). The gas phase modified combustion efficiency (MCE) declined throughout each burn from 100% to 97.8%; incorporation of the carbon within the particle emissions and unburnt residue (in this case, 29% by mass) significantly lowered this efficiency. The identified and quantified species in the emissions accounted for over 92% by mass of the combustion products. The unburned oil mass was 29% of the original crude oil mass, significantly higher than typically reported. Analysis of alkanes, major elements, and polycyclic aromatic hydrocarbons (PAHs) in the floating residual oil and water accounted for over 51% of the gathered mass.

More recently, EPA/ORD has conducted two efforts to characterize oil burning emission for BSEE. Both efforts were conducted at the US Army's Cold Regions Research Engineering Laboratory (CRREL) and involved extensive plume sampling of the emissions and water sampling of the residuals. The emissions were sampled by suspending an instrument platform into the plume by means of a crane. For the work reported here, EPA/ORD sampled emissions using a telescopic boom lift to bring the ORD customized instrument system into the plume. The instrument system, termed the "Kolibri", consists of advanced, lightweight real time sensors and bulk samplers measuring $PM_{2.5}$ (particulate matter less than 2.5 micrometers), carbon monoxide (CO), carbon dioxide (CO_2), BC, volatiles, and PAHs. Real time CO and CO_2 enabled calculation of a MCE and, together with analysis of each pollutant, enabled determination of an emission factor (pollutant mass/oil mass burned). Data gathered by the sampling system were logged aboard and transferred via telemetry to the operator on the ground.

1.2 Objective

This effort aimed to characterize emissions from a series of tests with a novel burner design as outlined in the section 2.2 matrix. Tests simulated conditions of at-sea oil burning technologies related to *in situ* burns (ISB).

2 MATERIALS AND METHODS

2.1 Test Location and Set-up

Testing took place at the NRL's Chesapeake Beach Detachment located in Chesapeake Beach, MD, south-southeast of Washington D.C. NRL 308 building's concrete testing platform was used for the testing. NRL conducted the burns with their crude oil spray burner system (Figure 2-1) and coordinated the EPA/ORD instrumentation location. The burner is comprised of the atomizer, ignition torches, combustor, and the associated flow system. It rests on a 3 ft × 3 ft × 3 ft Unistrut frame. A high-capacity air compressor was used to supply pressurized air to both atomize the crude oil and to provide air for the JP-5-fueled plasma ignition torches. A two-inch air hose conveyed the pressurized air to the test platform. A gear pump controlled by a data acquisition system, also located on the deck, fed the crude oil to the atomizer. For each burn test, members of NRL prepared the area with the test oil and then began the burn.

Figure 2-1. NRL's Crude Oil Spray Burner.

2.2 Test Matrix

Two different crude oils were tested: oil from Hoover offshore oil pipeline system ("HOOPS") and a middle-weight blend (MW) from Santa Clara, Point Arguello, and Alaska North Slope. The MW crude oil had higher density than HOOPS, 0.970 and 0.851 g/mL, respectively. The spray burner was tested when operating in full maximum flow state ("Full Max") with an average flow of 11.8 L/min ("Low Flow") with the HOOPS crude oil in its natural state (Table 2-1, Burns 1-3) and with HOOPS in an emulsified state (emulsion 13.1 L/min oil) (Table 2-1, Burns 4-6). The MW crude oil was tested when the spray burner was operating at two different flows: low flow (7.0 L/min, Burns 7-9) and full maximum flow (11.8 L/min, Burns 10-12). Each of the different test conditions were replicated three times resulting in 12 total burns.

Table 2-1. Test Matrix.

Burn No.	Oil type	Test Condition
1	HOOPS	Control – Full Max
2	HOOPS	Control – Full Max
3	HOOPS	Control – Full Max
4	HOOPS	Emulsified – Full Max
5	HOOPS	Emulsified – Full Max
6	HOOPS	Emulsified – Full Max
7	Middle-Weight Blend	Low Flow
8	Middle-Weight Blend	Low Flow
9	Middle-Weight Blend	Low Flow
10	Middle-Weight Blend	High Flow - Full Max
11	Middle-Weight Blend	High Flow - Full Max
12	Middle-Weight Blend	High Flow - Full Max

2.3 Target Emission Compounds

Target compounds included CO, CO_2, $PM_{2.5}$, BC/UVPM, total/organic/elemental carbons (TC/OC/EC), PAHs (as time and conditions allowed), and volatile organic compounds (VOCs). Measurements were used to calculate emission factors based on the carbon balance method, which uses the ratio of the sampled pollutant mass to the sampled carbon mass (determined from CO + CO_2 measurements) and the carbon percentage of the fuel (85%). The resultant emission factors are expressed as mass of pollutant per mass of oil burned.

Targeted emission constituents and their sampling methods are listed in Table 2-2.

Table 2-2. Target emission compounds, methods and sampling frequency.

Analyte	Method	Frequency
CO_2	SenseAir CO2 Engine® K30 Fast Response (FR), NDIR	Continuous
CO	EC4-500-CO, Electrochemical cell	Continuous
$PM_{2.5}$	Impactor/filter/gravimetric	Batch

Analyte	Method	Frequency
VOCs	Carbotrap 300	Batch
BC/UVPM	Aethalometer, MA200	Continuous
TC/OC/EC	Quartz filter	Batch
PAHs	PUF/XAD/PUF cartridge	Batch

While the goal was to gather samples that sufficiently exceeded analyte detection limits, the desired sampling volume to achieve this cannot be known *a priori*, as this would require knowledge of the emission factor itself. ORD's best engineering judgment based on similar past sampling, along with plume average CO_2 and CO concentration observed by the sampler, was used to estimate the necessary sampling time/volume.

2.4 Emission Sampling Instrumentation

The primary sampling instrument is the "Kolibri" (Figure 2-2). This ~3 kg system is a battery-powered, remotely controlled pollution sampler that was developed in EPA laboratories. The Kolibri's data acquisition system (DAS) consist of an onboard Teensy USB-based microcontroller board (Teensy 3.1, PJRC, LLC., Sherwood, OR, USA) running an Arduino based data acquisition and control program ("TeensyDAQ"). The main assignment for the TeensyDAQ is power regulation, data logging via a secure digital (SD) card, and data transmission. Also included in the DAS is a ground based computer which is running "KolibriDAQ" a Labview generated data acquisition and control program, which is used to view live data and run/control the onboard TeensyDAQ via a XBee wireless network (Xbee S1B, Digi International, Inc., Minnetonka, MN, USA). The KolibriDAQ is capable of plotting real time CO_2 and CO data, turning on and off sampling pumps, and displaying sampling time, sampling volume, battery level, and ambient temperature.

Figure 2-2. "Kolibri" sampling instrumentation.

2.5 Plume Sampling

A telescopic boom lift with an aerial platform was used to maneuver ORD's Kolibri sampling equipment into the plume (Figure 2-3). Two Kolibri systems were attached underneath the telescopic boom lift's aerial platform. The telescopic boom was attached to a freely rotating turntable enabling NRL's operator to maneuver the sampling equipment into the plume with guidance from the Kolibri's operator. The Kolibri's operator monitored the temperature and CO_2 levels; levels above ambient background concentrations indicated that the Kolibri sampler was within the plume.

Figure 2-3. Kolibri samplers mounted underneath boom lift platform (L) and burner in operation (R) while sampling.

2.6 Number of Samples Collected

The number of batch samples collected are shown in Table 2-3. One $PM_{2.5}$ sample was collected for each burn and one composite $PM_{2.5}$ sample was collected from all three replicate burns for each test condition. For example, the three HOOPS Control burns resulted in a single $PM_{2.5}$ sample from each burn and a 3-run composite $PM_{2.5}$ sample. The same sampling procedure was conducted for the TC/OC/EC samples. Single, composite samples for VOCs and PAHs were collected from the three replicate burns for each test condition in order to ensure collection of sufficient sample to obtain detectable levels.

Table 2-3. Number of batch samples collected.

Burn No.	Oil type	Test Condition	$PM_{2.5}$		TC		VOC	PAH
1	HOOPS	Control	1	1	1	1	1	1
2	HOOPS	Control	1		1			
3	HOOPS	Control	1		1			
4	HOOPS	Emulsified	1	1	1	1	1	1
5	HOOPS	Emulsified	1		1			
6	HOOPS	Emulsified	1		1			
7	Middle Weight	Low Flow	1	1	1	1	1	1
8	Middle Weight	Low Flow	1		1			
9	Middle Weight	Low Flow	1		1			
10	Middle Weight	High Flow	1	1	1	1	1	1
11	Middle Weight	High Flow	1		1			
12	Middle Weight	High Flow	1		1			
Ambient Air Background			1		1		1	1
Total No. of Samples			**17**		**17**		**5**	**5**

Control = Full Max Flow. High Flow = Full Max Flow.

2.7 Calculations

2.7.1 Emission Factors in Mass Analyte per Mass Initial Oil

Measurements were used to determine emission factors based on the carbon balance method, which uses the ratio of the sampled pollutant mass to the sampled carbon mass (determined from CO + CO_2 measurements and, where possible, TC from $PM_{2.5}$ analyses) and the carbon percentage of the fuel (85%). The resultant emission factors are expressed as mass of pollutant per mass of oil burned (Equation 1).

$$Emission\ Factor_{initial} = Fc \times \frac{Analyte_{ij}}{C_j} \qquad \textit{Equation 1}$$

Where:

$EF_{initial}$ = The emission factor for target analyte i (mg $Analyte_i$/kg oil initial)

Fc = Carbon fraction in the oil (0.85)

$Analyte_{ij}$ = background-corrected concentration (mg $Analyte_i/m^3$) of the target analyte i collected from the volume element j of the plume.

C_j = background-corrected concentration of carbon (kg Carbon/m^3) collected from volume element j of the plume

2.7.2 Emission Factors in Mass Analyte per Mass Oil Consumed

An alternative emission factor was calculated taking the oil not consumed into consideration as shown in Equation 2.

$$Emission\ Factor_{Consumed} = EF_{initial} \times \frac{mass\ oil}{mass\ oil \times oil\ mass\ loss} \qquad \textit{Equation 2}$$

Where:

$Emission\ Factor_{consumed}$ = The emission factor for target analyte i *taking oil consumed in consideration* (mg Analyte$_i$/kg oil consumed)

$EF_{initial}$ = The emission factor for target analyte i (mg Analyte$_i$/kg oil initial)

mass oil = mass of oil initial

oil mass loss = fraction of oil consumed in the burn

2.7.3 Modified Combustion Efficiency

The MCE was used to calculate how well the oil burned.

$$MCE = \frac{CO_2}{CO_2+CO+Total\ Carbon} \qquad \textit{Equation 3}$$

Where:

MCE = modified combustion efficiency

CO_2 = carbon dioxide in the plume in ppm

CO = carbon monoxide in the plume in ppm

Total Carbon = total carbon in the particulates (TC), at higher PM levels

2.7.4 Data Variability

Standard deviation (Stand. Dev.), relative standard deviation (RSD), and relative percent difference (RPD) were used as a measure of dispersion, calculations shown in Equations 4 to 6.

$$Standard\ Deviation = \sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}} \qquad \textit{Equation 4}$$

where:

x = each sample value
$\bar{x}$ = mean value of samples
n = number of samples

$$RSD\ (\%) = 100 \times \frac{Standard\ Deviation}{Sample\ Average} \qquad Equation\ 5$$

$$RPD\ (\%) = 100 \times \frac{x_1 - x_2}{\frac{x_1 + x_2}{2}} \qquad Equation\ 6$$

where:
x_1 = sample value one
x_2 = sample value two

3 MEASUREMENT AND QUALITY ASSURANCE PROCEDURES

3.1 CO_2 measurements

The Kolibri system's CO_2 sensor (CO_2 Engine® K30 Fast Response (FR), SenseAir, Delsbo, Sweden) measures CO_2 concentration by means of non-dispersive infrared absorption (NDIR). Sensor output voltage is linear from 0 to approximately 7900 ppm. The response time (t95) is less than 10 seconds and measurement is accurate within 5% error. The sensor operates at temperatures ranging from -10 to 40 °C and relative humidity (RH) from 0 to 95%. The CO_2 Engine® K30 FR sensor was calibrated prior to field departure from 0 to 8082 ppm with ± 2 ppm error using EPA Method 3A [2]. In the field, the CO_2 background was measured daily prior to sampling and it was calibrated for CO_2 on a daily basis in accordance with EPA Method 3A [2] using a three-point calibration. Data were recorded on the Teensy, a universal serial bus (USB)-based microcontroller board using an Arduino-generated data program.

A precision dilution calibrator Serinus Cal 2000 (American ECOTECH L.C., Warren, RI, USA) was used to dilute the high-level span gases for acquiring the mid-point concentrations for the K30 calibration curves. All calibration gases were certified by the suppliers that they were traceable to National Institute of Standards and Technology (NIST) standards.

The daily CO_2 system drift for the first and second test day for both units was less than 1.97% and 1.45%, respectively which is within the ±5% acceptance criteria of the sensor (Table 3-1).

Table 3-1. CO_2 system drift for each test day.

Calibration gas concentration	**First test day:**		**Second test day:**	
	Unit 1	**Unit 2**	**Unit 1**	**Unit 2**
400 ppm	0.29%	1.1%	-0.71%	0.86%
1500 ppm	1.97%	2.41%	-1.45%	0.07%
4000 ppm	0.31%	0.47%	0.83%	1.34%
6000 ppm	0.14%	0.77%	0.69%	0.49%

3.2 CO measurements

The Kolibri system's CO sensor (e2V EC4-500-CO) is an electrochemical gas sensor (SGX Sensortech Ltd, High Wycombe, Buckinghamshire United Kingdom) which measures CO concentration by means of an electrochemical cell through CO oxidation and changing impedance. The E2v CO sensor has a CO detection range of 0-500 ppm with resolution of 1 ppm and sensitivity of 55-85 nA/ppm. The temperature and RH operating range is -20 to +50 °C and 15 to 90% RH, respectively. The response time is less than 30 seconds and the noise level 1 ppm. Output is non-linear from 0 to 500 ppm. A calibration curve was calculated in the EPA Laboratory at 0 to 200 ppm with ± 2 ppm error using U.S. EPA Method 3A [2] prior to departure to the field. The sensor was calibrated daily for CO in accordance with U.S. EPA Method 3A [2]. The e2V CO concentration was recorded on the Kolibri Teensy a USB-based microcontroller board using an Arduino-generated data program and saved to a SD card.

A precision dilution calibrator Serinus Cal 2000 (American ECOTECH L.C., Warren, RI, USA) was used to dilute the high-level span gases for acquiring the mid-point concentrations for the e2V CO calibration curves. All calibration gases were certified by the suppliers that they were traceable to NIST standards.

The daily CO system drift for Kolibri Unit 2 for first and second test day was less than 4.1% and 0.58%, respectively which is within the ±5% acceptance criteria of the sensor (Table 3-2). The drift for Kolibri Unit 1 was slightly higher than the acceptance criteria of the sensor. However, the CO levels measured in the plume were most of the time less than 2 ppm.

Table 3-2. CO system drift for each test day.

Calibration gas concentration	**First test day:**		**Second test day:**	
	Unit 1	**Unit 2**	**Unit 1**	**Unit 2**
0 ppm	1.6 ppm*	0.6 ppm*	0.19 ppm*	0.11 ppm*
15 ppm	7.8 %	4.1%	8.2%	0.58%
25 ppm	NC	NC	5.7%	-0.43%
50 ppm	2.4%	2.6%	5.9%	-0.23%
100 ppm	2.5%	3.8%	NC	NC

* Absolute difference, which is within the noise level of the sensor. NC = not calibrated for that concentration.

3.3 $PM_{2.5}$

$PM_{2.5}$ was sampled with SKC's Personal Environmental Monitor (PEM) impactors (761-203B) using 37 mm tared Teflon™ filter with a pore size of 2.0 µm via a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) of 10 L/min. Particles larger than 2.5 µm were collected on a greased impaction disc mounted on the top of the filter in the $PM_{2.5}$ impactor. The constant flow pump was calibrated daily with a Sensidyne Go-Cal Air Flow Calibrator (Sensidyne LP, St. Petersburg, FL, USA). PM was measured gravimetrically following the procedures described in 40 CFR Part 50 Appendix L [3, 4]. The filters were pre- and post-weighed by Chester LabNet. The post weighing of the filters was completed within 12 days of sampling completion.

3.4 Total Carbon, Elemental Carbon, Organic Carbon

TC/OC/EC was sampled with SKC's $PM_{2.5}$ Personal Modular Impactor (PMI) using 37 mm quartz filter via a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) of 3 L/min. Particles larger than 2.5 µm in the $PM_{2.5}$ impactor were collected on an oiled 25 mm impaction disc mounted on the top of the filter cassette. The constant flow pump was calibrated daily with a Sensidyne Go-Cal Air Flow calibrator (Sensidyne LP, St. Petersburg, FL, USA). The TC/OC/EC was analyzed at EPA/ORD using a modified thermal-optical analysis (TOA) using Modified NIOSH Method 5040 [5] and Khan et al. [6]. The TC/OC/EC was analyzed within seven days of sampling completion. The RPD of the duplicate analyzed samples was 13%.

3.5 Black Carbon and UVPM

BC and UVPM were measured with an MA200 microaethalometer (AethlLabs, U.S.A.). The MA200 instrument measures BC concentrations in ng/m^3 using a calibrated filter-based light attenuation measurement, which is the same operating principle for all aethalometers. Concentrations are measured at five wavelengths, ranging from 375 nm (UV) to 880 nm (IR). The unit contains 85 sampling locations on an automatic filter tape advance system, allowing for long-term continuous measurements without the need for repeated filter replacements. Once attenuation reaches a user-specified value, the filter cartridge automatically advances to a clean part of the filter tape. The instrument also utilizes dual-spot sampling technology [7], in which two parallel spot measurements are recorded simultaneously at varying flow rates. Based on these measurements, a real-time compensation algorithm is implemented, accounting for and correcting filter loading effects [8-10], a common aethalometer phenomenon. The MA200 collected data every second. Flow rate was checked with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA).

3.6 Volatile Organic Compounds

VOCs were sampled using Carbotrap 300 stainless steel thermal desorption tubes (Supelco Inc., Bellefonte, PA, USA) via a constant micro air pump (3A120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) in accordance with U.S. EPA Method TO-17 [11]. The Carbotrap 300 tubes were obtained and analyzed by ALS Simi Valley for VOCs by thermal desorption GC/MS according to U.S. EPA Method TO-17 [11]. The sampling flow rate was 208 mL/min the first test day and 204 mL/min the second day. The VOC emission factors were background corrected.

3.7 Polyaromatic Hydrocarbons

PAHs were sampled using a polyurethane foam (PUF)/XAD-2/PUF sorbent preceded by a quartz microfiber filter with sampling rate of 0.005 m^3/min via a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA). The PUF/XAD-2/PUF cartridge was purchased pre-cleaned from Supelco (USA). The glass cartridge is 2.2 cm in outer diameter (OD) and 10 cm long with 1.5 g of XAD-2 sandwiched between two 3-cm PUF plugs. The Sensidyne sample pump was calibrated daily with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg FL, USA).

The target PAH compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene) were analyzed using EPA Method TO-13A. All pre-sampling recoveries were between 70-130%. Only napthalene was detected in the ambient background sample where the napththalene concentration in the plume samples were more than four times higher than in the ambient sample.

3.8 Other Measurements

The Kolibri was also equipped with a temperature and barometric pressure sensor (BMP 180, Adafruit, New York, USA) and a global position system (GPS) sensor (Ultimate GPS Breakout V3, Adafruit, New York, USA) as summarized in Table 3-3.

Table 3-3. GPS, Pressure, and Temperature Sensors.

Target	**Sensor**	**Sampling Rate**	**Range**	**Accuracy**
Temperature	BMP 180	Every second	-25 to 85°C	±2°C
Barometric pressure	BMP 180	Every second	300-1100 hPa	0.03hPa resolution
GPS	Ultimate GPS, Breakout V3	Every second	Velocity: 515 m/s	Position: < 3m Velocity: 0.1 m/s
Relative Humidity	Adafruit DHT22	0.5 hz	0-100%	±5%

4 RESULTS AND DISCUSSION

4.1 Combustion Gases

Minimal levels of CO were observed during all tests, with MCE ranging from 0.998 to 0.999 Table 4-1. These MCEs are higher than those observed from *in situ* oil burns 0.978±0.004 [1]. Most of the time the CO levels were less than two ppm or within the noise level of the sensor (1 ppm) (Figure 4-1), although CO peaks were clearly defined.

Table 4-1. Modified combustion efficiency and PM emission factors from each test.

Burn No.	**Oil type**	**Test Condition**	**MCE**	**$PM_{2.5}$**	**TC**	**OC**	**EC**	**BC**	**UVPM**
				g/kg oil	**g/kg oil**			**g/kg oil**	
1	HOOPS	Control	0.9995	3.7	0.47	0.47	ND	0.030	0.027
2	HOOPS	Control	0.9999	19.5	2.40	2.40	ND	0.020	0.023
3	HOOPS	Control	0.9998	4.0	1.02	1.02	ND	0.017	0.017
1-3	HOOPS	Control		2.5	0.16	0.15	0.006		
4	HOOPS	Emulsified	0.9997	37.7	0.64	0.64	ND	0.020	0.069
5	HOOPS	Emulsified	0.9987	40.8	0.73	0.73	ND	0.032	0.131
6	HOOPS	Emulsified	0.9991	2.6	0.47	0.47	ND	0.041	0.080
4-6	HOOPS	Emulsified		25.5	0.23	0.23	ND		
7	Middle Weight	Low Flow	0.9982	7.4	0.73	0.20	0.53	0.179	0.244
8	Middle Weight	Low Flow	0.9979	4.9	0.25	0.03	0.21	0.341	0.360
9	Middle Weight	Low Flow	0.9994	2.9	0.56	0.13	0.43	0.180	0.630
7-9	Middle Weight	Low Flow		6.1	1.31	0.31	1.00		
10	Middle Weight	High Flow	0.9996	19.8	0.17	0.17	ND	0.073	0.083
11	Middle Weight	High Flow	0.9989	24.1	0.31	0.05	0.26	0.175	0.195
12	Middle Weight	High Flow	0.9996	29.9	0.47	0.15	0.33	0.210	0.250
10-12	Middle Weight	High Flow		13.9	0.37	ND	0.37		

ND = not detected. Control = Full Max Flow. High Flow = Full Max Flow.

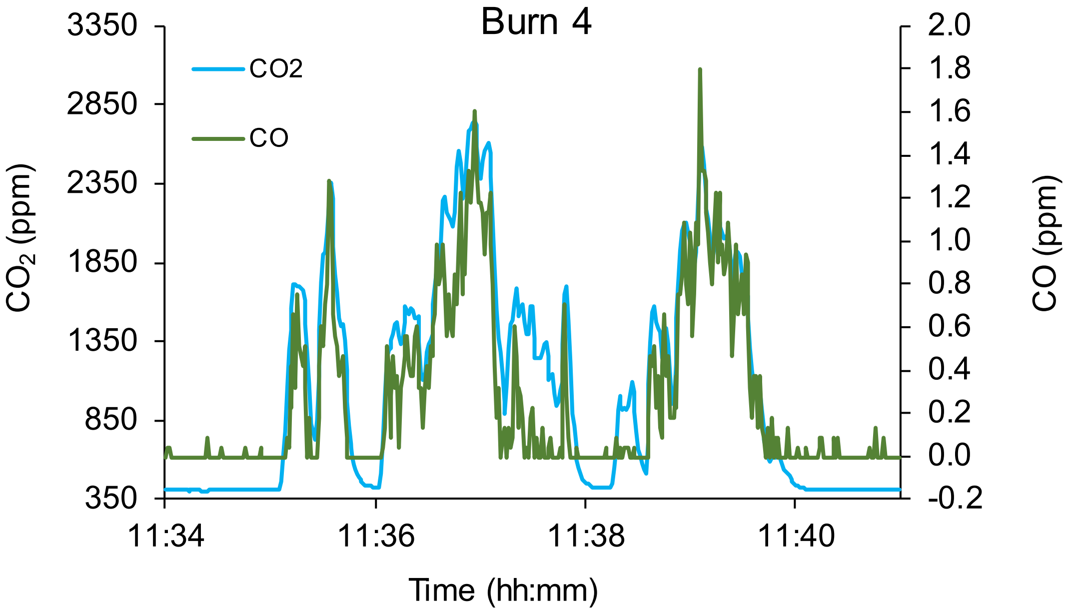

Figure 4-1. CO_2 and CO trace from Burn No. 4 with emulsified HOOPS.

4.2 $PM_{2.5}$

Lower $PM_{2.5}$ emission factors were found from HOOPS-Full Max and Middle Weight-Full Max than HOOPS Emulsified and Middle Weight-Low Flow (Table 4-1 and Figure 4-2). The emission factors ranged from 2.5 to 41 g/kg oil, which can be compared to simulated *in situ* oil burns with emission factors of 58±14 g/kg oil [1] and actual at-sea *in situ* oil burns during the Deepwater Horizon disaster of 74 g/kg oil [12].

One replicate sample was excluded when the average from HOOPS, Burn No. 2 was calculated, as the sample volume size was not large enough to obtain a true emission factor value. This was confirmed by the emission factor derived from the composite sample. One replicate sample was excluded from HOOPSs Emulsified, Burn No. 6, as the emission factor was in the same range as HOOPS non-emulsified tests. This lower emission factor was due to the oil on the bottom of the tank not being emulsified. The HOOPS emulsified composite $PM_{2.5}$ emission factor (Burn No 4-6, Table 4-1) was lower than the two replicate samples which most probably was due to the lower emission found in Burn No. 3. The run-weighted relative standard deviation for the remaining ten $PM_{2.5}$ samples and the composite samples ranged from 22 to 35 %. This value reflects both instrument and burner operation variation. The higher $PM_{2.5}$ emission factor for the emulsified HOOPS is likely due to the lower flame temperature– the water vapor would have displaced oxygen, acted as thermodynamic sink, and required additional evaporative energy. The lower temperature would have decreased the soot consumption reaction rates and left more soot in the plume.

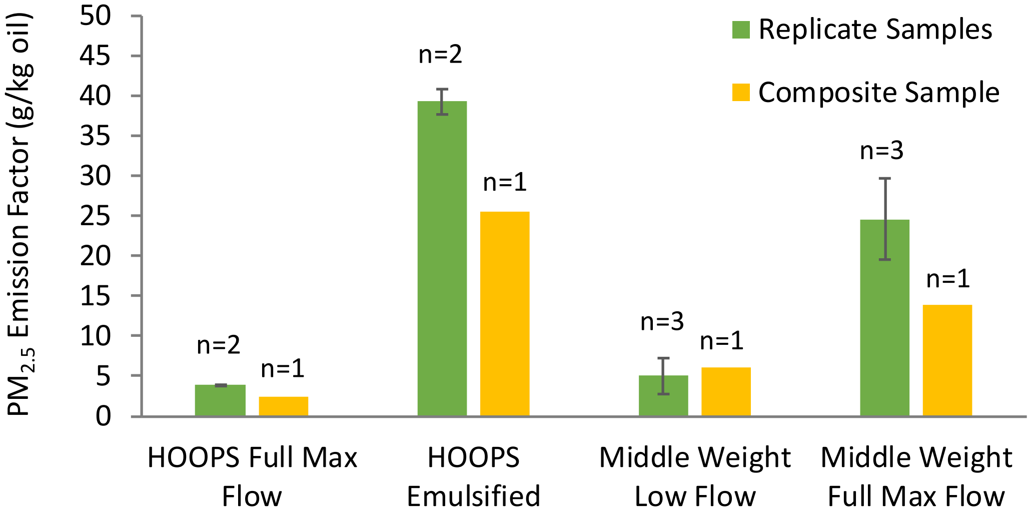

Figure 4-2. PM$_{2.5}$ emission factors. Error bars equal 1 Stand. Dev. if n =3 and range of data if n = 2.

4.3 Total Carbon, Elemental Carbon, and Organic Carbon

The TC, OC, and EC emissions were comparatively low, ranging from non-detect to 1.31 g/kg oil (Table 4-1). Most of the TC emissions from burning HOOPS were made up of OC which is the opposite from in *situ oil* burns where TC contains 92% EC [1]. TC emissions from MW contained on average 78% EC. The particulate carbon (TC) was 0.02-0.15% of the total particulate plus gas phase carbon which can be compared to 6.3% in the plumes from the gulf oil spill *in situ* oil burns [12].

One of the TC/OC/EC replicate samples was excluded when calculating the averages from the HOOPS Full Max Flow, Burn No. 2, as the sample volume size was not large enough to obtain a true emission factor value, as confirmed by comparison with the emission factor derived from the composite sample. The sample from HOOPS Emulsified, Burn No. 6, was also excluded on the same basis as the oil on the bottom of the tank was not emulsified.

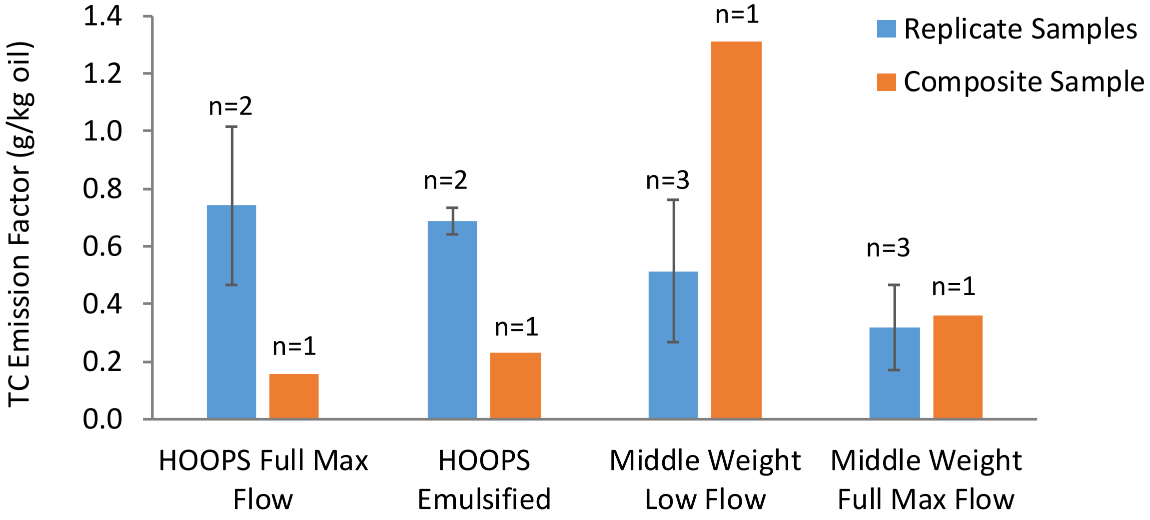

Figure 4-3. TC emission factors. Error bars equal 1 Stand. Dev. if n =3 and range of data if n = 2.

4.4 Black Carbon and UVPM

BC and UVPM were continuously measured in the plume. The MW oil type resulted in higher BC emission factors than HOOPS (Table 4-1 and Figure 4-4), which may be due to the different viscosities of the two oil types. An increase in emission factor with subsequent burns was found for HOOPS Emulsified and MW Max Flow (Figure 4-5). This may be attributed to changes in the burner configuration/operation or just by coincidence. The values here ranged from 0.017 to 0.36 g/kg oil which can be compared with values for open air pan burns of 53 g/kg oil [1].

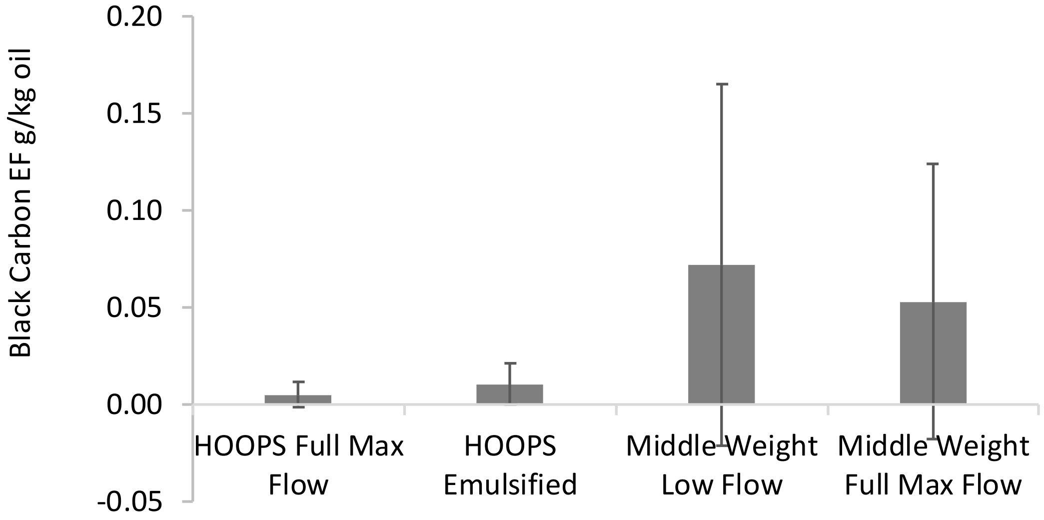

Figure 4-4. Black carbon emission factors. Average value from three burns. Error bar represents one standard deviation.

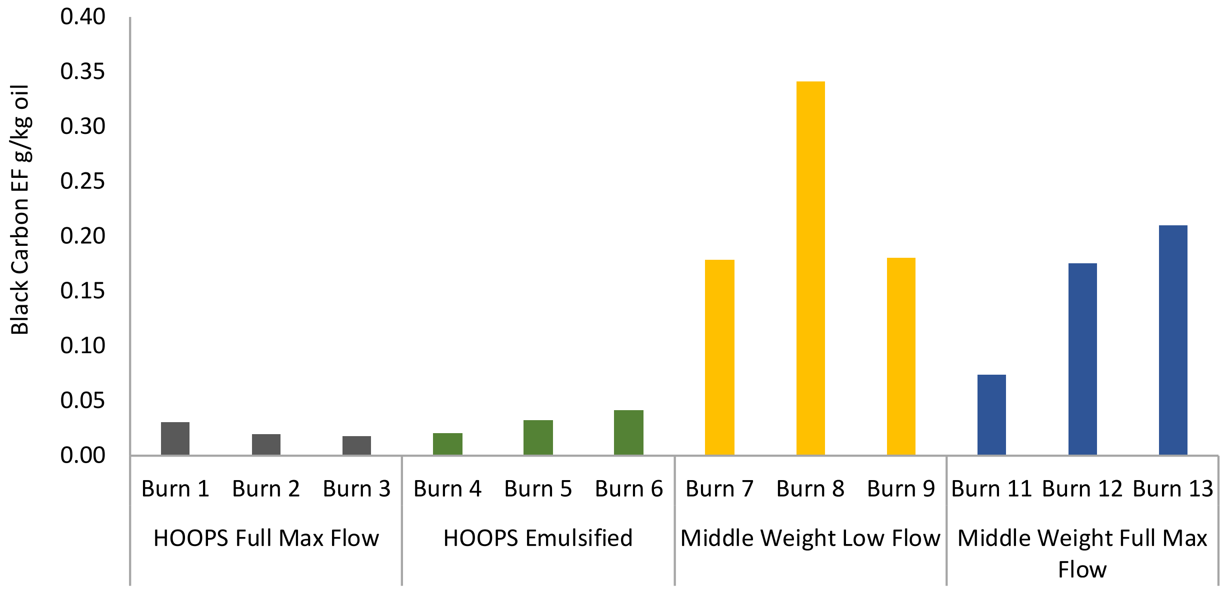

Figure 4-5. Black carbon emission factor from each burn.

4.5 Volatile Organic Compounds

VOC samples were composites of three runs, resulting in only a single VOC sample from each oil type and configuration. These run composites were done to promote adequate detection of VOC compounds. Approximately 60% of the 61 analyzed VOCs were detected (Table 4-2). The benzene values were low, ranging from 3.9 to 10.9 mg/kg oil (Figure 4-6) and were up to 100 times lower than from simulated *in situ* oil burns [1].

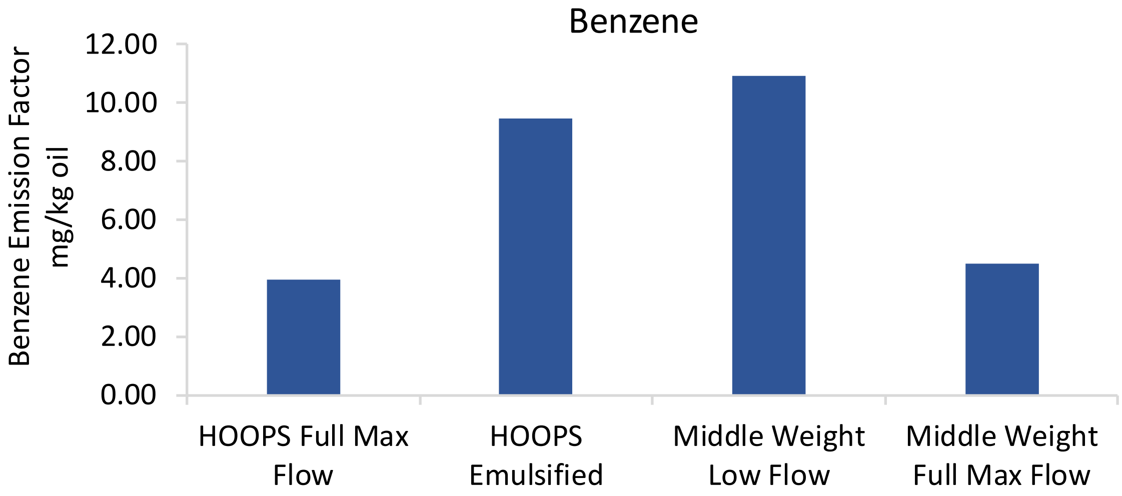

Figure 4-6. Benzene emission factors from each oil type and test configuration. Note: Single, 3-run composite samples only.

Surprisingly high emissions of methylene chloride were detected in the plume (also acetone and acetonitrile) (Figure 4-7). Methylene chloride is not naturally occuring in crude oil, but organic chlorides are used for cleaning pipelines and tanks. Methylene chloride has previously been found from *in situ* oil burns, but the emissions found in this study are 50 to 500 times higher than found in our other studies [13]. The cause of these high levels is not known.

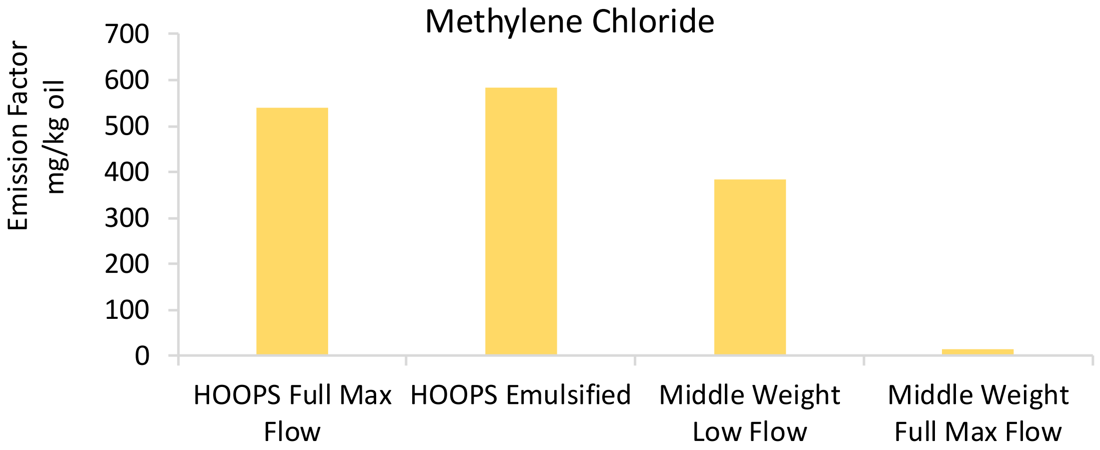

Figure 4-7. Methylene chloride emission factors from each oil type and test configuration. Note: Single samples only.

Table 4-2. VOC emission factors.

	HOOPS Full Max Flow		**HOOPS Emulsified**		**Middle Weight Low Flow**		**Middle Weight Full Max Flow**	
	EF	Method detection limit	EF	Method detection limit	EF	Method detection limit	EF	Method detection limit
VOC	mg/kg oil							
Dichlorodifluoromethane (CFC 12)	ND	0.12	1.21	0.08	8.58	0.07	0.89	0.04
Chloromethane	5.05	0.26	5.65	0.17	3.96	0.15	1.11	0.09
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	ND	0.16	ND	0.10	0.31	0.09	0.00	0.05
Vinyl Chloride	ND	0.14	ND	0.09	ND	0.08	ND	0.05
1,3-Butadiene	ND	0.27	1.08	0.18	2.86	0.15	0.25	0.09
Chloroethane	1.55	0.19	1.46	0.13	ND	0.11	ND	0.07
Ethanol	57.96	0.71	18.19	0.46	17.93	0.40	0.74	0.24
Acetonitrile	755.01	0.22	570.39	0.15	659.69	0.13	9.78	0.08
Acetone	137.12	1.85	224.66	1.21	117.58	1.05	8.51	0.62
Trichlorofluoromethane	ND	0.08	1.42	0.05	4.47	0.04	0.65	0.03
2-Propanol (Isopropyl Alcohol)	6.80	0.51	7.62	0.33	0.88	0.29	0.32	0.17
1,1-Dichloroethene	1.17	0.17	0.46	0.11	4.46	0.09	ND	0.06
Methylene Chloride	540.60	0.13	582.75	0.08	384.07	0.07	14.50	0.04
Trichlorotrifluoroethane	ND	0.14	0.03	0.09	1.46	0.08	0.08	0.05
Carbon Disulfide	ND	0.78	0.95	0.51	1.49	0.44	ND	0.26
trans-1,2-Dichloroethene	1.07	0.12	0.48	0.08	0.47	0.07	ND	0.04
1,1-Dichloroethane	ND	0.06	ND	0.04	0.05	0.03	ND	0.02
Methyl tert-Butyl Ether	ND	0.07	0.07	0.04	ND	0.04	ND	0.02
2-Butanone (MEK)	3.86	0.19	4.61	0.13	1.50	0.11	0.28	0.07
cis-1,2-Dichloroethene	ND	0.09	ND	0.06	ND	0.05	ND	0.03
n-Hexane	18.65	0.12	13.16	0.08	8.63	0.07	3.46	0.04
Chloroform	1.18	0.11	1.59	0.07	2.97	0.06	0.08	0.04
Tetrahydrofuran (THF)	1.36	0.24	1.97	0.16	1.43	0.14	0.23	0.08

1,2-Dichloroethane	ND	0.15	0.30	0.10	0.35	0.08	0.10	0.05
1,1,1-Trichloroethane	ND	0.12	ND	0.08	ND	0.07	ND	0.04
Benzene	3.94	0.91	9.47	0.60	10.93	0.52	4.47	0.31
Carbon Tetrachloride	ND	0.10	0.20	0.06	1.24	0.05	0.16	0.03
Cyclohexane	1.09	0.17	1.64	0.11	1.80	0.10	1.13	0.06
1,2-Dichloropropane	ND	0.19	ND	0.13	0.14	0.11	ND	0.07
Bromodichloromethane	0.20	0.09	ND	0.06	ND	0.05	ND	0.03
Trichloroethene	0.49	0.13	0.51	0.08	0.22	0.07	0.01	0.04
1,4-Dioxane	2.06	0.19	2.90	0.13	24.59	0.11	1.64	0.07
2,2,4-Trimethylpentane (Isooctane)	0.43	0.13	0.31	0.08	0.48	0.07	0.66	0.04
n-Heptane	5.16	0.14	5.42	0.09	5.74	0.08	3.04	0.05
cis-1,3-Dichloropropene	ND	0.11	ND	0.07	ND	0.06	ND	0.04
4-Methyl-2-pentanone	0.71	0.16	0.47	0.10	0.44	0.09	ND	0.05
trans-1,3-Dichloropropene	ND	0.11	ND	0.07	ND	0.06	ND	0.04
1,1,2-Trichloroethane	ND	0.19	ND	0.13	ND	0.11	ND	0.07
Toluene	73.50	0.46	44.23	0.30	39.41	0.26	12.56	0.15
2-Hexanone	ND	0.22	ND	0.15	ND	0.13	ND	0.08
Dibromochloromethane	ND	0.07	ND	0.04	0.08	0.04	ND	0.02
1,2-Dibromoethane	ND	0.10	ND	0.06	ND	0.05	ND	0.03
n-Octane	2.12	0.20	3.77	0.13	3.32	0.12	2.13	0.07
Tetrachloroethene	0.67	0.12	0.48	0.08	1.71	0.07	0.22	0.04
Chlorobenzene	0.10	0.08	0.19	0.05	ND	0.05	ND	0.03
Ethylbenzene	1.73	0.11	1.48	0.07	1.55	0.06	1.04	0.04
m,p-Xylenes	3.86	0.17	3.55	0.11	3.94	0.09	3.56	0.06
Bromoform	ND	0.14	ND	0.09	0.14	0.08	ND	0.05
Styrene	14.14	0.08	9.33	0.05	4.94	0.04	0.04	0.03
o-Xylene	1.26	0.07	1.31	0.05	1.63	0.04	1.38	0.02
1,1,2,2-Tetrachloroethane	ND	0.14	ND	0.09	ND	0.08	ND	0.05
Cumene	0.31	0.27	0.25	0.18	0.25	0.15	0.13	0.09
1,3,5-Trimethylbenzene	0.39	0.26	0.41	0.17	0.45	0.15	0.43	0.09
1,2,4-Trimethylbenzene	0.45	0.14	1.32	0.09	1.68	0.08	1.44	0.05

1,3-Dichlorobenzene	ND	0.15	ND	0.10	ND	0.08	ND	0.05
1,4-Dichlorobenzene	ND	0.14	0.02	0.09	ND	0.08	ND	0.05
1,2-Dichlorobenzene	ND	0.17	ND	0.11	ND	0.09	ND	0.06
1,2-Dibromo-3-chloropropane	ND	0.20	ND	0.13	ND	0.12	ND	0.07
1,2,4-Trichlorobenzene	ND	0.40	ND	0.26	ND	0.23	ND	0.13
Naphthalene	0.36	0.36	1.47	0.23	1.60	0.20	0.52	0.12
Hexachlorobutadiene	ND	0.29	ND	0.19	ND	0.17	ND	0.10

4.6 Polyaromatic Hydrocarbons

Only three of the 16 EPA PAHs were detected in the plume samples (Table 4-3). The sample collected from HOOPS Full Max wax excluded due to pump problems during sampling. However, only napthalene was detected in this sample -- a PAH that was also analyzed for in the VOC sample. Due to the few PAHs detected and lack of replicate samples, no definite comparison can be made. All collected samples had very low napthalene emission factors, 2.0-4.9 mg/kg oil consumed, compared to *in-situ* oil burns, 271.38 mg/kg oil [13].

Table 4-3. PAH emission factors.

PAHs	**HOOPS Emulsified**[1]	**Middle Weight Low Flow**[2]	**Middle Weight Full Max Flow**[3]
		mg/kg oil consumed	
Naphthalene	4.89	3.79	2.04
Acenaphthylene	ND	ND	ND
Acenaphthene	ND	ND	ND
Fluorene	ND	0.44	0.21
Phenanthrene	0.51	0.79	0.38
Anthracene	ND	ND	ND
Fluoranthene	ND	ND	ND
Pyrene	ND	ND	ND
Benzo(a)anthracene	ND	ND	ND
Chrysene	ND	ND	ND
Benzo(b)fluoranthene	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND
Indeno(1,2,3-cd)pyrene	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND
Benzo(ghi)perylene	ND	ND	ND
SUM 16-EPA PAH	**5.40**	**5.03**	**2.64**

[1] Detection limit 0.50 mg/kg oil consumed.

[2] Detection limit 0.43 mg/kg oil consumed.

[3] Detection limit 0.21 mg/kg oil consumed.

5 CONCLUSIONS

ISB with two oil types, non-emulsified and emulsified, and at two feed rates, show considerable improvement in $PM_{2.5}$ emissions and combustion efficiency with this burner compared to previous similar measurements of ISB. $PM_{2.5}$ emission factors from oil burn simulations in water-filled pans and from the actual Deepwater Horizon measurements in the Gulf of Mexico were over four times higher than the run-weighted average values obtained here, indicating significant improvement. Emulsified oil yielded $PM_{2.5}$ values that were over five times higher than the non-emulsified oil. CO emission factor values were 2 ppm or less, much lower than observed previously with *in situ* pan burn simulations (58 ppm). The low CO values resulted in high MCEs ($\geq$0.998).

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