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

Heat Transfer Technology: Flame Refluxer

Final Report

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EXECUTIVE SUMMARY

In situ burning of oil on water has been commonly used as a method of minimizing the environmental impacts of oil spill disasters. The spilled oil is typically collected or herded by towed booms until sufficiently concentrated to sustain combustion. An undesirable result of the oil burns is the production of copious black emissions. In an effort to minimize these emissions, technologies have been investigated to promote combustion of the oil. A recent study by Worcester Polytechnic Institute (WPI) examined the effect of enhancing the rate of heat transfer from the flame to the oil by using a porous, copper metal wool within the oil layer and conical cones extending above the oil into the flame zone.

Testing took place at the U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory (CRREL) located in Hanover, New Hampshire. The emission characterization from the different technologies was undertaken by U.S. EPA's Office of Research and Development (ORD).

CRREL's 47ft × 8ft × 8ft (14.3m × 2.4m × 2.4m) wave tank was used to simulate *in situ* oil burns using an initial oil mass of ~495 lb (225 kg). A test program exploring the three heat transfer structures including with or without waves was undertaken resulting in 11 burns conducted during a one-week campaign. ORD used their in-house developed, battery-powered, and remotely controlled sampling equipment called the "Flyer" to measure CO_2, CO, $PM_{2.5}$ (particulate matter of aerodynamic diameter 2.5 µm or less), black carbon (BC), total carbon/organic carbon/elemental carbon (TC/OC/EC), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/PCDF) from the oil burn plumes. PCDDs/PCDFs were collected from a single burn for the Baseline sample and a composite of multiple burns for the Refluxer sample resulting in two single samples: Baseline and Refluxer. The Flyer sampling instrumentation was mounted on an aluminum skid and suspended from a crane into the plume of the burning oil. The sampling instrumentation was maneuvered into the plume with the guidance from the Flyer's operator who monitored real-time temperature and CO_2 levels.

An increase in oil mass loss percentage with modified combustion efficiency (MCE, $CO_2/(CO_2 + CO)$) was found indicating that better combustion results in a more efficient oil burn. The $PM_{2.5}$ emission factors showed a clear relation to MCE, showing that higher MCE values lead to lower $PM_{2.5}$ emission factors. The lowest $PM_{2.5}$ emission factors were associated with the Grid structure particularly in the presence of waves. The benzene emission factors were found to decrease with increased MCE where the tests including waves had the lowest emission factors. The TC, BC and PAH emission factors showed similar ranges as previous oil burn studies. Vinyl chloride was detected in the plumes from the first six burns which is likely due to the polyvinyl chloride (PVC)-coated polyester fabric on the boom burning off. The burning of the PVC-coated fabric may also result in the higher PCDD/PCDF emission factors found in both the Baseline and

Refluxer samples compared to previous studies. Incineration of PVC is well known to form PCDD/PCDF. The PCDD/PCDF emission factors for the “Refluxer” sample were slightly higher than the “Baseline” sample, 14.9 ng TEQ/kg initial oil versus 10.5 ng TEQ/kg initial oil, suggesting that no enhanced PCDD/PCDF formation occurred due to the copper (Cu) material of the Refluxers. Among the three technologies the Grid heat transfer technology used with waves showed the overall highest MCE and oil mass loss percentage combined with lowest $PM_{2.5}$ emission factors.

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ACRONYMS

BC	Black carbon
BSEE	Bureau of Safety and Environmental Enforcement
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CRREL	Cold Regions Research and Engineering Laboratory
DCM	Dichloromethane
DNPH	2,4-Dinitrophenylhydrazine
EC	Elemental Carbon
EPA	Environmental Protection Agency
GC	Gas Chromatography
HPLC	High-Pressure Liquid Chromatography
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry
ISB	In Situ oil burns
MCE	Modified Combustion Efficiency
MS	Mass spectrometry
ND	Not detected
NDIR	Non-dispersive infrared
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NS	Not sampled
OC	Organic Carbon
OD	Outer diameter
ORD	Office of Research and Development
PAHs	Polycyclic aromatic hydrocarbons
PCDD/PCDF	Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans
PM	Particulate matter
$PM_{2.5}$	Particulate matter, with aerodynamic diameter equal to or less than 2.5 µm
PUF	Polyurethane foam plug
TC	Total Carbon
TEQ	Toxic equivalent
TOA	Thermal-optical analysis
TSP	Total suspended particles
UDRI	University of Dayton Research Institute
VOCs	Volatile Organic Compounds
WPI	Worcester Polytechnic Institute

1 INTRODUCTION

The objective of this effort was to characterize emissions and residues from a one week campaign of oil burns on water at U.S. Army Corps of Engineers, Cold Regions Research Engineering Laboratory (CRREL). The CRREL tests simulated conditions of at-sea burning to investigate development of technologies related to *in situ* oil burns (ISB). The technology tested was developed by Worcester Polytechnic Institute (WPI) through funding provided by the U.S. Department of the Interior/Bureau of Safety and Environmental Enforcement (DOI/BSEE). DOE/BSEE entered into an agreement with U.S. EPA to sample the emissions and discern potential distinctions from variants of WPI's Flame Refluxer (FR) technology. This technology enhances the rate of heat transfer from the flame to the oil by using a porous, copper metal wool "blanket" within the oil layer and conical cones extending above the oil into the flame zone [1]. Their experiments showed that the burning rate of oil slicks on water increased by a factor of six due to enhanced heat transfer to the oil slick from the flame. Reduced post-burn residue on the water was also observed. That effect on emissions required further study and was the objective of this effort.

2 MATERIALS AND METHODS

2.1 Test Location and Set-up

Testing took place at CRREL located in Hanover, New Hampshire. The facility used for the testing was the CRREL in-ground tank shown in the background of Figure 2-1. The interior dimensions of the wave tank are 47 ft × 8 ft × 8 ft (14.3 m × 2.4 m × 2.4 m). A tapered "beach" end opposite a wave generator absorbs the wave energy. The tank water depth is 6.5 ft, resulting in an operating capacity of about 16,700 gallons (63.2 m^3). To simulate at-sea ISB, approximately 495 lb (225 kg, or 270 L) crude oil was floated on the surface of the water-filled tank and ignited by CRREL. For each burn test, members of CRREL prepared the area and the burn tank with the test oil and then began the burn. CRREL handled oil storage, transport, ignition, and post-residue-collection cleanups. Tests were conducted from September 28 to October 2, 2020 with ambient temperatures ranging from 63ºF to 79ºF (17ºC to 26ºC).


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Figure 2-1. U.S. Army Corps of Engineers wave tank.

The mass of oil added and residue recovered was measured by CRREL to allow oil burn removal efficiency to be calculated. The burn plume was sampled using an EPA instrument system suspended from a crane and maneuvered into the plume as seen in Figure 2-1. Slight movements of the crane boom angle, rotational position, and cable length kept the instruments in the plume to accommodate wind shifts. The sampling system was mounted on an aluminum skid as shown in Figure 2-2.

05.15.2018 10:00

Figure 2-2. U.S. EPA's emission instrument system (the "Flyer") mounted on an aluminum skid.

2.2 Test Matrix

A test program exploring the three following heat transfer structures was undertaken (Figure 2-3):

- Ruffled
- Grid
- Bimetal

The three structures were supported at the oil/water/air interface by hemispherical floats underneath the heat flux grid. Unless otherwise indicated, two sections were used for each burn. The text matrix is shown in Table 2-1.

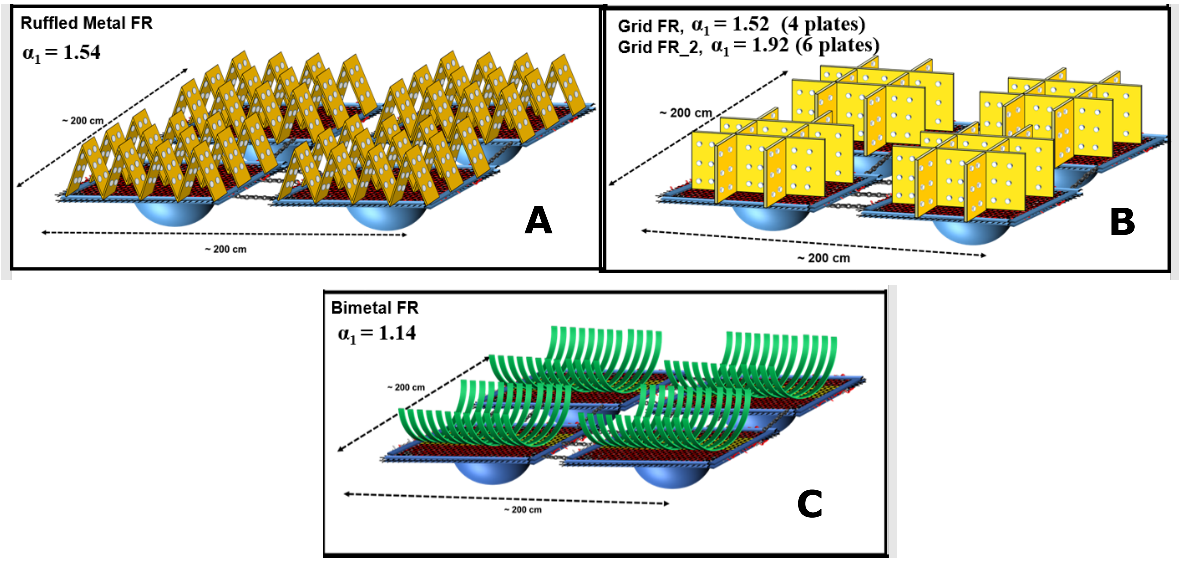

Figure 2-3. Heat transfer media and FR structures tested A) Ruffled, B) Grid, and C) Bimetal.

Table 2-1. Test Matrix.

Burn Number	Date	Test Condition	Mass initial oil[a] (lb)	Mass initial oil[a] (kg)
1	09/28/2020	Baseline #1	495	225
2	09/28/2020	Ruffled	486	221
3	09/29/2020	Grid[b]	495	225
4	09/29/2020	Bimetal	491	223
5	09/29/2020	Grid	497	226
6	10/01/2020	Grid Waves – 7 cm	497	226
7	10/01/2020	Grid Waves – 14 cm	495	225

Burn Number	Date	Test Condition	Mass initial oil[a] (lb)	Mass initial oil[a] (kg)
8	10/01/2020	Grid Solo Waves – 7 cm	504	229
9	10/01/2020	Bimetal Waves[c]	499	227
10	10/02/2020	Bimetal Waves	499	227
11	10/02/2020	Baseline #2	502	228

[a] Measured by CRREL. [b]One of the two grid sections toppled over. [c]Only one grid section used.

2.3 Target Emission Compounds

Target compounds include carbon monoxide (CO), carbon dioxide (CO_2), particulate matter less than 2.5 µm ($PM_{2.5}$), black carbon (BC), Elemental carbon/organic carbon and total carbon (EC/OC/TC), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) including carbonyls, and polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs). Targeted emissions and their sampling frequency are listed in Table 2-2. The number of batch samples collected for each test configuration is shown in Table 2-3.

Table 2-2. Oil Burn Emission Targets

Analyte	Method	Frequency
CO_2	LiCOR-820, NDIR	Continuous, 1Hz
CO	Electrochemical cell	Continuous, 1Hz
$PM_{2.5}$	Impactor/filter/gravimetric	Batch
PCDD/PCDF	Quartz filter/PUF, HRMS	Batch
PAH	Quartz filter/PUF/XAD/PUF, HRMS	Batch
VOCs	SUMMA cannister	Batch
BC	Aethalometer	Continuous, 1Hz
EC/OC/TC	Quartz filter	Batch
Carbonyls	DNPH cartridges	Batch

Table 2-3. Number of batch samples collected in each test configuration.

Burn		No. of collected samples					
Number	Test Condition	$PM_{2.5}$	EC/OC/TC	PAH	PCDD/ PCDF	VOC	Carbonyls
1	Baseline #1	2	2	1	1	1	1
2	Ruffled	2	2	1	1	1	1
3	Grid[a]	2	2	1		1	1
4	Bimetal	2	2	1		1	1
5	Grid	2	2	1		1	1
6	Grid Waves	2	2	1		1	1
7	Grid Waves	2	2	1		1	1
8	Grid Solo Waves	2	2	1		1	1
9	Bimetal Waves[b]	2	2	0		1	1
10	Bimetal Waves	2	2	1		1	1
11	Baseline #2	2	2	1		1	1
	Ambient	1	1	1	0	1	1
	Sum	**23**	**23**	**11**	**2**	**12**	**12**

[a] One of the two grid sections toppled over. [b] Only one grid section used.

2.4 Calculations

2.4.1 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

2.4.2 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.

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

Where:

$Emission\ Factor_{consumed}$ = The Emission Factor for target analyte *i* (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

2.4.3 Modified Combustion Efficiency

The Modified Combustion Efficiency (MCE) was used to calculate how well the oil burned in terms of plume emissions. Two approaches were used to determine the carbon in the plume. One approach includes gas phase (CO_2 and CO) MCE (Equation 3) and the other includes Total Carbon MCE_T (Equation 4), where the latter accounts for unburnt carbon in the particulate matter.

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

$$MCE_T = \frac{CO_2}{CO_2+CO+Total\ Carbon} \qquad Equation\ 4$$

Where:

MCE = modified combustion efficiency only including gas phase
MCE_T = modified combustion efficiency including TC
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)

3 MEASUREMENT AND QUALITY ASSURANCE PROCEDURES

3.1 CO_2 measurements

The CO_2 was continuously measured using a non-dispersive infrared (NDIR) instrument (LI-820 model, LI-COR Biosciences, Lincoln, USA). These units are configured with a 14 cm optical bench, giving it an analytical range of 0 to 20,000 ppm with an accuracy specification of less than 3% of reading. The LI-820 calibration range was set to 400 to 8,531 ppm and was calibrated for CO_2 on a daily basis in accordance with EPA Method 3A [2]. Concentration was recorded on the onboard computer using the FlyerDAQ program, a LabView generated data acquisition and control program. All gas cylinders used for calibration were certified by the suppliers that they are traceable to National Institute of Standards and Technology (NIST) standards.

The daily CO_2 system drift for the two LI-COR units were less than 1% for calibration gases 1,500, 4,000 and 8,531 ppm which is within the ±5% acceptance criteria of the sensor (Table 3-1). The drift at 400 ppm was either less than the ±5% acceptance criteria of the sensor or slightly higher.

Table 3-1. CO_2 System drift.

Calibration gas concentration	**LI-COR**		**LI-COR**		**LI-COR**		**LI-COR**	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
	09/28/2020		**09/29/2020**		**10/01/2020**		**10/02/2020**	
400 ppm	5.5%	6.2%	5.1%	5.05%	4.78%	3.39%	4.49%	5.74%
1,500 ppm	0.31%	0.37%	0.21%	0.031%	0.98%	0.83%	1.14%	1.18%
4,000 ppm	0.096%	0.13%	0.16%	0.289%	0.38%	0.309%	1.75%	1.75%
8,531 ppm	0.012%	0.065%	0.11%	0.18%	0.23%	0.11%	0.10%	0.09%

3.2 CO measurements

The CO sensor (e2V EC4-500-CO) was an electrochemical gas sensor (SGX Sensortech, Essex, 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 1 to 500 ppm with resolution of 1 ppm. The temperature and relative humidity (RH) operating range was -20 to +50°C and 15 to 90% RH, respectively. The response time is less than 30 seconds. Output is non-linear from 0 to 500 ppm. The sensor was calibrated for CO on a daily basis in accordance with U.S. EPA Method 3A [2].

All gas cylinders used for calibration were certified by the suppliers that they are traceable to NIST standards. The daily CO system drift for both sensors were less than 4.5% which is within the ±5% acceptance criteria of the sensor, with the exception for sensor #1 at 100 ppm

(09/29/2020) (Table 3-2). This drift had minimal impact on the results as the measured CO concentration in the plumes from the two burns conducted 09/29/2020 were mostly less than 50 ppm.

Table 3-2. CO System drift.

Calibration gas concentration	**e2V Sensor**		**e2V Sensor**		**e2V Sensor**		**e2V Sensor**	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
	09/28/2020		**09/29/2020**		**10/01/2020**		**10/02/2020**	
0 ppm	0.01*	0.01*	0.01*	0.01*	0.02*	0.01*	0.01*	0.01*
25 ppm	1.68%	0.19%	1.03%	0.41%	1.47%	1.35%	2.58%	1.94%
50 ppm	0.73%	1.87%	4.03%	2.15%	0.085%	0.12%	4.47%	3.25%
100 ppm	0.97%	4.52%	8.92%	4.47%	1.53%	2.47%	4.03%	2.67%

* Absolute difference in ppm, which is within the noise level of the sensor.

3.3 $PM_{2.5}$

$PM_{2.5}$ was sampled with SKC impactors using 47 mm tared Teflon™ filters with a pore size of 2.0 µm via a Leland Legacy sample pump (SKC Inc., USA) with a constant airflow of 10 L/min. PM was measured gravimetrically following the procedures described in 40 CFR Part 50 [3]. Particles larger than 2.5 µm in the $PM_{2.5}$ impactor were collected on an oiled 37 mm impaction disc mounted on the top of the first filter cassette. The Teflon™ filters were pre- and post-weight by Chester LabNet. The Leland Legacy Sample pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA). The post weighing of the filters was completed within thirty days of sampling completion.

3.4 Black Carbon, Elemental Carbon, Organic Carbon, and Total Carbon

BC was measured with an MA200 microaethalometer (AethLabs, USA). The microaethalometer is a small, portable, hand-held instrument capable of measuring BC concentration, the instrument measures light attenuation of particles deposited on a filter at five wavelengths (375, 470, 528, 625, 880 nm). The attenuation at the different wavelengths can be used to quantify light-absorbing species other than black carbon present in the sample (e.g., light-absorbing organic particulate matter), which can indicate differing sources of PM. The MA200 was sampling at increments of 1 seconds from 0 to 1 mg BC/m^3. The optical response of these instruments is factory calibrated. The pump flow was calibrated before leaving for the field via a Gilibrator Air Flow Calibration System (Sensidyne LP, USA). The MA200 is equipped with a filter cartridge that can advance to a new filter spot after PM loads the previous spot to a set attenuation (100).

EC/OC/TC was sampled with a SKC $PM_{2.5}$ personal modular impactor using 37 mm quartz filter via a Gilian 5000 sample pump (Sensidyne LP, USA) with a constant airflow of 3 L/min. Particles larger than 2.5 µm in the $PM_{2.5}$ impactor were collected on an oiled 37 mm impaction disc mounted on the top of the first filter cassette. The Gilian 5000 sample pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA). The EC/OC/TC was analyzed via a modified thermal-optical analysis (TOA) using NIOSH Method 5040 [4] and Khan et al. [5]. The EC/OC/TC was analyzed within twenty days of sampling completion. The laboratory was unable to do the EC-OC split due to high EC levels in each of the samples, thus only TC results are reported.

3.5 Volatile Organic Compounds and Carbonyls

SUMMA® canisters were used for collection of VOCs via EPA Method TO-15 [6]. Sampling for VOCs was accomplished using laboratory-supplied 6 L SUMMA® equipped with a manual valve, metal filter (frit), pressure gauge, pressure transducer, and an electronic solenoid valve. The canisters were analyzed by ALS, NY. The canisters were also used for analysis of CO, CO_2, and methane (CH_4) by gas chromatography (GC)/ flame ionization detector (FID) according to Method 25C [7]. Method 25 also specifies gas sample collection by evacuated cylinder determines the SUMMA®'s sampling rate.

Carbonyls were sampled with 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Sigma-Aldrich, PN 505323) using EPA Method TO-11A [8]. The cartridge flow was controlled by a calibrated a pump downstream of the cartridge at a sampling flow rate of 2 L/min. One background sample was taken. DNPH cartridges were extracted with carbonyl-free acetonitrile and analyzed by high-pressure liquid chromatography (HPLC) on an Agilent 1100 HPLC with a diode array detector in accordance with EPA Method TO-11A [8]. The samples were extracted and analyzed seven and eight weeks after sampling completion which is outside the two and four weeks hold time of the method, respectively. Due to high loading on the DNPH cartridge considerable coelution interferences occurred on the chromatogram as such only formaldehyde and acetaldehyde are reported.

The VOCs and carbonyl emission factors are background corrected.

3.6 Polyaromatic Hydrocarbons

PAHs were sampled using a polyurethane foam (PUF)/XAD-2/PUF sorbent preceded by a quartz microfiber filter with a sampling rate of 5 L/min (Leland Legacy pump (SKC Inc., Eighty Four, PA, USA)). The PUF/XAD-2/PUF cartridge was purchased pre-cleaned from Supelco (USA). The glass cartridge was 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 Leland Legacy sample pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg FL, USA). The target PAH compounds were the 16-EPA PAHs : 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-c,d)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene.

The PAHs were analyzed by Enthalpy Analytical (Durham, NC) using the analytical methods as described in EPA Method TO-13A [9]. Modifications to the method included use of a pre-sampling, pre-extraction, and pre-analysis spike. Labeled standards for PAHs were added to the XAD-2 trap before the sample was collected. Some of the sorbent traps had been spiked by EPA. The detection limit was 20 ng/sample. Surrogate recoveries were measured relative to the internal standards and are a measure of the sampling sorbent collection efficiency.

Not all samples met the 60-120% surrogate standards recovery criteria, these surrogates were those spiked by EPA suggesting that those surrogates had been spiked with higher concentrations than specified by EPA. However, the surrogates added by Enthalpy were within the 60-120% surrogate standards recovery criteria which concludes that the collection efficiency were equally good for all collected samples. All other surrogates and internal spikes were within the 60-120% criteria of the method for all samples. A one-hour background sample for ambient PAH was collected for analysis. The PAH concentrations in the collected plumes samples were more than 300 times higher than the ambient background sample's concentrations.

3.7 Polychlorinated Dibenzodioxins and Furans

PCDDs/PCDFs were collected onto a quartz microfiber filter (20.3×25.4 cm) and PUF plug using a low voltage Windjammer brushless direct current blower (AMETEK Inc., Berwyn, USA) with a nominal sampling rate of 0.65 m^3/min following EPA Method TO-9A [10]. The PUF was cleaned by the EPA laboratory before use by solvent extraction with dichloromethane and dried with flowing nitrogen to minimize contamination of the media with the target analytes and remove unreacted monomers from the sorbent.

PCDDs/PCDFs samples were analyzed by Enthalpy Analytical (Wilmington, NC) following EPA Method TO-9A [10]. Concentrations were determined using Agilent Technologies Model #6890 high resolution gas chromatography/Waters high resolution mass spectrometry (HRGC/HRMS). Two samples were analyzed consisting of

- Two PUFs and two filters
- Two PUFs and 16 filters

One of the four PUFs were spiked with surrogate standards by EPA and the other three PUFs by Enthalpy Analytical. All pre-extraction standard recoveries were 43-122% which is within the method criteria (25-130%).

PCDDs and PCDFs include 75 and 135 congeners, respectively. Of these 210 congeners, 17 are toxic and have been assigned toxic equivalency factor (TEF) values [11] (Table 3-3). The toxic equivalent (TEQ) value is obtained by multiplying the concentration of a PCDD/PCDF congener by its TEF-value and summing the result for all 17 toxic congeners. All TEF-weighted PCDD/PCDF congeners were detected in both samples.

Table 3-3. The 2005 World Health Organization PCDD/PCDF Toxic Equivalent Factors for mammals/humans [11].

PCDDs	TEF	PCDFs	TEF
2,3,7,8 - TCDD	1	2,3,7,8 - TCDF	0.1
1,2,3,7,8 - PeCDD	1	1,2,3,7,8 - PeCDF	0.03
1,2,3,4,7,8 - HxCDD	0.1	2,3,4,7,8 - PeCDF	0.3
1,2,3,6,7,8 - HxCDD	0.1	1,2,3,4,7,8 - HxCDF	0.1
1,2,3,7,8,9 - HxCDD	0.1	1,2,3,6,7,8 - HxCDF	0.1
1,2,3,4,6,7,8 - HpCDD	0.01	1,2,3,7,8,9 - HxCDF	0.1
1,2,3,4,6,7,8,9 - OCDD	0.0003	2,3,4,6,7,8 - HxCDF	0.1
		1,2,3,4,6,7,8 - HpCDF	0.01
		1,2,3,4,7,8,9 - HpCDF	0.01
		1,2,3,4,6,7,8,9 - OCDF	0.0003

4 RESULTS AND DISCUSSION

4.1 Oil Residue

The mass loss in Table 4-1 was derived by CRREL and used in this report to calculate the emission factor in mass pollutant per mass of oil consumed, see Equation 2 in Section 2.4.2. The mass loss varied from 57% to 99%, Figure 4-1. Table 4-1 shows a surprisingly low mass loss percent for Burns #1 (the Baseline #1 test) and #2 of 57% and 58%, respectively. The mass loss percentage of 95% for Baseline #2 is more in line with mass loss percentage found from previous baseline oil burns conducted at CRREL using the same wave tank and oil, 94-99% [12]. During Burn #3, one of the two grid sections toppled over on its side, presumably limiting its function. Burn #5 is a repeat of this test without mishap.

Table 4-1. Oil residue in each test.

Burn Number	Test Condition	Wave Height (cm)	Mass initial[a] oil (kg)	Mass Residue[a] (kg)	Mass loss (%)
1	Baseline #1		225	96.75	57
2	Ruffled		221	92.82	58
3	Grid[b]		225	NA	NA
4	Bimetal		223	15.61	93
5	Grid		226	13.56	94
6	Grid Waves	7	226	2.26	99

7	Grid Waves	14	225	2.25	99
8	Grid Solo Waves	7	229	2.29	99
9	Bimetal Waves[c]		227	2.27	99
10	Bimetal Waves		227	4.54	98
11	Baseline #2		228	11.4	95

[a] Measured by CRREL. NA – not applicable, not collected. [b] One of the two grid sections toppled over. [c] Only one grid section used.

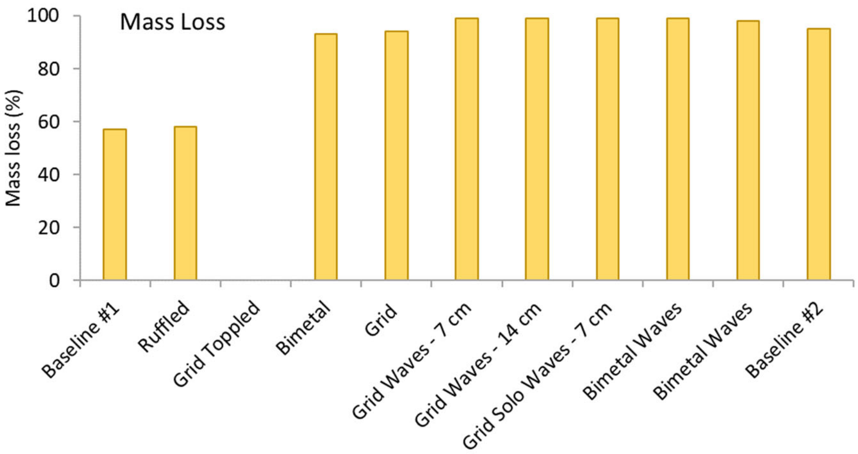

Figure 4-1. Mass loss in each test configuration. Residue not collected for "Grid Toppled".

4.2 Combustion Gases

CO and CO_2 were continuously measured every second throughout each burn. Two typical traces with resulting time-resolved MCE plotted in green are shown Figure 4-2. The MCE declines throughout the burn likely reflecting the initially more complete oxidation of the burning volatile components of the oil. The time-resolved concentrations of CO and CO_2 vary throughout the burn, which is mostly due to the crane operator more successfully positioning the sampler in the "thicker" parts of the plume.

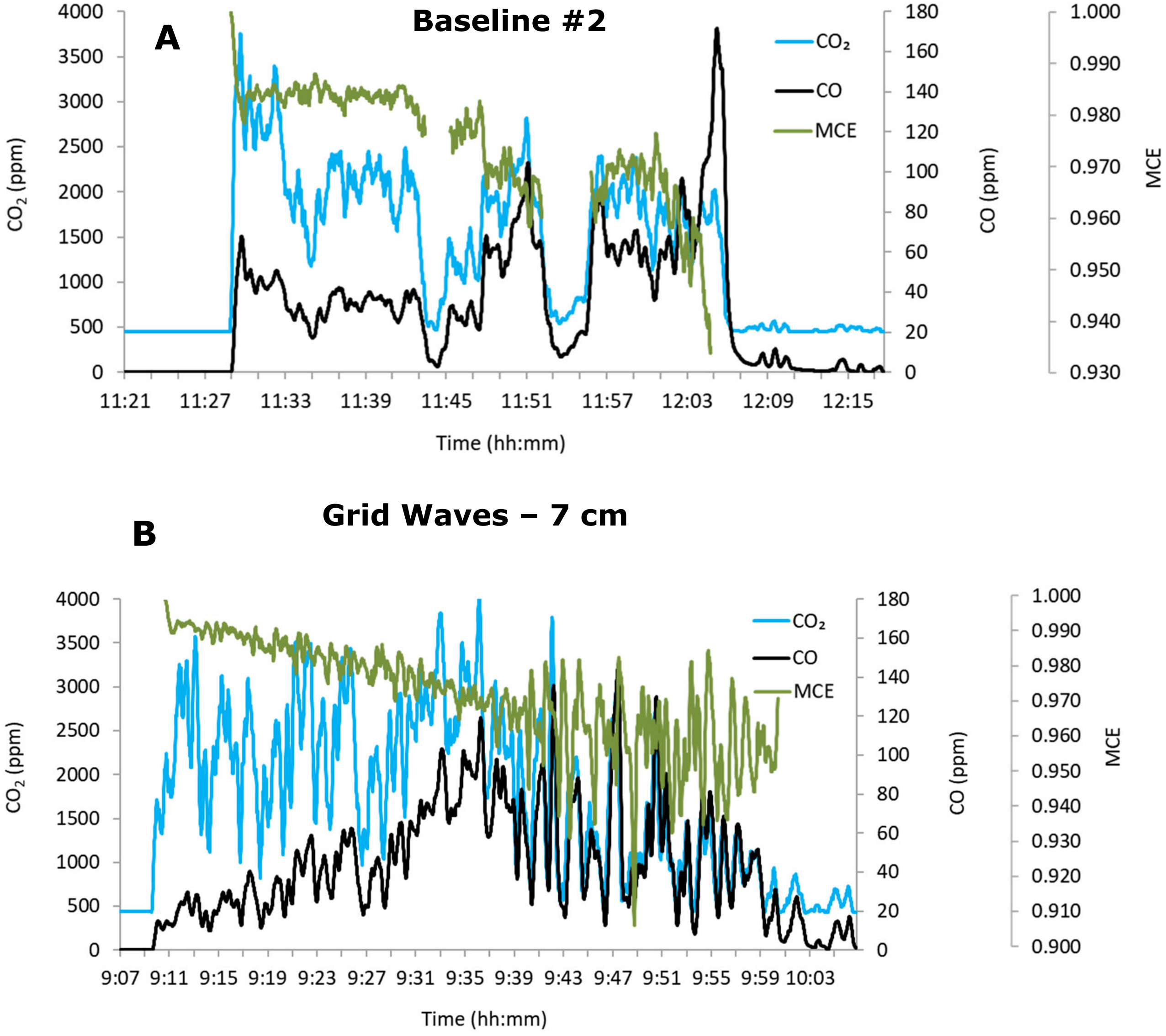

Figure 4-2. Typical CO_2 and CO concentration trace with corresponding MCE (20 seconds moving average, MCE calculated using CO_2 and CO): A) Baseline #2 and B) Grid Waves – 7 cm. The lower CO_2 and CO levels in graph A is due to wind shifts resulting in the sampling package sampling ambient levels.

The PM particles were analyzed for solid phase carbon to determine the TC content. This TC value was combined with carbon from CO and CO_2 to calculate MCE_T (MCE with TC) using Equation 4. Figure 4-3 shows chronological run data for MCE values both with and without TC as well as TC. When MCE is calculated with TC, MCE values typically decrease up to about 10%, indicating an unburnt carbon content emission in the particles. Figure 4-4 repeats this figure but uses oil mass loss instead of MCE as the ordinate value. Note that cases where $MCE_T > MCE_g$ are due to TC sampling during only a subset of the burn duration whereas MCE_g is based on the whole burn duration. In these cases, low values of CO and TC during this period would have resulted in the whole-burn MCE_g being lower than MCE_T.

The complete set of gas phase emission factors for each of the 11 tests are included in Table 4-2 .

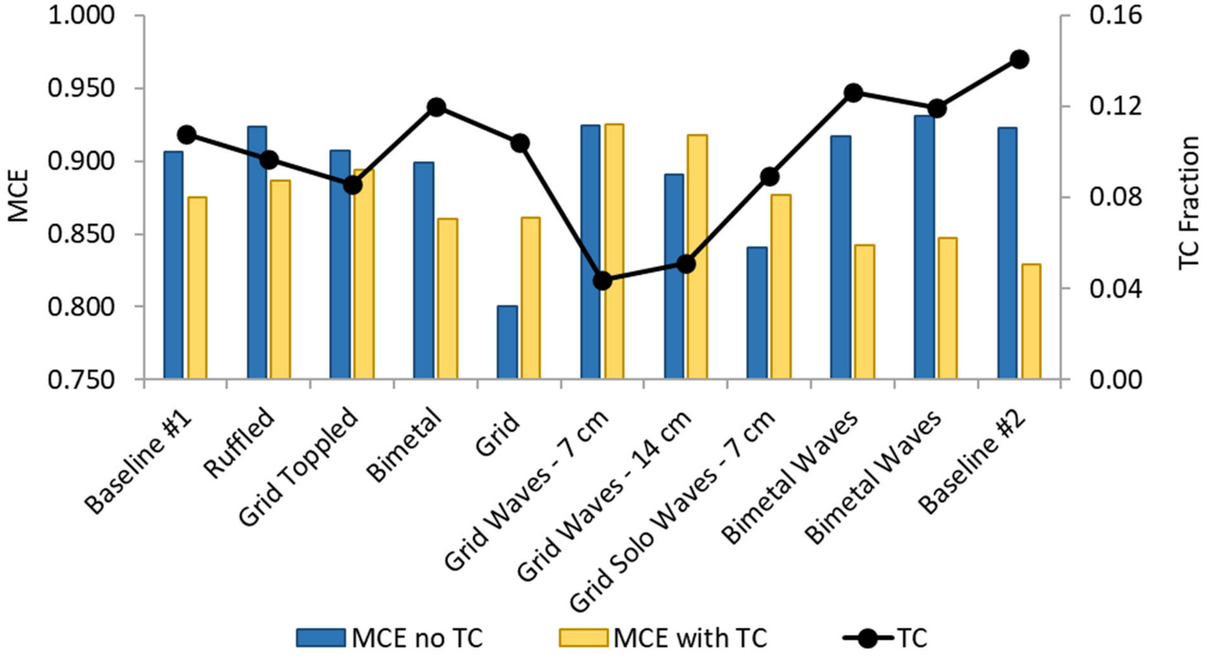

Figure 4-3. Modified combustion efficiency and TC in each of the test categories. MCE calculated with and without TC from particles. Error bar equals 1 Stand. Dev.

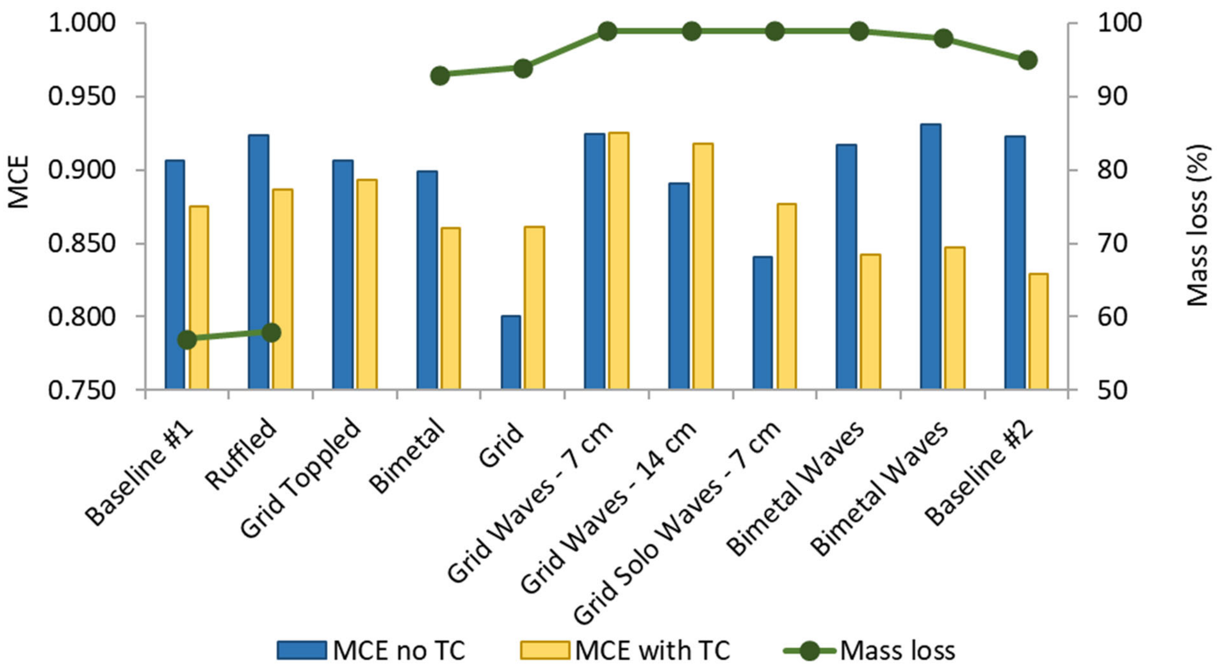

Figure 4-4. Modified combustion efficiency and oil mass loss in each of the test categories. MCE calculated with and without TC from particles. Error bar equal 1 Stand. Dev. There were no mass loss data taken for Grid Toppled.

Table 4-2. CO, CO_2, and CH_4 emission factors from each of the test configurations.

Burn Number	Test Condition	CO_2 g/kg oil initial	CO g/kg oil initial	CH_4 g/kg oil initial	CO_2 g/kg oil consumed	CO g/kg oil consumed	CH_4 g/kg oil consumed
1	Baseline #1	2,727	34	0.93	4,784	59.8	1.64
2	Ruffled	2,764	32	0.95	4,766	54.6	1.64
3	Grid[a]	2,785	41	0.50	NA	NA	NA
4	Bimetal	2,682	38	1.03	2,884	41.2	1.10
5	Grid	2,684	69	0.99	2,855	72.9	1.05
6	Grid Waves – 7 cm	2,885	61	0.85	2,914	61.2	0.86
7	Grid Waves – 14 cm	2,860	62	0.94	2,889	62.5	0.95
8	Grid Solo Waves – 7 cm	2,732	67	0.63	2,759	67.9	0.63
9	Bimetal Waves[b]	2,624	63	1.02	2,650	64.0	1.03
10	Bimetal Waves	2,640	67	0.61	2,694	68.0	0.62
11	Baseline #2	2,584	60	0.88	2,720	62.8	0.93

NA = not applicable, oil residue not collected. CH_4 emission factor derived from SUMMA canister. [a]One of the two grid sections toppled over. [b]Only one grid section used.

4.3 Oil Consumption and Modified Combustion Efficiency

The oil mass loss was compared with the MCE for all of the tests in Figure 4-5 (except for Burn No. 3) and for Burns No. 4-11 in Figure 4-6 (excluding the two first burns with exceptionally low mass loss percentage). Figure 4-6 shows a trend with increased mass loss percentage with increased MCE. This suggest that an efficient burn consumes more oil. Tests without waves result in less efficient combustion, leaving more residue than tests using waves. Table 4-3 reports the average oil consumption (weight loss) and the MCE for each test condition and burn.

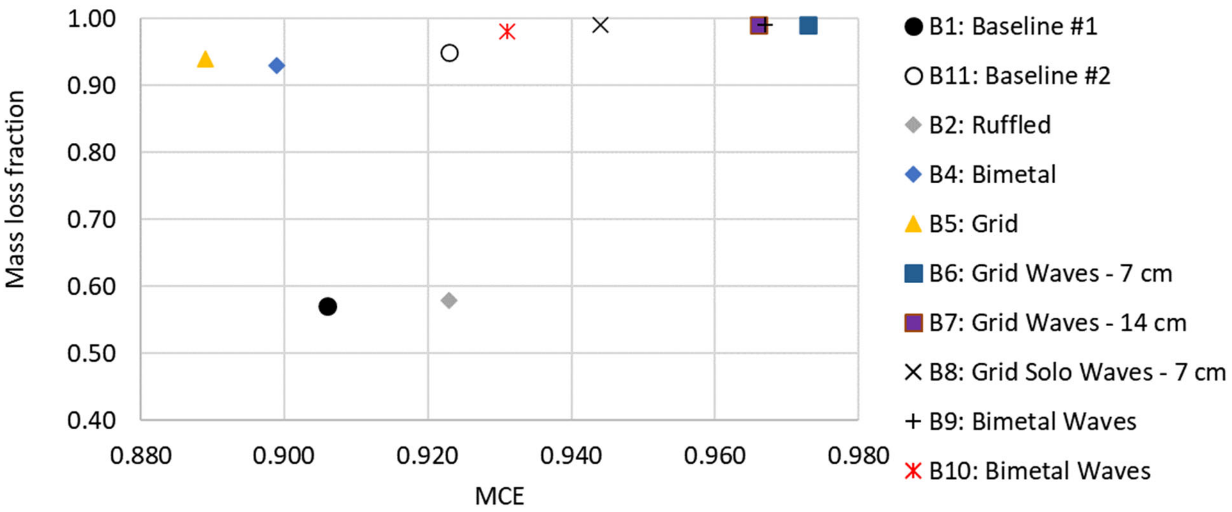

Figure 4-5. MCE (without TC from particles) versus mass loss for all tests.

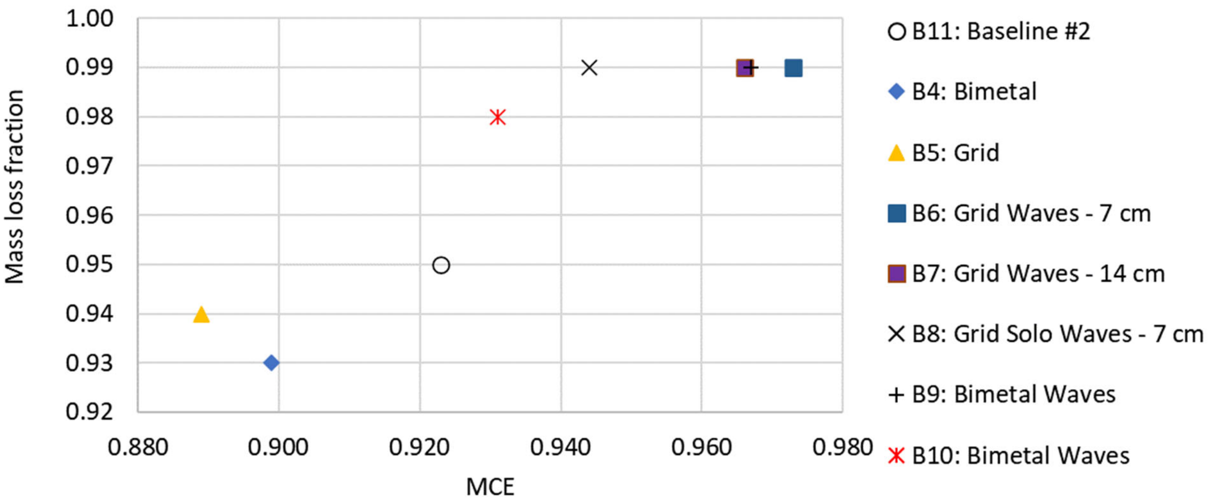

Figure 4-6. MCE (without TC from particles) versus mass loss for Burns No. 4-11.

Table 4-3. Average oil mass loss and MCE by test condition.

Burn Number	**Test Condition**	**Waves**	**Mass loss[a] (%)**	**MCE (unitless)**
1	Baseline #1		57	0.906
2	Ruffled		58	0.923
3	Grid[b]		NA	0.953
4	Bimetal		93	0.899
5	Grid		94	0.889
6	Grid Waves	7 cm	99	0.973
7	Grid Waves	14 cm	99	0.966
8	Grid Solo Waves	7 cm	99	0.944
9	Bimetal Waves[c]		99	0.967
10	Bimetal Waves		98	0.931
11	Baseline #2		95	0.923

MCE calculated for the entire burn. [a] Measured by CRREL. NA – not applicable, not collected. [b] One of the two grid sections toppled over. [c] Only one grid section used.

4.4 $PM_{2.5}$

The $PM_{2.5}$ emission factor was compared with the MCE_T for all tests and replicates in Figure 4-7. Figure 4-8 and Figure 4-9 shows the average value of the two $PM_{2.5}$ emission factors derived from each burn versus the MCE_T. When the $PM_{2.5}$ emission factor is compared with MCE_T a clear relation exists, showing that higher MCE values lead to lower $PM_{2.5}$ emission factors. The lowest $PM_{2.5}$ emission factors are associated with the Grid configuration particularly when used with waves. Figure 4-9 plots the $PM_{2.5}$ emission factors in g/kg oil consumed versus MCE_T and shows a good relationship when excluding the first two burns (Baseline #1 and Ruffled). No apparent trends were found when plotting the $PM_{2.5}$ emission factors against oil mass loss (Figure 4-10).

The $PM_{2.5}$ emission factor data versus test condition are shown in Table 4-4

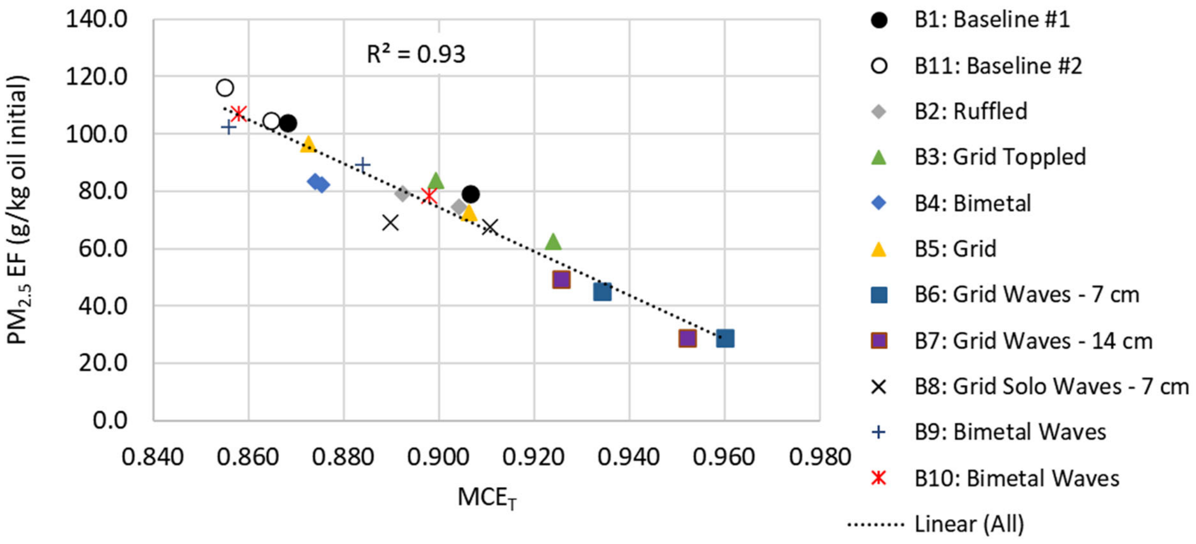

Figure 4-7. Change of $PM_{2.5}$ emission factor with modified combustion efficiency (MCE_T). Two $PM_{2.5}$ samples collected from each burn.

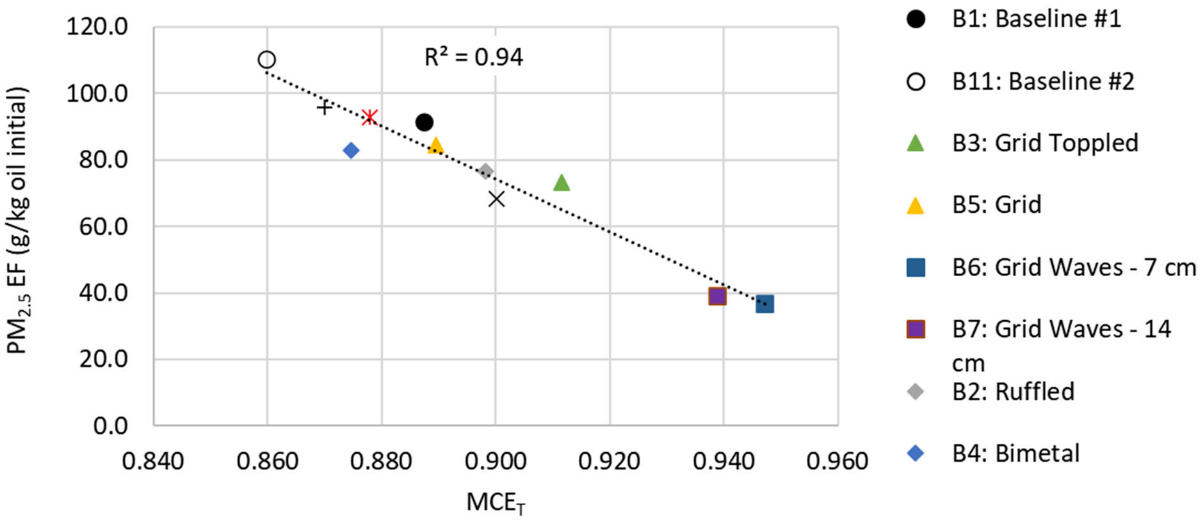

Figure 4-8. Change of $PM_{2.5}$ emission factor with modified combustion efficiency (MCE_T). Average $PM_{2.5}$ emission factor and MCE of two samples collected from each burn.

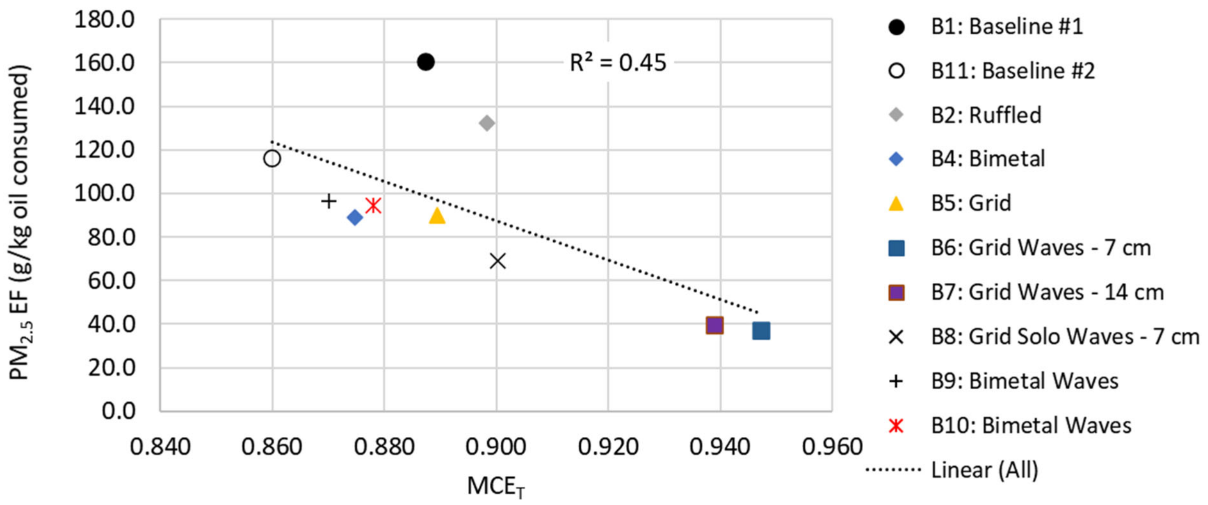

Figure 4-9. Change of PM$_{2.5}$ emission factor in g/kg oil consumed with modified combustion efficiency (MCE$_T$). Average PM$_{2.5}$ emission factor and MCE of two samples collected from each burn.

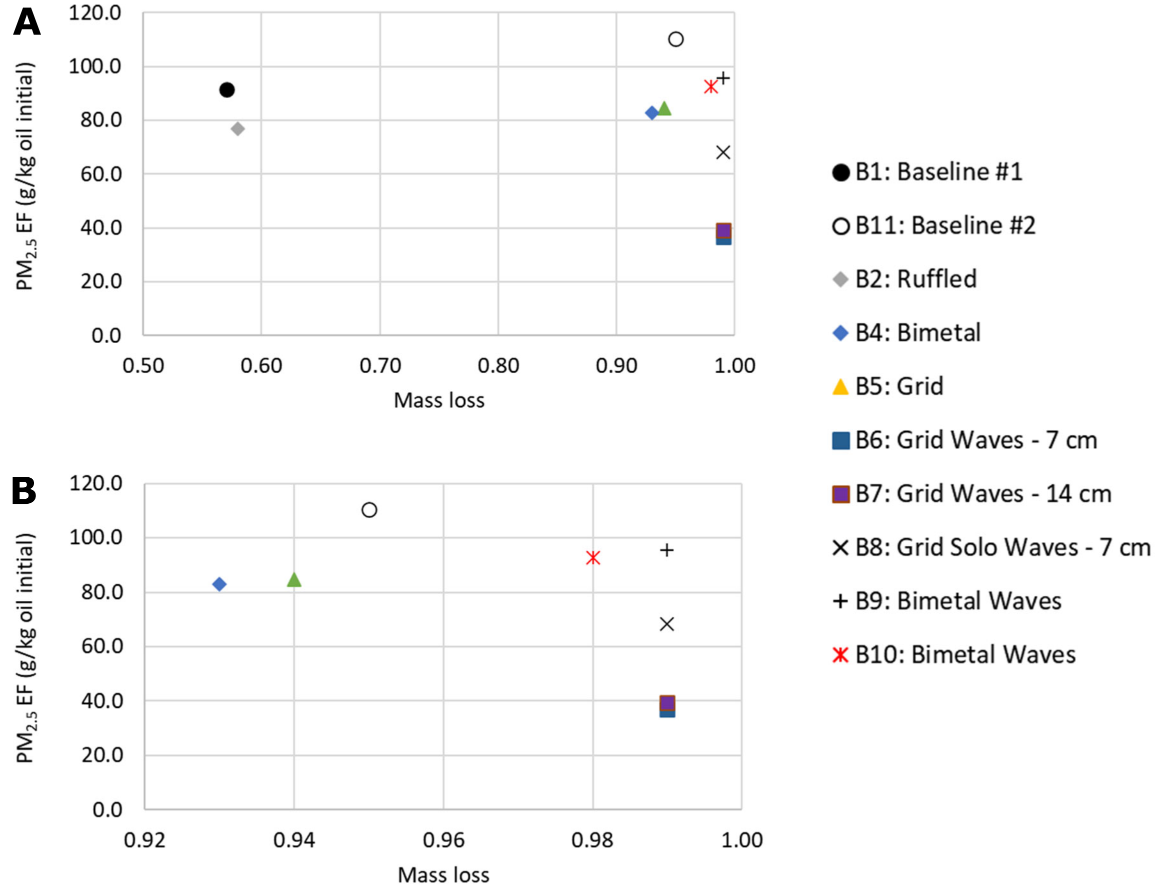

Figure 4-10. Change of $PM_{2.5}$ emission factor with oil mass loss. A) All tests except Burn No. 3 and B) Burns No. 4-11 (excluding Burn No. 1, 2 and 3).

Table 4-4. $PM_{2.5}$ emission factors from each test condition.

Burn Number	Test Condition	$PM_{2.5}$ g/kg oil initial	$PM_{2.5}$ g/kg oil consumed
1	Baseline #1	91.6	160.8
2	Ruffled	76.7	132.2
3	Grid[a]	73.2	NA
4	Bimetal	82.9	89.2
5	Grid	84.6	90.0
6	Grid Waves – 7 cm	36.9	37.3
7	Grid Waves – 14 cm	39.3	39.7
8	Grid Solo Waves – 7cm	68.2	68.9
9	Bimetal Waves[b]	95.7	96.6
10	Bimetal Waves	92.6	94.5
11	Baseline #2	110.5	116.3

NA – not applicable, oil residue not collected. [a] One of the two grid sections toppled over. [b] Only one grid section used.

4.5 Total Carbon

Analysis of the particles for TC is reported in Table 4-5. The TC values ranged from 37.7 to 160.8 g/kg oil consumed, compared with values of 51.3 to 138.0 g/kg oil consumed from studying TC emissions from oil burn using different boom ratios [12].

Table 4-5. Total carbon emission factors.

Burn Number	Test Condition	TC g/kg oil initial	TC g/kg oil consumed
1	Baseline #1	91.6	160.8
2	Ruffled	82.6	142.4
3	Grid[a]	72.9	NA
4	Bimetal	102.12	109.8
5	Grid	88.4	94.1
6	Grid Waves – 7 cm	37.3	37.7
7	Grid Waves – 14 cm	43.5	43.9
8	Grid Solo Waves – 7 cm	76.2	77.0

9	Bimetal Waves[b]	107.2	108.3
10	Bimetal Waves	101.5	103.6
11	Baseline #2	119.8	126.1

NA – not applicable, oil residue not collected. [a] One of the two grid sections toppled over. [b] Only one grid section used.

4.6 Black Carbon

BC emission factors are reported in Table 4-6. BC were not measured for all burns due to high plume concentration the MA200 enhanced its filter tape more often than anticipated resulting in filter tape shortage. The BC emission factors were in the same range (12.4 to 43.1 g/kg fuel initial) as found from oil burns plumes using different boom ratios (BC 35.7 to 165.1 g/kg oil initial) [12].

Table 4-6. Black carbon (BC) emission factors.

Burn Number	Test Condition	BC (880 nm)	
		g/kg oil initial	g/kg oil consumed
1	Baseline #1	43.1	75.6
2	Ruffled	12.4	21.4
3	Grid[a]	NA	NA
4	Bimetal	61.3	65.9
5	Grid	37.3	39.6
6	Grid Waves – 7 cm	NA	NA
7	Grid Waves – 14 cm	NA	NA
8	Grid Solo Waves – 7 cm	NA	NA
9	Bimetal Waves[b]	NA	NA
10	Bimetal Waves	NA	NA
11	Baseline #2	NA	NA

NA – not applicable, not measured. [a] One of the two grid sections toppled over. [b] Only one grid section used.

4.7 Polyaromatic Hydrocarbons

The PAH_{16} emission factors ranged from 215.8 to 1,155.1 mg/kg oil initial (Figure 4-11 and Table 4-7). The highest emission factor (1,155 mg/kg oil) was derived from the “Ruffled” test condition. The lowest emission factor of 215.8 mg/kg oil initial was derived from “Grid Waves – 7 cm” which was in similar range as from both the baseline tests 287.0 and 224.9 mg/kg oil initial. PAH_{16} values of 106.3 to 456.2 mg/kg oil initial obtained during testing of different boom ratios [12] are similar to those found here, 215.8 to 521.7 mg/kg oil initial.

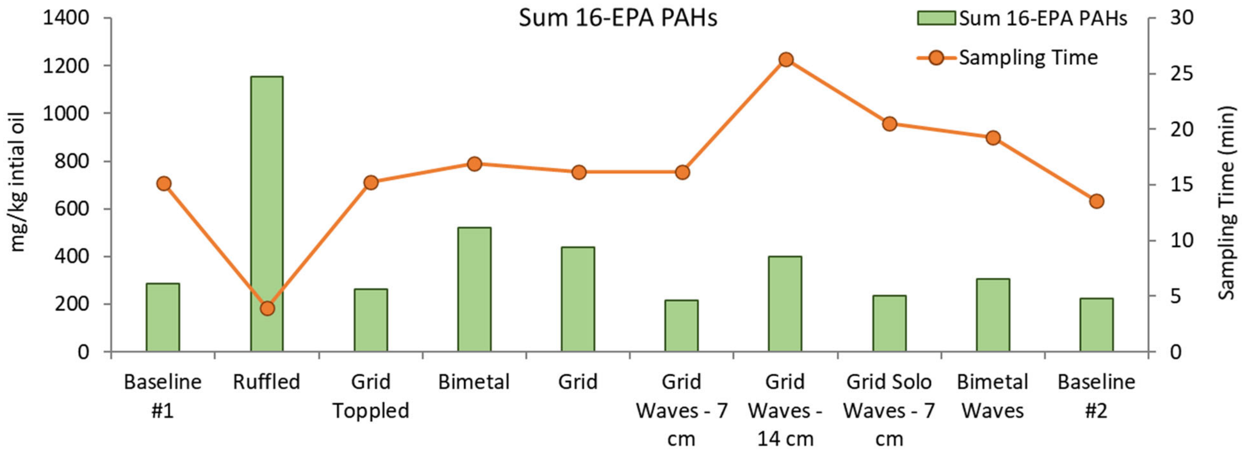

Figure 4-11. PAH emission factors for the different test configurations.

Table 4-7. PAH emission factors in mg/kg initial oil.

Burn Number	**Baseline #1 1**	**Ruffled 2**	**Grid[a] 3**	**Bimetal 4**	**Grid 5**	**Grid Waves - 7 cm 6**	**Grid Waves - 14 cm 7**	**Grid Solo Waves - 7 cm 8**	**Bimetal Waves 10**	**Baseline #2 11**
Targets						**mg/kg initial oil**				
Naphthalene	115.93	500.96	109.36	223.83	179.89	89.49	170.55	108.45	116.13	87.01
Acenaphthylene	39.00	138.20	32.72	67.72	62.92	25.53	51.17	35.54	32.03	30.30
Acenaphthene(CCC)	ND	5.48	0.46	ND	0.79	0.35	0.63	0.37	0.35	ND
Fluorene	4.78	39.77	5.92	9.72	32.20	5.14	10.31	6.43	6.63	4.53
Phenanthrene	36.64	153.02	34.23	60.84	51.69	29.83	49.13	25.04	45.43	32.61
Anthracene	4.86	25.34	4.91	8.23	8.33	5.36	10.45	4.29	7.57	4.18
Fluoranthene(CCC)	27.43	84.01	23.90	42.47	32.20	18.26	31.92	15.00	32.17	21.79
Pyrene	28.07	84.40	24.33	40.56	31.90	18.97	33.48	15.23	32.59	22.22
Benzo(a)anthracene	3.39	17.76	3.14	6.73	4.79	3.25	5.93	2.72	4.05	2.27
Chrysene	4.41	22.81	4.11	9.26	6.17	4.00	7.32	3.25	5.23	3.06
Benzo(b)fluoranthene	3.86	19.43	3.42	7.73	4.58	2.88	5.34	2.67	3.94	2.89
Benzo(k)fluoranthene	2.06	9.90	1.86	4.32	2.95	1.61	3.21	1.57	2.09	1.53
Benzo(a)pyrene(CCC)	6.02	21.25	4.65	10.87	7.06	4.33	7.89	4.50	5.95	4.47
Indeno(1,2,3-cd)pyrene	4.05	14.21	3.06	11.36	4.61	2.72	4.80	3.75	3.82	2.97
Dibenz(a,h)anthracene	0.46	ND	ND	1.55	0.66	0.41	0.78	0.52	0.49	0.29
Benzo(ghi)perylene	6.02	18.52	4.46	16.53	6.53	3.71	6.48	5.18	5.39	4.75
SUM 16-EPA PAH	**286.99**	**1,155.06**	**260.54**	**521.73**	**437.25**	**215.84**	**399.40**	**234.50**	**303.85**	**224.86**

ND = not detected. [a] One of the two grid sections toppled over.

4.8 Volatile Organic Compounds

VOC emission factors are reported in Table 4-8 and Table 4-9. The benzene emission factors ranged from 278 to 694 mg/kg fuel, which is within the same range as previous oil burns testing different boom aspect ratios conducted in CRREL's wave tank [12]. The MCE_g from each collected VOC sample were similar, ranging from 0.975 to 0.987. Regardless of the similarity in their values, the benzene emission factors were still found to be proportional to the MCE_g as shown in Figure 4-12. This was, however, not true for all the detected VOCs.

It is important to note that the VOC samples from Burns #1 to #6 include vinyl chloride, which has only previously been detected from oil burns when using carbon fiber insulation as a means to increase the combustion efficiency [13]. Vinyl chloride was not detected in any samples from previous oil burn efforts studying the effect of different boom ratios on the combustion efficiency [12] or oil consumed from 1 m^2 pan burns [14] using the same sampling and analytical methods. Burn #1 (Baseline #1) has the highest vinyl chloride emissions factor, which is five times higher than found from Burn #2. Additionally Burns #7 to #11 have no detectable levels of vinyl chloride. Burn #1 has also higher emission factors of methylene chloride, chloromethane, and chlorobenzene. One possible explanation for detecting vinyl chloride in the plumes from the first six burns is that it may originate from the boom material. The boom includes a polyvinyl chloride (PVC)-coated polyester fabric which is below the water line of the boom. The vinyl chloride emissions in the first six burns can be due to the PVC coating burning off where most of it burned off during the first burn (Baseline #1) explaining the higher vinyl chloride emission factor for Baseline #1.

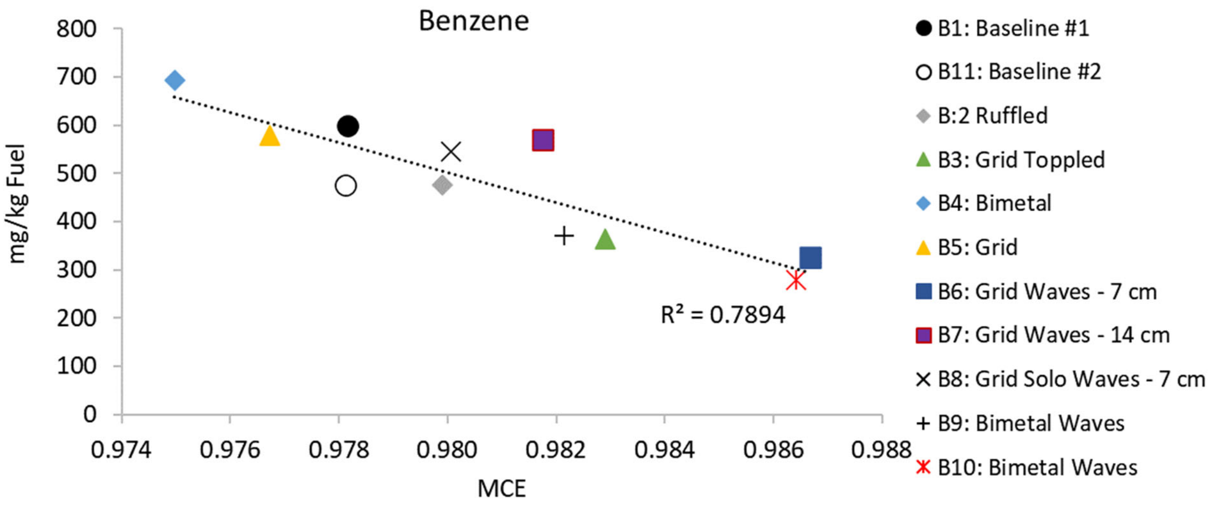

Figure 4-12. MCE_g (without TC) versus benzene emission factor for all tests and configurations.

Table 4-8. Carbonyl emission factors in mg/kg initial oil.

Burn Number	**Test Condition**	**Formaldehyde**	**Acetaldehyde**
		g/kg oil initial	**g/kg oil initial**
1	Baseline #1	74	45
2	Ruffled	90	30
3	Grid[a]	42	ND
4	Bimetal	60	27
5	Grid	93	31
6	Grid Waves – 7 cm	70	23
7	Grid Waves – 14 cm	120	80
8	Grid Solo Waves – 7 cm	32	34
9	Bimetal Waves[b]	72	26
10	Bimetal Waves	149	45
11	Baseline #2	291	46

ND = not detected. [a] One of the two grid sections toppled over. [b] Only one grid section used.

Table 4-9. VOC emission factors in mg/kg initial oil.

VOC	Burn 1 Baseline #1	Burn 2 Ruffled	Burn 3 Grid[a]	Burn 4 Bimetal	Burn 5 Grid	Burn 6 Grid Waves 7 cm	Burn 7 Grid Waves 14 cm	Burn 8 Grid Solo Waves 7 cm	Burn 9 Bimetal Waves[b]	Burn 10 Bimetal Waves	Burn 11 Baseline #2
Propene	20.00	13.98	7.93	18.52	17.91	58.28	93.02	17.86	15.22	11.72	118.90
Dichlorodifluoromethane (CFC 12)	0.47	0.14	0.19	0.17	0.11	0.11	0.32	0.10	0.09	ND	0.89
Chloromethane	7.49	1.65	0.18	1.63	1.44	0.20	2.28	1.28	0.90	0.56	1.00
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Vinyl Chloride	10.43	2.03	0.40	0.99	0.38	0.30	ND	ND	ND	ND	ND
1,3-Butadiene	15.80	10.71	6.62	13.03	12.90	27.15	39.64	13.40	8.62	7.30	41.70
Bromomethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethanol	451.87	ND	ND	ND	ND	ND	4.76	3.83	ND	ND	ND
Acetonitrile	266.86	109.87	123.71	206.55	76.23	103.08	156.83	132.93	136.92	0.53	3.43
Acrolein	34.36	21.35	18.96	34.31	18.01	30.14	39.25	25.60	20.46	4.08	43.75
Acetone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichlorofluoromethane	0.79	ND	1.15	ND	ND	ND	ND	0.19	ND	ND	0.15
2-Propanol (Isopropyl Alcohol)	16.13	ND	ND	ND	ND	0.17	6.52	ND	0.35	ND	ND
Acrylonitrile	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methylene Chloride	5.39	ND	2.79	2.10	0.66	0.55	1.76	ND	ND	ND	ND
3-Chloro-1-propene (Allyl Chloride)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichlorotrifluoroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon Disulfide	9.16	3.62	4.61	ND	4.52	2.28	5.71	4.21	17.23	2.32	23.83
trans-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl tert-Butyl Ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Vinyl Acetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

2-Butanone (MEK)	1.42	ND	ND	ND	0.22	ND	1.90	ND	15.34	ND	1.27
cis-1,2-Dichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl Acetate	10.27	ND	2.98	ND	ND	ND	ND	4.69	ND	ND	ND
n-Hexane	ND	ND	ND	ND	ND	ND	66.60	17.23	ND	ND	30.53
Chloroform	ND	ND	ND	ND	ND	0.18	ND	ND	ND	ND	ND
Tetrahydrofuran (THF)	ND	ND	ND	ND	4.73	0.85	ND	ND	1.21	ND	0.46
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	599.14	476.54	363.95	693.50	579.78	325.00	569.63	544.73	369.84	278.09	476.03
Carbon Tetrachloride	0.25	ND	0.01	ND	ND	0.02	ND	ND	ND	ND	ND
Cyclohexane	1.42	ND	1.06	ND	ND	4.45	8.25	1.72	3.19	1.00	8.94
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dioxane	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.79	ND
Methyl Methacrylate	30.02	2.90	0.35	2.26	ND	ND	22.20	ND	ND	ND	ND
n-Heptane	2.37	1.88	3.46	2.78	2.04	13.03	28.54	5.17	10.34	2.79	32.77
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Methyl-2-pentanone	1.17	ND	ND	ND	ND	ND	ND	ND	1.21	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Toluene	32.28	16.55	15.77	35.49	35.95	35.22	73.63	31.04	17.60	10.24	45.75
2-Hexanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Butyl Acetate	1.90	ND	ND	ND	ND	ND	ND	ND	0.79	ND	ND
n-Octane	1.33	1.27	1.54	1.72	1.40	7.60	20.62	5.17	5.08	1.33	20.11
Tetrachloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorobenzene	1.90	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene	3.79	1.45	1.06	2.26	1.94	3.80	7.61	2.49	1.72	0.93	6.63
m,p-Xylenes	7.43	1.59	1.06	3.13	2.04	7.17	17.44	4.40	3.27	1.19	14.89

Bromoform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Styrene	37.92	21.71	12.48	31.27	27.96	26.07	45.99	30.62	14.65	9.95	29.04
o-Xylene	3.79	0.85	0.46	1.36	0.85	2.93	7.14	2.01	1.46	0.57	6.11
n-Nonane	1.58	1.24	0.77	1.69	1.08	4.89	15.86	5.17	3.27	1.13	14.15
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cumene	ND	ND	ND	ND	ND	0.21	0.65	ND	ND	ND	0.54
alpha-Pinene	7.11	ND	ND	ND	ND	0.33	1.27	ND	ND	ND	0.97
n-Propylbenzene	0.90	ND	ND	ND	ND	0.39	1.00	ND	ND	ND	0.97
4-Ethyltoluene	ND	ND	ND	ND	ND	0.68	1.74	0.58	0.38	ND	1.71
1,3,5-Trimethylbenzene	1.74	ND	ND	ND	ND	0.58	1.74	0.64	0.36	ND	1.56
1,2,4-Trimethylbenzene	4.74	1.03	0.36	1.34	0.68	2.06	6.03	2.39	1.29	0.51	5.73
Benzyl Chloride	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
d-Limonene	10.90	0.43	ND	1.91	0.97	5.21	9.51	3.45	ND	0.53	2.01
1,2-Dibromo-3-chloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Naphthalene	204.83	187.66	95.63	259.95	182.40	103.88	189.72	171.91	120.32	72.73	163.57
Hexachlorobutadiene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected. [a] One of the two grid sections toppled over. [b] Only one grid section used.

4.9 Polychlorinated Dibenzodioxins and Furans

PCDDs/PCDFs were collected from a single burn for the Baseline sample (Burn #1, Baseline #1) and multiple burns (Burns #2 to #10) for the “Refluxer” sample resulting in two single samples: Baseline and Refluxer. The PCDD/PCDF emission factors for the “Refluxer” sample were only slightly higher than the “Baseline” sample, 14.9 ng TEQ/kg initial oil and 10.5 ng TEQ/kg initial oil, respectively (Table 4-10). This suggests that no enhanced PCDD/PCDF formation occurs due to the Refluxer materials. However, both the Baseline and Refluxer samples were approximately ten times higher than reported from previous oil burn studies (Figure 4-13) with values ranging from 0.41 to 3.25 ng TEQ/kg oil initial [12, 14, 15]. An elevated PCDD/PCDF emission factor of 8.0 ng TEQ/kg initial oil was previously found when studying the use of carbon fiber as an insulation to increase the combustion efficiency [13] (Figure 4-13).

As discussed in the VOC Section 4.8 above regarding elevated vinyl chloride emissions, these higher PCDD/PCDF emission factors may also be due to combustion of the material on the boom itself as the boom includes a PVC-coated polyester fabric. PCDDs/PCDFs are well known to form from incineration of PVC. Some of this PVC-coating may burn off resulting in an enhanced PCDD/PCDF formation. This could explain how all the TEF congeners were detected in the Baseline sample from only a single burn. Detectable levels of vinyl chloride were also found when studying the use of carbon fiber as an insulation to increase the combustion efficiency [13] which also saw higher PCDD/PCDF emission factors.

Table 4-10. PCDD/PCDF emission factors.

Sum	**Unit**	**Baseline**	**Refluxer**
		Burn #1	**Burn #2-#10**
PCDD Total	ng/kg initial oil	45.5	66.5
PCDF Total	ng/kg initial oil	746.0	860.3
PCDD/PCDF Total	ng/kg initial oil	791.6	926.8
PCDD TEQ	ng TEQ/kg initial oil	1.43	2.62
PCDF TEQ	ng TEQ/kg initial oil	9.06	11.68
PCDD/PCDF TEQ	ng TEQ/kg initial oil	10.49	14.29

All seventeen TEQ congeners were detected in both samples.

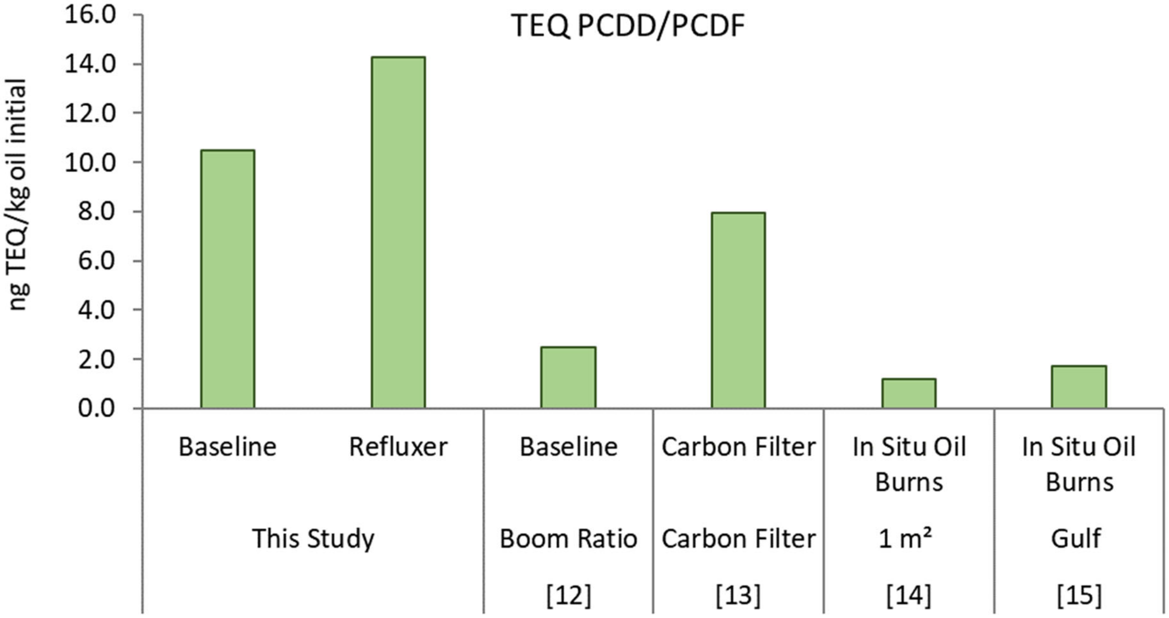

Figure 4-13. Comparison of PCDD/PCDF TEQ emission factors with Boom Ratio Study [12], Carbon Filter study [13], 1 m^2 in situ oil burns [14], and Deepwater Horizon in situ oil burn data [15]. The baseline was a single burn and the Refluxer was a composite of nine burns.

5 CONCLUSIONS

An increase in mass loss percentage with higher MCE was found suggesting that an efficient burn results in more oil mass loss. The $PM_{2.5}$ emission factors showed a clear relation to MCE_T, showing that higher MCE_T values lead to lower $PM_{2.5}$ emission factors. The lowest $PM_{2.5}$ emission factors were associated with the Grid configuration particularly when used with waves. Benzene was found to be proportional to MCE_g where the tests including waves had the lowest emission factors. The TC, BC, and PAH emission factors showed similar ranges as previous oil burn studies. Vinyl chloride was detected in the plumes from the first six burns which may be due to the PVC-coated polyester fabric on the boom burning off. The burning of the PVC-coated fabric may also result in the higher PCDD/PCDF emission factors found in both the Baseline and Refluxer samples compared to previous studies. Incineration of PVC is well known to form PCDD/PCDF. The PCDD/PCDF emission factors for the "Refluxer" sample were slightly higher than the "Baseline" sample, indicating that likely no enhanced PCDD/PCDF formation occurred due to the copper material of the Refluxers, a known PCDD/PCDF catalyst.

Among the three technologies, the Grid heat transfer configuration used with waves showed the overall highest MCE and mass loss percentage combined with lowest $PM_{2.5}$ emission factors. The Grid configuration used with waves also showed the lowest emission factors for other classes of compounds including total carbon, PAH_{16}, and carbonyls. The Grid configuration appears to have the best potential for improving combustion efficiency and reducing emissions than the Ruffled or Bimetal configurations.

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