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

Final Report

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ABSTRACT

A modified boom system was tested for its ability to improve the combustion efficiency of in situ oil burns at sea. The boom system served to concentrate the skimmed oil to promote combustion. Test trials of oil burns on water were conducted at the US Army Corps of Engineers (ACE) facility in Hanover, New Hampshire. Emission measurements were taken with the Kolibri, a system of gas and particle sensors developed by the US Environmental Protection Agency's Office of Research and Development, attached to an unmanned aircraft system (UAS). The UAS was flown into the plume of the burns to measure gas and particle compositions.

Six in situ oil burns were conducted within a contained boom with length:width aspect ratio of 3:1 using three different initial oil masses per area 25.6, 12.8 and 6.4 kg/m^2. In four of the six tests additional oil was added as the burn progressed to mimic real offshore oil burns where oil is continually collected during the burn. The modified combustion efficiency, MCE_T, ranged from 0.87 to 0.65 (unitless) and emissions of particles of aerodynamic diameter of 2.5 μm, $PM_{2.5,}$ ranged from 159 to 629 g/kg initial oil. $PM_{2.5}$ emissions decreased with increased MCE_T. The lowest $PM_{2.5}$ emission factors were emitted when burning 160 gallons of oil all at once (25.6 kg/m^2) and when oil was continuously added to an initial 40 gallons burn (starting at 6.4 kg/m^2, 40+40+20+20+20 gallons, total of 140 gallons,). These lower $PM_{2.5}$ emission factors and corresponding MCEs were similar those found from a previous boom aspect ratio study at the ACE facility using a boom aspect ratio of 1:1. The larger scale used in this study with a burn area of 20.1 m^2 (versus 3.4 m2) and 1136 kg initial oil (versus 31 kg) may be why these two studies had similar results despite different boom aspect ratios. The larger scale used in this current study resulted in similar mass loss percentage (93.8-97.1%) as in the boom aspect ratio study (94.3-99.6%) when the initial oil area density was less than 12.8 kg/m^2.

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ACRONYMS

BSEE	Bureau of Safety and Environmental Enforcement
CEMM	Center for Environmental Measurement and Modeling
CO	Carbon monoxide
CO_2	Carbon dioxide
CRREL	Cold Regions Research and Engineering Laboratory
EC	Elemental Carbon
EPA	Environmental Protection Agency
FR	Fast Response
GRF	Geophysical Research Facility
ISB	In-situ burning
MCE	Modified Combustion Efficiency
MOBE	Multi-Partner Research Initiative Offshore Burn Experiments
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
ORD	Office of Research and Development
OTM	Other Test Method
PEM	Personal Environmental Monitor
PM	Particulate matter
$PM_{2.5}$	Particulate matter, with diameter equal to or less than 2.5 μm
PMI	Personal Modular Impactor
ppm	Parts per million
RH	Relative humidity
SOP	Standard operating procedure
TC	Total Carbon
TOA	Thermal-optical analysis
UAS	Unmanned aircraft system
UDRI	University of Dayton Research Institute

1 INTRODUCTION

In-situ burning (ISB) is the controlled burning of oil spilled from a vessel or pipeline. There were multiple ISB events after the Deepwater Horizon oil spill on April 20, 2010, including 410 ISBs conducted by the Coast Guard [1]. Proponents of ISB suggest that it offers a rapid and simple means of reducing the environmental impact of oil spills. During ISBs, the majority of spilled oil is converted to gaseous combustion products. ISB emits a black plume composed of 80-84% by weight carbon dioxide (CO_2) and water; the remaining components are other gases and soot particles. One of the main concerns with ISB is the trace gas constituents and particulate matter (PM) in the smoke plume. Measuring smoke/combustion emission is crucial to quantify the potential release of air toxics, PM, and other pollutants.

The Department of Interior, Bureau of Safety and Environmental Enforcement (BSEE), the project sponsor, is pursuing a line of research to conduct full-scale tests of modified boom configurations in the Canadian Multi-Partner Research Initiative Offshore Burn Experiments (MOBE) planned for the summer of 2023. This current effort reported here intends to determine if alternate boom geometries will result in a reduction of particulate matter (PM) and trace pollutants in the plume and reduced amounts of burn residue. Lessons learned from this current effort are intended to be applied to the MOBE effort.

The US Environmental Protection Agency's Office of Research and Development (ORD) deployed its lightweight emission sampling/sensor system, the "Kolibri," on an unmanned aircraft system (UAS) for particle and gas measurements in the ISB plume. Among other measurements, the Kolibri is comprised of sensors for CO_2 and carbon monoxide (CO), both critical measurements for determination of emission factors, as well as lightweight systems for batch and online sampling of $PM_{2.5.}$

This effort measured emissions from a five-day campaign of oil burns on water at the U.S. Army Corps of Engineers, Cold Regions Research Engineering Laboratory (CRREL). The objective of this study was to evaluate the relationship between emissions and burn efficiency from ISB of crude oil on water using a new boom technique called the "burning tongue" that aims to improve burn efficiencies (Figure 1-1). The name is derived from the physical configuration of the boom which is deployed to corral and concentrate the oil into a narrow ("tongue") section for ignition. The study also derived emission factors from the in-situ oil burns.

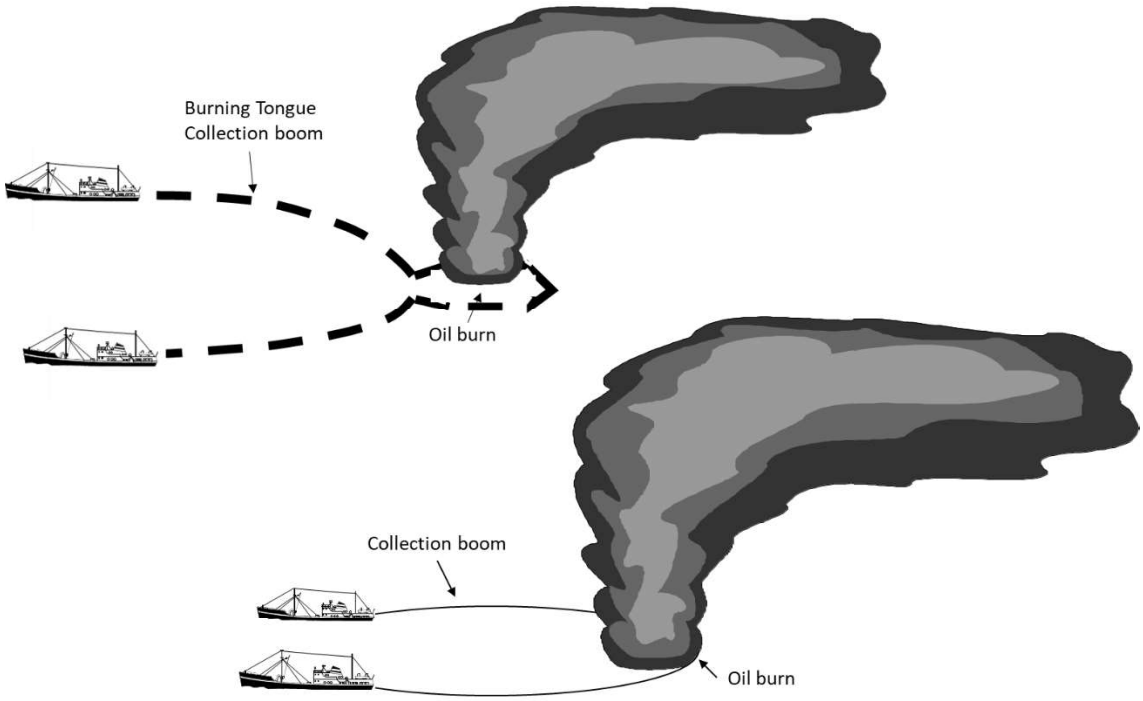

Figure 1-1. Schematic of the new burning tongue collection boom (top) and standard boom (bottom). Not to scale.

2 MATERIALS AND METHODS

2.1 Test Location

Testing took place at the CRREL facility located in Hanover, New Hampshire. The facility used for the testing was CRREL's Geophysical Research Facility (GRF) water-filled, in-ground tank shown in Figure 2-1.

Figure 2-1. Geophysical Research Facility at CRREL - 20m x 6.7m x 2.1m; water-filled tank.

2.2 Test Set-Up

The boom in the GRF tank was assembled to simulate the narrow part of the burning tongue boom configuration (Figure 2-2). The narrow tongue part of the boom was 30 feet (9.1 m) long and 10 feet (3.05 m) wide boom with a boom ratio of 3:1 and a burn area of 217 ft^2 (20.14 m^2). A hydraulic gate was configured between the wide and narrow part of the boom to control the amount of oil released into the tongue. The GRF tank was equipped with propellers to generate a 0.75 knot current simulating an actual towed boom used for oil spilled at sea. The crude oil (Alaska North Slope) was introduced into the GRF through an underwater oil-injection system developed by CRREL at a speed of approximately 10 gal/min. The boom setup, pre- and postburn is shown in Figure 2-3. For each burn test, members of CRREL handled the oil injection, ignition, and post-burn residue collection.

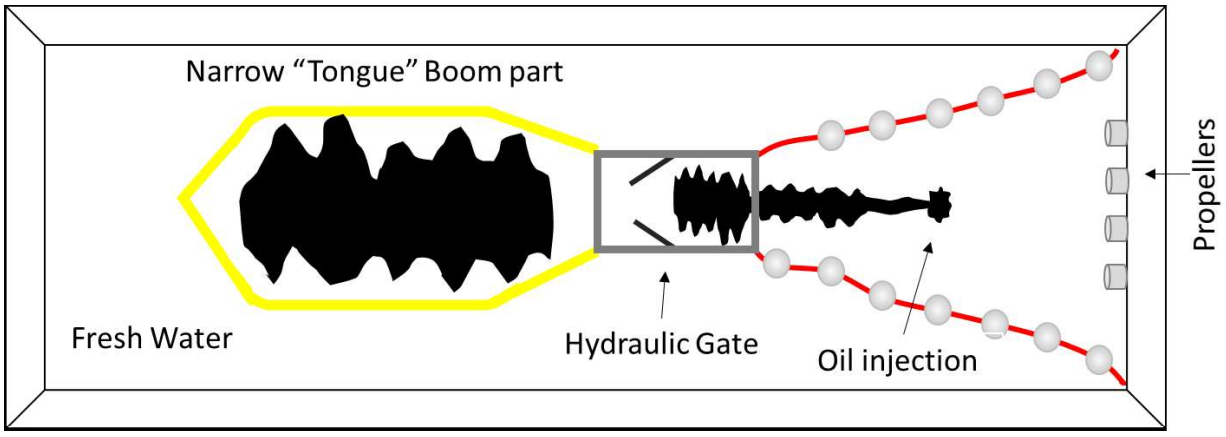

Figure 2-2. Schematic of GRF tank from above (not to scale).

Figure 2-3. Boom configuration A) before and B) after test burn 1.

2.3 Test Matrix

Four different test scenarios were studied using the same boom configuration in each test. Two baseline tests were conducted with two different initial oil amounts (160 and 80 gallons). Three other scenarios were studied with the same start amount of initial oil (40 gallons) but varying the number of times and amount of oil was added to the ongoing burn to mimic the reality of offshore burning (Table 2-1). The initial start mass oil per area was different for two first burns (25.6 and 12.8 kg/m^2) compared to the other four burns (6.4 kg/m^2 each) (Table 2-1).

The added oil was added continuously with the hydraulic gate open when the initial oil or when first or second additional oil had burned for approximately 4 min.

Table 2-1. Test Matrix.

Burn Number	Date	Test Condition	Oil gallons	Mass Total initial oil lbs (kg)	Initial mass start oil per area kg oil/m^2
1	11/01/2022	Baseline – initial oil	160	1136 (515)	25.6
2	11/01/2022	Baseline – initial oil	80	568 (258)	12.8
3	11/02/2022	Oil added during burn once	40+40	568 (258)	6.4
4	11/02/2022	Oil added during burn once	40+40	568 (258)	6.4
5	11/02/2022	Oil added during burn twice	40+40+20	710 (322)	6.4
6	11/03/2022	Oil added during burn three times	40+40+20+20+20	994 (451)	6.4

2.4 Sampling Approach

ORD's small, light-weight emission sampling package termed the "Kolibri" was used for the aerial emission sampling, Figure 2-4. Aerial sampling was conducted by a UAS carrying the Kolibri at a height of less than 400 feet above ground level. The main sampling platform for this study was the UAS Alta X Freefly and the backup UAS was the Aurelia X8.

Figure 2-4. U.S. EPA's Kolibri emission instrument system mounted on the undercarriage of the UAS Aurelia X8.

2.5 Target Emission Compounds

Target compounds include carbon monoxide (CO), carbon dioxide (CO_2), particulate matter of 2.5 µm aerodynamic diameter ($PM_{2.5}$), elemental/organic carbon (EC/OC), and total carbon (TC). Targeted emissions and their sampling methods 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	Instrument/Method	Frequency
CO_2	K30 FR, NDIR	Continuous
CO	E2V EC4-500-CO, Electrochemical cell	Continuous
$PM_{2.5}$	PEM Impactor, Teflon filter, gravimetric	Batch
EC/OC/TC	PMI impactor, Quartz filter, thermal-optical	Batch

Table 2-3. Number of Batch Samples Collected in Each Test Configuration.

Burn #	Test Condition	$PM_{2.5}$	TC/OC/EC
1	Baseline	2	2
2	Baseline	2	2
3	Oil added during burn once	1	1
4	Oil added during burn once	1	1
5	Oil added during burn twice	1	1
6	Oil added during burn three times	2	2

2.6 Calculations

2.6.1 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).

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

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

2.6.2 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

2.6.3 Modified Combustion Efficiency

The Modified Combustion Efficiency (MCE) was used to calculate how well the oil burned.

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

$$MCE_G = \frac{CO_2}{CO_2 + CO} \qquad Equation\ 4$$

Where:

MCE_T = modified combustion efficiency gas + particulate phase
MCE_G = modified combustion efficiency gas phase
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)

4 MEASUREMENT AND QUALITY ASSURANCE PROCEDURES

4.1 CO_2 measurements

The Kolibri system uses a CO_2 Engine® K30 Fast Response (FR) (SenseAir, Delsbo, Sweden) to measure CO_2 concentration by means of non-dispersive infrared absorption (NDIR). Sensor output voltage is linear from 0 to approximately 7900 ppmv. The response time (t_{95}) is less than 10 seconds and measurement is accurate within 5% error. The sensor can operate at temperature ranges -10-40ºC and RH 0-95%. In the field, a particulate filter will precede the sensor's optical lens and CO_2 background samples was taken daily prior to sampling. The CO_2 Engine® K30 FR was calibrated for CO_2 on a daily basis in accordance with EPA OTM-48 [2]. All gas cylinders used for calibration were certified by the suppliers that they are traceable to NIST standards. Data were recorded on a USB-based microcontroller board using an Arduino-generated data program.

The daily CO_2 system was less than 2% for each of the calibration gases which is within the ±5% acceptance criteria of the sensor (Table 3-1).

Table 3-1. CO_2 System drift.

Calibration gas concentration	11-01-2022	11-02-2022	11-03-2022
408 ppm	1.98%	0.09%	0.93%
1534 ppm	1.02%	0.15%	0.80%
1986 ppm	0.84%	0.25%	1.15%

4.2 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 1-500 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 EPA OTM-48 [2]. All gas cylinders used for calibration were certified by the suppliers that they are traceable to NIST standards. Data were recorded on a USB-based microcontroller board using an Arduinogenerated data program.

The daily CO system drift was less than 4.5% which is within the ±5% acceptance criteria of the sensor, with the exception for 11-03-2022 at 100 ppm with drift of 5.67% (Table 3-2). This drift had minimal impact on the results as the measured CO concentration in the plume was less than 22 ppm.

Table 3-2. CO System drift.

Calibration gas concentration	11-01-2022	11-02-2022	11-03-2022
0 ppm	0.03*	0.07*	0.020*
20 ppm	1.28%	0.51%	4.19%
100 ppm	0.65%	1.33%	5.67%

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

4.3 $PM_{2.5}$

The Kolibri sampled $PM_{2.5}$ with SKC Personal Environmental Monitor (PEM) impactors (SKC Inc., PA USA) 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 in the $PM_{2.5}$ impactor was collected on an oiled impaction disc mounted on the top of the filter cassette. The sample pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA). The Teflon filters were pre- and post-weigh according to 40 CFR Part 50 Appendix J and L [3, 4].

4.4 Total Carbon, Elemental Carbon, Organic Carbon

OC/EC/TC was sampled with a SKC $PM_{2.5}$ 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 was collected on an oiled 25 mm impaction disc mounted on the top of the filter cassette. The sample pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA). The OC/EC/TC was analyzed via a modified thermal-optical analysis (TOA) using NIOSH Method 5040 [5] and Khan et al. [6].

5 RESULTS

5.1 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 consumed oil, see Equation 2 in Chapter 2.6.2. The largest mass loss percentage (97.1%) was found when initial start mass oil per area was 6.4 kg/m^2 and oil was added four times (Burn 6, Figure 4-1). The lowest mass loss percentage (90.8%) occurred when the initial start mass oil per area was the highest, 25.6 kg/m^2, and all oil was burned at once (Burn 1, Figure 4-1). These data can be compared to the previous boom ratio study with mass losses of 94.3, 97.1 and 99.6% with boom ratios 1:1, 4:1 and 9:1, respectively with an initial oil mass per area of 9.3 kg/m^2 [7].

Table 4-1. Oil residue in each test.

Burn Number	Test Condition	Initial Oil gallons	Mass initial[a] Total oil (kg)	Residue[a] (kg)	Mass loss (%)	Burn Time (min:sec)
1	Baseline – initial oil	160	515	104.5	90.8	10:00
2	Baseline – initial oil	80	258	33.5	94.1	5:45
3	Oil added during burn	40+40	258	28.7	94.9	12:12
4	Oil added during burn	40+40	258	35.0	93.8	11:40
5	Oil added during burn	40+40+20	322	29.5	95.8	9:30
6	Oil added during burn	40+40+20+20+20	451	28.4	97.1	

[a] Measured from collected oil residue by CRREL.

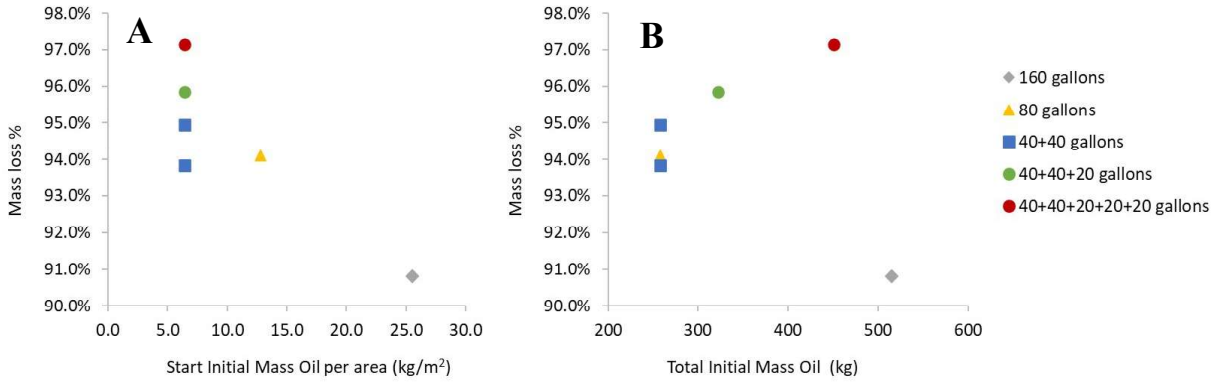

Figure 4-1. Mass loss versus A) mass start oil per area and B) total initial mass oil.

5.2 Combustion Gases

The MCE_T ranged from 0.653 to 0.870 (Table 4-2) where the higher MCE_T was similar to those found from oil burns using a boom ratio of 1:1 (0.864) [7].

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

Burn No.	Test Condition	CO_2 g/kg oil initial	CO g/kg oil initial	CO_2 g/kg oil consumed	CO g/kg oil consumed	MCE_G	MCE_T
1	160 gallons	2648	40	2916	45	0.967	0.866
2	80 gallons	2678	57	2419	51	0.945	0.730
3	40+40 gallons	2351	21	2476	22	0.987	0.774
4	40+40 gallons	2398	53	2556	57	0.966	0.778
5	40+40+20 gallons	2012	56	2099	59	0.961	0.653
6	40+40+20+20+20 gallons	2598	49	2674	51	0.977	0.870

5.3 Oil Consumption and Modified Combustion Efficiency

Figure 4-2 shows the MCE_T versus mass loss. No trends or correlations were found between the oil consumption and MCE_T.

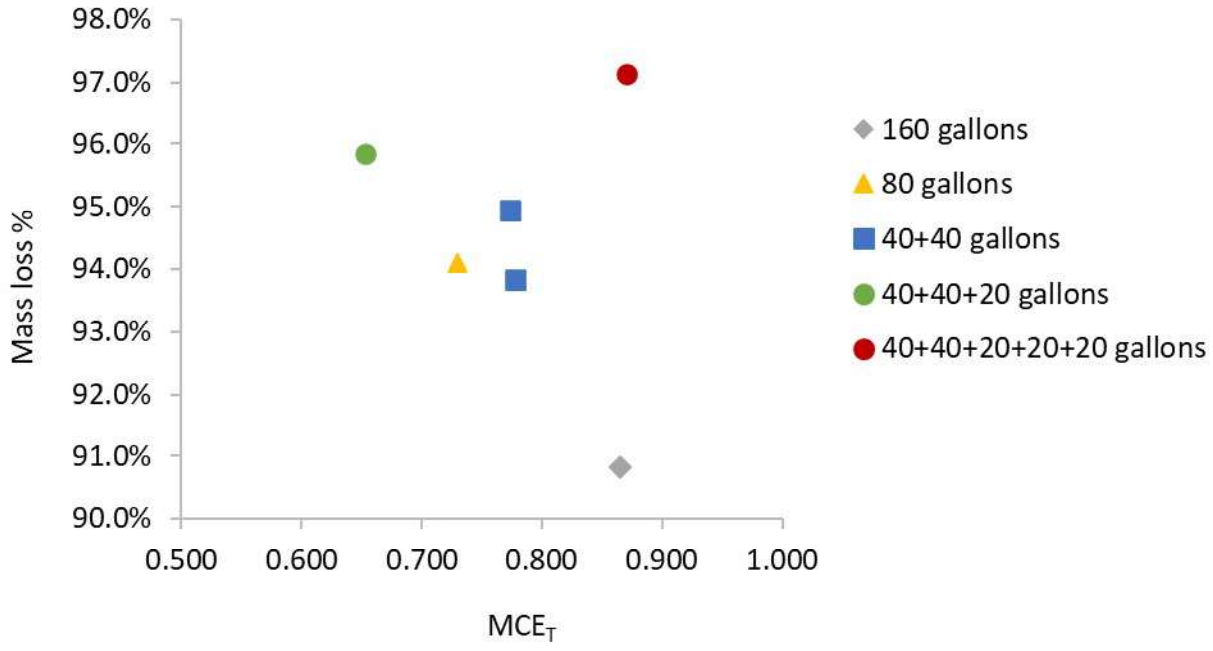

Figure 4-2. Modified combustion efficiency versus mass loss.

5.4 $PM_{2.5}$

The $PM_{2.5}$ emissions were found to decrease with increased combustion efficiency (Figure 4-3), consistent with previous results [7]. The lowest emission factors were emitted when burning 160 gallons of oil all at once and when burning 140 gallons of oil continuously added. These $PM_{2.5}$ emission factors were in similar range to those emitted from oil burns using a boom ratio of 1:1 conducted in November 2018 [7] as shown in Figure 4-4.

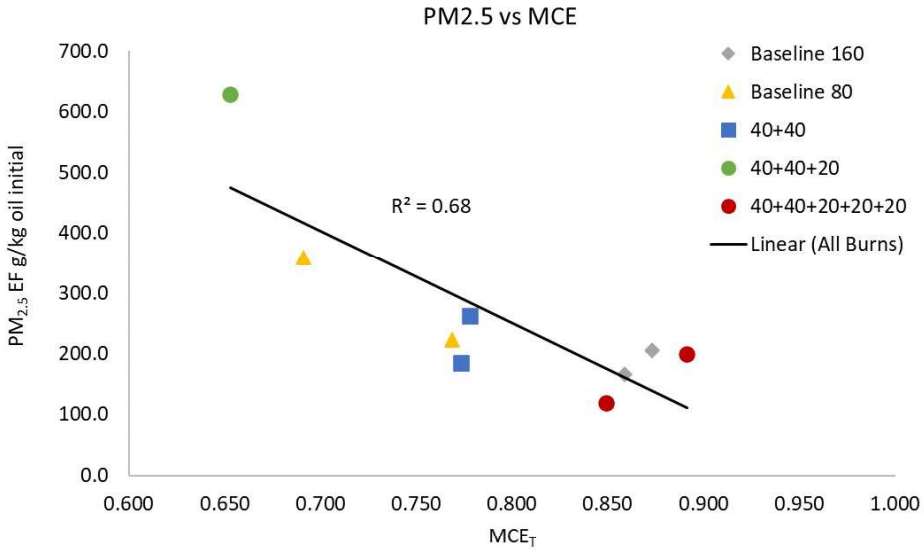

Figure 4-3. Modified combustion efficiency versus $PM_{2.5}$. Two $PM_{2.5}$ samples collected from some test configurations.

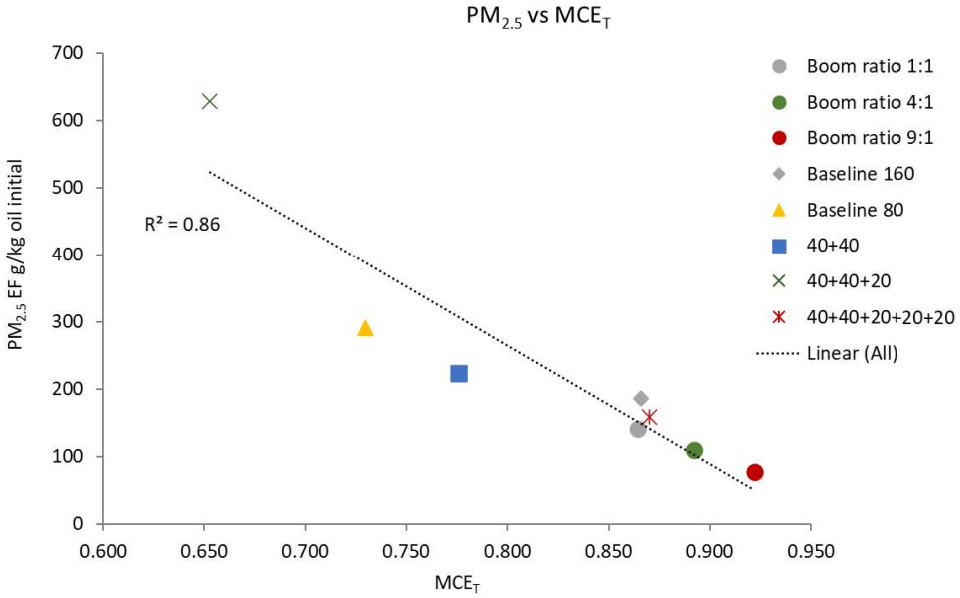

Figure 4-4. $PM_{2.5}$ emission factors versus modified combustion efficiency from this study and a previous study using different boom ratios Aurell et al., 2021 [7].

No apparent trend was found between $PM_{2.5}$ emissions and Oil Mass Loss (Figure 4-5), which is in agreement with the previous boom aspect ratio study conducted in November 2018 that did not see any trends between PM emissions and Oil Mass Loss [7]. Emission factors from each test configuration are shown in Table 4-3.

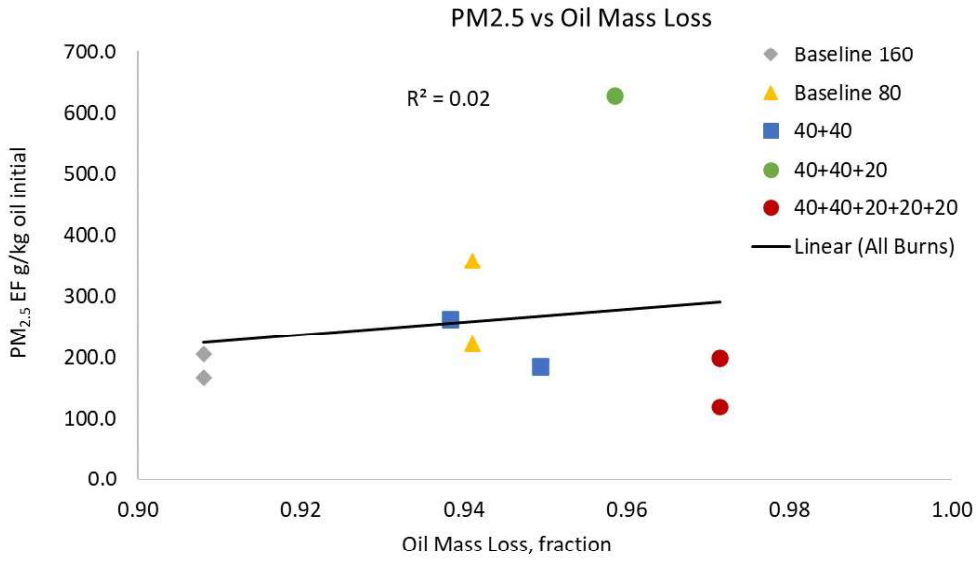

Figure 4-5. Oil mass loss versus $PM_{2.5}$.

Table 4-3. $PM_{2.5}$ emission factors from each test configuration.

Burn No.	Test Condition	$PM_{2.5}$ g/kg oil initial	$PM_{2.5}$ g/kg oil consumed	MCE_T	MCE_G
1	160 gallons	186.1	204.9	0.866	0.967
2	80 gallons	290.7	308.9	0.730	0.945
3	40+40 gallons	185.5	195.4	0.774	0.989
4	40+40 gallons	262.3	279.5	0.778	0.958
5	40+40+20 gallons	628.9	656.2	0.653	0.851
6	40+40+20+20+20 gallons	159.1	163.8	0.870	0.977

5.5 Total Carbon, Elemental Carbon and Organic Carbon

The TC/EC/OC emission factors are shown in Table 4-4. On average, 81% of the PM mass was carbon, of which 74% was elemental carbon.

Table 4-4. Total carbon, elemental carbon, and organic carbon emission factors.

Burn No.	Test Condition	OC	EC	TC	OC	EC	TC
		g/kg oil initial			g/kg oil consumed		
1	160 gallons	10.2	96.6	106.8	11.2	106.4	117.6
2	80 gallons	130.7	154.8	285.5	138.9	164.5	303.4
3	40+40 gallons	139.4	97.4	236.8	146.8	102.6	249.4
4	40+40 gallons	40.9	164.1	205.0	43.6	174.8	218.5
5	40+40+20 gallons	138.6	299.1	436.9	144.6	312.0	455.9
6	40+40+20+20+20 gallons	12.6	85.4	98.1	13.0	88.0	101.0

6 CONCLUSIONS

Six in situ oil burns were conducted using a boom ratio of 3:1 using three different initial oil masses per area 25.6, 12.8 and 6.4 kg/m^2. In four of the six tests additional oil was added as the burn progressed in order to mimic real offshore oil burns with continual oil collection. The MCE_T and $PM_{2.5}$ emissions ranged from 0.87 to 0.65 and 159 to 629 g/kg initial oil, respectively, where the $PM_{2.5}$ emissions decreased with increased MCE_T. This near four-fold range in the $PM_{2.5}$ emission factor for similar conditions of oil addition (40+40+20 gallons and 40+40+20+20+20 gallons) is both promising and challenging, indicating that further study would be necessary to understand the combustion phenomena that lead to these differences. The lowest $PM_{2.5}$ emission factors were emitted when burning 160 gallons of oil all at once (25.6 kg/m^2) and when oil was continuously added to an initial 40 gallons burn (starting at 6.4 kg/m^2, 40+40+20+20+20 gallons, total of 140 gallons). These lower $PM_{2.5}$ emission factors and corresponding MCEs were similar to those found from a previous in-ground tank study at CRREL using a boom aspect ratio of 1:1. The larger scale used in this study with a burn area of 20.1 m^2 and 1136 kg initial oil compared to the 3.4 m^2 and 31 kg initial oil used in the boom aspect ratio study may be why the results in this study using a boom ratio of 3:1 were similar to those with a boom ratio of 1:1. The larger scale did not affect the mass loss as the mass loss percentage was in the same range in this study (93.8-97.1%) as in the boom ratio study (94.399.6%) when the initial oil mass per area was less than 12.8 kg/m^2. While conclusions are tempered by lack of repeats, it appears that incremental addition of oil results in greater oil consumption (Figure 4-1) and lower $PM_{2.5}$ emission factors.

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