

**Emission Measurements from Thermal Decontamination of  
Potentially Explosive Materials:  
Naval Surface Warfare Center Indian Head Division**



Supplemental Report

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## ABSTRACT

The Naval Surface Warfare Center Indian Head Division (NSWC IHD) uses a thermal method to decontaminate items that are potentially contaminated with trace amounts of energetics. These materials are termed “material potentially presenting an explosive hazard” or MPPEH. Included in their current thermal methods for decontaminating MPPEH, is open-air incineration using an array of stacked wooden pallets as the fuel source. As an alternative fuel source, NSWC IHD is looking to use an array of propane-fueled burner nozzles. The objective of this study was to compare emissions from the current practice using pallet piles with the alternative proposed practice of using a propane-fueled burner. The emission characterization from the two fuel sources was undertaken by U.S. EPA’s Office of Research and Development (ORD).

ORD used their in-house developed light-weight battery-powered and remotely controlled sampling equipment called the “Kolibri” to measure carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), PM<sub>2.5</sub> (particulate matter of mass median diameter 2.5 μm or less), Black Carbon (BC), total carbon/organic carbon/elemental carbon (TC/OC/EC), and volatile organic compounds (VOCs) from the plumes of the two fuel sources. The Kolibri package was attached to the body of an unmanned aerial system (UAS) owned and operated by University of Maryland (UMD) UAS Test Site. UMD’s UAS operator maneuvered the sampling equipment into the plume with guidance from the Kolibri’s operator who monitored real-time temperature and CO<sub>2</sub> levels.

Two propane burns and one pallet pile burn were conducted. One PM<sub>2.5</sub> and one TC/OC/EC batch sample was collected for each burn. A single, composite sample for VOCs was collected from the two propane burns in order to ensure collection of sufficient sample to obtain detectable levels. The first propane burn ignited the adjacent pallet pile within a few minutes of the propane ignition. As a result, the PM<sub>2.5</sub> and TC/OC/EC batch samples collected from the first propane burn were excluded from the results.

The propane burner had a lower modified combustion efficiency (MCE, CO<sub>2</sub>/(CO<sub>2</sub> + CO)) than the burning pallet piles, 0.975 compared to 0.992. Due to the wood’s lower energy value the CO<sub>2</sub> emission factor in g CO<sub>2</sub>/kWh fuel from the wood pallet pile burn was almost two times higher than from the propane burner. The CO emission factor was two times higher from the propane burner than the wood pallet pile burn. It’s not clear from the limited tests whether this was an operational issue.

The PM<sub>2.5</sub> and BC emission factors on an energy basis were, respectively, approximately 14 and 26 times less for the propane burner than the pallet pile burn. The propane PM<sub>2.5</sub> emission factor on a fuel mass basis was in the same range as previous, similar measurements. The benzene emission factor from the wood pallet burn was three times higher than the propane burner. However, the propane burner emitted surprisingly high emissions of methylene chloride and of other chlorinated VOCs not found from previous similar measurements. These higher chlorinated VOC emissions may be a byproduct of the natural gas and crude oil refining where chlorides occur naturally or due to trace chemicals from fracking processes.

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## ACRONYMS

BC	Black carbon
C	Carbon
CA	California
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
CRTDA	Caffee Road Thermal Decontamination Area
DAS	Data acquisition system
EC	Elemental carbon
FL	Florida
FR	Fast response
GC/MS	Gas chromatography/mass spectrometry
GPS	Global position system
IR	Infrared
MCE	Modified combustion efficiency
MD	Maryland
MPPEH	Material Potentially Presenting an Explosive Hazard
NDIR	Non-dispersive infrared
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute for Standards and Technology
NSF	Naval Support Facility
NSWC	US Navy Surface Warfare Center, Dahlgren
NSWC DD	Naval Surface Warfare Center Dahlgren Division
NSWC IHD	Naval Surface Warfare Center Indian Head Division
OC	Organic carbon
ORD	Office of Research and Development
PEM	Personal environmental monitor
PM	Particulate matter
PM <sub>2.5</sub>	Particulate Matter equal or less than 2.5 microns
PMI	Personal modular impactor
ppm	parts per million
QAPP	Quality assurance project plan
RH	Relative humidity
RPD	Relative percent difference
SD	Secure digital
TC	Total carbon
TOA	Thermal optical analysis
UAS	Unmanned aircraft system
UDRI	University of Dayton Research Institute
UMD	University of Maryland

USB  
UV  
VOCs

Universal serial bus  
Ultraviolet  
Volatile organic compounds

# **1 INTRODUCTION**

## **1.1 Background**

The U.S. Environmental Protection Agency's Office of Research and Development (ORD) is participating in a test program with the Naval Surface Warfare Center Indian Head Division (NSWC IHD) to develop methods of measuring and quantifying emissions from open area combustion [1]. IHD plans to use the Caffee Road Thermal Decontamination Area (CRTDA) located at Indian Head, Maryland, to process material generated on-site and classified as Material Potentially Presenting an Explosive Hazard (MPPEH). Thermal methods will be used to decontaminate items that are contaminated with trace amounts of energetics, such as materials accumulated as a result of demolition, out-of-service processing equipment, and empty production containers and materials. The CRTDA is an open-air decontamination area suitable for large combustible items. NSWC IHD currently employs procedural controls to ensure that thermal decontamination operation will be effective by using pre-burn waste materials surveys and monitoring surface thermocouples placed on the material being treated. The purpose of ORD's involvement is to sample, measure, and characterize the pollutants to provide a further level of assurance that emissions pose no undue risk.

## **1.2 Objective**

The objective is to compare emissions from the current practice of open-air incineration using an array of stacked wooden pallets as the fuel source versus a proposed practice of burning atop an array of propane-fueled burner nozzles.

## 2 MATERIALS AND METHODS

### 2.1 Test Location

Testing took place at CRTDA located at the southern end of Naval Support Facility (NSF) Indian Head Cornwallis Neck MD, at the end of Caffee Road along the Mattawoman Creek shoreline (Figure 2-1).



Figure 2-1. Location of the CRTDA. Second inset shows relation to Washington, D.C.

### 2.2 Test Set-up and Test Matrix

The CRTDA burn pad is approximately 40 feet square and consists of a layer of CR6 stone (i.e., blue stone ranging in size from rock dust to  $\frac{3}{4}$  inch). Reflective berms, approximately four to six feet in height, flank the north, east, and south sides of the burn pad. Two different fuels were tested: propane and wood pallets (Figure 2-2). Two propane burns were conducted (Table 2-1). The first propane burn ignited the wood pallets burn, which were placed too close to the propane burner.



Figure 2-2. A) Propane burner and B) pallets.

Table 2-1. Test Matrix.

Burn No.	Fuel
1	Propane
2	Pallets
3	Propane

### 2.3 Target Emission Compounds

Target compounds included carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), particulate matter < 2.5 μm (PM<sub>2.5</sub>), black carbon/ultraviolet particulate matter (BC/UVPM), total/organic/elemental carbons (TC/OC/EC), and volatile organic compounds (VOCs). Measurements were used to calculate emission factors based on the carbon balance method as described in section 2.7.1. 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 <sub>2</sub>	SenseAir CO2 Engine® K30 Fast Response (FR), NDIR	Continuous
CO	EC4-500-CO, Electrochemical cell	Continuous
PM <sub>2.5</sub>	Impactor/Teflon® filter/gravimetric	Batch
VOCs	Carbotrap 300	Batch
BC/UVPM	Aethalometer, MA200	Continuous
TC/OC/EC	Impactor/Quartz filter	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<sub>2</sub> 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 2-3). 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<sub>2</sub> and CO data, turning on and off sampling pumps, and displaying sampling time, sampling volume, battery level, and ambient temperature.

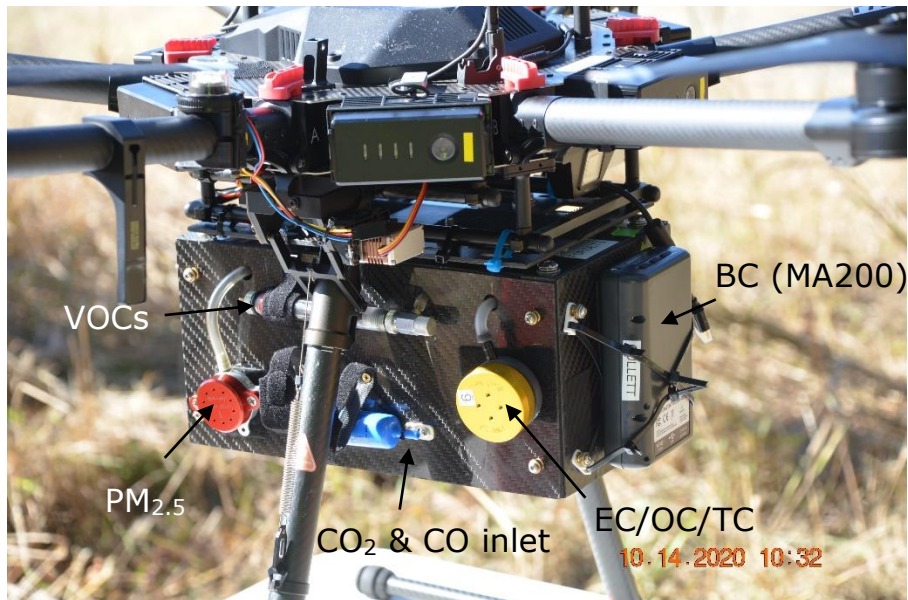


Figure 2-3. "Kolibri" sampling instrumentation.

## 2.5 Plume Sampling

Aerial plume sampling was conducted by an unmanned aircraft system (UAS) operated by University of Maryland (UMD) UAS Test Site. UMD's UAS is a DJI Matrice M600 which is a 6-rotor diameter (hexacopter) with a 9.1 kg weight and a 15.1 kg maximum acceptable gross take-off weight. It is controlled automatically or by pilot-in-command modes and provides the operator a global position system (GPS) display screen of location in real time with a 900 MHz telemetry system. The M600 has a triple redundant inertial measurement unit and GPS with a return to base function at a preset battery level charge.

ORD's Kolibri sampling system was attached underneath the body of the DJI M600 (**Error! Reference source not found.** A). UMD's UAS operator maneuvered the sampling equipment into the plume with guidance from the Kolibri's operator. The Kolibri's operator monitored the temperature and CO<sub>2</sub> and CO levels; levels above ambient background concentrations indicated that the Kolibri sampler was within the plume.

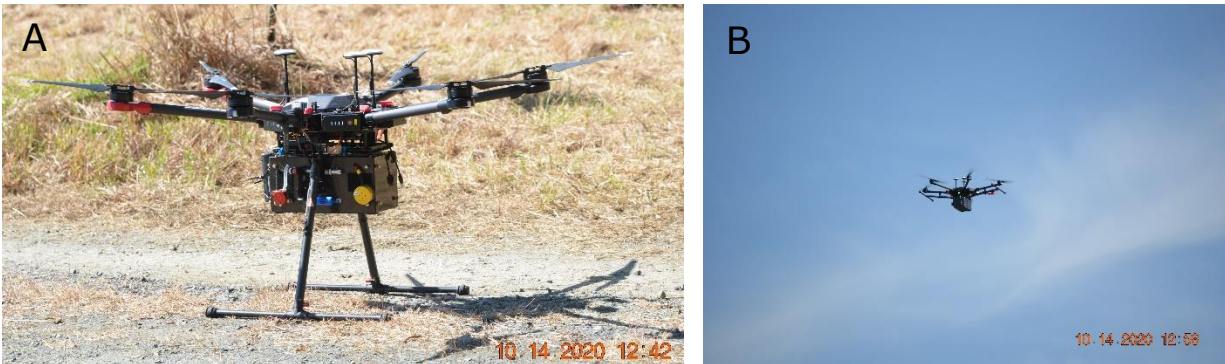


Figure 2-4. A) Kolibri sampler mounted on the UAS (DJI M600) and B) UAS and Kolibri in the air.

## 2.6 Number of Samples Collected

The number of batch samples collected are shown in Table 2-3. One PM<sub>2.5</sub> and one TC/OC/EC sample was collected for each burn. A single, composite sample for VOCs was collected from the two propane burns in order to ensure collection of sufficient sample to obtain detectable levels. Ambient air background samples were collected for 30 minutes upwind of the burn site and after the burns concluded.

Table 2-3. Number of batch samples collected.

Burn No.	Fuel Type	PM <sub>2.5</sub>	TC/OC/EC	VOC
1	Propane	1	1	1
2	Pallets	1	1	1
3	Propane	1	1	Same as Burn #1

Burn No.	Fuel Type	PM <sub>2.5</sub>	TC/OC/EC	VOC
Ambient Air Background		1	1	1
<b>Total No. of Samples</b>		<b>4</b>	<b>4</b>	<b>3</b>

## 2.7 Calculations

### 2.7.1 Emission Factors in Mass Analyte per Mass Initial Fuel

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<sub>2</sub> measurements) and the carbon percentage of the fuel. The resultant emission factors are expressed as mass of pollutant per mass of fuel burned (Equation 1).

$$EF = F_C \times \frac{\text{Analyte}_{ij}}{c_j} \quad \text{Equation 1}$$

Where:

$EF$  = The emission factor for target analyte  $i$  (mg Analyte <sub>$i$</sub> /kg fuel)

$F_C$  = Carbon fraction in the fuel, see **Error! Reference source not found.**

$\text{Analyte}_{ij}$  = background-corrected concentration (mg Analyte <sub>$i$</sub> /m<sup>3</sup>) of the target analyte  $i$  collected from the volume element  $j$  of the plume.

$c_j$  = background-corrected concentration of carbon (kg Carbon/m<sup>3</sup>) collected from volume element  $j$  of the plume

### 2.7.2 Emission Factors in Mass Analyte per kWh Fuel

$$EF_E = \frac{EF}{C_V} \quad \text{Equation 2}$$

Where:

$EF_E$  = The emission factor for target analyte  $i$  (mass Analyte <sub>$i$</sub> /kwh Fuel)

$EF$  = The emission factor for target analyte  $i$  (mg Analyte <sub>$i$</sub> /kg fuel)

$C_V$  = Calorific value of the fuel, see **Error! Reference source not found.**

Table 2-4. Carbon Fraction and Calorific value of the fuel.

Fuel	F <sub>c</sub>	Calorific Value kWh/kg Fuel
Propane	0.82	13.99
Pallets	0.50	4.50

### 2.7.3 Modified Combustion Efficiency

The modified combustion efficiency (MCE) was used to calculate how well the fuel burned. Two approaches were used. One approach includes gas phase (CO<sub>2</sub> and CO) MCE<sub>g</sub> (Equation 3) and the other includes Total Carbon MCE<sub>T</sub> (Equation 4).

$$MCE_g = \frac{CO_2}{CO_2+CO} \quad \text{Equation 3}$$

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

Where:

MCE<sub>g</sub> = modified combustion efficiency only including gas phase

MCE<sub>T</sub> = modified combustion efficiency including TC

CO<sub>2</sub> = 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

Relative percent difference (RPD) were used as a measure of dispersion, calculations shown in Equation 5.

$$RPD (\%) = 100 \times \frac{x_1 - x_2}{\frac{x_1 + x_2}{2}} \quad \text{Equation 5}$$

where:

x<sub>1</sub> = sample value one

x<sub>2</sub> = sample value two

### 3 MEASUREMENT AND QUALITY ASSURANCE PROCEDURES

#### 3.1 CO<sub>2</sub> Measurements

The Kolibri system's CO<sub>2</sub> sensor (CO<sub>2</sub> Engine® K30 Fast Response (FR), SenseAir, Delsbo, Sweden) measures CO<sub>2</sub> concentration by means of non-dispersive infrared absorption (NDIR). Sensor output voltage is linear from 0 to approximately 8,000 ppm. The response time (t<sub>95</sub>) 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<sub>2</sub> Engine® K30 FR sensor was calibrated prior to field departure from 0 to 8082 ppm with ± 2 ppm error using EPA Method 3A [2]. The K30 was calibrated for CO<sub>2</sub> on the day of the sampling effort in accordance with EPA Method 3A [2] using a three-point calibration at 400, 1000, and 6000 ppm. The system drift of the K30 was determined by measuring calibration gas concentrations post-sampling and calculating the difference between the pre- and post-sampling calibration measurements. In the field, the CO<sub>2</sub> background was measured prior to sampling. Data were recorded on the Teensy, a universal serial bus (USB)-based microcontroller board using an Arduino-generated data program.

All calibration gases were certified by the supplier that they were traceable to National Institute of Standards and Technology (NIST) standards. The daily CO<sub>2</sub> system drift for the Kolibri unit was less than 1.56% which is within the ±5% acceptance criteria of the sensor (Table 3-1).

Table 3-1. CO<sub>2</sub> system drift.

Calibration gas concentration	Kolibri
400 ppm	0.02%
1000 ppm	1.56%
6000 ppm	1.04%

#### 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 at the field site the day of sampling for CO in accordance

with U.S. EPA Method 3A [2] using a three-point calibration at 0, 10, and 50 ppm. The system drift of the e2V was determined by measuring calibration gas concentrations post-sampling and calculating the difference between the pre- and post-sampling calibration measurements. In the field, the CO background was measured prior to sampling. 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.

All calibration gases were certified by the supplier that they were traceable to NIST standards. The daily CO system drift for the Kolibri unit was less than 3.5% which is within the  $\pm 5\%$  acceptance criteria of the sensor (Table 3-2).

Table 3-2. CO system drift.

Calibration gas concentration	Kolibri
0 ppm	0.86 ppm*
10 ppm	3.5%
50 ppm	2.2%

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

### 3.3 PM<sub>2.5</sub>

PM<sub>2.5</sub> 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<sub>2.5</sub> impactor. The constant flow pump was calibrated the day of sampling effort 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 fourteen days of sampling completion.

### 3.4 Total Carbon, Organic Carbon, and Elemental Carbon

TC/OC/EC was sampled with SKC's PM<sub>2.5</sub> 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<sub>2.5</sub> impactor were collected on an oiled 25 mm impaction disc mounted on the top of the filter cassette. The constant flow pump was calibrated the day of sampling effort 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 fourteen days of sampling completion.

### 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  $\text{ng}/\text{m}^3$  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) with a sampling flow rate of 267 mL/min in accordance with U.S. EPA Method TO-17 [11]. The constant flow pump was calibrated the day of the sampling and checked after testing with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg, FL, USA).

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 VOC emission factors were background corrected. The target VOCs analyzed from Carbopack 300 are stated in Table 3-3. The surrogate spikes (1,2-dichloroethane- $d_4$ , toluene- $d_8$ , bromofluorobenzene) used for the QA/QC had recoveries of 77-132% for all samples including laboratory method blank, which is within the accuracy of the method; recoveries of 70-140%. The duplicate run lab control sample had RPDs less than 17% for all VOCs which is within the 25% RPD accuracy limit of the method.

Table 3-3. VOCs analyzed by U.S. EPA Method TO-17.

VOCs		
1,1,1-Trichloroethane*	2-Hexanone	Ethanol

1,1,2,2-Tetrachloroethane*	2-Propanol (Isopropyl Alcohol)	Ethylbenzene*
1,1,2-Trichloroethane*	4-Methyl-2-pentanone	Hexachlorobutadiene*
1,1-Dichloroethane	Acetone	m,p-Xylenes*
1,1-Dichloroethene	Acetonitrile*	Methyl tert-Butyl Ether
1,2,4-Trichlorobenzene*	Benzene*	Methylene Chloride*
1,2,4-Trimethylbenzene	Bromodichloromethane	Naphthalene*
1,2-Dibromo-3-chloropropane	Bromoform*	n-Heptane
1,2-Dibromoethane	Carbon Disulfide*	n-Hexane
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	Carbon Tetrachloride*	n-Octane
1,2-Dichlorobenzene	Chlorobenzene*	o-Xylene*
1,2-Dichloroethane	Chloroethane	Styrene*
1,2-Dichloropropane	Chloroform*	Tetrachloroethene
1,3,5-Trimethylbenzene	Chloromethane*	Tetrahydrofuran (THF)
1,3-Butadiene*	cis-1,2-Dichloroethene	Toluene*
1,3-Dichlorobenzene	cis-1,3-Dichloropropene*	trans-1,2-Dichloroethene
1,4-Dichlorobenzene	Cumene*	trans-1,3-Dichloropropene
1,4-Dioxane	Cyclohexane	Trichloroethene
2,2,4-Trimethylpentane (Isooctane)	Dibromochloromethane	Trichlorofluoromethane
2-Butanone (MEK)*	Dichlorodifluoromethane (CFC 12)	Trichlorotrifluoroethane
		Vinyl Chloride*

\* On U.S. EPA's list of hazardous air pollutants [12].

### 3.7 Other Measurements

The Kolibri was also equipped with a temperature and barometric pressure sensor (BMP 180, Adafruit, New York, USA) and RH (DHT22 Adafruit, New York, USA) as summarized in Table 3-4.

Table 3-4. GPS, Pressure, and Temperature Sensors.

Target	Sensor	Range
Temperature	BMP 180	-25 to 85°C
Barometric pressure	BMP 180	300-1100 hPa
Relative Humidity	Adafruit DHT22	0-100%

## 4 RESULTS AND DISCUSSION

The first propane burn ignited the pallet pile within a few minutes of the propane ignition. When this was noted after approximately 4 minutes of sampling time, the sampling equipment was turned off and the UAS returned to its takeoff/landing area. The data below revealed that the propane plume mixed with the pallet pile burn plume after approximately 2 min (see Figure 4-1A). As a result, the PM<sub>2.5</sub> and TC/OC/EC batch samples collected from the first propane burn have been excluded from the emission factor results.

### 4.1 Black Carbon and UVPM

BC and UVPM were continuously measured in the plume. The BC and CO<sub>2</sub> concentration traces from each burn are shown in Figure 4-1, which shows that the propane plume from the second half of Burn No. 1 (at approximately 12:00, Figure 4-1A) is mixed with emissions from the pallets. The pallets resulted in approximately 26 times higher BC emission factors than propane when comparing Burns 2 and 3 (Table 4-1, IR BC column). The BC emission factor from the pallets was 76 mg/kg fuel which is lower than values for open burns of timber slash piles of 240 mg/kg fuel [14]. The propane emission factor of 8.7 mg/kg fuel is higher than found from flaring of propane 1.0 mg/kg fuel (calculated from 0.51 kg soot/10<sup>3</sup> m<sup>3</sup> fuel and propane density of 493 kg/m<sup>3</sup>) [15].

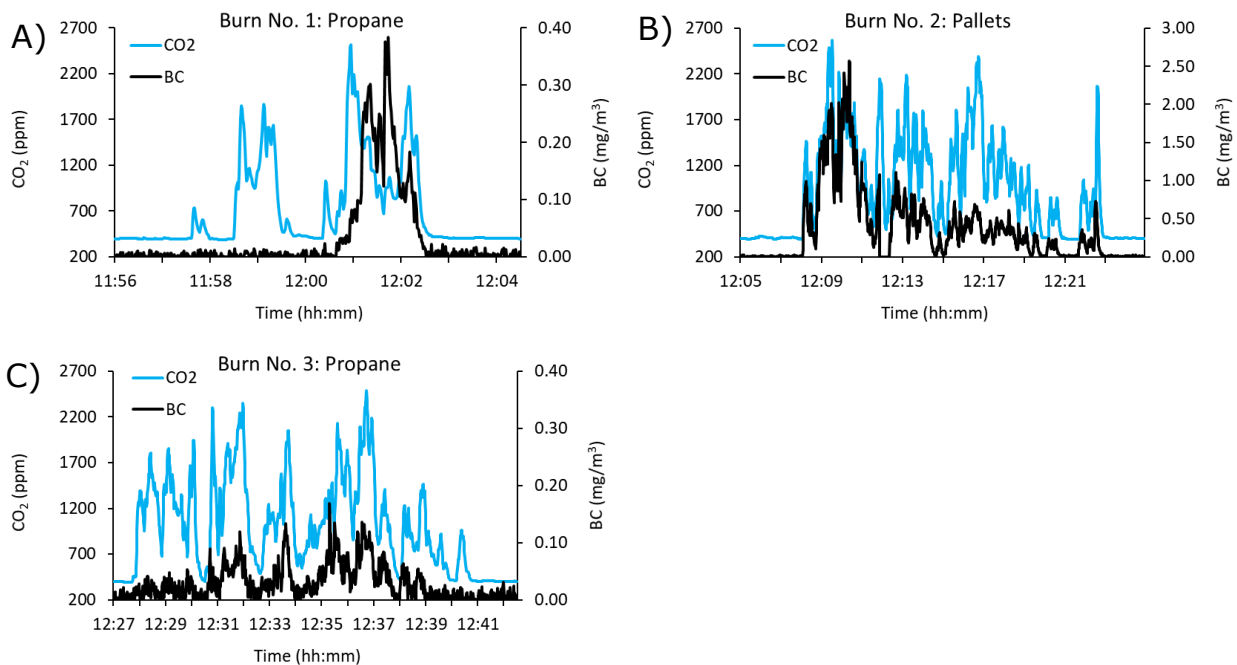


Figure 4-1. Black carbon and CO<sub>2</sub> concentration traces from each burn: A) Burn No. 1 Propane, B) Burn No. 2 Pallets, and C) Burn No. 3 Propane.

Table 4-1. UVPM and BC emission factors in g/kWh fuel from each burn.

Burn. No.	Fuel	UVPM	Blue BC	Green BC	Red BC	IR BC
g/kWh Fuel						
1	Propane	ND	ND	ND	ND	ND
1	Mix: Propane + Pallets	2.25	2.27	2.16	2.11	2.00
2	Pallets	18.19	19.22	18.43	18.08	16.81
3	Propane	0.68	0.68	0.65	0.64	0.62

Table 4-2. UVPM and BC emission factors in mg/kg fuel from each burn.

Burn. No.	Fuel	UVPM	Blue BC	Green BC	Red BC	IR BC
mg/kg fuel						
1	Propane	ND	ND	ND	ND	ND
1	Mix: Propane + Pallets	31.48	31.75	30.17	29.51	28.00
2	Pallets	81.88	86.50	82.92	81.37	75.65
3	Propane	9.52	9.56	9.11	9.00	8.71

## 4.2 Combustion Gases

The CO levels were lower from the pallet burn than the propane burns as shown in Figure 4-2, resulting in a higher MCE of 0.994 from the pallet burn than propane burns with MCEs of 0.977 and 0.975 (Table 4-3). The propane burn’s MCEs reported here are lower than those observed from propane burns previously measured from a propane burner at the Naval Surface Warfare Center Dahlgren Division (NSWCDD) of  $0.993 \pm 0.001$  [13]. The MCE from the pallets (0.994) were higher than MCE from open burning of timber slash piles ( $0.941 \pm 0.030$ ) [14], as might be expected for the thinner, drier pallets.

The CO<sub>2</sub> emission factor was lower from the pallet burn than the propane burns when presented as g/kg fuel, 497 g/kg fuel and on average 803 g/kg fuel, respectively (Table 4-3). Due to the wood’s lower energy value (4.5 kWh vs 13.99 kWh/fuel for propane) the CO<sub>2</sub> emission factor from the pallets (110 g/kWh) was almost two times higher than from the propane burn (57 g/kWh). The CO emission factor was lower from the pallets burn for both emission factor units.

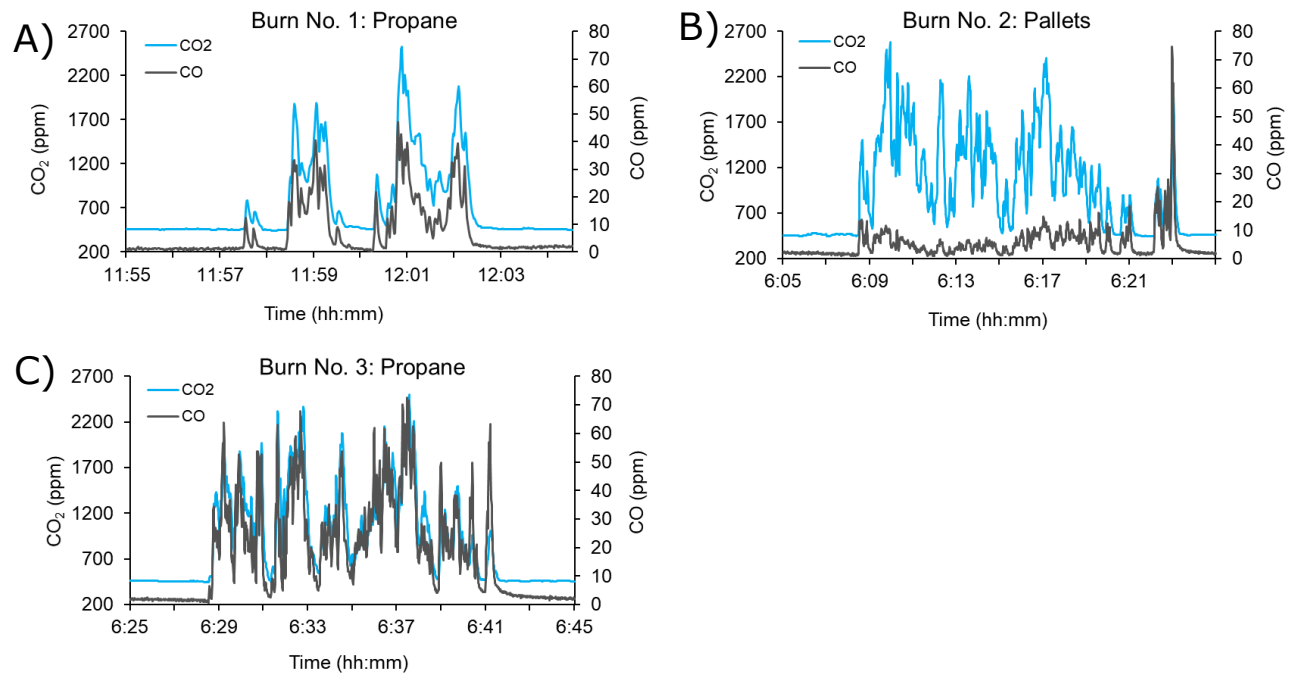


Figure 4-2. CO<sub>2</sub> and CO trace from A) Burn No. 1, B) Burn No. 2, and C) Burn No. 3.

Table 4-3. MCE and CO<sub>2</sub> and CO emission factors from each burn.

Burn No.	Fuel	Sample Duration min	MCE <sub>g</sub>	MCE <sub>τ</sub>	ΔCO <sub>2</sub> CO		ΔCO <sub>2</sub> CO		ΔCO <sub>2</sub> CO	
					ppm	g/kg fuel	g/kg fuel	g/kWh fuel	g/kWh fuel	
1*	Propane	1.9	0.977	NA	363	8.4	807	13.4	57.65	0.96
2	Pallets	13.7	0.994	0.992	601	3.4	497	2.6	110.52	0.59
3	Propane	12.8	0.975	0.969	543	14.1	800	20.4	57.16	1.46

\* Derived from the first part of burn 1 (time period 11:57-12:00, Figure 4-1A). NA – not applicable as no TC sample collected during the time period.

### 4.3 PM<sub>2.5</sub>

Lower PM<sub>2.5</sub> emission factors were found from the propane, 0.029 g/kWh fuel, than the pallets, 0.42 g/kWh fuel (Table 4-4). The propane PM<sub>2.5</sub> emission factor (0.40 g/kg fuel) is lower than the value obtained during previous testing of the propane burner at NSWCD 0.890±0.20 g/kg fuel [13] (Figure 4-3). The pallet PM<sub>2.5</sub> (emission factor of 1.9 g/kg fuel) was also lower than PM<sub>2.5</sub> emitted from open burning of timber slash piles (emission factor 4.9±1.8 g/kg fuel) [14] (Figure 4-3).

Table 4-4. *PM<sub>2.5</sub> Emission factors from each burn.*

Burn No.	Fuel	MCE <sub>g</sub>	PM <sub>2.5</sub>	PM <sub>2.5</sub>
			g/kg fuel	g/kWh fuel
1*	Propane	0.977	NA	NA
2	Pallets	0.994	1.87	0.42
3	Propane	0.975	0.40	0.029

\* Derived from the first part of burn 1 (time period 11:57-12:00, Figure 4-1A). NA – not applicable as no PM<sub>2.5</sub> sample was collected during the time period.

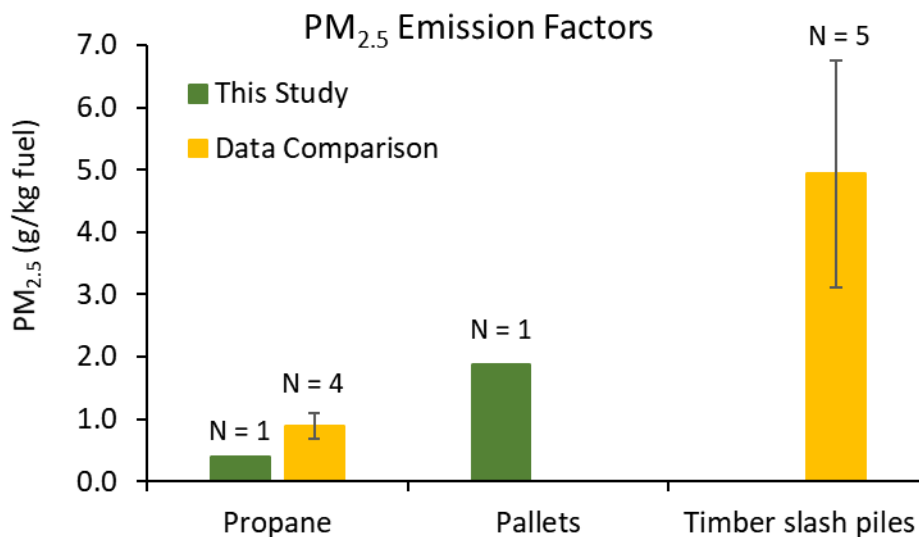


Figure 4-3. *PM<sub>2.5</sub> emission factors. Error bars equal 1 Stand. Dev. Data comparison for propane from Aurell et al., 2017 [13] and timber slash piles from Aurell et al., 2017 [14].*

#### 4.4 Total Carbon, Organic Carbon, and Elemental Carbon

Lower TC emission factors were found from the propane, 0.0024 g/kWh fuel, than the pallets, 0.22 g/kWh fuel (Table 4-45). Most of the TC emissions from burning pallets was made up of OC (72%) while 52% of the TC from the propane was made up by OC. Higher OC values are expected for wood combustion. The TC emission factors from both the propane burn and pallets burn were lower those emitted from NSWCD's propane burner [13] and open burning of timber slash piles [14] as shown in Figure 4-4.

Table 4-5. TC/OC/EC emission factors from each burn.

Burn No.	Fuel	MCE <sub>g</sub>	g/kg fuel			g/kWh fuel		
			TC	OC	EC	TC	OC	EC
1*	Propane	0.977	NA	NA	NA	NA	NA	NA
2	Pallets	0.994	1.00	0.72	0.28	0.222	0.159	0.063
3	Propane	0.975	0.033	0.017	0.016	0.0024	0.0012	0.0011

\* Derived from the first part of burn 1 (time period 11:57-12:00, Figure 4-1A). NA – not applicable as no EC/OC/TC sample was collected during the time period.

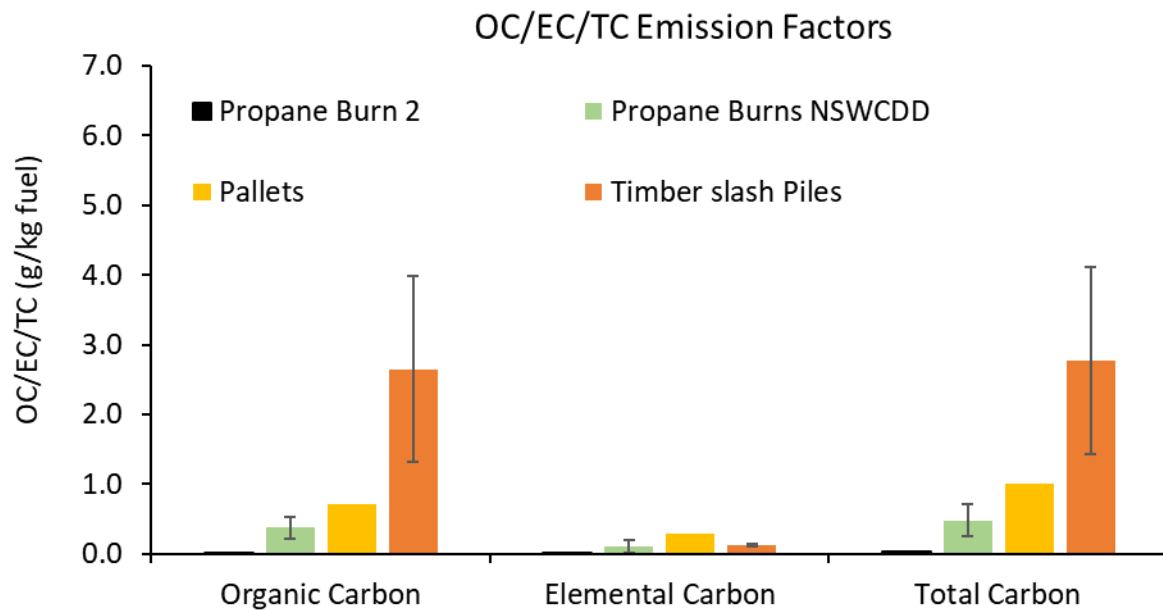


Figure 4-4. OC/EC/TC emission factors. Error bars equal 1 Stand. Dev. Data comparison Propane from Aurell et al., 2017 [13] and Timber slash piles Aurell et al., 2017 [14].

#### 4.5 Volatile Organic Compounds

Only a single VOC sample from each fuel type was taken. The propane VOC sample was composite sampled from both Burn No. 1 and Burn No. 2 where 84% of the sampled volume was collected from Burn No. 2 and the first part of Burn No. 1. Approximately 40% of the 61 analyzed VOCs were detected (Table 4-6). The benzene value was three times higher from the pallet burn (3.22 g/kWh fuel) than from the propane burner (1.11 g/kWh fuel) due to the wood's lower energy value (Table 2-4). When examining the emission factors per kg fuel burned, the

benzene values were low for both fuels, approximately 15 mg/kg fuel (Figure 4-5). These benzene levels are higher than from the NSW CDD's propane burner  $2.5 \pm 2.0$  mg/kg [13] and lower than from timber slash burn piles 115 mg/kg fuel [14].

Surprisingly, methylene chloride emissions (as well as other C-Cl compounds) were detected in the propane burn plume at high values, 1,803 mg/kg fuel. Similarly, high concentration values were found for acetone, acetonitrile, and ethanol for the propane burn (Figure 4-6). Methylene chloride has previously been found from propane burns (0.22 mg/kg fuel [13]), but at levels much lower than found here. Propane is a by-product from processing of natural gas and crude oil refining where chlorides naturally occur and may also be used in the fracking industry. Thus, the level of chlorides in the propane may differ depending on the location/vendor of the propane source, which may be a reason for the different methylene chloride levels found in this study compared to the NSW CDD's propane burner study. The source of these compounds remains to be determined.

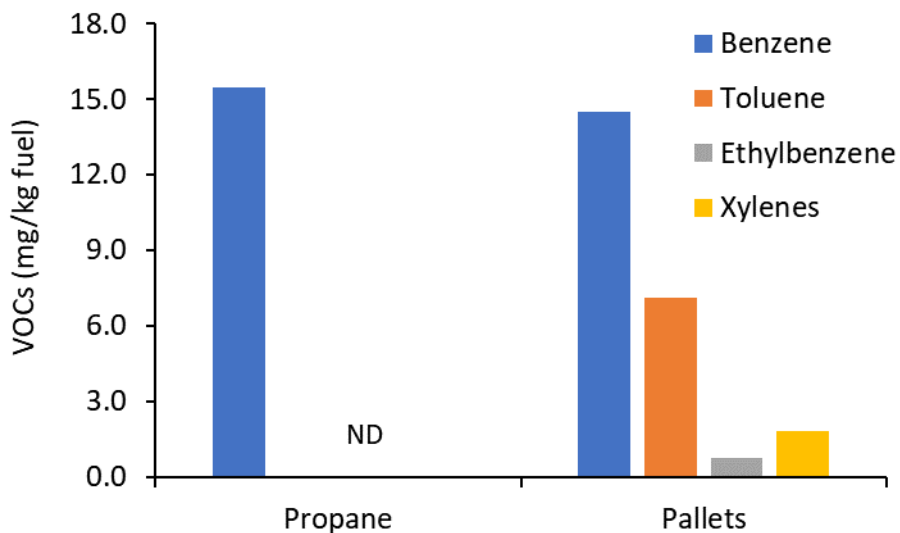


Figure 4-5. Benzene, toluene, ethylbenzene, and xylenes emission factors from each fuel. Note: Single samples only.

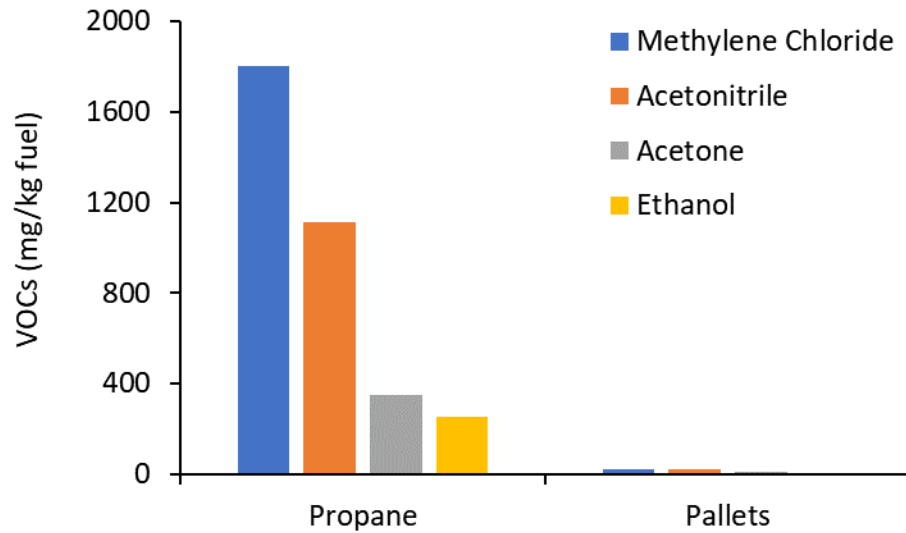


Figure 4-6. Methylene chloride, acetonitrile, acetone, and ethanol emission factors from each fuel type. Note: Single samples only.

Table 4-6. VOC emission factors.

VOC	Propane	Pallets	Propane	Pallets
	mg/kg fuel		mg/kWh Fuel	
Dichlorodifluoromethane (CFC 12)	9.88	ND	0.71	ND
Chloromethane	9.11	0.45	0.65	0.10
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 14)	0.80	ND	0.057	ND
Vinyl Chloride	ND	ND	ND	ND
1,3-Butadiene	9.64	0.57	0.69	0.13
Chloroethane	4.12	ND	0.29	ND
Ethanol	251.78	2.50	18.00	0.56
Acetonitrile	1111.84	21.69	79.47	4.82
Acetone	348.70	10.45	24.92	2.32
Trichlorofluoromethane	5.70	ND	0.41	ND
2-Propanol (Isopropyl Alcohol)	15.00	ND	1.07	ND
1,1-Dichloroethene	0.70	ND	0.050	ND
Methylene Chloride	1803.36	22.70	128.90	5.04
Trichlorotrifluoroethane	1.33	ND	0.10	ND
Carbon Disulfide	6.96	ND	0.50	ND
trans-1,2-Dichloroethene	2.25	ND	0.16	ND
1,1-Dichloroethane	ND	ND	ND	ND
Methyl tert-Butyl Ether	ND	ND	ND	ND

VOC	Propane	Pallets	Propane	Pallets
	mg/kg fuel		mg/kWh Fuel	
2-Butanone (MEK)	7.50	1.48	0.54	0.33
cis-1,2-Dichloroethene	ND	ND	ND	ND
n-Hexane	19.62	6.97	1.40	1.55
Chloroform	5.89	ND	0.42	ND
Tetrahydrofuran (THF)	3.91	0.45	0.28	0.10
1,2-Dichloroethane	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND
Benzene	15.48	14.51	1.11	3.22
Carbon Tetrachloride	0.13	0.35	0.0094	0.077
Cyclohexane	4.93	ND	0.35	ND
1,2-Dichloropropane	1.18	ND	0.084	ND
Bromodichloromethane	ND	ND	ND	ND
Trichloroethene	ND	ND	ND	ND
1,4-Dioxane	ND	0.91	ND	0.20
2,2,4-Trimethylpentane (Isooctane)	ND	0.82	ND	0.18
n-Heptane	ND	0.92	ND	0.20
cis-1,3-Dichloropropene	ND	ND	ND	ND
4-Methyl-2-pentanone	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND
Toluene	ND	7.13	ND	1.58
2-Hexanone	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND
n-Octane	ND	0.51	ND	0.11
Tetrachloroethene	ND	ND	ND	ND
Chlorobenzene	ND	ND	ND	ND
Ethylbenzene	ND	0.76	ND	0.17
m,p-Xylenes	ND	1.31	ND	0.29
Bromoform	ND	ND	ND	ND
Styrene	ND	2.31	ND	0.51
o-Xylene	ND	0.53	ND	0.12
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND
Cumene	ND	ND	ND	ND
1,3,5-Trimethylbenzene	ND	ND	ND	ND
1,2,4-Trimethylbenzene	ND	0.38	ND	0.084
1,3-Dichlorobenzene	ND	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND
1,2-Dibromo-3-chloropropane	ND	ND	ND	ND

VOC	Propane	Pallets	Propane	Pallets
	mg/kg fuel		mg/kWh Fuel	
1,2,4-Trichlorobenzene	ND	ND	ND	ND
Naphthalene	0.59	2.80	0.042	0.62
Hexachlorobutadiene	1.23	ND	0.088	ND

## 5 CONCLUSIONS

The propane burner emitted approximately 14 and 26 times less PM<sub>2.5</sub> and BC emissions, respectively than the pallet pile burn. The propane PM<sub>2.5</sub> emission factor was in the same range as previous, similar measurements from NSWCCD's propane burner. The propane burner combusted the propane fuel less efficiently than the burning pallet piles as revealed by the lower MCE, 0.975 compared to 0.992. Due to the wood's lower energy value the CO<sub>2</sub> emission factor in g/kWh fuel from the pallets was almost two times higher than from the propane burner. The CO emission factor was two times higher from the propane burner than the wood pallet pile burn. The benzene emission factor from wood pallet burn was three times higher than the propane burner. However, the propane burner emitted surprisingly high emissions of methylene chloride and of other chlorinated VOCs not found from previous similar measurements from NSWCCD's propane burner. These higher chlorinated VOC emissions may be due to the processing of natural gas and crude oil refining where chlorides occur naturally or is a result of organochlorinated fracking chemicals.

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