

Forest Biomass Diversion - Tracking the Economic Costs and Air Emissions of Forest Biomass Diversion and Allocating the Air Emissions Credits Generated - *Emissions Sampling and Determination of Emission Factors*

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Introduction

The objective was to quantify emission factors of major carbon species, PM_{2.5}, Black Carbon, and NO/NO_x gases produced from open-air burning of a large pile resulting from forestry activities. This field experiment was conducted at Blodgett Forest Research Station, CA. on January 17, 2014. It was a cloudless sunny day with minimal wind and a temperature in the 40's at ignition and 60's later in the afternoon.

Sampling and Analysis Methods

Fuel analysis

Representative fuel samples were collected prior to ignition for determining the moisture content. Samples were weighed in the field, shipped to the Fire Lab, oven dried at 105°C for 48 hours and reweighed to calculate moisture content on a dry weight basis. The fuel samples were subsequently ground (40 mesh) in a Wiley mill and analyzed for carbon and nitrogen content with a LECO Tru-Spec CN analyzer.

Emissions

The pile was sampled using a 20 foot steel probe angled over the edge of the pile. Within five minutes of ignition flame heights were approximately 100 feet with a strong convective column of emissions. During this time emissions could only be sampled over burning fuel at a lower edge. A 150 ft. flexible ¾ inch stainless steel sampling line brought the emissions to the point where samples and measurements were taken. Here the line connected to a manifold that distributed the sample. The manifold had four outlets:

- 1) *PM_{2.5}* - half inch convective black tubing to the filter box. *PM_{2.5}* was collected on 37 mm Teflon filters with the filter box flow at 42 lpm, with a 2.5 micron cutoff hi-volume cyclone. The system had previously been calibrated with a BGI Federal Reference Monitor (FRM). It was controlled, logged, and monitored from a laptop computer.
- 2) *NO/NO_x* - a ¼ inch Teflon line to an 1 l/min. flow external pump which drew the sample through a LICOR LI-820 and nephelometer upstream from a Thermo Model 42i NO/NO_x Analyzer. The LICOR and nephelometer provided continuous real time monitoring of CO₂ and aerosols to assess when to sample canisters and filters. The analyzer was calibrated with a 1 ppm NO standard at the lab prior to deployment. NO/NO_x concentration was measured continuously during the burning of the pile and logged on a laptop computer.
- 3) *Carbon gases* - The emissions samples were collected in 850 ml stainless steel SUMMA canisters by a portable sampling package consisting of a battery powered 12 volt DC KNF Neuberger PTFE chemical resistant diaphragm air sampling pump. Inline is a stainless steel inlet filter (NUPRO) with replaceable 15 micron fritted stainless steel element. A stainless steel adjustable pressure relief valve (NUPRO) controls fill pressure of canister. Mounted on an aluminum frame. The time to fill a canister is approximately one minute.. The canisters were pressurized with sampled to 25 psia (~ 2 atm.). Background air samples were taken at the start of each day. Three canisters were sampled during the active flaming phase from the edge of the pile. Canister samples after approximately 40 minutes after ignition were collected at 10 minute intervals. All of these canisters were characteristic of smoldering emissions. A total of thirty four fire emissions canisters were sampled.
- 4) *Black Carbon* - was measured with a microAeth Model AE51 aethelometer. A sample is collected on T60 (Teflon coated glass fiber) filter media (internal pump- 150 ml/min.), and analyzed in real time by measuring the rate of change in absorption of transmitted light due to continuous collection of aerosol deposit on the filter. Measurement at 880 nm interpreted as concentration of Black Carbon (BC). The data is logged on the instrument and downloaded.

Analysis of Canisters

The concentrations of methane, carbon dioxide (CO₂), and carbon monoxide (CO), and non-methane hydrocarbons (NMHC) will be determined by gas chromatography (Hao et al., 1996). Canister samples will be analyzed with an Agilent model 7890 gas chromatograph equipped with dual flame ionization detectors (FIDs at 300° C). Analysis for CO₂ and CO uses a 1 ml sample loop to inject the sample onto a 1/8" diameter x 6 ft. Carbosphere column with helium carrier gas at a flow rate of 16 ml/minute. The oven temperature is 50° for 6 minutes, then increasing 10/min. to 130° the 130° for 6 min. Exiting the column the gases pass through a nickel catalyst methanizer (375° C), to convert the CO₂ and CO to methane, before the detector (FID). The analysis for CH₄, and C₂ – C₄ occurs simultaneously on another sample with a .25 ml sample loop injecting onto a 6 m HP-1 pre-column, and then after 2 minutes to a 50 m HP/ALS .53mm mega-bore capillary column, helium carrier gas at 6 ml/min. The FID has a makeup helium gas flow of 14 ml/ min. Two 10-port valves are installed on the GC, for the gas loop sampling and to vent the pre-column and back-flush the packed column. Chromatograms are collected and processed by Agilent ChemStation software. A set of gas standards bracketing the sample concentrations are analyzed with each set of samples to construct a standard curve for each compound. Based on the integrated peak areas, the sample concentrations are calculated from the standard curves and written into an Excel spreadsheet. Duplicate analyses are performed every sixth sample. NIST primary standards for CO₂, CO, CH₄, and propane are analyzed daily to validate the standard curves.

Filter Analysis

After sampling 37 mm .Teflon filters were pre-weighed and post weighed after sampling using the same method . The filters are conditioned for 48 hours in a controlled temperature and humidity weighing room, and weighed at to within 1 microgram with a Mettler MT5 micro-balance. The balance is calibrated with NIST standard weights. Control filters are also weighed and deployed to the field. The particulate sample weights are corrected based on changes in pre and post weights of controls, due to handling, changes in temperature, etc. The PM_{2.5} concentration, in units of mg/m³ is calculated from corrected sample weights and total volume of air that was sampled.

Emissions Results and Emission Factors

The emission factors were calculated via the carbon mass balance method (Hao et. al) using the concentrations of CO₂, CO, and CH₄ and NMHC gas concentrations, and the carbon content of the fuels. The concentration from the clean air background canisters was subtracted from the sample concentrations to calculate the emission factors, which are in units of g/kg fuel consumed. An integrated emission factor was calculated for each emission species for the whole fire as well as the smoldering phase, which occurred after the first 40 minutes of burning.

Carbon monoxide (CO) is an indicator of less efficient combustion of wood, vs. CO₂. Other products of this inefficient combustion include methane, and hydrocarbons, and particulates. For natural biomass burning emissions there is usually a high degree of correlation between CO and hydrocarbons. This makes CO concentration a good predictor of CH₄, hydrocarbons and particulates, with r² values often greater than .9 in regression equations.

Combustion Efficiency describes the percent of carbon released in the form of CO₂ vs. CO. Totally efficient combustion, such as essentially occurs in biomass power plants, results in 99.99 percent of the carbon emitted as CO₂. As less efficient combustion occurs more CO is produced. The CO/CO₂ ratio is normalized by dividing the CO₂ by the sum of carbon contained with the CO and CO₂, and it then becomes linearly correlated with other products of incomplete combustion (MCE).

$$\text{MCE} = \text{CO}_2 \text{ ppm} / (\text{CO ppm} + \text{CO}_2 \text{ ppm})$$

MCE is a good predictor of low pollution (high MCE), as well as high concentration of methane, hydrocarbons, aerosols (low MCE). An intense forest fire is in the MCE range of .92 -.95. Grass fires are usually highly efficient with little smoldering and are in the MCE range of .95 -1. Typical prescribed fires under less extreme conditions have MCE values near .90. Smoldering combustion is indicated by MCE values of .60 to .85.

Results

Fuel Content

The fuel samples included four size classes present in the pile (Table 1). Large logs or other 1000 hour fuels were not sampled. Fuel moistures ranged from 8.8 to 17.7 percent and averaged 14.7 percent. These values indicate low fuel moistures and dry conditions. The carbon content was similar for all of the fuels, with needles the highest at 51.3 percent but representing a small fraction of the biomass in the pile. Nitrogen was similar with the needles having a much higher value for N but again representing a small fraction of the biomass, with the woody fuels in a range of .46 to .58 percent.

	H ₂ O	C	N
Rotten Wood	17.7	48.8	.58
Needles, Fine	15.3	51.3	1.29
Branches 1-3''	8.8	50.2	.46
Branches > 3''	17.0	50.0	.48
<i>Mean</i>	14.7	50.2	.70

Table 1. Fuel moisture (by dry weight) content of pile fuels, and carbon and nitrogen content.

Canister and Filter Results

Due to the intense and rapid combustion of the pile only the first three canisters can be characterized as flaming phase combustion samples. These were of lower concentration than later smoldering phase canisters but contained adequate concentrations of gases for analysis. In Figure 1 regressions of the concentrations of methane, NMHC, PM_{2.5} and C₂ gases vs. CO indicate that there is a high correlation between all of the hydrocarbons and CO. The PM_{2.5} concentration is generally not highly correlated with CO ($r^2=.17$) as it is formed by a different process as the gases. NMHC is the sum of all of the C₂ – C₄ hydrocarbons measured, and has an r^2 of .93 with CO.

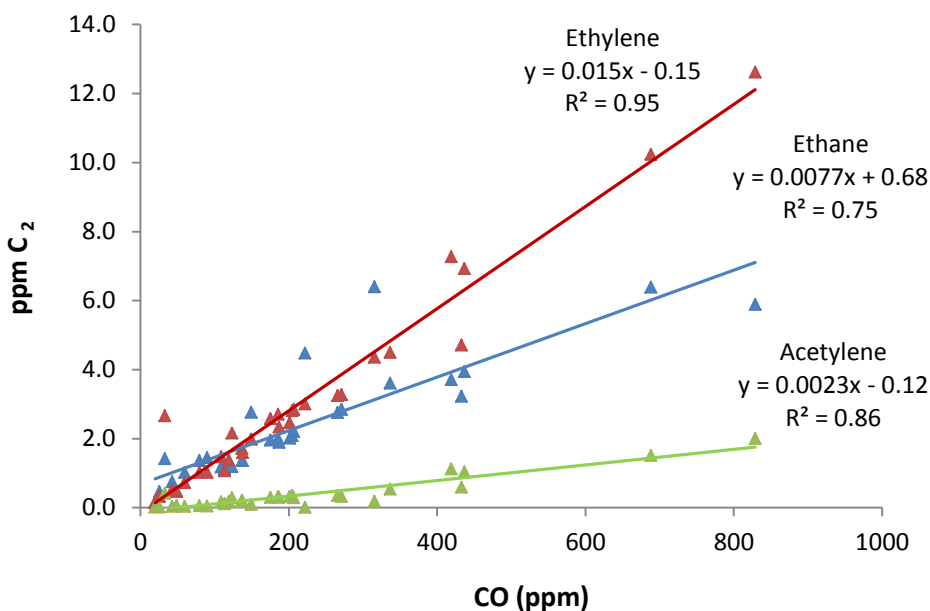
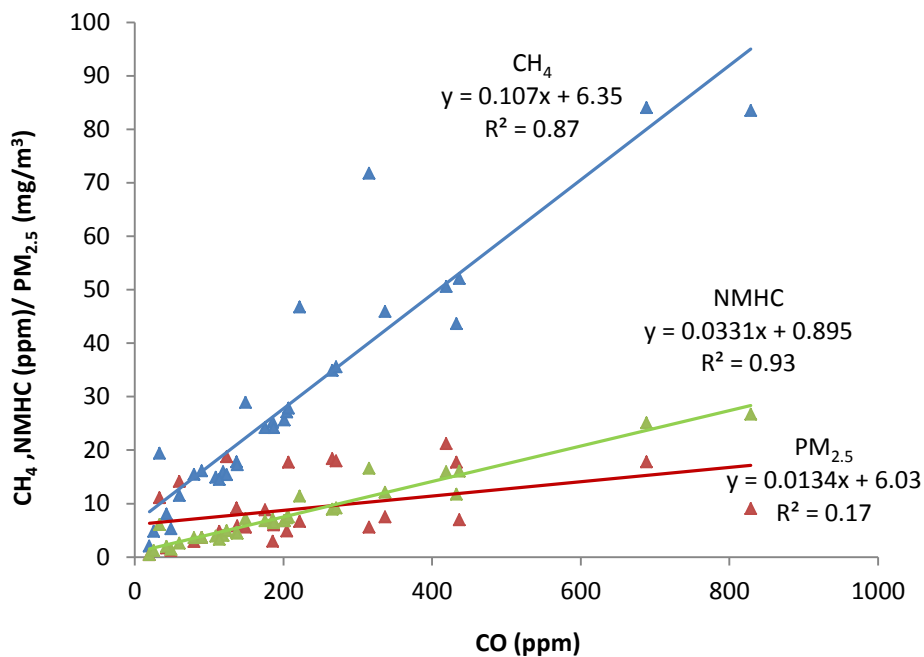


Figure 1. Results of hydrocarbons and CO concentrations from 34 canister samples collected from the pile burn. The Upper graph includes CH₄, NMHC (total non-methane hydrocarbons), and PM_{2.5} (mg/m³) vs. CO. The lower graph displays three 2-carbon gas emissions vs. CO.

Emission Factors

The emission factors are presented in in Table 2. The first set is a weighted average for the total fire. This is based on visual estimates that approximately 80 percent of the fuel was consumed in the first 45 minutes during the active flaming phase. Sampling after this characterized a mix with smoldering combustion and subsequently smoldering only. The total fire emission factors are similar to what would be obtained from a prescribed fire under good burning conditions. The smoldering emission factors demonstrate how much higher levels of CO and hydrocarbons are produced under poorer burning conditions with high fuel moistures. For comparison this project conducted a set of 7 pile burn experiments near Flagstaff, Ariz. in December of 1993. The results for the major carbon emissions (Table 3) are comparable to the BFRS pile burn with the exception of the EF $PM_{2.5}$ which was significantly higher in Arizona. The average MCE value for the Arizona piles was .89 vs. .94 for BFRS. This is may be due to over-estimation of the flaming phase for the BFRS burn, or that the Arizona piles were burned in snow and cold temperatures in December. The smoldering EFs are similar for the two experiments with the exception of $PM_{2.5}$.

	<i>Total</i>		<i>Smoldering</i>	
	EF (g/kg)	Std. Dev.	EF (g/kg)	Std. Dev.
CO	66.3	45.8	157.6	33.2
CO ₂	1708	89.6	1511	56.7
CH ₄	5.0	4.6	13.5	3.5
ethylene	0.42	0.90	2.08	0.70
ethane	0.42	0.72	2.11	0.40
acetylene	0.04	0.11	0.21	0.10
propylene	0.12	0.32	0.61	0.28
propane	0.25	0.46	1.26	0.30
propyne	0.00	0.03	0.01	0.03
n-butane	0.03	0.10	0.15	0.10
isobutene	0.01	0.03	0.04	0.03
1-butene	0.05	0.10	0.26	0.07
isobutene	0.04	0.09	0.18	0.08
cis-2-butene	0.02	0.04	0.09	0.03
trans-2 butene	0.03	0.06	0.13	0.05
1,3-butadiene	0.05	0.13	0.26	0.11
NMHC	1.48	2.66	7.39	1.68
NO	0.94	0.41		
NO _x	1.03	0.41		
PM _{2.5}	5.27	5.31	5.31	5.92
BC			0.32	
MCE	0.94	0.04	0.86	0.03

Table 2. Emission factors for 1/17/14 pile burn at BFRS.

	EFCO ₂	EFCO	EFCH ₄	EFNMHC	EFPM _{2.5}	CE
Average A	1722	49.6	3.11	3.42	7.02	0.94
Average B	1546	128.9	10.75	6.48	18.44	0.84
Average All	1634	89.3	6.93	4.95	12.73	0.89

Table 3. Average emission factors and combustion efficiency for 7 pile burns measured in Northern Arizona in 1993. Fire codes ending in A are for the mostly flaming fire start, while B refers to the later smoldering of the pile. (Ward and Susott, 1998)

NO/NO_x

The pile burn emission factors were produced from the integrated NO and NO_x measurements for the first day only. The NO and NO_x emission factors for the total fire were 1.03 and .92 g/kg respectively. These values are on the low range in comparison to results from wildland and prescribed fire emission factors. Laboratory and field experiments suggest that NO_x emission factors, even for similar vegetation types, vary significantly (Yokelson et al., 2011). Burning conditions and the nitrogen content of the fuel likely drive biomass burning NO_x emission factor variability (Yokelson et al., 2008). McMeeking et al. (2009) reported on laboratory measurements of NO_x emission factors from burning 33 different plant species that varied from 0.04 to 9.6 g NO /kg. The NO_x emission factors typically increased linearly with the modified combustion efficiency (MCE).

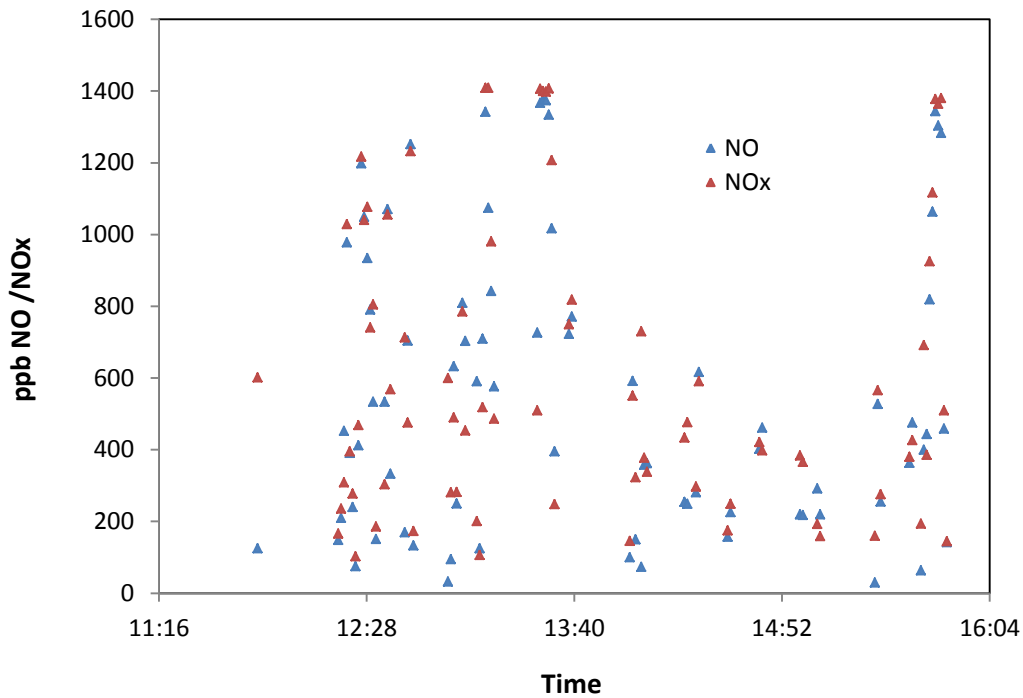


Figure 2. NO and NO_x (ppb) values from the BFRS pile burn 1/17/14

Black Carbon

Black carbon measurements were obtained only for sections of both days, and no results were obtained for the flaming phase. so only smoldering combustion was characterized. This is the combustion phase however when most black carbon is emitted. The emission factor integrated from both days for black carbon was 0.32 g/kg. This characterizes smoldering emissions only and not the total fire. A sample of output for the BC results is shown in Figure 3.

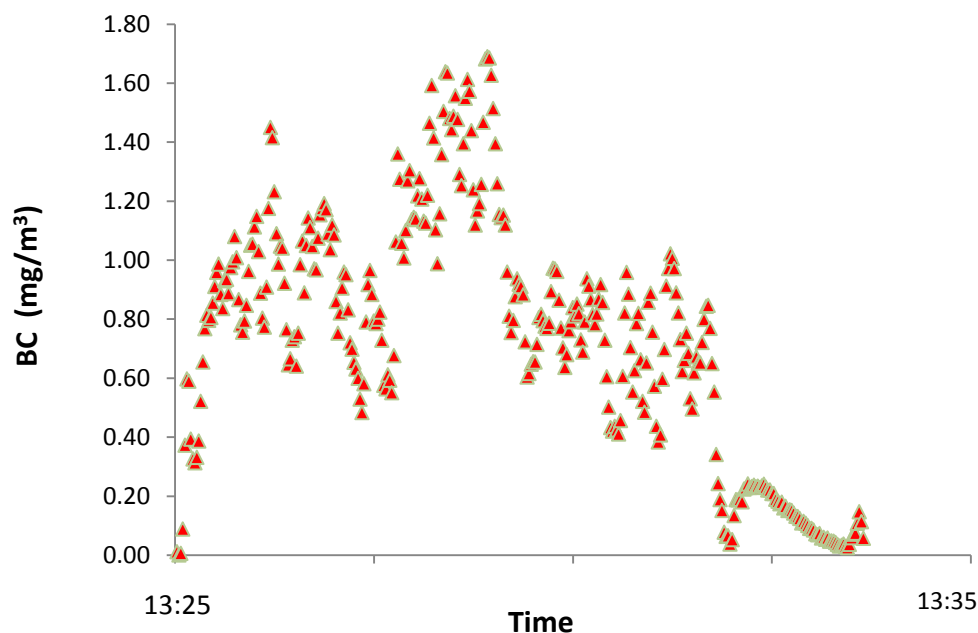


Figure 3. Sample output of black carbon (mg/m^3) output from aethelometer for BFRS pile burn 1/17/14.

Conclusion

The emission factors for this pile burn reflect a fairly high combustion efficiency, with an overall MCE value of .94. Fuel moistures were low and conditions were ideal for efficient burning, producing moderate emission factors for CO, methane and hydrocarbons. At the start vigorous flaming combustion was observed with a large convective plume. Subsequent smoldering combustion produced significant smoke, which continued the next day and beyond. Emission factors for the smoldering phase are reported separately, and are high for CO and hydrocarbons. This pile burn experiment was conducted under conditions that favor more efficient combustion but should provide a reasonable estimate of emission factors for the practice in this region.

References

Hao, W. M.; Flores Garnica, G.; Baker, S. P.; Urbanski, S. P., 2009. Carbon and Aerosol Emissions from Biomass Fires in Mexico. *American Geophysical Union, Fall Meeting 2009*, abstract #B53E-0446.

Hao, W., D.E. Ward, G. Olbu and S.P. Baker. 1996: Emissions of CO₂, CO and hydrocarbons from fires in diverse African savanna ecosystems. *Journal of Geophysical Research*, 101(D19), 23577-23584.

McMeeking, G. R., S. M. Kreidenweis, S. Baker, C. M. Carrico, J. C. Chow, J. L. Collett, Jr., W. M. Hao, A. S. Holden, T. W. Kirchstetter, W. C. Malm, H. Moosmüller, A. P. Sullivan, and C. E. Wold, 2009. Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory, *J. Geophys. Res.*, 114, D19210, doi:10.1029/2009JD011836,

Ward, D. E. (Principal Investigator) and R. A. Susott. (1998). Final Report for Arizona Burns in 1993 and 1994 Smoke Emissions from Ponderosa Pine Fuels Exposed to a Variety of Fire Histories and Site Preparation Treatments. USDA Forest Service Rocky Mountain Research Station Intermountain Fire Sciences Laboratory Fire Chemistry Project 4404.

Yokelson, R. J., Burling, I. R., Urbanski, S. P., Atlas, E. L., Adachi, K., Buseck, P. R., C. W., Akagi, S. K., Toohey, D., and Wold, C. E.: Trace gas and particle emissions from open biomass burning in Mexico, *Atmos. Chem. Phys.*, 11, 6787–6808, doi:10.5194/acp-11-6787-2011,10 2011.

Yokelson, R. J., Christian, T. J., Karl, T. G., and Guenther, A.: The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data, *Atmos.Chem. Phys.*, 8, 3509–3527, doi:10.5194/acp-8-3509-2008, 2008.