ANALYSIS OF CO_2, CO, $PM_{2.5}$, AND PM_{10} FROM FLAMING AND SMOLDERING COMBUSTION IN A HOME WOOD STOVE

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ABSTRACT: It is advantageous to study carbon monoxide, carbon dioxide, and particulate matter smaller than 2.5µm because these pollutants have known negative health and climate implications. We will use three instruments: a trace level gas CO analyzer from Thermo Environmental Instruments, a non-dispersive infrared gas analyzer from Licor Biosciences for CO_2*, and an aerosol monitor from TSI for particulate matter, to continuously measure the output of these pollutants from a wood stove with two types of combustion, flaming and smoldering. The CO instrument model 48C has a lower detectable limit of 0.04ppm, with linearity ± 1% of readings ≤ 1000ppm. The* CO_2 *instrument model LI-820 has measurement range is 0-20000ppm with an accuracy of <3% of the reading. The DustTrak, using gravimetric and photometric analysis to filter and analyze particulate matter, has a flow rate accuracy of ±5% of factory set point and can measure concentrations from 0.001-150 mg/*m^3*.*

In heating homes, using wood for fuel in wood stoves is becoming an increasingly common practice in the Pacific Northwest (Tonn & White, 1990). The combustion of wood in stoves releases pollutants which may have a connection with respiratory illness in households that use them and a definite connection with atmospheric pollution (Larson & Koenig, 1994). Major pollutants of atmospheric importance are carbon monoxide (CO), carbon dioxide (CO_2), sulfur and nitrogen compounds, and large and small particulate matter (PM_{10}, $PM_{2.5}$). The carbon-containing pollutants contribute to ozone increases in the lower atmosphere (which worsens smog in densely populated areas) and decreases in the upper atmosphere (Haagen-Smit & Fox, 1954). The connection between carbon monoxide and ozone formation can be shown by the following overall equation (there are more steps and intermediate species, but the net is shown) (Reeves et al., 2002):

$$CO + 2O_2 \longrightarrow hv + CO_2 + O_3$$

From this equation, we can see how carbon monoxide released from the combustion of wood in wood stoves may contribute to atmospheric issues. Particulate matter with diameter smaller than 2.5µm is of particular importance has been shown to be linked to respiratory health because it is small enough to bypass the nose into the lungs (Lea-Langton et al., 2015). There are many other respiratory illnesses associated with wood smoke from stoves: emphysema, anthracosis (build-up of carbon dust in the lungs), lung fibrosis (scarring of lung tissue), and asthma are some issues (Bruce, Perez-Padilla & Albalak, n.d.).

Under ideal conditions, wood burns according to the combustion reaction:

$$C_XH2_{X+2} + O_2 \longrightarrow H_2O + CO_2$$

Under real conditions, though, this reaction is never complete and depending on the burning conditions and type of wood, side reactions occur to release different pollutants. Smoldering combustion can be characterized by "slow, low temperature, and flameless … combustion" which takes place on the surface of a material, whereas flames arise as material goes into the gas phase, instead of solid (Chao & Wang, 2001; Moghtaderi & Fletcher, 1988; Rein, 2009).

Gas chromatography, dilution tunnel, and mass spectrometry have all been used to test emissions of varying fuel types and combustion environments for particulate matter and carbonaceous matter (Hedberg, 2002; Lea-Langton et al., 2015; McDonald et al., 2000). A dilution tunnel is a useful method to measure flow of particulate matter from combustion. This method was used to monitor particulate size from a combustion reaction running for 90 minutes. The results of this experiment showed an average value of 4.22E14 particles of particulate matter with diameter less than 0.9µm per kilogram of wood taken over 10 minute periods (Hedberg, 2002). In a recent study, researchers used gas chromatography to identify the amount of carbon monoxide produced from wood combustion. This method, testing for semi-volatile and volatile organic compounds showed an increase in carbon monoxide release as compared to other similar studies (McDonald et al., 2000). Mass Spectrometry has proven especially helpful in identifying the different types of particulate matter that result from wood stove combustion. One study used aerosol time of flight mass spectrometry (ATOFMS) to measure the particulate matter (large and small) products of flame and smoldering combustion of wood (Lea-Langton et al., 2015). This method gave results that there is a higher concentration of particulate matter from smoldering than flaming combustion for different wood types.

In comparing fuel types, soft has been tested against hardwood for emission types and amounts (McDonald et al., 2000). This study showed that when examining carbon monoxide and particulate matter, softwood generally expelled more carbon monoxide, and hardwood generally expelled more particulates of varying sizes. Another study compared combustion of wood in different environments: an open fireplace, a closed fireplace, and a traditional stove (Ozgen et al., 2014). This research showed that, when comparing emissions factors for carbon monoxide versus particulate matter, there was not a significant difference in emissions factors for the two pollutants. That data comes from combustion cycles not shorter than 45 minutes. In a different part of the combustion cycle, the air valve was closed and the fuel load increased by 50% at the latter part of the cycle. This change resulted in a higher emission factor for CO for a closed fireplace than in a stove.

We are presenting research and data to contribute to the study of particulate matter and carbon monoxide resulting from the combustion of wood in wood stoves. Two parts in the combustion cycle were studied: flaming and smoldering. We wish to examine the question: What is the effect on the concentrations of pollutants during flaming vs. smoldering combustion? We hypothesize that for flaming combustion, concentrations of particulate matter will be relatively low compared to concentrations of carbon monoxide and carbon dioxide, due to a more complete reaction. For smoldering combustion, we hypothesize that concentrations of particulate matter will be relatively high compared to low concentrations of carbon dioxide and carbon monoxide due to the incomplete burning of fuel.

Materials and Methods

1. Overview/setup

We will monitor three pollutants with a respective instrument to examine the hypothesis that smoldering combustion in a wood stove produces high concentrations of particulate matter and flaming combustion produces high concentrations of carbon dioxide and carbon monoxide because smoldering combustion results in an incomplete breakdown of organic material and flaming combustion gives a more complete reaction. We will analyze pollutant data by comparing concentrations from smoldering combustion with concentrations from flaming combustion. Data will be collected using a wood stove in Covington, WA. The stove is located in a back room of a 6-member family home, and is only used for heating. The Rainier 90 model stove from Avalon Firestyles will be used. A diagram available on the company's website shows an inner area of 58.89 square centimeters, and other specifications of the stove (Avalon Firestyles, 2016).

The stove we will be using has an exhaust flue connected, which leads up through the ceiling to the roof. For consistency, wood burned will be from a single source and stored indoors away from moisture.

The exhaust will be monitored for CO, $PM_{2.5}$, PM_{10}, and CO_2 using the setup described below. We will use a trace level gas CO analyzer from Thermo Environmental Instruments (model 48C). For CO_2, we will use a non-dispersive infrared gas analyzer from Licor Biosciences (model LI-820). Finally, to measure particulate matter, we will use an aerosol monitor from TSI (model DustTrak DRX 8533/8534). The instruments will be connected to the gas source via a rubber tube which is connected to the exhaust flue with a gasket. We will place a particulate matter filter downstream from the DustTrak and upstream from the Licor and 48C, to ensure that the latter two do not take in any particulates. A pump will be placed upstream of the Licor because it is not included in the instrument itself.

2. Theory of Operation

2.1. Theory of Operation of the DustTrak

The DustTrak works to measure the size and amount of particulate matter using photometry and gravimetric analysis. Air is drawn into the instrument using an included pump, and some of it is diverted to a HEPA filter to be used as sheath air. The unfiltered air is passed through a laser emitted from a laser diode. The amount and intensity of light that is not absorbed is measured by a sensor and then recorded as a voltage. This signal is separated into the photometric signal and the single particle pulses. The air that passes through the laser then is passed through a gravimetric filter, which separates particles by size (TSI Incorporated, 2012).

2.2. Theory of Operation of the 48C

Sample gas is passed through an infrared light source set to 4.6 microns, because CO absorbs at that wavelength. The absorption is measured with an IR detector, and from this, the concentration of CO in the sample gas can be calculated (TSI Incorporated, 2012).

2.3. Theory of Operation of the LI-820

The LI-820 instrument is an NDIR (non-dispersive infrared) gas analyzer. It works to analyze air for carbon dioxide by directing infrared light through an air sample to a detector. There are two chambers, one with sample and one with reference sample which consists of ambient air. Depending on the amount of light absorbed, and our knowledge that carbon dioxide absorbs at 4.24 microns, we can measure the amount of carbon dioxide in a given sample. There are two absorption bands, one at 4.24 microns, and one non absorption band (Licor Biosciences, n.d.).

3. Calibration of Instruments

3.1. Calibration of the DustTrak

The DustTrak comes calibrated to Arizona Test Dust (ISO 12103-1, A1). This dust is used because it covers the size range of particles that the DustTrak can measure. To blank the instrument, we will use a zero air filter provided by the manufacturer. For our collection, we will calibrate according to the manual, by using a reference instrument and calibration gas of a known concentration of PM2.5 and PM10 (TSI Incorporated, 2012). The LI-820 and reference instrument will be simultaneously sampled and their average concentrations of aerosol recorded.

3.2. Calibration of the 48C

The 48C will be calibrated using NIST/EPA certified CO and zero calibration gas and relating flow rate to CO concentration using equations provided in the manual by the manufacturer (Thermo Environmental Instruments, 2007). “Blank” or zero air must have less than 0.01ppm CO, so we must remove any CO from the zero gas by scrubbing and drying it according to procedures detailed by the manufacturer. We will connect a flow rate meter to the instrument and by changing the flow rate, we can change the concentration of CO in the standard gas to create a calibration curve by recording and plotting the standard CO concentration and the instrument's response.

3.3 Calibration of the LI-820

To blank the instrument, a CO2 free gas will be passed through it. Similar to work done by Gibert et al. (2009), we will choose two standard gases (one at high and one at low CO2 concentration) chosen to contain the high and low readings expected from measurements. In the study, the low standard was 365.922 ± 0.045 ppm, the high standard was 401.292 ± 0.045 ppm, and were chosen to reflect the range of concentrations expected from what they measured. Reference gas was dried ambient air. We can expect our highest concentration to be higher than 400 ppm because we will be measuring direct products of combustion and not atmospheric concentrations as in Gibert et al. (2009), so we will choose a higher concentration standard for the upper limit of our calibration range. Calibrations for the LI-820 can either be done manually or at set time intervals to create a linear calibration curve using the voltages from the detector.

4. Data Collection and Error Reduction

4.1. Overview

Data will be collected in January 2015, over the span of three continuous weeks. Data will be collected continuously and recorded electronically for each instrument, at a minimum of two repetitions per instrument (one for each burn type). Similar to an experiment done by Grieshop et al. (2008), we will cut wood into small pieces (in the previously mentioned study dimensions of 4 x 4 x 20 cm were used). For each repetition, the combustion chamber will be cleared of all ashes, charred wood, and other reside. As in Grieshop et al. (2008), wood will be allowed to burn for approximately 30 minutes before recording data, to keep as many variables (temperature, flow rate, etc.) as constant as possible. All instruments will be calibrated in the lab before transport to field site, and brought back to the lab when not in use to prevent damage. No instrument will be left unattended.

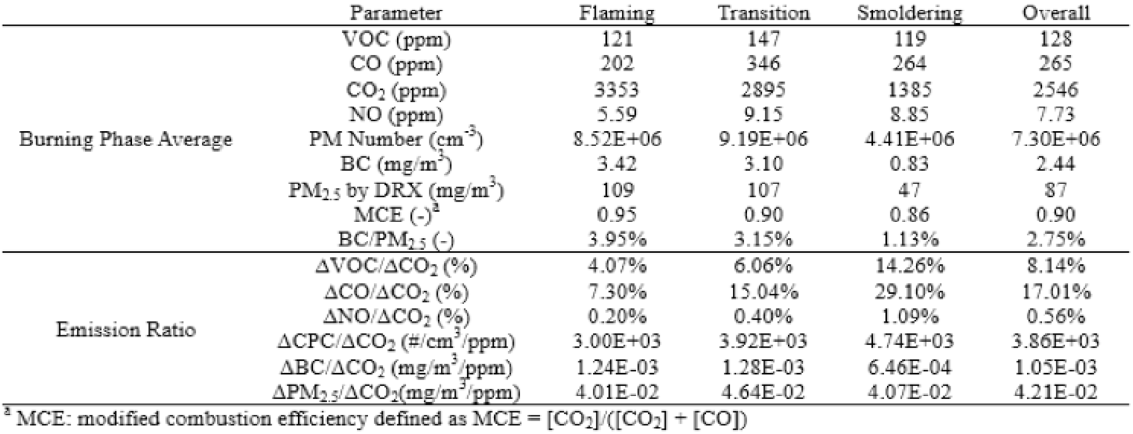
4.2. Data Collection and Error Reduction for the DustTrak

For the DustTrak, the voltage across the detector is proportional to the $PM_{2.5}$ fraction of the total sampled aerosol. A calibration constant is determined using the equation in section 3.1 of the manual, and the recorded voltage from $PM_{2.5}$ is multiplied by this factor. The aerosol stream is surrounded by clean, filtered air (sheath air), to prevent particles from circulating and changing results. A study by Ramachandran et al. (2003) shows possible error due to the method of analysis of the DustTrak. This study mentions that because the instrument samples at ambient humidity, concentration measurements change with increased humidity due to increased average size of particles. To correct for this error, a correction factor using relative humidity has been developed by Laulainen et al. (1993), cited in Ramachandran et al. (2003).

We expect to see data similar to that collected in an experiment by Wang et al. (2012), in which they studied pollutants from wood fires, and developed a test for instruments measuring those pollutants. For smoldering combustion, they showed high relative concentrations of $PM_{2.5}$ compared to smoldering combustion using the DustTrak. This is the opposite result in regards to our hypothesis, but it is useful to see what data we could possibly obtain using the same instrument.

4.3 Data Collection and Error Reduction for the 48C

We expect to see carbon monoxide data similar to that collected by Grieshop et al. (2008). For a certain wood type, their data shows high relative CO concentration released by flaming combustion vs. smoldering combustion. Even though they used a different instrument than we will and recorded data under laboratory conditions while we will be measuring at a field site, they are researching wood combustion



	Parameter	Flaming	Transition	Smoldering	Overall
Burning Phase Average	VOC (ppm)	121	147	119	128
	CO (ppm)	202	346	264	265
	CO_2 (ppm)	3353	2895	1385	2546
	NO (ppm)	5.59	9.15	8.85	7.73
	PM Number (cm^{-3})	8.52E+06	9.19E+06	4.41E+06	7.30E+06
	BC (mg/m^3)	3.42	3.10	0.83	2.44
	$PM_{2.5}$ by DRX (mg/m^3)	109	107	47	87
	MCE (-)[a]	0.95	0.90	0.86	0.90
	$BC/PM_{2.5}$ (-)	3.95%	3.15%	1.13%	2.75%
Emission Ratio	$\Delta VOC/\Delta CO_2$ (%)	4.07%	6.06%	14.26%	8.14%
	$\Delta CO/\Delta CO_2$ (%)	7.30%	15.04%	29.10%	17.01%
	$\Delta NO/\Delta CO_2$ (%)	0.20%	0.40%	1.09%	0.56%
	$\Delta CPC/\Delta CO_2$ ($\#/cm^3/ppm$)	3.00E+03	3.92E+03	4.74E+03	3.86E+03
	$\Delta BC/\Delta CO_2$ ($mg/m^3/ppm$)	1.24E-03	1.28E-03	6.46E-04	1.05E-03
	$\Delta PM_{2.5}/\Delta CO_2$($mg/m^3/ppm$)	4.01E-02	4.64E-02	4.07E-02	4.21E-02

[a] MCE: modified combustion efficiency defined as MCE = $[CO_2]/([CO_2] + [CO])$

Figure 1: Table 4 from Wang, et al., 2012. The Burning Phase Averages of PM2.5 measured by the DustTrak is relatively high for flaming combustion as compared to smoldering combustion.

and found results that are consistent with our hypothesis.

The detector in the 48C is responsive to the intensity of light hitting it, and the response is proportional to the light's intensity. Span error can be calculated for this instrument as detailed by the manufacturer. This is done by testing with a gas with CO level around 80% of the upper range limit. It ensures that span error can be recognized and minimized.

4.4 Data Collection and Error Reduction for the LI-820

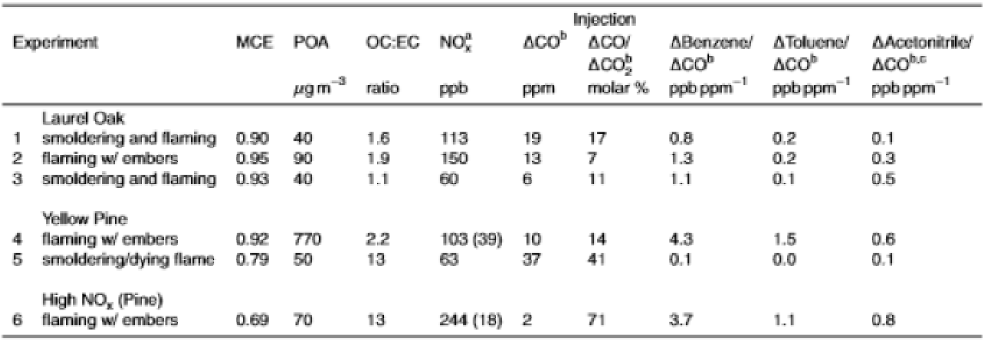
CO_2 absorbance in the LI-820 is measured by comparing the output of the two detectors. From these values we can calculate the mole fraction of CO_2 in the gas we pass through the instrument, using equations specified in the instrument manual (Licor Biosciences, n.d.). The measurement range for the instrument is 0-20000ppm with an accuracy of <3% of the reading.

Broader Impacts

This is a useful experiment in that there are many possibilities for expansion. For instance, future researchers could change variables such as fuel type, combustion environment, length of combustion, etc. There are many pollutants aside from CO, CO_2, and particulate matter that, depending on the conditions, can be detected from combustion. So, it's possible to study and analyze other compounds and their effects on the environment and respiratory health.

We will use this experiment to teach non-scientists about the effects of the pollutants we'll be studying. Doing the data collection in a family home will provide an opportunity to demonstrate what we'll be doing and the methods used to collect and analyze data. As we're actually collecting data, we can talk a small audience of five college-age people through the setup and operation of the instrument(s). Because of the home setting of the experiment, the audience will be residents of the home who have previously expressed an interest in science. We will describe and display the instruments we will be using to help gain attention, and then describe how we will analyze the data and use it to evaluate a hypothesis. Allowing the students to learn not only about instruments, but also about data analysis, will help them to decide to pursue a STEM major or career.

Another way to share findings would be to display a poster at the University of Washington Bothell, and speak about the findings. This could be used to convey information to a

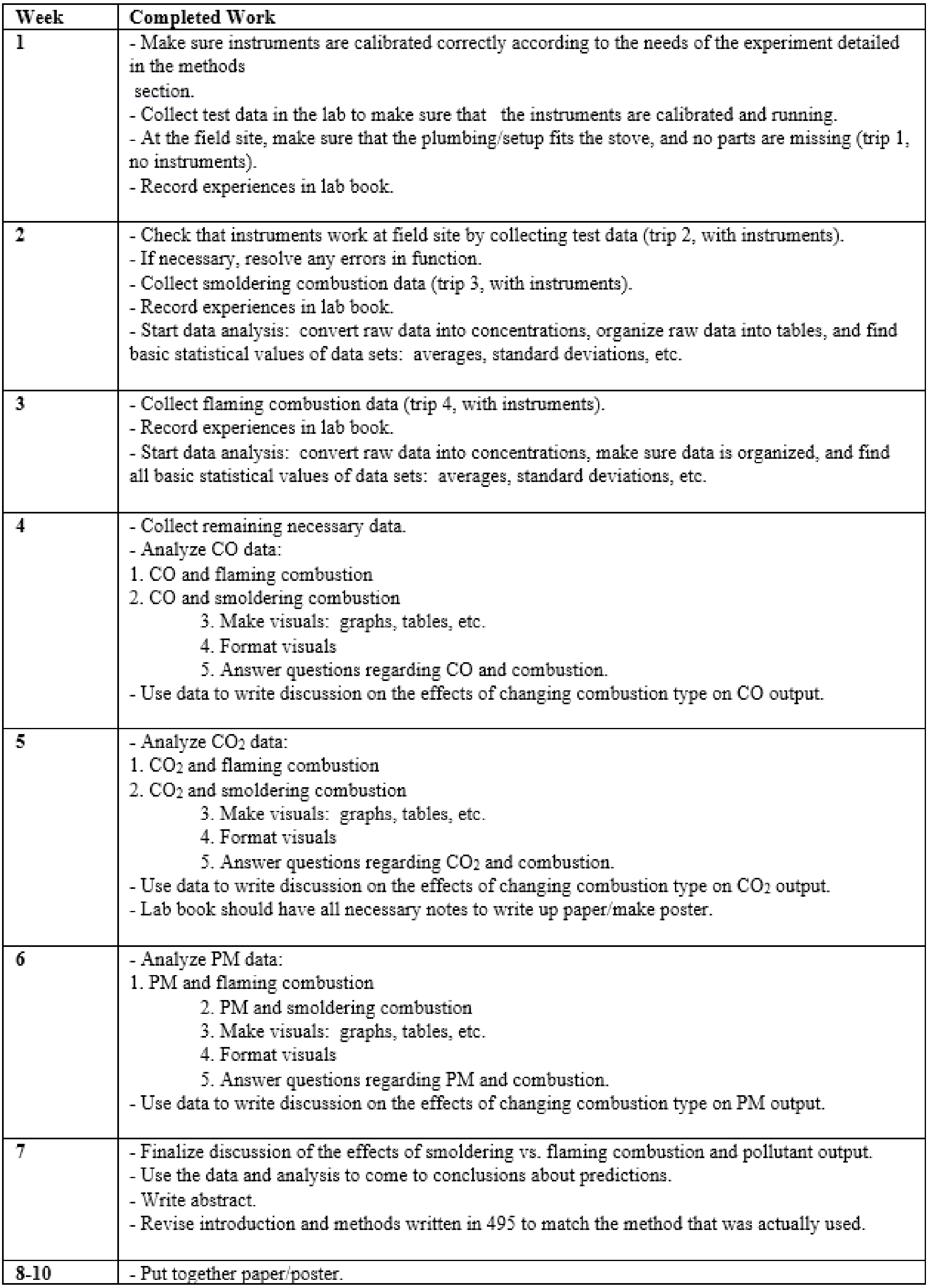


Experiment	MCE	POA	OC:EC	NO_x^a	ΔCO^b	Injection			
						$\Delta CO/\Delta CO_2^b$	ΔBenzene/ΔCO^b	ΔToluene/ΔCO^b	ΔAcetonitrile/$\Delta CO^{b,c}$
		$\mu g\,m^{-3}$	ratio	ppb	ppm	molar %	ppb ppm^{-1}	ppb ppm^{-1}	ppb ppm^{-1}
Laurel Oak									
1 smoldering and flaming	0.90	40	1.6	113	19	17	0.8	0.2	0.1
2 flaming w/ embers	0.95	90	1.9	150	13	7	1.3	0.2	0.3
3 smoldering and flaming	0.93	40	1.1	60	6	11	1.1	0.1	0.5
Yellow Pine									
4 flaming w/ embers	0.92	770	2.2	103 (39)	10	14	4.3	1.5	0.6
5 smoldering/dying flame	0.79	50	13	63	37	41	0.1	0.0	0.1
High NO_x (Pine)									
6 flaming w/ embers	0.69	70	13	244 (18)	2	71	3.7	1.1	0.8

Figure 2: Table 1 from Grieshop, et al., 2008 We expect to obtain results similar to those from experiments 1, 2, and 3, column 5 for change in CO in ppm.

more technical audience, which would allow us to include most of the details and technical language of the research. Specifically, the audience would be STEM students and teachers who have a background in scientific language.

Timeline



Week	Completed Work
1	- Make sure instruments are calibrated correctly according to the needs of the experiment detailed in the methods section. - Collect test data in the lab to make sure that the instruments are calibrated and running. - At the field site, make sure that the plumbing/setup fits the stove, and no parts are missing (trip 1, no instruments). - Record experiences in lab book.
2	- Check that instruments work at field site by collecting test data (trip 2, with instruments). - If necessary, resolve any errors in function. - Collect smoldering combustion data (trip 3, with instruments). - Record experiences in lab book. - Start data analysis: convert raw data into concentrations, organize raw data into tables, and find basic statistical values of data sets: averages, standard deviations, etc.
3	- Collect flaming combustion data (trip 4, with instruments). - Record experiences in lab book. - Start data analysis: convert raw data into concentrations, make sure data is organized, and find all basic statistical values of data sets: averages, standard deviations, etc.
4	- Collect remaining necessary data. - Analyze CO data: 1. CO and flaming combustion 2. CO and smoldering combustion 3. Make visuals: graphs, tables, etc. 4. Format visuals 5. Answer questions regarding CO and combustion. - Use data to write discussion on the effects of changing combustion type on CO output.
5	- Analyze CO_2 data: 1. CO_2 and flaming combustion 2. CO_2 and smoldering combustion 3. Make visuals: graphs, tables, etc. 4. Format visuals 5. Answer questions regarding CO_2 and combustion. - Use data to write discussion on the effects of changing combustion type on CO_2 output. - Lab book should have all necessary notes to write up paper/make poster.
6	- Analyze PM data: 1. PM and flaming combustion 2. PM and smoldering combustion 3. Make visuals: graphs, tables, etc. 4. Format visuals 5. Answer questions regarding PM and combustion. - Use data to write discussion on the effects of changing combustion type on PM output.
7	- Finalize discussion of the effects of smoldering vs. flaming combustion and pollutant output. - Use the data and analysis to come to conclusions about predictions. - Write abstract. - Revise introduction and methods written in 495 to match the method that was actually used.
8-10	- Put together paper/poster.

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