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A comparison of two methods to measure pyrolysis gases in a wind tunnel and in prescribed burns

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Abstract

Pyrolysis products from wildland fuels are typically measured under tightly controlled conditions using fuels which have been processed to remove water content and physical shape. Different instruments can be used to identify and quantify the composition of these gases. Measurement of pyrolysis gases under conditions typical of wildland fires has seldom occurred. We used FTIR spectroscopy and GC/FID analysis to measure pyrolysis gases produced in wind tunnel experiments and small prescribed burns in longleaf pine needle fuel beds with live shrubs. Use of compositional data techniques on the 8 common gases measured by both methods showed that the compositions were affected by the measurement method and interaction between method and location was significant.

1. Introduction

A wide variety of methods and instruments are available to identify and quantify the hundreds of gaseous and particulate compounds produced by the heating and combustion of wildland fuels. The methods and instrumentation have been compared (e.g., Fehsenfeld *et al.* 1987; Christian *et al.* 2004; Li *et al.* 2019) as well as used in a complementary fashion to increase the detection and quantification of as large a suite of compounds as possible (e.g., Yokelson *et al.* 2013). Linking laboratory results to field scale phenomena has long been a topic of interest and the field of wildland fire and smoke emissions is no exception (Ward and Radke 1993).

Ward and Radke (1993) compared different methods of describing smoke emissions from bench-scale measurement to aircraft and satellite measurement. Combustion efficiency, defined as the ratio of CO_2 to the sum of CO_2, CO, hydrocarbons, and particulate matter emitted by a fire, was proposed as a measure to link results across scales. Further development of this concept led to the use of CO/CO_2 and modified combustion efficiency (MCE) as descriptors of a fire and as an “independent” predictor of other smoke components (Ward and Hao 1991; Yokelson *et al.* 1996) because MCE was often “well-correlated” with other emission components. However, the problematic use of correlation measures on proportional and relative data has long been known (Pearson 1896; Aitchison 1986) and the measured gas mixtures formally correspond with multivariate relative data known as compositional data. Thus, the widely assumed convention that CO/CO_2, and thus MCE, was an independent predictor for other smoke components has been shown to be in error (Weise *et al.* in press). Given the above, the objective of this manuscript is to properly compare the composition of pyrolysis gases measured in a series of wind tunnel and field fires by FTIR spectroscopy and GC/FID using a compositional data analysis (CoDA) approach to determine if the two sampling methods produced similar results.

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2. Methods

Gas sampling was performed in a series of wind tunnel experiments and field prescribed burns in longleaf pine (*Pinus palustris* Mill.) needle fuel beds containing a live shrub component. See Scharko *et al.* 2019 and Weise *et al*. 2022 for details of the sampling methodology and analytical methods used to determine quantity and composition of the gases. Eight gases (CO_2, CO, CH_4, C_2H_2, C_2H_4, C_3H_6, C_4H_6 and C_4H_8) were measured by both FTIR and GC/FID. The relative amounts of these gases will be analyzed in this paper using version 4.1.2 of the public domain software R (R Core Team 2021). The data were preprocessed using the *multLN* function to impute random values below the minimum observed concentrations (Palarea-Albaladejo and Martín-Fernández 2013, 2015).

The common approach to analysis of compositional data is to express them through adequate log-ratios coordinates (balances) and then applying ordinary statistical techniques (Egozcue *et al.* 2003). The purpose of the various log-ratio transformations used in CoDA is to put the data in ordinary real space as opposed to their original simplex space. Seven log-ratio balances representing meaningful contrasts between subsets of gases were obtained by sequential binary partitioning (Egozcue and Pawlowsky-Glahn 2005). Multivariate analysis of variance (MANOVA) tested the effects of method (FTIR, GC/FID) and location (wind tunnel, field) on the entire composition and ANOVA tested the effects on these 7 balances individually. The data were unbalanced (Table 1); there are a variety of approaches to use ANOVA to test the significance of effects for unbalanced data. Based on Langsrud (2003), we used the *Anova* function which calculated Type II sums of squares to test the effects. Because there are only two levels of each factor, the significance of the difference between the two levels is tested by default; the probability was adjusted to account for the multiple t-tests using Benjamini and Hochberg's (1995) false discovery rate. A total of 21 t-tests (7 balances x 3 effects (method, location, interaction)) were performed because the intercept term was not included.

3. Results

The gases common to the GC/FID and FTIR samples were CO, CO_2, CH_4, C_2H_2, C_2H_4, C_3H_6, C_4H_6 and C_4H_8. These gas concentrations, constituting a subcomposition of the original composition, were "normalized" ("closed" in the CoDA parlance) to put them on a proportion (0,1) scale. Note that within a CoDA framework, these values can be expressed in the original ppm units, proportions or be converted to percentages without affecting the statistical results (scale invariance property). The relative amounts of the gases were similar in terms of highest to lowest proportions (Table 2); however, the relative amount of CO measured by FTIR at Ft. Jackson was an order of magnitude larger than the wind tunnel or GC/FID measurements. The MANOVA showed that the GC/FID and FTIR methods had a significant effect on the relative composition of the common gases (Table 2) and there was a significant interaction between location and method.

Because of the significant interaction, the mean values of the 4 combinations of location and method were calculated for each balance (Table 4). The overall mean for each balance is a weighted mean so the values were strongly influenced by the large number of GC/FID observations in the wind tunnel. The presence of significant interaction prevents clearly attributing differences in the balances to method alone. Since location was not significant as a main effect, the probability values are not presented.

Method significantly affected 4 of the 7 balances and the interaction term for method and location significantly affected a single balance. The 1st two balances containing CO_2 were smaller for the FTIR measurements at Ft. Jackson; relatively less CO_2 and more CO and CH_4 were measured (Table 2) resulting in smaller balances. The FTIR measured more CO relative to CH_4 than GC/FID; however, relatively more CH_4 was measured by GC/FID in the field burns. The interaction term affected the CO_2 vs CO & CH_4 balance. The FTIR balance values were smaller than GC/FID for Alkenes vs Alkynes. Note that the GC/FID values for this balance were close to zero which implies that the actual ratio between these subsets of gases was close to 1 in the original units, suggesting that the relative amounts of these two groups are approximately equal. The propene vs isobutene balance suggested that more propene relative to isobutene was present in the FTIR samples compared to the GC/FID.

Table 1. Number of pyrolysis gas samples analyzed by FTIR and GC/FID in the wind tunnel (RFL) and prescribed fires in Ft. Jackson, SC (FJ).

Method	Location	
	RFL	FJ
FTIR	22	5
GC/FID	88	7

Table 2. Mean relative amount of pyrolysis gases common to two sampling methods in wind tunnel (RFL) and prescribed fires in Ft. Jackson, SC (FJ). Expressed in proportions.

	RFL FTIR	RFL GC/FID	FJ FTIR	FJ GC/FID
Carbon dioxide (CO_2)	9.22E-01	9.43E-01	8.07E-01	9.81E-01
Carbon monoxide (CO)	6.85E-02	4.82E-02	1.58E-01	1.47E-02
Methane (CH_4)	5.25E-03	6.13E-03	1.64E-02	3.32E-03
Ethene (C_2H_4)	2.38E-03	1.87E-03	9.86E-03	3.33E-04
Acetylene (C_2H_2)	1.23E-03	4.89E-04	6.29E-03	1.48E-04
Propene (C_3H_6)	4.15E-04	8.56E-05	1.45E-03	3.65E-05
1,3-butadiene (C_4H_6)	9.92E-05	3.87E-05	4.29E-04	2.47E-05
Isobutene (C_4H_8)	3.86E-06	2.15E-05	7.43E-05	1.44E-05

Table 3. Summary of multivariate analysis of variance testing effects of sampling method (FTIR, GC/FID) and fire location (wind tunnel, Ft. Jackson) on mean relative composition of pyrolysis gases measured by both methods.

Source	df[a]	Pillai's[b] trace	F[c]	Num df	Den df	Pr(>F)
Method	1	0.39	10.66	7	112	<0.0001
Location	1	0.07	1.15	7	112	0.34
Interaction	1	0.16	2.97	7	112	0.007

a. Degrees of freedom of effect.
b. Pillai's trace used to test equality of means.
c. F-statistic associated with Pillai's trace.

4. Discussion and Conclusions

Direct comparison of gas measurements in a fire environment produced with different instruments is challenging and influenced by many factors. Different instruments and analytical techniques may measure the same gases with differing resolution or are unable to detect the same compounds (Ward and Radke 1993). Because of this, a wide variety of instrumentation is deployed to measure a large suite of compounds (e.g., Yokelson *et al.* 2013). The present study used two methods readily adapted to field use. The inherent spatial, temporal and compositional variability in fuels as well as the conditions under which the fuels were heated can affect the composition of the pyrolysis and combustion products. Some of this variability can be controlled by using a common sample line or assuming sample collection points in close proximity are true replicates. In small-scale experiments, fuel variability is reduced by homogenizing samples to eliminate shape and moisture effects and heating methods are closely controlled. In the present study, the assumption was made that samples taken in proximity in wind tunnel fuel beds or in small, prescribed burns in natural fuels each represented true replicates. In 3 of the 4 location × method combinations, samples were collected in canisters for subsequent analysis (either later in the day (FTIR) or several weeks after collection (GC/FID). The wind tunnel FTIR spectroscopic measurements were collected in real time.

While all these factors may affect the values of the absolute values for the pyrolysis gases collected, it is the relative values which are important since these are compositional data. Based on the subcomposition of gases measured by both FTIR and GC/FID, it is not possible to state that fire location (wind tunnel versus field) did not significantly affect relative composition of pyrolysis gases based on the presence of significant interaction. While the analytical method effect was significant, it cannot be separated from location. In the present study, the FTIR sampling was confounded with real-time measurement in the wind tunnel versus analysis of canister samples from the field. Canisters were used as a necessary safety precaution since the field fires were much less controlled than the wind tunnel burns and the FTIR setup precluded field use. Use of real-time measurement by FTIR provided other benefits (Banach *et al.* 2021).

Pyrolysis gases have been successfully measured in a wind tunnel and in small field prescribed burns using two different methods: FTIR-spectroscopy and GC/FID analysis. Using CoDA techniques on the subcomposition of gases measured by both methods showed that the compositions were affected by the measurement method.

Table 4. Estimated mean values for selected log-ratio balances of pyrolysis gases by method, location and overall mean. P-values adjusted to control false discovery rate (Benjamini and Hochberg 1995) < 0.05 are in bold.

		RFL		FJ		Mean	p-values	
Balance	Gases involved	FTIR	GC/FID	FTIR	GC/FID		Method	Interaction
Dominant gases vs Hydrocarbons	$\frac{[CO_2, CO, CH_4]}{[C_2H_2, C_2H_4, C_3H_6, C_4H_6, C_4H_8]}$	7.90	8.36	6.35	8.82	8.22	**0.043**	0.262
CO_2 vs CO & CH_4	$\frac{[CO_2]}{[CO, CH_4]}$	3.17	3.27	2.26	4.04	3.25	**0.001**	**0.004**
CO vs CH_4	$\frac{[CO]}{[CH_4]}$	1.82	1.46	1.60	1.05	1.51	0.375	0.763
Alkenes vs Alkynes	$\frac{[C_2H_4, C_3H_6, C_4H_8]}{[C_2H_2, C_4H_6]}$	-0.88	0.10	-0.52	-0.09	-0.11	**0.043**	0.474
Ethene vs Alkenes	$\frac{[C_2H_4]}{[C_3H_6, C_4H_8]}$	3.34	3.08	2.78	2.18	3.06	0.478	0.763
Acetylene vs 1,3-butadiene	$\frac{[C_2H_2]}{[C_4H_6]}$	1.78	1.79	1.90	1.27	1.77	0.474	0.474
Propene vs isobutene	$\frac{[C_3H_6]}{[C_4H_8]}$	3.31	0.98	2.10	0.66	1.43	**0.001**	0.474

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