Joint Measurements of $PM_{2.5}$ and light-absorptive PM in woodsmoke-dominated ambient and plume environments

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Abstract. DC, also referred to as Delta-C, measures enhanced light absorption of particulate matter (PM) samples at the near-ultraviolet (UV) range relative to the near-infrared range, which has been proposed previously as a woodsmoke marker due to the presence of enhanced UV light absorbing materials from wood combustion. In this paper, we further evaluated the applications and limitations of using DC as both a qualitative and semi-quantitative woodsmoke marker via joint continuous measurements of $PM_{2.5}$ (by nephelometer pDR-1500) and light-absorptive PM (by 2-wavelength and 7-wavelength Aethalometer®) in three Northeastern U.S. cities/towns including Rutland, VT, Saranac Lake, NY and Ithaca, NY. Residential wood combustion has been shown to be the predominant source of wintertime primary $PM_{2.5}$ emissions in both Rutland and Saranac Lake, where we conducted ambient measurements. In Ithaca, we performed woodsmoke plume measurements. We compared the pDR-1500 against a FEM $PM_{2.5}$ sampler (BAM 1020), and identified a close agreement between the two instruments in a woodsmoke-dominated ambient environment. The analysis of seasonal and diurnal trends of DC, BC (880 nm) and $PM_{2.5}$ concentrations supports the use of DC as an adequate qualitative marker. The strong linear relationships between $PM_{2.5}$ and DC in both woodsmoke-dominated ambient and plume environments suggest that DC can reasonably serve as a semi-quantitative woodsmoke marker. We proposed a DC-based indicator for woodsmoke emission, which was then shown to exhibit relatively strong linear relationship with heating demand. While we observed reproducible $PM_{2.5}$-DC relationships in similar woodsmoke-dominated ambient environments, those relationships differ significantly with different environments, and among individual woodsmoke sources. Our analysis also indicates the potential for $PM_{2.5}$-DC relationships to be utilized to distinguish different combustion and operating conditions of woodsmoke sources, and that DC-Heating demand relationships could be adopted to estimate woodsmoke emissions. However, future studies are needed to elucidate those relationships.

1 Introduction

Woodsmoke resulting from anthropogenic activities is a widespread air pollution problem in many parts of the world. For example, residential woodsmoke is estimated to account for 20% of total stationary and mobile polycyclic organic matter

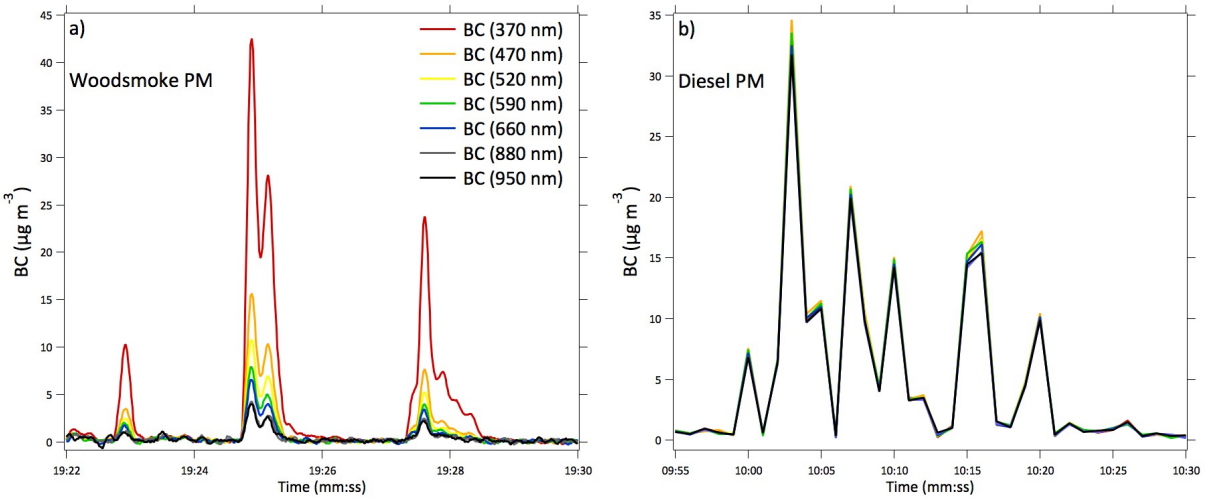
emissions, and 50% of all area source air toxic cancer risks according to the 2011 National Air Toxics Assessment in the U.S. (https://www.epa.gov/national-air-toxics-assessment). It is reported that around 35% of total $PM_{2.5}$ emissions in the United Kingdom came from domestic wood burning in 2015, while road transport only contributed around 13% of the total $PM_{2.5}$ emissions (DEFRA, 2016). In addition to its contribution to regional air quality, residential woodsmoke may cause significant near-source air quality impacts due to relatively low stack heights and low exhaust temperatures. While in some sense wood burning products may be considered natural substances, the health effects of wood smoke are found to be comparable to those of fossil-fuel combustion sources (Naeher et al., 2007).

Chemicals that are enriched in woodsmoke relative to other sources have been used to quantify woodsmoke impacts on ambient particulate matter (PM). Among them, levoglucosan, a sugar anhydride derived from the pyrolysis of the major wood polymer cellulose, has been used extensively as a molecular marker for woodsmoke because it is emitted at high concentrations and relatively stable in the atmosphere (Fine et al., 2001; Simoneit et al., 1999). However, detecting levoglucosan in PM samples at present requires detailed chemical analysis, and the related information is not widely available.

The widely deployed Aethalometer® has made possible continuous aerosol light absorption measurements, commonly referred to as Black Carbon (BC), at either two wavelengths (880 nm and 370 nm) or seven wavelengths (370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm, and 950 nm). Allen et al. (2004) first proposed using enhanced light absorption of ambient particulate matter (PM) at 370 nm relative to 880 nm, due to the presence of light absorbing materials from wood combustion near ultraviolet (UV) range, as a marker for woodsmoke PM. Figure 1 depicts the distinct responses of a seven-wavelength Aethalometer (Magee Scientific AE-33) to woodsmoke (Figure 1a) and diesel (Figure 1b) plumes, providing a context for our discussions in this paper. The source of the diesel plume was a backup diesel generator, and the measurement was conducted in 2015. The woodsmoke plume data was collected near a residential woodstove source in early 2016. Note that the purpose of Figure 1 was to reveal the qualitative differences between the two sources, rather than making a quantitative comparison.

The wavelength-dependent responses to woodsmoke were clearly shown in Figure 1a. At the longer wavelength end, there were virtually no differences in the signals from the 880 nm and 950 nm channels. At the shorter wavelength end, the 370 nm channel recorded the highest reading. We referred to the augmented responses at shorter wavelengths compared to the 880 nm and 950 nm as "UV enhancement". By contrast, virtually no wavelength-dependence (i.e., no UV enhancement) was observed for diesel exhaust (Figure 1b). There are some slight discrepancies among the different wavelength channels, likely due to the limitations of the real-time dynamic spot loading correction scheme used by the AE-33. The patterns of the wavelength-dependent responses shown in Figure 1 were consistent with the findings from several previous studies, which suggested that UV absorbing compounds are enriched in biomass-combustion PM but scarce in diesel PM (Chen et al., 2015; Olson et al., 2015) or traffic-related PM (Kirchstetter et al., 2004). Broadly, the light-absorbing organic compounds, referred to as "brown carbon" or BrC, have been shown to strongly absorb UV (Andreae and Gelencsér, 2006).

The concept of DC (also referred to as Delta-C) originated from using the level of the UV enhancement as a marker for woodsmoke PM (Allen et al., 2004). Traditionally, DC was calculated by the differences between 370 nm and 880 nm signals, i.e., DC = BC (370 nm) – BC (880nm), due to the availability of two-channel Aethalometer models. But the concept is not limited to those two particular wavelengths. Figure 1a indicates that woodsmoke UV enhancement started appearing at 660



(a) (b)

Figure 1. Wavelength-dependent responses of AE-33 to (a) woodsmoke and (b) diesel plumes. Note that the purpose of this figure is to reveal the qualitative differences, rather than making a quantitative comparison, between the two types of plumes.

nm, and more enhancement can be expected at even shorter wavelength (than 370 nm) not available in current Aethalometer models. Studies showed that woodsmoke enhancement peaks at ~300 nm (Kirchstetter et al., 2004; Kirchstetter and Thatcher, 2012). It is possible that including shorter wavelength in future instrumentation development would improve the sensitivity to woodsmoke PM (Olson et al., 2015). Another approach taking advantage of UV enhancement (or wavelength dependence of the aerosol absorption coefficient in general), as reported by Sandradewi et al. (2008a), derives light absorption Ångström exponents (AAE, or α) from multi-wavelength Aethalometer readings. α is close to 1 for traffic sources, and varies for woodsmoke, but generally much larger than 1. Assuming certain value of α for woodsmoke, Sandradewi et al. (2008b) conducted quantitative analysis of source contributions to PM. This approach often requires light absorption measurements at multiple wavelengths to have a reliable estimate on α (Chen et al., 2015). Sandradewi et al. (2008b) showed that using different pairs of wavelengths led to different values of α for woodsmoke. Since the ambient data to be presented in this paper were collected by a two-wavelength Aethalometer and given the uncertainties associated with values of α for woodsmoke, we did not perform a direct source apportionment analysis similar to that presented by Sandradewi et al. (2008a), but presented a qualitative analysis to be presented later (Section 3.2).

Wang et al. (2011) reported a strong correlation between DC and woodsmoke markers such as levoglucosan during the heating season, and no statistically significant correlation between DC and vehicle exhaust markers based on field data collected in Rochester, NY. A follow-up study from the same research group used DC as an input variable in source apportionment models, where it was found to play an important role in separating traffic (especially diesel) emissions from wood combustion emissions (Wang et al., 2012). Allen et al. (2011) adopted DC as woodsmoke marker for their fixed-site measurements in Northern New York State, and revealed temporally and spatially resolved patterns of woodsmoke PM (Fuller et al., 2014).

However, Harrison et al. (2013) analyzed data for DC from an Aethalometer network in UK and suggested the presence of other UV absorbing contributors (such as coal burning) to the DC signal. Laboratory experiments conducted by Olson et al. (2015) showed that besides biomass burning other sources such as uncontrolled coal (e.g., lignite) and kerosene combustion in lamps can also lead to high DC values. In addition, some secondary organic aerosol (SOA) products have also been found to result in UV enhancement (Zhang et al., 2011; Zhong and Jang, 2011), and increase DC responses.

Motivated by the findings from those previous investigations, we aim to further evaluate the applications and limitations of using DC as a qualitative and semi-quantitative woodsmoke marker. Our work is based on recent joint wintertime measurements of $PM_{2.5}$ and light-absorptive PM in woodsmoke-dominated ambient environments and woodsmoke plume environments in three cities/towns located in the Northeastern U.S. Woodsmoke is known to be the major PM source during wintertime, and predominant PM source during winter nighttime, in the three studied cities/towns. Neither heating by coal nor kerosene lamps are common in this region. Furthermore, SOA formation is typically slow during wintertime. Our study can be regarded as a "necessary condition test" for DC serving as a woodsmoke PM marker. In other words, DC would be deemed an inappropriate marker if it were unable to track woodsmoke PM patterns even under woodsmoke-dominated environments. The paper is organized in such a way that we distinguish the ambient and plume environments by discussing their field measurements and results separately, as the potential implications based on the two types of environments are inherently different. Data from multiple locations and different environments contribute to a more robust evaluation on DC.

2 Field Measurements

2.1 Woodsmoke-dominated environments: Ambient (Rutland, Clinton and Lakeview) and Plume (Ithaca)

In this paper, we reported the results from field measurements conducted in four sites in three Northeastern U.S. cities, i.e., Rutland, VT, Saranac Lake, NY and Ithaca, NY. Table 1 describes the general site characteristics.

Rutland is the third largest city in the state of Vermont with a population of 16,500, where residential wood combustion is a major source of winter space heating (Frederick and Jaramillo, 2016). According to the 2014 National Emission Inventory, residential woood combustion (RWC) contributes to approximately 38.6% of the annual $PM_{2.5}$ emissions in Rutland County. In comparison, on-road mobile sources only account for 1.4%. Considering the seasonal patterns of various emission sources, it is clear that RWC is the predominant primary $PM_{2.5}$ source in Rutland during wintertime. The ambient air quality monitoring site in Rutland (EPA AQS site number: 50-021-0002) is one of very few routine monitoring stations in the U.S. heavily influenced by woodsmoke (http://dec.vermont.gov/air-quality/monitoring/network/rutland). Even though Rutland is not a nonattainment area for annual or 24-hr $PM_{2.5}$ National Ambient Air Quality Standards, its $PM_{2.5}$ design value is among the highest in New England. The next two sites were located in Saranac Lake, a rural town of 5,400 people in Upstate New York. The 2014 National Emission Inventory indicated that RWC accounts for approximately 22.4 to 25.4% of the annual $PM_{2.5}$ emissions, while the contribution of on-road mobile sources is between 2.8 to 3.9%, which indicated that it is also a woodsmoke-dominated environment during wintertime. Ambient PM concentrations are generally low in Ithaca, the final site and a city of 30,500 in Central New York. While residential wood combustion is not widespread in Ithaca, it has caused localized air pollution hotspots

Table 1. Descriptions of field measurement sites

Site Name		Environment	Monitoring Method	Operation Period	Site Descriptions
Rutland, VT		Ambient	Fixed-site	October 2011 to June 2013	Co-located with FEM/FRM at AQS 50-021-0002, no nearby woodsmoke sources
Saranac Lake, NY	Clinton	Ambient		December 2014 to April 2015	Located in the backyard of a residential property on Clinton Street, minimal woodsmoke sources
	Lakeview	Ambient		January to April 2015	Located in the backyard of a residential property on Lakeview Street, no nearby woodsmoke sources
Ithaca, NY		Plume	Mobile	December 2015 to March 2016	Right outside the property lines of woodsmoke sources at downwind direction

and complaints against woodsmoke were filed by affected residents living in the densely populated neighborhoods. A primary goal for the field measurements in Ithaca was to capture those hotspots. It is woodsmoke-dominant in nature as we purposefully sampled woodsmoke plumes.

In short, a common feature for the three cities/towns is that woodsmoke is the predominant PM source during winter nighttime, and the only known major source of DC. Furthermore, the Rutland, Clinton and Lakeview sites represent ambient environments since they captured the mixture of multiple sources, not dominated by any one individual source. By contrast, the mobile monitoring technique employed in Ithaca was designed to capture individual sources, thus, representing plume environments.

Table 2 summarizes the major equipment deployed in the different sites. Detailed descriptions of the experimental methods are provided in Sections 2.2 and 2.3.

The Vermont State Department of Environmental Conservation maintains an air quality monitoring site in Rutland, VT (43.608056° N, 72.982778° W; Elevation: 179 m, EPA site number: 50-021-0002). This site is located in the downtown area of Rutland, not adjacent to any known woodsmoke sources. Routine measurements of $PM_{2.5}$, O_3, CO, SO_2, NO, NO_2, VOCs and meteorological variables are conducted.

We deployed a personal DataRAM™ Aerosol Monitor (Model pDR-1500, ThermoFisher Scientific, USA) and a two-wavelength AethalometerTM (370 and 880 nm, Model AE-21, Magee Scientific, USA) for continuous monitoring of $PM_{2.5}$ and Black Carbon (BC), respectively, at the Rutland monitoring site. Operating at 5 min time resolution, both pDR-1500 (1 L

Table 2. Descriptions of air quality instruments deployed in various field measurements

Site Names		$PM_{2.5}$	Light-absorptive PM	PAH	Others
Rutland, VT		pDR-1500 at 5 min time resolution, 2.5 μm cyclone inlet	AE-21 at 5 min time resolution, 2.5 μm cyclone inlet	N/A	FEM and FRM $PM_{2.5}$ monitors
Saranac Lake, NY	Clinton	pDR-1500 at 1 min time resolution, 2.5 μm cyclone inlet	AE-42 at 1 min time resolution, 2.5 μm cyclone inlet	EcoChem PAS2000 at 30 s time resolution	2-D Sonic Anemometer for wind speed and direction
	Lakeview				
Ithaca, NY		pDR-1500 at 1 s time resolution, 2.5 μ m cyclone inlet	AE-33 1 s time resolution, 2.5 μm cyclone inlet	N/A	CO_2 probe

min-1, no RH and temperature correction) and AE-21 (2L min-1) were equipped with 2.5 μm sharp-cut cyclone inlets (BGI model SCC 0.732) placed 1.5 m above the roof of a trailer and ambient air was drawn to the instruments through an aluminum sample line. The pDR-1500 was running from December 2011 to April 2012, during which we were able to compare the $PM_{2.5}$ readings from both pDR-1500 and the collocated Federal Equivalent Method (FEM) instrument (BAM 1020, Met One, USA). The AE-21 was in operation from October 2011 to June 11, 2013.

All Aethalometer data were corrected for filter spot optical loading saturation effects (Drinovec et al., 2015; Park et al., 2010; Virkkula et al., 2007) using the "binned" approach, first described by Park et al. (2010), as implemented by version 7.1 of the Aethalometer "data masher" program (Allen et al., 2012). This correction provides a more robust measurement of the DC metric, since the optical attenuation for BC at 370 nm is 2.4 times larger than at 880 nm, resulting in a larger loading artifact at the shorter wavelength. If only BC is present, this results in a negative DC instrument response when the loading is not corrected for.

2.1.1 Saranac Lake, NY (Clinton and Lakeview)

Both sites in Saranac Lake, i.e., Clinton and Lakeview, were located in the backyards of residential properties that did not burn wood for either recreational or heating purposes. Both pDR-1500 (1L min-1, no RH and temperature correction) and AE-42 (2 L min-1) were deployed with the same 2.5 μm sharp-cut cyclone inlets as described in Section 2.2.1, mounted 1.83 m (or 6 feet) above the ground. Both sites were equipped with a 2-D Sonic Anemometer (Model Windsonic, Gill Instruments, UK) for wind speed and direction. In addition, the Lakeview site also included a Photoelectric Aerosol Sensor (Model PAS2000, EcoChem, USA) for continuous particle-bound PAH measurement. The operation periods for the three fixed sites are listed in Table 1.

2.2 Mobile Monitoring at Ithaca, NY

As mentioned earlier, we adopted mobile monitoring techniques in Ithaca, NY to identify air pollution hotspots caused by woodsmoke. The sampling inlet of both pDR-1500 and the seven-wavelength Aethalometer (370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm, and 950 nm; Model AE-33, Magee Scientific, USA), equipped with 2.5 μm sharp-cut cyclones (BGI SCC 1.197 cyclone at 2.3 L min-1 for pDR-1500; BGI SCC 1.829 cyclone at 5 L min-1 for AE-33), were mounted one foot above the sunroof of a hybrid electric vehicle (HEV). Although the AE-33 employs automated real-time loading compensation (Drinovec et al., 2015), and thus no post data processing was attempted to account for filter loading effect. To account for the filter loading effect, that correction was not used here, since it is not appropriate for mobile monitoring where different combustion sources are sampled in rapid succession. Filter loading was kept relatively low to minimize any loading effects. A flow-through type CO_2 probe (Model CARBOCAP® GMP343, Vaisala, Finland) was connected to the outlet of AE-33 to record the CO_2 level. The pDR-1500 operated without RH correction. RH in the pDR-1500 sensing chamber was always less than 35% without additional sample heating as the instrument was inside a heated vehicle and the chamber temperature was well above ambient dew point. The pDR-1500 was zeroed prior to each mobile run. The pDR-1500 and AE-33 both operated at 1 s time resolution, and the GMP343 at 2 s time resolution to capture individual woodsmoke plumes.

The mobile monitoring occurred periodically from December 2015 to March 2016. Assisted by the weather forecast from New York State Department of Environmental Conservation (NYSDEC) staff, we chose to conduct mobile runs only during low temperature and low wind speed conditions, when the local air quality impacts from woodsmoke were expected to be significant. We made a total of 20 mobile runs (two in December 2015, seven in January, five in February and six in March 2016). The monitoring routes were recorded at 1 s intervals from a Delorme BU-353S4 GPS receiver using Delorme Street Atlas 2015 PLUS software.

At the beginning of the field campaign, we employed the mobile measurements as an efficient way to survey the air quality levels in the Ithaca area, which then enabled us to identify a few recurring hotspots. The rest of the field campaign focused on those recurring hotspots. Specifically, we parked the HEV right outside the property lines of residential woodsmoke sources in the downwind direction, and all instruments were powered primarily by the HEV battery without self-pollution. The internal combustion engine of the HEV occasionally turned on to recharge the battery, and caused brief periods of self-pollution. We recorded those conditions, generally characterized by high CO_2 and low $PM_{2.5}$ levels, and removed them from subsequent data analysis.

3 Results and Discussions

3.1 Evaluation of pDR against BAM (and maybe FRM)

As mentioned in Section 2.2.1, we collocated a pDR-1500 with BAM 1020, which is a FEM $PM_{2.5}$ sampler, from December 2011 to April 2012 at the Rutland site. Figure 2 illustrates the comparisons of 24-hour average (Figure 2a), nighttime (10 pm to 6 am) average (Figure 2b), hourly (Figure 2c) and hourly nighttime-only (Figure 2d) $PM_{2.5}$ from the two instruments. The

main reason to present the nighttime results was that PM during that period almost exclusively came from woodsmoke sources in Rutland. Therefore, Figure 1 not only presents the overall comparisons between the two instruments (Figures 2a and 2c), but also how their readings correlated for woodsmoke-dominated environments (Figures 2b and 2d). Note that the apparent horizontal lines in Figure 2c and Figure 2d result from the 1 μg m^{-3} resolution of the hourly BAM readings.

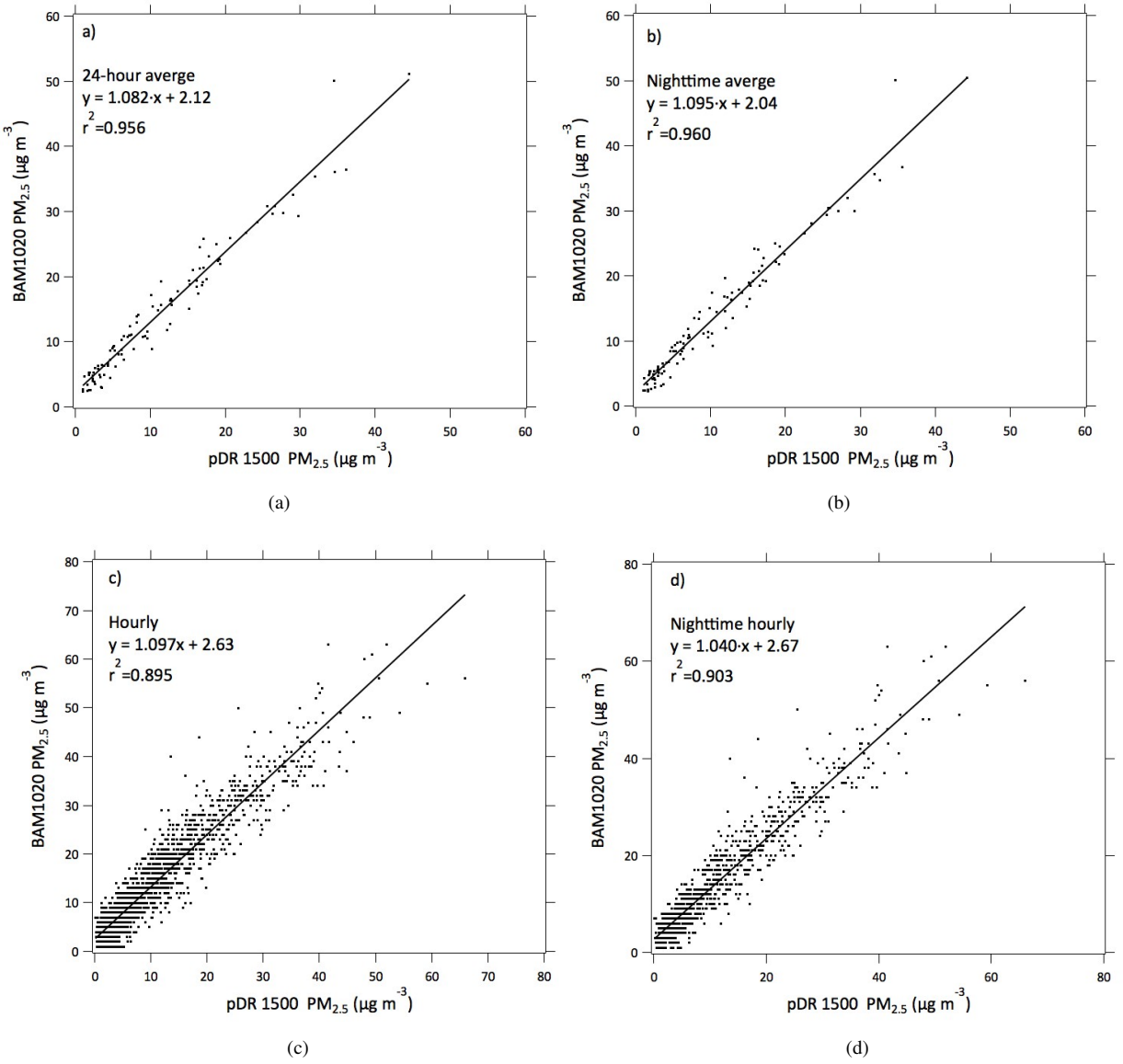


Figure 2. Comparisons between $PM_{2.5}$ values from BAM 1020 (FEM) and pDR-1500 in terms of (a) 24-hour average, (b) Nighttime (10 pm to 6 am) average, (c) hourly average and (d) nighttime hourly average. The apparent horizontal lines in (c) and (d) result from the 1 μg m^{-3} resolution of the hourly BAM readings.

Table 3 lists the metrics for the regressions. Overall, we found a good agreement between the two instruments. The coefficients of determination, r^2, ranged from 0.895 to 0.960. As expected, the daily and nighttime multi-hour averages (0.956 and 0.960, respectively) showed better correlations than hourly and nighttime hourly averages (0.895 to 0.903, respectively). For the hourly data plots, we observed the BAM noise at the origin where pDR-1500 reads very low and the BAM PM is 2 ± 5 μg m^{-3}. In general, the comparison results gave us confidence in deploying pDR-1500 for other woodsmoke studies.

Table 3. Comparisons between BAM 1020 (y) and pDR-1500 (x) from December 2011 to April 2012 in Rutland, VT. The values inside the parentheses represent the corresponding one standard deviation.

	Regression	r^2
Daily Average	y = 1.082(± 0.023)·x+2.12(± 0.33)	0.956
Nighttime average	y = 1.095(± 0.022)·x+2.04(± 0.32)	0.960
Hourly average	y = 1.097(± 0.007)·x+2.63(± 0.10)	0.895
Nighttime hourly average	y = 1.040(± 0.011)·x+2.67(± 0.16)	0.903

The FRM sampler (Model 2025 $PM_{2.5}$ Sequential Air Sampler w/VSCC, R&P, USA) at the Rutland site operates every third day so that we did not include the FRM data in the comparisons. The $PM_{2.5}$ Continuous Monitor Comparability Assessment at the site reported $PM_{2.5}$, FEM = 0.97$PM_{2.5}$, FRM + 1.76 (R=0.97) for Year 2011 and $PM_{2.5}$, FEM = 1.07$PM_{2.5}$, FRM + 0.74 (R=0.92) for Year 2012 (https://www.epa.gov/outdoor-air-quality-data/pm25-continuous-monitor-comparability-assessments).

3.2 DC as a qualitative marker for woodsmoke PM

Figure 3 shows the two-week moving average for DC, BC (880 nm), and $PM_{2.5}$ values measured at the Rutland site from October 2011 to June 2013. DC is strongly linked to the season, with highest values in the winter months and much lower values during the summer months. The summertime DC was close to zero, and the non-zero values could be attributed to Canadian forest fires events typically taking place during summer months (Dreessen et al., 2016; Dutkiewicz et al., 2011) and other recreational biomass burning activities. DC, BC (880nm) and $PM_{2.5}$ all peaked at winter months, when they showed very similar temporal trends. This is as expected since a fraction of woodsmoke PM is BC and woodsmoke sources led to high $PM_{2.5}$ concentrations in heating seasons. Nevertheless, unlike DC, the concentrations of BC (880nm) and $PM_{2.5}$ were also significant on occasion in the summertime, likely driven by traffic and other emission sources. This comparison supports DC as a qualitative woodsmoke marker.

Figure 4 illustrates the diurnal variations of DC, BC (880 nm), and $PM_{2.5}$ concentrations, for both summer months (July to September 2012) and winter months (December 2012 to March 2013) at Rutland. As expected, DC showed a strong diurnal pattern in the winter months, elevated during nighttime and peaking around 10 pm, and little variation during the summer months. The diurnal patterns of BC (880 nm) persisted over seasons, but driven by woodsmoke sources in the winter months and likely by traffic sources in the summer months. The wintertime $PM_{2.5}$ exhibited a strong diurnal pattern, driven by woodsmoke sources, and less significant but still noticeable diurnal pattern in the summertime, driven by traffic sources, which were not

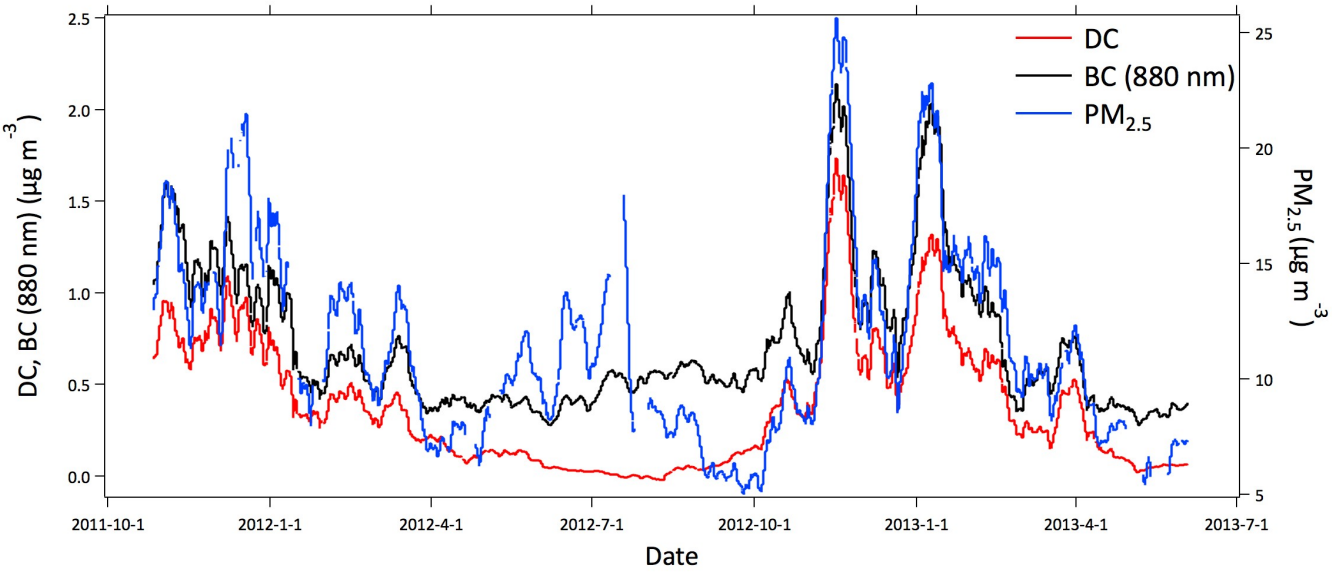
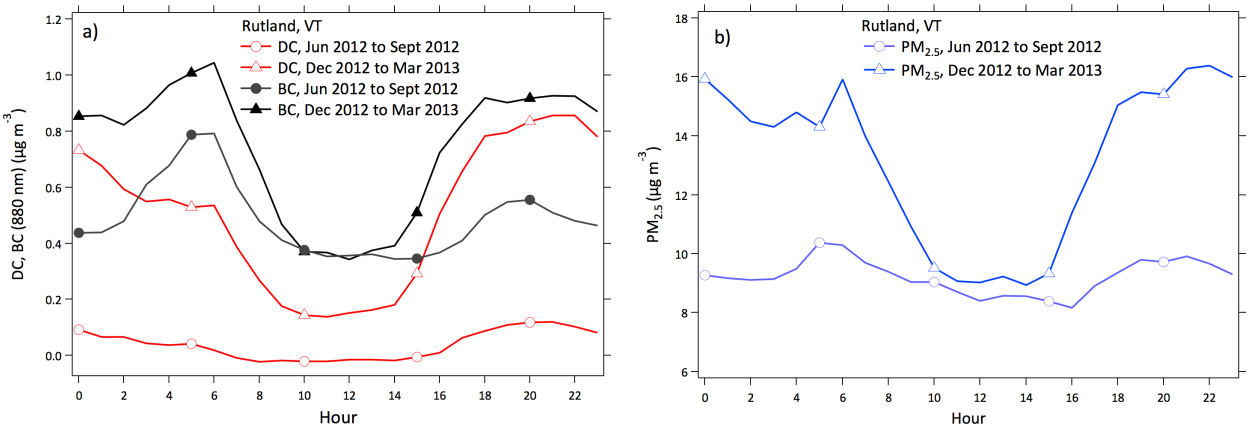


Figure 3. Two-week moving average DC (i.e., BC (370 nm)-BC (880 nm)), BC (880 nm), and $PM_{2.5}$ values measured at the Rutland site from October 2011 to June 2013

as dominant as woodsmoke sources in Rutland, VT. The nighttime enhancement in pollutant concentrations due to changes in the atmospheric boundary layer also contributed to the diurnal patterns both in summertime and wintertime. This comparison further supports DC as a qualitative woodsmoke marker. As mentioned earlier, previous studies found that SOA products may result in DC signals (Zhang et al., 2011; Zhong and Jang, 2011). If SOA formation were significant, we would expect that $PM_{2.5}$ and/or DC would peak around mid-day. The distinct diurnal patterns illustrated in Figure 4 is more consistent with strong influence of local emissions. Moreover, the seasonal trend shown in Figure 3 indicates that DC peaked during wintertime when SOA production is small and approached zero during summertime when SOA production is expected to be high. Therefore, both the diurnal and seasonal patterns indicate that SOA is not likely to be a main driver for DC in Rutland.

Figure 5 depicts the diurnal profiles of AAE (also known as α), derived from the two-wavelength AE-21 (i.e., 370 nm and 880 nm) data in Rutland, for both summer months (July to September 2012) and winter months (December 2012 to March 2013). Overall, the values of α in the winter months (ranging from 1.37 to 1.76) are much greater than those in the summer months (ranging from 0.93 to 1.24). Zotter et al. (2017) recommended values of α for traffic and woodsmoke as 0.9 and 1.68, respectively, by comparing the source apportionment of equivalent black carbon using the Aethalometer model originally proposed by Sandradewi et al. (2008a, b) with ^{14}C measurements of the elemental carbon fraction from several locations and campaigns across Switzerland. Those α values are also marked in Figure 5. Therefore, Figure 5 suggests, qualitatively, that woodsmoke PM dominates during the winter months, while traffic (or fossil fuel combustion) PM is a major source of PM during the summer months, which is consistent with the findings based on the emission inventory described earlier.



(a) (b)

Figure 4. Diurnal plots (i.e., averaged into 24 hours) of a) DC (i.e., BC (370 nm)-BC (880 nm)) and BC (880 nm), and b) $PM_{2.5}$ values measured at the Rutland site from October 2011 to June 2013.

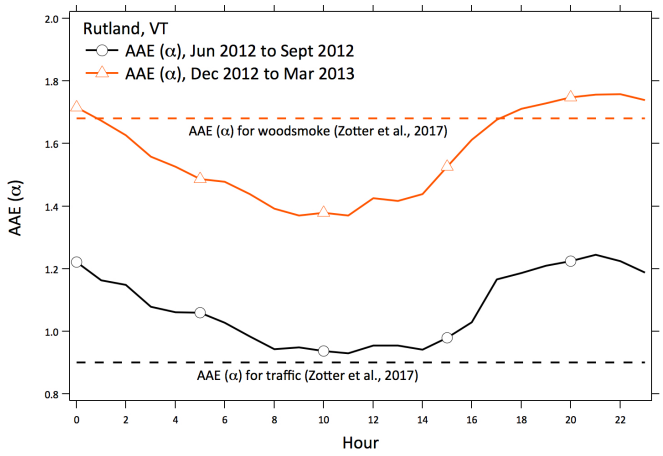
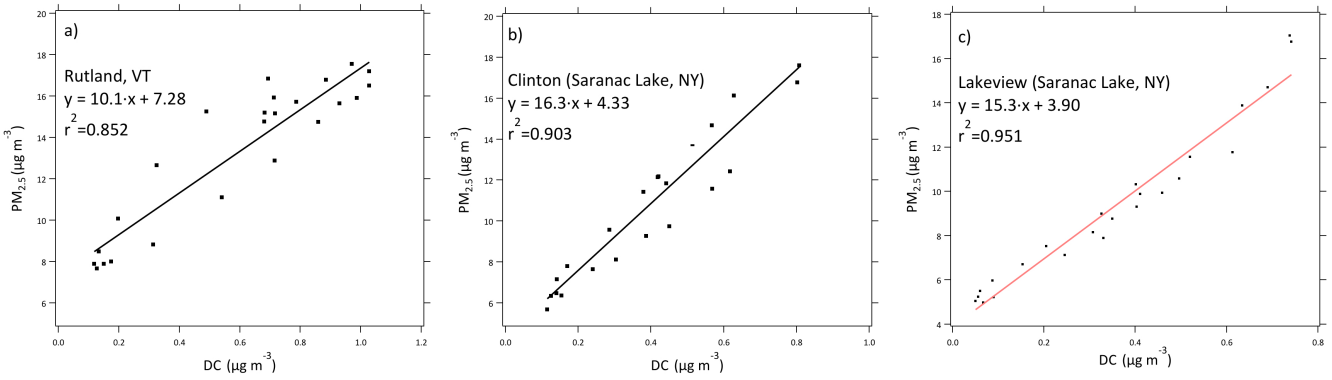


Figure 5. Diurnal profiles of absorption Ångström exponents (AAE) derived from the two-wavelength Aethalometer data measured at the Rutland site from October 2011 to June 2013. The recommended AAE values for traffic and woodsmoke, respectively, by Zotter et al. (2017) are also marked.

It is worth mentioning that both Figures 4 and 5 indicate that the woodsmoke activities are small but non-zero during the summer months, especially during nighttime. This phenomena will be investigated in a future study.

3.3 DC as a semi-quantitative marker for woodsmoke PM

Under woodsmoke-dominated environments we were studying, woodsmoke is the leading source of $PM_{2.5}$. Thus, we explored in this section the relationships between measured $PM_{2.5}$ and DC to assess whether DC can be used as semi-quantitative



(a) (b) (c)

Figure 6. Diurnal $PM_{2.5}$ vs DC (i.e., BC (370 nm)-BC (880 nm)) averaged over the wintertime operation periods for a) the Rutland site, and over the entire operation periods for b) the Clinton site and c) the Lakeview site, respectively, into 24 hours.

predictor of woodsmoke $PM_{2.5}$, for both ambient and plume environments. We used the terms "semi-quantitative" for two reasons. One is that both highly time-resolved $PM_{2.5}$ and BC measurements contains significant uncertainties. The other reason is that the DC cannot be quantitatively interpreted as an exact amount of a specific compound unless the mixture of UV-absorbing species remains constant enough and an average absorption cross-section can be assumed.

3.3.1 Ambient environments (Rutland, Clinton and Lakeview)

Figure 6 depicts $PM_{2.5}$ vs DC for the three ambient sites, where we averaged all the hourly data, binned by hours of the day (i.e., 24 data points), over the wintertime operation periods for Rutland and over the entire operation periods for Clinton and Lakeview, respectively. The slopes derived from the linear regressions represent Δ(Ambient $PM_{2.5}$)/ΔDC. Table 4 presents the linear regression results with all correlation coefficients of determination exceeding 0.85, which indicates strong positive correlations between changes in DC and changes in ambient $PM_{2.5}$ changes at the three sites. The most plausible explanation is that DC is an indicator of woodsmoke PM, which typically have a strongly diurnal pattern, considering that wood burning and traffic are the only two major local PM emissions sources, and that wood burning is typically the dominant source of DC in ambient atmosphere. DC signals only occur in the presence of wood burning. Furthermore, Figure 5 suggests that averaging stationary PM and BC data over a long period of time (e.g., over a winter month or longer in a fixed location) may lead to an average absorption cross section, i.e., a constant Δ(Ambient $PM_{2.5}$)/ΔDC, even though PM composition and the resulting absorption cross section may vary with time.

Furthermore, the regression coefficients for Clinton and Lakeview, the two ambient sites in Saranac Lake, NY, were very similar, suggesting that the Δ(Ambient $PM_{2.5}$)/ΔDC is reproducible for similar ambient environments. However, the same relationship did not hold for the different environment of Rutland. The inclusion of two heating seasons for the Rutland site, compared to one season in Clinton and Lakeview, may have also contributed to the discrepancy.

Table 4. Semi-quantitative relationship between DC (μg m^{-3}) and $PM_{2.5}$ (μg m^{-3}) in woodsmoke dominated ambient environments. The values inside the parentheses represent the corresponding one standard deviation.

Site		**Regression**	r^2
Rutland, VT		$PM_{2.5}$ = 10.1($\pm$0.90)·DC+7.28($\pm$0.60)	0.852
Saranac Lake, NY	Clinton	$PM_{2.5}$ = 16.3($\pm$1.14)·DC+4.33($\pm$0.52)	0.903
	Lakeview	$PM_{2.5}$ = 15.3($\pm$0.74)·DC+3.85($\pm$0.31)	0.951

3.3.2 Plume environments (Ithaca)

Figure 7 presents the $PM_{2.5}$-DC relationships from two reoccurring woodsmoke sources based on the plume measurements, reported as 5-second moving averages, that were conducted in Ithaca, NY. Figure 7a-7d, and Figure 7e-7f characterized two sources different days, respectively. Both sources were woodstoves as the configurations of the exterior stacks were consistent with this type of heating equipment. We estimated the background $PM_{2.5}$ concentrations for each day, and the values were $\sim$ 3 μg m^{-3}. Thus, we only included data points with $PM_{2.5}$ concentrations larger than 5 μg m^{-3} in Figure 7 in order to capture the plume signals. The slopes derived from the linear regressions represent Δ(Woodsmoke $PM_{2.5}$)/ΔDC, as we conducted sampling in woodsmoke plume environments.

Overall, we observed a dominant set of correlated measurements, likely representing the average woodstove combustion conditions, on each day. On both Figure 7c and 7f, "Condition 2" marked data points that define a different correlation are plotted with different symbols and a separate regression line. Each "Condition 2" line consisted of plume data recorded continuously. Possibly, during those conditions the woodstove combustion had been disturbed for some reasons (such as reloading the stove) for both Sources 1 and 2, thus significant deviation from the average conditions (denoted as "Condition 1" on both Figure 7c and 7f). For both Conditions 1 and Conditions 2, the correlations are generally strong. PM vs. DC slopes vary significantly for individual sources (from 3 to 9.6 for Source 1, and from 7.4 to 28.6 for Source 2). Even for the same source, the slopes can change considerably during different operating conditions. Our analysis also suggests that the $PM_{2.5}$-DC relationships can be potentially utilized to distinguish different combustion and operating conditions of woodsmoke sources. It is expected that cleaner burns would have a larger slope, i.e., less organic aerosol per unit woodsmoke PM (Chandrasekaran et al., 2011, 2013). In other words, the different combustion conditions lead to different chemical compositions and absorption cross sections, which can be potentially captured by high time resolution light absorption measurements. However, further studies are needed to link the $PM_{2.5}$-DC relationships to specific conditions.

3.3.3 DC and Heating degree days

Heating degree days (HDD), counted as the number of degrees that the daily average ambient temperature (F) is below 65°F, have been shown to be a better way to estimate energy use for space heating than actual temperature, as most homes or

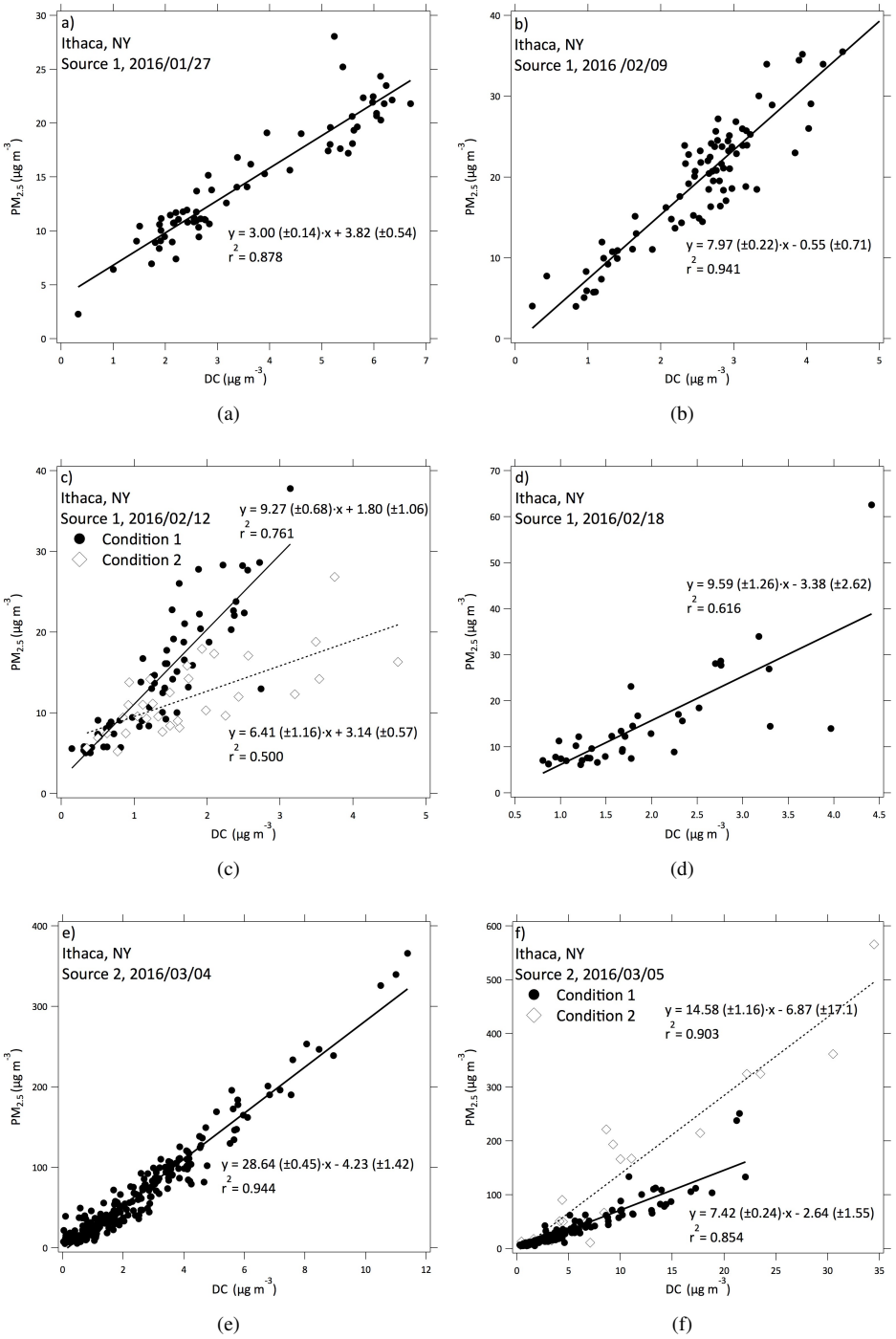


Figure 7. PM2.5 vs. DC relationships from two reoccurring woodsmoke sources based on the plume measurements conducted in Ithaca, NY. Data are reported as 5-second averages. The dates are expressed in YYYY/MM/DD. The values inside the parentheses represent the corresponding one standard deviation.

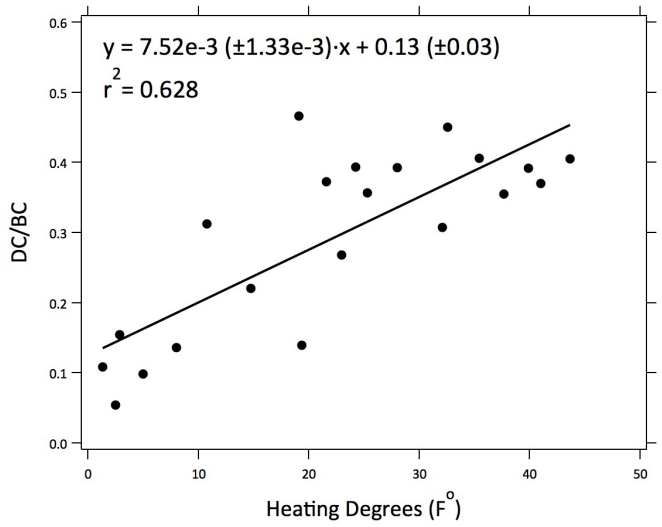


Figure 8. The relationship between DC/BC and HDD, both presented as monthly averaged values based on Rutland data. DC/BC is proposed as a woodsmoke PM emission indicator. The values inside the parentheses represent the corresponding one standard deviation.

facilities are maintained at a temperature above 65°F. In a woodsmoke-dominated environment, we expected more woodsmoke with higher HDD.

We calculated the monthly average HDD for Rutland using the temperature data recorded at the weather station located in the Rutland-Southern Vermont Regional Airport (KRUT). In our analysis, DC/BC was adopted as a semi-quantitative woodsmoke emission indicator.

The rationale to use DC/BC, rather than DC directly, was to take BC as a dilution indicator to normalize DC. Even though the absolute values of DC change with meteorological conditions, DC/BC should be driven by the amount of woodsmoke PM emissions generated, not woodsmoke PM concentrations.

Figure 8 illustrates the relationship between DC/BC and HDD, both presented as monthly averaged values. We observed a relatively strong linear relationship between DC/BC, which is an indicator for woodsmoke PM emissions, and HDD, which is a surrogate for space heating energy use. In other words, Figure 8 reveals not only a qualitative relationship (i.e., colder the weather, the more woodsmoke PM), but also a potentially semi-quantitative relationship linking space heating energy and woodsmoke PM emissions. Note that the proportionality between DC/BC and HDD will vary from place to place, depending on various factors such as fraction of heating obtained from biomass, and types of biomass fuels burned.

4 Conclusions

We presented the results from the joint wintertime measurements of $PM_{2.5}$ and light-absorptive PM in woodsmoke-dominated ambient and plume environments in three Northeastern U.S. cities/towns, where other types of sources contributing to DC such

as uncontrolled coal and kerosene burnings are usually rare. Our main conclusion is that DC can be a useful woodsmoke PM marker, both qualitatively and semi-quantitatively.

As a qualitative marker, DC can track the diurnal and seasonal woodsmoke PM patterns, approaching zero in the summertime, reaching highest values in the wintertime, and peaking at winter nights.

As a semi-quantitative marker, we showed strong linear relationships between $PM_{2.5}$ and DC in the ambient environments, and the resulting nearly constant Δ(Ambient PM2.5)/ΔDC values can be potentially estimate woodsmoke contributions to $PM_{2.5}$. $PM_{2.5}$ vs DC relationship has been shown to be reproducible for similar ambient environments (like the Clinton and Lakeview sites in Saranac Lake, NY). Nevertheless, the same relationship did not hold for the different environment (like Rutland, VT). In other words, the relationship depends on the environment and combustion conditions.

This paper also presented several other potentially interesting findings: the $PM_{2.5}$-DC relationships can be utilized to distinguish different combustion and operating conditions of woodsmoke sources; the semi-quantitative relationship between DC vs. HDD could link space heating energy and woodsmoke PM emissions. Those findings could have important implications and applications in air quality management. However, as elaborated in the paper, further studies are needed to elucidate those findings.

Competing interests. There are no competing interests.

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