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Can $\Delta PM_{2.5}/\Delta CO$ and $\Delta NO_y/\Delta CO$ Enhancement Ratios Be Used to Characterize the Influence of Wildfire Smoke in Urban Areas?

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ABSTRACT

In this study we investigate the use of $\Delta PM_{2.5}/\Delta CO$ and $\Delta NO_y/\Delta CO$ normalized enhancement ratios (NERs) in identifying wildfire (WF) smoke events in urban areas. Nine urban ambient monitoring sites with adequate CO, $PM_{2.5}$, and/or NO_y measurements were selected for this study. We investigated if WF events could be distinguished from general urban emissions by comparing NERs for wildfires with NERs calculated using yearly ambient data, which we call the ambient enhancement ratios (AERs). The $PM_{2.5}/CO$ and NO_y/CO AERs represent typical urban concentrations and can provide insight into the dominant emission sources of the city. All 25 WF events were distinguished because they had $\Delta PM_{2.5}/\Delta CO$ NERs that were significantly greater than the $PM_{2.5}/CO$ AER for each site. The $\Delta PM_{2.5}/\Delta CO$ NERs for the WF events ranged from 0.057–0.228 μg m^{-3} $ppbv^{-1}$. In contrast, we were only able to calculate useful $\Delta NO_y/\Delta CO$ NERs (correlations with $R^2 > 0.65$) for 4 of 17 events (only 17 of 25 events had NO_y data). For these 4 events, $\Delta NO_y/\Delta CO$ NERs ranged from 0.044–0.075 ppbv $ppbv^{-1}$, not all of which were significantly different from the NO_y/CO AERs at the site. We conclude that $\Delta PM_{2.5}/\Delta CO$ NERs are a very useful tool for identifying WF events, but that the high and variable NO_y concentrations in urban areas present problems when trying to use $\Delta NO_y/\Delta CO$ NERs.

Keywords: Wildfire; Normalized Enhancement Ratio; Urban AQS; $PM_{2.5}$; CO; NO_y

ABBREVIATIONS

WF = Wildfire
NER = Normalized Enhancement Ratio
ER = Emission Ratio
AER = Ambient Enhancement Ratio

INTRODUCTION

Wildfire (WF) smoke can significantly influence regional air quality (Popovicheva *et al.*, 2016). When this smoke is transported to urban areas, it can have severe negative public health implications (Roberts *et al.*, 2011). Chronic respiratory diseases, cardiovascular diseases, and increased risk of mortality have been attributed to exposure to fine particulate matter ($PM_{2.5}$) from WF smoke (Pope III *et al.*, 2002; Johnston *et al.*, 2012; Monsalve *et al.*, 2013; Díaz-Robles *et al.*, 2015; Adetona *et al.*, 2016; Kochi *et al.*, 2016). Due to climate change WFs are expected to increase in the US (Westerling *et al.*, 2006; Liu *et al.*, 2014; Val Martin *et al.*, 2015; Abatzoglou and Williams, 2016; Westerling, 2016). Air Quality System (AQS) monitoring stations provide real-time $PM_{2.5}$ measurements at a high temporal resolution, but it is hard to directly discriminate between forest fire smoke and other emission sources with only $PM_{2.5}$ measurements. While there are many tracers of WF smoke, such as acetonitrile (Andreae and Merlet, 2001; de Gouw *et al.*, 2003), water soluble potassium (K^+) (Ramadan *et al.*, 2000; Kim *et al.*, 2003; Popovicheva *et al.*, 2016), levoglucosan, and other organic molecular markers (Simoneit *et al.*, 1999; Simoneit, 2002; Khamkaew *et al.*, 2016), but these measurements either require intensive measurement techniques or have a low time resolution. In this paper we will assess the use of enhancement ratios of commonly measured pollutants (CO, $PM_{2.5}$, and NO_y) from AQS sites to identify WF smoke in urban areas.

Normalized enhancement ratios (NERs), also known as normalized excess mixing ratios, are a good way to help identify the source of a pollution plume observed at ambient monitoring sites (Andreae and Merlet, 2001; Briggs *et al.*, 2016). During a pollution or smoke event in which concentrations of two species (X and Y) increase substantially above background levels, NERs relate the excess concentrations of a target species X with that of a reference species Y (NER = $\Delta X/\Delta Y$, where Δ is the enhancement

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over background concentrations). The reference species Y has most commonly been carbon monoxide (CO) or carbon dioxide (CO_2), which are thought of as conserved, inert products of combustion (Andreae and Merlet, 2001; Hobbs *et al.*, 2003). McClure *et al.* (2016) showed that this is not always the case for CO_2. Vegetation uptake can deplete CO_2 in WF plumes within the boundary layer, distorting the NER. For this reason, it is typically best to use CO as the Y species. There are two common ways of calculating NERs: (1) by determining the absolute enhancement above the local background concentrations $(X_{plume} - X_{bkg})/(Y_{plume} - Y_{bkg})$, and (2) by determining the regression slope of X and Y during the smoke (or pollution) event.

Emission ratios (ERs) are the ratio of two species (X and Y) at the emission source. There is a difference between ERs and NERs, which should be kept in mind throughout this paper. NERs are calculated in plumes far from the emission source and therefore represent the sources plus any atmospheric processing that has occurred, whereas ERs reflect the ratio of the species at the emission source.

One purpose of calculating the NER of a plume is to try to identify the source of the plume by relating it to known ERs. For the NER of a plume to be equal to the ER it must be assumed that (1) there is a fixed emission X/Y ratio from the source; (2) there is no chemical or physical loss of the species with transport, only dilution; and (3) background dilution is constant. For aerosols or reactive gas species such as reactive nitrogen (NO_y), the NER measured downwind of a fire may be different than the ER of the same fire due to the production or loss of the target species. In addition, Yokelson *et al.* (2013) has argued that the two primary methods for calculating NERs mentioned previously can be inaccurate due to changes in background concentrations during plume transport. Briggs *et al.* (2016) used the two primary NER methods (absolute enhancement over background, and regression analysis), as well as a third method developed to address Yokelson *et al.* (2013)'s concerns, while studying WF plumes at the Mt. Bachelor Observatory. Briggs *et al.* (2016) found little difference between $\Delta\sigma_{scat}/\Delta CO$ and $\Delta NO_y/\Delta CO$ NERs calculated using the three methods if the enhancement of the species in the plumes was large relative to the background concentrations (σ_{scat} is the aerosol scattering coefficient, which is well correlated to $PM_{2.5}$). Large differences were found for $\Delta O_3/\Delta CO$ and $\Delta CO/\Delta CO_2$, where the enhancement is small relative to the background. This result verified that if the plume concentration is significantly larger than the background the regression method for calculating NERs is acceptable. The study also showed that despite possible production or loss of the target species during transportation, NERs are useful in determining plume sources.

Review articles of WF emissions show $PM_{2.5}$/CO ERs ranging from ~0.10 to 0.20 μg m^{-3} $ppbv^{-1}$ (Andreae and Merlet, 2001; Janhäll *et al.*, 2010; Akagi *et al.*, 2011). Although these studies primarily characterized fresh smoke emissions, there was no clear consensus whether PM mass increases (Hobbs *et al.*, 2003; Reid *et al.*, 2005; Yokelson *et al.*, 2009; Vakkari *et al.*, 2014; Briggs *et al.*, 2016) or stays the same (Akagi *et al.*, 2012; Jolleys *et al.*, 2015; May *et al.*, 2015) with plume age. Even with the complexities of plume aging on PM mass, NERs of aged WF events measured in the field mostly fit within the range of WF ERs measured at the fire source. Studies of boreal forest fire plumes observed $\Delta PM_{2.5}/\Delta CO$ of 0.13–0.15 μg m^{-3} $ppbv^{-1}$ (DeBell *et al.*, 2004; Dutkiewicz *et al.*, 2011). A wide range in $\Delta PM_{2.5}/\Delta CO$ NERs have been found in long-range transported WF events observed at the Mt. Bachelor Observatory in Oregon (0.18–0.43 μg m^{-3} $ppbv^{-1}$) (Wigder *et al.*, 2013; Laing *et al.*, 2016). Similar wide ranges have been observed in aged WF plume ΔOA/ΔCO (OA = organic aerosol, which makes up ~95% of $PM_{2.5}$ mass) (Jolleys *et al.*, 2012; Sakamoto *et al.*, 2015).

Mobile emission and urban background $PM_{2.5}$/CO ratios are significantly lower than WF ratios. $PM_{2.5}$/CO ratios from measurements near major highways and urban background range from 0.021 to 0.045 μg m^{-3} $ppbv^{-1}$ (Dimitriou and Kassomenos, 2014; Patton *et al.*, 2014). The differences between the urban background ratios and ratios from WF emissions suggests that the $\Delta PM_{2.5}/\Delta CO$ may be useful in distinguishing WF contribution in urban areas.

In urban settings vehicles are the dominant source of nitrogen oxides (NO_x), which are converted to NO_y through oxidation (Seinfeld and Pandis, 2006). The atmospheric lifetime of NO_y is longer than NO_x, making NO_y a more conserved measure. Both NO_x and NO_y have substantially shorter lifetimes than CO. NO_x and NO_y have lifetimes of ~1 day under normal background concentrations (Seinfeld and Pandis, 2006), and hours in urban areas (Spicer, 1982; Beirle *et al.*, 2011). Despite this difference in lifetimes between CO and NO_x(y), it has previously been assumed that NO_x/CO ERs are relatively conserved within the urban environment since the predominant emission sources of NO_x and CO are local vehicular traffic (Hassler *et al.*, 2016). Measurements of NO_x/CO and NO_y/CO in cities have similar ranges, which verifies that NO_x and NO_y are comparable within urban environments. Studies of urban and near-road ambient measurements observed NO_y/CO ranging from 0.058 to 0.112 ppbv $ppbv^{-1}$ (Wang *et al.*, 2003; Patton *et al.*, 2014), and NO_x/CO ranging from 0.063 to 0.150 ppbv $ppbv^{-1}$ (Kirchstetter *et al.*, 1999; Magliano *et al.*, 1999; Long *et al.*, 2002). NO_x(y)/CO ratios are dictated by vehicle emissions, so the ratio varies from city to city depending on the composition of their mobile fleet (e.g., gasoline vs diesel) (Hassler *et al.*, 2016). In the past three decades CO emissions from gasoline-powered vehicles decreased faster than those of NO_x, which has led to an increasing trend in urban ambient NO_x/COs from the 1970s to the early 2000s (Parrish *et al.*, 2002; Parrish, 2006; Parrish *et al.*, 2011). The mean observed NO_x/CO ratio for 28 US cities was 0.118 ppbv $ppbv^{-1}$ in 2000, and 0.139 ppbv $ppbv^{-1}$ in 2003 (Parrish, 2006; Parrish *et al.*, 2009). Hassler *et al.* (2016) similarly found that the NO_x/CO ratio measured in the LA Basin steadily increased from the 1970s until 2007, and from 2007–2016 it has been steady.

NO_x/CO and NO_y/CO ratios for WF events are significantly smaller than NO_x/CO urban ratios. Akagi *et al.* (2011) reports ERs for different forest types; boreal forests have a NO_x/CO ER of 7.0×10^{-3} ppbv $ppbv^{-1}$, temperate

forests an ER of 0.026 ppbv ppbv^{-1}, and extratropical forest an ER of 9.0×10^{-3} ppbv ppbv^{-1}. DeBell *et al.* (2004) found $\Delta NO_y/\Delta CO$ NERs of aged smoke events at three rural locations to range from 2.4×10^{-3} to 7.4×10^{-3} ppbv ppbv^{-1}, much higher than the ambient background $\Delta NO_y/\Delta CO$ ratios (0.12 ppbv ppbv^{-1}). WF events observed at Mt. Bachelor during the summer of 2012–2013 had $\Delta NO_y/\Delta CO$ NERs in a similar range (3.0×10^{-3} to 1.3×10^{-2} ppbv ppbv^{-1}) (Briggs *et al.*, 2016). All of these studies were conducted in locations with low NO_y background concentrations, which makes distinguishing $\Delta NO_y/\Delta CO$ NERs easier. We will evaluate if $\Delta NO_y/\Delta CO$ NERs can be used in urban areas with high NO_y concentrations.

The use of NERs to identify WF smoke has been predominantly used previously at background locations with low ambient concentrations. In this study we plan to examine whether $\Delta PM_{2.5}/\Delta CO$ and $\Delta NO_y/\Delta CO$ NERs can be used to distinguish WF events in typical urban areas using US EPA AQS data, and will address the following scientific questions:

- What are the characteristics of ambient urban measurements that make it useful for NER analysis?
- Can WF smoke events be identified in urban areas using $\Delta PM_{2.5}/\Delta CO$ and $\Delta NO_y/\Delta COs$ NERs?
- How do $PM_{2.5}/CO$ and NO_y/CO AERs fluctuate for different monitoring sites and different cities?
- How do $PM_{2.5}/CO$ and NO_y/CO AERs compare to ERs derived from emission inventory data?

METHODS

Data Collection

For our study we chose urban AQS monitoring sites in the US with collocated hourly ambient CO and $PM_{2.5}$ data available on the US Environmental Protection Agency (EPA) AQS API/Query AirData website [*https://aqs.epa.gov/api*] (Fig. 1; Table S1). Only sites with adequate CO measurements were used. CO data was deemed adequate if it was measured with an instrument whose EPA method code was greater than 500 (e.g., 554, 588, and 593; See EPA codes: https://aqs.epa.gov/aqsweb/documents/codetables/methods_all.html). These instruments report CO concentrations at a 1 ppb resolution and have a method detection limit (MDL) of 20 ppb. Instruments with an EPA method code of less than 500 did not have enough resolution to identify WF events. These instruments measure CO concentrations at only a 100 ppb resolution and have MDLs of 500 ppb. At the Reno and Stockton sites, the CO instrumentation was changed from instruments with method codes 88 and 54 to instruments with method code 593 on 12/29/2010 and 5/31/2012, respectively. Due to this upgrade, we were able to use data collected after the upgrade from these sites. We highly recommend that EPA monitoring sites currently using CO instruments associated with an EPA method code less than 500 upgrade their CO instrumentation. This will result in more useful and useable CO data nationwide.

Wildfire Identification

We limited our study to the summer and fall, when large forest fires occur in the Western US and are most likely to affect urban air quality. We selected WF events by selecting time periods in the summer and fall in which there was a noticeable increase in $PM_{2.5}$ and CO, and a strong correlation ($R^2 > 0.65$) between them. We have used this method of identifying WF events successfully in previous studies (Wigder *et al.*, 2013; Baylon *et al.*, 2015; Briggs *et al.*, 2016;

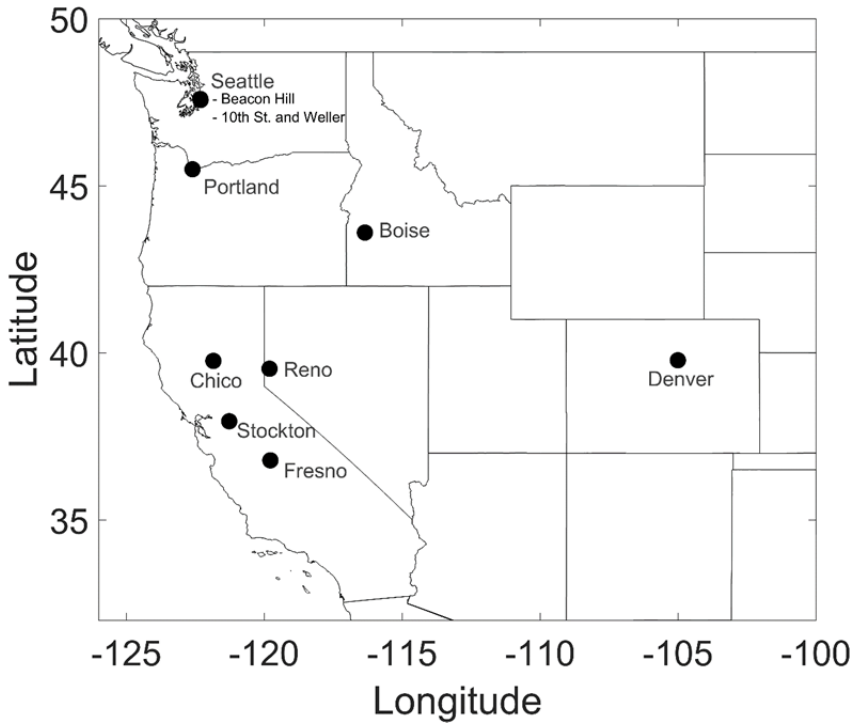

Fig. 1. Location of US Cities with sample sites used in this study.

Laing *et al.*, 2016). We verified the fire events by one of two ways. The first was confirming transport to the monitoring stations from known fire locations using the National Oceanic and Atmospheric Administration Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) back-trajectories (Stein *et al.*, 2015). Fire locations were identified using Moderate Resolution Imaging Spectroradiometer (MODIS) satellite-derived active fire counts (Justice *et al.*, 2002). Some of the smoke events were further verified by search for local or national news articles pertaining to forest fire smoke in the selected cities.

Wildfire Plume Normalized Enhancement Ratios (NERs)

An NER depicts the relative enhancement of two species above background concentrations (e.g., $\Delta X/\Delta Y$; Δ is the enhancement over the background concentration) (Andreae and Merlet, 2001; Wigder *et al.*, 2013; Laing *et al.*, 2016). We calculated $\Delta PM_{2.5}/\Delta CO$ NERs and $\Delta NO_y/\Delta CO$ NERs from the slope of the Reduced Major Axis (RMA) regression. $\Delta PM_{2.5}/\Delta CO$ NERs were calculated for all WF events; $\Delta NO_y/\Delta CO$ NERs were calculated when NO_y data was available (17 of the 25 events).

Ambient Enhancement Ratios (AERs)

We calculated $PM_{2.5}/CO$ and NO_y/CO AERs at each site using an RMA regression using all hourly data in the year. AERs reflect typical urban emissions at a given monitoring site. For the $PM_{2.5}/CO$ ratios, we used $PM_{2.5}$ data up to the 99th percentile to mitigate the influence of WF events on the AERs or other exceptional events. The NO_y/CO AERs were calculated using all available data.

Emission Inventory–Derived Emission Ratios (ERs)

For comparison with AERs, we calculated $PM_{2.5}/CO$ and NO_x/CO ERs from county emission inventories. For each site, we obtained county emission inventories for CO, $PM_{2.5}$, and NO_x from the US EPA 2011 National Emissions Inventory (NEI11) (*https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data*). ERs were calculated for each source sector (fuel combustion, mobile sources, industrial processes, etc.), as well as in sum across all sources.

RESULTS AND DISCUSSION

We identified 25 WF events at nine different monitoring sites in US cities that met our criteria. All 25 had CO and $PM_{2.5}$ data, and 17 of the events also had NO_y data. As described in the Methods section we could not use data for many other sites due to low CO data resolution. We conclude that only measurements with EPA method code > 500 can be used for NER analysis. First we will discuss AERs in order to determine an urban baseline ratio from which the WF events can be compared. Then we will discuss the NERs of specific events and evaluate their use in identifying WF smoke.

Urban $PM_{2.5}$/CO and NO_y/CO AERs

Our goal is to determine whether enhancement ratios from WF events can be distinguished from urban background conditions. The background is represented by Ambient Enhancement Ratios (AERs), which reflect typical urban emissions and can vary city to city depending on the predominant emission source. To mitigate influence of large WF events, we calculated $PM_{2.5}/CO$ AERs using up to the 99th percentile of $PM_{2.5}$ data. Large WF events with high $PM_{2.5}$ concentrations can positively bias $PM_{2.5}/CO$ AERs calculated from yearly data. The most significant differences in $PM_{2.5}/CO$ slope between using all data and using only the 99th percentile were seen in the Boise and Reno datasets, each of which experienced extended periods of WF smoke with very high $PM_{2.5}$ concentrations. Due to the exceptional WF events at these two sites, the $PM_{2.5}/CO$ ratios were ~30% higher using the full dataset compared to the using up to the 99th percentile. Given that these fire events were anomalous in that they occurred during only one summer, the $PM_{2.5}/CO$ AERs using up to the 99th percentile of $PM_{2.5}$ data provide a more accurate representation of typical non-WF concentrations.

For the sites we studied, $PM_{2.5}/CO$ AERs ranged from 0.021–0.066 μg m^{-3} ppbv^{-1} with the majority falling between 0.030–0.046 μg m^{-3} ppbv^{-1} (Table 1). These values match other studies characterizing $PM_{2.5}/CO$ ratios of ambient urban background concentrations (Dimitriou and Kassomenos, 2014; Patton *et al.*, 2014). The lowest $PM_{2.5}/CO$ AERs were at the Seattle 10th St site and Denver (0.021 μg m^{-3} ppbv^{-1}). Both of these sites are in close proximity to and highly influenced by heavily trafficked highways. The Seattle 10th St site has a significantly lower $PM_{2.5}/CO$ AER (0.021 μg m^{-3} ppbv^{-1}) compared to Seattle Beacon Hill (0.035 μg m^{-3} ppbv^{-1}). The reasons for the difference will be discussed further in the Seattle Case Study section but underscore the fact that the location of the monitoring site can have a major influence on the AERs and therefore may not be representative of the entire city. The highest $PM_{2.5}/CO$ AER was observed in Boise (0.066 μg m^{-3} ppbv^{-1}). $PM_{2.5}$ and CO data for Boise was only available for 2015, during which extended periods of WF events were observed. This likely skewed the ratio higher despite using only data up to the 99th percentile of $PM_{2.5}$.

We compared the measured AERs to $PM_{2.5}/CO$ ERs calculated for each county using the NEI11 from the EPA. $PM_{2.5}/CO$ ERs were calculated for fuel combustion sources, mobile sources, the sum of all emission sources, the sum of all sources except fires, and the sum of all sources except fires and dust (Table S2). Comparing the measured $PM_{2.5}/CO$ AERs to $PM_{2.5}/CO$ ERs calculated for the sum of all sources except fires and dust, all sites except Portland were within 30%; but compared to $PM_{2.5}/CO$ ERs calculated for the sum of emissions except fires, only 5 of the 9 sites are within 30% of the measured $PM_{2.5}/CO$ AERs. Additional information on the NEI derived $PM_{2.5}/CO$ ERs is available in the Supplemental Material.

The NO_y/CO AERs using all data ranged from 0.070–0.185 ppbv ppbv^{-1} (Table 1). All sites had slight diurnal differences with an increase in NO_y/CO during the day and minimal seasonal differences. To try to isolate traffic emissions, we calculated NO_y/CO AERs using only weekday

Table 1. $PM_{2.5}$/CO and NO_y/CO AERs for each site. The $PM_{2.5}$/CO AERs were calculated using an RMA regression of all data up to the 99th percentile of $PM_{2.5}$ mass. The NO_y/CO AERs are calculated using an RMA regression of all data at each site. NA means NO_y data was not available.

Site location	Site county	$PM_{2.5}$/CO AERs ($\mu g\ m^{-3}\ ppbv^{-1}$)*		NO_y/CO AERs ($ppbv\ ppbv^{-1}$)			
				All data		Weekday rush hour data	
		slope	R^2	slope	R^2	slope	R^2
Seattle - Beacon Hill	King	0.035	0.379	0.185	0.711	0.218	0.753
Seattle - 10th St	King	0.021	0.407	NA	NA	NA	NA
Portland, OR	Multnomah	0.030	0.537	0.088	0.947	0.095	0.876
Boise, ID	Ada	0.066	0.348	0.136	0.718	0.158	0.780
Denver, CO	Denver	0.021	0.188	0.145	0.801	0.160	0.831
Stockton, CA	San Joaquin	0.046	0.351	NA	NA	NA	NA
Fresno, CA	Fresno	0.041	0.454	0.070	0.918	0.079	0.812
Reno, NV	Washoe	0.029	0.315	0.130	0.858	0.141	0.910
Chico, CA	Butte	0.046	0.565	NA	NA	NA	NA

*All data up to the 99th percentile of $PM_{2.5}$ concentration used for RMA analysis.

(Monday–Friday) data during peak morning traffic (5:00–9:00 AM). This method has been used previously as it captures fresh vehicle emissions and minimized the effects of reactive nitrogen species produced through photochemical oxidation (Parrish *et al.*, 2002; Parrish, 2006; Hassler *et al.*, 2016). NO_y/CO AERs calculated using the morning rush hour data were slightly higher (7–14%) for all sites compared to AERs calculated using all data. The difference may be attributed to NO_y deposition and loss during the day. The high R^2 values for the NO_y/CO AERs at all sites and lack of significant temporal changes in NO_y/CO ratio indicates a homogenously mixed source dominated by on-road vehicle emissions. The range of observed NO_y/CO AERs in this study is similar to previous studies of urban NO_y/CO AERs (Wang *et al.*, 2003; Patton *et al.*, 2014) and urban NO_x/CO AERs (Kirchstetter *et al.*, 1999; Magliano *et al.*, 1999; Long *et al.*, 2002).

We compared the NO_y/CO AERs to the corresponding NO_x/CO ERs derived from the NEI11 (Table S3). NO_x/CO ERs calculated from the EPA NEI11 for the sum of all emission sources, the sum of all sources except fires, mobile sources, and fuel combustion sources. As the principal source of NO_x and CO are vehicles, the NO_x/CO ERs are dominated by the mobile NO_x/CO ER. The NO_x/CO ERs sum of all sources were within 30% of the NO_y/CO AERs for 4 of the 6 sites. For Portland and Fresno, the NO_x/CO ERs were higher by a factor of 2 and 5, respectively. These differences are discussed in greater detail in the Supplemental Material.

$\Delta PM_{2.5}/\Delta CO$ and $\Delta NO_y/\Delta CO$ NERs during WF Events

Table 2 shows $\Delta PM_{2.5}/\Delta CO$ NERs for the 25 WF events range from 0.057–0.228 $\mu g\ m^{-3}\ ppbv^{-1}$, with the majority being between 0.085 and 0.170 $\mu g\ m^{-3}\ ppbv^{-1}$. These values are consistent with previous measurements of WF events (DeBell *et al.*, 2004; Dutkiewicz *et al.*, 2011; Chen and Xie, 2014), and estimates of emission factors for forest fires (Andreae and Merlet, 2001; Janhäll *et al.*, 2010; Akagi *et al.*, 2011).

The $PM_{2.5}$ vs CO scatter plots for individual sites are shown in Figs. 2 and 3. The WF events (orange dots and lines) are generally consistent with the ER for temperate forests (solid red line; (Akagi *et al.*, 2011)). All WF events had $\Delta PM_{2.5}/\Delta CO$ NERs that were significantly greater than the $PM_{2.5}$/CO AER at the site, which confirms that $\Delta PM_{2.5}/\Delta CO$ NERs can be used to distinguish and identify WF events in urban locations. The mobile $PM_{2.5}$/CO ER derived from the NEI11 is significantly lower than the AER at all sites and bounds the lower edge of the scatter plot (green dotted line).

Although most of the $\Delta NO_y/\Delta CO$ NERs were lower than the NO_y/CO AER for all sites (Fig. 4), only 4 of the 17 events had a good correlation between NO_y and CO ($R^2 > 0.65$). The low occurrence of a good correlation between NO_y and CO is most likely due to the high and variable NO_y background in the urban areas. For the 4 WF events we were able to characterize (with $R^2 > 0.65$), the $\Delta NO_y/\Delta CO$ ranged from 0.044–0.075 $ppbv\ ppbv^{-1}$. These values are higher than NO_x/CO ERs for forest fires (Andreae and Merlet, 2001; Akagi *et al.*, 2011), and higher than $\Delta NO_y/\Delta CO$ NERs observed in WF plumes measured in rural areas (DeBell *et al.*, 2004). This is likely be caused by the high NO_y background in the urban areas in this study due to mobile emission compared to rural background concentrations. In addition, only 3 of the 4 had $\Delta NO_y/\Delta CO$ NERs lower than the NO_y/CO AER at the site. Therefore even if a $\Delta NO_y/\Delta CO$ NER can be calculated for a WF, it is not necessarily distinguishable from the background NO_x/CO ratio. Due to the high and variable urban NO_y background concentrations, we found $\Delta NO_y/\Delta CO$ NERs not suitable for use in identifying WF events in urban locations.

Seattle Case Study

The Seattle sites provide an interesting comparison of WF events captured by two sites in close proximity to each other. As previously mentioned, the $PM_{2.5}$/CO AER for the 10th St site was the lowest of all of the sites ($0.021\ \mu g\ m^{-3}\ ppbv^{-1}$), and substantially lower than Beacon Hill ($0.035\ \mu g\ m^{-3}\ ppbv^{-1}$), due to the heavy mobile emission influence at 10th St. We investigated how the different backgrounds at these two sites affected their WF NERs.

Fig. 5 shows the time-series of $PM_{2.5}$ and CO during the WF events. We observed simultaneous increases in $PM_{2.5}$

Table 2. Wildfire event NERs from the monitoring sites and ERs from Akagi *et al.* (2011) and EPA NEI11 emission inventories. Events with $R^2 > 0.65$ are bolded. NA means NO_y data was not available.

Site	Date Time (local)	$\Delta PM_{2.5}/\Delta CO$ ($\mu g\ m^{-3}\ ppbv^{-1}$)		$\Delta NO_y/\Delta CO$ ($ppbv\ ppbv^{-1}$)	
		slope	R^2	slope	R^2
Seattle - Beacon Hill	8/22/15 15:00–8/23/15 1:00	**0.108**	**0.920**	0.088	0.161
Seattle - Beacon Hill	8/23/15 10:00–8/23/15 19:00	**0.158**	**0.876**	0.123	0.082
Seattle - 10th St	8/23/15 6:00–8/23/15 20:00	**0.057**	**0.677**	NA	NA
Portland	8/22/15 00:00–8/24/15 00:00	**0.228**	**0.978**	NA	NA
Boise	8/14/15 12:00–8/16/15 12:00	**0.104**	**0.675**	0.059	0.156
Boise	8/21/15 8:00–8/22/15 00:00	**0.116**	**0.955**	0.017	0.043
Boise	10/11/15 16:00- 10/12/15 18:00	**0.133**	**0.928**	0.051	0.423
Boise	10/12/15 20:00–10/13/15 20:00	**0.129**	**0.731**	0.076	0.322
Boise	10/13/15 20:00–10/14/15 14:00	**0.092**	**0.820**	0.069	0.511
Boise	10/15/15 15:00–10/16/15 15:00	**0.107**	**0.776**	0.078	0.372
Stockton	8/15/15 4:00–8/16/15 19:00	**0.158**	**0.844**	NA	NA
Denver	8/22/15 9:00–8/23/15 10:00	**0.166**	**0.762**	NA	NA
Fresno	8/15/15 10:00–8/16/15 15:00	**0.087**	**0.815**	**0.047**	**0.707**
Fresno	8/17/15 18:00–8/18/15 15:00	**0.091**	**0.778**	**0.075**	**0.820**
Fresno	9/11/15 15:00–9/11/15 20:00	**0.141**	**0.986**	0.012	0.227
Fresno	9/13/15 14:00–9/14/15 18:00	**0.086**	**0.749**	**0.044**	**0.758**
Reno	8/18/13 14:00–8/19/13 14:00	**0.126**	**0.743**	0.057	0.366
Reno	8/22/13 8:00–8/26/13 00:00	**0.145**	**0.918**	0.034	0.306
Reno	8/27/13 12:00–8/28/13 18:00	**0.161**	**0.868**	0.042	0.097
Reno	9/18/14 00:00–9/19/14 00:00	**0.128**	**0.886**	0.006	0.579
Reno	8/20/15 19:00–8/21/15 19:00	**0.119**	**0.767**	**0.075**	**0.716**
Chico	7/28/13 20:00–7/31/13 12:00	**0.153**	**0.892**	NA	NA
Chico	7/29/14 19:00–7/30/14 10:00	**0.093**	**0.979**	NA	NA
Chico	9/22/14 5:00–9/22/14 15:00	**0.161**	**0.895**	NA	NA
Chico	9/13/15 14:00–9/14/15 10:00	**0.142**	**0.925**	NA	NA
All sites mean ± SD		0.128 ± 0.036		0.060 ± 0.015[#]	
Akagi ER for boreal forests*		0.138		0.0066	
Akagi ER for temperate forests*		0.163		0.0263	
EPA WF ER range[t]		0.096–0.164		0.010–0.048	
EPA fuel combustion ER range[t]		0.155–0.245		0.096–0.669	
EPA mobile ER range[t]		0.008–0.014		0.178–0.365	

[#] Only events with an $R^2 > 0.65$ were used to calculate the mean (4 of 17 events).
[*] Calculated using emission factors from Akagi *et al.* (2011).
[t] Calculated using EPA NEI11 from all 8 Counties (https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data).

at both sites. The red boxes show the identified WF events for each site detailed in Table 2. Despite capturing the same WF events, the $\Delta PM_{2.5}/\Delta CO$ NERs are different for the two sites. The $\Delta PM_{2.5}/\Delta CO$ NER for Seattle 10th St was the lowest of all the WF events (0.057 $\mu g\ m^{-3}\ ppbv^{-1}$), and significantly lower than the $\Delta PM_{2.5}/\Delta CO$ NERs for the same event at the Beacon Hill site (0.158 $\mu g\ m^{-3}\ ppbv^{-1}$). The difference is due to the location of the monitoring sites. The 10th St site is located in very close proximity to a major highway (I-5) in downtown Seattle and is heavily influenced by traffic emissions. The Beacon Hill site is located in a park ~350 feet above the city and much less influenced by traffic. The background CO concentration is significantly higher at the 10th St site than the Beacon Hill as can be seen in Fig. 5. During the WF event on 8/23/2015, the maximum CO concentration at 10th St (1312 ppbv) was more than double that at Beacon Hill (568 ppbv). Due to this high and variable CO background, the correlation between $PM_{2.5}$ and CO is not as strong at the 10th St site during the WF events. During the event observed at both sites on 8/23/2015, the Beacon Hill site had a much better correlation ($R^2 = 0.876$) than the 10th St site ($R^2 = 0.677$).

The difference in NERs of the same fire event seen at two sites with different backgrounds substantiates Yokelson *et al.* (2013)'s argument that changes in background concentrations can significantly affect calculated NERs. Despite the NERs being different, at both sites the WF event NER was significantly larger than the $PM_{2.5}/CO$ AERs and thus the WF event on 8/23/2015 could be discerned.

On 8/22/2015 there was a clear increase in $PM_{2.5}$ observed at both sites. For this time period the $PM_{2.5}$ and CO were much better correlated at Beacon Hill ($\Delta PM_{2.5}/\Delta CO$ $R^2 = 0.92$) compared to the 10th St site ($\Delta PM_{2.5}/\Delta CO$ $R^2 = 0.33$). Since the event at 10th St site did not meet our criteria, it

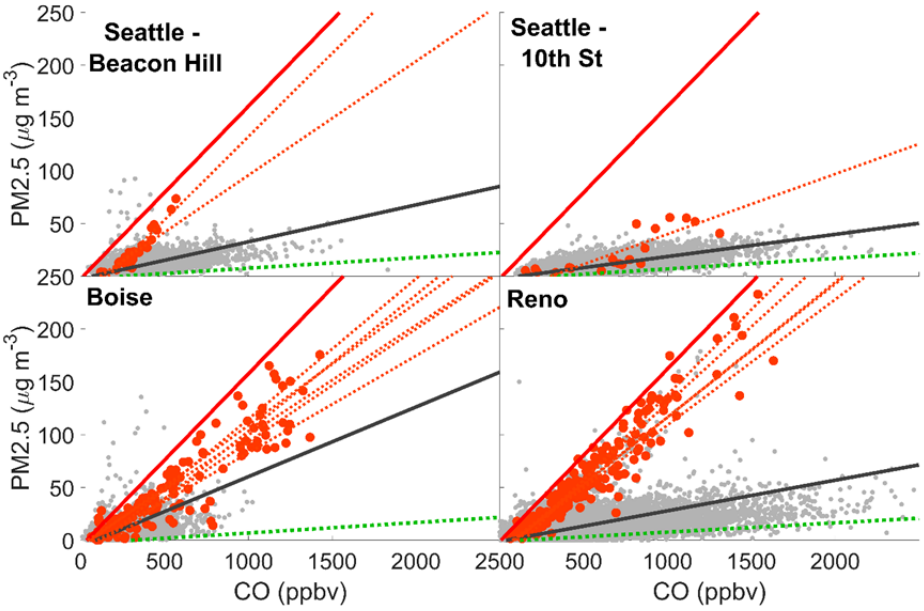

Fig. 2. $PM_{2.5}$ vs. CO scatter plots for Seattle - Beacon Hill, Seattle - 10th St, Boise, and Reno. All points are hourly averages. The grey dots are all of the data points at the site, and the orange dots represent the identified WF events. The lines are defined as follows. Solid dark grey line: $PM_{2.5}$/CO AERs calculated (RMA slope) at each site using data up to the $PM_{2.5}$ 99th percentile. Dotted orange line(s): $\Delta PM_{2.5}/\Delta CO$ NERs for WF events. Dotted green line: Mobile EPA County Emission Inventory $PM_{2.5}$/CO ER. Solid red line: $PM_{2.5}$/CO ER for Temperate Forests (0.164 μg m^{-3} ppbv^{-1}; Akagi *et al.* (2011)).

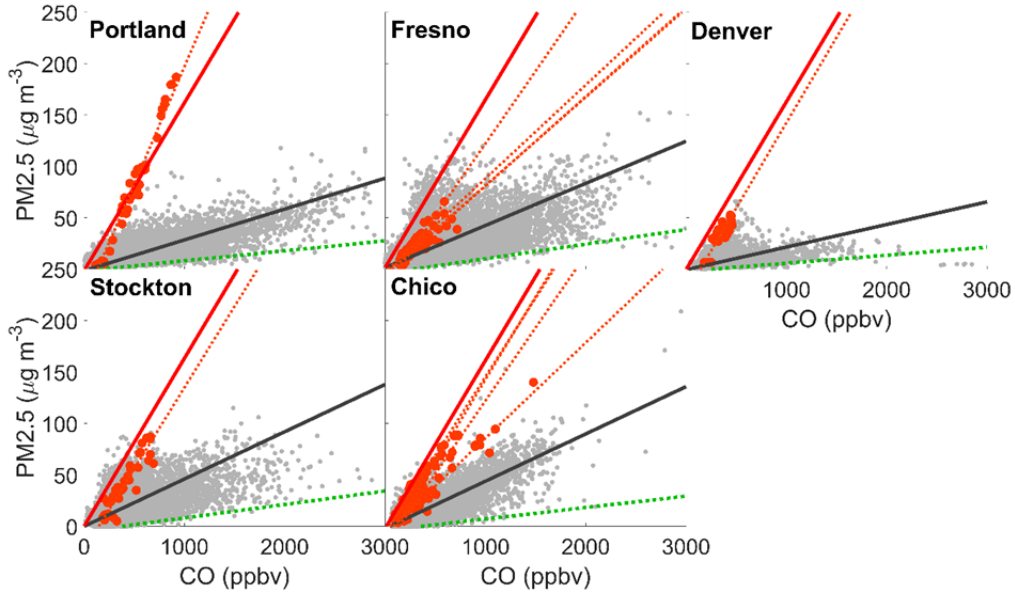

Fig. 3. $PM_{2.5}$ vs. CO scatter plots for Portland, Fresno, Denver, Stockton, and Chico. Color and line designations are the same as in Fig. 2.

was not counted as a WF event. This is an example of high background concentrations impeding the use of enhancement ratios in identifying WF events. The lower and less variable the background concentrations are, the easier WF events will be able to be identified. For site with high background, such as Seattle 10th St, only larger WF plumes will be identifiable, whereas smaller plumes can be identified at the Beacon Hill site.

CONCLUSIONS

In this paper we evaluated the use of normalized enhancement ratios in identifying WF events at nine monitoring sites in US cities using commonly measured AQS criteria pollutants ($PM_{2.5}$, CO, and NO_y). Our main conclusions are as follows:

- Some monitoring sites had CO measurements that had a

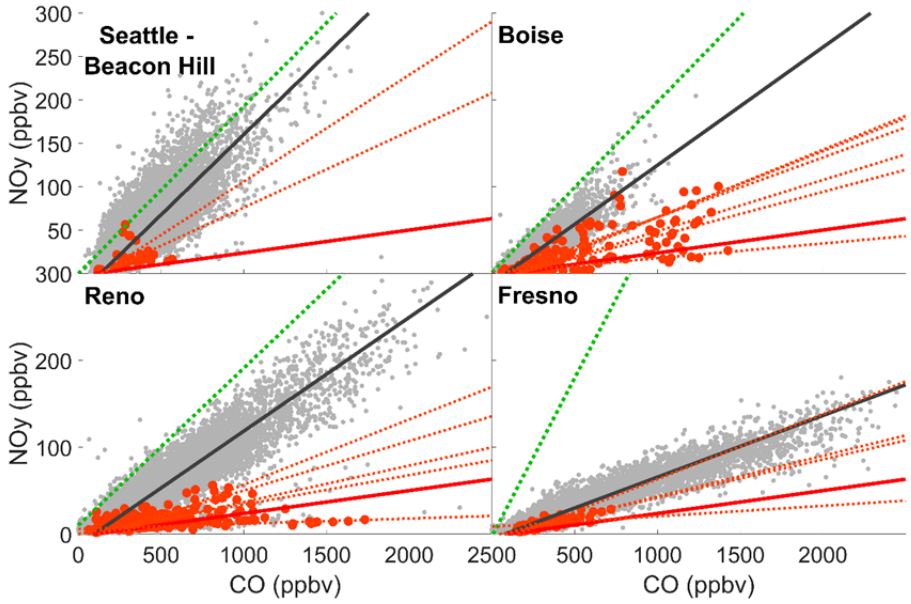

Fig. 4. NO_y vs. CO scatter plots for Seattle - Beacon Hill, Boise, Reno, and Fresno. All points are hourly averages. The grey dots are all of the data points at the site, and the orange dots represent the identified WF events. The lines are defined as follows. Solid dark grey line: NOy/CO AERs calculated (RMA slope) at each site. Dotted orange line(s): $\Delta NO_y/\Delta CO$ NERs for WF events. Dotted green line: Mobile EPA County Emission Inventory NOx/CO ER. Solid red line: NO_x/CO ER for Temperate Forests (0.026 ppbv ppbv^{-1}; Akagi *et al.* (2011)).

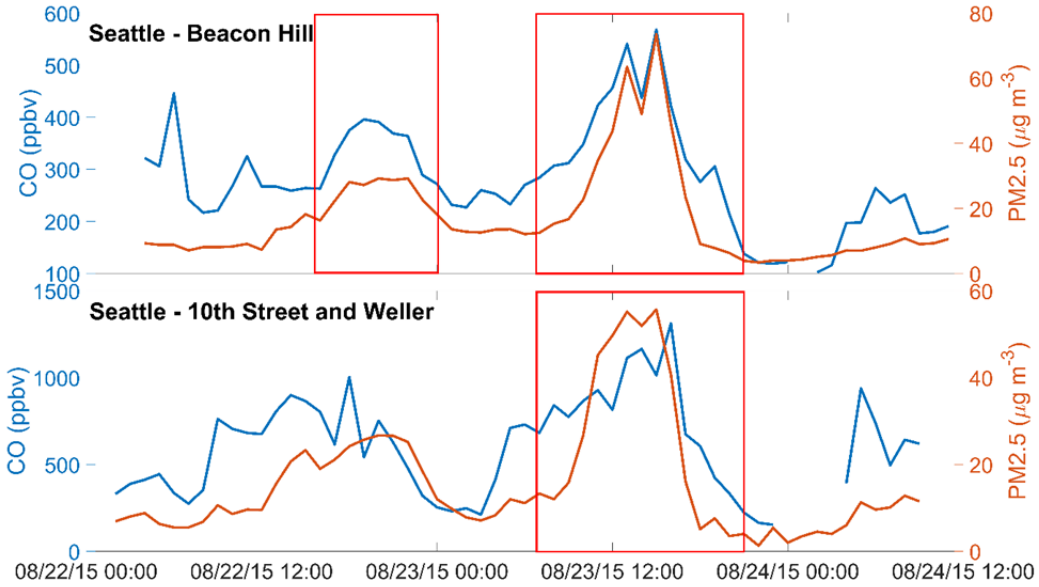

Fig. 5. Time series of $PM_{2.5}$ and CO at the two Seattle locations during WF events in August 2015. The red boxes represent the WF events for each site characterized in Table 2.

lower resolution than was necessary for the analysis in this paper. There is a need to improve CO measurements at EPA AQS monitoring sites by upgrading older CO instruments to ones with an EPA method code > 500.

- For AQS sites with adequate CO data, $\Delta PM_{2.5}/\Delta CO$ NERs provide an excellent tool for identifying or confirming WF events in urban areas, while $\Delta NO_y/\Delta CO$ NERs were less reliable in confirming WF events due to high and variable NO_y concentrations in urban areas.
- $\Delta PM_{2.5}/\Delta CO$ NERs for the identified WF events ranged from 0.057–0.228 μg m^{-3} ppbv^{-1}. The $\Delta PM_{2.5}/\Delta CO$ NERs for WF events were significantly greater than the $PM_{2.5}$/CO AERs for each site and can be used successfully to identify WF events in urban areas.
- A case study in Seattle of a WF event observed at two monitoring sites showed that the ability to identify WF events by $\Delta PM_{2.5}/\Delta CO$ NERs is contingent on the background levels of CO and the total enhancement of CO during the WF event. The higher the background levels of CO, the larger the enhancement in CO must be

in order to identify the event with $\Delta PM_{2.5}/\Delta CO$ NERs.

- Only 4 WF events had $\Delta NO_y/\Delta CO$ NERs with an $R^2 > 0.65$, making it an unreliable tool for identifying or confirming WF smoke in most urban areas. The lack of good correlations between NO_y and CO are likely due to high and variable urban NO_y background concentrations due primarily to mobile emissions. Ostensibly this method could still be used in areas with lower and less variable NO_y concentrations.
- Urban $PM_{2.5}$/CO AERs ranged from 0.021–0.066 μg m^{-3} $ppbv^{-1}$, and 8 of the 9 sites were within 30% when compared with the $PM_{2.5}$/CO ERs calculated from the county emission inventories (NEI11).
- Urban NO_y/CO AERs ranged from 0.071–0.185 ppbv $ppbv^{-1}$, and 4 of the 6 sites were within 30% when compared to NO_x/CO ERs derived from the NEI11 county emission inventories.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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