



## Can $\Delta\text{PM}_{2.5}/\Delta\text{CO}$ and $\Delta\text{NO}_y/\Delta\text{CO}$ 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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  and  $\Delta\text{NO}_y/\Delta\text{CO}$  normalized enhancement ratios (NERs) in identifying wildfire (WF) smoke events in urban areas. Nine urban ambient monitoring sites with adequate CO,  $\text{PM}_{2.5}$ , and/or  $\text{NO}_y$  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  $\text{PM}_{2.5}/\text{CO}$  and  $\text{NO}_y/\text{CO}$  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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  NERs that were significantly greater than the  $\text{PM}_{2.5}/\text{CO}$  AER for each site. The  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  NERs for the WF events ranged from 0.057–0.228  $\mu\text{g m}^{-3} \text{ppbv}^{-1}$ . In contrast, we were only able to calculate useful  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs (correlations with  $R^2 > 0.65$ ) for 4 of 17 events (only 17 of 25 events had  $\text{NO}_y$  data). For these 4 events,  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs ranged from 0.044–0.075  $\text{ppbv ppbv}^{-1}$ , not all of which were significantly different from the  $\text{NO}_y/\text{CO}$  AERs at the site. We conclude that  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  NERs are a very useful tool for identifying WF events, but that the high and variable  $\text{NO}_y$  concentrations in urban areas present problems when trying to use  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs.

**Keywords:** Wildfire; Normalized Enhancement Ratio; Urban AQS;  $\text{PM}_{2.5}$ ; CO;  $\text{NO}_y$

### 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 ( $\text{PM}_{2.5}$ ) 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  $\text{PM}_{2.5}$  measurements at a high temporal resolution, but it is hard to directly discriminate between forest fire smoke and other emission sources with only  $\text{PM}_{2.5}$  measurements. While there are many tracers of WF smoke, such as acetonitrile (Andreae and Merlet, 2001; de Gouw *et al.*, 2003), water soluble potassium ( $\text{K}^+$ ) (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,  $\text{PM}_{2.5}$ , and  $\text{NO}_y$ ) 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 ( $\text{NER} = \Delta\text{X}/\Delta\text{Y}$ , where  $\Delta$  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<sub>2</sub>), 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<sub>2</sub>. Vegetation uptake can deplete CO<sub>2</sub> 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  $(X_{\text{plume}} - X_{\text{bkg}})/(Y_{\text{plume}} - Y_{\text{bkg}})$ , 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<sub>y</sub>), 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  $\Delta\sigma_{\text{scat}}/\Delta\text{CO}$  and  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs calculated using the three methods if the enhancement of the species in the plumes was large relative to the background concentrations ( $\sigma_{\text{scat}}$  is the aerosol scattering coefficient, which is well correlated to PM<sub>2.5</sub>). Large differences were found for  $\Delta\text{O}_3/\Delta\text{CO}$  and  $\Delta\text{CO}/\Delta\text{CO}_2$ , 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<sub>2.5</sub>/CO ERs ranging from ~0.10 to 0.20  $\mu\text{g m}^{-3} \text{ppbv}^{-1}$  (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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  of 0.13–0.15  $\mu\text{g m}^{-3} \text{ppbv}^{-1}$  (DeBell *et al.*, 2004; Dutkiewicz *et al.*, 2011). A wide range in  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  NERs have been found in long-range transported WF events observed at the Mt. Bachelor Observatory in Oregon (0.18–0.43  $\mu\text{g m}^{-3} \text{ppbv}^{-1}$ ) (Wigder *et al.*, 2013; Laing *et al.*, 2016). Similar wide ranges have been observed in aged WF plume  $\Delta\text{OA}/\Delta\text{CO}$  (OA = organic aerosol, which makes up ~95% of PM<sub>2.5</sub> mass) (Jolleys *et al.*, 2012; Sakamoto *et al.*, 2015).

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

In urban settings vehicles are the dominant source of nitrogen oxides (NO<sub>x</sub>), which are converted to NO<sub>y</sub> through oxidation (Seinfeld and Pandis, 2006). The atmospheric lifetime of NO<sub>y</sub> is longer than NO<sub>x</sub>, making NO<sub>y</sub> a more conserved measure. Both NO<sub>x</sub> and NO<sub>y</sub> have substantially shorter lifetimes than CO. NO<sub>x</sub> and NO<sub>y</sub> 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<sub>x</sub>(y), it has previously been assumed that NO<sub>x</sub>/CO ERs are relatively conserved within the urban environment since the predominant emission sources of NO<sub>x</sub> and CO are local vehicular traffic (Hassler *et al.*, 2016). Measurements of NO<sub>x</sub>/CO and NO<sub>y</sub>/CO in cities have similar ranges, which verifies that NO<sub>x</sub> and NO<sub>y</sub> are comparable within urban environments. Studies of urban and near-road ambient measurements observed NO<sub>y</sub>/CO ranging from 0.058 to 0.112 ppbv ppbv<sup>-1</sup> (Wang *et al.*, 2003; Patton *et al.*, 2014), and NO<sub>x</sub>/CO ranging from 0.063 to 0.150 ppbv ppbv<sup>-1</sup> (Kirchstetter *et al.*, 1999; Magliano *et al.*, 1999; Long *et al.*, 2002). NO<sub>x</sub>(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<sub>x</sub>, which has led to an increasing trend in urban ambient NO<sub>x</sub>/COs from the 1970s to the early 2000s (Parrish *et al.*, 2002; Parrish, 2006; Parrish *et al.*, 2011). The mean observed NO<sub>x</sub>/CO ratio for 28 US cities was 0.118 ppbv ppbv<sup>-1</sup> in 2000, and 0.139 ppbv ppbv<sup>-1</sup> in 2003 (Parrish, 2006; Parrish *et al.*, 2009). Hassler *et al.* (2016) similarly found that the NO<sub>x</sub>/CO ratio measured in the LA Basin steadily increased from the 1970s until 2007, and from 2007–2016 it has been steady.

NO<sub>x</sub>/CO and NO<sub>y</sub>/CO ratios for WF events are significantly smaller than NO<sub>x</sub>/CO urban ratios. Akagi *et al.* (2011) reports ERs for different forest types; boreal forests have a NO<sub>x</sub>/CO ER of  $7.0 \times 10^{-3} \text{ppbv ppbv}^{-1}$ , temperate

forests an ER of 0.026 ppbv ppbv<sup>-1</sup>, and extratropical forest an ER of  $9.0 \times 10^{-3}$  ppbv ppbv<sup>-1</sup>. DeBell *et al.* (2004) found  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs of aged smoke events at three rural locations to range from  $2.4 \times 10^{-3}$  to  $7.4 \times 10^{-3}$  ppbv ppbv<sup>-1</sup>, much higher than the ambient background  $\Delta\text{NO}_y/\Delta\text{CO}$  ratios (0.12 ppbv ppbv<sup>-1</sup>). WF events observed at Mt. Bachelor during the summer of 2012–2013 had  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs in a similar range ( $3.0 \times 10^{-3}$  to  $1.3 \times 10^{-2}$  ppbv ppbv<sup>-1</sup>) (Briggs *et al.*, 2016). All of these studies were conducted in locations with low  $\text{NO}_y$  background concentrations, which makes distinguishing  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs easier. We will evaluate if  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs can be used in urban areas with high  $\text{NO}_y$  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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  and  $\Delta\text{NO}_y/\Delta\text{CO}$  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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  and  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs?
- How do  $\text{PM}_{2.5}/\text{CO}$  and  $\text{NO}_y/\text{CO}$  AERs fluctuate for different monitoring sites and different cities?
- How do  $\text{PM}_{2.5}/\text{CO}$  and  $\text{NO}_y/\text{CO}$  AERs compare to ERs derived from emission inventory data?

## METHODS

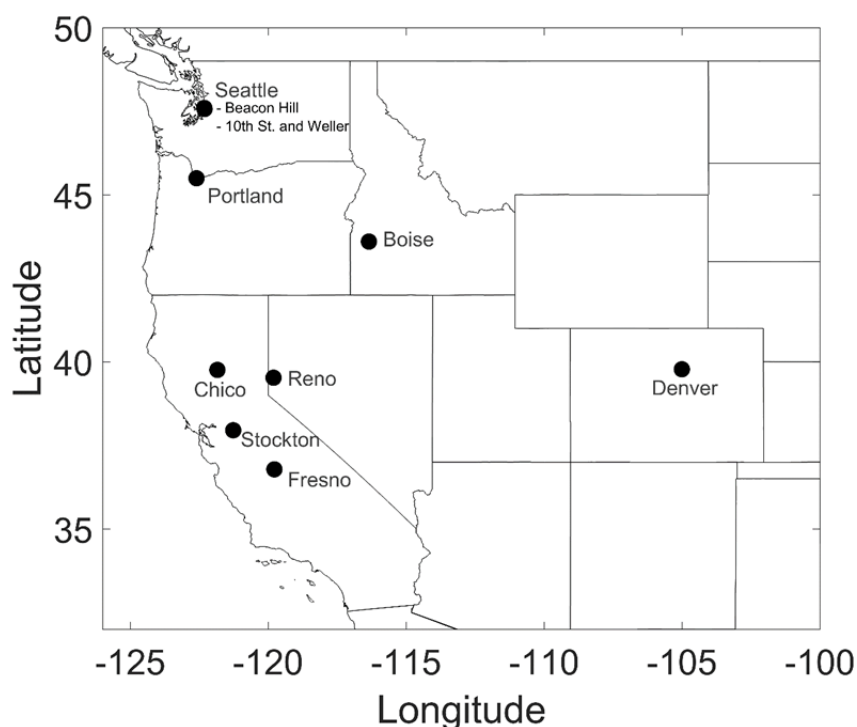
### Data Collection

For our study we chose urban AQS monitoring sites in

the US with collocated hourly ambient CO and  $\text{PM}_{2.5}$  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](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  $\text{PM}_{2.5}$  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.,  $\Delta X/\Delta Y$ ;  $\Delta$  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 99<sup>th</sup> 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 99<sup>th</sup> 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 99<sup>th</sup> 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 99<sup>th</sup> 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 99<sup>th</sup> 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  $\mu g m^{-3} ppbv^{-1}$  with the majority falling between 0.030–0.046  $\mu g m^{-3} ppbv^{-1}$  (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  $\mu g m^{-3} ppbv^{-1}$ ). 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  $\mu g m^{-3} ppbv^{-1}$ ) compared to Seattle Beacon Hill (0.035  $\mu g m^{-3} ppbv^{-1}$ ). 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  $\mu g m^{-3} ppbv^{-1}$ ).  $PM_{2.5}$  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 99<sup>th</sup> 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<sub>2.5</sub>/CO and NO<sub>y</sub>/CO AERs for each site. The PM<sub>2.5</sub>/CO AERs were calculated using an RMA regression of all data up to the 99<sup>th</sup> percentile of PM<sub>2.5</sub> mass. The NO<sub>y</sub>/CO AERs are calculated using an RMA regression of all data at each site. NA means NO<sub>y</sub> data was not available.

Site location	Site county	PM <sub>2.5</sub> /CO AERs		NO <sub>y</sub> /CO AERs (ppbv ppbv <sup>-1</sup> )			
		(μg m <sup>-3</sup> ppbv <sup>-1</sup> )*		All data		Weekday rush hour data	
		slope	R <sup>2</sup>	slope	R <sup>2</sup>	slope	R <sup>2</sup>
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 99<sup>th</sup> percentile of PM<sub>2.5</sub> 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<sub>y</sub>/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<sub>y</sub> deposition and loss during the day. The high R<sup>2</sup> values for the NO<sub>y</sub>/CO AERs at all sites and lack of significant temporal changes in NO<sub>y</sub>/CO ratio indicates a homogeneously mixed source dominated by on-road vehicle emissions. The range of observed NO<sub>y</sub>/CO AERs in this study is similar to previous studies of urban NO<sub>y</sub>/CO AERs (Wang *et al.*, 2003; Patton *et al.*, 2014) and urban NO<sub>x</sub>/CO AERs (Kirchstetter *et al.*, 1999; Magliano *et al.*, 1999; Long *et al.*, 2002).

We compared the NO<sub>y</sub>/CO AERs to the corresponding NO<sub>x</sub>/CO ERs derived from the NEI11 (Table S3). NO<sub>x</sub>/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<sub>x</sub> and CO are vehicles, the NO<sub>x</sub>/CO ERs are dominated by the mobile NO<sub>x</sub>/CO ER. The NO<sub>x</sub>/CO ERs sum of all sources were within 30% of the NO<sub>y</sub>/CO AERs for 4 of the 6 sites. For Portland and Fresno, the NO<sub>x</sub>/CO ERs were higher by a factor of 2 and 5, respectively. These differences are discussed in greater detail in the Supplemental Material.

#### ΔPM<sub>2.5</sub>/ΔCO and ΔNO<sub>y</sub>/ΔCO NERs during WF Events

Table 2 shows ΔPM<sub>2.5</sub>/ΔCO NERs for the 25 WF events range from 0.057–0.228 μg m<sup>-3</sup> ppbv<sup>-1</sup>, with the majority being between 0.085 and 0.170 μg m<sup>-3</sup> ppbv<sup>-1</sup>. 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<sub>2.5</sub> 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 ΔPM<sub>2.5</sub>/ΔCO NERs that were significantly greater than the PM<sub>2.5</sub>/CO AER at the site, which confirms that ΔPM<sub>2.5</sub>/ΔCO NERs can be used to distinguish and identify WF events in urban locations. The mobile PM<sub>2.5</sub>/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 ΔNO<sub>y</sub>/ΔCO NERs were lower than the NO<sub>y</sub>/CO AER for all sites (Fig. 4), only 4 of the 17 events had a good correlation between NO<sub>y</sub> and CO (R<sup>2</sup> > 0.65). The low occurrence of a good correlation between NO<sub>y</sub> and CO is most likely due to the high and variable NO<sub>y</sub> background in the urban areas. For the 4 WF events we were able to characterize (with R<sup>2</sup> > 0.65), the ΔNO<sub>y</sub>/ΔCO ranged from 0.044–0.075 ppbv ppbv<sup>-1</sup>. These values are higher than NO<sub>x</sub>/CO ERs for forest fires (Andreae and Merlet, 2001; Akagi *et al.*, 2011), and higher than ΔNO<sub>y</sub>/ΔCO NERs observed in WF plumes measured in rural areas (DeBell *et al.*, 2004). This is likely caused by the high NO<sub>y</sub> 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 ΔNO<sub>y</sub>/ΔCO NERs lower than the NO<sub>y</sub>/CO AER at the site. Therefore even if a ΔNO<sub>y</sub>/ΔCO NER can be calculated for a WF, it is not necessarily distinguishable from the background NO<sub>x</sub>/CO ratio. Due to the high and variable urban NO<sub>y</sub> background concentrations, we found ΔNO<sub>y</sub>/ΔCO 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<sub>2.5</sub>/CO AER for the 10th St site was the lowest of all of the sites (0.021 μg m<sup>-3</sup> ppbv<sup>-1</sup>), and substantially lower than Beacon Hill (0.035 μg m<sup>-3</sup> ppbv<sup>-1</sup>), 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<sub>2.5</sub> and CO during the WF events. We observed simultaneous increases in PM<sub>2.5</sub>

**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  $\text{NO}_y$  data was not available.

Site	Date Time (local)	$\Delta\text{PM}_{2.5}/\Delta\text{CO}$ ( $\mu\text{g m}^{-3}$ ppbv $^{-1}$ )		$\Delta\text{NO}_y/\Delta\text{CO}$ (ppbv ppbv $^{-1}$ )	
		slope	$R^2$	slope	$R^2$
Seattle - Beacon Hill	8/22/15 15:00–8/23/15 1:00	<b>0.108</b>	<b>0.920</b>	0.088	0.161
Seattle - Beacon Hill	8/23/15 10:00–8/23/15 19:00	<b>0.158</b>	<b>0.876</b>	0.123	0.082
Seattle - 10th St	8/23/15 6:00–8/23/15 20:00	<b>0.057</b>	<b>0.677</b>	NA	NA
Portland	8/22/15 00:00–8/24/15 00:00	<b>0.228</b>	<b>0.978</b>	NA	NA
Boise	8/14/15 12:00–8/16/15 12:00	<b>0.104</b>	<b>0.675</b>	0.059	0.156
Boise	8/21/15 8:00–8/22/15 00:00	<b>0.116</b>	<b>0.955</b>	0.017	0.043
Boise	10/11/15 16:00–10/12/15 18:00	<b>0.133</b>	<b>0.928</b>	0.051	0.423
Boise	10/12/15 20:00–10/13/15 20:00	<b>0.129</b>	<b>0.731</b>	0.076	0.322
Boise	10/13/15 20:00–10/14/15 14:00	<b>0.092</b>	<b>0.820</b>	0.069	0.511
Boise	10/15/15 15:00–10/16/15 15:00	<b>0.107</b>	<b>0.776</b>	0.078	0.372
Stockton	8/15/15 4:00–8/16/15 19:00	<b>0.158</b>	<b>0.844</b>	NA	NA
Denver	8/22/15 9:00–8/23/15 10:00	<b>0.166</b>	<b>0.762</b>	NA	NA
Fresno	8/15/15 10:00–8/16/15 15:00	<b>0.087</b>	<b>0.815</b>	<b>0.047</b>	<b>0.707</b>
Fresno	8/17/15 18:00–8/18/15 15:00	<b>0.091</b>	<b>0.778</b>	<b>0.075</b>	<b>0.820</b>
Fresno	9/11/15 15:00–9/11/15 20:00	<b>0.141</b>	<b>0.986</b>	0.012	0.227
Fresno	9/13/15 14:00–9/14/15 18:00	<b>0.086</b>	<b>0.749</b>	<b>0.044</b>	<b>0.758</b>
Reno	8/18/13 14:00–8/19/13 14:00	<b>0.126</b>	<b>0.743</b>	0.057	0.366
Reno	8/22/13 8:00–8/26/13 00:00	<b>0.145</b>	<b>0.918</b>	0.034	0.306
Reno	8/27/13 12:00–8/28/13 18:00	<b>0.161</b>	<b>0.868</b>	0.042	0.097
Reno	9/18/14 00:00–9/19/14 00:00	<b>0.128</b>	<b>0.886</b>	0.006	0.579
Reno	8/20/15 19:00–8/21/15 19:00	<b>0.119</b>	<b>0.767</b>	<b>0.075</b>	<b>0.716</b>
Chico	7/28/13 20:00–7/31/13 12:00	<b>0.153</b>	<b>0.892</b>	NA	NA
Chico	7/29/14 19:00–7/30/14 10:00	<b>0.093</b>	<b>0.979</b>	NA	NA
Chico	9/22/14 5:00–9/22/14 15:00	<b>0.161</b>	<b>0.895</b>	NA	NA
Chico	9/13/15 14:00–9/14/15 10:00	<b>0.142</b>	<b>0.925</b>	NA	NA
All sites mean $\pm$ SD		0.128 $\pm$ 0.036		0.060 $\pm$ 0.015 <sup>#</sup>	
Akagi ER for boreal forests*		0.138		0.0066	
Akagi ER for temperate forests*		0.163		0.0263	
EPA WF ER range <sup>†</sup>		0.096–0.164		0.010–0.048	
EPA fuel combustion ER range <sup>†</sup>		0.155–0.245		0.096–0.669	
EPA mobile ER range <sup>†</sup>		0.008–0.014		0.178–0.365	

<sup>#</sup> 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).

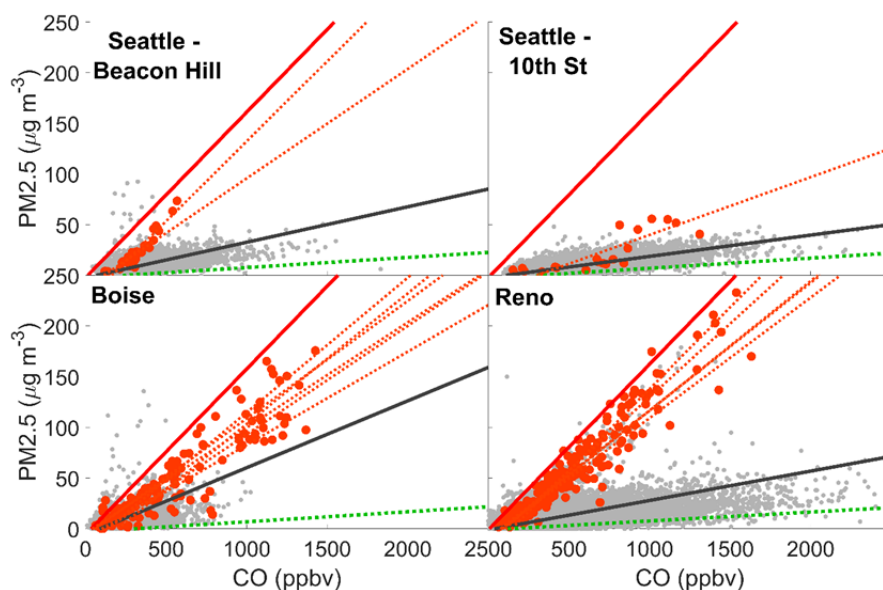
<sup>†</sup> Calculated using EPA NEI11 from all 8 Counties (<https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data>).

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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  NERs are different for the two sites. The  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  NER for Seattle 10th St was the lowest of all the WF events ( $0.057 \mu\text{g m}^{-3}$  ppbv $^{-1}$ ), and significantly lower than the  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$  NERs for the same event at the Beacon Hill site ( $0.158 \mu\text{g m}^{-3}$  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

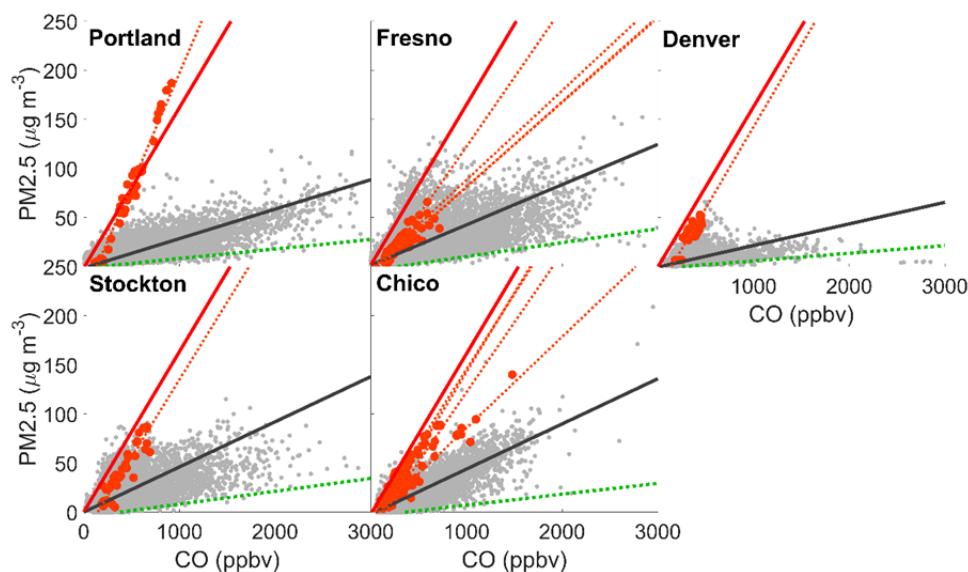
between  $\text{PM}_{2.5}$  and CO is not as strong at the 10th St site during the WF events. During the event observed at both sites on 8/23/2015, the Beacon Hill site had a much better correlation ( $R^2 = 0.876$ ) than the 10th St site ( $R^2 = 0.677$ ).

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  $\text{PM}_{2.5}/\text{CO}$  AERs and thus the WF event on 8/23/2015 could be discerned.

On 8/22/2015 there was a clear increase in  $\text{PM}_{2.5}$  observed at both sites. For this time period the  $\text{PM}_{2.5}$  and CO were much better correlated at Beacon Hill ( $\Delta\text{PM}_{2.5}/\Delta\text{CO}$   $R^2 = 0.92$ ) compared to the 10th St site ( $\Delta\text{PM}_{2.5}/\Delta\text{CO}$   $R^2 = 0.33$ ). Since the event at 10th St site did not meet our criteria, it was not counted as a WF event. This is an example of high background concentrations impeding the use of enhancement



**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  $PM_{2.5}$  99<sup>th</sup> 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 ( $0.164 \mu g m^{-3} ppbv^{-1}$ ; 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.

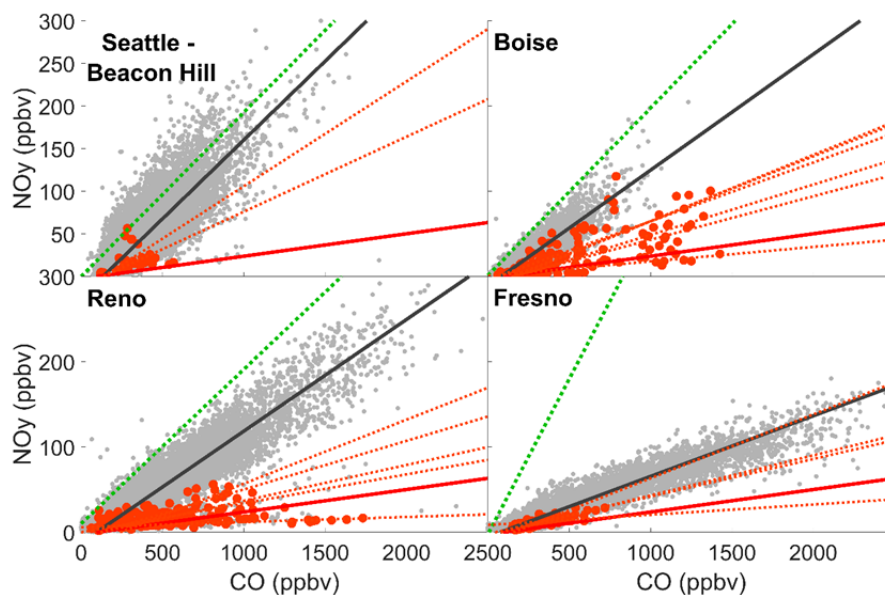
ratios in identifying WF events. The lower and less variable the background concentrations are, the easier WF events will be able to be identified. For site with high background, such as Seattle 10<sup>th</sup> St, only larger WF plumes will be identifiable, whereas smaller plumes can be identified at the Beacon Hill site.

## CONCLUSIONS

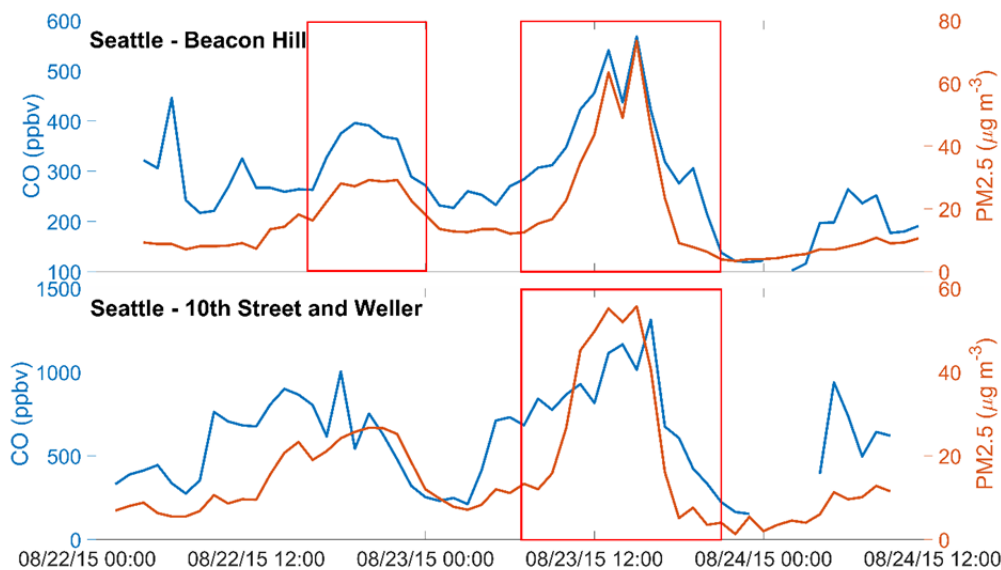
In this paper we evaluated the use of normalized

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 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,  $\Delta PM_{2.5}/\Delta CO$



**Fig. 4.**  $\text{NO}_y$  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:  $\text{NO}_y/\text{CO}$  AERs calculated (RMA slope) at each site. Dotted orange line(s):  $\Delta\text{NO}_y/\Delta\text{CO}$  NERs for WF events. Dotted green line: Mobile EPA County Emission Inventory  $\text{NO}_x/\text{CO}$  ER. Solid red line:  $\text{NO}_x/\text{CO}$  ER for Temperate Forests ( $0.026 \text{ ppbv ppbv}^{-1}$ ; Akagi et al. (2011)).



**Fig. 5.** Time series of  $\text{PM}_{2.5}$  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.

- $\text{NERs}$  provide an excellent tool for identifying or confirming WF events in urban areas, while  $\Delta\text{NO}_y/\Delta\text{CO}$   $\text{NERs}$  were less reliable in confirming WF events due to high and variable  $\text{NO}_y$  concentrations in urban areas.
- $\Delta\text{PM}_{2.5}/\Delta\text{CO}$   $\text{NERs}$  for the identified WF events ranged from  $0.057\text{--}0.228 \mu\text{g m}^{-3} \text{ ppbv}^{-1}$ . The  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$   $\text{NERs}$  for WF events were significantly greater than the  $\text{PM}_{2.5}/\text{CO}$  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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$   $\text{NERs}$  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  $\Delta\text{PM}_{2.5}/\Delta\text{CO}$   $\text{NERs}$ .
- Only 4 WF events had  $\Delta\text{NO}_y/\Delta\text{CO}$   $\text{NERs}$  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  $\text{NO}_y$  and CO are likely due to high and variable urban  $\text{NO}_y$  background concentrations due primarily to mobile emissions. Ostensibly this method



could still be used in areas with lower and less variable  $\text{NO}_y$  concentrations.

- Urban  $\text{PM}_{2.5}/\text{CO}$  AERs ranged from 0.021–0.066  $\mu\text{g m}^{-3}$   $\text{ppbv}^{-1}$ , and 8 of the 9 sites were within 30% when compared with the  $\text{PM}_{2.5}/\text{CO}$  ERs calculated from the county emission inventories (NEI11).
- Urban  $\text{NO}_y/\text{CO}$  AERs ranged from 0.071–0.185  $\text{ppbv}$   $\text{ppbv}^{-1}$ , and 4 of the 6 sites were within 30% when compared to  $\text{NO}_x/\text{CO}$  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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