Can ΔPM$_{2.5}$/ΔCO and ΔNO$_y$/ΔCO 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$_{2.5}$/ΔCO and $\Delta$NO$_y$/ΔCO 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$_{2.5}$/ΔCO NERs that were significantly greater than the PM$_{2.5}$/CO AER for each site. The $\Delta$PM$_{2.5}$/ΔCO 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$_y$/ΔCO 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$_y$/ΔCO 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$_{2.5}$/ΔCO 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$_y$/ΔCO 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 = ΔX/ΔY, where Δ is the enhancement...
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 ($X_{\text{plume}} - X_{\text{bkg}}$)/($Y_{\text{plume}} - Y_{\text{bkg}}$), 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of 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$_x$), the NER measured downwind of a fire may be different than the ER of the source; (2) there is no chemical or physical loss of the species with transport, only dilution; and (3) background dilution is constant.

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 PM$_{2.5}$/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$_x$ is longer than NO$_y$, making NO$_x$ 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$_y$(y), it has previously been assumed that NO$_y$/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$_y$/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$_x$/CO 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$_y$/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 \times 10^{-3} ppbv ppbv⁻¹. DeBell et al. (2004) found ΔNOy/ΔCO 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⁻¹, much higher than the ambient background ΔNOy/ΔCO ratios (0.12 ppbv ppbv⁻¹). WF events observed at Mt. Bachelor during the summer of 2012–2013 had ΔNOy/ΔCO NERs in a similar range (3.0 \times 10^{-3} to 1.3 \times 10^{-2} ppbv ppbv⁻¹) (Briggs et al., 2016). All of these studies were conducted in locations with low NOy background concentrations, which makes distinguishing ΔNOy/ΔCO NERs easier. We will evaluate if ΔNOy/ΔCO NERs can be used in urban areas with high NOy 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 ΔPM2.5/ΔCO and ΔNOy/ΔCO 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 ΔPM2.5/ΔCO and ΔNOy/ΔCOs NERs?
- How do PM2.5/CO and NOy/CO AERs fluctuate for different monitoring sites and different cities?
- How do PM2.5/CO and NOy/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 PM2.5 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 PM2.5 and CO, and a strong correlation (R² > 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;
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., ΔX/ΔY; Δ is the enhancement over the background concentration) (Andreae and Merlet, 2001; Wigder et al., 2013; Laing et al., 2016). We calculated ΔPM2.5/ΔCO NERs and ΔNOX/ΔCO NERs from the slope of the Reduced Major Axis (RMA) regression. ΔPM2.5/ΔCO NERs were calculated for all WF events; ΔNOX/ΔCO NERs were calculated when NOx data was available (17 of the 25 events).

Ambient Enhancement Ratios (AERs)

We calculated PM2.5/CO and NOx/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 PM2.5/CO ratios, we used PM2.5 data up to the 99th percentile to mitigate the influence of WF events on the AERs or other exceptional events. The NOx/CO AERs were calculated using all available data.

Emission Inventory–Derived Emission Ratios (ERs)

For comparison with AERs, we calculated PM2.5/CO and NOx/CO ERs from county emission inventories. For each site, we obtained county emission inventories for CO, PM2.5, and NOx 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 PM2.5 data, and 17 of the events also had NOx 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 PM2.5/CO and NOx/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 PM2.5/CO AERs using up to the 99th percentile of PM2.5 data. Large WF events with high PM2.5 concentrations can positively bias PM2.5/CO AERs calculated from yearly data. The most significant differences in PM2.5/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 PM2.5 concentrations. Due to the exceptional WF events at these two sites, the PM2.5/CO ratios were ~30% higher using the full dataset compared to using the up to the 99th percentile. Given that these fire events were anomalous in that they occurred only during one summer, the PM2.5/CO AERs using up to the 99th percentile of PM2.5 data provide a more accurate representation of typical non-WF concentrations.

For the sites we studied, PM2.5/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 PM2.5/CO ratios of ambient urban background concentrations (Dimitriou and Kassomenos, 2014; Patton et al., 2014). The lowest PM2.5/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 PM2.5/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 PM2.5/CO AER was observed in Boise (0.066 µg m–3 ppbv–1). PM2.5 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 PM2.5.

We compared the measured AERs to PM2.5/CO ERs calculated for each county using the NEI11 from the EPA. PM2.5/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 PM2.5/CO AERs to PM2.5/CO ERs calculated for the sum of all sources except fires and dust, all sites except Portland were within 30%; but compared to PM2.5/CO ERs calculated for the sum of emissions except fires, only 5 of the 9 sites are within 30% of the measured PM2.5/CO AERs. Additional information on the NEI derived PM2.5/CO ERs is available in the Supplemental Material.

The NOx/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 NOx/CO during the day and minimal seasonal differences. To try to isolate traffic emissions, we calculated NOx/CO AERs using only weekday
day. The high $R^2$ values for the NO$_y$/CO AERs at all sites range from 0.057–0.228 µg m$^{-3}$ ppbv$^{-1}$, with the majority of 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 and indicate a homogenously mixed source dominated by on-road vehicle emissions. 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. Although most of the $\Delta$NO$_y$/ACO NERs were lower than the NO$_x$/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$_y$/ACO 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$_y$/ACO 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$_y$/ACO NERs lower than the NO$_x$/CO AER at the site. Therefore even if a $\Delta$NO$_y$/ACO NER can be calculated for a WF, it is not necessarily distinguishable from the background NO$_y$/CO ratio. Due to the high and variable urban NO$_y$ background concentrations, we found $\Delta$NO$_y$/ACO 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 µg m$^{-3}$ ppbv$^{-1}$), and substantially lower than Beacon Hill (0.035 µg 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$_{2.5}$ (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 reductive 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 captures fresh vehicle emissions and minimized the effects of reductive 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.

### 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.

<table>
<thead>
<tr>
<th>Site location</th>
<th>Site county</th>
<th>PM$_{2.5}$/CO AERs (µg m$^{-3}$ ppbv$^{-1}$)</th>
<th>NO$_y$/CO AERs (ppbv ppbv$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>All data</td>
<td>Weekday rush hour data</td>
</tr>
<tr>
<td></td>
<td></td>
<td>slope</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Seattle - Beacon Hill</td>
<td>King</td>
<td>0.035</td>
<td>0.379</td>
</tr>
<tr>
<td>Seattle - 10th St</td>
<td>King</td>
<td>0.021</td>
<td>0.407</td>
</tr>
<tr>
<td>Portland, OR</td>
<td>Multnomah</td>
<td>0.030</td>
<td>0.537</td>
</tr>
<tr>
<td>Boise, ID</td>
<td>Ada</td>
<td>0.066</td>
<td>0.348</td>
</tr>
<tr>
<td>Denver, CO</td>
<td>Denver</td>
<td>0.021</td>
<td>0.188</td>
</tr>
<tr>
<td>Stockton, CA</td>
<td>San Joaquin</td>
<td>0.046</td>
<td>0.351</td>
</tr>
<tr>
<td>Fresno, CA</td>
<td>Fresno</td>
<td>0.041</td>
<td>0.454</td>
</tr>
<tr>
<td>Reno, NV</td>
<td>Washoe</td>
<td>0.029</td>
<td>0.315</td>
</tr>
<tr>
<td>Chico, CA</td>
<td>Butte</td>
<td>0.046</td>
<td>0.565</td>
</tr>
</tbody>
</table>

*All data up to the 99th percentile of PM$_{2.5}$ concentration used for RMA analysis.
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 NOy data was not available.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date Time (local)</th>
<th>$\Delta PM_{2.5}/\Delta CO$ (µg m$^{-3}$ ppbv$^{-1}$) slope</th>
<th>$R^2$</th>
<th>$\Delta NO_y/\Delta CO$ (ppbv ppbv$^{-1}$) slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seattle - Beacon Hill</td>
<td>8/22/15 15:00–8/23/15 1:00</td>
<td>0.108</td>
<td>0.920</td>
<td>0.088</td>
<td>0.161</td>
</tr>
<tr>
<td>Seattle - Beacon Hill</td>
<td>8/23/15 10:00–8/23/15 19:00</td>
<td>0.158</td>
<td>0.876</td>
<td>0.123</td>
<td>0.082</td>
</tr>
<tr>
<td>Seattle - 10th St</td>
<td>8/23/15 6:00–8/23/15 20:00</td>
<td>0.057</td>
<td>0.677</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Portland</td>
<td>8/22/15 00:00–8/24/15 00:00</td>
<td>0.228</td>
<td>0.978</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Boise</td>
<td>8/14/15 12:00–8/16/15 12:00</td>
<td>0.104</td>
<td>0.675</td>
<td>0.059</td>
<td>0.156</td>
</tr>
<tr>
<td>Boise</td>
<td>8/21/15 8:00–8/22/15 00:00</td>
<td>0.116</td>
<td>0.955</td>
<td>0.017</td>
<td>0.043</td>
</tr>
<tr>
<td>Boise</td>
<td>10/11/15 16:00–10/12/15 18:00</td>
<td>0.133</td>
<td>0.928</td>
<td>0.051</td>
<td>0.423</td>
</tr>
<tr>
<td>Boise</td>
<td>10/12/15 20:00–10/13/15 20:00</td>
<td>0.129</td>
<td>0.731</td>
<td>0.076</td>
<td>0.322</td>
</tr>
<tr>
<td>Boise</td>
<td>10/13/15 20:00–10/14/15 14:00</td>
<td>0.092</td>
<td>0.820</td>
<td>0.069</td>
<td>0.511</td>
</tr>
<tr>
<td>Boise</td>
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<td>0.107</td>
<td>0.776</td>
<td>0.078</td>
<td>0.372</td>
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<tr>
<td>Seattle - Beacon Hill</td>
<td>8/23/15 10:00–8/23/15 19:00</td>
<td>0.158</td>
<td>0.844</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Seattle - Beacon Hill</td>
<td>8/23/15 10:00–8/23/15 19:00</td>
<td>0.166</td>
<td>0.762</td>
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<tr>
<td>Seattle - Beacon Hill</td>
<td>8/23/15 10:00–8/23/15 19:00</td>
<td>0.087</td>
<td>0.815</td>
<td>0.047</td>
<td>0.707</td>
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<td>Seattle - Beaver Hill</td>
<td>8/23/15 10:00–8/23/15 19:00</td>
<td>0.091</td>
<td>0.778</td>
<td>0.075</td>
<td>0.820</td>
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<td>0.012</td>
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<td>0.979</td>
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<td>0.142</td>
<td>0.925</td>
<td>NA</td>
<td>NA</td>
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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*: $0.096–0.164$; $0.010–0.048$
EPA fuel combustion ER range*: $0.155–0.245$; $0.096–0.669$
EPA mobile ER range*: $0.008–0.014$; $0.178–0.365$

* 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).

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 µg 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 µg 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 8/22/2015, the Beacon Hill site had a much better correlation ($R^2 = 0.876$) than the 10th St site ($R^2 = 0.767$). 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 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$_x$). 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$_{2.5}$/ΔCO
Fig. 4. NOy 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): ΔNOy/ΔCO NERs for WF events. Dotted green line: Mobile EPA County Emission Inventory NOx/CO ER. Solid red line: NOx/CO ER for Temperate Forests (0.026 ppbv ppbv⁻¹; Akagi et al. (2011)).

Fig. 5. Time series of PM2.5 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.

NERs provide an excellent tool for identifying or confirming WF events in urban areas, while ΔNOy/ΔCO NERs were less reliable in confirming WF events due to high and variable NOy concentrations in urban areas.

- ΔPM2.5/ΔCO NERs for the identified WF events ranged from 0.057–0.228 µg m⁻³ ppbv⁻¹. The ΔPM2.5/ΔCO NERs for WF events were significantly greater than the PM2.5/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 ΔPM2.5/ΔCO 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 ΔPM2.5/ΔCO NERs.

- Only 4 WF events had ΔNOy/ΔCO NERs with an R² > 0.65, making it an unreliable tool for identifying or confirming WF smoke in most urban areas. The lack of good correlations between NOy and CO are likely due to high and variable urban NOy background concentrations due primarily to mobile emissions. Ostensibly this method...
could still be used in areas with lower and less variable NO\textsubscript{x} concentrations.

- Urban PM\textsubscript{2.5}/CO AERs ranged from 0.021–0.066 \(\mu\)g m\textsuperscript{-3} ppbv\textsuperscript{-1}, and 8 of the 9 sites were within 30% when compared with the PM\textsubscript{2.5}/CO ERs calculated from the county emission inventories (NEI11).

- Urban NO\textsubscript{x}/CO AERs ranged from 0.071–0.185 ppbv ppbv\textsuperscript{-1}, and 4 of the 6 sites were within 30% when compared to NO\textsubscript{x}/CO ERs derived from the NEI11 county emission inventories.

**ACKNOWLEDGEMENTS**

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**SUPPLEMENTARY MATERIAL**

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

**REFERENCES**


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