ESTIMATING CONTRIBUTIONS OF PRESCRIBED RANGELAND BURNING IN KANSAS TO AMBIENT PM$_{2.5}$ THROUGH SOURCE APPORTIONMENT WITH THE UNMIX RECEPTOR MODEL

Z. Liu, Y. Liu, R. Maghirang, D. Devlin, C. Blocksome

ABSTRACT. The Unmix receptor model was applied to the 2002-2014 speciated PM$_{2.5}$ data from the IMPROVE site at Tallgrass National Preserve near Strong City, Kansas, to investigate the contributions of prescribed rangeland burning on local air quality. This investigation found the following five source categories that contribute to annual local ambient PM$_{2.5}$: nitrate/agricultural (22%), vegetative burning (5%), secondary organic aerosol (29%), sulfate/industrial (30%), and crustal/soil (14%). In the month of April, the contributions of vegetative burning and secondary organic aerosol increased to 11% and 49%, respectively, indicating the influence of the prescribed burning season. The contribution of smoke from prescribed burning was estimated to be 1.05 µg m$^{-3}$ as primary aerosols and 4.03 µg m$^{-3}$ as secondary aerosols, which in total accounted for 42% of the average PM$_{2.5}$ concentration in April.

Keywords. IMPROVE, Rangeland burning, Secondary organic aerosols, Smoke, Source apportionment.

Prescribed rangeland burning is a long-standing practice in Kansas that is used to enhance the nutritional value of native grasses, control woody plants, and is vital to the maintenance of the tallgrass prairie ecosystem. The Flint Hills tallgrass region of eastern Kansas covers 13 Kansas counties, and approximately 2 million of the 7 million acres of rangeland in the region are burned each year, mostly in April. The smoke plumes originating from these fires have contributed to air quality concerns in downwind communities (KDHE, 2010; Liu, 2014). Modeling tools are being developed to assist in developing improved smoke management practices related to prescribed fires. However, the modeling efforts are often limited due to lack of detailed local source profiles of smoke emissions as well as knowledge gaps regarding the contribution of smoke emissions to secondary organic aerosols (Riebau and Fox, 2010).

The principles of source apportionment were established decades ago, and various receptor modeling approaches have been developed to resolve the contributions of important emission sources to ambient concentrations, such as chemical mass balance (CMB), positive matrix factorization (PMF), and Unmix. Unmix has been applied in several key source apportionment studies in both rural and urban sites, and investigators have been able to generate realistic results in good agreement with results from other approaches (Poirot et al., 2001; Coutant et al., 2002; Lewis et al., 2003; Maykut et al., 2003; Hu et al., 2006; Mijic et al., 2012). Unmix has also been successfully used for apportionment of secondary pollutants (Anderson et al., 2006) and for evaluation of VOC source profiles (Ethirajan and Mohan, 2012).

Unmix is gaining broader applicability in air quality research. The Unmix receptor model assumes that for each source there are some samples at the receptors that contain little or no contribution from that source, and these samples produce edges in the measured data. By definition, each edge defines the points where a single source is not contributing. Unmix determines the number of sources and their respective species profiles based on these highly dimensional edges (Henry, 2003). The Unmix modeling process is explained using simple graphical examples by Henry (1997). Unlike chemical mass balance models, the Unmix model does not require externally supplied source profiles, but it requires a large data quantity for multivariate analysis. The IMPROVE (Interagency Monitoring of Protected Visual Environments) sampling network (http://vista.cira.colostate.edu/improve/) provides multiple years of quality-assured data on speciated PM$_{2.5}$, which is well suited to the large data quantity requirements of multivariate analysis in Unmix.

The objective of this work is to perform a source apportionment analysis of a dataset at a rural IMPROVE site using Unmix and to specifically investigate the contributions of prescribed rangeland burning on local ambient concentrations of PM$_{2.5}$. While numerous receptor modeling studies have been conducted, this is the first known study in rural...
Kansas to unravel the contributions of local smoke emissions.

SITE AND DATA

The Tallgrass IMPROVE site is centrally located in the Tallgrass Prairie National Preserve, near Strong City, Kansas, 390 m above sea level. The site is at the center of the Flint Hills region (fig. 1) and thus is an ideal site to evaluate the effects of prescribed rangeland burning on local air quality. The IMPROVE particulate sampler has four sampling modules. Three modules collect PM$_{2.5}$ using Teflon, nylon, and quartz filters, respectively, and the other module collects PM$_{10}$ using a Teflon filter. Every three days, a 24 h filter sample set (Teflon, nylon, and quartz filters sampling in parallel) was collected. A total of 1428 valid filter sample sets from 26 September 2002 to 31 December 2014 were collected and included in the Unmix analysis. All filter samples were analyzed using the IMPROVE protocols (Malm et al., 1994). The Teflon filters were analyzed at the University of California-Davis for gravimetric mass and for analysis of elements in PM$_{2.5}$ using Cu-anode XRF. The denuded nylon filters were analyzed by Research Triangle Institute (RTI) for nitrate, sulfate, and chloride using ion chromatography. The quartz filters were analyzed by Desert Research Institute for organic and elemental carbon (OC and EC) using the thermal/optical reflectance method.

Fine potassium (K) particles have two major sources, soil and smoke, with the smoke potassium on much smaller particles than the soil potassium. The soil potassium can be estimated from the measured concentration of Fe. In order to provide a tracer associated with vegetative burning, a calculated species “non-soil potassium (K$_{non}$)” was included in the Unmix modeling (K$_{non}$ = K – 0.34Fe). The Fe coefficient of 0.34 was derived from the lower edge of the K versus Fe scatterplot. The speciated PM$_{2.5}$ mass concentrations and the total PM$_{10}$ mass concentrations were assembled in a conventional data matrix as Unmix model input, with each row containing the measured variables from a 24 h sampling period.

UNMIX MODEL IMPLEMENTATION

The U.S. EPA Unmix 6.0 model (http://www2.epa.gov/air-research/epa-unmix-60-fundamentals-user-guide) was used. Source apportionment can be sensitive to the presence of outliers or large noise in the data. Hence, the first step was to examine the data set for data validation, outlier detection, and quality assurance. Factor analysis was used to estimate the fraction of the variance of each species, and species with more than 50% of their variance due to error and those with a low number of concentrations above the detection limit were excluded. Scatter plots of one species versus another were examined as a part of the process and were used to identify the species with good edges. A nearly linear scatter plot, as was seen in the plot of Si versus Fe, indicates that there may be only one major source of the two species, since they were usually produced at the same ratio. A wedge-shaped plot indicates at least two major sources of the pair species, as was seen in the plot of K versus Fe. If the middle section of the wedge has few high concentration points, there may be only two major sources, and the high concentrations from one source usually do not co-occur with the high concentrations of the other source (Coutant et al., 2002). All the above considerations provide hints for selecting species or identifying sources.

The general objective in running Unmix was to maximize the number of input species and resultant sources while producing physically realistic and interpretable results. In initial runs of Unmix, the species were selected for their ability to obtain a minimal solution whose diagnostic indicators are acceptable, rather than for their utility in identifying the sources. PM$_{2.5}$ was assigned as the total species. The solutions for Unmix were augmented to include more species (such as PM$_{10}$) than those used for fitting by regressing the remaining species with the source contributions in current output from Unmix. Species with $r^2 > 0.8$ were added one by one in follow-up runs to test the stability of the solution and to explore whether any of the additional species can lead to a better solution with a larger number of sources. The species were selected through multiple trial-and-error processes. If

Figure 1. NOAA satellite image of Kansas Flint Hills burning activities in 2014 and location of the Tallgrass IMPROVE sampling site.
the number of significant species in solution abruptly decreased after adding a species, the species was removed and another species was tried. A feasible solution of contributing sources should ensure that at least 80% of the variance of each species could be explained by these sources. The total species (PM$_{2.5}$) should have little influence of outliers, and each source should have multiple species not strongly influenced by outliers. Uncertainties in the solutions of source contributions to PM$_{2.5}$ were estimated by a bootstrap procedure (Efron and Tibshirani, 1993) in which the data are resampled more than 100 times with replacement and the standard deviation of these resampled results gives the estimate of the 1-sigma uncertainty.

**RESULTS AND DISCUSSION**

The most satisfactory result of applying Unmix to the Tallgrass data set was a five-source solution using ten species (PM$_{2.5}$, OC, EC, nitrate, sulfate, Al, Fe, Si, S, and K$_{non}$). The estimated minimum signal-to-noise ratio was 2.02, while the measured and Unmix-predicted PM$_{2.5}$ had an r$^2$ of 0.97. Solutions with six or more sources have been observed; however, satisfying diagnostic indicators consistent with recommendations were not obtained. The contributions of the five Unmix-derived sources (labeled S1 to S5) to PM$_{2.5}$ are shown in figure 2. Table 1 presents the contributions to PM$_{2.5}$ and to its constituent species from each source for the five-source solution, averaged over the 1428-sample data set. Table 2 shows the correlation, differences, and regression coefficients for predicted (model) and measured (input) values of the ten selected species. Table 3 presents a correlation matrix for the five sources, PM$_{2.5}$, PM$_{10}$, and several measured species not included in the Unmix modeling. To highlight the effect of intensive rangeland burning in April, time series plots of the contributions of each source on PM$_{2.5}$ are presented in figure 3.

### Table 1. Unmix-derived source contribution and 1-sigma uncertainties for selected species ($\mu$g m$^{-3}$)$^{[a]}$

<table>
<thead>
<tr>
<th>Species</th>
<th>PM$_{2.5}$</th>
<th>O$_{C}$</th>
<th>E$_{C}$</th>
<th>N$_{itrate}$</th>
<th>S$_{ulfate}$/industrial</th>
<th>S$_{ulfate}$/soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1: Nitrate/agricultural</td>
<td>1.680 ±0.200</td>
<td>0.067 ±0.014</td>
<td>0.021 ±0.003</td>
<td>0.679 ±0.047</td>
<td>0.100 ±0.026</td>
<td>0.001 ±0.000</td>
</tr>
<tr>
<td>S2: Vegetative burn</td>
<td>0.367 ±0.161</td>
<td>0.302 ±0.157</td>
<td>0.203 ±0.171</td>
<td>0.034 ±0.027</td>
<td>-0.149 ±0.348</td>
<td>0.006 ±0.004</td>
</tr>
<tr>
<td>S3: Secondary organics</td>
<td>2.220 ±0.291</td>
<td>0.481 ±0.054</td>
<td>0.051 ±0.042</td>
<td>0.022 ±0.010</td>
<td>0.130 ±0.028</td>
<td>0.001 ±0.001</td>
</tr>
<tr>
<td>S4: Sulfate/industrial</td>
<td>2.250 ±0.263</td>
<td>0.022 ±0.033</td>
<td>0.021 ±0.010</td>
<td>-0.001 ±0.004</td>
<td>0.566 ±0.034</td>
<td>0.003 ±0.001</td>
</tr>
<tr>
<td>S5: Crustal/soil</td>
<td>1.080 ±0.122</td>
<td>0.078 ±0.032</td>
<td>0.001 ±0.001</td>
<td>0.028 ±0.003</td>
<td>0.189 ±0.037</td>
<td>0.047 ±0.006</td>
</tr>
</tbody>
</table>

$^{[a]}$ S1 to S5 represent the five Unmix-derived sources.
aerols. The volatilization of NH₃ is highly temperature dependent, and low wind speeds, low temperatures, high pressures, stagnant conditions, and strong inversions and large-scale inversion conditions in winter were the meteorological drivers for episodic pollution by these nitrates (Kim et al., 2014). The regional agricultural NH₃ emission supported aerosol nitrate formation, and low wind speeds, low temperatures, high pressures, stagnant conditions, and strong inversions and large-scale inversion conditions in winter were the meteorological drivers for episodic pollution by these nitrates (Kim et al., 2014). The source profiles in table 1 indicate that 89% of the ambient nitrate in PM₂.₅ came from S1, which exhibited a strong seasonal dependence. Because the volatilization of NH₃ is highly temperature dependent, agricultural NH₃ emissions usually have their own seasonal variation, which also depends on agricultural practices, such as how livestock are raised and when manure or fertilizer are applied to the land. Higher NH₃ emissions and concentrations are often observed in summer rather than winter (Mukhtar et al., 2008). However, translating seasonality in NH₃ emissions to seasonality of nitrate aerosol is not straightforward because gas-to-particle conversion reactions have important influences on the formation of nitrate aerosols, and the dynamic NH₃/aerosol relationship is confounded by the seasonality in nitric and sulfuric acid concentrations (Aneja et al., 2003). More research is needed to model the influence of seasonality in NH₃ emissions on nitrate aerosols.

S2: VEGETATIVE BURNING (5% OF PM₂.₅)

This source is characterized by non-soil potassium and OC/EC. Compared to other sources, it had relatively high relative uncertainties for its PM₂.₅ contributions. This source contributed 87% of the smoke tracer non-soil potassium in PM₂.₅ and had an OC concentration greater than EC. It also included some soil elements (Al, Fe, and Si). In addition, the source strength of S2 had consistent spikes in April (fig. 3 and table 4), which is the same month when intensive prescribed rangeland burning occurs in the Flint Hills region. There were no S2 spikes in April 2013, which was consistent with the fact that only 0.2 million acres were burned in 2013 due to the dry weather, while the 12-year average of acres burned in April is 2.1 million in the Flint Hills region. Relatively smaller spikes were also observed on the following dates: 5 July 2003, 5 July 2007, 5 July 2008, 5 July 2011, 5 July 2012, 6 July 2013, and 4 July 2014. These were most likely due to Fourth of July firework events. All of the above provide evidence for identifying this source as smoke primarily from vegetative burning. The existence of Fe, Si, and Al in S2 indicated that a part of the smoke particles were from soil.

S3: SECONDARY ORGANIC AEROSOL (29% OF PM₂.₅)

This source category is characterized by large OC components and lacks tracers to identify it as a specific source. The large OC/EC ratio (9:1) was an indication of a secondary formation. The source category also contains some sulfate, which could come from distant sources that allow secondary sulfate formation during transport. Secondary organic aerosols can be generated from various sources, such as biogenic, mobile, or stationary anthropogenic sources. Figure 3 shows that spikes in the source strength of S3 occurred consistently...
Figure 3. Time series plots of source contributions on PM2.5 (dates are m/d/y).
in April, indicating that emission from rangeland burning was a major source of secondary organic aerosols. The spikes in S3 and S2 did not always occur on the same day (table 4) because the secondary aerosols have different pathways with the primary smoke emissions. Fourth of July fireworks could explain the observed S3 spikes in July and could have contributed to the sulfate and organic compounds in S3. Table 3 shows that S3 correlated with S2 with a Pearson correlation coefficient of 0.49. The S3 and S2 sources contributed 51% and 32%, respectively, of the OC in PM$_{2.5}$.

**S4: SULFATE/INDUSTRIAL (30% of PM$_{2.5}$)**

This source category is characterized by high sulfate and is the major mass contributing source. It contributed about 50% of the sulfate in PM$_{2.5}$. In most cases, the sulfate is fully neutralized and in the form of ammonium sulfate. This source represents secondary sulfate from regional SO$_2$ emissions, including coal-fired power plants, residual oil use, and other industrial processes. Although there was a lack of tracers to identify S4 as a specific source, Se correlated with S4 with a Pearson correlation coefficient of 0.60 (table 3), indicating that power plants could be important contributors to S4. Figure 3 shows that the contributions of S4 were generally higher during summer than during winter, which is consistent with the effect of photochemistry and the presence of oxidants on the formation of secondary sulfate. From 2005 to 2014, S4 showed a decreasing trend, which may be attributed to long-term reductions in regional SO$_2$ emissions due to rules such as the Clean Air Nonroad Diesel Rule and the Acid Rain Program for utilities. Similar long-term decreasing trends of atmospheric sulfate in the U.S. have been reported in other studies and have been linked to the implementation of a number of regulations and associated controls on sulfur emissions in the U.S. (Hubbell et al., 2009; Henne-man et al., 2015).

**S5: CRUSTAL/SOIL (14% of PM$_{2.5}$)**

This source is the most easily identified source as it is characterized by typical crustal/soil elements, such as Fe, Si, and Al. Other typical crustal/soil elements such as Ti, Ca, and K also correlated well with S5 (table 3), although they were not selected species in the Unmix solution. Spikes in the source strength of S5 were observed occasionally in the summer when the wind was strong (table 5). Table 4 shows that S5 is negatively related with S1, S3, and S4. It is hypothesized that S5 represents resuspended soil and thus was enhanced by strong wind, while S1, S3, and S4 are mainly secondary aerosols and thus could be suppressed or easily dispersed by strong wind.

The seasonal variation of the identified sources was examined, and the results indicated strong effects of the prescribed rangeland burning (fig. 4). April had the highest PM$_{2.5}$ compared to other months. The contributions of S2 and S3 were 11% and 49%, respectively, in April, as compared with 5% and 29%, respectively, on average. In April, the S2 contribution was more than three times higher and the S3 contribution was more than two times higher than in March or May. The differences between contributions in April and the average contributions of all other months were 1.05 and 4.03 µg m$^{-3}$ for S2 and S3, respectively. It is reasonable to hypothesize that these increases in the S2 and S3 contributions are attributable to the intensive prescribed rangeland burning in April. Therefore, it can be estimated that prescribed rangeland burning contributed about 8.7% as primary smoke aerosols and 33% as secondary aerosols, respectively, of the average 24 h PM$_{2.5}$ concentration in April (12.12 µg m$^{-3}$). It was found that S3, S4, and S5 shared a similar seasonality, and they were all generally high in summer and low in winter. In contrast, S1 was generally low in summer and high in winter. As a result, the seasonality of total PM$_{2.5}$ was not obvious, as can be seen in figure 4. October had the lowest PM$_{2.5}$ compared to other months, as the

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**Table 4. Spikes in the source strength of S2 and S3.**

<table>
<thead>
<tr>
<th>Date (m/d/y)</th>
<th>Contribution (µg m$^{-3}$)</th>
<th>Date (m/d/y)</th>
<th>Contribution (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/12/2003</td>
<td>1.73</td>
<td>4/9/2003</td>
<td>72.10</td>
</tr>
<tr>
<td>4/16/2005</td>
<td>4.04</td>
<td>4/16/2005</td>
<td>15.87</td>
</tr>
<tr>
<td>4/21/2008</td>
<td>2.73</td>
<td>4/21/2008</td>
<td>10.81</td>
</tr>
<tr>
<td>4/22/2009</td>
<td>4.73</td>
<td>4/-/2009</td>
<td>No spike</td>
</tr>
<tr>
<td>4/3/2012</td>
<td>2.50</td>
<td>4/-/2012</td>
<td>No spike</td>
</tr>
<tr>
<td>4/-/2013</td>
<td>No spike</td>
<td>4/-/2013</td>
<td>No spike</td>
</tr>
</tbody>
</table>

12-year average 0.38  2.22  2.1

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**Table 5. Spikes in the source strength of S5.**

<table>
<thead>
<tr>
<th>Date (m/d/y)</th>
<th>Wind Speed (mph)</th>
<th>Maximum Wind Speed (mph)</th>
<th>S5 Contributions in PM$_{2.5}$ (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/13/2006</td>
<td>6</td>
<td>23</td>
<td>12.21</td>
</tr>
<tr>
<td>10/5/2006</td>
<td>3</td>
<td>10</td>
<td>18.27</td>
</tr>
<tr>
<td>8/10/2007</td>
<td>7</td>
<td>18</td>
<td>12.06</td>
</tr>
<tr>
<td>6/26/2008</td>
<td>9</td>
<td>20</td>
<td>18.48</td>
</tr>
<tr>
<td>7/17/2012</td>
<td>9</td>
<td>20</td>
<td>15.38</td>
</tr>
<tr>
<td>6/27/2013</td>
<td>5</td>
<td>16</td>
<td>17.43</td>
</tr>
<tr>
<td>8/29/2013</td>
<td>5</td>
<td>13</td>
<td>14.93</td>
</tr>
<tr>
<td>6/22/2014</td>
<td>8</td>
<td>20</td>
<td>13.87</td>
</tr>
<tr>
<td>8/24/2014</td>
<td>11</td>
<td>22</td>
<td>14.57</td>
</tr>
</tbody>
</table>

12-year average 1.08

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[a] Wind speed data is from MHK airport, which is about 57 miles from analysts at Kansas State University and KDHE. They have been generally counted from late February or early March to the first week of May.
contributions from all the five source categories were not at high levels in that month.

Figure 5 shows that all PM$_{2.5}$ concentrations higher than 30 $\mu$g m$^{-3}$ were observed in April and are likely associated with prescribed rangeland burning. Similarly, all PM$_{10}$ concentrations higher than 50 $\mu$g m$^{-3}$ were observed in April, except on 7 June 2006. Table 3 shows that total PM$_{2.5}$ and total PM$_{10}$ both correlated well with S2 and S3, indicating...
that vegetative burning primary emissions and secondary organic aerosols are the two major contributors to the variations of not only PM$_{2.5}$ but also PM$_{10}$. The following regression equation was developed to relate the total PM$_{10}$ with the five Unmix-derived PM$_{2.5}$ sources, with $r^2 = 0.7$:

$$\text{PM}_{10} = 4.795 + 0.700(\text{SI}) + 2.169(\text{S2}) + 1.275(\text{S3}) + 1.106(\text{S4}) + 2.436(\text{S5})$$

(1)

Based on the above equation, for every 1 $\mu$g m$^{-3}$ contribution from vegetative burning primary emissions to PM$_{2.5}$, more than twice that contribution (2.169 $\mu$g m$^{-3}$) can be expected to PM$_{10}$, indicating that less than half of the PM$_{10}$ from vegetative burning primary emissions is PM$_{2.5}$. For every 1 $\mu$g m$^{-3}$ contribution from secondary organic aerosols to PM$_{2.5}$, a similar contribution (1.275 $\mu$g m$^{-3}$) can be expected to PM$_{10}$, indicating that the majority of PM$_{10}$ from secondary organic aerosols is PM$_{2.5}$. On average, it could be estimated that the sources associated with vegetative burning primary emissions and secondary organic aerosols contributed about 6% and 19%, respectively, of PM$_{10}$.

**CONCLUSION**

Application of the Unmix receptor model to the 2002-2014 data set from the IMPROVE site at Tallgrass National Preserve resulted in a realistic solution that contains the following five source categories that contribute to local ambient PM$_{2.5}$: nitrate/agricultural (22%), vegetative burning (5%), secondary organic aerosol (29%), sulfate/industrial (30%), and crustal/soil (14%). In April, contributions of vegetative burning and secondary organic aerosol increased to 11% and 49%, respectively, indicating the influence of the prescribed rangeland burning season at Flint Hills. The contribution of smoke from prescribed burning was estimated to be 1.05 $\mu$g m$^{-3}$ as primary aerosols and 4.03 $\mu$g m$^{-3}$ as secondary aerosols, which in total accounted for 42% of the average PM$_{2.5}$ concentration in April. The estimated contribution of secondary aerosols was four times higher than that of primary aerosols, which highlighted the importance of secondary aerosols in smoke management. This information could be useful in the development of effective air quality management strategies.

Comparison studies of the various models and analytical techniques have been recommended in order to obtain solid results in source apportionment (Engel-Cox and Weber, 2007). In our results, the sulfate/industrial source category may contain multiple unidentified sources, and secondary tools and methods may be needed to refine the source apportionment. It is expected that much can be gained from integrated studies of Unmix and other receptor models, or dispersion and photochemical models, in future work. In addition, in ongoing source apportionment studies at Kansas City and Wichita, more complicated source profiles are expected. The smoke source information obtained in this study may provide insights when estimating smoke contributions to air quality in those big cities.

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**REFERENCES**


