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Trends in concentrations of atmospheric gaseous and particulate species in rural eastern Tennessee as related to primary emissions reductions

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Trends in Meteorology at Look Rock

This analysis uses data from both Look Rock (LRK) and TYS when examining meteorological influences on the Look Rock site. Temperature and precipitation are the most readily compared parameters between the two sites but other data are described that provide some insight into conditions that affect air quality--and aerosols in particular. All data statistics cover the entire 15 year period (1999-2013) unless otherwise noted. As done in the main paper, data were summarized by calendar quarter: January-March (1st), April-June (2nd), July-September (3rd) and October-December (4th). These quarters are sometimes denoted as “winter”, “spring”, “summer” and “autumn”, respectively. Due to solar elevation, these seasonal definitions make winter and autumn closely aligned as are spring and summer.

Surface Air Temperature

Surface air temperature is normally measured at about 2 m above the ground in a location well removed from surface structures. The Look Rock data do not meet the strict monitoring requirements followed by the NWS so some amount of disagreement is expected. However, of greater importance is the elevation difference between TYS (299 m) and LRK (805 m). The ridge top temperatures are expected to be lower than those in the valley below due to the near adiabatic decrease (on average) in temperature with height. Look Rock-TYS average temperature differences for quarters 1-4 were -1.7°, -2.4°, -2.6° and -1.1°C, respectively. Spring and summer differences were larger than those for winter and autumn. These differences were consistent from one year to the next with the only exception being the 4th quarter of 1999 when LRK averaged 0.2°C warmer than TYS. All quarterly mean temperatures are plotted in Figure S-1 to illustrate the high correlation (r^2=0.994) and consistent bias between the two locations.

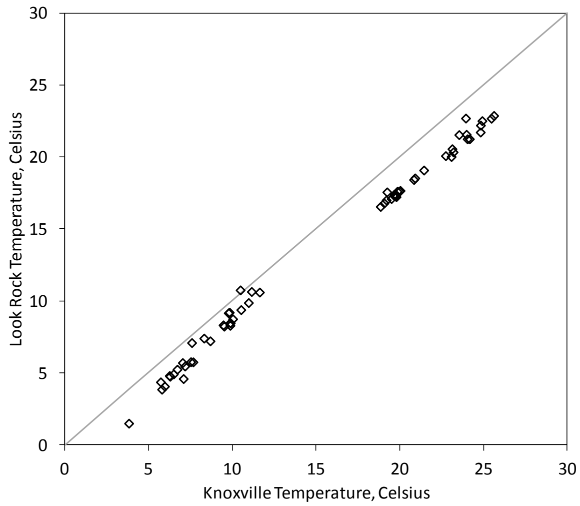

Figure S-1. LRK and TYS quarterly mean temperatures compared for 1999-2013.

There is high confidence because of this correlation that the temperature departures (or anomalies) from normal of each quarter/year based on the TYS NWS 30-year climate “normal” (average) temperatures (for 1980-2010) represent an equivalent anomaly at LRK. LRK quarterly average temperatures and the TYS quarterly temperature anomalies are plotted in Figure S-2 for 1999-2013. No season shows a clear temperature trend over the period. Fifteen-year mean anomalies (negative values denote cooler than average), by quarter, were 0.25°, 0.43°, -0.27° and -0.01°C (1st - 4th quarters, respectively). The largest positive anomaly was in the 1st quarter of 2012 (3.5°C) whereas the largest negative anomaly was two years earlier (1st quarter 2010) at -2.7°C. The most notable quarterly deviation trend occurred during the spring (2nd) quarter for which 11 of 15 years had positive anomalies.

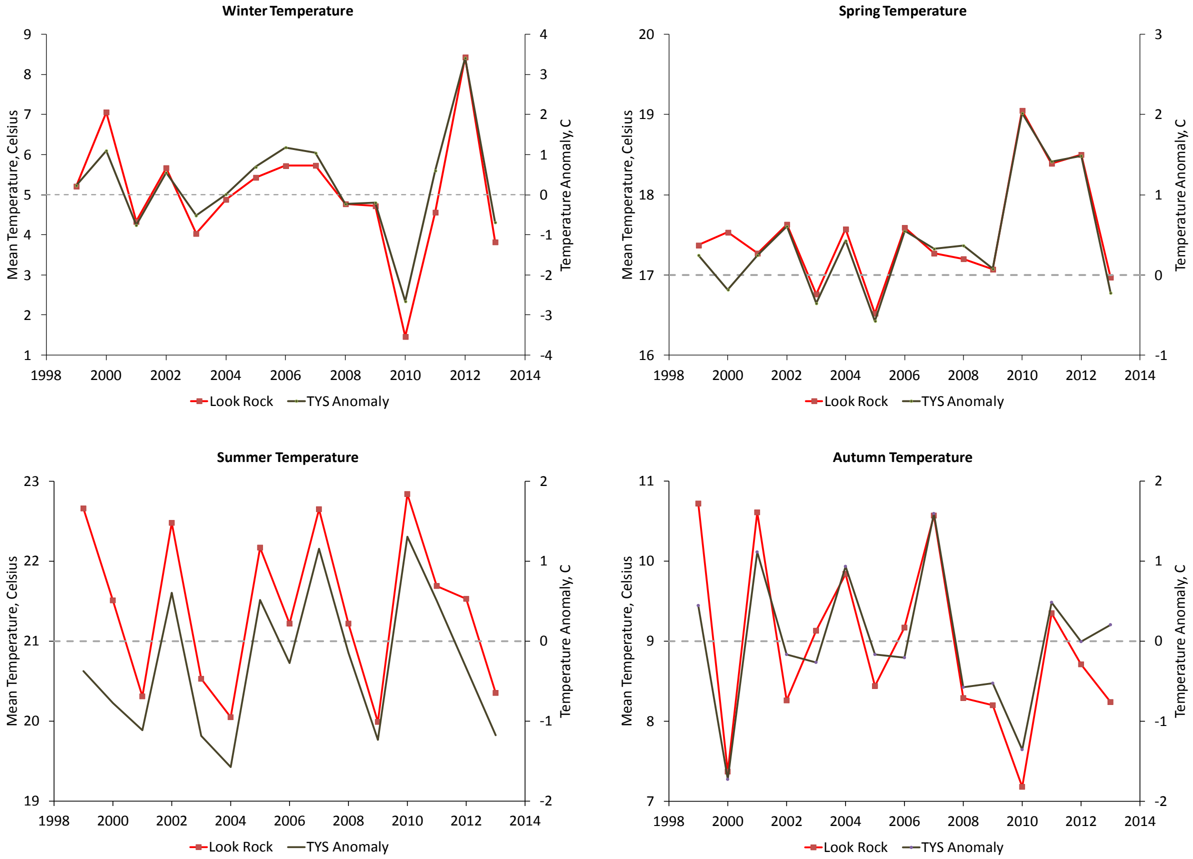

Figure S-2. Time series of quarterly mean LRK temperatures and TYS temperature anomalies for 1999-2013.

During calendar year 2013 (the year when the Aerodyne ACSM aerosol analyzer was operated at Look Rock), TYS temperature deviations from the 15-yr mean were -0.69°C (i.e., below average) for the winter (1st) quarter, -0.22°C for the spring (2nd) quarter, -1.18°C for the summer (3rd) quarter) and 0.20°C for the autumn (4th) quarter. Thus, spring and autumn were near the 15-yr seasonal mean for temperature whereas winter and summer were cooler than average.

Precipitation

Measurements of precipitation are subject to more spatial variability than measurements of temperature because of the inhomogeneous nature of rainfall, the stochastic nature of convective precipitation and topographic influences on precipitation formation. The NWS uses heated rain gages capable of recording precipitation amount when freezing precipitation occurs. LRK uses similar measurement technology. Thus, the measurement itself should be similar for the two sites. One issue affecting a site-to-site comparison is the more frequent occurrence of power outages at LRK. Outages are more likely to occur under extreme weather conditions, especially thunderstorms (but can also include freezing precipitation and high winds), and these are the very conditions most likely to experience precipitation. Thus, the LRK data record may exclude portions of some precipitation events producing an underestimation of actual quarterly precipitation amount. Figure S-3 compares quarterly precipitation totals for TYS and LRK for 1999-2013. The level of agreement is not as high as for temperature (r^2=0.64) but does not have a consistent site bias as was found for temperature. In addition, a comparison (not shown) of the difference between LRK and TYS precipitation totals against the number of hours of missing LRK precipitation data does not show a relationship consistent with a bias affected by missing data. Some quarters experienced substantial differences in precipitation totals and these seem more likely due to convective precipitation occurring at only one site.

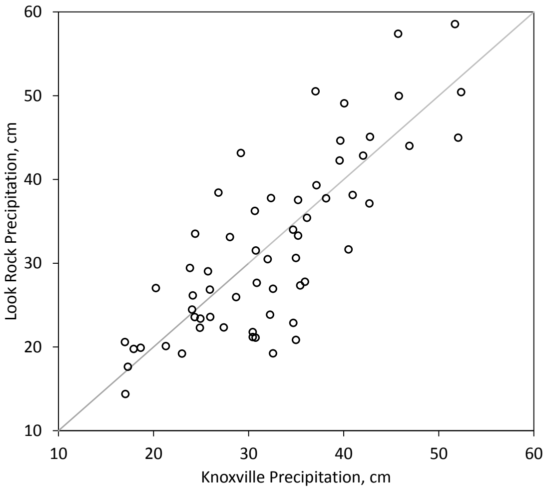

Figure S-3. Comparison of LRK and TYS quarterly precipitation amounts.

Table S-1. Precipitation statistics (cm).

Qtr	1999-2013		2013	
	TYS	LRK	TYS	LRK
1	33.6	29.9	52.4	50.4
2	32.2	33.8	51.7	58.6
3	34.9	36.1	38.2	37.8
4	28.4	28.0	35.2	33.3
Annual	129.2	127.7	177.4	180.0

Figure S-4 plots time series of quarterly precipitation totals for LRK along with the corresponding 30-year anomalies for TYS. Table S-1 lists the 1999-2013 average quarterly precipitation amounts for both TYS and LRK along with the 2013 totals. Precipitation is distributed rather evenly across all seasons with the last quarter being the driest on average. There are no clear trends in quarterly precipitation amounts during 1999-2013. Several periods stand out as anomalous when compared to the 30-year climatological reference data. High anomalies >15 cm occurred for winters of 2002 and 2013, spring 2013, and summers of 2003, 2009 and 2012. In addition, a negative anomaly <-15 cm occurred in winter 2007.

The year 2013 experienced a substantial surplus in precipitation compared to the 15-yr averages for both TYS and LRK. Above average precipitation was measured during all quarters of the year (Table S-1). Annual totals were 37% above average at TYS and 40% above average at LRK. Experiencing above average precipitation across all seasons is exceptional and suggests that the 2013 weather patterns that affected east Tennessee were considerably different from what has typically occurred during recent years.

Wind Speed

Characterizing airflow is a more complex problem than summarizing single parameters like temperature and precipitation because it implies three-dimensional motion. Local winds like those measured near the surface at both LRK and TYS provide only partial information because air transported to the site over long distances can significantly impact local air quality. We make a distinction, therefore, between local and regional airflow with local wind data providing limited information on transport in the immediate vicinity of LRK. Regional transport is described in a later section.

“Local” in the current context refers to surface winds, measured at roughly 10 m above the surface, representing transport within at most a kilometer of the measurement location. The limitation on data applicability is due to the three-dimensional nature of airflow (vertical and horizontal) as well as the numerous influences on transport forced by terrain, surface conditions, atmospheric turbulence and convection. Nevertheless, surface wind data provide some insight into local phenomena that can impact air quality at the site on a regular, sometimes diurnal, basis.

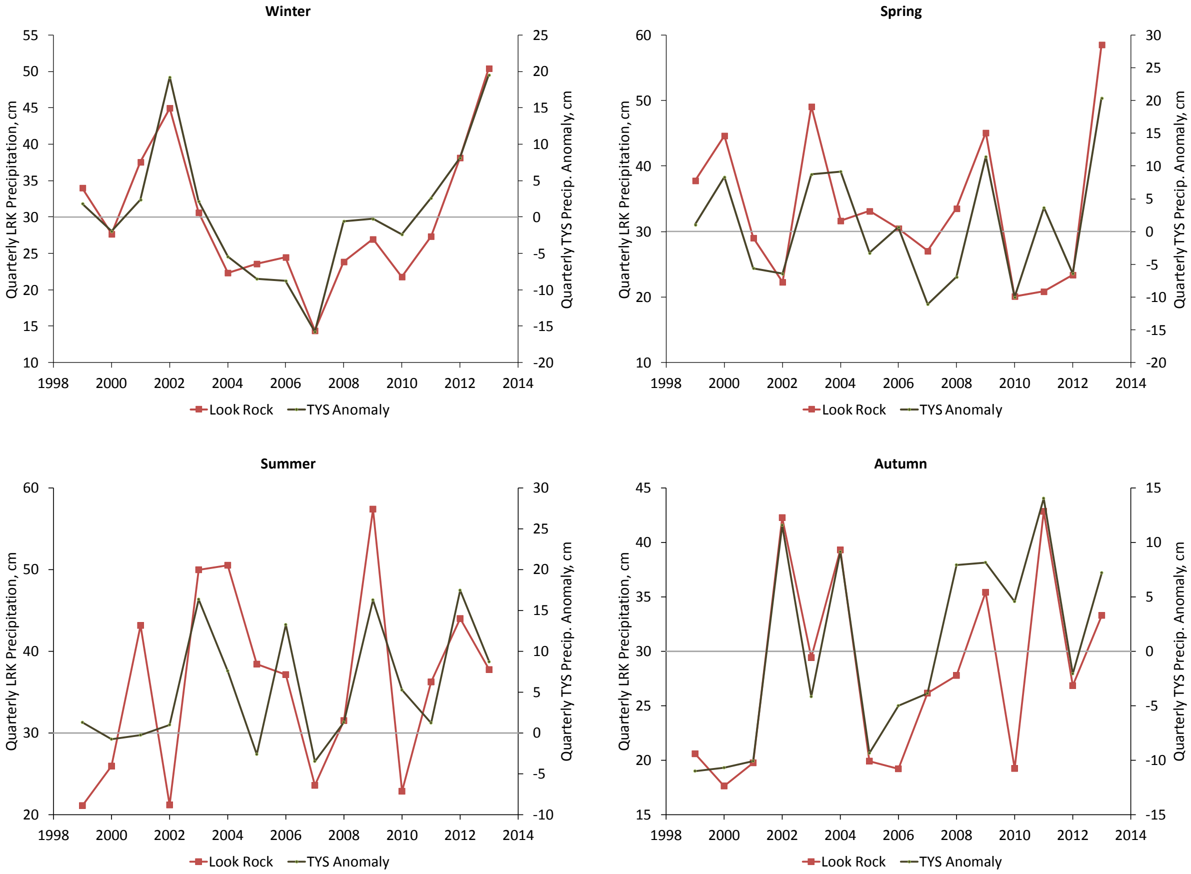

Figure S-4. Time series of quarterly LRK precipitation and TYS precipitation anomalies for 1999-2013.

Wind speed measured at both TYS and LRK tends to be lowest in the early morning hours between midnight and sunrise when the atmosphere is most stable and the vertical turbulent transfer of momentum is at a minimum. Conversely, highest wind speeds usually occur during the afternoon when higher momentum is transported toward the surface from aloft. The exception is winds produced by convective precipitation which can occur at any time of day. The regular waning and waxing of wind speed implies that local influences (on the order of a few hundred meters) on air quality in the vicinity of LRK are greatest at night when speeds are lowest. With higher daytime winds comes an increase in influence from locations farther away. Another transport phenomenon associated with the light nighttime winds is vertical transport. Sinking air tends to occur at night as slightly cooler air moves down the ridge sides into the adjacent valleys. This is unlikely to occur during the day when solar heating drives vertical motions and vertical mixing increases the influence of winds aloft on horizontal transport.

Quarterly mean hourly wind speeds from LRK and TYS indicates are correlated (r^2=0.55). This level of agreement probably reflects the seasonal and synoptic-scale influences (such as cyclones and anticyclones) on wind that affect both locations. LRK speed is slightly lower than that at TYS. This small difference, on the order of <10 percent, is most likely due to the vertical and horizontal proximity of the LRK forest canopy to the wind sensor. The NWS sensor is located in an open field devoid of major obstacles that influence airflow.

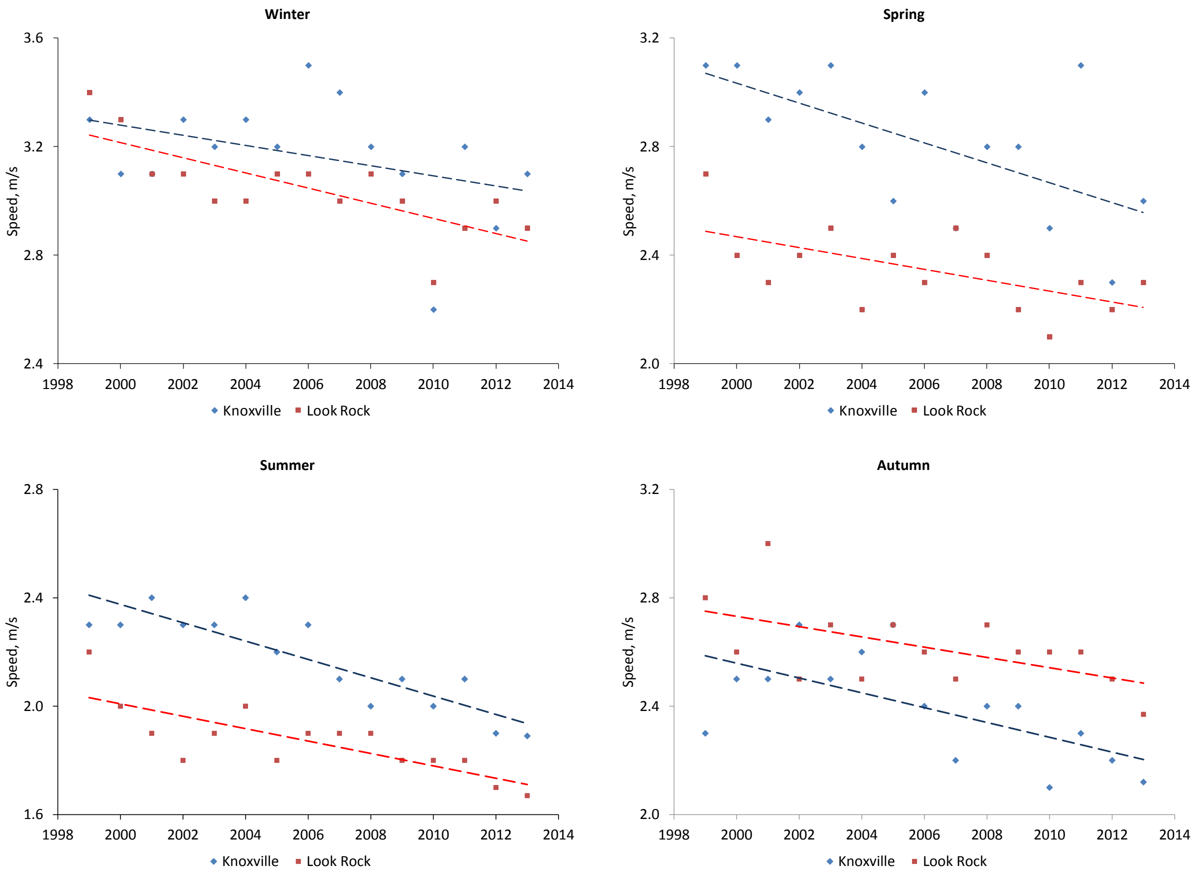

Figure S-5. Time series of mean quarterly wind speed at LRK and TYS for 1999-2013. Dashed lines represent the mean linear trends in each plot. All trends are statistically significant.

Inter-annual differences in quarterly average wind speed are generally not large at either site. However, of all the meteorological parameters available at TYS and LRK, none show a consistent trend like that for wind speed. Figure S-5 illustrates this trend with time series plots of quarterly averages for both sites. Trends are negative and are similar at both sites and for each quarter. By fitting a linear trend line to each quarterly time series and computing the average slope and correlation (coefficient of determination, r^2) we get a mean trend across all quarters that is equal to -2.2 and -2.9 cm s^{-1} per year at LRK and TYS, respectively, with a corresponding mean r^2 of 0.69 and 0.59. Thus, 60-70 percent of the variation in annual wind speed measured at LRK and TYS during 1999-2013 was associated with this downward trend while the remaining variation was due to inter-annual factors. While this trend is significant and rather robust, it is also not unexpected because similar trends have been reported elsewhere (Pryor et al., 2009; Milton, 2010; Pryor and Ledolter, 2010). The causal factors for such a trend are unknown but may be associated with a recent climatic shift (Pryor and Ledolter, 2010). The more immediate impact is that ventilation at LRK has been steadily diminishing with local influences on air quality growing in importance over time.

Comparison of Pollutant Species Sensitivities to Meteorological Factors

In the main paper the normalized variable $\hat{x}$ was defined as

$$\hat{x} = \frac{x - \bar{x}}{\sigma_x}$$

where $\bar{x}$ represents the mean value of x with standard deviation σ_x. The quotient $\Delta\hat{x}_2/\Delta\hat{x}_1$ compares the relative changes in two normalized variables over time and is referred to here as the sensitivity of $\hat{x}_2$ to $\hat{x}_1$. This quotient can be computed statistically as the slope of a regression line between $\hat{x}_2$ and $\hat{x}_1$ over the period of record used in this study (nominally 15 years except for SO_2 for which quarterly data are incomplete before 2007).

Sensitivity data from the aforementioned regressions between air quality and emissions and meteorological variables are summarized in Table S-2. The values in the table represent the fractional standard deviation change in each air pollutant concentration in response to a one standard deviation change in a corresponding emissions or meteorological variable. Sensitivities >1 indicate a greater relative response in pollutant than in the independent variable. Regarding comparisons of air pollutants with emissions: results are presented for those data pairings that are expected to be most likely associated due to a strong physical/chemical connection. This is because of the covariance of NO_x and SO_2 emissions ($\frac{\Delta\hat{x}_{NOx}}{\Delta\hat{x}_{SO2}} = 0.95$; r^2=0.90). Both species responded similarly to regulatory requirements and changing economic drivers but there is no reason to believe that both contributed equally to changes in the different air pollutant levels. For example, Look Rock gas-phase SO_2 levels were significantly associated with NO_x emissions but it is unreasonable to conclude that NO_x emissions changes have been driving changes in $SO_{2(g)}$. Instead, the linkage is a statistical artifact of the SO_2-NO_x emissions association. In a similar manner, ozone was significantly associated with SO_2 emission changes but NO_x is the more likely species influencing ozone. Both OC and EC aerosol components were found to have significant associations with SO_2 and NO_x emission changes. However, the statistical link between OC and NO_x was greater than was the OC:SO_2 link and the latter results are assumed to be an artifact. The opposite was true for EC. It was more sensitive to SO_2 emission changes than NO_x emission changes. The reason for this is not clear but might be due to the possibility that EC emissions are sometimes associated with diesel truck emissions and diesel fuel sulfur levels have also been declining due to EPA regulations.

In summer both ozone and OC increase with temperature although ozone has slightly greater sensitivity to temperature than OC. These same pollutants are negatively linked to precipitation during summer. EC is negatively linked with precipitation during the 1st quarter. A positive link between pollutant concentrations and wind speed was found in most quarters. Ozone, OC and EC associations with solar radiation were positive when significant links were found. The negative association between sulfate and solar radiation during the second (spring) quarter was unexpected because of the role played by solar radiation in gas-phase SO_2 oxidation to sulfate. This association was not a surrogate for a sulfate:cloud cover link (i.e., more cloud cover—and less solar radiation—leading to more heterogeneous sulfate formation) because the sulfate:cloud cover comparison was found to be purely random for the same time period. In fact, sulfate was never significantly associated with cloud cover during any quarter. Though infrequent, an association between pollutant and the frequency of high Look Rock relative humidity (i.e., relative humidity at the site exceeding 90 percent) was negative when found. The role of high ridgetop humidity may be an indicator of pollutant scavenging by clouds in direct contact with the high-elevation site.

Table S-2. Sensitivity of quarterly measured Look Rock air pollutants to annual emissions and quarterly meteorological factors based on significant regression slopes expressed as $\Delta\hat{x}_2/\Delta\hat{x}_1$.[a]

Air Pollutant [b]	Averaging Period	SO_2 Emissions	NO_x Emissions	T [c]	Pcp. [d]	Wind Speed	CC [e]	Sol. Rad.	High RH
Ozone	1st Qtr.	-	-	-	-	-	-	-	-
	2nd Qtr.	-	0.77	-	-	0.57	-	-	-
	3rd Qtr.	-	0.69	0.68	-0.68	0.68	-0.49	-	-
	4th Qtr.	-	-	-	-	-	-	0.74	-0.57
SO_2 [f]	1st Qtr.	-	-	NA	NA	NA	NA	NA	NA
	2nd Qtr.	1.44	-						
	3rd Qtr.	1.27	-						
	4th Qtr.	1.37	-						
Sulfate	1st Qtr.	0.92	0.73	-	-	0.56	-	-	-
	2nd Qtr.	0.97	0.75	-	-	0.55	-	-0.57	-
	3rd Qtr.	0.97	0.76	-	-	0.69	-	-	-
	4th Qtr.	0.76	0.61	-	-	-	-	-	-
OC	1st Qtr.	-	-	-	-	-	-	-	-
	2nd Qtr.	0.56	0.66	-	-	0.54	-	-	-
	3rd Qtr.	0.65	0.76	0.52	-0.57	0.80	-0.43	-	-
	4th Qtr.	0.44	-	-	-	0.70	-0.44	0.64	-0.56
EC	1st Qtr.	0.87	0.80	-	-	0.78	-	-	-
	2nd Qtr.	0.87	0.79	-	-	0.68	-	-	-
	3rd Qtr.	0.92	0.86	-	-	0.67	-	-	-
	4th Qtr.	0.73	0.65		-0.59	0.62	-	0.55	-

[a] Sensitivities are included here only for comparisons in which $p \leq 0.05$. Subscript "2" denotes the average normalized air pollutant deviation and subscript "1" denotes the emissions or meteorological factor.

[b] All data records cover the period 1999-2013 unless otherwise indicated.

[c] Temperature.

[d] Precipitation.

[e] Cloud cover.

[f] SO_2 was only compared against emissions data and sufficient concentration data were unavailable before 2007.

Overall, the highest average pollutant sensitivity was computed for $SO_{2(g)}$, sulfate and EC to SO_2 emissions. This was driven in large part by sensitivities >1 for $SO_{2(g)}$. Sensitivities >1 imply that $SO_{2(g)}$ experienced relative declines in excess of those for emissions within the Look Rock domain as defined in the paper. One way for this to occur is by way of SO_2 emissions decreases well outside the Look Rock domain but it also implies that a significant amount of unreacted $SO_{2(g)}$ reaches the site from outside the perimeter region (domain) that is expected to have the greatest impact on Look Rock air quality. A second hypothesis is that a larger reduction in SO_2 emissions occurred within the domain than quantified by the EPA emissions data. More than 50 percent of the SO_2 originated from EGUs (as high as 75 percent early in the analysis period) and their emissions are accurately known because of stack monitoring required by law. It is possible that, as the EGU SO_2 emissions decline, the remaining SO_2 emissions are becoming more uncertain because of the sources involved and limitations on how their emissions are quantified. An increase in emissions uncertainty over time could be a major factor determining the apparent sensitivity of pollutants to SO_2 emissions.

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