Climate impact on ambient PM$_{2.5}$ elemental concentration in the United States: A trend analysis over the last 30 years

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**Abstract**

Weather impacts on the chemical composition of PM$_{2.5}$ varies significantly over space and time given the diversity of particle components and the complex mechanisms governing particle formation and removal. In this study, we employed generalized additive models (GAMs) to estimate weather-associated changes in PM$_{2.5}$ composition in the US during 1988–2017. We considered seven components of ambient PM$_{2.5}$, which included elemental carbon (EC), organic carbon (OC), nitrate, sulfate, sodium, ammonium, and silicon. The impact of long-term weather changes on each PM$_{2.5}$ component was defined in our study as “weather penalty”. During our study period, temperature increased in four regions, including the Industrial Midwest and Northeast during the warm and cold season; and Upper Midwest and West in the cold season. Wind speed decreased in both seasons. Relative humidity increased in the warm season and decreased in the cold season. The weather changes between 1988 and 2017 were associated with most PM$_{2.5}$ components during both warm and cold seasons. The direction and the magnitude of the weather penalty varied considerably over the space and season. In the warm season, our findings suggest a nationwide weather penalty for EC, OC, nitrate, sulfate, sodium, ammonium, and silicon of 0.04, 0.21, 0.04, 0.35, −0.01, 0.05, and 0.01 μg/m$^3$, respectively. In the cold season, the estimated total penalty was 0.04, 0.21, 0.06, 0.04, −0.01, −0.02, and 0.02 μg/m$^3$, respectively.

**1. Introduction**

Over the last 50 years, a large body of the literature has assessed the impact of weather changes on air pollutant levels (Fiore et al., 2015; He et al., 2017; Mahmud et al., 2010; Mickley et al., 2004; Stelson and Seinfeld, 1982; Tai et al., 2010). Recently, investigators have also focused on the impacts of climate change on air pollution-related health effects (Jhun et al., 2015; Sun et al., 2015; Tainio et al., 2013). Among the air pollutants, fine particulate matter (PM$_{2.5}$) and ground level ozone (O$_3$) have been the most studied. Specifically, a previous investigation estimated that daily variation in meteorology factors can explain up to 50% of PM$_{2.5}$ variability in the United States – US (Tai et al., 2010). Jhun et al. (2015) report that past (1994–2012) weather-related increases in PM$_{2.5}$ in the US were 0.056 and 0.027 μg/m$^3$ per year in the warm and cold seasons, respectively. For O$_3$, Jhun et al. (2015) estimated an increase of 0.18 and 0.07 ppb per year during the warm and cold seasons, respectively. The authors also showed that this impact of long-term weather changes on PM$_{2.5}$ and O$_3$ in the US was associated with an excess of 770 and 290 annual deaths, respectively.

The weather impact on air quality has been extensively studied. It is well known that O$_3$ is primarily resulted from photochemical reactions between nitrogen oxides (NO$_x$) and organic compounds in the presence of sunlight (Fenger, 2009). Low humidity, high temperature, and low wind speed favor O$_3$ formation (Koo et al., 2012). For PM$_{2.5}$, atmospheric chemistry studies have shown that weather conditions are directly associated with the particle formation (e.g., nucleation, condensation, coagulation, and mechanical formation) and removal (e.g., coagulation, diffusion, wet deposition, and sedimentation) mechanisms (Feng et al., 2012; Hua et al., 2016). Given the particle formation and removal mechanisms, and the diversity of particle components, weather impacts on PM$_{2.5}$ are more complex than the impacts on O$_3$. The literature has described some process representing this complexity: i) high temperature favors the formation of water vapor, which subsequently condenses onto primary particles (Wang et al., 2013), ii) particles are efficiently scavenged through wet deposition (particles removed by a cloud or rain) (Balkanski et al., 1993), and meteorological conditions...
play an important role (it determines the formation of clouds and rain), iii) high temperatures can increase oxidation and production of sulfate particles, but also reduce nitrate particles through volatilization from particle to gas phase (Phalen, 2012; Weichenthal et al., 2016).

Given the complexity of weather impacts on PM$_{2.5}$, some studies have defined the chemical species of PM$_{2.5}$ as the outcome in weather-related air pollution models (Jihua et al., 2009; Price et al., 2016; Pye et al., 2009; Tai et al., 2010). These studies have shown that the relationship between particle components and weather variables varies significantly over space and time depending on the chemical components of PM$_{2.5}$. For example, Tai et al. (2010) found that temperature is positively correlated with nitrate in California, but negatively correlated in the Southeast. Relative humidity is negatively correlated with organic and elemental carbon but positively correlated with sulfate and nitrate. Sheehan and Bowman (2001) showed that a 10 °C decrease in temperature can increase secondary organic aerosol concentrations by 20–150%.

Prior investigations on the relationship between PM$_{2.5}$ chemical components and weather variables focused primarily on future climate scenarios or laboratory experiments. Little research has focused on spatial and seasonal models based on observational data to estimate the relationship between particle components and weather. Our research addresses this gap by quantifying the impacts of climate change on ambient PM$_{2.5}$ composition and levels in the US. Specifically, we performed a trend analysis based on a large temporal datasets of PM$_{2.5}$ species concentrations and weather over the last 30 years.

2. Materials and methods

2.1. Air quality data

We evaluated the impacts of weather changes on seven major components of ambient PM$_{2.5}$, including elemental carbon (EC), organic carbon (OC), nitrate, sulfate, sodium (Na$^+$), ammonium, and silicon. Daily air pollution data for the period 1988 and 2017 were obtained from the US Environmental Protection Agency (EPA) Air Data Monitoring Program - air quality data collected at outdoor monitors across the US (https://www.epa.gov/outdoor-air-quality-data). Of note, data for ammonium was only available starting 1997.

We considered air pollution monitoring stations with at least 10 years of year-round (January–December) data and at least 14 daily measurements each month. This resulted in 110 EC sites, 109 OC sites, 321 nitrate sites, 331 sulfate sites, 315 sodium sites, 122 ammonium sites, and 307 silicon sites. Using the selected data, we aggregated the air pollution monitoring stations into seven regions, including: Industrial Midwest (IM), North East (NE), North West (NW), South East (SE), South West (SW), Upper Midwest (UM), and West (W). The definition of these regions was based on the National Morbidity Mortality Air Pollution Study - NMMAPS (Samet et al., n.d.), Fig. 1 shows the spatial distribution of the air pollution monitoring stations by pollutants and the seven regions defined in our study.

The EPA air pollution monitoring data are measured by two networks, Chemical Speciation Monitoring Network (CSN) and IMPROVE. Overall, CSN sites are mainly located in urban and suburban areas, while most of the IMPROVE sites are in rural areas. These networks use different sampling methods, analytical protocols, and quality assurance (Solomon et al., 2014). Given the differences between the measurements of air pollution in CSN and IMPROVE, we adjusted the EC and OC data based on the factors reported by (Hand et al., 2011; Malm et al., 2011). In short, for CSN data, we subtracted monthly averaged blank values from the data if they were measured by Thermal Optical Reflectance (TOR) method. If the data were measured by Thermal Optical Transmittance (TOT) method, EC data was adjusted by multiplying 1.3 for compatibility with EC data from IMPROVE, whereas OC data was adjusted using the parameters recommended by Copeland et al. (2011) and Malm et al. (2011). This same adjustment for EC and OC was used recently by (Meng et al., 2018) to estimate space-time trends of PM$_{2.5}$ constituents in the US. We did not apply adjustments for the other components (nitrate, sulfate, sodium, ammonium, and silicon), since the literature has shown that the measurements from CSN and IMPROVE for these components are consistent (the analytical methods are very similar) (Hand et al., 2012b, 2011; Meng et al., 2018; Solomon et al., 2014).

Finally, we used the blanks data files provided by EPA in order to identify the data below the detection limits. The EPA recommends that if samples are reported below the detection limit, they have to be replaced by ½ the MDL - Method Detection Limit (the minimum sample concentration detectable for the monitor and method). The percentage of observation below detection limit (for the dataset used in our analysis, after apply the sites selection criteria, as described above) for each component of PM$_{2.5}$ was as follows: 4% for EC and OC, 7% for sodium, 2% for silicon, and 1% for ammonium and silicon. The data used for nitrate and sulfate did not present samples below the detection limit.

2.2. Weather data

The meteorological data were provided by the National Oceanic Atmospheric Administration’s National Climatic Data Center (ftp://ftp.ncdc.noaa.gov/pub/data/gisd/). This data contains daily information on temperature (°C), wind speed (Knots), and relative humidity (%). We selected 241 weather stations which operated during all 30 years (1988–2017) collecting year-round data for at least 21 days per month. We used a spatial matching process to merge daily weather data with those from the corresponding air pollution sites (daily air pollution data). This spatial join was based on the nearest weather station’s data, with an average distance between air pollution monitor and weather station of 29.5 km.

2.3. Statistical analysis

We used a framework composed by five steps to estimate the impacts of weather change on air pollution: i) central estimates, ii) bootstrap analysis, iii) standard error calculation, iv) merging process of the central estimates and the standard error, and; v) meta-analysis. Fig. 2 shows an overview of these steps.

2.3.1. Weather trends

We applied a general linear regression model to estimate changes in temperature, wind speed and humidity per year in 1988–2017. We stratified the analysis by season and regions. We defined two seasons, cold (November–April) and warm (May–October). Then, region-specific trends were meta-analyzed to estimate national average trends by season.

2.3.2. Weather-related increases in air pollution

We used a framework composed by five steps to estimate the impacts of weather change on air pollution: i) central estimates, ii) bootstrap analysis, iii) standard error calculation, iv) merging process of the central estimates and the standard error, and; v) meta-analysis. Fig. 2 shows an overview of these steps.

2.3.2.1. Central estimates. In the first step (central estimates), we employed generalized additive models (GAMs) to estimate weather-associated changes in PM$_{2.5}$ composition for each season (warm and cold - the same definition as mentioned above) and each of the seven regions. We used two GAM models to estimate long-term trends of daily PM$_{2.5}$ components. The first model was adjusted for weather variables (adjusted model), whereas weather variables were not included in the second (unadjusted model). The adjusted and unadjusted models are described in the Eqs. (1) and (2), respectively.
Y_{i,j,p} = \alpha + \beta_{\text{adjusted}} \text{year}_{i,j,p} + \gamma \text{month}_{i,j,p} + \sigma \text{weekdays}_{i,j,p} + s_1(\text{temp}) + s_2(\text{ws}) + s_3(\text{rh}) + e_{i,j,p} \tag{1}

Y_{i,j,p} = \alpha + \beta_{\text{unadjusted}} \text{year}_{i,j,p} + \gamma \text{month}_{i,j,p} + \sigma \text{weekdays}_{i,j,p} + e_{i,j,p} \tag{2}

where, \( Y \) is the daily concentration of the chemical specie \( p \) of PM_{2.5} (EC, OC, nitrate, sulfate, sodium, ammonium, and silicon) at site \( i \) and on date \( j \); \( \alpha \) is the regression intercept; \( \beta_{\text{adjusted}} \) and \( \beta_{\text{unadjusted}} \) are the regression coefficients representing the linear weather-adjusted and unadjusted pollutant trends (μg/m³ per year), respectively, in 1988–2017 for a specific season and region; \( \gamma \) and \( \sigma \) are the vectors of coefficients that represent monthly and weekday variability, respectively, of specie \( p \) at site \( i \); \( s() \) are the smoothing splice function to characterize nonlinear relationships between weather variables and daily concentration of specie \( p \); and \( e \) are normal residual errors with homoscedastic residual variance. Note that this is only applied in the adjusted model (Eq. (1)). The weather variables are represented by temperature (temp), wind speed (ws), and relative humidity (rh).

Finally, we highlight that we assumed constant seasonal/weekly variation based on the results observed in a pre-analysis. In this pre-analysis, we checked whether the year, month, and weekday interactions are significant. We checked that in the full model with the temperature variable and the results shown no significance. We used the software R - version 2.13.1 to perform the statistical analysis. We used GAM function in the MGCV package, which the Generalized Cross Validation (GCV) is the default method for selecting the smoothing parameters in a GAM model. Then we used \( \beta_{\text{adjusted}} \) and \( \beta_{\text{unadjusted}} \) values to quantify past weather-related increases ("weather penalty") in each PM_{2.5} component (item 1.3, Fig. 2). We derived the weather penalties (μg/m³ per year) for each season and region by obtaining the differences between \( \beta_{\text{unadjusted}} \) and \( \beta_{\text{adjusted}} \) (\( \beta_{\text{unadjusted}} - \beta_{\text{adjusted}} \)). While the weather impact is incorporated into the unadjusted trends, the adjustment with weather variables in model 2 removes the impact of inter-annual weather variation on air pollution trends. Therefore, we considered that any differences between the unadjusted and weather-adjusted trends are entirely attributable to the impact of long-term weather changes. A positive penalty (\( \beta_{\text{unadjusted}} > \beta_{\text{adjusted}} \)) suggests that an increase in species \( p \) of PM_{2.5} is associated with long-term weather changes in 1988–2017.

2.3.2.2. Bootstrap analysis. We applied a bootstrap analysis to estimate standard error for the penalties. This approach is recommended when the coefficients are estimated from the same input dataset and from related regression models (Härdle et al., 2003; Politis, 2003). The bootstrap was based on randomized subsets (pseudo-datasets) of the input dataset that accounted for serial correlation structures among the observations of PM_{2.5} components. We defined a block size of 20 days to create 100 pseudo-datasets for each season and region. Then we applied the same models described in Eqs. (1) and (2) (adjusted and unadjusted, respectively) for each pseudo-dataset. Finally, we estimated the penalty, as illustrated in Fig. 2, item 2.3.

2.3.2.3. Standard error calculation and merging process. We estimated standard errors (by season and region) for the unadjusted trend, weather adjusted trend, and penalty by obtaining standard deviation from the 100 estimate in the bootstrap analysis (Fig. 2, items 3.1, 3.2, and 3.3). Then, we linked the standard error obtained here with the central estimates according to the model type (adjusted, unadjusted, penalty), season, and region, as illustrated in Fig. 2, items 4.1, 4.2, and 4.3.
2.4. Meta-analysis

In the last stage (step 5), we applied meta-analysis to estimate national $\beta_{\text{adjusted}}$, $\beta_{\text{unadjusted}}$ and weather penalties by season. Specifically, we accounted for intra- and inter-region variability by applying regression meta-analysis with random effects (Berkey et al., 1998).

3. Results

3.1. Temporal distribution of air pollution

The national average time series of the raw monitored concentrations for each component of PM$_{2.5}$ were assessed by month and season (Fig. 3–5). Trends derived from regression analyses are discussed in section 3.3.

Slight decreases in EC were observed during our study period (1988–2017), while OC had a small increase (Fig. 3). Nitrate concentration showed substantial increases (Fig. 4) with an annual average concentration of 0.35 $\mu$g/m$^3$ in 1988 to 0.63 $\mu$g/m$^3$ in 2017. Over the entire study period, the highest nitrate concentration was observed in the cold season while the highest sulfate concentrations were observed in the warm season (Fig. 4). In contrast to nitrate, sulfate had a considerable increase until 2006, and thereafter exhibited a drastic decrease. Sodium and ammonium presented significant decreases during the study period, while silicon had a modest decrease (Fig. 5). Annual average sodium concentrations decreased from 0.21 $\mu$g/m$^3$ in 1988 to 0.07 $\mu$g/m$^3$ in 2017; ammonium concentrations decreased from 1.47 $\mu$g/m$^3$ in 1997 to 0.40 $\mu$g/m$^3$ in 2017; and silicon decreased from 0.17 $\mu$g/m$^3$ in 1988 to 0.11 $\mu$g/m$^3$ in 2017.

3.2. Weather trends

We assessed raw time series and annual trends of temperature, wind speed, and relative humidity (Fig. 6).

Our results showed temperature increases in four regions, including IM and NE during the warm and cold season; and UM and W only in the cold season. NE was the region with the highest increases in the study period (1988–2017). Trends analysis of temperature in NE shows an annual increase of 0.036 °C (95% CI: 0.035; 0.037) and 0.031 °C (95% CI: 0.030; 0.032) during the warm and cold season, respectively. In contrast, SW and NW had the lowest temperature change in the warm and cold season, respectively. A national meta-analysis presented a temperature variation of −0.005 °C (95% CI: −0.02; 0.01) in the warm season, and 0.003 °C (95% CI: −0.03; 0.02) during the warm and cold season, respectively. In contrast to nitrate, sulfate had a considerable increase until 2006, and thereafter exhibited a drastic decrease. Sodium and ammonium presented significant decreases during the study period, while silicon had a modest decrease (Fig. 5). Annual average sodium concentrations decreased from 0.21 $\mu$g/m$^3$ in 1988 to 0.07 $\mu$g/m$^3$ in 2017; ammonium concentrations decreased from 1.47 $\mu$g/m$^3$ in 1997 to 0.40 $\mu$g/m$^3$ in 2017; and silicon decreased from 0.17 $\mu$g/m$^3$ in 1988 to 0.11 $\mu$g/m$^3$ in 2017.
season and 0.031 knots (95% CI: 0.007; 0.054) per year during the cold season (Fig. 6).

Trends of relative humidity varied significantly by season and region. During the warm season, relative humidity increased in most regions. Only the West Coast regions (NW and W) exhibited decreases in relative humidity. The national meta-analysis showed an increase in relative humidity by $5.4 \times 10^{-4}$ (95% CI: $7.31 \times 10^{-5}; 1.01 \times 10^{-3})$ per year in the warm season. In the cold season, trends of relative humidity increased only in the SE and UM, $2.64 \times 10^{-4}$ (95% CI: $6.12 \times 10^{-5}; 4.68 \times 10^{-4})$ and $3.87 \times 10^{-4}$ (95% CI: $1.02 \times 10^{-4}; 6.72 \times 10^{-4}$) per year, respectively. A national meta-analysis in the cold season yielded a relative humidity variation of $−4.50 \times 10^{-5}$ (95% CI: $−2.50 \times 10^{-4}; 1.60 \times 10^{-4}$) per year (Fig. 6).

### 3.3. Impacts of weather change on air pollution

Our results suggest that impacts of weather change on air pollution vary considerably over region and season depending on the PM$_{2.5}$ component. Figs. 7–9 show the unadjusted trends, weather-adjusted trends, and weather penalties by region and season during the study period, 1988–2017. The estimates of the month and weekday terms gamma and sigma (seasonal and weekday parameters) are presented in as supplementary material (Excel file). Below, we describe the results for each PM$_{2.5}$ component assessed in our study.

#### 3.3.1. Weather-related EC changes

EC decreased in most of the regions during the warm season (Fig. 7). In contrast, the trends (EC increases/decreases) among the regions in the cold season were more heterogeneous. The national meta-analysis by warm and cold season showed a variation in daily EC concentration by $−0.002 \mu g/m^3$ (95% CI: $−0.006; 0.001$) and $−0.001 \mu g/m^3$ (95% CI: $−0.004; 0.002$) per year, respectively. Over 30 years, these amount to a total weather-related increase in daily EC of 0.04 $\mu g/m^3$. Our weather-adjusted model of the EC trend showed that had the weather variables (temperature, wind speed, and relative humidity) not changed between 1988 and 2017, the annual decrease in EC in both warm and cold seasons would have been larger, $−0.003 \mu g/m^3$ (95% CI: $−0.007; 0.0001$) in the warm period and $−0.002 \mu g/m^3$ (95% CI: $−0.006; 0.01$) in the cold period. This indicates an annual weather penalty for warm and cold season of $0.0012 \mu g/m^3$ (95% CI: $0.0011; 0.0013$) and $0.0013 \mu g/m^3$ (95% CI: $0.0006; 0.0012$), respectively.

#### 3.3.2. Weather-related OC changes

OC decreased in all regions in both warm and cold seasons, except in NW and SW (Fig. 7). The results of the national meta-analysis were similar to EC. Nationally, OC concentration had an annual change of $−0.008 \mu g/m^3$ (95% CI: $−0.02; 0.0008$) in the warm season and $−0.0005 \mu g/m^3$ (95% CI: $−0.009; 0.007$) in the cold period. Over a 30-year period, the weather penalty on OC was approximately 0.21 $\mu g/m^3$. Without weather changes, OC concentration in the warm and cold season would have changed by $−0.01 \mu g/m^3$ (95% CI: $−0.004; −0.02$) and $−0.007 \mu g/m^3$ (95% CI: $−6.8 \times 10^{-5}; −0.01$), respectively. This reflects an annual weather penalty similar in both seasons, 0.007 $\mu g/m^3$ (95% CI: $0.005; 0.008$) in the warm and 0.007 $\mu g/m^3$ (95% CI: $0.006;
3.3.3. Weather-related nitrate changes

Overall, the unadjusted nitrate trend showed a decrease by 0.003 \( \mu g/m^3 \) (95% CI: 0.001; 0.006) per year in the warm season and increased by 0.004 \( \mu g/m^3 \) per year in the cold season (Fig. 8). Removing the impact of inter-annual weather variation on nitrate trends (adjusted model), the annual decrease in nitrate concentration would have been 0.005 \( \mu g/m^3 \) (95% CI: 0.001; 0.009) in the warm season and an increase by 0.002 \( \mu g/m^3 \) in the cold period. The annual weather penalty was 0.001 \( \mu g/m^3 \) (95% CI: \(-4.66 \times 10^{-5}; 0.003\)) and 0.002 \( \mu g/m^3 \) (95% CI: 0.001; 0.003) for the warm and cold seasons, respectively. Total national weather penalty on nitrate between 1988 and 2017 was 0.04 \( \mu g/m^3 \) and 0.06 \( \mu g/m^3 \) in the warm and cold season, respectively.

3.3.4. Weather-related sulfate changes

Sulfate decreased in all regions and in both seasons, with larger decreases in the warm season (Fig. 8). Nationally, sulfate decreased by 0.11 \( \mu g/m^3 \) (95% CI: 0.04; 0.19) per year in the warm season, compared to 0.05 \( \mu g/m^3 \) (95% CI: 0.02; 0.08) per year in the cold season. Without weather changes, sulfate would have decreased by 0.13 \( \mu g/m^3 \) (95% CI: 0.04; 0.21) per year in the warm season and 0.05 \( \mu g/m^3 \) (95% CI: 0.02; 0.08) per year in the cold season, reflecting a weather penalty of 0.01 \( \mu g/m^3 \) (95% CI: 0.006; 0.02) and 0.001 \( \mu g/m^3 \) (95% CI: –0.0003; 0.003) per year, respectively. Over 30 years, the total penalty on sulfate was 0.35 \( \mu g/m^3 \) in the warm season and 0.04 \( \mu g/m^3 \) in the cold season.

3.3.5. Weather-related sodium changes

Similar to sulfate, sodium also decreased in all regions in both warm and cold seasons (Fig. 9). During the warm season, sodium decreased by 0.005 \( \mu g/m^3 \) (95% CI: 0.003; 0.006) per year nationally. SE had the highest decrease of 0.008 \( \mu g/m^3 \) (95% CI: 0.007; 0.009) per year. Weather changes had minimal effects on sodium concentrations in the warm season with a very small weather penalty of –0.0005 \( \mu g/m^3 \) per year. During the cold season, national meta-analysis showed a decrease by 0.003 \( \mu g/m^3 \) (95% CI: 0.002; 0.004) per year. As in the warm period, SE was also the region with the highest sodium decrease in the cold season, 0.006 \( \mu g/m^3 \) (95% CI: 0.005; 0.007) per year. Without weather changes, sodium would have decreased by 0.002 \( \mu g/m^3 \) (95% CI: 0.002; 0.003) per year, indicating a very small weather penalty (–0.0004 \( \mu g/m^3 \) per year). We estimated a total penalty on sodium between 1988 and 2017 of –0.01 \( \mu g/m^3 \).

3.3.6. Weather-related ammonium changes

As with sulfate and sodium, ammonium decreased in all regions during both warm and cold seasons (Fig. 9). The IM, W, NE, and SE regions presented the highest decreases in the warm season, between 0.10 and 0.11 \( \mu g/m^3 \) per year. In the cold season, the West had the highest decrease (0.11 \( \mu g/m^3 \) per year). Nationally, ammonium decreased by 0.08 \( \mu g/m^3 \) (95% CI: 0.05; 0.1) and 0.06 \( \mu g/m^3 \) (95% CI: 0.04; 0.08) per year in the warm and cold seasons, respectively. This reflects a total penalty during our study period of 0.05 \( \mu g/m^3 \) in the warm season and –0.02 \( \mu g/m^3 \) in the cold season. Our results indicated no statistically significant influence of weather changes on ammonium,
with a small weather penalty for ammonium (0.002 and \(-0.0008 \mu g/m^3\) per year in the warm and cold seasons, respectively).

### 3.3.7. Weather-related silicon changes

Unlike sulfate, sodium and ammonium, trends of silicon presented more regional variation (Fig. 9). Silicon decreased in all regions during the warm and cold seasons, except SW and UM regions. Nationally, silicon presented an annual variation by \(0.0009 \mu g/m^3\) (95% CI: \(-0.002; 0.0003\)) in the warm season and \(-0.0002 \mu g/m^3\) (95% CI: \(-0.001; 0.0007\)) in the cold season. Over 30 year, these amount to a total weather-related increase in daily silicon of 0.01 \(\mu g/m\) and 0.02 \(\mu g/m\) in the warm and cold season respectively. Without weather changes in the warm season, silicon would have decreased by \(0.002 \mu g/m^3\) (95% CI: \(0.0006; 0.003\)) per year, reflecting a weather penalty of \(0.0009 \mu g/m^3\) (95% CI: \(0.0008; 0.001\)) per year. Finally, without weather changes in the cold season, silicon would have decreased by \(0.001 \mu g/m^3\) (95% CI: \(0.0002; 0.002\)) per year. This reflects an annual weather penalty of \(0.0007 \mu g/m^3\) (95% CI: \(0.0004; 0.001\)).
4. Discussion

Overall, we found substantial spatiotemporal variation in each parameter examined in our study, including raw time series of ambient PM$_{2.5}$ elemental concentration, trends of weather variables using general linear regression model, and trends of ambient PM$_{2.5}$ elemental concentration using adjusted and unadjusted GAMs.

Weather trends derived from regression analysis (Fig. 6) showed that temperature increased in two regions (IM and NE) during the warm season and in four regions during the cold season (IM, NE, UM, and W). Wind speed decreased in all regions and seasons, except in SW during the cold period. Relative humidity had opposite trends in depending on the season. For example, in the warm season, the relative humidity increased in most of the regions (except in NW and W), whereas in the cold season decreased (except in SE and UM). Nationally, temperature decreased in the warm season (statistically insignificant) and increased in cold season (statistically insignificant), wind speed decreased in the both seasons (statistically significant), and relative humidity increased in the warm season (statistically significant) and decreased in the cold season (statistically insignificant). Overall, the weather trends observed in our study were in agreement with those reported in the literature, which include the temperature trends study reported by the U.S. Global Change Research Program (USGCRP, 2017) and Jhun et al. (2015), wind speed trends previously estimated by Pryor et al. (2009) and Jhun et al. (2015), and relative humidity trends analysis reported Brown and Degaetano (2013).

The weather changes between 1988 and 2017 were associated with penalties for most PM$_{2.5}$ components during both warm and cold seasons in the US (Figs. 7–9). We observed this association in both unadjusted and adjusted models. The unadjusted model represents the trends of individual chemical component of PM$_{2.5}$ in each region and season resulting from a combination of weather changes and emission changes. The model adjusted by weather variables (adjusted model) removes the influence of inter-annual changes in temperature wind speed, and relative humidity on PM$_{2.5}$ elemental concentration. Finally, the differences between unadjusted- and adjusted-models, defined in our study as weather penalty, reflect the impact of long-term weather changes on each component of PM$_{2.5}$. We highlight that this weather penalty account for direct (e.g., photochemical reactions) and indirect (e.g., more heating use on cold days) effects of weather conditions, and those of other meteorological phenomena with ground-level manifestations (e.g., transport of cold, dry, air mass). The comparison of our results observed in the unadjusted models with those presented in the literature (modeling and observational studies) is presented as follows. Then we discuss the findings representing the weather penalties.

Our results show that EC had a slight decrease during 1988 and 2017 - the national meta-analysis by warm and cold season showed a variation in daily EC concentration by $-0.002 \mu g/m^3$ and $-0.001 \mu g$/ per year, respectively. This is in agreement with previous observational and modeling findings (Murphy et al., 2011; Xing et al., 2015). For example, Murphy et al. (2011) showed that EC concentrations in the US decreased by over 25% during the period 1990–2004. Our unadjusted model showed that sulfate and ammonium decreased in the US. Sulfate decreased approximately 0.11 \mu g/m³ (95% CI: 0.04; 0.19) and 0.05 \mu g/m³ (95% CI: 0.02; 0.08) per year in the warm and cold seasons, respectively. Ammonium decreased by 0.08 \mu g/m³ (95% CI: 0.05; 0.1) and 0.06 \mu g/m³ (95% CI: 0.04; 0.08) per year in the warm and cold seasons, respectively. Silvern et al. (2017) also show that aerosol sulfate and ammonium decreased between 2003 and 2013 in response to SO$_2$ emission controls. Xing et al. (2015) compared observational and modeling air quality trends for some PM2.5 components, including sulfate. The authors reported that both observational and modeling analyses indicate sulfate decreases in the US between 1990 and 2010. For unadjusted nitrate trend, our results show a decrease by 0.003 \mu g/m³ (95% CI: 0.001; 0.006) per year in the warm season and an increase by 0.004 \mu g/m³ per year in the cold season. Xing et al. (2015) estimated the trends between 1990 and 2010 without stratifying by season and found that nitrate in the US monitored by IMPROVE network decreased 0.003 \mu g/m³ per year, while the nitrate trends for the CASNET network was $-0.006 \mu g/m³$ per year. For sodium, we observed a decrease in all regions by 0.005 \mu g/m³ (95% CI: 0.003; 0.006) per year nationally in the warm season and 0.003 \mu g/m³ (95% CI: 0.002; 0.004) per year in the cold season. This result is in agreement with the recent global trends of air pollution (Li et al., 2017), which the authors estimated that nitrate in the US decreased by 0.003 \mu g/m³ per year between 1989 and 2013.

Fig. 6. Changes per year in temperature (left chart), wind speed (middle chart) and relative humidity (right chart) in 1988-2017.
The weather penalties on carbon particles (EC and OC, as shown in Fig. 7) were greatest in the west coast (region W, represented by the state of California and Nevada), especially the penalties on OC during the warm season. This reflects the significant EC and OC emissions from wildfire, most strongly in California and Nevada (Bendix and Commons, 2017; Doerr and Santín, 2016; Marlon et al., 2012). Previous investigations have found positive correlation of temperature with carbon particles - EC and OC; and negative correlation of those carbon particles with relative humidity (Tai et al., 2010). These correlations in the warm season are mostly driven by wildfire occurrence (Marlon et al., 2012). Our weather trends analysis shows that the West has become drier in the last 30 years. Temperature and relative humidity were important determinants of the EC and OC trends in most of the regions, including the West. Strong effects of temperature and relative humidity in determining EC and OC concentrations have also been reported in the literature (Hand et al., 2013; Murphy et al., 2011; Tai et al., 2010). Wind speed was also an important weather parameter. Reduced winds over the last 30 years impacted adversely concentrations of both primary and secondary pollutants, including EC, OC, and the other pollutants evaluated in our study.

The West demonstrated the highest weather penalty on nitrate

Fig. 7. Unadjusted trends, weather-adjusted trends, and weather penalties of EC and OC in 1988–2017 by region and season.
Fig. 8 (with a notably high penalty in the cold season compared to the warm season). This reflects a strong influence of the weather phenomena on the nitrate formation in the atmosphere. Studies show that high temperature can decrease nitrate levels due to ammonium nitrate volatilization (Fan and Li, 2010). Therefore, nitrate is expected to increase during cold season. The net effect depends by the relative abundance of ammonium nitrate, which the major sources are sea salt, motor vehicle, and power generation (Meng et al., 2017; Van Pul et al., 2009). These emission sources are significant in the West (Nowak et al., 2012).

Our results indicate minimal influences of weather changes on sulfate in the cold season. If the weather variables had not changed in the cold season over the last 30 years, sulfate would have very similar concentration. During the warm season, the weather penalties on sulfate were greater. This is in agreement with the literature that shows that sulfate dominates in summer days due to more rapid SO2 oxidation (Hand et al., 2012a; Tai et al., 2010). Warmer summers and less wind (stagnations) favor photochemical reactions so a larger fraction of SO2 is oxidized to form sulfates. Most sulfate aerosols in the atmosphere come from the photochemical conversion of SO2 (Roberts and
We found the greatest weather penalties on sulfate in the IM, NE, SE, and UM regions in the warm season. This reflects the major source of SO₂ – power plants (Fu et al., 2013; Huang et al., 2012). According to the US Energy Information Administration (EIA), in 2015, about 40% of the SO₂ emissions from power plants in the US occurred in New England, Middle Atlantic, Mid-West, and in the East North Central region (EIA, 2015). Finally, we highlight that the sharp decrease of sulfate across the US during both the warm and cold seasons are a result of the acid rain rule, which enforced stringent sulfur dioxide emissions from power plans and diesel engines.

Comparing the trends of nitrate and sulfate, our results show that while nitrate increased, sulfate decreased during our study period. This may be a result of greater availability of ammonia to react with nitric acid to form ammonium nitrate. When nitric acid and sulfuric acid are present, the reaction between ammonia and sulfuric acid is thermodynamically favored.

The distribution of the weather penalties on ammonium across regions (Fig. 9) is very similar to those of sulfate, especially during the warm season. This is due to the chemistry of these elements, which there is an interdependence during the reactions - sulfuric acid and ammonia to form ammonium sulfate. Indeed, sulfate is mostly present in the atmosphere in the form of ammonium sulfate. Studies show that reduction in sulfate will increase the available free ammonium (Ciuraru et al., 2012). Also, ammonia from sources such as fertilizer contributes to the formation of sulfates and nitrates that exist in the atmosphere as ammonium sulfate and ammonium nitrate (Shen et al., 2011).

The weather penalties for sodium (Fig. 9) were negative in all coastal regions (NE, NW, SE, and W) during the warm season. This reflects the presence of sea salt, the main source of sodium (Bersenkovitsch et al., 2018; Laskin et al., 2003). The west coast (W) had the lowest penalty during both warm and cold periods. This may be related to decreases in wind speed, resulting in decreases in sodium carried from the ocean (Saul et al., 2006). In addition, less wind from the ocean may reduce both sodium and relative humidity as there is an interdependence between sodium concentration, wind, and relative humidity in coastal areas. The WC region had the greatest decreases in relative humidity in the last 30 years.

Compared to sodium, the weather penalties on silicon were positive in all regions in both warm and cold seasons (Fig. 9). The W and UM regions had the highest penalties in the warm season. During the cold period, the highest penalties were observed in SW and W. Wind is also an important factor related to silicon concentration. Weakening of
wind, as observed in our study, decreases soil resuspension into the atmosphere and thus silicon levels.

Our study has several limitations. First, over the last 30 years the EPA changed some measurement techniques used to estimate PM$_{2.5}$ composition in various locations throughout the US. This change may have the potential to confound the interpretation of long-term trends (Hyslop et al., 2015). Second, we applied spatial join to match weather data (NOAA stations) to air pollution data (EPA stations) given some EPA air pollution stations do not simultaneously monitor weather data. A larger distance between air pollution and weather stations is more likely to yield a weaker association, and subsequently an underestimation of the weather penalty. The matching average distance between air pollution stations and weather stations was 29.5 km. Third, the spatial distribution of the air pollution stations in the continental US is not homogeneously distributed. Consequently, weather penalties estimated for some regions may not be representative of the entire region (e.g., SW region, where most stations are located in Texas). Fourth, we estimated linear trends for individual weather variables due to computational capacity. Ideally, we would estimate non-linear trends and their uncertainty via bootstrap model. Finally, we only accounted for three weather variables (temperature, wind speed, and relative humidity) in order to maximize the completeness of the data. Other additional variables (e.g., cloud cover, precipitation, and atmospheric mixing height) may be strongly correlated with the variables that we included in our analyses.

5. Conclusions

Ambient PM$_{2.5}$ components are strongly linked to weather variables such as temperature, relative humidity, and wind conditions. Our findings suggest that weather changes over the last 30 years increased the ambient concentration of most PM$_{2.5}$ components in the US. This impact was defined in our study as weather penalty. The direction and the magnitude of the weather penalty varied considerably over the region and season. Fig. 10 presents the national map showing the distribution of the weather penalties for each species of PM$_{2.5}$ region, and season.

This study contributes to the understanding on the impacts of weather on PM$_{2.5}$ composition. The evidence of historical weather penalty should be of interest to policy makers to devise future strategies related to environmental health and climate change. During the warm season, our findings suggest an overall national weather penalty on EC, OC, nitrate, sulfate, sodium, ammonium, and silicon between 1988 and 2017 of 0.04, 0.21, 0.04, 0.35, −0.01, 0.05, and 0.01 μg/m$^3$, respectively. In the cold season, the estimated total penalty was 0.04, 0.21, 0.06, 0.04, −0.01, −0.02, and 0.02 μg/m$^3$, respectively.

Taken together, the weather penalty on some of the most toxic particulate pollutants (Rivas et al., 2014; Rohr and Wyzga, 2012; Zanobetti et al., 2009) highlight potential future challenges of regulating land use and air pollution sources, given that the weather trends observed in our study period are projected by climate prediction models to continue in the future. Therefore, reliable projections of weather changes and air pollution levels will be necessary to implement actions and policies necessary to protect public health.

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