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LETTER

Impacts of transboundary air pollution and local emissions on PM$_{2.5}$ pollution in the Pearl River Delta region of China and the public health, and the policy implications

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Abstract

Despite a downward trend in pollutant levels because of a series of emission control policies, the Pearl River Delta (PRD) region continues to suffer from a high number of fine particulate matter (PM$_{2.5}$) events and the resultant public health impacts. To effectively control PM$_{2.5}$ in the region, a comprehensive understanding of source contribution and PM$_{2.5}$ responses to various emission species is critical. We applied the Community Multiscale Air Quality Modeling System together with the high-order decoupled direct method, to simulate air quality and PM$_{2.5}$ sensitivity and examined PM$_{2.5}$ responses to emission species in the PRD region in the four seasons of 2010. We employed a concentration-response function to quantify the resultant number of premature mortalities attributable to outdoor PM$_{2.5}$. We estimated that local and transboundary air pollution (TAP) contributed 27% and 73%, respectively, of the region’s PM$_{2.5}$. In absolute terms, the largest impacts from local and TAP occurred in winter. With respect to relative contributions among the different sources, regional TAP (between cities in the region) (R-TAP) and local contributions had the largest effect in summer, whereas superregional TAP (from outside of the region) contributed the most in fall and winter. Outdoor PM$_{2.5}$ pollution caused 20 160 (95% confidence interval: 5100–39 310) premature mortalities every year in the PRD region. Averaging among cities, 50%, 20%, and 30% of these deaths were attributable to S-TAP, R-TAP, and local contributions, respectively. Precursor gas emissions (i.e. NH$_3$, volatile organic compounds, SO$_2$, and NO$_x$) affect PM$_{2.5}$ level in a nonlinear manner; thus, individual pollutant control strategies are less effective for improving PM$_{2.5}$ pollution than an integrated strategy. On the basis of our findings, we recommend that controls for multiple emission species should be implemented to control PM$_{2.5}$ pollution in the region.

1. Introduction

Fine particulate matter (PM$_{2.5}$; particles with an aerodynamic diameter $\leq$ 2.5 $\mu$m) pollution is a critical environmental problem in China, causing approximately 1.37 million premature deaths yearly (Gu and Yim 2016, Liu et al 2016, Gu et al 2018). The Pearl River Delta (PRD) region is one of the fastest growing regions in China and has experienced serious air pollution issues (Yim et al 2010, Yang et al 2018, Wang et al 2019) because of its highly intensive energy consumption, which causes a high level of air pollution emissions. In recent decades, PM$_{2.5}$ has emerged as the major ambient air pollutant in the PRD region, with an annual level of approximately 50 $\mu$g m$^{-3}$ (Zhang and Cao 2015), which is higher than three times the limit set in
the new National Ambient Air Quality Standards of China (15 μg m⁻³ for a Category I zone) (Jin et al 2016). If the annual PM$_{2.5}$ level could be reduced below the World Health Organization guidelines (i.e. 10 μg m⁻³), approximately 40 000 PM$_{2.5}$-related premature deaths would be avoided in the PRD region every year (Xie et al 2011).

To effectively control the PM$_{2.5}$ level, fully understanding the contributors to PM$_{2.5}$ pollution and its sensitivity to emission species is crucial. The PRD region is a highly urbanized city cluster, and the distances between its major cities are shorter than 10 km (Shao et al 2006). Scholars have reported transboundary air pollution (TAP) between the cities is a major contributor to the air pollution in the region (Louie et al 2005, Deng et al 2008, Gu and Yim 2016, Luo et al 2018, Tong et al 2018a, 2018b). Wu et al (2013) demonstrated that approximately 8.6% of the PM$_{2.5}$ level in Guangzhou was attributable to mobile sources originating in adjacent regions (i.e. Dongguan, Foshan, and Shenzhen). Another study reported that emissions from Shenzhen contributed to 55% and 47% of sulfate and nitrate pollution, respectively, in Hong Kong in winter (Lu and Fung 2016). Previous studies have focused on PM$_{2.5}$ source apportionment in the PRD region at the city level, but how the ambient PM$_{2.5}$ level responds to changes in both primary and gaseous emissions of secondary PM should also be investigated; detecting the major emission species and sources that contribute to the PM level is vital for formulating effective emission control measures.

Past studies have intensively investigated TAP in China, but the public health impact of TAP has yet to be fully understood, especially in the PRD region (Hou et al 2015, Gu and Yim 2016, Zhang et al 2017, Zhao et al 2017). As limited research has been conducted concerning the effect of TAP on the PM$_{2.5}$-related public health at the city level in the PRD region during different seasons, the significance of this research is to evaluate the effect of TAP on air quality in cities in this region and the resultant public health effect.

Research has also demonstrated nonlinear responses of PM$_{2.5}$, and its species to changes in precursor emissions (Tsimpidi et al 2008, Henze et al 2009, Megaritis et al 2013). Ambient PM$_{2.5}$ may respond differently to changes in individual or multiple emission species (i.e. primary PM emissions and gaseous emissions for secondary PM) (Dunker 1984). Comprehensively assessing the responses of ambient PM$_{2.5}$ to multiple emission species is necessary, especially for a region with a high ambient PM$_{2.5}$ level. Knowledge of these nonlinear responses and the transboundary nature of PM$_{2.5}$ is particularly critical for policymakers and atmospheric scientists.

To address the aforementioned points of emphasis, this study applied a regional air quality model to examine the simultaneous nonlinear PM$_{2.5}$ response to multipollutant emissions and then estimated the contributions of local and nonlocal emissions to PM$_{2.5}$ levels in ten major cities in the PRD region during various seasons. We also employed a CRF to quantify the resultant air pollution-related premature mortality rate in the PRD region.

2. Method

This study applied the Community Multiscale Air Quality Model (CMAQ; version 4.7.1) (Byun and Schere 2006) in conjunction with the high-order decoupled direct method (HDDM) (Dunker 1984) to simulate air quality and PM$_{2.5}$ sensitivity to its precursor emissions in the PRD region using three nested modeling domains with a spatial resolution of 27 km (D1), 9 km (D2), and 3 km (D3). D1 covered almost the entirety of China, D2 encompassed southern China, and the innermost domain (D3) covered the PRD region (figure 1).

The CMAQ-HDDM model was configured to have 26 vertical layers. The meteorological fields were simulated using the Advanced Research Weather Research and Forecasting Model (Skamarock et al 2008), which was driven by Final Operational Global Analysis data having 6 h temporal resolution and 1° × 1° spatial resolution (National Centers for Environmental Prediction, National Weather Service, National Oceanic and Atmospheric Administration and US Department of Commerce 2000). The details are provided by Wang et al (2019). The gridded hourly emissions were preprocessed using Sparse Matrix Operator Kernel Emissions (Houyoux et al 2006). The emissions within PRD except HK were provided by Zheng et al (2009). The Hong Kong Environmental Protection Department (HKEPD) provided the emissions data for Hong Kong including public electricity generation, road transport, navigation, civil aviation, other combustion sources, non-combustion sources and hill fires. The emissions data for outside the PRD region were based on the INTEX-B 2006 regional emission inventory (Zhang et al 2009) which included all major anthropogenic sources, excluding biomass burning. Biogenic emissions were based on Guenther et al (2006), whereas shipping emissions were based on Streets et al (2003). Both meteorological and emissions data were utilized to drive the CMAQ. The results from the 6 d spin-up period were discarded to minimize the effect of the initial conditions on the modeling results. Boundary conditions were generated from the mother domain simulations.

Because of the heavy computation required for CMAQ-HDDM model simulations, we selected January (winter), April (spring), July (summer), and October (fall) of 2010 as a representative of seasonal variation in which the air pollutants including both gaseous pollutants and particulate matter show different seasonal characteristics (Kwok et al 2010). The model was evaluated by observations collected in the PRD region (see table S1 which is available online: Environ. Res. Lett. 14 (2019) 034005).
We employed the integrated CRF to estimate the PM$_{2.5}$-attributable premature mortality rate, which is appropriate for assessing the effect of China’s relatively high PM$_{2.5}$ concentrations (Gu and Yim 2016). The detailed information of the CRF is provided in the section 4 in the SI.

We applied the Monte Carlo method to estimate uncertainties with 95% confidence intervals (CI). The uncertainties took into account CMAQ-HDDM model performance and the parameters adopted in the CRFs (Gu and Yim 2016). To eliminate the overestimation of PM$_{2.5}$-related mortality contributed by S-TAP due to nonlinear CRFs, the premature mortality with total PM$_{2.5}$ concentration was calculated as baseline and was then apportioned with the source contribution share.

### 3. Results and discussion

We first apportioned the contribution of local (i.e. receptor city), regional (i.e. the PRD region but not including the receptor city), and superregional (i.e. outside the PRD region) emissions to ambient PM$_{2.5}$ in the major cities in the PRD region and quantified the resultant number of premature mortalities. To provide valuable scientific references for policymakers for use in formulating effective emission control measures in the PRD region, we discuss the contribution of PM$_{2.5}$ precursor gases to ambient PM$_{2.5}$ and account for nonlinearity through assessing the PM$_{2.5}$ sensitivity to individual emission species and cross-sensitivity between two emission species at various VOC/NO$_x$ ratios.

#### 3.1. Source contributions of PM$_{2.5}$ and corresponding health impacts

The superregional contribution (emissions outside the PRD region) emerged as the dominant contributor to ambient PM$_{2.5}$ for all the cities (figure 2), contributing approximately 53% on average, and was especially high in winter (60.5%) and fall (65.0%). The contribution ranged from approximately 50% (DG) to 77% (HK) in winter; 54% (DG and ZS) to 83% (HZ) in fall, 46% (DG) to 71% (HK) in spring, and 13% (HZ) to 52% (ZQ) in summer. HK (63.5%) and ZQ (67.3%) were the two largest receivers. The highest absolute contribution to the PM$_{2.5}$ level in an individual city occurred in winter (~18.2 μg m$^{-3}$ on average), followed by fall (~15.9 μg m$^{-3}$ on average), which was most likely because the strong prevailing northeasterly wind in those seasons (figure S2 in SI) was favorable for the long-range transport of pollutants from outside the PRD region. In spring, the northwesterly wind also carried pollutants from western areas of the continent to the region, and this transport accounted for approximately 8.8 μg m$^{-3}$ of the PM$_{2.5}$ concentration. In general, roughly 2.4 μg m$^{-3}$ of the PM$_{2.5}$ concentration in each city in summer was because of superregional emission sources.

Approximately 20% of annual PM$_{2.5}$ was attributable to regional emissions. This was generally less than the S-TAP. However, in summer, PM$_{2.5}$ concentration in several cities—HZ, DG, GZ, and FS—was more attributable to regional sources than superregional ones. Overall, the relative regional contribution peaked in summer (25.7%), in which GZ (25.8%), FS (25.6%), and ZS (28.5%) experienced the largest relative regional contributions. Seasonal variation in the regional contributions to the ambient concentrations is presented in figure S2 in the SI.
PM$_{2.5}$ level was similar to that in S-TAP contribution; the highest PM$_{2.5}$ level occurred in winter (∼6.2 μg m$^{-3}$), followed by fall (∼4.8 μg m$^{-3}$), spring (∼3.2 μg m$^{-3}$), and summer (∼2.6 μg m$^{-3}$). At the city level, the R-TAP was higher in western PRD region (i.e. FS, JM, ZS, and ZH) in winter and fall owing to the southwesterly wind, and it was lower in eastern PRD region (i.e. HZ, SZ, and HK). In HZ, which is located in the east of the PRD region, 1% of the ambient PM$_{2.5}$ concentration was attributable to regional sources. However, emissions from GZ were the most significant city contributor to the other nine cities in winter and fall, contributing roughly 14.9 μg m$^{-3}$ and 13.2 μg m$^{-3}$ PM$_{2.5}$ in total, respectively. In spring and summer, emissions from SZ significantly contributed to ambient PM$_{2.5}$ in quantities of approximately 6.0 μg m$^{-3}$ and 4.4 μg m$^{-3}$, respectively. The emission rates of cities in northeast PRD region were higher than in southwest PRD region (figure S3 in SI).

Approximately 27% of ambient PM$_{2.5}$ was due to local emission sources—higher than the R-TAP contribution. The relative local contribution was the largest (44.3%) in summer, in which SZ (40.5%) and DG (34.0%) received the largest percentages of the relative local contribution. In magnitude, the local contribution was slightly higher in winter (∼2.0–12.2 μg m$^{-3}$) than in other seasons (∼1.4–7.9 μg m$^{-3}$) ($p = 0.0022$). The marginal seasonal variation in local contributions indicated that the seasonal variation in ambient PM$_{2.5}$ concentration (i.e. higher in winter and fall but lower in summer) was mainly because of the long-range transport of air pollutants into the PRD region. The most substantial local contribution occurred in northern PRD region, especially in FS (∼8.4 μg m$^{-3}$ on average).

Our health effect estimation (table 1) indicates that outdoor air pollution resulted in roughly 20 160 (95% CI: 5100–39 310) PM$_{2.5}$-attributable premature mortalities in the PRD region in the year 2010; the lowest incidence rate was that in ZH (∼120) and the highest was that in SZ (∼1320). The results were consistent with those of other studies (Gu and Yim 2016, Liu et al 2016). For instance, the HKEPD reported that air pollution-related mortalities totaled approximately 2000 in HK in one year (Environment Bureau 2017), and our study estimated 1900 PM$_{2.5}$-attributable mortalities in HK.

In general, local emissions resulted in 29.3% of the premature mortalities in the ten major cities in the PRD region, which is equivalent to roughly 5900 (95% CI: 1500–11 480) premature deaths. We note that both the characteristics of the exposed population and PM$_{2.5}$ attribution could affect the PM$_{2.5}$-related premature mortality rate. In SZ, local emissions had a significant effect on the incidence rate (∼1320, 95% CI: 320–2580) because of this city’s large population and the contribution of local emissions to the PM$_{2.5}$ level (7.2 μg m$^{-3}$). In ZH, the local contribution to PM$_{2.5}$-attributable mortality was the smallest (∼120, 95% CI: 30–240) because of the city’s small population, despite it having a higher local contribution (3.0 μg m$^{-3}$) than other cities.

Regional emissions contributed to roughly 4090 (95% CI: 1070–7930), or 20.3%, of premature mortalities in 2010, which was a smaller number than those caused by the local contribution. The PM$_{2.5}$-attributable mortality ranged from 90 (95% CI: 20–170) in ZH to approximately 1100 (95% CI: 300–2120) in GZ.

The emissions contributed from the superregion were the largest cause of PM$_{2.5}$-attributable premature mortality, accounting for roughly 10 170 (95% CI: 2530–19 900), or 50.4%, of the premature mortalities in the PRD region due to outdoor air pollution. For ZQ, our results indicate that approximately 67.3%—the largest S-TAP among the cities—of PM$_{2.5}$-attributable premature mortalities were because of emissions from outside of the region.
Table 1. Estimated PM$_{2.5}$-attributable premature mortalities in 2010 in the ten major cities in the PRD region (including 95% CI in parentheses); results were rounded to the nearest integer.

<table>
<thead>
<tr>
<th>City</th>
<th>Baseline mortality</th>
<th>Mortality due to local contributions</th>
<th>Regional contribution</th>
<th>Mortality due to superregional contributions</th>
<th>Superregional contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HK</td>
<td>1913 (357–3971)</td>
<td>462 (86–959)</td>
<td>12.40</td>
<td>1214 (227–2,520)</td>
<td>63.45</td>
</tr>
<tr>
<td>SZ</td>
<td>3262 (796–6381)</td>
<td>1321 (322–2583)</td>
<td>11.82</td>
<td>1556 (380–3043)</td>
<td>47.70</td>
</tr>
<tr>
<td>HZ</td>
<td>1284 (263–2610)</td>
<td>323 (66–656)</td>
<td>15.40</td>
<td>764 (157–1552)</td>
<td>59.47</td>
</tr>
<tr>
<td>DG</td>
<td>2772 (761–5316)</td>
<td>943 (259–1808)</td>
<td>22.56</td>
<td>764 (157–1552)</td>
<td>43.44</td>
</tr>
<tr>
<td>GZ</td>
<td>4277 (1173–8206)</td>
<td>1213 (333–2328)</td>
<td>25.79</td>
<td>1204 (331–2309)</td>
<td>45.84</td>
</tr>
<tr>
<td>FS</td>
<td>2628 (795–5316)</td>
<td>776 (235–1448)</td>
<td>25.39</td>
<td>1961 (538–3761)</td>
<td>45.84</td>
</tr>
<tr>
<td>ZQ</td>
<td>1178 (265–2338)</td>
<td>179 (40–356)</td>
<td>17.52</td>
<td>1178 (356–2197)</td>
<td>45.84</td>
</tr>
<tr>
<td>JM</td>
<td>1365 (316–2690)</td>
<td>313 (72–618)</td>
<td>21.04</td>
<td>792 (178–1572)</td>
<td>44.82</td>
</tr>
<tr>
<td>ZS</td>
<td>1021 (269–1977)</td>
<td>251 (66–486)</td>
<td>28.52</td>
<td>764 (177–1507)</td>
<td>67.26</td>
</tr>
<tr>
<td>ZH</td>
<td>2628 (795–4901)</td>
<td>251 (66–486)</td>
<td>28.52</td>
<td>1213 (333–2328)</td>
<td>56.00</td>
</tr>
<tr>
<td>SUM</td>
<td>20 162 (5097–39 310)</td>
<td>5901 (1506–11 480)</td>
<td>29.27</td>
<td>10 167 (2525–19 898)</td>
<td>50.43</td>
</tr>
</tbody>
</table>

The baseline mortality estimates are given in parentheses. The mortalities due to local contributions, regional contributions, and superregional contributions are rounded to the nearest integer, with 95% CIs in parentheses.
3.2. Emission contribution and PM$_{2.5}$ sensitivity to emission species

Previous section analyzed the effect of local and transboundary pollutants on the ambient PM$_{2.5}$ concentration in the ten major cities in the PRD region as well as the corresponding health effects. To formulate effective PM$_{2.5}$ control strategies, it is critical to comprehensively understand the sources that contribute to ambient PM$_{2.5}$ and the response of PM$_{2.5}$ to different emission species; it is noted that even though our emission inventory may not be the most updated information due to limited data availability, this study aimed to examine the nonlinear relationship between PM$_{2.5}$ concentration and precursor gas emissions in particular to identify key gaseous species. Our analysis focused on local source contributions and R-TAP to provide a useful reference for local governments and policymakers in the PRD region.

3.2.1. Primary PM

In general, primary PM emissions (local + regional) were the major contributor to the PM$_{2.5}$ concentration, accounting for roughly 40% of ambient PM$_{2.5}$ in the PRD region (figure 3). Primary PM emissions were mainly from local sources and demonstrated clear seasonal variation whereby the highest contribution occurred in January ($\sim 7.0$ $\mu g$ m$^{-3}$ or 21%); contributions in April ($\sim 4.3$ $\mu g$ m$^{-3}$ or 25%) and October ($\sim 4.4$ $\mu g$ m$^{-3}$ or 17%) were similar; and the smallest contribution occurred in July ($\sim 3.75$ $\mu g$ m$^{-3}$ or 43%). The regional primary PM contribution (up to $\sim 26.5\%$) was smaller than the local contribution for most cities in the PRD region but exhibited a comparable seasonal variation. The sensitivity of PM$_{2.5}$ to primary PM was linear (Koo et al 2009). Thus, we did not conduct a sensitivity analysis for primary PM.

Moreover, because of the nonlinear relationship between secondary aerosols, which are formed through oxidation and neutralization of precursor gases (i.e. NO$_x$, SO$_2$, VOC, and NH$_3$), and their precursor gaseous emissions, the contribution of individual emission species to the PM$_{2.5}$ level may vary with emissions and background chemical composition. Thus, from an environment protection perspective, we analyzed the hourly seminormalized first-order and second-order sensitivity coefficients, which reflect the responses of pollutants’ concentration to perturbations in parameters such as gaseous emissions (Cohan et al 2005) (figure 4). A positive sensitivity coefficient indicates that pollutant concentration demonstrates positive feedback to a change in emissions, whereas a negative sensitivity coefficient means that pollutant concentration increases or decreases when emissions decrease or increase, respectively.

3.2.2. NH$_3$

The contribution of gaseous emissions to the PM$_{2.5}$ level ranged from approximately $-4\%$ to $25\%$ (figure 3). Among gaseous emissions, emissions of NH$_3$—the main base for neutralizing SO$_2$ and NO$_x$—contributed to the PM$_{2.5}$ concentration more (from $\sim 2\%$ to $\sim 11\%$) than those of other gases (i.e. VOC, SO$_2$, and NO$_x$), despite low NH$_3$ emissions in the PRD region. The index of the gas ratio (GR, less than zero) and the degree of sulfate neutralization (DSN, less than 1.5) indicate that the PRD was a NH$_3$-poor region (figures S5 and S6 in SI for details).

The sensitivity coefficients of PM$_{2.5}$ and its components to NH$_3$ emissions were positive under various VOC and NO$_x$ ratios (figure 4(a)). The highest sensitivity coefficients were calculated when the ratio of VOC to NO$_x$ was approximately 6. Ammonium
concentration reduced in correspondence with reduction in ammonia, as expected. Nitrate concentration was also significantly lower because nitrate formation was highly dependent on the NH3 emissions in such a NH3-poor region. Compared with nitrate, sulfate concentration was less sensitive (or exhibited smaller positive sensitivity coefficients) to NH3 emissions. Ammonia preferred to react with sulfuric acid; thus, sulfate was maintained in its aerosol phase although ammonia was reduced. The effect of NH3 emission on SOA level is minimal due to the sensitivity coefficient of SOA to NH3 emission is close to zero. Overall, the level of PM2.5 and in particular ammonium and nitrate, reduced in response to reduced NH3 emissions, even though the response of sulfate level was marginal. The results indicate that ammonia should be one of the targeted species to effectively reduce PM2.5 in the region.

3.2.3. VOC

The VOC contribution to PM2.5 was relatively small (figure 3): 3% in spring. VOC contribution shows a clear spatial difference and was the highest in July, followed by April, on the west side of the Pearl River, but highest in April, followed by January and July, on the east side.

Figure 4(b) depicts that the sensitivity coefficients of nitrate, sulfate, and ammonium to VOC emissions switched from positive to negative at a VOC/NOx ratio of roughly 6, which meant their concentrations responded positively to a change in VOC emissions but negatively with an increased VOC/NOx ratio. Notably, previous studies in Europe and United States found that when the VOC/NOx ratio is around 5.5:1, OH reacts with VOC and NOx at an equal rate (Seinfeld and Pandis 2006, Tsimpidi et al 2008, Megaritis et al 2013). This means that our finding is consistent with those reported by previous studies.

Low VOC/NOx ratios (<6) typically occur in urban areas, which have substantial NOx emissions from traffic and were more likely a VOC-limited region for photochemistry. At a low VOC/NOx ratio (VOC-limited regions), the rate of O3 formation decreased linearly in relation to a reduction in VOC emissions, resulting in a lower hydroxyl radical (OH) concentration. Consequently, the levels of sulfate and nitrate decreased because of a lack of oxidants, and the ammonium concentration was also reduced. However, at a high VOC/NOx ratio (>6), which typically occurs in rural areas (NOx-limited regions), a reduction of VOC emissions resulted in an increase in OH and O3 concentrations (Tsimpidi et al 2008). Consequently, sulfate, nitrate, and ammonium concentrations increased through oxidation and neutralization when VOC emissions were reduced. Moreover, as an important precursor to SOA, it is expected that a reduction (increment) of VOC leads to decreases (increases) in SOA. As the VOC/NOx ratio increased, the sensitivity coefficient of SOA to VOC went up to equilibrium. Overall, the sensitivity coefficients of PM2.5 were the highest at a VOC/NOx ratio of approximately 6, and at higher than that ratio, they were lower because of lower concentrations of nitrate, sulfate, and ammonium.

3.2.4. NOx

The contribution of NOx emissions to the PM2.5 concentration was negative in most of the PRD cities (figure 3), especially in January and April. A reduction in NOx emissions might cause an increase in the level of PM2.5 components (i.e. nitrate). Conversely, the PM2.5 concentration attributable to NOx emissions was positive in HZ (∼25%) and ZQ (∼7%). It may be because of their relatively low NOx emissions. The sensitivity coefficient of PM2.5 to NOx emissions explains the different contributions.
As with sensitivity to VOC emissions, a VOC/NOx ratio of roughly 6 was a turning point for NOx emissions (figure 3(c)). At a low VOC/NOx ratio (<6), the sensitivity coefficients of PM2.5 and its components were negative, which meant their concentration responded inversely to a change in NOx emissions. O3 and OH levels increased as a result of reduced NOx emissions in VOC-limited regions (typically urban areas). Increasing oxidant concentration may lead to increases in nitrate and sulfate levels by accelerating the formation of NOx and SO2 through reactions with oxidants (Dong et al 2014, Zhao et al 2015). Overall, the reduction in NOx emissions caused an increase in the number of OH radicals that were supposed to react with NOx to form nitric acid, and the excessive OH radicals reacted with SO2 to form sulfuric acid and thus sulfate. The simultaneous increases in sulfate and nitrate also resulted in an increase in the ammonium level. Therefore, in VOC-limited regions (i.e. most parts of the PRD region), contribution of NOx emissions to PM2.5 to NOx emissions was negative.

At a high VOC/NOx ratio (>6), PM2.5, nitrate, and ammonium levels show a positive response to a perturbation in NOx emissions. Decreasing NOx emissions resulted in a linear reduction in ambient oxidant levels in NOx-limited regions (typically rural areas). The simultaneous decreases in both oxidants and NOx consequently reduced the extent of nitrate formation. The effect of a perturbation in NOx emissions on nitrate was thus decreased. Furthermore, in rural areas, sulfate level still negatively responded to changes in NOx emissions at first but then switched to a positive response. When the VOC/NOx ratio was higher than 6 but below 15, which occurred in transition zones, a reduction in NOx emissions led to the existence of excessive OH radicals. Reactions between SO2 and OH led to elevated levels of sulfuric acid and sulfate. However, with an increase in the VOC/NOx ratio (especially >16), chiefly in NOx-limited regions, a small NOx reduction resulted in a reduction in the number of free OH radicals, thereby decreasing the overall oxidant level. The sulfate level consequently reduced along with a reduction in NOx emissions.

Moreover, the sensitivity of SOA to NOx emission was all negative which means a reduction in NOx emissions could lead to an increase in SOA especially in urban areas (low VOC/NOx ratio). It is because VOC competes with NOx for an oxidant to form SOA.

In sum, a reduction in NOx emissions in urban areas may lead to an increase in secondary inorganic aerosol species, resulting in an overall increase in the PM2.5 concentration (Tsimplidi et al 2008, Zhao et al 2015). An emission control policy that focuses on NOx emissions alone may thus be an ineffectual means of reducing the PM2.5 level in urban areas in the PRD region. Conversely, the PM2.5 level decreased in relation to reduced NOx emissions because of decreased levels of nitrate and ammonium and may thus offer a more promising reduction strategy.

3.2.5. SO2
The contribution of SO2 emissions to the PM2.5 concentration was marginal (figure 3): up to 3%. The effect was slightly stronger in summer (up to ∼3.3 μg m⁻³) than in other seasons (up to ∼0.8 μg m⁻³).

The sensitivity coefficients of PM2.5 and its components to a perturbation in SO2 emissions were positive except for nitrate (figure 4(d)), regardless of the ratio of VOC to NOx. Additionally, the sensitivity of SOA to SO2 emission is close to zero, indicating a negligible impact of SO2 emissions on SOA formation. Positive sensitivity coefficients indicate that a reduction in SO2 emissions lowered the sulfate, ammonium, and PM2.5 levels. The sulfate concentration changed linearly according to a perturbation in SO2. The response of nitrate to SO2 emissions was negative, which might be because nitrate formed by combining with NH3 and was freed up because of a reduction in SO2 emissions. In such an NH3-poor region, the formation of nitrate is highly dependent on the availability of ammonia (Huang et al 2014), which is acquired through competing with SO2. Ammonia reacts preferentially with sulfuric acid, even though it also reacts with nitric acid to form nitrate aerosol when sufficient ammonia is available. Thus, a reduction in SO2 emissions led to an increase in free ammonia level, and consequently, more nitric acid was transferred to the particulate phase. Overall, when SO2 emissions were reduced, PM2.5 increased because of the relatively larger quantities of ammonium and sulfate, even though this was partly offset by a decreased nitrate level. This result also indicates that reducing the PM2.5 level by controlling SO2 emissions alone is ineffective because SO2 control results in an increase in nitrate concentrations.

3.2.6. NOx and SO2
At low VOC/NOx ratios (i.e. <15), the cross-sensitivity coefficients of PM2.5, sulfate, and ammonium were negative (figure 4(e)), indicating that a reduction in the levels of NOx (or SO2) species led to an increase in sensitivity of PM2.5, sulfate, and ammonium to SO2 (or NOx). Thus, simultaneously controlling SO2 and NOx could maximize the reduction in PM2.5 concentration. In urban areas, the most effective measure for controlling PM2.5 is to reduce the amount of SO2 and NOx simultaneously. Conversely, at high VOC/NOx ratios (i.e. >15), the cross-sensitivity coefficient of PM2.5 was positive, which indicates that a reduction in the levels of NOx (or SO2) species could lead to a reduction in the sensitivity of PM2.5 to SO2 (or NOx), causing PM2.5 level to increase because of a reduction in SO2 (or NOx). This result implies that reductions in SO2 and NOx in areas with high VOC/NOx ratios—that is, rural areas—would be unable to control PM2.5 effectively.
4. Conclusion

Local contribution to ambient PM$_{2.5}$ was on average lower than the S-TAP but higher than the R-TAP. The highest PM$_{2.5}$ levels in the PRD region typically occurred during winter and autumn, followed by spring, because of the significant S-TAP, whereas the absolute local contribution was slightly higher in winter than in the other three seasons. The R-TAP was relatively higher in southwestern PRD cities in winter and fall than in northeastern cities because of the prevailing northeasterly wind. With respect to overall relative contributions, the highest local contribution and R-TAP occurred in summer: approximately 44.3% and 25.7%, respectively. At the city level, emissions from northeastern PRD cities were a major contributor because these cities had high emission rates, especially GZ, the emissions of which contributed approximately 14.9 μg m$^{-3}$ to the ambient PM$_{2.5}$ levels in the other nine cities in winter and fall, respectively. Emission from SZ contributed roughly 6.0 μg m$^{-3}$ and 4.4 μg m$^{-3}$ PM$_{2.5}$ in spring and summer, respectively. The S-TAP, R-TAP, and local contributions resulted in approximately 10 170, 4090 and 5900 annual premature mortalities in the PRD region, respectively.

Given that regional and local emissions contributed almost half of the ambient PM$_{2.5}$ concentration in the PRD region, our study analyzed the main emission species to gain insight with respect to the efficacy of various control measures. Simulations revealed that primary PM emissions, especially from local regions, were the major contributor to PM$_{2.5}$ concentration in the PRD region, contributing up to roughly 43% in summer. To control PM$_{2.5}$ levels in the region, one effective strategy would be to reduce emissions from primary PM emissions sources (e.g. power plants, industries, and vehicles). Among gaseous emissions, NH$_3$ emissions were the largest contributor to PM$_{2.5}$ levels, contributing 11%.

Secondary aerosol concentrations responded non-linearly to changes in the levels of their precursors. Reducing NH$_3$ and VOC emissions would lessen the PM$_{2.5}$ level to the greatest extent. However, most parts of the PRD region are NH$_3$ poor and VOC-limited; thus, it would not be practical to control ammonia and VOC emissions. A reduction in NO$_3$ emissions could lead to an increase in the PM$_{2.5}$ concentration in a low VOC/NO$_y$-ratio region (<6; i.e. urban areas), whereas a decrease in the PM$_{2.5}$ concentration in a high VOC/NO$_y$-ratio region. We note that substantially curtailting NO$_x$ emissions might be effective at reducing the regional PM$_{2.5}$ level through reforming the VOC/NO$_x$-limited pattern. In addition, from analyzing the cross-sensitivity coefficient, we determined that controlling SO$_2$ or NO$_x$ individually would not be effective at reducing the PM$_{2.5}$ concentration because these species competed for bases and oxidants, especially when the VOC and NO$_x$ ratio was less than 15. Considering the nonlinear relationship, multi-pollutant control strategies should therefore be implemented to achieve the greatest reduction in ambient PM$_{2.5}$ level.

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Declarations of interest

None.

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