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Mapping ozone source-receptor relationship and apportioning the health impact in the Pearl River Delta region using adjoint sensitivity analysis

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Abstract

While fine particulate matters are decreasing in the Pearl River Delta (PRD) region, the regional ozone (O₃) shows an increasing trend that affects human health, leading to an urgent need for scientific understanding of source–receptor relationship between O₃ and its precursor emissions given the changing background composition. We advanced and applied an adjoint air quality model to map contributions of individual O₃ precursor emission sources [nitrogen oxides (NO_x) and volatile organic compound (VOC)] at each location to annual regional O₃ concentrations and to identify the possible dominant influential pathways of emission sources to O₃ at different

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2019.117026>.

spatiotemporal scales. Additionally, we introduced the novel adjoint sensitivity approach to assess the relationship between precursor emissions and O₃-induced premature mortality. Adjoint results show that Shenzhen was a major source contributor to regional O₃ throughout all seasons, of which 49.4% (3.8%) were from its NO_x (VOC) emissions. Local emissions (within PRD) contributed to 83% of the regional O₃ whereas only ~54% of the estimated ~4000 regional O₃-induced premature mortalities. The discrepancy between these two contributions was because O₃-induced mortalities are dependent on not only O₃ concentration, but incident rate and population density. We also found that a city with low O₃-induced mortalities could have significant emission contributions to health impact in the region since the transport pathways could be through transport of local O₃ or through transport of O₃ precursors that form regional O₃ thereafter. It is therefore necessary to formulate emission control policies from both air quality and public health perspectives, and it is also critical to have better understanding of influential pathways of emission sources to O₃.

Graphical Abstract

Keywords

Ozone; Adjoint sensitivity analysis; Source apportionment; Health impact assessment

1. Introduction

Exposure to surface ozone (O₃) has been associated with increased mortality and morbidity (Atkinson et al., 2016; Kan et al., 2012; Raza et al., 2018; Turner et al., 2016), and it became the leading contributor to global disease burden that caused an additional 254,000 deaths in 2015 (Cohen et al., 2017). Epidemiological studies have established a link between O₃ exposure and adverse health risk of respiratory (Guo et al., 2016; Raza et al., 2018) and cardiovascular (Cakmak et al., 2016; Khaniabadi et al., 2017) diseases. As the world's second largest energy consumer, China has experienced severe problems due to air pollution, especially O₃ pollution (Gu et al., 2018; Verstraeten et al., 2015; Wang et al., 2015). Several studies in China have addressed the association between O₃ exposure and increased health risk (Liu et al., 2018a, b; Tian et al., 2018; Xie et al., 2017). However, studies regarding the effect of O₃ exposure on health in the Pearl River Delta (PRD) region are few despite serious O₃ pollution in this region.

With the reform and opening-up policy implementation in 1979, the PRD region has become the “World’s Factory” (Wang et al., 2017), with rapid industrialization and urbanization. Therefore, the PRD region has severe O₃ pollution problems (Yim et al., 2019c) due to large amounts of anthropogenic emissions (Chan and Yao, 2008). PRD was one of the first regions in China to experience serious photochemical smog pollution (Tao et al., 2012). The Chinese government launched the Air Pollution Prevention and Control Action Plan in 2013 to reduce anthropogenic emissions. While PM_{2.5} shows a decreasing trend, O₃ pollution is increasing due to NO_x emission reduction (Li et al., 2018). The annual average ground-level O₃ mixing ratio in PRD increased by 10 µg/m³ from 2006 to 2014 (Liu et al., 2018a). Decrease in PM_{2.5} was reported to stimulate O₃ production through reduction in the reactive uptake of HO₂ radicals by aerosol particles (Li et al., 2018). Hence, a complete understanding of the source–receptor (S–R) relationship between O₃ and its precursor emissions (Butler et al., 2018; Cohan et al., 2005) is required to develop expeditious and cost-effective regulations for emission reduction to control O₃ in the PRD.

Several studies have aimed at attributing O₃ to sources at different spatial, temporal, and sectoral resolutions (Fiore et al., 2009; Itahashi et al., 2015; Zhang et al., 2017). Literature has reported the significant transboundary air pollution nature in China (Gu and Yim, 2016; Yim et al., 2019a), especially in the Pearl River Delta (Luo et al., 2018; Tong et al., 2018b, 2018a; Yang et al., 2019; Yim et al., 2010, Yim et al., 2019b). Apart from local emission sources, previous studies have found transboundary emission sources to be crucial in affecting regional O₃ levels (Itahashi et al., 2013; Sudo and Akimoto, 2007; Wang et al., 2011; Zhang et al., 2009). Super-regional sources were a dominant contributor to mean O₃ levels, whereas local and regional sources were crucial for high O₃ levels in June and November in the PRD (Li et al., 2012). Source contributions to O₃ in the PRD have been studied mainly through the identification of source contributions for a specific location or area and for a specific period (Cheng et al., 2010; Ling et al., 2011; Wang et al., 2010). No studies have comprehensively assessed the grid-based association between O₃ and its precursor emissions in the region and quantified the contributions of emissions from various cities and their effects on health.

The main objectives of this study are to investigate S–R relationships between changes in O₃ and its precursor emissions at each grid/location and to identify potential dominant influential pathways of precursor emissions that affect regional O₃. Additionally, we assessed the annual and seasonal variations of source contributions at the city level, and we quantified the contribution of emissions from various cities to the O₃-related health effects in the PRD.

2. Material and method

2.1. Model configurations

The Community Multi-scale Air Quality (CMAQ) modeling system (version 4.7.1) (Byun and Schere, 2006) was used to simulate the concentrations of pollutant species in PRD in 2010. The input meteorological fields of CMAQ were obtained from the Weather Research and Forecasting (WRF) Model (version 3.7) (Powers et al., 2017). The initial and boundary conditions of WRF were obtained from the meteorological data of National Centers for

Environmental Prediction/Final at 6-h intervals. Both WRF and CMAQ models were configured to have three nested domains, with a spatial resolution of 27 km (D1), 9 km (D2), and 3 km (D3) (Fig. 1). WRF configuration description is provided in our previous study by Wang et al. (2019b). The Hong Kong Environmental Protection Department (HKEPD) provided the emission datasets in HK including public electricity generation, road transport, navigation, civil aviation, other combustion sources, non-combustion sources and wild burning. The Multi-resolution Emission Inventory for China (MEIC) developed by Tsinghua University in 2010 was used to provide emission datasets outside HK in China (Li et al., 2018), which estimated for all major anthropogenic sources, excluding biomass burning. Biogenic emissions generated in this study were based on (Guenther et al., 2006) whereas shipping emissions were based on (Streets et al., 2003). The details about emission generation in the PRD can be found in our previous study by Hou et al. (2019). Both emission and meteorological data were utilized to drive CMAQ simulations in D3 covering the whole PRD. In this study, CMAQ was configured with a 10-day spin-up to minimize the influence of the initial condition. Boundary conditions in D3 were provided by the mother domain simulations.

This study used the CMAQ adjoint (CMAQ ADJ) model developed during our previous work (Wang et al., 2019), which integrated the CMAQ ADJ v4.5 model (Hakami et al., 2007) into the CMAQ v4.7.1 model framework. The CMAQ ADJ model was configured with the same chemical mechanism and schemes in CMAQ to avoid erroneous results (Zhang et al., 2008). When using the CMAQ ADJ model, we ran only the backward part of it to improve the computational efficiency by reading the checkpointed concentrations of pollutants in CMAQ at the beginning of each time step.

2.2. Health impact assessment (HIA)

We evaluated the health effects of air pollution based on four main datasets: air pollution levels, the population exposed, background mortality and morbidity rates, and the corresponding concentration-response function (CRF). The health endpoints (E) were defined as health problems caused by exposure to O₃ and were estimated based on the adapted China-specific CRF function. The basic form of E is shown as Equation (1). The health impact functions for O₃ are based on a log-linear relationship between relative risk (RR) and concentrations defined by previous epidemiology studies (Jerrett et al., 2009). In the present study, we used the coefficients of a CRF equation from a previous study (Gu et al., 2018), and the details are shown in Table S1.

$$E = \sum_k (RR_k - 1) / RR_k \times P_k \times f_k \quad (1)$$

where RR for O₃ was calculated using Equation (2):

$$RR_k = \begin{cases} \exp[\gamma \times (X_k - X_0), if(X_k \geq X_0)] \\ 1, if(X_k < X_0) \end{cases} \quad (2)$$

where k refers to the grid index; P_k is the population size based on 1-km Grid GDP Data of China in 2010 (<http://www.geodoi.ac.cn/weben/doi.aspx?Id131>) and the Gridded Population

of the World v4 (<http://sedac.ciesin.columbia.edu/data/collection/gpw-v4>); f refers to the background incident rate for individuals aged older than 30 years based on statistical results from Mainland China, Hong Kong (HK), and Taiwan in 2010; X_k refers to the maximum daily 8-h average of O_3 concentration (MDA8 O_3) in the target scenario; and X_0 is the threshold value below which no additional risk was assumed to exist. The values of γ were estimated based on the meta-regression analysis of previous epidemiological studies in China.

2.3. Adjoint sensitivity analysis and cost functions definition

The adjoint sensitivity method has been implemented in air quality models such as GEOS-Chem adjoint (Henze et al., 2007), CMAQ ADJ (Hakami et al., 2007; Wang et al., 2019), and GRAPES-CUACE adjoint (An et al., 2016) to calculate the gradient of a concentration-dependent cost function over a given receptor to all model input parameters in a single model run and is propitious to large-scale nonlinear complex calculation (Zhao et al., 2013). The adjoint version of CMAQ model involved all chemical reactions of O_3 formation and included contributions of precursor emissions as model inputs. Although our adjoint model did not trace the proportional contribution of each reaction and tagged species, it accounted for both positive and negative source contributions from all emission species to ozone production.

In CMAQ ADJ, adjoint sensitivity calculations were driven by the adjoint forcing term (ϕ) in the same manner as the concentrations were driven by emissions in CMAQ. The adjoint forcing term ϕ was the derivative of the local cost function (J) with respect to the state variables [e.g. pollutant concentration (C)], reflecting the local and marginal influence of a change in concentration on J ($\phi = \frac{\partial J}{\partial C}$). The saved ϕ and C from baseline case were taken as input data for adjoint backward integration. Thus, the derivative of J with respect to control variables [e.g. emissions (E)] can be computed simultaneously backward in time by the adjoint model (Zhai et al., 2018).

In this study, the first J was defined as annual average O_3 concentrations in the PRD (J_c) simulated by CMAQ model. Subsequently, the adjoint model can estimate change in J_c due to small perturbations in emissions (E) across all grids/locations and times, as denoted by $\frac{\partial J_c}{\partial E}$. The larger the values of $\frac{\partial J_c}{\partial E}$, the greater the influences of E on J_c . However, the amount of emission varies geographically, and different emission species may differ in units as well as orders of magnitude. To determine the actual influence of different E on J_c , the definition of semi-normalized sensitivity coefficients (ϕ) was used by multiplying the adjoint sensitivity with respective emission species (Wang et al., 2018). We calculated and summed the adjoint sensitivity coefficients for each individual NO_x ($NO_x = NO + NO_2$) and VOC [$VOC = OLE + \text{Acetaldehyde (ALD2)} = \text{Ethene} + \text{formaldehyde (FORM)} + \text{Isoprene (ISOP)} + \text{Paraffin (PAR)} + \text{TOL} + \text{XYL}$] emission species, as denoted by $\phi_{O_3 - E_{NO_x}}$ and $\phi_{O_3 - E_{VOC}}$, respectively, where E_{NO_x} and E_{VOC} refer to the total NO_x and VOC emissions, respectively. The description of chemical species used in this study are presented in Table S2. The adjoint sensitivity coefficients shared the same unit with the cost function and had

physical meanings (An et al., 2016). We note that the values of $\varphi_{O_3 - E_{NO_x}}$ and $\varphi_{O_3 - E_{VOC}}$ can be used for determining the relative contributions from each emission species to J_c .

Association between O_3 precursor emissions and the O_3 -related health impact in the adjoint model was established through defining of an appropriate adjoint cost function (J_m) as the premature mortalities over PRD due to O_3 exposure. As ϕ only included a concentration–response factor for O_3 , the NO_x and VOC emissions were linked to J_m in CMAQ. We estimated the source attribution to O_3 -related health impact over PRD due to NO_x and VOC emissions at each grid cell based on the adjoint sensitivity coefficients

$\varphi_{Mort - E_{NO_x}} \left(\frac{\partial J_m}{\partial E_{NO_x}} \times E_{NO_x} \right)$ and $\varphi_{Mort - E_{VOC}} \left(\frac{\partial J_m}{\partial E_{VOC}} \times E_{VOC} \right)$. The details of simulation design are shown in Table S3.

2.4. Definition of the percentage relative source contribution to cost function

We summed adjoint sensitivity coefficients across different dimensions (i.e. emission species and source areas) and interpreted them as contributions (Contri). This can be expressed as follows:

$$\text{Contri} = \sum_{k=1}^s \sum_{i=0}^{n-1} \sum_{j=0}^{m-1} \left(\frac{\partial J_c}{\partial E_{k,i,j}} \times E_{k,i,j} \right)$$

where n and m are the numbers of rows and columns in the region, respectively; s is the number of emission species; and E refers to species' emission.

The percentage of relative contributions (%Contri) is the ratio between Contri and total sensitivity coefficients within the model domain. In this study, we calculated the annual and seasonal percentage relative contributions from each city in PRD. The four seasons were defined as follows: spring (March–May), summer (June–August), fall (September–November), and winter (December–February).

2.5. Uncertainty analysis

We used the Monte Carlo approach to obtain empirical confidence intervals (CIs) and to assess health outcome uncertainty in CRF. A central estimation with 95% CI of overall uncertainty for each impact was conducted based on random 20,000 calculations assuming a triangular probability distribution T (low, nominal, and high). Uncertainties of health impact estimation originated from the uncertainties of coefficients in CRF. For an adjoint simulation with defining J_c , adjoint sensitivity uncertainty arises from the nonlinear response of O_3 with respect to its precursor emissions NO_x and VOC. The discrepancy between the total adjoint sensitivity coefficients within the model domain and the simulated O_3 over PRD was mainly attributed to the nonlinear response of O_3 to its precursor emissions and the sources outside the model domain (Henze et al., 2007; Zhang et al., 2015). Furthermore, adjoint simulation uncertainty with defining J_m was evaluated based on the O_3 -exposure-induced premature mortalities in the PRD. The ultimate impact uncertainty was estimated based on the median (50%) and 95% confidential interval (2.5%–97.5%) from the impact distribution T .

3. Results

3.1. Model evaluation and validation

3.1.1. Finite difference—We applied and advanced the gas-phase of CMAQ ADJ v4.5 model (the adjoint version of CMAQ v4.5) to CMAQ v4.7.1. The CMAQ ADJ v4.5 was developed and publicly released (Hakami et al., 2007). Our modified CMAQ ADJ was validated through comparison with the CMAQ ADJ v4.5 model for each scientific subroutine and complete subroutines. Each process showed an R^2 value of 1, whereas the full adjoint had an R^2 value of 0.999, indicating the robust performance of our modified CMAQ ADJ model. The grid-to-grid comparison of adjoint sensitivity of O_3 with NO_2 emissions for complete subroutines on a randomly selected date (June 29, 2010) is presented in Fig. S1.

The accuracy of the adjoint model was verified to confirm its reliability by comparing with the finite difference method [i.e. “brute force” (BF)]:

$$S_{ij}^{BF} = \frac{C^{+10\%} - C^{-10\%}}{0.2}$$

where $C^{+10\%}$ ($C^{-10\%}$) is the simulated concentration at a 10% increase (decrease) at baseline emissions level. S_{ij}^{BF} refers to the approximate semi-normalized first-order BF sensitivity. The 20% difference ($\pm 10\%$) was chosen to be large enough to avoid numerical noise and small enough to capture the local derivative at the base-level parameter of emission sensitivities (Napelenok et al., 2006).

Because each pair of BF and adjoint sensitivities were achieved through the propagation of perturbations forward and backward in time, only point-to-point comparisons were available for validation purposes (Gou and Sandu, 2011). For the first-order BF sensitivities of O_3 with respect to emissions (i.e. NO_2 emissions), a $\pm 10\%$ perturbation was applied on NO_2 emissions at a random grid (X_{ij}). After running a 24-h simulation, the scaled semi-normalized first-order BF sensitivity coefficient (S_{ij}^{BF}) was calculated through the division of O_3 changes by the emission scaling factor (0.2). The semi-normalized adjoint sensitivity coefficient of O_3 with respect to NO_2 emissions was calculated through multiplication of the adjoint sensitivity with corresponding emission species (i.e. NO_2 emissions). For implementing adjoint simulations, the receptor region was defined as the grid (X_{ij}) and the cost function was the O_3 concentration at the last hour of a day in a defined receptor grid. The validation tests were performed by running a series of BF simulations over various randomly selected grids with $\pm 10\%$ perturbation on NO_2 emissions, and adjoint simulations were conducted by defining the perturbed grid in BF as the receptor. Previous study (Zhai et al., 2018) found that 10–30% perturbations on emissions were proved to have a high agreement between accumulated adjoint sensitivity coefficients and finite difference results. BF and adjoint emission sensitivity coefficients for daily averages in a single grid cell on a randomly selected date (June 29, 2010) were compared in Fig. S2. The R^2 value was observed to be close to 1 (0.999987), indicating that adjoint sensitivity coefficients have a high accuracy of representing O_3 changes within a modest range of emission perturbations.

Therefore, our modified CMAQ ADJ has high efficiency in quantifying the source-receptor relationships of surface O₃.

3.1.2. Forward model evaluation—The CMAQ model performance was evaluated by comparing it with in situ O₃ observations. The geographical coordinates of monitoring sites used in this study are presented in Table S4. The monthly observations were obtained from the report of Monitoring results in 2010, Pearl River Delta, Regional Air Quality Monitoring Network, released by Environmental Protection Department, the Government of the Hong Kong Special Administrative Region (https://www.epd.gov.hk/epd/english/resources_publications/m_report.html). In general, the model could capture the monthly and daily variations of surface O₃ at most monitoring sites (Fig. S3). A large difference between observations and simulations occurred at sites located in upwind urban areas of PRD (i.e. Tianhu and Chengzhong). On average, the values of the correlation coefficient (R) and normalized mean bias were approximately 0.73% and 6.37%, respectively, based on daily variations. Our results were comparable with those of other studies (Wang et al., 2010; Zhang et al., 2006). Due to the available data in HK, the hourly observations in HK were compared with simulated air pollutants including O₃, NO₂, and SO₂ concentrations. As shown in Table S5, the statistical results for individual sites in HK were comparable with those reported by previous studies (Cai et al., 2013; Kwok et al., 2010; Liu et al., 2018a, b). The annual average observations and simulated O₃ in PRD monitoring sites are shown in Fig. S4. In the urban areas of PRD, our model showed robustness and consistency with observations. Overall, our model simulations were satisfactory for this study.

3.2. Baseline simulation

Figure S4 depicts the spatial distributions of annual average O₃ concentration in PRD. The lowest O₃ concentrations (<31 µg/m³) were observed in the urban areas of Shenzhen (SZ) and Guangzhou (GZ). Furthermore, the core area of PRD (Cai et al., 2013) had relatively lower regional O₃ levels, such as in SZ (49.6 µg/m³) and Foshan (FS) (50.2 µg/m³). In highly urbanized areas with substantial anthropogenic NO_x emissions, the lower levels of O₃ were due to the NO_x titration. The minimum O₃ (25.1 µg/m³) occurred in FS, whereas the maximum O₃ (73.1 µg/m³) occurred in Huizhou (HZ). The simulated surface O₃ in urban areas of PRD, such as in SZ, Dongguan (DG), HZ, Zhuhai (ZH), and Zhongshan (ZS), exhibited strong monthly variations with a maximum in September and a minimum in January. In addition, the highest O₃ concentration in HK was observed in October, which was consistent with the Air Quality Report in Hong Kong (http://www.aqhi.gov.hk/api_history/english/report/files/AQR2010e_final.pdf). Overall, O₃ concentration in the PRD and HK increased in summer and fall, as reported in previous studies (Chan and Chan, 2000; Lam et al., 2005; Shao et al., 2009). This could be because summer and fall seasons are associated with a favorable weather condition (i.e. hot weather), which promotes photochemical formation and O₃ accumulation. Furthermore, PRD was influenced by subsiding air induced by a tropical cyclone located in the Western Pacific Ocean near Taiwan in summer and fall.

3.3. S-R relationships of surface ozone in PRD

To explain the influences of emission sources on PRD O₃, O₃ photochemical indicators (e.g. H₂O₂/HNO₃, O₃/NO_y, and O₃/NO_z ratios) were applied to distinguish the local O₃ photochemical production regime (i.e. NO_x-limited and VOC-limited). Previous studies have suggested a threshold value of 0.55 for H₂O₂/HNO₃ ratio to discriminate and characterize local O₃ production regimes in PRD (Jin and Holloway, 2015; Ye et al., 2016). We note that an area is under the VOC-limited regime when nitric acid (HNO₃) is the dominant radical sink (low H₂O₂/HNO₃ ratios), whereas the area is under the NO_x-limited regime when peroxide (H₂O₂) is the dominant radical sink (high H₂O₂/HNO₃ ratios). In this study, the H₂O₂/HNO₃ ratio with the suggested threshold was used (Fig. S5) to determine the O₃ production regimes. The results show that most of the areas in PRD are NO_x-limited except for some areas (H₂O₂/HNO₃ < 0.55), which have substantial NO_x emissions (Fig. S6) and relatively low O₃ levels. These exceptional areas were determined to be VOC-limited.

Fig. 2a and b shows the spatial distribution of annual average O₃ sensitivity coefficients with respect to NO_x($\varphi_{O_3} - E_{NO_x}$) and VOC($\varphi_{O_3} - E_{voc}$) emissions, respectively. A positive value of O₃ sensitivity coefficient implies a decrease in PRD O₃ with a reduction in both NO_x and VOC emissions at the location. This indicates that O₃ benefit (i.e. PRD O₃ reduction) could be achieved through removal of NO_x and VOC emissions in these positive locations. Summing the values of $\varphi_{O_3} - E_{NO_x}$ and $\varphi_{O_3} - E_{voc}$ over all the grids in the PRD gave the value of 47.8 µg/m³, approximately 83% of the simulated annual average PRD O₃ (57.8 µg/m³).

The adjoint sensitivity coefficients can be used to locate where the emissions would have the larger influence on the cost function (An et al., 2016). Large positive $\varphi_{O_3} - E_{NO_x}$ values were observed within the PRD, particularly in urban cores with intense NO_x emissions (Fig. S6) (e.g. downtown SZ), indicating larger contributions from NO_x emissions of the urban cores to PRD O₃. In addition, $\varphi_{O_3} - E_{NO_x}$ shows a notable pattern of navigation in the open water areas of HK. This pattern is associated with international shipping business in the Pearl River Estuary region (Li et al., 2012).

The influential behaviors of NO_x emissions from local source areas to PRD O₃ were investigated by considering different O₃ photochemical regimes in the PRD. In VOC-limited areas inside the PRD, a positive relationship between NO_x emissions and PRD O₃ was observed. Although local O₃ formation decreases with an increase of NO_x and increasing rate nitric acid formation ($OH + NO_2 \rightarrow HNO_3$) in the VOC-limited regime, local O₃ reduction would not hinder an overall increase of PRD O₃. This may be because the transport process could offset local O₃ loss in locations with positive $\varphi_{O_3} - E_{NO_x}$. It is rather straightforward to explain positive $\varphi_{O_3} - E_{NO_x}$ in the NO_x-limited regime: local increasing NO_x would increase the local O₃ formation rate, which directly increases PRD O₃. Because the O₃ formation was relatively unaffected by changes in VOC in the NO_x-limited regime (Sillman, 1999), the magnitude of positive $\varphi_{O_3} - E_{NO_x}$ was larger than that of $\varphi_{O_3} - E_{voc}$.

Positive $\varphi_{O_3 - E_{voc}}$ values were found in most areas of the PRD, especially in urban areas with substantial anthropogenic VOC emissions, in which vehicular exhaust dominated the sources (Chang et al., 2014). In contrast to $\varphi_{O_3 - E_{NO_x}}$, large positive $\varphi_{O_3 - E_{voc}}$ occurred only in areas inside the PRD, indicating the dominant local source contributions to PRD O_3 . In addition, large $\varphi_{O_3 - E_{voc}}$ was more dispersed than large $\varphi_{O_3 - E_{NO_x}}$. Some negative $\varphi_{O_3 - E_{voc}}$ values were observed, but their magnitude was significantly smaller than that of positive $\varphi_{O_3 - E_{voc}}$, indicating the marginal negative influences of VOC emissions there.

Fig. S7 shows the annual average O_3 sensitivity coefficients with respect to each individual VOC emission species. We observed that O_3 sensitivities to species of ALD2, FORM, and PAR had a greater magnitude than to the other VOC species. The photolysis of ALD2 and FORM could result in HO_2 radical formation, which could contribute substantially to ambient O_3 in polluted areas through the reaction (Ling et al., 2016) $HO_2 + NO \rightarrow NO_2 + OH$. The reaction of PAR with OH formed ALD2 and HO_2 , which could indirectly increase ambient O_3 (Yu et al., 2010). The negative sensitivity coefficients of O_3 to VOC emissions might originate from alkane oxidation by O_3 (Calvert et al., 2008), ozonolysis of alkynes (Bailey, 2012), and O_3 depletion by HCHO (Riedel et al., 2005) and ISOP (Dunker et al., 2016).

In nonlocal source areas (i.e. areas outside PRD), there might be different influential pathways of precursor emissions (NO_x and VOC) to PRD O_3 . To determine the most likely dominant pathways, the sensitivity coefficients of O_3 concentration with respect to background O_3 concentration ($\varphi_{O_3 - O_3}$) was observed (Fig. S8). The annual prevailing wind direction was northeasterly (~25%; Fig. S9). The positive $\varphi_{O_3 - O_3}$ in the northeastern part of the PRD appeared along the prevailing wind pathway, whereas the negative $\varphi_{O_3 - O_3}$ was found in the northwestern and western part of the PRD. Considering the signs of $\varphi_{O_3 - O_3}$, we identified two possible influential pathways that dominated the influences of emissions on PRD O_3 (Table S6). It could be interpreted from positive $\varphi_{O_3 - O_3}$ that O_3 precursors might enhance background O_3 along the prevailing wind pathway. By contrast, the precursor emissions at a grid with negative $\varphi_{O_3 - O_3}$ would probably be transported to PRD instead of forming O_3 locally in the region.

Because the nonlocal source areas had limited NO_x (high VOC/ NO_x ratios), the local O_3 formation in those areas was more sensitive to changes in local NO_x emissions (Thornton, 2002). Thus, locally formed O_3 that enhanced PRD O_3 mainly came from NO_x emissions transported from nonlocal source areas. Furthermore, if precursor emissions from nonlocal source areas contribute to O_3 formation in the PRD, PRD O_3 would be more sensitive to changes in NO_x emissions as most areas in PRD had limited NO_x . Hence, whatever the major role of precursor emissions (form local O_3 or transport to receptor) from nonlocal source areas was, the influence of NO_x emissions on PRD O_3 was larger than that of VOC. This could explain the larger magnitude of $\varphi_{O_3 - E_{NO_x}}$ compared with $\varphi_{O_3 - E_{voc}}$ in nonlocal source areas of the PRD. Therefore, decreasing NO_x would be an effective strategy

to control O₃ in PRD, whereas NO_x emission reductions would lead to larger gains in NO_x-limited areas (Chameides et al., 1992).

3.4. Annual and seasonal source contributions from each city

Fig. 3 shows the annual and seasonal average percentage of relative source contributions of NO_x and VOC emissions from different cities in the region to PRD O₃. For NO_x emissions, the top source contributor was SZ (49.4%), followed by HK (10.9%), GZ (8.8%), and DG (8.2%). For VOC emissions, SZ, GZ, and DG were the top three contributors to PRD O₃, which accounted for 3.8%, 3.3%, and 1.5% of the total source contributions, respectively. By contrast, VOC emissions in all the cities except Jiangmen (JM) made smaller source contributions to PRD O₃ compared with their NO_x emissions. Thus, reducing NO_x emission would be the key for controlling PRD O₃.

NO_x emissions in SZ were the largest contributor (>31%) to PRD O₃ throughout the year, followed by HK (13.0%) and DG (7.4%) in spring, HK (10.4%) and DG (10.2%) in summer, GZ (23.7%) and FS (8.4%) in fall, and HK (12.5%) and DG (8.4%) in winter. The largest source contributions from VOC emissions varied seasonally. In spring, VOC emission contributions to PRD O₃ were relatively large from SZ (4.6%), GZ (3.2%), JM (2.7%), and DG (2.1%). In summer, the top contributors were GZ (4.1%), SZ (3.3%), and DG (2.1%). In fall, top contributors were GZ (6.0%), SZ (2.6%), and DG (1.1%). Large source contributions of emissions from GZ and FS, which are both upwind cities, were probably due to the prevailing northwesterly winds and relatively large wind speed (~39% and 6 m/s) in fall.

In winter, in all cities, NO_x emission (84.6%) was the dominant contributor to PRD O₃ when compared with VOC emission (5.0%). This can be explained by relatively lower levels of isoprene and terpene emissions in winter than in other seasons. Both NO_x (50.4%) and VOC (3.6%) emissions in SZ were dominant contributors to PRD O₃. The level of emitted NO_x in SZ was the highest among all PRD cities in winter. Under the low VOC/NO_x ratio condition, relatively high levels of VOC emissions could promote the rate of O₃ formation in SZ and even the PRD region.

3.5. Attribution of O₃ health impacts to emissions in the PRD

Table 1 shows the estimated premature mortalities due to ambient O₃ exposure and the city's contributions in the baseline scenario. The exposure to ambient O₃ caused 3639 (95% CI: 1837–6383) premature mortalities in the PRD region in 2010. The three largest contributors to the total premature mortalities in the PRD region were GZ [683 (95% CI: 291–1303)], JM [676 (95% CI: 376–1118)], and HZ [595 (95% CI: 339–961)]. When combined, the three cities (GZ, JM, and HZ) accounted for ~54% of the total mortalities in the PRD region. Among all PRD cities, ZH has the smallest contribution to the PRD regional total O₃-related premature mortalities due to its lowest population levels (3% population ratio = total population in Zhuhai/total population in PRD) compared with the other cities.

The sensitivity coefficients of J_m (premature mortalities over PRD due to O₃ pollution) with respect to NO_x and VOC emissions were calculated and are respectively denoted by

$\phi_{O_3 - ENO_x}$ and $\phi_{O_3 - Evoc}$. Summing $\phi_{O_3 - ENO_x}$ and $\phi_{O_3 - Evoc}$ over the model domain indicated 2853 deaths, approximately 78% of the baseline premature mortalities (3639 deaths).

Relative source contributions of each city to J_m were calculated (Table 1). Of the total source contributions, local emissions (inside PRD) contributed to ~54% of J_m , whereas contributions from regional emissions (outside PRD) accounted for ~46%. Among cities, the SZ (28.4%) was the largest source contributor. Thus, SZ had the largest emission density among all cities, and the prevailing southerly and southeasterly wind could lead to large population exposure to O_3 pollution in the PRD. A city with a high percentage of source contribution does not necessarily have many premature mortalities. For example, SZ's NO_x and VOC emissions caused approximately 1033 premature mortalities (28.4% of the regional total), but only 144 premature mortalities occurred in SZ as shown in the baseline scenario. This could be because the premature mortalities due to O_3 pollution were estimated based on population, background incident rate, and MDA8 O_3 concentrations. GZ had high baseline mortalities as well as high source contributions (6.42%). However, JM and HZ had high premature mortalities but low source contribution to PRD regional mortalities, which was due to the relatively low levels of emissions.

4. Discussion

Studies have analyzed the importance of determining regional source contributions to O_3 in the PRD mainly for a specific location or area or a specific time (Cheng et al., 2010; Li et al., 2012; Wang et al., 2010). One highlight of this study is that we estimated the grid-based emission contributions within the model domain to PRD O_3 . The results imply that NO_x -focused emission control must be strengthened across all PRD regions, whereas parallel VOC reductions should also be implemented in polluted urban areas to effectively abate regional O_3 in the PRD. Regarding contributions at the city level, efforts should be made to reduce NO_x and VOC emissions in SZ, GZ, and FS. Among these three cities, stringent emission control policy is required for SZ because it is the largest contributor (>31%) to PRD O_3 .

In China, the effect of O_3 pollution on health was the highest in the PRD (Gu et al., 2018); however, studies on the PRD are limited. A recent study estimated the acute effects of ambient O_3 on mortality for only four cities, namely GZ, FS, ZS, and ZH, based on five monitoring stations in the PRD (Tao et al., 2012). This study estimated the health effects of O_3 exposure based on CMAQ-simulated MDA8 O_3 concentrations. Furthermore, this study is the first to attribute the health effects of O_3 exposure to NO_x and VOC emissions across all locations in PRD to quantify how emissions from different locations influence human health metrics. It appears that reducing NO_x or VOC emissions in an area can reduce its O_3 , which can lower the health effects in that area. However, a city having a high O_3 mortality may not necessarily have a high O_3 emission influencing the total PRD mortalities, e.g. JM and HZ. According to our results, reducing emissions in SZ will be the most efficient method for reducing total PRD mortalities despite SZ not having the highest mortality.

Therefore, a health-oriented O₃ control strategy would be beneficial to ensure low risk to public health.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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HIGHLIGHTS

- We applied adjoint sensitivity approach to map O₃ source-receptor relationship.
- Dominant influential pathways of O₃ precursor emissions in the PRD were identified.
- Transboundary air pollution contributed to ~46% of O₃-induced premature mortality.
- Emission contributions to ambient O₃ and the health impact may not be consistent.

Fig. 1.

(a) Nested domains used in CMAQ model. Color shades refer to DEM based on the Chinese National Datum (i.e. the Yellow Sea Datum in 1985). The areas colored in red represent the PRD region. (b) The PRD region and locations of PRD Regional Air Quality Monitoring Stations (red dots). DG, Dongguan; FS, Foshan; GZ, Guangzhou; HK, Hong Kong; HZ, Huizhou; JM, Jiangmen; SZ, Shenzhen; ZH, Zhuhai; ZQ, Zhaoqing; and ZS, Zhongshan. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 2. Spatial distributions of annual average semi-normalized sensitivity coefficients of O_3 with respect to (left) NO_x emissions ($\mu g/m^3$) and (right) VOC emissions ($\mu g/m^3$) over the PRD in 2010.

Fig. 3.

Annual and seasonal average relative source contributions (%) of individual NO_x and VOC emissions from each city to PRD O₃. The cities included are DG (Dongguan), FS (Foshan), GZ (Guangzhou), HK (Hong Kong), HZ (Huizhou), JM (Jiangmen), SZ (Shenzhen), ZH (Zhuhai), ZQ (Zhaoqing), and ZS (Zhongshan).

Table 1

Annual O₃-exposure-induced premature mortalities (95% confidence intervals) in the Pearl River Delta (PRD) region and its major cities, and the percentage of relative source contributions from each city in the region to the annual O₃-exposure-induced premature mortalities of baseline scenario over the PRD. The values in parentheses are 2.5 and 97.5 percentiles. The premature mortalities were rounded up to the nearest integer.

City	Baseline scenario [deaths]	Population ratio [%]	Source contributions [%]	Emission density [$\mu\text{g}/\text{m}^3$]
Dongguan	170 (80–312)	6	4.70	0.57
Foshan	385 (171–719)	13	2.25	0.29
Guangzhou	683 (291–1303)	25	6.42	0.25
Hong Kong	356 (176–635)	10	7.33	0.24
Huizhou	595 (339–961)	11	0.99	0.10
Jiangmen	676 (376–1118)	14	0.88	0.12
Shenzhen	144 (63–277)	6	28.40	0.63
Zhuhai	140 (77–232)	3	1.02	0.12
Zhaoqing	324 (184–527)	6	0.01	0.08
Zhongshan	166 (81–297)	5	1.86	0.28