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Assessment of regional air quality resulting from emission control in the Pearl River Delta in China

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Abstract: The paper combined observation, reduction measures, and atmospheric modeling to provide scientific support for assessing air quality in the Pearl River Delta (PRD) in China. Statistical data revealed that energy consumption doubled from 2004 to 2014 and vehicle usage increased significantly from 2006 to 2014. Due to the controlling efforts, primary emission of SO_2, NO_x (NO_2+NO) and $PM_{2.5}$ decreased, resulting in the reductions of ambient SO_2, NO_2 and PM_{10} by 66%, 20% and 24%, respectively. However, O_3 increased by 19%. Comprehensive air quality modellings were made to evaluate the responses of air pollutants to changes in NO_x, VOCs and NH_3 emissions. Three scenarios, a baseline scenario, a CAP scenario (control strength followed as past tendency), and a REF scenario (strict control referred to latest policy/plans) were conducted to investigate the sensitivities and mechanisms. NO_x, nitrate and $PM_{2.5}$ reduced by 1.8%, 0.7% and 0.2% under NO_x CAP and reduced by 7.2%, 1.8% and 0.3% under NO_x REF scenario, respectively. The results indicated that in certain area reducing NO_x emission elevated the atmospheric oxidizability, which resulted in a compensation of $PM_{2.5}$ due to the increase of nitrate or sulfate. NH_3 controlling scenarios showed that nitrate was sensitive to NH_3 emission in PRD, with the decrease of nitrate by 0 - 10.6% and 0 - 48% under CAP and REF, respectively.

Controlling VOCs emission could benefit $PM_{2.5}$ in southwestern PRD where photochemical pollution frequently occurred. Furthermore, O_3 formation in PRD was generally VOCs-limited while the regime turned to NO_x-limited in the afternoon, therefore reducing VOCs emission benefits the reduction of overall O_3 and controlling NO_x emission in the afternoon could reduce peak O_3.

Keyword: Emission control, Air quality in PRD, WRF/CMAQ, Scenario analysis

1. Introduction

The Pearl River Delta (PRD), situated in southern China, is one of the largest city clusters in China. Covering only 0.57% area, housing 4.2% of total population, this region however contributes to nearly 10% gross domestic product of China. (Guangdong Statistical Yearbook, 2013) Driven by its rapid economization, increasing industrialization and continuous urbanization, the PRD region has been suffering from severe air pollution in the past decades. Studies have shown that air quality in PRD is an integrated result of complicated atmospheric pollution, among which haze and photochemical pollution are the most typical ones. They are usually accompanied with exceeded particulate matter with aerodynamic diameters less than or equal to 2.5μm ($PM_{2.5}$), low visibility and high mixing ratio of Ozone (O_3). (Louie et al. 2005b; Chan and Yao, 2008; Tan et al. 2009; Wang and Hao, 2012; Zhong et al 2013a). Characterized by high levels of primary emissions (i.e. Nitrogen oxides (NO_x), volatile organic compounds (VOCs) etc.), as well as complicated secondary air pollutions (O_3, secondary organic aerosol (SOA), etc.), emission control strategy are urgently needed for better air quality.

In fact, a series of strategies to improve air quality were implemented by both national and regional government. In national, during 2001-2005 (the 10th Five-Year Plan), the State Environmental Protection Administration (SEPA) set the target aiming to reduce 10% national sulfur dioxide (SO_2) emission between 2001 and 2005. Though the target wasn't fulfilled (SO_2 emission increased 27.8% instead), the 11th Five-Year Plan (2006-2010) sequentially targeted to reduce SO_2 emission with more aggressive strategy and regulation. The controlling measures included installing flue gas desulfurization (FGD) and shutting down small, inefficient power units. Finally, the Plan resulted in 14.3% decrease of national SO_2 emissions (Chinese Environmental Statistical Bulletin, http://www.mep.gov.cn/zwgk/hjtj/). Before 2010, NO_x emission control in China was merely about power plants and on-road vehicles. Till the 12th Five-Year Plan (2011-2015), a national campaign against NO_x emission was firstly executed together with the emission control of SO_2. The 12th plan was characterized by the targets of 10% NO_x reduction and 8% SO_2 reduction with 2010 as the base year. In an attempt to further improve air quality, the State Council issued Air Pollution Control Action Plan in 2013, with specific goals for three typical city clusters in China: 15%, 25% and 20% reduction of $PM_{2.5}$ in PRD, BTH (Beijing-Tianjin-Hebei) and YRD (Yangtze River Delta) from 2012 to 2017, respectively. In regional, the joint governments of Guangdong Province and Hong Kong have been closed collaborated in response to national control target. In particular, there has been noticeable improvement in regional air quality since the two governments jointly announced the "Joint Statement on Improving Air Quality in the PRD Region for 2002-2010" and subsequently enforced a series of vigorous emission reduction measures. In November 2012, both sides took the co-operation into a new phase by endorsing "The PRD Air Pollutant Emission Reduction Plan up to 2020" (APERP). The plan aims that the 2020 emission of SO_2, NO_x and VOCs within the mainland PRD would be 20%~35%, 20%~40% and 15%~25% less than those in 2010. Typically, it is the first time a specific controlling target was set on VOCs emissions in inland PRD.

To provide scientific support for improving air quality in PRD, several studies on policy assessment have been carried out. For example, Xing et al. (2011) projected four emission scenarios to assess air quality in three city clusters in China and appealed for stricter NO_x emission control; By using a response surface modeling technique, Wang et al. (2011) claimed controlling NH_3 emissions in parallel with current SO_2 and NO_x controls would be an effective approach in improving regional air quality; Liu et al.

(2013) studied the relationship between emission control and concentrations of air pollutants in Guangzhou based on the controlling method during Guangzhou Asian Games and suggested that O_3 pollution should be attached with more attention. Though much efforts were conducted, we must bear in mind that the current air quality in PRD is still of big concern and improving air quality is needed in a sustainable way. With the influence of past control measures, certain emission sources are altered and yearly trends of some pollutants are also changed (Zhong et al. 2013a). Therefore, understanding past-to-present air quality and assessing the potential impact of the recent control policy become critically important. By reviewing environmental published data, the campaign against SO_2 emission control in PRD has already set a good example around the country, the annual concentration of SO_2 in 2014 is 15.7 μg/m^3, compared to 48.4 μg/m^3 in 2006, SO_2 concentration has met China's Grade I standard (20μg/m^3, MEP, 2012). On the other hand, there are more potential space in reducing NO_x, VOCs and NH_3 emissions due to the lack/inadequacy of concerning control policy. Besides, studies suggested that these primary emissions play important roles in the formation of secondary pollutants. (Louie et al., 2005a; Edgerton et al. 2008; Chan and Yao. 2008; Wang et al. 2011; Ling et al. 2012; Li et al. 2013; Wang et al. 2013) Hence, in this study we choose to assess air quality ($PM_{2.5}$ and O_3) responses to emission controls of NO_x, VOCs and NH_3 based on the recent regional policy (APERP).

The remainder of this paper is organized as follows. First, yearly variations of air pollutants from observations and emission inventories were investigated in order to understand the changes of air quality in PRD. Next, three emission scenarios for NOx, VOCs and NH_3 were proposed, the potential impacts of emission controls on air quality were further assessed via numerical simulations. Major air quality issues, including nitrate, sulfate, ammonium, SOA, $PM_{2.5}$ and O_3 were discussed in details under different scenarios. The purpose of this study is to evaluate air quality profited by recent policy legislations and plans, and also provide concerning implications of chemistry mechanisms affecting the effectiveness of control strategies in the PRD region.

2. Method and material

2.1 Statistical Data

Monitoring air quality data (SO_2, NO_2, O_3, and PM_{10}) were collected from the PRD Regional Air Quality Monitoring Network (Zhong et al., 2013b). The network is consisted of 16 sites with 13 sites in the mainland PRD and 3 sites in Hong Kong, which could well reflect the spatial patterns of air quality in this region. Since the network provides monthly statistical results of regional air pollutants and seasonal air quality report to the public (http://www.epd.gov.hk/epd/eindex.html, accessed on 24 Dec 2015), the annual trend of air pollutants (from 2006 to 2014) were investigated. Besides, environment related statistical data, such as energy consuming, coal burning and vehicle usage, were also analyzed in order to help understand the change of past-to-present air quality in PRD. (Guangdong Statistical Yearbook, 2004-2014).

Observed hourly air pollutants including $PM_{2.5}$, O_3 and NO_x were employed to evaluate model performance. These data were collected from surface monitoring stations founded by either CMA (China Meteorological Administration) or HKEPD (Hong Kong Environmental Protection Department) within PRD (Fig. 2.). In general, these sites were regularly maintained following the rules of USEPA and previous studies have already shown good performance with convinced quality control in terms of both scientific research and operational service. (HKEPD report, 2012; Zou et al., 2015; Wang et al., 2015)

In addition, we introduced satellite remote sensing data to further validate the model performance. The derived method includes two MODIS aerosol optical depth (AOD) products, Terra and Aqua. The 1 km AOD data in the PRD region was retrieved at 0.55 μm based on a MODIS dark target algorithm and a self-developed look-up table. By using a self-developed physical model of AOD-$PM_{2.5}$, the satellite-derived $PM_{2.5}$ could be estimated. (Details refer to Li et al. 2015.) Based on satellite-derived surface $PM_{2.5}$, the magnitude and spatial distribution could be further evaluated.

2.2 Emission inventories

In this study, four types of emission inventories from 2006 to 2012 were applied. They were a developed 2006-based PRD regional emission inventory (Zheng et al., 2009), a 2008-based Multi-resolution Emission Inventory for China (MEIC), a 2010-based MEIC and a 2012-based MEIC (He et al., 2012), respectively. Specifically, the 2006-

based PRD emission inventory has a high grid resolution of 3 km × 3 km and considers sources of power plant, industry, mobile, VOCs products and others in the PRD region with convinced high quality. Developed by Tsing Hua University, MEIC refers to a series of Chinese national emission inventories with a resolution of 0.25° x 0.25° (~ 25 km), which includes the emissions of agriculture (AGR), transport (TRA), industry (IND), power plant (PP) and residence (RES). Though some uncertainties existed between the PRD EI and MEIC, we employed both to study the emission trend in PRD since the trends were reasonably comparable with other data. (Details refer to the Supplement) In addition, **biogenic emissions** calculated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.04) were used for driving chemical transport model. As a biogenic emission model, MEGAN could provide biogenic emission for both global and regional modeling with the highest resolution around 1 km (Guenther et al., 2006).

In order to stretch our understanding on the variation of air quality in PRD, trends of anthropogenic (SO_2, NO_x, $PM_{2.5}$ and VOCs) emissions based on the above inventories were investigated together with agricultural NH_3 emission data. (Obtained from Zheng et al., 2012; Shen et al., 2014)

2.3 Scenarios and emission projection

Based on recent evolution of emission control in PRD, this paper presents one baseline and two possible future emission scenarios for NO_x, NH_3, and VOCs. Simulations were conducted in four months (January, April, July and November), representing the winter, spring, summer and autumn, respectively. Also, the meteorological conditions were assumed unchanged among these scenarios meaning that same meteorological conditions in year 2010 were used for all scenarios.

The baseline was conducted by using the 2010-based MEIC, which was deemed to represent the air quality in 2010 and also used to compare with future scenarios. The comparison method is defined as:

$$Area\ Mean\ Change\ of\ X\ = \frac{1}{n}\sum_{i=1}^{n}\frac{B_i - C_i}{\mathrm{B}_i}$$

,where *X* refers to air pollutants such as $PM_{2.5}$ or O_3, *n* is the total grid number within the simulated PRD region, i is the ground computational grid, B_i is the predicted baseline value of X in the i grid and C_i is the predicted value of X in the i grid under the controlling scenarios.

A CAP future scenario was proposed, referring to a theoretical scenario, the control strength in the future was assumed to follow the past control tendency. The goal is to evaluate air quality in 2020 if governments just maintain past control strength with no further actions. To achieve this, activity data based on past emission inventories were used. A general extrapolation function is given below:

$$EI_{cap} = f_x(\, EI_{past}, activity, time)$$

, where *EI* refers to emission inventory, *activity* refers to PP, TRA, IND, AGR and RES, respectively.

The other future scenario was REF, a reference control scenario based on APERP. The REF assumed the NO_x and VOCs control would be stringently implemented based on the government plan and the 2020 emission inventory was projected by assigning the referred emission amount into four activities (TRA, PP, IND and RES). However, there was no direct controlling strategy implemented for NH_3 emission. In this study, we chose to assess the NH_3 controlling effect of AGR since AGR was its dominant source in PRD (Zheng et al., 2012). According to the study on the potential control of AGR emission by Shen et al., (2014) and Klimont et al., (2004), the controlling potentiality of AGR NH_3 ranges from ~15% to ~80% through a series of cleaning/effective technology. Besides, Wang et al., (2013) studied the responses of inorganic aerosols by adopting 30% NH_3 emission reduction in national scale, we therefore employed the same reduction for AGR NH_3 control (30% reduction) in REF to study the impacts in regional scale.

Fig. 1 summarizes the emissions of NO_x, VOCs and NH_3 for each scenario. The CAP showed that total emission of NO_x, NH_3 and VOCs would reduce by 18%, 5% and increased by 28%, respectively, while the REF showed that NO_x, VOCs and NH_3 were reduced by 30%, 20% and 30%, respectively. In particular, VOCs emissions increased in most activities under CAP, implying the increasing trend of VOCs emission and the ignorance of VOCs control in the past. Besides, NO_x emission contributed by transportation also increased under CAP (35% higher than baseline). This was due to the significant increase of vehicle usage. (Fig. 1 and Table 1).

2.4 Model set up and evaluation

In this study, US Environmental Protection Agency (EPA) Multi-scale Air Quality (CMAQ, version 4.7.1, http://cmascenter.org/cmaq/) modeling system driven by Weather Research and Forecasting (WRF, version 3.3.1, http://www.wrf-model.org/index.php) was applied for assessing air quality in PRD region. As open sources, the CMAQ modelling system is a third-generation air quality model and is designed for applications ranging from investigating complex mechanism of atmospheric chemistry and physics to regulatory and policy analysis.

A two-nested domain was applied for model setting in this study (Fig. 2), with horizontal grid spacing of 36 km and 12 km, respectively. Vertically, there were 39 sigma levels for all domains, with the top level fixed at 100 hPa. The outmost domain covered nearly entire region of China, Southern China Sea, Korea, Japan and parts of Western Pacific Ocean, which aimed to provide enough boundary condition for the nested domain. The inner domain covered whole area of Guangdong Province with the PRD region highly focused. The detailed WRF-CMAQ configuration was provided in Table S1. Given the resolution of 0.25°× 0.25° (~ 25 km) for original emissions, the emission data are linearly interpolated into the inner domain (12 km) considering the earth curvature effect. Similar method can be found in other studies. (Jiang et al., 2010; Xing et al., 2011; Liu et al., 2013)

Statistical metrics were used so as to compare the relationship between observation and simulation, which included the averaged values (Obs_{mean} and Sim_{mean}), mean bias (MB, Obs_{mean} - Sim_{mean}), absolute bias (ME), root mean square error (RMSE, $\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(Sim(i)-Obs(i))^2}$) and the index of agreement (IOA, $\mathrm{IOA} = 1 - \frac{\sum_{i=1}^{n}(sim(i)-Obs(i))^2}{\sum_{i=1}^{n}(|Sim(i)-\overline{Obs}|+|Obs(i)-\overline{Obs}|)^2}$). Usually, an IOA value ranges from 0 to 1, and a higher value of IOA indicates the better agreement between the simulation and observation. Additionally, in order to further quantify the performance of chemical simulations, normalized mean bias (NMB, $\mathrm{NMB} = \sum_{i=1}^{n}[(Sim(i)-Obs(i))/\mathrm{Obs(i)}]$) and normalized mean error (NME, NME $= \sum_{i=1}^{n}[|Sim(i) - Obs(i)|/Obs(i)])$ were also introduced.

3. Results and discussion

3.1 Analysis of statistical results

Fig. 3 shows the temporal variations of the energy consumption and the concentrations of air pollutants in PRD. From 2004 to 2014, the total energy consumption in this region increased 1.97 times, among which electricity ranked the top, followed by oil product and coal. Besides, the possession of vehicles (Table 1) increased 3.1 times (2006-2014), occupying nearly 80% of whole Guangdong province. These ascending activities might potentially rise the emissions of primary air pollutants, therefore further insight was given on the emission variations.

It was found that the emissions of SO_2, NO_x and $PM_{2.5}$ all relatively reduced in these years (Table 2) owing to the effectiveness of emission controls in inland PRD and Hong Kong. In fact, the joint governments of Guangdong and Hong Kong have been dedicated in emission reduction during the past decade. Basically, the control measures included using more efficient desulfurization and denitrification techniques, phasing out high emitting vehicles, shutting down small/inefficient industries, popularizing clean energy and production, controlling the emission of non-road mobile sources and etc. Accordingly, the monitored trend of pollutants generally agreed with emission data for those major air pollutants, for example, SO_2, NO_2 and PM_{10}, reduced by 66%, 20% and 24%, respectively. (Fig. 3) In particular, a noticeable reduction was SO_2, the annual concentration in 2014 was 15.7 μg/m^3, much less than China's Grade I standard (20μg/m^3), showing a successful example of SO_2 control around China. On the other hand, despite these measures, VOCs emissions increased and NH_3 emissions slightly changed (Table 2) owing to the limited/inadequate VOCs or NH_3 emission control in PRD. Since VOCs and NO_x were the precursors of tropospheric O_3, the poor regulation of VOCs emission and/or unbalanced NO_x reduction possibly resulted in the increasing of O_3 concentration (Fig. 3, rising rate=1.1μg/m^3/year) in PRD, which implied that photochemical pollution was becoming a problematic concern.

Because that the emission trends played key roles in future CAP scenarios, we further compared the trends with ECLIPSE global emission trends and other published paper (See details in Supplement). The comparisons showed that relatively consistent variations were discovered for SO_2, NO_2, PM and VOCs emissions (Fig. S1, Fig. S2 and Fig. S3), indicating that the combining use of MEIC with PRD EI was reasonably acceptable. Indeed, similar responses of annual SO_2 NO_2 PM_{10} and O_3 concentrations confirmed again the emission trends in this study were convincing. (Table 2 and Fig. 3)

3.2 Evaluation of model performance

Simulated surface meteorological parameters were verified with observed hourly data in the PRD region. Generally, the results revealed that the model could well reproduce weather conditions in 2010 (Table 3). The results of MB, ME, NMB, NME, RMSE and IOA are basically in the typical range of meteorological modeling studies (Huang and Fung, 2005; Jiang et al., 2010; Wang et al., 2015).

Simulated NO_x, O_3 and $PM_{2.5}$ were also verified with surface monitoring data. (Fig. 4 and Table 4) The mean bias of O_3 ranged from 7.1ppb to 10.6 ppb and the averaged IOA was 0.8, showing a good simulation of O_3. The prediction of NO_x was generally underestimated (MB=7.71ppb), which could be attributed to two main aspects. One was NO_x could be easily affected by local emissions, i.e., mobile emission, and such sources were usually the weakness for the consideration of emission inventories, especially in urban area. The other aspect was owing to the limited model resolution, the second domain only had a grid resolution of 12 km, thus it could not reflect the highly-precised underlying ground information. (i.e., street urban canopy, which could trap and sustain high spatial gradients in primary pollutants such as NO, Jiang et al., 2010; Li et al., 2013) For $PM_{2.5}$, the simulated average was 32.5 $\mu g/m^3$ and the observed average was 47.7$\mu g/m^3$. Though the model missed several high polluted events, (i.e., Jan 20 and Jan 26) the trend and magnitude were comparable with observed data (IOA=0.6).

In order to further validate the model performance, the modelled $PM_{2.5}$ were compared to those derived from satellite products (Fig. 5). Noticeably, the modelled $PM_{2.5}$ agreed well with remote sensing data in both spatial distribution and seasonal variation. Though the modelled $PM_{2.5}$ was ~10 ug/m^3 lower than the satellite-derived ones in certain area, the distribution pattern agreed well especially for the reproduce of those high concentration areas. The spatial distribution showed that relatively high $PM_{2.5}$ were observed and simulated in the highly developed urban cores, i.e. Guangzhou, Foshan, Dongguan and Shenzhen. Besides, the seasonality showed that $PM_{2.5}$ were relatively higher during dry season (Nov. and Jan.) compared to wet season (Apr. and Jul.), which might be attributed to the seasonality emission as well as meteorological factors (i.e., boundary layer, wet deposition, radiation and etc.).

Based on the above evaluations, the magnitudes and trends of O_3, NO_x and $PM_{2.5}$ were reasonably well reproduced. The overall performance was comparable with previous studies (Jiang et al., 2008; Li et al., 2013) and thus was accepted for further analysis.

3.3 Controlling Impact on $PM_{2.5}$

Since the model performed well in reproducing spatial and temporal $PM_{2.5}$, this section aimed to study responses of the secondary pollutant, $PM_{2.5}$ (including nitrate, sulfate, ammonium and SOA), to emission controls of NO_x, VOCs and NH_3, respectively. The spatial distributions of baseline nitrate (0 -10 μg/m^3), ammonium (0.3 - 6.3 μg/m^3), sulfate (1.8 -16.4 μg/m^3) and SOA (0.3 -2.4 μg/m^3) were provided in Fig. S5, taking up 34.6%, 14.6%, 15.5% and 2.4% of $PM_{2.5}$, respectively.

3.3.1 Controlling impact of NO_x scenario

The NO_x CAP scenario showed that NO_x concentration (ranging from -15.1% to 9.6%) could either increase or reduce at different areas (Fig. 6a). Generally, the area mean NO_x concentration reduced by 1.8%, while Zhaoqing experienced an overall NO_x increase, which was due to the increase of mobile source. The NO_x REF showed an average of 7.2% reduction of NO_x in the PRD (Fig. 6d), among which Guangzhou, Dongguan, Foshan and Jiangmen were the main cities subject to NO_x reduction. The expected NO_x variation led to the changes of nitrate and $PM_{2.5}$. Accordingly, nitrate and $PM_{2.5}$ each reduced by 0.7% and 0.2% when the control strength remained unchanged (CAP), while the reduction percentages were 1.8% and 0.3%, respectively, when the REF reduction scenario was enforced.

Interestingly, nitrate and $PM_{2.5}$ increased at Guangzhou, Huizhou and Shenzhen, even though the precursors were reduced. (red areas in Fig. 6b and Fig. 6c) It should be noted that both the formation pathways of HNO_3 in the daytime and night were through the oxidation of NO_2 by atmospheric oxidants (daytime: NO_2+OH+M->HNO_3+M; night: NO_2+O_3->NO_3+O_2, NO_3+NO_2+M -> N_2O_5+M, N_2O_5+H_2O(s)->HNO_3) Section 3.4 revealed that the corresponding area was VOCs-limited in O_3 formation, therefore the rate of O_3 formation increased as the consequence of NO_x reduction, leading to higher oxidants (i.e. OH radical, O_3 etc.). As a result, the HNO_3 formations in both daytime and night pathways were enhanced, resulting in more formation of HNO_3 and NO_3^-. The findings were similar to the work of Zhao et al. (2013) On the other hand, the REF NO_x scenario showed that $PM_{2.5}$ in Guangzhou, Huizhou and Shenzhen increased while the corresponding nitrate was reduced (Fig. 6f). This was related to the compensation of sulfate aerosol. Since H_2SO_4 and HNO_3 were neutralized mainly by NH_3, and NH_3 preferentially reacts with H_2SO_4 due to the stability of $(NH_4)_2SO_4$. The oxidation of SO_2 occurred in both heterogeneous and homogeneous, and OH radical is the key reactive species in the formation of sulfate. Due to the increase of atmospheric oxidizability caused by reducing NO_x (Fig. 9, O_3 increased), the oxidation of SO_2 would be enhanced. Indeed, the increase of sulfate in the corresponding area offset the overall $PM_{2.5}$ (sulfate increased 1%, see Fig. S6). Therefore, an effective way in reducing $PM_{2.5}$ was to reduce NO_x emission together with SO_2 emission.

3.3.2 Controlling impact of NH_3 scenario

Fig. 7. shows the responses of ammonium, nitrate and $PM_{2.5}$ when controlling NH_3 emission. Due to the fact that NH_3 emission in the past showed small fluctuations in PRD, the NH_3 CAP scenario also showed minor responses. In general, ammonium, nitrate and $PM_{2.5}$ would reduce by 0.5%, 1.6% and 0.5%, respectively. If agricultural NH_3 emission reduced by 30% (NH_3 REF scenario), ammonium, nitrate and $PM_{2.5}$ changed noticeably with the maximum reduction of 13%, 48% and 7.2%, respectively. The reduction areas were mainly located in those agriculture intensive cities such as Jiangmen, Zhaoqing and Foshan. In addition, sulfate slightly changed (not shown), with area mean reduction by 0.16% and 0.20% under CAP and REF, respectively.

It should be noted that the reduction of NH_3 emission resulted in the significant reduction of nitrate (Fig. 7e) while sulfate changed little Indeed, the inorganic aerosol chemistry much differs under NH_3-poor and NH_3-rich conditions. We used an experience-based method by comparing [TA] (total molar concentration of ammonia) and [TS] (total molar concentration of sulfate).（John and Spyros, 2006） If [TA] < 2[TS], it is NH_3-poor condition; otherwise, it is NH_3-rich. In this study, [TA]-2[TS] < 0, meaning there was limited free ammonia thus the region was generally the NH_3-poor conditions. The result was consistent with the result of Wang et al., (2011). Usually, NH_3-poor condition means the atmospheric available ammonia is insufficient to balance the remaining of other anions and cations, resulting that even a small perturbation in the ammonia emissions might have a significant effect on inorganic aerosols. On the other hand, sulfate slightly changed under NH_3-poor condition, which was mainly due to the fact that the formation of $PM_{2.5}$ bound sulfate was relatively free of acid-base balance. Namely, it might be not strongly dependent upon the amount of NH_3, because the heterogeneous and in-cloud processes enabled sulfate existed in the form of sulphuric acid in $PM_{2.5}$

Due to the fact that controlling NH_3 emission could not only reduce ammonium, but also significantly reduced nitrate, implementing NH_3 controlling strategy is highly suggested in PRD.

3.3.3 Controlling impact of VOCs scenario

Fig. 8 shows the change in SOA and $PM_{2.5}$ concentrations under the anthropogenic VOCs controlling scenario. Generally, SOA responses with the same trend as the precursors' change. Under the VOCs CAP scenario, the PRD VOCs emissions increased by 28.7% from 2010, and the corresponding SOA and $PM_{2.5}$ would increase by 10.7% and 0.4%, respectively. If strict VOCs controls were applied, the VOCs emissions reduced by 20% while the average reduction of SOA and $PM_{2.5}$ were 13% and 1%, respectively. Both scenario showed that the noticeable increase and reduction area were consistently located at Foshan, Zhongshan, Guangzhou and Jiangmen, with the highest increase of 34% and 1.7% for SOA and $PM_{2.5}$ under CAP scenario and highest decrease of 27.4% and 5.3% for those under REF scenario, respectively. Usually, severe photochemical pollution occurred in late summer and autumn in PRD, when the prevailing winds were from the north, and was often aggravated by stagnant weather.(Wang et al., 2015) These areas were downwind areas compared to the less polluted area, (i.e., northern Guangzhou) thus subjecting to the gathering and accumulation of air pollutants. Such responses indicated that though SOA was not the major components of $PM_{2.5}$ (compared to nitrate or sulfate), the control of anthropogenic VOCs at Foshan, Zhongshan, Guangzhou and Jiangmen with severe photochemical pollution, might be effective on the control of $PM_{2.5}$ concentrations.

3.4 Controlling impact on O_3

The implement of VOCs and NO_x controlling strategy would inevitably affect tropospheric O_3. Due to the fact that photochemical pollution in PRD is increasingly significant, as indicated by the upward trend of O_3 in Fig. 3, it is urgent to fully understand the O_3 formation mechanisms and to further control O_3 pollution. Based on the proposed scenarios of controlling NOx and VOCs, we investigated the effects of NOx and VOCs controls on O_3 production, respectively.

Given that O_3 usually peaks in the early afternoon, we selected the 14:00 O_3 as the study objects. Similar with the patterns of SOA, the baseline (Fig. 9a) revealed that high O_3 polluted area located in the southwestern PRD, with the highest mixing ratio over 70ppbv, indicating that these areas suffered from severer photochemical pollution. Besides, a relatively high O_3 polluted area was simulated in the Pearl River Estuary (PRE). One possible reason was the unique “horn mouth” topography, which could geographically trap and sustain pollutants. In addition, NO_x emission might be weaker over PRE, and the weaker NO titration caused higher O_3 as compared to the urban areas. Fig. 9b and Fig. 9c depicted O_3 changes under two VOCs scenarios. The responses of 14:00 O_3 increased by 3.3% under CAP scenario while reduced by 8% under REF scenario, suggesting that O_3 formation was VOCs-limited in PRD region. Such results implied that reducing VOCs emissions would be beneficial to O_3 control in PRD. On the other hand, the NO_x scenarios presented different patterns. It was interesting to see that O_3 concentration would reduce in most areas of PRD when NOx emission was constrained. The results showed that the mixing ratio of O_3 could be furthest reduced by 5.8% under NO_x CAP scenario and 6.5% under NO_x REF scenario, respectively, which means that the peak O_3 formation was also limited by NO_x in PRD. However, in the adjacent area of Guangzhou, Dongguan and Shenzhen (the white and red area in Fig. 9d and Fig. 9e), O_3 increased in the context of NO_x control. Furthermore, we divide PRD into two representing areas. Area A was the O_3 reduced area, including Foshan, Jiangmen, Zhuhai, and Zhongshan, while the cities with O_3 increment (Guangzhou, Dongguan and Shenzhen) were defined as Area B.

Fig. 10 showed the average diurnal variation of O_3 in the two divided areas under NO_x scenario. The overall result revealed that both Area A and Area B were dominated by VOCs-limited regime. For Area A, it could be seen that O_3 concentration increased when NO_x emission was controlled, the peak value increased 0.6ppb and 1.6ppb for CAP and REF, respectively. However, the controlling regime of Area B was not as monotonous as Area A, the dominating regime was VOCs limited in the morning, then switched to NO_x limited in the afternoon (13:00 - 17:00) and finally turned to VOCs limited in the rest hours. Such a pattern revealed that though controlling NO_x might raise the overall O_3 concentration, peak O_3 could be reduced if controlling NO_x emission in the afternoon.

In order to further convince the result, we introduced the production rate ratio of H_2O_2 to HNO_3 (P_{H2O2}/P_{HNO3}) to identify O_3 formation regime. (Sillman, 1995) Previous study in Hong Kong has showed that P_{H2O2}/P_{HNO3} is a good ratio to characterize NOx-VOCs-O_3 regime in PRD. (Lam et al., 2004; Li et al., 2013) In this study, we adopted the ratio, P_{H2O2}/P_{HNO3}, of 0.4 as the value to separate NO_x- and VOCs-sensitivity of O_3 chemistry in this study. Fig. 11 compared the afternoon regime with the whole day regime. The result revealed that the PRD was generally under VOCs-limited, while most area of PRD were NO_x-limited in the afternoon. Those areas were VOCs-limited in the afternoon were mainly located at the Guangzhou, Dongguan, Shenzhen and downwind seashore areas, which was consistent with the diagnosis of Fig. 9. Such results implied again that controlling VOCs emissions could reduce the overall O_3 concentrations and controlling the afternoon NO_x emissions could help to reduce peak O_3.

4. Summary and Conclusion

The PRD region in China has been suffered from air quality issues in the past decade. In an attempt to provide scientific support for improving air quality, this study investigates the concerning past-to-present air quality data and assesses air quality resulting from emission control through numerical simulation.

Statistical data revealed that the region's total energy consumption almost doubled from 2004 to 2014, the demand of electricity, oil and coal take up the major parts of energy consumption in PRD. A significant increase of vehicle usage had been seen which increases 3.1 times in 2014 from the 2006 level. The ascending vehicle usage results in a predicted increase of 35% NO_x emission and 13.3% VOCs emission in 2020. By investigating the past-to-present emission inventories, agricultural NH_3 emission in PRD showed rather stable, the primary emission of SO_2, NO_x and $PM_{2.5}$ depicted decreasing trends, while VOCs emission showed an increasing trend which was due to the lack of available controlling policy. Thanks to the controlling efforts, the surface monitoring air quality data agreed with the emission data. Ambient concentrations of SO_2, NO_2 and PM_{10} decreased by 66%, 20% and 24%, respectively. On the contrary, O_3 showed an increasing trend, about 19% higher from 2014 to 2006 (rising rate = 1.1ug/m^3/year), which showed a strong signal that photochemical pollution in PRD was becoming more stringent.

A three-dimensional chemical transport model, CMAQ, was employed to evaluate the responses of nitrate, ammonium, SOA, $PM_{2.5}$ and O_3 to changes in NO_x, VOCs and NH_3 emissions. Three scenarios, baseline, CAP (control strength followed as past tendency), and REF (strict control referred to recent policy and plans), were conducted to investigate the responses and mechanisms. The baseline results were validated with observed data by using point-to point and area-to-area comparison. Statistical metrics showed that the modelling results were reasonably reproduced with the IOA of O_3, NO_x and $PM_{2.5}$ were 0.8, 0.6 and 0.6, respectively. The comparison of simulated $PM_{2.5}$ with satellite-derived ones also agreed well in magnitude and spatial distribution, demonstrating a good performance in numerical simulation.

If the control of NO_x emission follows the tendency of past strength (CAP), NO_x concentration could reduce by 1.8%, resulting a little change in nitrate and $PM_{2.5}$

(reduced by 0.7% and 0.2%). It should be noted that secondary pollutants as nitrate and $PM_{2.5}$ do not response linearly as the change of NO_x emission. Instead, a relative increasing area (Guangzhou, Huizhou and Shenzhen) of nitrate and $PM_{2.5}$ was found even NO_x emission were reduced, which was attributed to enhancing oxidation of NO_2 caused by the increase of atmospheric oxidants. In the strict REF scenario, the concentration of NO_x, nitrate and $PM_{2.5}$ would reduce by 7.2%, 1.8% and 0.3%, respectively. The results indicate that $PM_{2.5}$ could be compensated by the increase of sulfate even the reduction of NO_x emission. Therefore, it is highly suggested reducing NOx emission together with SO_2 emission. Under the NH_3 CAP scenario, ammonium, nitrate and $PM_{2.5}$ would reduce by 0.5%, 1.6% and 0.5%, respectively. While the corresponding ammonium, nitrate and $PM_{2.5}$ reduced noticeably under NH_3 REF scenario. The reduce sensitivity showed that reducing NH_3 emission could not only reduce ammonium but also significantly reduce nitrate. Since nitrate aerosol was sensitive to NH_3 emissions in PRD, it should be effective in controlling $PM_{2.5}$ by reducing NH_3 emission. The VOCs controlling scenario shows that SOA responses with the same trend as VOCs emissions change. Though the contribution of SOA to $PM_{2.5}$ in PRD is minor, the controlling of VOCs emission might take effect in southwestern areas where photochemical pollution usually occurs. The study on the controlling effect of NO_x and VOCs on O_3 in PRD shows that the PRD is generally VOCs-sensitive, while the diurnal pattern shows that the regime turns to be NO_x-sensitive in the afternoon, such phenomenon was further analyzed by analyzing the ratio of $P_{H2O2}/P_{HNO3.}$ The results indicate that reducing VOCs emission would benefit in reducing the overall O_3 and reducing NO_x emission in the afternoon would result in reducing peak O_3.

Supplementary Information

Assessment of regional air quality resulting from emission control in the Pearl River Delta in China

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Table S1 WRF-CMAQ domain setting and configuration

Item	Domain 1	Domain 2
Grid spacing	36km	12km
Microphysics	WRF single-moment 5-class microphysics	
Short-wave radiation	Goddard	
Long-wave radiation	RRTM	
Surface layer	MM5 similarity surface layer	
Land-surface model	Noah	
Boundary layer	ACM2	
Cumulus parameterization	Grell-Devenyi ensemble scheme	
Chemistry option	CB05	
Biogenic emission	MEGAN v2.04	
Aerosol option	AERO5	

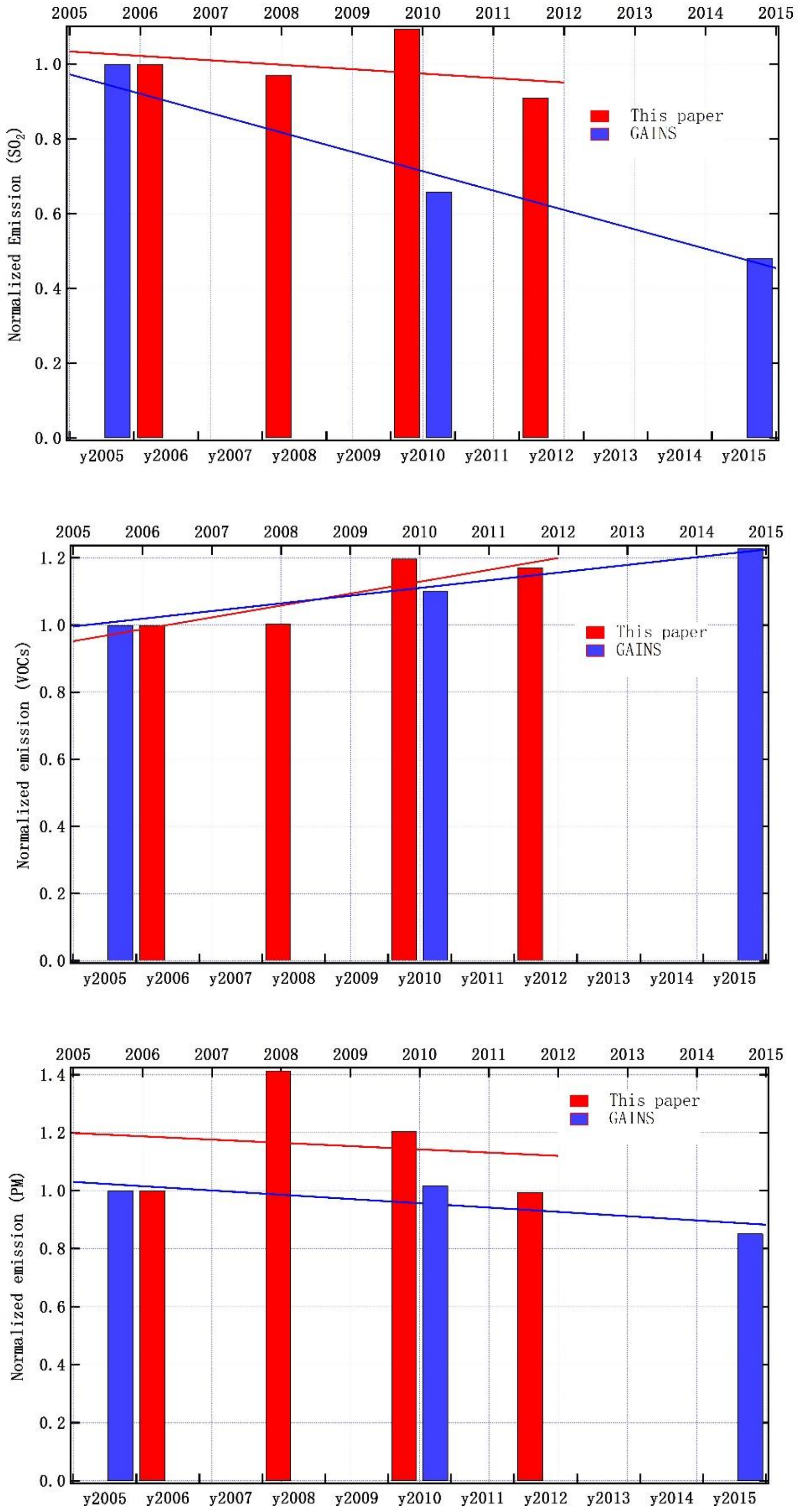


Fig. S1. Comparison of emission trend in this study with GAINS (ECLIPSE) emissions. (All data are normalized to the first year)

ECLIPSE V5 global emission is a global emission provided by International Institute for Applied Systems Analysis, which can be accessed at http://www.iiasa.ac.at. The concerning PRD emission in this study is retrieved by the GAINS model (Greenhouse Gas – Air Pollution Interactions and Synergies, http://gains.iiasa.ac.at/models/). One of the functional features of GAINS is to calculate the ECLIPSE emissions in a specific area. Since the ECLIPSE emission has a time resolution of 5 years, we compare the 2005-, 2010- and 2015-emissions with the 2006-, 2008-, 2010- and 2012-emissions in this study. The results show that the declining trend of PM and SO_2 and the increasing trend of VOCs matched well between the comparisons, the rake ratio of SO_2, PM and VOCs is -0.02, -0.01 and 0.03 for this study and -0.05, -0.01 and 0.02 for ECLIPSE, respectively, indicating the combining use of MEIC and PRD emission is reasonably acceptable.

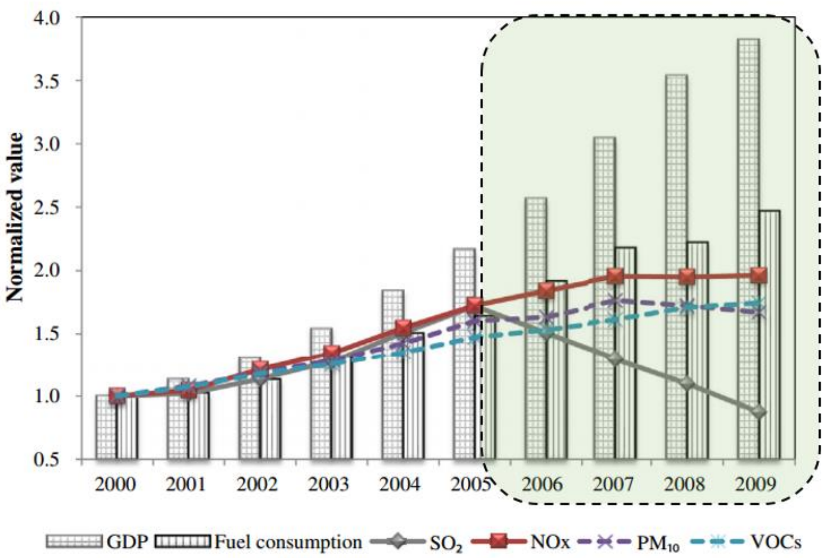
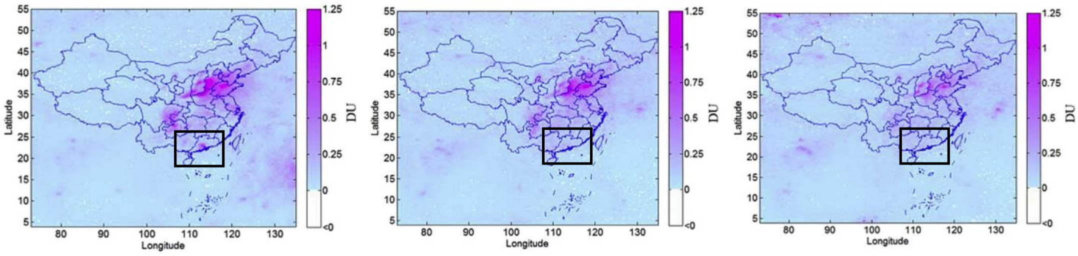


Fig. S2. Trends in pollutant emissions, GDP and fuel consumption. (All data are normalized to the year 2000) From Lu et al., (2013)



(a) 2005 (b) 2012 (c) 2014

Fig. S3. Spatial distribution of SO2 VCDs in 2005 (a), 2012 (b) and 2014 (c). (The black blank highlights the PRD region) From Xia et al., (2016)

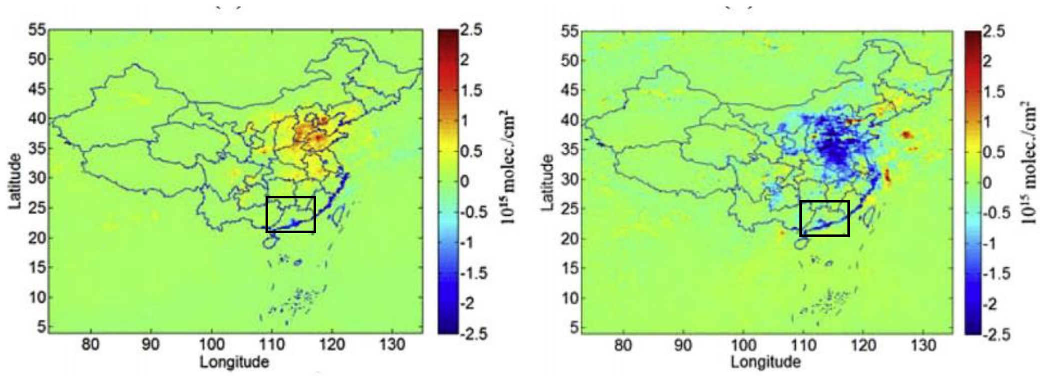


Fig. S4. The inter-annual variation of NO_2 VCDs between 2005 and 2012 (left, 2012 - 2005) and that between 2012 and 2014 (right, 2014 - 2012). (The black blank highlights the PRD region) From Xia et al., (2016)

We also compare the trend in this study with previous published work and it could be concluded that our trend in this study is consistent with previous work. Lu et al., (2013) studied emission trends and variations in source contributions of SO_2, NO_x, PM_{10} and VOCs in the PRD region from 2000 to 2009 by using a dynamic methodology. Parts of the results revealed that SO_2 and PM_{10} emissions dropped from 2005 to 2009 owing to the effectiveness of control measures adopted by governments (11th 5-Year Plan), however, VOCs emissions presented continuous increase during the study period (Fig. S2). Xia et al., (2016) used bottom-up methods to evaluate the national emissions of SO_2, NO_x, CO and CO_2 and claimed that the emission trend generally matched with satellite vertical column densities (VCDs). By comparing the national spatial emissions with VCDs, it could be also found that similar variations in PRD region for SO_2 and NO_x emissions. (Fig. S3 and Fig. S4).

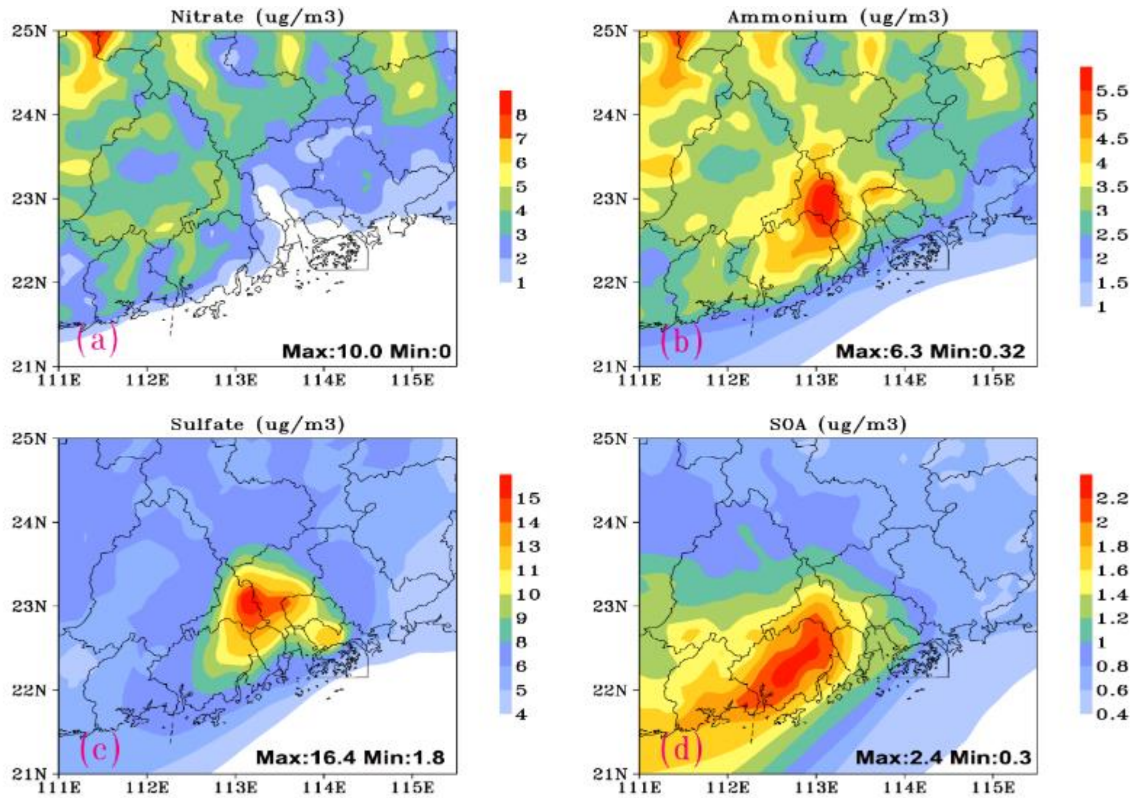


Fig. S5. Simulated annual mean distribution of nitrate (a), ammonium (b), sulfate(c) and SOA (d) under baseline scenario

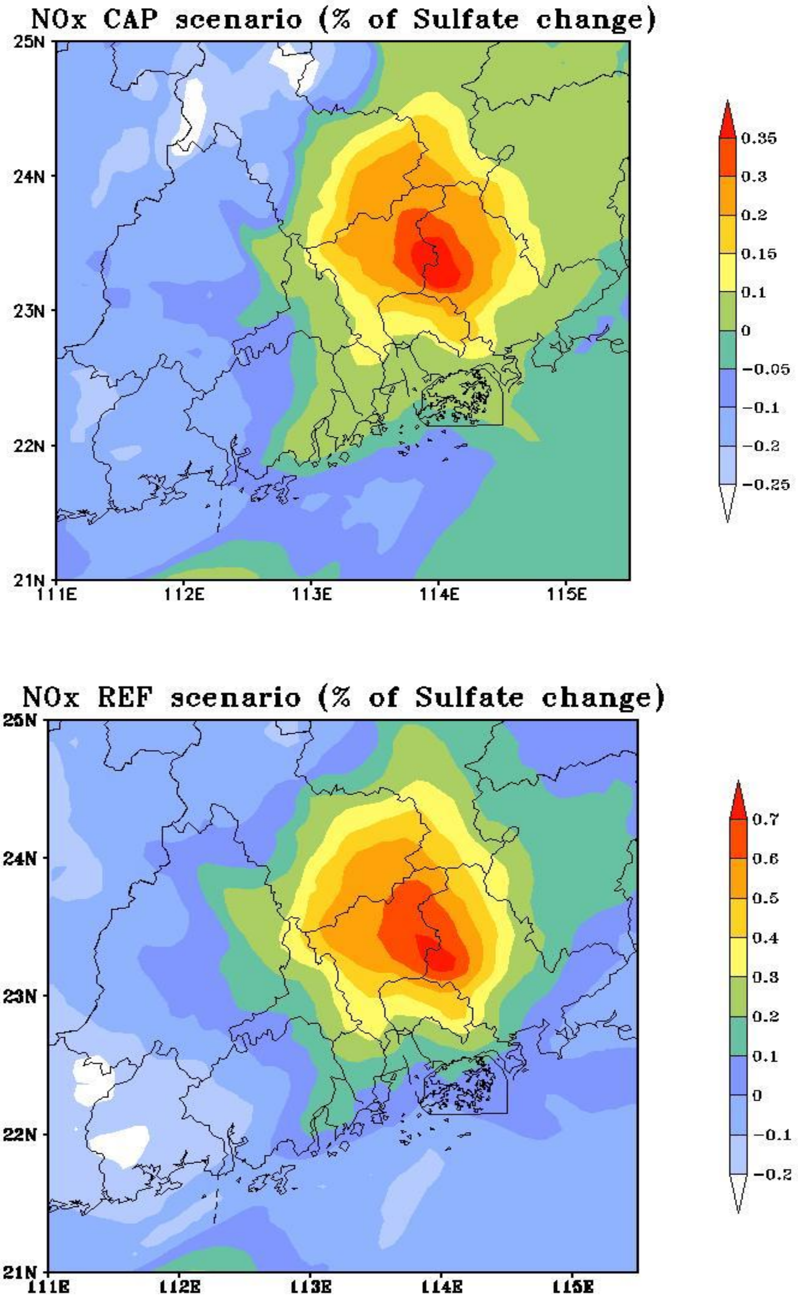


Fig. S6. Simulated annual mean distribution of sulfate under NO_x CAP scenario (top) and NO_x REF scenario (down).