Anonymous Referee #1:

I think it is an important work adding to the discussion of the PM pollution in China. Indeed understanding of the past trends and chemical speciation is an important element of the work towards future strategy or evaluation of that strategy to reduce the PM exposure in China. Below are a number of comments and few questions that I hope are helpful to the authors and could potentially increase the value of the paper for several readers.

Response: We thank Referee #1 for the encouragement and for the valuable comments to improve our manuscript. Responses to each point are addressed as below.

There is a lot of focus on high concentration areas and on the typical three regions for China. This is pretty common in many papers and there are good reasons for that. However, as Figure 1 shows, there are several stations in the range of 50-100 ug/m3 for which the model seem to underestimate the concentrations and these are in the 'other' areas where possibly large population lives to and so for the overall health impact assessment it might be very important. I think this deserves more discussion in the text and possibly this is something that can be highlighted for further work.

Response: We checked the locations of those estimates that were underestimated in 'other region'. They are located in Liaoning, Inner Mongolia and Fujian province, which are all places less populated than the typical three regions. But still, the underestimation could introduce biases in the health impact studies.

We have added some discussions in the revised manuscript: 'However, satellite-derived $PM_{2.5}$ concentrations were underestimated by a factor of 2 in some places outside the three regions (e.g. Liaoning, Inner Mongolia and Fujian province), which might affect the health impact estimates in these regions. The underestimation was mainly caused by the biases in modeled $PM_{2.5}$ concentrations, and the satellite-derived data improved compared to the model results (Figure S1).'

We have also added the analysis of $PM_{2.5}$ composition in seven regions and 20 major cities over China, and compared them with available ground measurements data, which is shown in the new Figure 3 and Figure 4.

In the conclusion part, we also added the following paragraph: 'In this study, our analysis mainly focused on the three selected regions (i.e., ECN, SCB and PRD), because they have high $PM_{2.5}$ levels, large anthropogenic emissions and large population densities. However, other places outside the three regions also experienced rapid industrialization and urbanization in recent years due to the national development strategies, which is important but has been paid less attention to. Future works could further improve the estimation of $PM_{2.5}$ composition datasets in these area and investigate the spatiotemporal variations of $PM_{2.5}$ concentrations and its driving forces.'

The paper does not address the possible issues associated with changing aerosol load on satellite retrievals affecting potentially the trend analysis as well as the absolute comparison. The SI mentions issue of 'anomalies' in post 2007 period where less valid readings from OMI exist. I think this deserves a mention in the main paper and a short discussion of what it means for the error over time. I think some of that discussion can be added to the section 3.2.

Response: We thank the referee for raising up these issues. Aerosols can have a significant impact on the retrieval of tropospheric trace gases (e.g. SO_2 and NO_2) in their magnitude. For polluted regions like China, the annual mean NO_2 columns are enhanced by 15–40 % when considering aerosol effects (Lin et al., 2015). However, Boersma et al. (2004) showed that satellite-derived cloud fractions are also sensitive to aerosols with a high single scattering albedo. An increase in cloud fractions as a result of higher aerosol concentrations leads to a similar AMF correction for aerosols as would be accomplished through a direct radiative transfer calculation without cloud correction. So the trend of trace gases are less affected by the aerosol trend. The 'row anomaly' issue occurred in the OMI instrument since 2007 and affected the valid number of retrievals in both SO_2 and NO_2 vertical column densities. Different numbers of valid pixels among years could affect the trend of SO_2 and NO_2 column densities.

In this study, we used SO_2 and NO_2 vertical column densities to evaluate the model performance of simulating $PM_{2.5}$ precursors. We have added the following sentence to Section 3.2 to mention the uncertainties here: 'It is worth noting that the satellite retrieved SO_2 and NO_2 column densities have uncertainties in their trends because of the row anomaly issue happened to the CCD detectors in OMI instrument and the impact of changing aerosol loadings on the satellite retrievals, which might contribute to the discrepancies between modeled and satellite data.'

Line 58-64: I think these two sentences should be reformulated. I do not believe that 'disparities in pollution characteristics' are the reason. It is the nature of air pollution that it does not know the borders and a mix of substances forms, travels over long distances making development of a comprehensive regional or national air quality strategy difficult, requiring knowledge of many different elements and measurements are essential factor. But only in combination with models (both CTM and remote sensing data) full understanding of the close and far sources on specific location can be understood and consequently managed.

Response: We thank the referee for the valuable suggestion. We have reformulated the sentences as: 'Measurements from individual cities are insufficient to support a comprehensive national analysis or health impact studies because air quality issues are usually regional problems and require knowledge of many different elements. Full understanding of the pollution sources can be achieved in combination with CTMs (Wang et al., 2013; Xing et al., 2015).'

Line 68-69: This sentence (conclusion) follows on the previous statements which to my mind do not fully characterize the complexity of the problem or the existing approaches. One has to consider that a lot of tools (CTMs) used in China were originally developed elsewhere where situation was different in many respects, including different level of pollutant concentrations, often existing networks of monitors with long time series, staff and laboratories with long term experience, existence of agencies monitoring pollution sources, etc. Obviously taking a set of tools from that context and trying to apply to China, or several Asian regions for that matter, will face challenges and the authors name a few. This sentence (line 68-69) reads a bit like the 'other' methods are disqualified to provide insight; I'd suggest to think of a more modest statement highlighting the additional approaches and analysis that can help to alleviate the issues and improve understanding the pm2.5 problem in china in the past years.

Response: We thank the referee for the constructive suggestions. We have revised the sentence to more accurately describe the limitations in CTMs as following: 'However, CTMs have limitations in $PM_{2.5}$ simulations over China, since many models have been originally developed in other regions that have different pollution levels compared to China. Application of these models in China might introduce problems including missing precursors and formation mechanisms of secondary organic aerosols (Baek et al., 2011) and the lack of heterogeneous reactions, which may lead to underestimations of sulfate in haze events (Wang et al., 2014; Zheng et al., 2015)'
We also reformulated the last sentence as: 'Therefore, additional information is needed to alleviate the issues and improve the simulations of historical $PM_{2.5}$ chemical compositions.'

More specific comments:

TITLE

Suggest replacing 'Chemical compositions' with 'Chemical composition'

Response: Revised.

ABSTRACT

Line 17: 'other correction factors'. . .I am not sure this is the best formulation; this is not informative. Suggest to reformulate

Response: We have revised the sentence as ‘We estimated the changes in chemical composition of ambient $PM_{2.5}$ over China during 2005–2012 using satellite-based aerosol optical depth (AOD) data and the GEOS-Chem chemical transport model, and investigated the driving forces behind the changes by examining the changes in precursor emissions using a bottom-up emission inventory.’

Line 23: Suggest replacing ‘dominated’ with ‘dominating’

Response: Revised.

INTRODUCTION

Line 36: replace ‘a mixture of complex materials from . . .’ with ‘a complex mixture originating from ..’

Response: Revised.

Line 41-43: It is not only ‘direct’ effects that are relevant and when mentioning BC, I would also add the reference to the ‘Bounding BC study’ by Bond et al. (2013) published in JGR. Consider rewriting the sentence; for example: ‘Several components (e.g., sulfate, BC, OC) have significant impact on the global energy budget and consequently contribute to climate change (IPCC, 2013; Bond et al., 2013).

Response: Revised as suggested: ‘Some components (e.g., sulfate, OC and BC) have significant impacts on the global energy budget system and consequently contribute to climate change (Bond et al., 2013; IPCC, 2013).’

Line 43-44: This sentence shall be reformulated and I would focus on stressing on the role pm2,5 plays in haze formation as well as affecting visibility rather than public attention since currently also health issues attract attention. If you want to add a historical perspective then it should be a more comprehensive.

Response: Revised as suggested: ‘$PM_{2.5}$ can also trigger visibility degradation or cause extreme haze events.’

Line 54-55: ‘cloud help design future plans’ should be changed to ‘could help design future control policies’

Response: Revised.

Line 56: add ‘concentrations’ after pm2.5

Response: Revised.

Line 95: Suggest replacing ‘dominated’ with ‘dominating’

Response: Revised.

Line 97: suggest deleting ‘figure out’

Response: Revised.

METHODOLOGY

Line 107: ‘randomly distributed over time. . .’? A rather strange statement and I do not understand what the authors are trying to communicate here

Response: In an ideal condition, the measurements data used to evaluate the estimations should cover the whole study time period from 2005 to 2012. However, we don’t have temporal continuous observations in China prior to 2013, and the measurements data used in this study are collected from publications. These observation data only represent parts of the study period (e.g., several months or years), however, they were randomly distributed during 2005-2012, which we believe can be representative for the study time period. To better describe the issue, we have revised the sentence as: ‘Although spatio-temporal continuous observation data are unavailable, the collected measurements cover most of the eastern provinces, are randomly distributed in time, and are considered to be representative of our study time and region.’

Line 142: maybe modify to “. . .due to missing AOD data”

Response: Revised.

Figure 1 and S1: I think it would be useful to see how the Figure S1 looks like when the points are shown with the same colour scale as in Figure 1 where regional allocation is indicated. From the Figure 1 it appears that there is pretty consistent about factor 2 underestimation for the low to moderate (well, in fact an average of 50-100 ug is not moderate but it is relative to 100-200 yg) concentrations in ‘other’ regions (yellow dots). I think this deserves few words of discussion in the text as there might be significant number of people leaving in these areas.

Response: We have revised Figure S1 to show same colour scale as Figure 1.

We also checked the locations of those estimates that were about factor 2 underestimation in ‘other region’. They are located in Liaoning, Inner Mongolia and Fujian province, which are all places less populated than the typical three regions. But still, the underestimation could introduce biases in the health impact studies. We have added some discussions here: ‘However, satellite-derived $PM_{2.5}$ concentrations were underestimated by a factor of 2 in some places outside the three regions (e.g. Liaoning, Inner Mongolia and Fujian province), which might affect the health impact estimates in these regions. The underestimation was mainly caused by the biases in modeled $PM_{2.5}$ concentrations, and the satellite-derived data improved compared to the model results (Figure S1).’

RESULTS

Line 259: Many readers might be interested about the possibly reasons for the overestimation of BC. Since this is a non-reactive species, does it mean that the emission are overestimated in bottom-up inventories or there are issues with the transport-deposition in the model?

Response: The GEOS-Chem modeled BC concentrations are underestimated compared to ground measurement data as shown in Figure S1, which is consistent with previous studies (Zhang et al., 2015). This underestimation is possibly due to underestimation in BC emission inventory (Zhang et al., 2015).

The satellite-derived BC concentrations in this study are overestimated compared to observations (Figure 1), which is caused by the overestimation of simulated BC fractions in $PM_{2.5}$. As can be seen in Figure S1, GEOS-Chem modeled BC is less underestimated than other species like sulfate and OM, which resulted in higher BC fractions in the simulated $PM_{2.5}$.

We have revised the sentence as: ‘Satellite-based data performed well for estimating OM concentrations but tended to overestimate the BC concentrations in polluted regions, which was caused by the overestimation of modeled BC fractions by the GEOS-Chem model’

Line 271: The first few lines of this section highlight the findings but are these really so new? I think a number of other papers have shown similar trends in emissions so this work compares the consistency of those estimates, at least in terms of emission trends. A couple of references can be added.

Response: We have added reference that describe the SNA concentrations trend using CTMs: ‘Based on the analysis described above, we found that sulfate and nitrate were the two dominant components driving the variations in the $PM_{2.5}$ concentration during 2005–2012, which is consistent with previous studies using CTMs (Xing et al., 2015).’

We also added reference in Section 4.2 when describing SO_2 and NO_x emissions: 'The emissions trends estimated by the MEIC model are consistent with other studies (Lu et al., 2010; Lu et al., 2011; Zhao et al., 2013; Zhao et al., 2013).'

Line 278: Only vehicles are the cause? The level of control of SO2 and NOx has been different and only recently the power sector is asked to mitigate NOx while SO2 was longer on the agenda.

Response: We have revised the discussion here as: 'The NO_3^-/SO_4^{2-} ratios were larger in the eastern part of China, because eastern part of China had stricter emissions standards and higher vehicle populations (Zheng et al., 2014), and in western China (e.g., Sichuan, Chongqing, and Ningxia), where coal with higher sulfur contents is burned (Tang et al., 2008), resulting in higher emission factors of SO_2. During 2005–2012, the NO_3^-/SO_4^{2-} ratios over China exhibited an increasing trend, further supporting the changes in the relative abundances of sulfate and nitrate in the atmosphere and the distinct process of controlling SO_2 and NO_x emissions in China.'

Line 280: Is S content the only reason? I thought that there has been also different requirements with respect to the emission standards for power and industrial sources across provinces with Western Provinces having slower pace in introducing strict standards.

Response: We have revised the discussion here as: 'The NO_3^-/SO_4^{2-} ratios were larger in the eastern part of China, because eastern part of China had stricter emissions standards and higher vehicle populations (Zheng et al., 2014), and in western China (e.g., Sichuan, Chongqing, and Ningxia), where coal with higher sulfur contents is burned (Tang et al., 2008), resulting in higher emission factors of SO_2. During 2005–2012, the NO_3^-/SO_4^{2-} ratios over China exhibited an increasing trend, further supporting the changes in the relative abundances of sulfate and nitrate in the atmosphere and the distinct process of controlling SO_2 and NO_x emissions in China.'

Line 359: This statement reads like it would be a fact but in fact it is an estimate and even if the total value appear to fit the overall satellite trends there are several uncertainties. I think that here and in other discussion in this section one needs to stress that these are estimates and also that a real confirmation might come from the CMS (cont monitoring systems) if such data will be available.

Response: We thank the referee for pointing out the issue. The $PM_{2.5}$ composition trend and precursor emission trend are estimates of this study and have their uncertainties. We have revised our manuscript as suggested and also provide references here to support our conclusion:

‘In comparison to 2011, the NO_x emissions reduction caused by a decline in the activity level in the power sector in 2012 was estimated to be 26.5 Gg, much less than the estimated emission reduction of 897.5 Gg, implying that SCR promotion might have begun to take effect. The reduction of NO_x emissions have also been noticed by other studies using satellite retrievals (de Foy et al., 2016; Liu et al., 2016; van Der A et al., 2016).’

Line 362: It might be useful to highlight in this section of the paper how policies outside of the three focus regions affected the total emissions in China. TO give an example; Figure 10 shows for example for SO2 a larger change due to EF (power and total) in China as in any other three focus regions so I believe the contribution has to come from elsewhere.

Response: Regions outside the three selected regions had larger reduction rates due to EF in power sector, which contributed to the larger change due to EF over China. This is related to the study period selected in this region, i.e. 2005~2012. In the year 2005, more developed regions like ECN, PRD has already took actions to reduce the power emissions, which had a higher SO_2 control efficiency above the national average level. At meanwhile, SO_2 control efficiency in other regions were below the national average level.

In the year 2012, FGD devices were installed in most power plants over China. The SO_2 control efficiency are similar among different regions. Therefore, the change between 2012 and 2005 were larger in ‘other region’ that the three selected regions.

Line 387: Linking to one of my earlier comments; this section could include also a word about the potential impact of changing aerosol load on the satellite retrievals

Response: Aerosols can have a significant impact on the retrieval of tropospheric trace gases (e.g. SO_2 and NO_2). For polluted regions like China, the annual mean NO_2 columns are enhanced by 15–40 % when considering aerosol effects (Lin et al., 2015). However, Boersma et al. (2004) showed that satellite-derived cloud fractions are also sensitive to aerosols with a high single scattering albedo. An increase in cloud fractions as a result of higher aerosol concentrations leads to a similar AMF correction for aerosols as would be accomplished through a direct radiative transfer calculation without cloud correction. So the trend of trace gases are less affected.

However, we used SO_2 and NO_2 vertical column densities here to evaluate the model performance of simulating $PM_{2.5}$ precursors. We have added the following sentence to Section 3.2 to mention the uncertainties here: ‘The satellite retrieved SO_2 and NO_2 column densities have uncertainties in their trends because of the row anomaly issue happened to the CCD detectors in OMI instrument and the impact of changing aerosol loadings on the satellite retrievals.’

CONCLUSIONS

In general some repletion here of the discussion in chapter 4 so it could be shortened a bit. However, the issues I mentioned in the beginning of the review about the regions outside the three focus regions could be highlighted here as a possible area of further work.

Response: Thanks for the suggestions. We have deleted the first paragraph in conclusion to avoid repletion, and added the following paragraph to the revised manuscript: 'In this study, our analysis mainly focused on the three selected regions (i.e., ECN, SCB and PRD), because they have high $PM_{2.5}$ levels, large anthropogenic emissions and large population densities. However, other places outside the three regions also experienced rapid industrialization and urbanization in recent years due to the national development strategies, which is important but has been paid less attention to. Future works could further improve the estimation of $PM_{2.5}$ composition datasets in these area and investigate the spatiotemporal variations of $PM_{2.5}$ concentrations.'

References:

Boersma, K. F., Eskes, H. J., and Brinksma, E. J.: Error analysis for tropospheric NO_2 retrieval from space, Journal of Geophysical Research-Atmospheres, 109, doi:10.1029/2003jd003962, 2004.

Lin, J. T., Liu, M. Y., Xin, J. Y., Boersma, K. F., Spurr, R., Martin, R., and Zhang, Q.: Influence of aerosols and surface reflectance on satellite NO_2 retrieval: seasonal and spatial characteristics and implications for NO_x emission constraints, Atmos. Chem. Phys., 15, 11217-11241, doi:10.5194/acp-15-11217-2015, 2015.

Zhang, L., Henze, D. K., Grell, G. A., Carmichael, G. R., Bousserez, N., Zhang, Q., Torres, O., Ahn, C., Lu, Z., Cao, J., and Mao, Y.: Constraining black carbon aerosol over Asia using OMI aerosol absorption optical depth and the adjoint of GEOS-Chem, Atmos. Chem. Phys., 15, 10281-10308, doi:10.5194/acp-15-10281-2015, 2015.

Anonymous Referee #2:

1. Page 1, line 19. Which population was used to do the population weighting?

Response: The population data used in this study are taken from the LandScan Global Population database (ORNL, 2010, Bright et al., 2011). We have added this information and the following reference to the revised manuscript.

Page 6, line 15 is revised as: 'The population-weighted mean mass concentrations of $PM_{2.5}$ over China were estimated using population data taken from the LandScan Global Population database (ORNL, 2010, Bright et al., 2011). The annual population-weighted mean concentrations were in the range of 63.9–75.2 $\mu g/m^3$ during 2005–2012 and were nearly twice the Chinese national standard.'

Reference: Bright, E. A., Coleman, P. R., Rose, A. N., and Urban, M. L.: LandScan 2010, in, 2010 ed., Oak Ridge National Laboratory, Oak Ridge, TN, 2011.

2. Page 3, "2.2 Satellite-derived PM2.5 and chemical composition concentrations": what's spatial resolution for data integration and model fitting? what's the detailed meanings of AODCTM in equation (1) and (2)? Although the method has been published in Geng. et al. 2015, it would be easier for readers' understanding if more information given in this manuscript.

Response: The satellite AOD data is at the spatial resolution of 0.1° × 0.1°, and the conversion factors are taken from the nested-grid GEOS-Chem model, which has a spatial resolution of 0.5° × 0.666°. The output datasets ($PM_{2.5}$ composition data) are at 0.1° × 0.1°. AOD_{CTM} means AOD data comes from a CTM model.

We have revised the manuscript to better describe our method: 'The satellite-derived $PM_{2.5}$ concentration datasets used in this work were adopted from Geng et al. (2015). These data were calculated using satellite AOD and conversion factors between AOD and $PM_{2.5}$ simulated by a CTM, and the spatial resolution of the dataset is 0.1° × 0.1°. Following Philips et al. (2014), the satellite-derived chemical compositions of $PM_{2.5}$ at 0.1° × 0.1° were estimated by applying composition-specific conversion factors to satellite AOD. The equations used for the $PM_{2.5}$ and composition calculations are:

$$\mathrm{PM}_{2.5,satellite} = \mathrm{AOD}_{satellite} \cdot \frac{\mathrm{PM}_{2.5,CTM}}{\mathrm{AOD}_{CTM}} \tag{1}$$

$$\mathrm{Composition}^{k}_{satellite} = \mathrm{AOD}_{satellite} \cdot \frac{\mathrm{Composition}^{k}_{CTM}}{\mathrm{AOD}_{CTM}} \tag{2}$$

where subscript ‘satellite’ and ‘CTM’ represent data from satellite and model respectively; *k* represents different chemical compositions, including SO_4^{2-}, NO_3^-, NH_4^+, BC, OM, dust and sea salt, in this study.’

3. Why is population-weighted concentrations used to evaluate the inter-annual variation? What’s the advantages of population-weighted concentrations comparing with unweighted concentrations in analysis the effects of controlling policies and emissions on PM2.5?

Response: We believe that the population-weighted mean concentrations can better reflect the changes of anthropogenic emissions, because anthropogenic emissions are usually emitted in populous regions. Putting more weights in populated area could partially avoid the influence of natural sources, such as dust from the desert. The northwestern part of China has very high $PM_{2.5}$ concentrations due to dust, but there is little population and emissions in that region. Using population-weighted mean concentrations can reduce the contribution of dusty region in the mean $PM_{2.5}$.

Chemical composition of ambient PM$_{2.5}$ over China and relationship to precursor emissions during 2005–2012

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Abstract. In this work, we presented the characteristic of PM$_{2.5}$ chemical composition over China for the period of 2005–2012, by synthesis of in-situ measurement data collected from literatures and satellite-based estimates using aerosol optical depth (AOD) data and the GEOS-Chem chemical transport model. We revealed the spatiotemporal variations in PM$_{2.5}$ composition during 2005–2012 and investigated the driving forces behind the variations by examining the changes in precursor emissions using a bottom-up emission inventory. Both in-situ observations and satellite-based estimates identified that secondary inorganic aerosols (i.e., sulfate, nitrate, and ammonium, SNA) ranked the highest fraction in dust-free PM$_{2.5}$ concentrations, followed by organic matters (OM) and black carbon (BC). For instance, satellite-based estimates found that SNA, OM and BC contributed to 59%, 33% and 8% of national population-weighted mean dust-free PM$_{2.5}$ concentrations respectively during 2005–2012. National population-weighted mean PM$_{2.5}$ concentration increased from 63.9 μg/m^3 in 2005 to 75.2 μg/m^3 in 2007, and subsequently decreased to 66.9 μg/m^3 from 2007 to 2012. Variations in PM$_{2.5}$ concentrations are mainly driven by the decrease of sulfate and the increase of nitrate. Population-weighted mean sulfate concentration decreased by 2.4% per year during 2005–2012 (from 14.4 μg/m^3 to 12.9 μg/m^3), while population-weighted mean nitrate concentration increased by 3.4% per year during 2005–2012 (from 9.8 μg/m^3 to 12.2 μg/m^3), largely offsetting the decrease of sulfate concentrations. By examining the emission data from the MEIC emission inventory, we found that the changes in sulfate and nitrate concentrations were in line with the decrease in SO_2 emission and increase in NO_x emissions during the same period. The desulfurization regulation in power plants enforced around 2005 was the primary contributor to the SO_2 emissions reduction since 2006. In contrast, growth of energy consumption and lack of control measures for NO_x resulted in persistent increase in NO_x emissions until the installation of denitrification devices on power plants late in 2011, which began to take effect in 2012. The results of this work indicate that the synchronized abatement of emissions for multi-pollutants are necessary for reducing ambient PM$_{2.5}$ concentrations over China.

1 Introduction

Fine particulate matter with aerodynamic diameters of less than 2.5 μm (PM$_{2.5}$) is composed of a complex mixture originating from multiple sources, including sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), black carbon (BC), organic carbon (OC), crustal elements, and water. PM$_{2.5}$ and its chemical composition can penetrate deeply into human lungs and cause adverse health effects, including increased cardiovascular and respiratory morbidity and all-cause mortality (Dockery et al., 1993; McDonnell et al., 2000; Pope et al., 2002). Some components (e.g., sulfate, OC and BC) have significant impacts on the global energy budget system and consequently contribute to climate change (Bond et al., 2013; IPCC, 2013). $PM_{2.5}$ can also trigger visibility degradation or cause extreme haze events.

Measurements of the historical trends in air quality represent the basis of health impact studies and control policy assessments. However, such datasets are usually limited in developing countries, including China. Indeed, before 2013, the Chinese national monitoring network did not report measurements of $PM_{2.5}$ or its chemical composition, and thus, it is difficult to elucidate the historical changes in aerosols and their driving forces across China. Air quality changes prior to 2013 have attracted substantial attention because China experienced rapid economic growth and urbanization during that time, along with increased energy demand. Additionally, the Chinese government has begun taking actions to mitigate emissions. Knowledge of the variations in the $PM_{2.5}$ chemical composition and their relationship to precursor emissions can be used to improve the design of future plans.

Previous studies focusing on historical $PM_{2.5}$ concentrations trend analysis typically depended on measurement data from several sites (He et al., 2001; Sun et al., 2015) or simulations using chemical transport models (CTMs) (Wang et al., 2013; Xing et al., 2015). Measurements from individual cities are insufficient to support a comprehensive national analysis or health impact studies because air quality issues are usually regional problems and require knowledge of many different elements. Full understanding of the pollution sources can be achieved in combination with CTMs (Wang et al., 2013; Xing et al., 2015). However, CTMs have limitations in $PM_{2.5}$ simulations over China, since many models have been originally developed in other regions that has different pollution levels compared to China. Application of these models in China might introduce problems including missing precursors and formation mechanisms of secondary organic aerosols (Baek et al., 2011) and the lack of heterogeneous reactions, which may lead to underestimations of sulfate in haze events (Wang et al., 2014; Zheng et al., 2015). Therefore, additional information is needed to alleviate these issues and improve the simulations of historical $PM_{2.5}$ chemical compositions.

Satellite remote sensing of atmospheric pollutants has been widely used to understand the spatial and temporal distributions of air pollutants in recent years (Martin, 2008; Streets et al., 2013). Satellite retrievals can fill in the gaps in ground observations because of their high spatial and temporal coverage. Satellite remote sensing provides the column densities of trace gases (e.g., SO_2 and NO_2) and parameters that are related to aerosol concentrations, such as the aerosol optical depth (AOD), which has been widely used to estimate surface $PM_{2.5}$ concentrations (Chu et al., 2003; Wang and Christopher, 2003; van Donkelaar et al., 2016). Different types of methods can be used to retrieve ground-level $PM_{2.5}$ concentrations from satellite AOD data, including the use of CTMs to obtain conversion factors between $PM_{2.5}$ and AOD (Liu et al., 2004; van Donkelaar et al., 2010) and the use of statistical models (Hu et al., 2014; Zheng et al., 2016) or semi-empirical models (Lin et al., 2015; Zhang et al., 2015) to investigate the relationship among $PM_{2.5}$, AOD and other factors. Compared to statistical models and semi-empirical models, CTMs do not require ground measurements as input data and can also derive $PM_{2.5}$ composition concentrations (Philip et al., 2014), making them suitable for studies seeking to explore the historical $PM_{2.5}$ chemical composition prior to 2013 over China. Our previous work improved the method of retrieving $PM_{2.5}$ concentrations using CTMs over China (Geng et al., 2015), and the method is used in this study.

In this work, we first attempted to fill in the gaps in $PM_{2.5}$ chemical composition measurements during 2005–2012 over China by using satellite AOD and conversion factors derived from a CTM. We also collected ground measurements of $PM_{2.5}$ composition from literatures to support the satellite-based analysis. The satellite-based concentrations were evaluated against the collected ground measurements. Based on in situ measurements and satellite-derived datasets, we investigated the spatial and temporal variations of $PM_{2.5}$ composition over China and identified the dominant species involved in these variations. We further compared the chemical composition concentrations with precursor emissions to better understand their relationship and the driving forces behind the changes.

2 Methodology

2.1 Ground-based measurement data

As mentioned previously, national-scale $PM_{2.5}$ and chemical composition measurements are unavailable over China during the study period (2005–2012). Therefore, we collected $PM_{2.5}$ and chemical composition measurements from the literatures. The sources, site locations, sampling period, and other information relevant to the collected data are summarized in Table S1. In total, we collected 96, 46, 46, 44, 53 and 55 records for $PM_{2.5}$, SO_4^{2-}, NO_3^-, NH_4^+, OC and BC, respectively. Although spatio-temporal continuous observation data are unavailable, the collected measurements cover most of the eastern provinces, are randomly distributed in time, and are considered to be representative of our study time and region for model evaluation.

2.2 Satellite-derived $PM_{2.5}$ and chemical composition concentrations

The satellite-derived $PM_{2.5}$ concentration datasets used in this work were adopted from Geng et al. (2015). These data were calculated using satellite AOD and conversion factors between AOD and $PM_{2.5}$ simulated by a CTM, and the spatial resolution of the dataset is 0.1° × 0.1°. Following Philips et al. (2014), the satellite-derived chemical compositions of $PM_{2.5}$ at 0.1° × 0.1° were estimated by applying composition-specific conversion factors to satellite AOD. The equations used for the $PM_{2.5}$ and composition calculations are:

$$\mathrm{PM}_{2.5,satellite} = \mathrm{AOD}_{satellite} \cdot \frac{\mathrm{PM}_{2.5,CTM}}{\mathrm{AOD}_{CTM}} \tag{1}$$

$$\mathrm{Composition}^{k}_{satellite} = \mathrm{AOD}_{satellite} \cdot \frac{\mathrm{Composition}^{k}_{CTM}}{\mathrm{AOD}_{CTM}} \tag{2}$$

where subscript ‘satellite’ and ‘CTM’ represent data from satellite and model respectively; *k* represents different chemical compositions, including SO_4^{2-}, NO_3^-, NH_4^+, BC, OM, dust and sea salt, in this study. The AOD retrievals were provided by the Moderate Resolution Imaging Spectroradiometer (MODIS, Levy et al., 2007) and Multi-angle Imaging SpectroRadiometer (MISR, Kahn et al., 2007) instruments onboard the Terra satellite. Daily AOD data at 0.1° × 0.1° from the two instruments were filtered against ground AOD measurements from the Aerosol Robotic Network (AERONET, Holben et al., 1998) and China Aerosol Remote Sensing NETwork (CARSNET, Che et al., 2009) before averaging them to reduce the uncertainties. We used the nested-grid GEOS-Chem model v9-01-02 (Bey et al., 2001; for more details, see the Support Information) over Southeast Asia and year-by-year emission inventory over China to simulate the conversion factors between $PM_{2.5}$ species and AOD. The nested-grid model has a spatial resolution of 0.5° lat × 0.667° lon (Chen et al., 2009), which was driven by assimilated GEOS-5 meteorology from the Goddard Earth Observing System (GEOS) at the NASA Global Modeling and

Assimilation Office (GMAO; http://gmao.gsfc.nasa.gov/). A total of eight years of simulations were conducted with initialization on January 1, 2005 after a one-year spin-up simulation. The study time period (i.e., 2005–2012) could not be expanded because of the restrictions imposed by the GEOS-5 meteorology data. In addition, the aerosol vertical profiles from the space-based Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP, Winker et al., 2007) used to adjust the model simulations and corrections for incomplete sampling were also taken into account. More details are provided in Geng et al. (2015) and Philips et al. (2014).

The uncertainties associated with satellite-derived $PM_{2.5}$ compositions mainly relate to the satellite AOD retrievals, the modeled conversion factor between $PM_{2.5}$ and AOD, the modeled $PM_{2.5}$ composition fractions and incomplete sampling because of missing AOD data (Philip et al., 2014). Since the satellite AOD data were filtered against ground AOD measurements, the uncertainty of the AOD was restricted to the larger bound of ±20% or ±0.1. Vertical profiles from the CALIOP instrument were used to adjust the modeled profile; therefore, the uncertainties in the modeled $PM_{2.5}$/AOD ratio were estimated as their annual mean differences. The normalized mean bias between each modeled component and ground observations was used as the error of the simulated $PM_{2.5}$ composition fraction. Uncertainty resulting from incomplete sampling was estimated as the relative difference between the modeled full-time mean value and the value coincidently sampled using satellite data. The total error was the sum of the described errors in quadrature.

2.3 Bottom-up emission inventory

The bottom-up emission information used in this study was taken from the Multi-resolution emission inventory for China (MEIC, http://www.meicmodel.org/). The MEIC model, which was developed and is maintained by Tsinghua University, is a technology-based, dynamic process emission model. The MEIC inventory is an update of the bottom-up emission inventory developed by the same group (Zhang et al., 2009) and includes estimated emissions from ~700 anthropogenic sources over China. The power sector was estimated using a unit-based dataset, and the spatial distribution of the power emission was significantly improved (Wang et al., 2012; Liu et al., 2015). The on-road emissions were calculated using estimated county-level vehicle population data combined with an emission factor model (Zheng et al., 2014). We also built a framework to speciate the non-methane volatile organic compounds (NMVOCs) and provided model-ready NMVOC emissions for major chemical mechanisms (Li et al., 2014). In this work, the year-by-year emissions of SO_2, NO_x, NH_3, CO, OC, BC and NMVOCs during 2005–2012 were taken from the MEIC inventory as the GEOS-Chem model input to simulate the conversion factors between $PM_{2.5}$ and AOD, and to support the emission driving force analysis.

In the bottom-up method, large uncertainties lie in the activity data, emission factors, removal efficiency and distribution of control technology, and spatial proxies (Zhang et al., 2009), which could affect the estimation of emission trends. To evaluate the estimated emission trends in the MEIC inventory, simulated tropospheric vertical SO_2 and NO_2 columns from the GEOS-Chem model were compared with satellite observations from the Ozone Monitoring Instrument (OMI, Levelt et al., 2006). The satellite SO_2 products were taken from Wang et al. (2015), which were improved based on the standard NASA products to reduce uncertainties. The satellite NO_2 product was the OMI standard product, OMNO2 (version 2.1) (Bucsela et al., 2013). More descriptions of the satellite SO_2 and NO_2 columns are provided in the Support Information.

3 Model Evaluation

3.1 Satellite-derived concentration

Figure 1 compares the satellite-derived $PM_{2.5}$ and chemical composition concentrations with ground measurement data collected from the literature. Satellite-based data were extracted and averaged according to the corresponding sample period and location before comparison. All symbols were colored according to their site locations. Three regions covering most of the anthropogenic sources over China were defined in this study as follows: Eastern China (ECN, 28–42°N, 110–123°E), the Pearl River Delta (PRD, 20–25°N, 110–117°E) and the Sichuan Basin (SCB, 27–33°N, 102–110°E). We found good agreement between the satellite-based and in situ $PM_{2.5}$ concentrations, with R = 0.72, slope = 0.80 and intercept = 10.18 $\mu g/m^3$. However, satellite-derived $PM_{2.5}$ concentrations were underestimated by a factor of 2 in some places outside the three regions (e.g. Liaoning, Inner Mongolia and Fujian province), which might affect the health impact estimates in these regions. The underestimation was mainly caused by the biases in modeled $PM_{2.5}$ concentrations, and the satellite-derived data improved compared to the model results (Figure S1).

The chemical compositions estimated in this study also had good consistency with ground measurements, with R values in the range of 0.65-0.75 for different species. The satellite-derived data had relatively small biases in SO_4^{2-} and OM estimations but overestimated NO_3^-, NH_4^+ and BC over polluted regions. The overestimation of NO_3^- and NH_4^+ was caused by overestimation of the NO_3^- fractions by the GEOS-Chem model, which was a common problem encountered in previous model studies (Park et al., 2004; Zhang et al., 2012; Wang et al., 2013). The overestimation of satellite-derived BC concentrations mainly occurred in the ECN region. In general, the satellite-derived concentrations were improved relative to the model simulations (Figure S1).

3.2 Modeled SO_2 and NO_2 columns

To examine the model's capability for capturing the trends in $PM_{2.5}$ precursors, we also compared the normalized inter-annual trends of model-simulated and satellite-observed tropospheric SO_2 and NO_2 column densities over China, as shown in Figure 2. Satellite-derived SO_2 and NO_2 relative trends were well captured by the model simulations, with slight overestimation of the growth rates in some years. ECN had the best performance for both SO_2 and NO_2, with only a small overestimation of the NO_2 growth rates during 2008–2009 and an underestimation of the SO_2 growth rate in 2007. The relative increases in the NO_2 columns were generally overestimated for PRD and SCB, indicating the possible overestimation of the NO_x emissions growth rates. The negative values in the satellite SO_2 columns over PRD were mainly caused by the strong interference of ozone absorption in the retrieval process, especially over clean regions where the SO_2 concentrations were low. However, the satellite-observed SO_2 columns showed a decreasing trend in PRD, which was consistent with the modeled results. It is worth noting that the satellite retrieved SO_2 and NO_2 column densities have uncertainties in their trends because of the row anomaly issue happened to the CCD detectors in OMI instrument and the impact of changing aerosol loadings on the satellite retrievals, which might contribute to the discrepancies between modeled and satellite data.

4 Results and Discussion

4.1 Spatiotemporal variations in the $PM_{2.5}$ chemical composition

Figure 3 presents the mass concentrations of $PM_{2.5}$ species and their speciation in $PM_{2.5}$ in seven regions over China. Ground measurements obtained from the literature were classified into the seven regions, in companion with coincidently sampled satellite-based data. North, Central, Northwest and Southwest China had a high observed $PM_{2.5}$ level (above 100.0 μg/m^3), which were well reproduced by the satellite-based estimation. The observed secondary inorganic aerosols (sulfate, nitrate and ammonium [SNA]) concentration exceeded half of the dust-free $PM_{2.5}$ concentration in six regions over China, with large values in Central (49.8 μg/m^3) and Northwest (46.5 μg/m^3) China, indicating the significant contribution of secondary aerosols to $PM_{2.5}$ mass. The observed OM and BC fractions varied between 29–57% and 3–10% respectively, comparing to 27–40% and 9–14% from sampled satellite data. The main difference between observed and satellite-derived speciation occurred in Northeast China where few ground measurement were available. OM had a larger fraction in South (36%) and Northeast (57%) China, possibly due to larger biogenic emissions in these regions.

We also provided the population-weighted mean concentrations of satellite-derived $PM_{2.5}$ species for each region, which were estimated using population data taken from the LandScan Global Population database (ORNL, 2010, Bright et al., 2011). North China ranked the highest $PM_{2.5}$ level (94.7 μg/m^3), followed by Central (88.8 μg/m^3) and Northwest (70.9 μg/m^3) China. SNA concentrations were most abundant in North (46.9 μg/m^3) and Central (43.3 μg/m^3) China, while their fractions in the dust-free $PM_{2.5}$ were highest in East (63%) and North (61%) China. The regional population-weighted mean $PM_{2.5}$ composition concentrations were quite different from the averaged observations, implying the possible biases when using measurements data from several sites to represent the region's level.

Figure 4 summarizes the $PM_{2.5}$ speciation from ground measurements and corresponding satellite-based data for 20 major cities across China. Only observations covering more than one year were used. Dust and sea salt were also excluded in the comparison. In general, $PM_{2.5}$ speciation patterns were well captured by satellite-derived data in most cities. SNA were major components of $PM_{2.5}$ over Chinese cities, which contributed 46–70% of the dust-free $PM_{2.5}$ concentrations in the 20 cities, comparable to the observed fractions of 44–73%. The city with the largest SNA fraction in dust-free $PM_{2.5}$ was Qinghai Lake, from both observation (73%) and satellite-based estimation (70%). OM was also an important component in $PM_{2.5}$, with averaged fraction of 31% and 32 % from ground measurements and satellite data separately among the cities. Baotou has the largest observed fraction of OM in dust-free $PM_{2.5}$, which was underestimated by satellite-based data. The fractions of BC were overestimated by satellite-based data in many cities, which was caused by the overestimation of BC concentration mentioned above.

Figure 5 shows the multi-year mean spatial distributions of the satellite-derived $PM_{2.5}$ concentrations over China overlaid with ground measurements with sample periods exceeding one year during the corresponding timeframe. The spatial patterns of $PM_{2.5}$ were well captured by the satellite-based data, with concentration enhancements of the anthropogenic pollution sources, including in the North China Plain, the Yangtze River Delta, the SCB and Hunan-Hubei province. The population-weighted mean mass concentrations of $PM_{2.5}$ over China were in the range of 63.9–75.2 μg/m^3 during 2005–2012 and were nearly twice the Chinese national standard. China had an overall negative $PM_{2.5}$ trend of 0.3% per year during 2005–2012; a positive trend of 18.2% per year was estimated in 2005–2007, followed by a negative trend of 2.7% per year in 2008–2012. According to the inter-annual $PM_{2.5}$ changes over China shown in Figure 6a, the $PM_{2.5}$ level exhibited a general downward trend after the peak year (2007), although a slight rebound of the $PM_{2.5}$ concentration was found in 2011. The $PM_{2.5}$ trend estimated in this work was consistent with those of previous studies (Boys et al., 2014; Ma et al., 2015).

The inter-annual changes in the satellite-derived $PM_{2.5}$ concentrations for ECN, PRD and SCB are presented in Figure 6b-6d. Regional disparities were found in the time series of $PM_{2.5}$ concentrations, especially at the inflection points beginning decreases or rebounds. ECN's trend was similar to the national trend, whereas in the PRD, a persistent negative trend of 2.6 μg/m^3 per year in $PM_{2.5}$ after 2007 was observed, with no rebound. $PM_{2.5}$ levels in the SCB peaked in 2006, which was one year before the national peak; subsequently, it increased again beginning in 2008 until decreasing in 2012.

The spatial distributions and time series of SNA are shown in Figure 7. The spatial patterns of SNA in the eastern part of China were similar to those of $PM_{2.5}$. Satellite-based data could well reproduce the regional heterogeneity of SNA, although NO_3^- was overestimated over ECN. The sulfate concentrations over eastern China generally exceeded 15.0 μg/m^3, and the highest values occurred in the SCB (≥ 30 μg/m^3). Regarding the nitrate concentrations, the highest values were found in the North China Plain, reflecting the different emission characteristics of sulfate and nitrate. SNA showed quite different temporal variations relative to the total $PM_{2.5}$. The population-weighted mean sulfate concentrations over China showed a negative trend of 2.4% per year during the study period (from 14.4 μg/m^3 in 2005 to 12.9 μg/m^3 in 2012), as shown in Figure 7j, with a peak value in 2006 (15.9 μg/m3) and a rebound in 2011 (Figure 6e). In contrast to SO_4^{2-}, the nitrate concentrations over China had an increasing trend of 3.4% per year (from 9.8 μg/m^3 in 2005 to 12.2 μg/m^3 in 2012), which partially compensated for the reduction in sulfate and caused the total $PM_{2.5}$ to drop one year after sulfate. In 2012, nitrate decreased for the first time, and sulfate decreased again, causing the total $PM_{2.5}$ to decline as well. The temporal trends of sulfate and nitrate also differed among the three regions. ECN and SCB had SO_4^{2-} trends similar to the national trend, whereas in the PRD, the SO_4^{2-} concentrations decreased consistently after 2007. The SCB had a larger NO_3^- growth rate compared to other regions, which could explain the earlier rebound of $PM_{2.5}$ in this region.

Figure 8 presents the spatial and temporal changes of carbonaceous aerosols. Satellite-based data performed well for estimating OM concentrations but tended to overestimate the BC concentrations in polluted regions, which was caused by the overestimation of modeled BC fractions by the GEOS-Chem model. The estimated OM concentrations were highlighted in densely populated regions because organic carbon is mainly produced by residential combustion. BC hotspots were most apparent in populous regions and large cities, consistent with previous ground observation studies (Cao et al., 2007). Negative trends of 0.9% and 0.1% per year were found for OM and BC, respectively, and these trends held nearly steady over this period.

The spatial and temporal changes in mineral dust and sea salt are presented in Figure 9. High values of mineral dust (exceeding 80.0 μg/m^3) were found over the desert regions (e.g., the Taklimakan Desert), which were the largest contributors to $PM_{2.5}$ in northwestern China. Sea salt was mainly distributed along the coast, and its concentrations were less than 1.0 μg/m^3. Dust and sea salt were mainly produced from natural sources and fluctuated during this period.

Based on the analysis described above, we found that sulfate and nitrate were the two dominant components driving the variations in the $PM_{2.5}$ concentration during 2005–2012, which is consistent with previous studies using CTMs (Xing et al., 2015). Decreases in SO_4^{2-} caused the total $PM_{2.5}$ concentrations to decline beginning in 2007, whereas NO_3^- was the main reason for the $PM_{2.5}$ rebound observed in 2011. We also compared the relative abundances of nitrate and sulfate (i.e., NO_3^-/SO_4^{2-}) in different years to confirm the variations of these two species. The NO_3^-/SO_4^{2-} ratio over China was generally less than 2, lower than the values reported for developed cities (e.g., 2–5 in Los Angeles, Kim et al., 2000). The NO_3^-/SO_4^{2-} ratios were larger in the eastern part of China, because eastern part of China had stricter emissions standards and higher vehicle populations (Zheng et al., 2014), and in western China (e.g., Sichuan, Chongqing, and Ningxia), where coal with higher sulfur contents is burned (Tang et al., 2008), resulting in higher emission factors of SO_2. During 2005–2012, the NO_3^-/SO_4^{2-} ratios over China exhibited an increasing trend, further supporting the changes in the relative abundances of sulfate and nitrate in the atmosphere and the distinct process of controlling SO_2 and NO_x emissions in China. Thus, the contribution of the mobile sector to $PM_{2.5}$ increased, while the contribution from point sources decreased. Ground measurements also reflected the increasing trend in the NO_3^-/SO_4^{2-} ratio over China. For example, Fu et al. (2014) found that the NO_3^-/SO_4^{2-} ratio in Guangzhou increased from 0.31 to 0.69 during 2007–2011. Additionally, Tan et al. (2016) observed an increase in the NO_3^-/SO_4^{2-} ratio from 0.73 to 0.92 in Foshan during 2008–2012.

4.2 Relationship between the $PM_{2.5}$ composition and precursor emissions

The sulfate and nitrate concentrations were compared with the precursor emissions of SO_2 and NO_x to elucidate the driving forces underlying the changes in the $PM_{2.5}$ components, as shown in Figure 10. We used the percent changes relative to the 2005 benchmark for the direct comparison of the concentrations and emissions. The relative changes in the SO_2 and NO_x emissions were consistent with the changes in the sulfate and nitrate concentrations, respectively, although discrepancies were noted in the growth and reduction rates.

On the national scale, the relative changes in SO_4^{2-} from 2005 to 2012 corresponded almost linearly to the relative changes in SO_2 emissions, whereas the relative increase in NO_3^- during 2005–2012 was less than that of NO_x emissions. During this time period, NH_3 emissions remained steady, and the magnitude was less than the sum of the SO_2 and NO_x emissions on a molecular basis, indicating that NH_3-limited conditions existed in China. Although the decrease of SO_4^{2-} released free NH_3 in a 1:2 ratio, the amount of NH_3 released could not fully neutralize the increased nitric acid because the increase in the NO_x emissions was more than twice the decrease in the SO_2 emissions (e.g., an 11% reduction in SO_2 emissions vs. a 48% increase in NO_x emissions in 2012). This explains why the relative increase of NO_3^- was less than that of NO_x emissions (e.g., a 24% increase of NO_3^- in 2012).

Among the three regions, the PRD had the largest reduction rates of SO_2 emissions and the lowest growth rates of NO_x emissions, consistent with the faster decline of SO_4^{2-} concentrations and slower increase of NO_3^- concentrations in this region. The SCB had a larger growth rate of NO_x emissions compared to other regions, which could explain the rapid increase of NO_3^- concentrations. Differences were observed in the relative change rates of SO_4^{2-} concentrations and SO_2 emissions. Possible explanations for these differences include uncertainties in the bottom-up SO_2 emission trend, as described in Sect. 3.2, and the influences of the varying meteorological conditions over the years. Similar to the national trend, the growth of the NO_3^- concentration was not only affected by the NO_x emission increase but also by changes in the SO_4^{2-} concentrations via the thermodynamic equilibrium of SNA.

Figure 11 presents the inter-annual emission trends of SO_2 and NO_x in four sectors taken from the MEIC inventory. The emissions trends estimated by the MEIC model are consistent with other studies (Lu et al., 2010; Lu et al., 2011; Zhao et al., 2013; Zhao et al., 2013). We also established a hypothetical scenario of emission trends that assumed that the emission factors and technology distributions remained unchanged during 2005–2012 to separate the effects of activity (A) and emission factor (EF) changes. The hypothetical scenario represented the emission changes caused by A changes alone, and the differences between the hypothetical scenario and the actual emissions reflected the emission changes caused by EF variations.

As shown in Figure 11, the total SO_2 emissions peaked in 2006 (34.3 Tg) and subsequently decreased. This reduction was mainly driven by the power sector, which is a major source of SO_2 emissions over China. China set a target to reduce national SO_2 emissions by 10% in the 11th Five Year Plan (FYP, 2006–2010) and took corresponding actions, including the mandatory installation of flue-gas desulfurization (FGD) in coal-fired power plants and the optimization of generation unit fleets by promoting large power plants and decommissioning small plants (The State Council of the People's Republic of China 2006). Although the increasing electricity demand tended to increase SO_2 emissions by 68% during 2005–2011, the reduced SO_2 EFs completely reversed the SO_2 emissions in the power sector, causing them to decrease at a rate of 1.4 Tg/yr and confirming the success of FGD operation and the optimization of the mix of generation unit fleets. After reaching a bottom value of 28.4 Tg in 2010, the SO_2 emissions subsequently increased. This rebound was mainly caused by the growing activity rates in the industrial sector and limited control measures in iron and steel production. Therefore, successful control of SO_2 emissions in the power sector was the key factor relating to SO_4^{2-} reduction after 2007, whereas limited controls in the industrial sector contributed to the SO_4^{2-} rebound.

The total NO_x emissions over China showed completely different trends compared to SO_2 emissions because of the distinct control processes implemented for SO_2 and NO_x by the Chinese government. China established a goal to reduce NO_x emissions by 10% late in the 12th FYP (2011–2015) and pursued the installation of selective catalytic reduction (SCR) equipment at power plants beginning in 2011. Previously, the control measures on NO_x in the power sector were limited, whereas the energy demand increased continuously, leading to a dramatic increase in NO_x emissions from the power sector during 2005–2011. Meanwhile, the Chinese government promoted the construction of precalciner kilns, which are the most energy-efficient cement kilns, to replace the shaft kilns for cement production. However, the NO_x EF increased because the higher operational temperatures and more automated air-flow systems of precalciner kilns resulted in higher NO_x emissions compared to shaft kilns. In the transport sector, NO_x emissions increased by 19.3% in 2012 relative to 2005; this value was the result of a 17.4% decline because of the implementation of staged regulations and a 36.7% increase attributed to vehicle population growth. In comparison to 2011, the NO_x emissions reduction caused by a decline in the activity level in the power sector in 2012 was estimated to be 26.5 Gg, much less than the estimated emission reduction of 897.5 Gg, implying that SCR promotion might have begun to take effect. The reduction of NO_x emissions have also been noticed by other studies using satellite retrievals (de Foy et al., 2016; Liu et al., 2016; van Der A et al., 2016). The rapid increase of NO_x emissions caused the NO_3^- concentrations to rise, compensating for the reductions in the SO_4^{2-} concentration and even leading to a rebound in the $PM_{2.5}$ concentration.

Figure 12 summarizes the region-specific by-sector emission change rates caused by A and EF changes, which could facilitate understanding the regional disparities in $PM_{2.5}$ composition variations. ECN exhibited emission patterns that were very similar to those observed at the national level, and the SO_2 control measures implemented in the power sector were most effective in ECN. Indeed, in this region, a reduction rate of 17.4% per year was attributed to the EF reduction, larger than those observed in the PRD (11.4%/year) and SCB (9.9%/year).

The PRD had more effective control of power sector NO_x emissions, and the vehicle population in this region grew more slowly, contributing to slower growth of the total NO_x emission and, thus, persistent $PM_{2.5}$ reduction after 2007. In the SCB, coal consumption in the industrial sector grew quickly, and as a result, the SO_2 and NO_x emissions increased by 20.9% and 20.0% per year, respectively. Reductions in the sulfur content of the coal burned in the SCB reduced the SO_2 EFs and offset a large fraction of the increased emissions. In contrast, for NO_x emissions, the EFs continued to increase, causing the NO_x emissions and NO_3^- concentrations over the SCB to increase dramatically.

4.3 Uncertainties and limitations

The national population-weighted mean uncertainties were estimated to be 3.4 μg/m^3 for sulfate, 2.7 μg/m^3 for nitrate, 2.0 μg/m^3 for ammonium, 1.2 μg/m^3 for BC and 4.6 μg/m^3 for OM. Despite the large uncertainties in the magnitudes of the estimated $PM_{2.5}$ compositions, the trend analysis performed here was relatively unaffected because most of the uncertainties were systematic errors, and we used the normalized trend to cancel out most of them. The bottom-up emissions used to elucidate the driving forces were also expected to include large uncertainties, but we focused on the emission trend, which could be more reliable. In addition, we used a CTM and satellite observations from the OMI instrument to further support the estimated precursor emissions, which increased the robustness of our study.

Another limitation of our study is that the influence of meteorological conditions was not considered. Indeed, meteorological parameters, such as temperature, humidity and precipitation, influence the gas-phase formation of sulfate, gas-to-aerosol partitioning, and the wet and dry depositions of aerosols, which all contribute to the inter-annual variations in the $PM_{2.5}$ concentrations. According to Mu and Liao (2014), $PM_{2.5}$ concentrations exhibit large inter-annual variations in North China, especially during winter, when the meteorological parameters vary greatly. Indeed, North China had larger inter-annual variations in summer, whereas the SCB exhibited the smallest inter-annual variations among the polluted regions. In this work, we used annual mean values to compare concentrations and emissions, which might have partially reduced the variation of the uncertainties between seasons. However, future work is needed to more accurately quantify the relationship between precursor emissions and aerosol concentrations.

5 Concluding Remarks

In this study, we investigated the spatiotemporal variations of $PM_{2.5}$ compositions over China during 2005–2012, a period for which national ground measurements are unavailable, based on ground measurements obtained from literature and satellite-derived datasets, and sought to identify the driving forces underlying these changes. We found that SNA ranked the highest fraction in dust-free $PM_{2.5}$ concentrations (52–63% in different regions), followed by OM and BC, which accounted for 29–39% and 7–10% of $PM_{2.5}$ respectively. The estimated national population-weighted mean $PM_{2.5}$ concentration increased from 2005 to 2007, and subsequently decreased from 2007 to 2012. Of the three polluted regions studied here, the PRD was the only one to exhibit a persistent decrease in $PM_{2.5}$ after 2007; other regions had different peak and rebound years. The decline in the total $PM_{2.5}$ concentrations after 2007 was mainly attributable to sulfate reduction, whereas the rebound in $PM_{2.5}$ in 2011 was caused by persistent nitrate growth and a rebound in the sulfate concentration. The ratios between nitrate and sulfate increased over China from 2005 to 2012, further confirming the relative abundance changes of these two species.

Bottom-up emission inventories of the precursors SO_2 and NO_x were examined to explain the variations in these species. FGD operation in the power sector was the primary contributor to SO_2 reduction, whereas the growth of industrial emissions caused SO_2 emissions to rebound in 2011. Limited control measures implemented during 2005–2011 caused the NO_x emissions to increase rapidly, whereas the

SCR system installed in the power sector during the 12th FYP caused the NO_x emissions to decline in 2012. The SO_2 and NO_x emission trends were generally consistent with the sulfate and nitrate concentrations, respectively, but exhibited different relative change rates, which could be explained by the thermodynamic equilibrium of SNA.

In this study, our analysis mainly focused on the three selected regions (i.e., ECN, SCB and PRD), because they have high $PM_{2.5}$ levels, large anthropogenic emissions and large population densities. However, other places outside the three regions also experienced rapid industrialization and urbanization in recent years due to the national development strategies, which is important but has been paid less attention to. Future works could further improve the estimation of $PM_{2.5}$ composition datasets in these area and investigate the spatiotemporal variations of $PM_{2.5}$ concentrations and its driving forces.

This study's findings show that the simultaneous regulation of SO_2 and NO_x is crucial for $PM_{2.5}$ mitigation in China. A recent study (Cheng et al., 2016) reported that NO_x is not only a precursor for nitrate but is also an important oxidant contributing to sulfate formation in northern China. This finding highlights the importance of controlling NO_x emissions. The government has already implemented stricter control measures to reduce SO_2 and NO_x emissions in recent years. FGD devices have been promoted in iron and steel production to reduce industrial SO_2 emissions, and the use of SCR devices in the power sector also resulted in significant effects, causing the trend in NO_x emissions to decline since 2011 (de Foy et al., 2016; Liu et al., 2016; van Der A et al., 2016). Ground measurements from the national monitoring network established in 2013 demonstrate a decreasing trend in $PM_{2.5}$ over China since 2013, confirming the efficacy of the emissions controls implemented in China. In the future, more attention should be paid to curbing NO_x emissions.

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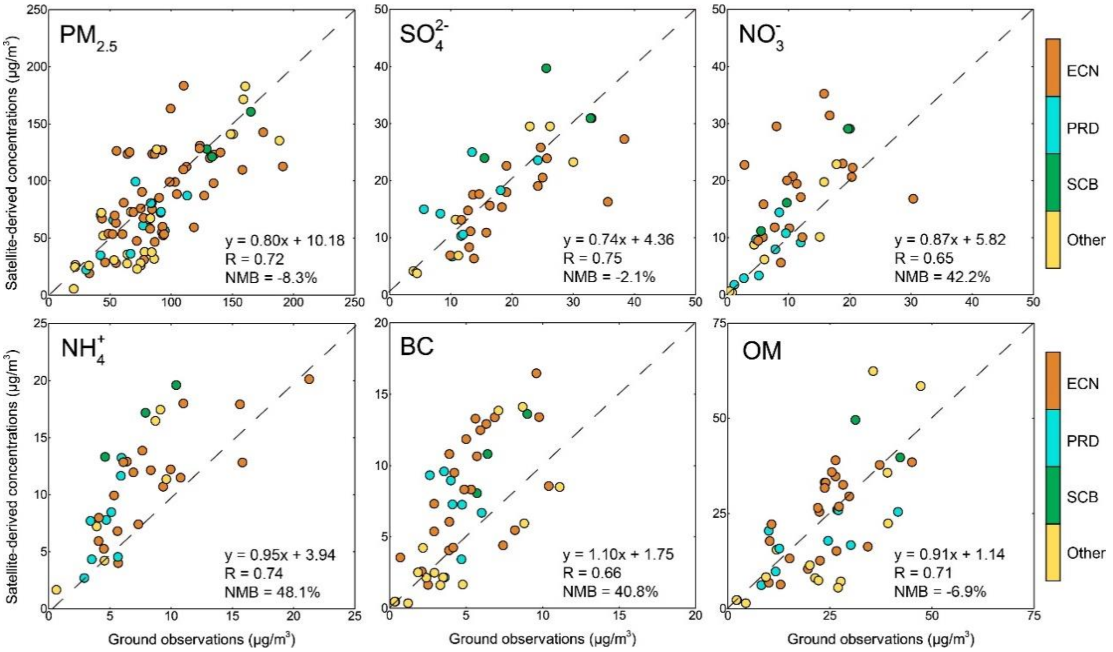


Figure 1. Evaluation of satellite-derived $PM_{2.5}$ and chemical composition concentrations using in situ data collected from the literature. The colors of the symbols represent the locations of the collected in situ data. The three defined regions are ECN (28–42°N, 110–123°E), PRD (20–25°N, 110–117°E) and SCB (27–33°N, 102–110°E). The dashed line corresponds to the 1:1 line in each panel.

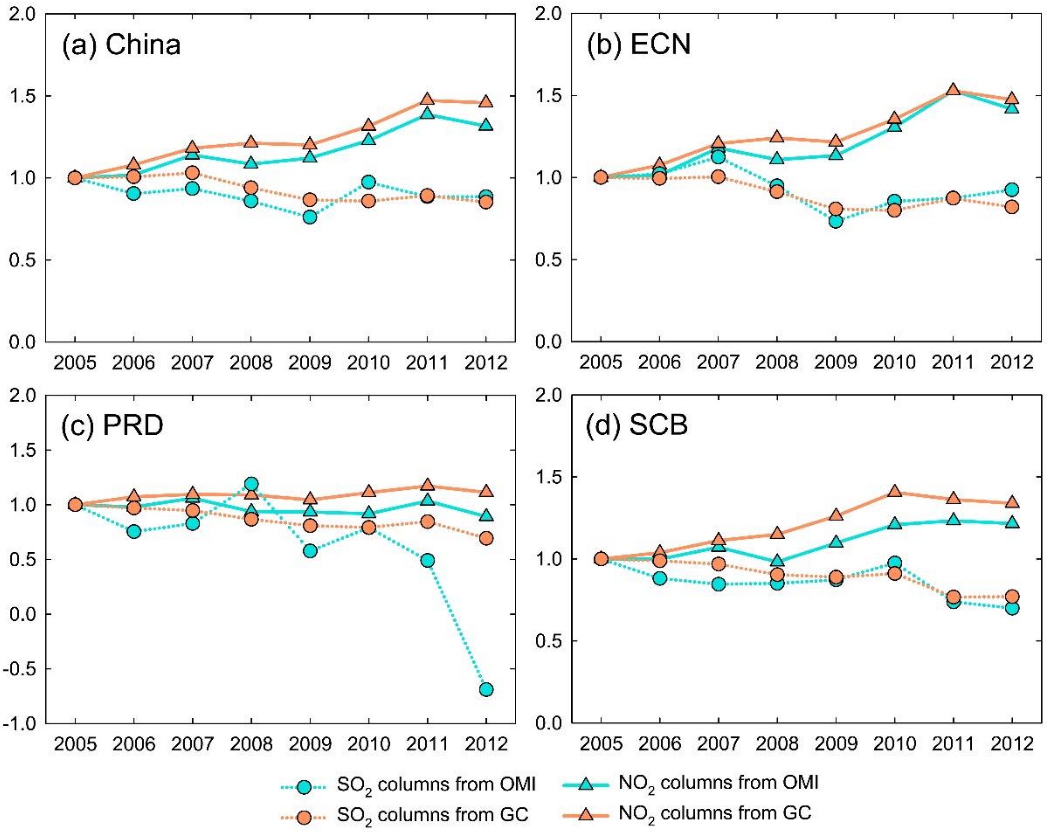
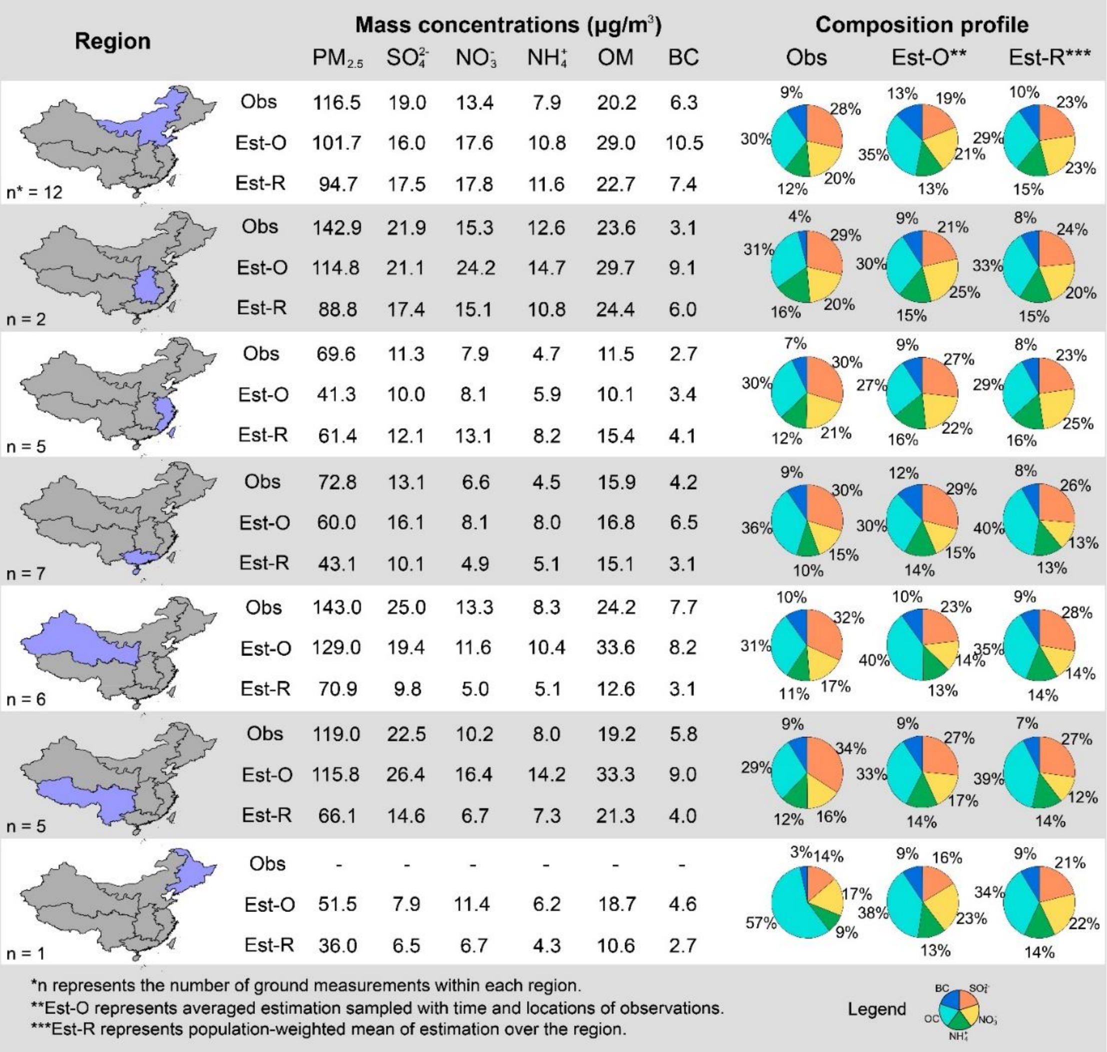


Figure 2. The inter-annual trends of the simulated and observed tropospheric column densities for SO_2 and NO_2 over (a) China, (b) ECN, (c) PRD and (d) SCB during 2005–2012. All data are normalized by the value in 2005. The dotted lines with circles denote SO_2, and the solid lines with triangles denote NO_2. Cyan and orange represent the satellite (OMI) and model (GC) values, respectively.



Region		Mass concentrations (μg/m^3)					
		PM$_{2.5}$	SO$_4^{2-}$	NO$_3^-$	NH$_4^+$	OM	BC
n* = 12	Obs	116.5	19.0	13.4	7.9	20.2	6.3
	Est-O	101.7	16.0	17.6	10.8	29.0	10.5
	Est-R	94.7	17.5	17.8	11.6	22.7	7.4
n = 2	Obs	142.9	21.9	15.3	12.6	23.6	3.1
	Est-O	114.8	21.1	24.2	14.7	29.7	9.1
	Est-R	88.8	17.4	15.1	10.8	24.4	6.0
n = 5	Obs	69.6	11.3	7.9	4.7	11.5	2.7
	Est-O	41.3	10.0	8.1	5.9	10.1	3.4
	Est-R	61.4	12.1	13.1	8.2	15.4	4.1
n = 7	Obs	72.8	13.1	6.6	4.5	15.9	4.2
	Est-O	60.0	16.1	8.1	8.0	16.8	6.5
	Est-R	43.1	10.1	4.9	5.1	15.1	3.1
n = 6	Obs	143.0	25.0	13.3	8.3	24.2	7.7
	Est-O	129.0	19.4	11.6	10.4	33.6	8.2
	Est-R	70.9	9.8	5.0	5.1	12.6	3.1
n = 5	Obs	119.0	22.5	10.2	8.0	19.2	5.8
	Est-O	115.8	26.4	16.4	14.2	33.3	9.0
	Est-R	66.1	14.6	6.7	7.3	21.3	4.0
n = 1	Obs	-	-	-	-	-	-
	Est-O	51.5	7.9	11.4	6.2	18.7	4.6
	Est-R	36.0	6.5	6.7	4.3	10.6	2.7

*n represents the number of ground measurements within each region.
**Est-O represents averaged estimation sampled with time and locations of observations.
***Est-R represents population-weighted mean of estimation over the region.

Figure 3. PM$_{2.5}$ composition concentrations and their fractions in seven regions over China. Region specific data were averaged from available ground measurements and satellite-derived data. Species shown only include sulfate, nitrate, ammonium, OM and BC. The observation data in Northeast China (Harbin) is only available in fractions, which is adopted from Wang et al. (2017). More details about the observation data and references are provided in Support Information.

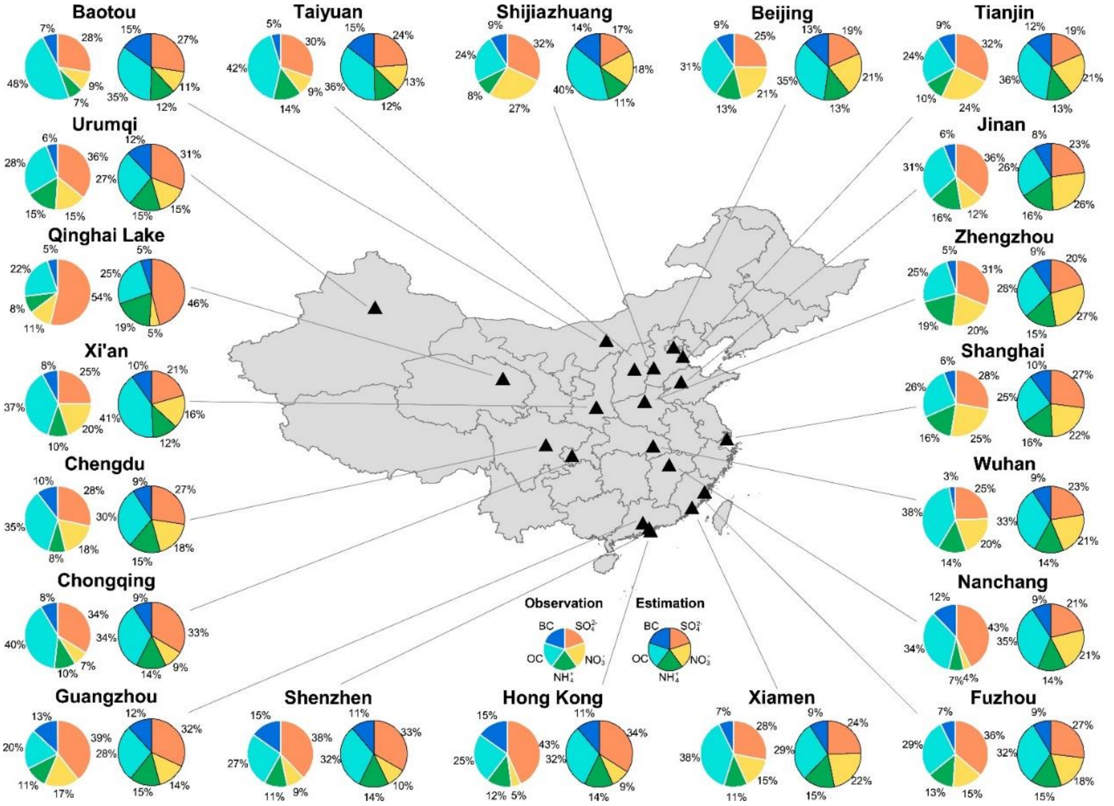


Figure 4. Observed and estimated $PM_{2.5}$ speciation for 20 major cities across China. Species shown only include sulfate, nitrate, ammonium, OC and BC. All observation data covered more than one year period. Details of the observations and references are provided in Support Information.

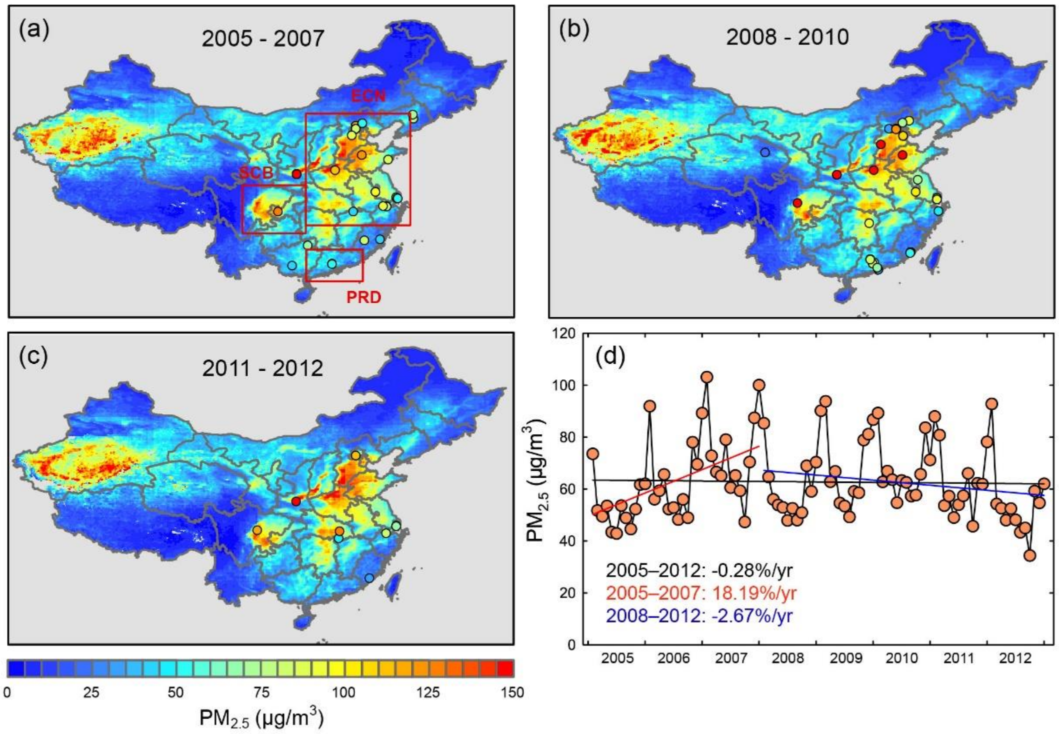


Figure 5. Spatial distributions of averaged PM$_{2.5}$ over China during (a) 2005–2007, (b) 2008–2010 and (c) 2011–2012 overlaid with ground measurements collected during the corresponding time period. (d) The population-weighted monthly mean PM$_{2.5}$ concentrations over China and their regression trend. Boxed areas outline the regions defined in this study.

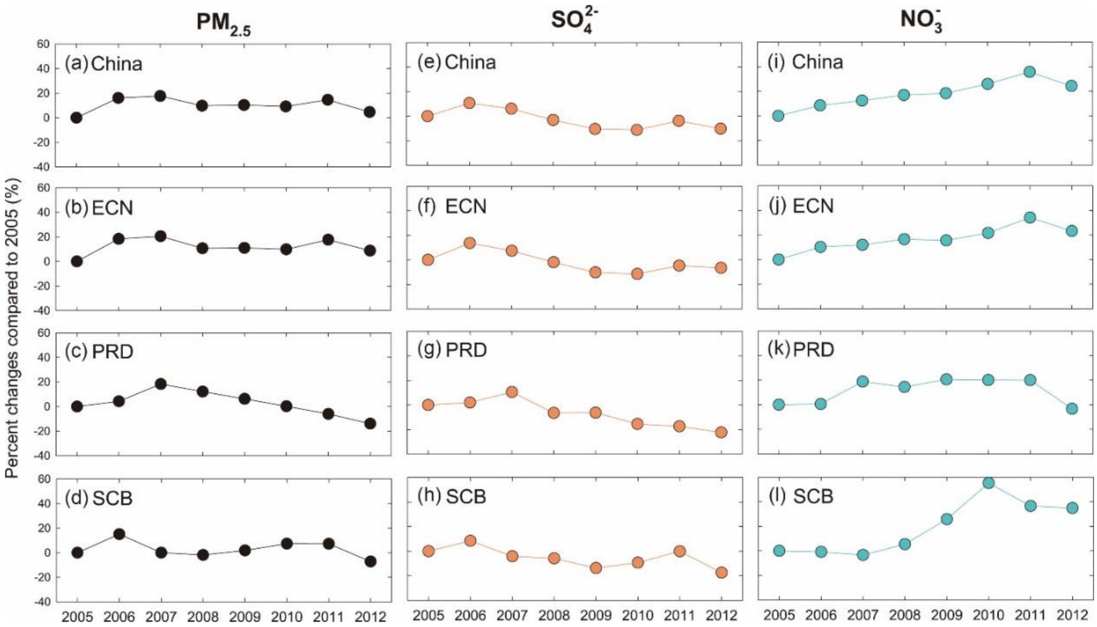


Figure 6. Inter-annual percent changes of (a-d) $PM_{2.5}$, (e-h) SO_4^{2-} and (i-l) NO_3^- concentrations compared to 2005 over China, ECN, PRD and SCB.

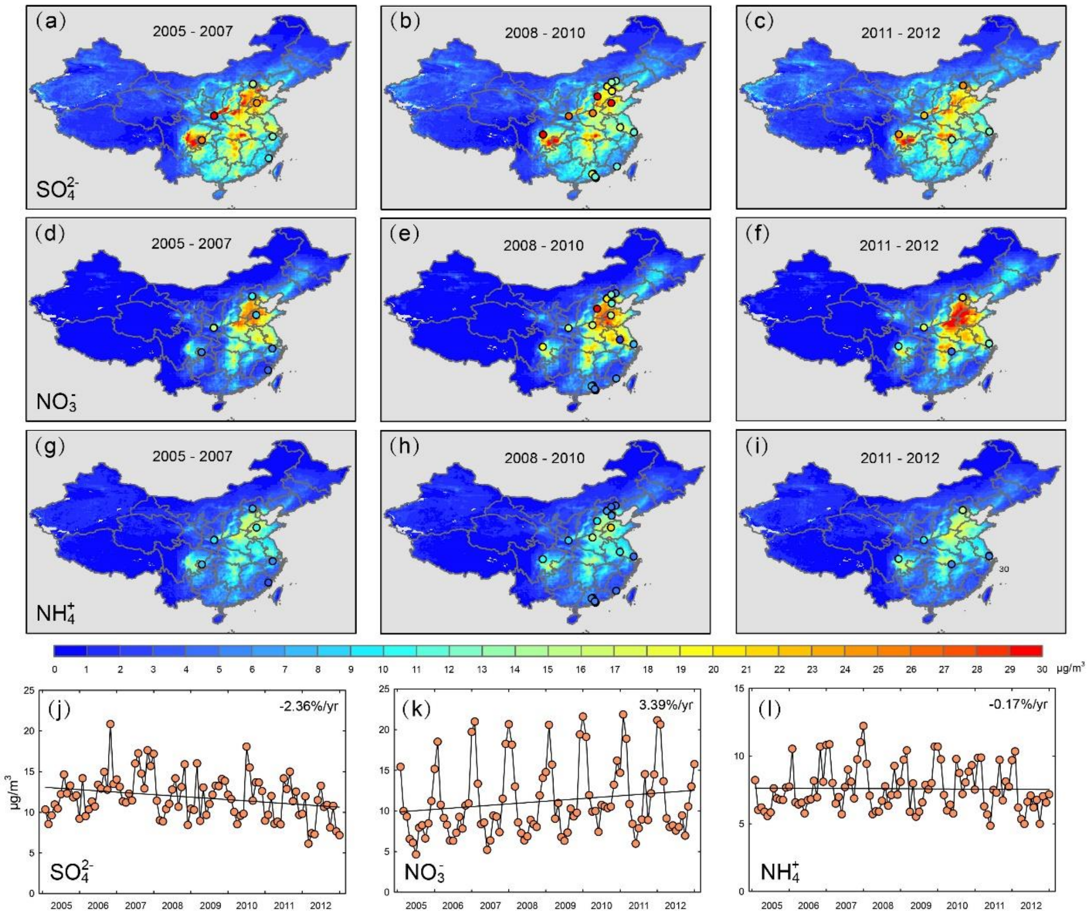


Figure 7. Spatial distributions of averaged (a-c) SO_4^{2-}, (d-f) NO_3^- and (g-i) NH_4^+ over China during 2005–2007, 2008–2010 and 2011–2012 overlaid with ground measurements collected during the corresponding time period. (j-l) The population-weighted monthly mean SO_4^{2-}, NO_3^- and NH_4^+ concentrations over China and their regression trends.

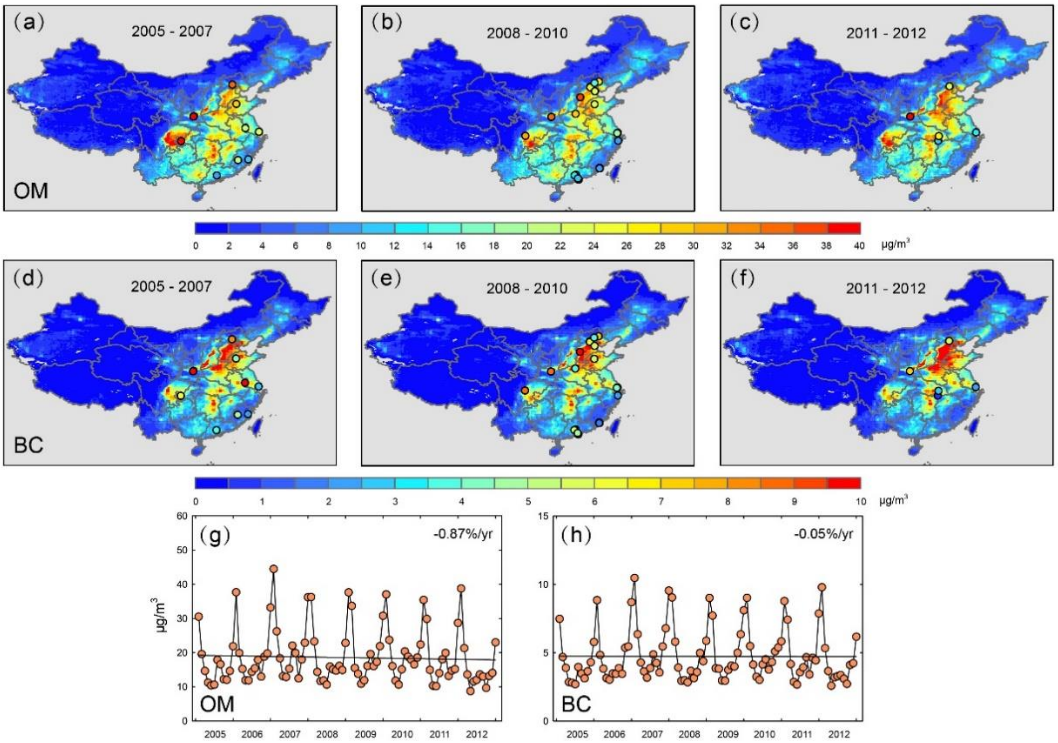


Figure 8. Spatial distributions of averaged (a-c) OM and (d-f) BC over China during 2005–2007, 2008–2010 and 2011–2012 overlaid with ground measurements collected during the corresponding time period. (g-h) The population-weighted monthly mean OM and BC concentrations over China and their regression trends.

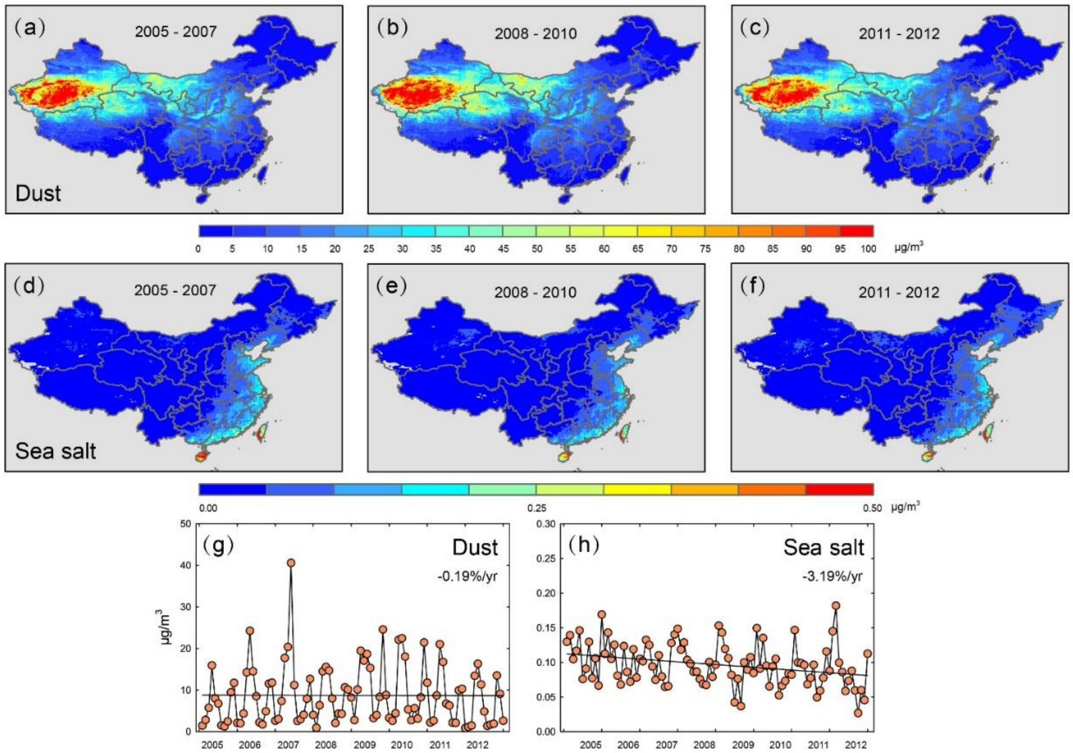


Figure 9. Spatial distributions of averaged (a-c) dust and (d-f) sea salt over China during 2005–2007, 2008–2010 and 2011–2012. (g-h) The population-weighted monthly mean dust and sea salt concentrations over China and their regression trends.

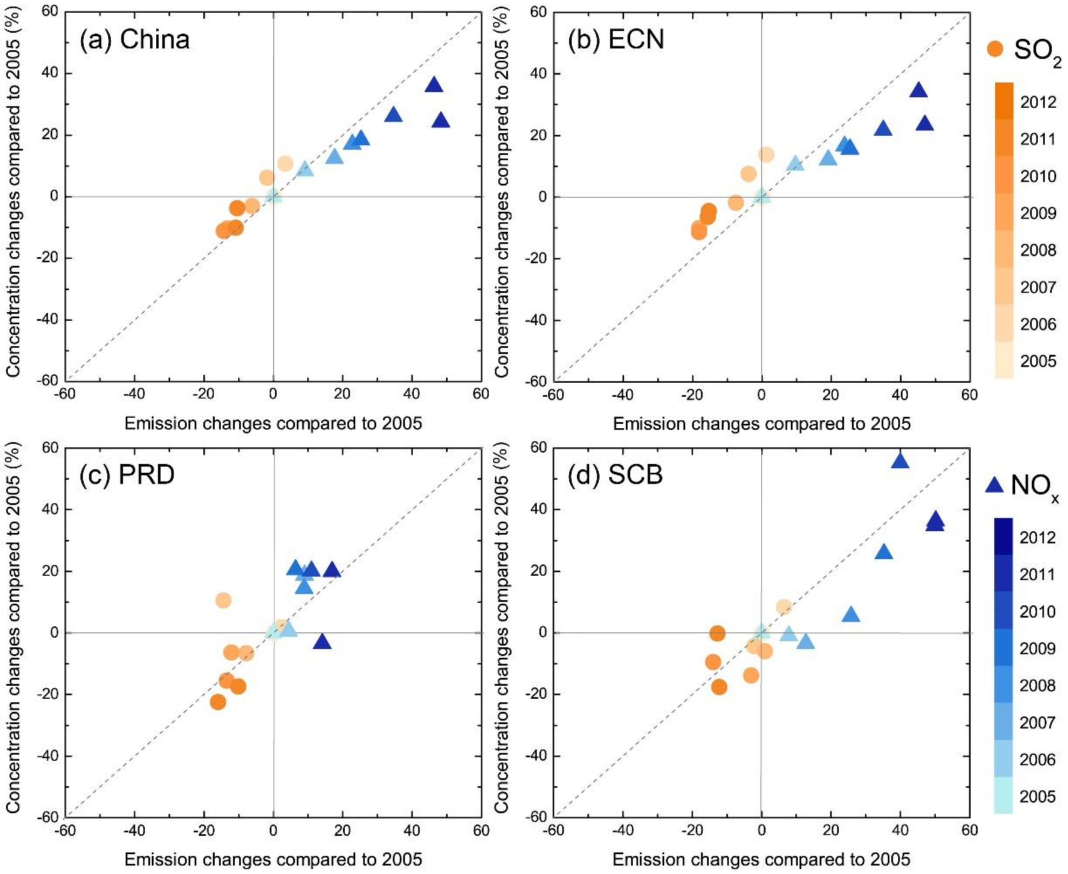


Figure 10. Comparisons of changes in the SO_4^{2-} and NO_3^- mass concentrations and their precursor emissions during 2005–2012. All data are presented as percent changes relative to 2005. The oranges circles and blue triangles represent SO_4^{2-} and NO_3^-, respectively, and the shades of the symbols' colors denote the year.

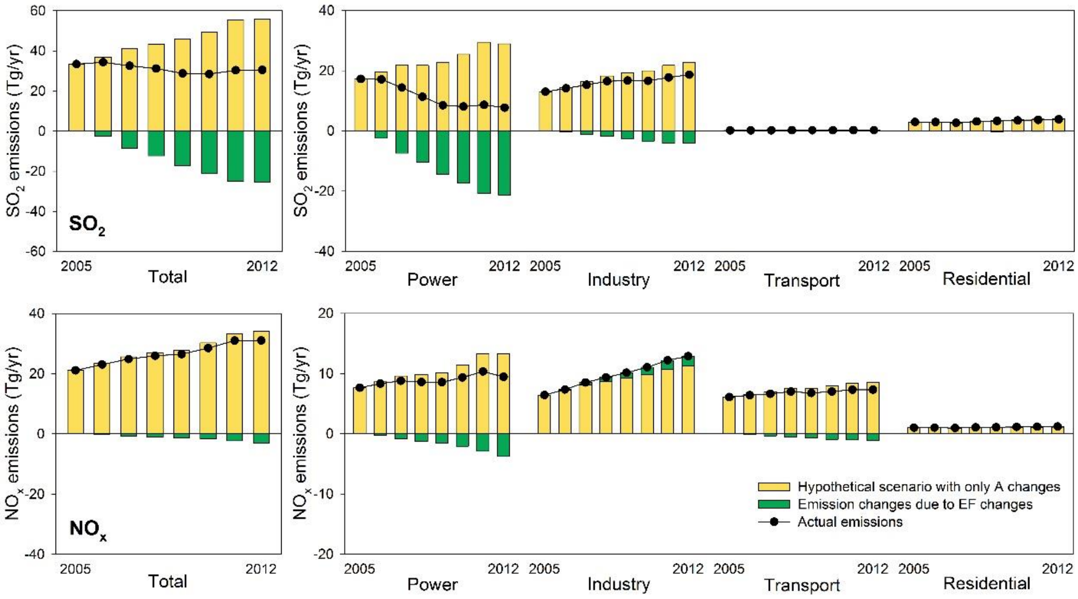


Figure 11. SO_2 and NO_x emissions by sector during 2005–2012 over China. The black circles denote the actual inter-annual emission trends estimated using the MEIC inventory. The yellow bars represent the hypothetical scenario involving only activity (A) changes. The green bars indicate the emission changes resulting from variations in the emission factor (EF). The top row illustrates the SO_2 emissions, and the bottom row presents the NO_x emissions.

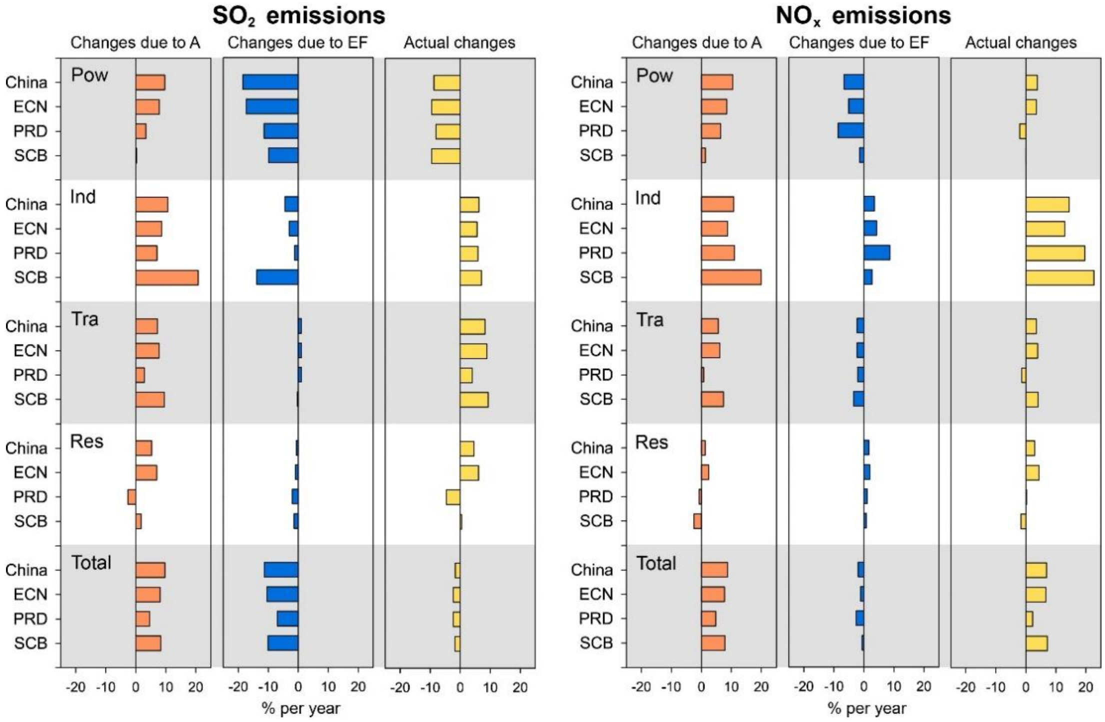


Figure 12. Summary of the average emission changes (% per year) during 2005–2012 for the power (Pow), industry (Ind), transport (Tra) and residential (Res) sectors over China and the three regions. Orange bars indicate the emission changes caused by activity (A) changes, and blue bars represent the emission changes caused by emission factor (EF) changes. Yellow bars present the actual emission changes estimated using the MEIC model.