

Authors reply to reviewer's comments:

Dear Anonymous Referees,

Thanks for your careful review of the manuscript. We read the reviewer's comments carefully, and have responded and taken all of reviewer's comments into consideration and revised the manuscript accordingly. All the changes have been highlighted and tracked changes in the revised manuscript. My detailed responses, including a point-by-point response to the review and a list of all relevant changes, is as follows:

“Interactive comment on “Changes in chemical components of aerosol particles in different haze regions in China from 2006 to 2013 and contribution of meteorological factors” by X. Y.

Zhang et al.

Anonymous Referee #1

Received and published: 23 September 2015

General Comment: Based on chemical composition of aerosol in different haze regions in China from 2006 and 2013 with 24h filter samples collected at 13 CAWNET stations, the authors discuss the sources of PM₁₀ and contribution of meteorological factors especially during haze episodes in key regions of China. As this dataset is obtained from a well-organized and continuously running network and filter samples have gone through the same analytical protocol and quality control, results from different sites and years are comparable, which provides valuable spatial and temporal trend information of PM₁₀ composition and sources in China. To understand sources of China is very much needed in China now in order to improve air quality and visibility. It provides a more complete picture of aerosol in China and valuable dataset for future study. The authors carry out detailed analysis of data and provide important and interesting results. Therefore, I would recommend to publish this manuscript. Some comments and suggestions are provided below to improve the quality of the manuscript.”

Responds: Thanks for the positive comments.

“Specific Comments:

“1) One of the key conclusion of this work is that dust is important source in PM₁₀ in China. Dust is probably calculated by the oxides of Al, Si, Fe etc. As these “crustal” elements are also found in coal fly ash, I would recommend the authors to show the equation for calculating dust and try to differentiate the contribution from dust and coal fly ash. If not possible, at least coal combustion during winter cold season in the northern China should be emphasized. ”

Responds: As mentioned by reviewer, mineral aerosol observed in China indeed contains coal-ash from incomplete combustion in most area of China. This is also the major point of us in our previous work (Zhang et al., AE, 2002) and in this manuscript (P10, L2-10). The original text in last version of the manuscript is “In general, a high mineral concentration was observed in northwest China, thereby indicating the influence of dust from natural Asian dust sources. However, in the southern margin of the Loess Plateau in XiAn, the mineral level exceeded those in stations closer to natural dust sources (Dunhuang, Galanshan etc). Thus, urban fly coal ash and fugitive dust sources were also observed to affect the mineral levels in these areas. Based on the measurement results of non-crustal Ca in coarse particle fractions, especially during non-spring seasons (with fewer occurrences of Asian sand and dust storm (SDS)), part of the mineral dust is hypothesized to originate from construction activities and coal ash (Zhang et al., 2002).”

Actually mineral dust is estimated by using the surrogate concentration of element (Fe) in this manuscript, which is around 4% in the Chinese mineral dust mass (see in P10, L10-13). This approach has been used in our previous works in various ambient conditions and areas in China, and has been proved to be able to estimate mineral dust content properly (Zhang et al., AE, 1993; Zhang et al., AE, 2002; Zhang et al., JGR, 2003; Zhang et al., ACP, 2012), although the uncertainties are still there. We didn't use the oxides of Al, Si, Fe, Ca, Mg, Ti to estimate mineral dust concentration, mainly because we found, in our previous work, that we can get similar concentration of mineral aerosol by using the simple method (just on the basis of Fe, like this manuscript) and by using oxides of various element, which will probably bring the extra uncertainties due to limitation of elemental analysis; another reason is that we can not obtain Si, Al in relative higher accuracy by using Whatman quartz microfibre filters as the filtration media that we used to measure water-soluble constituents, carbonaceous species and mineral aerosol simultaneously.

Of course, we found we don't want to distinguish the relative contributions of coal-ash and other sources to mineral mass by only using Fe (no one can do this). But we added some more descriptions about the approach how to estimate the mineral mass, and some text to emphasis the existence of coal ash in mineral aerosol concentration (P10, L12-25), which also reinforce the major conclusion of this manuscript that “coal-combustion was still the largest anthropogenic source of aerosol pollution in various areas in China”

“2) Page 19219: the last paragraph in section 3, the authors suggest the contribution from biomass burning and motor vehicle simply based on EC/OC ratio. This ratio is not very specific to sources. Even for the same source type, e.g., biomass burning, this ratio can have a range under different fuel types and combustion conditions. Therefore, it should be careful in such discussion if it is only based on EC/OC ratio. “

Responds: As reviewer's comment, it is not very precise to pinpoint the contributions from biomass burning and motor vehicle by simply using EC/OC ratio, but it still can provide some insights into it, because the large differences do exist in OC/EC ratios for biomass burning (5.9-8.9) and motor vehicle (1.4-3.0) emission.

We added some sentences to mention the uncertainties and weaken this speculation according to reviewer's suggestion in P17, L6-7.

“3) The discussion and description in this manuscript contain many numbers and details. It would be easier to read if it is better organized and more clear after revision.”

Responds: Some revisions have been made. We provide less number as possible as we can to increase the readability of this manuscript. We also added a “Table 3” in summary section to put all numbers on to make a comparison between the normal regional background and winter concentration of major chemical components in major haze regions of China. That makes text more clear (P34, Table 3).

4) The summary is too detailed and long. It should contain key points and conclusions from this work.”

Responds: Revised. We simplified many text, and place lots of number on the table 3.

“Interactive comment on “Changes in chemical components of aerosol particles in different haze regions in China from 2006 to 2013 and contribution of meteorological factors” by X. Y. Zhang et al.

Anonymous Referee #2

Received and published: 15 August 2015

This study reveals the reasons for severe haze-fog event formation in Jan. 2013 by investigating the changes in major chemical components over recent years in different haze regions. The authors also evaluate the relative contribution of meteorological conditions during the haze process by introducing a parameterized index. The paper presents solid findings that are of interest to the readers to understand the aerosol characteristics and emission sources over a large area in China. The data reported are valuable to validate regional/global models. The paper is of good scientific and well structured, worth of being published in ACP after some revisions.”

Responds: Thanks for the positive comments from reviewer.

Major comments:

“1. There is no clear statement to describe how to retrieve mineral aerosol or dust mass concentration. A description of the approach to calculate mineral aerosol is necessary.”

Responds: We revised the text to have more detailed description about the estimation approach of mineral dust concentration (P10, L12-25).

“2. In figure 2, it gives the information of “dust”, but in the text and other tables and figures, the authors use “mineral”. They should keep consistent if they refer to the same component.”

Responds: In this figure we used “dust” for saving space season to simply denote “mineral dust” that is we commonly used in the text and other tables.

“3. P17, L4-5, it is not clear that in which winter, the EC concentration is 21 $\mu\text{g}\cdot\text{m}^{-3}$. P18, L27, Dose the 23 $\mu\text{g}\cdot\text{m}^{-3}$ refer to the mass concentration of ammonium in winter 2013?”

Responds: Revised and pointed out that it is winter of 2012

“4. P21L5-9, do these processes the author mentioned, coal ash, fugitive dust, etc. have significant seasonal variation, which can be the reason for higher mass concentration of mineral dust in winter?”

Responds: Thank you for the suggestion. We made a further statement that coal-ash contribute the increased mineral dust mass in winter season (P25, L2-7).

5. P11, Pragraph 1, it should be clarified that if “PM level” in this section represents the PM10 mass concentration. The English shall be polished by a native speaker.

Responds: Changed and polished

Some specific points are shown below:

1. In the abstract, the name of “Yangtzi River Delta” is used, but in other sections, it is “Yangtze River Delta”. It should be consistent and “Yangtze River Delta” should be used.

Responds: Accepted and unified.

2. P4, L13: “questions was” should be changed as “questions were”. P8, L15: please keep these parameters, c'andc;_'(c) and _(c)beingconsistent: P8, L22, “_e” the letter “e” should be the subscript, “_e”.

Responds: Revised.

3. P11, L11, it should be “went up to 160.”

Responds: Revised

4. P11, L14, it should be “PRD areas”.

Responds: Revised

5. P12, L10, “OC accounted 8 P12, L20, “ accounted 33

Responds: The “~” is correct, it means about.

6. P13, L23, the unit of 2.5, “ τ m” should be supplemented. It is the same in P28L15.

Responds: Added

7. P18, L9, “plenary boundary” should be changed as “planetary boundary layer”.

Responds: Corrected

8. In Figure 2a, the unit of mass concentration should be given in the legend.

Responds: Changed

9. There are some other grammar mistakes that the authors should pay more attention to.

Responds: Modified.

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Changes in Chemical Components of Aerosol Particles in Different Haze Regions in China from 2006 to 2013 and Contribution of Meteorological Factors

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1 **Abstract:**

2 Since individuals experienced persistent haze-fog events in January 2013 in central-eastern
3 China, questions on factors causing differences in drastic changes in 2013 from those in adjacent
4 years have been raised. Changes in major chemical components of aerosol particles over the years
5 also remain unclear. The extent of meteorological factors contributed to such changes is yet to be
6 determined. The study intends to present the changes in daily-based major water-soluble
7 constituents, carbonaceous species and mineral aerosol in PM₁₀ at 13 stations within different haze
8 regions in China from 2006 to 2013, associated with specific meteorological conditions that are
9 highly related with aerosol pollution (parameterized as an index called “PLAM”). No obvious
10 changes were found in annual mean concentrations of these various chemical components and PM₁₀
11 in 2013, relative to 2012. By contrast, wintertime mass of these components were quite different, in
12 Hua Bei Plain (HBP), sulfate, OC, nitrate, ammonium, EC, and mineral dust concentrations in
13 winter were approximately 43 μg m⁻³, 55 μg m⁻³, 28 μg m⁻³, 23 μg m⁻³, 21 μg m⁻³ and 130 μg m⁻³,
14 respectively; these masses were approximately two to four times higher than those in background
15 mass, also exhibiting a decline during 2006 to 2010, and then a rise till 2013. The mass of these
16 concentrations and PM₁₀, except mineral, respectively increased by approximately 28% to 117%
17 and 25% in January 2013 compared with that in January 2012. Thus, persistent haze-fog events
18 occurred in January 2013, and approximately 60% of this increase in component concentrations
19 from 2012 to 2013 can be attributed to severe meteorological conditions in the winter of 2013. In
20 Yangtze River Delta (YRD) area, winter masses of these components, unlike HBP, did not
21 significantly increase since 2010; PLAM was also maintained at a similar level without significant
22 changes. In the Pearl River Delta (PRD) area, the regional background concentrations of the major
23 chemical components were similar to those in YRD; accounted approximately 60-80% of these in
24 HBP. Since 2010, a decline was found for winter concentrations, which can be partially attributable
25 to a persistent bettering meteorological conditions and the emission cutting with an emphasis on
26 coal-combustion in this area.

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1 In addition to the scattered and centralized coal-combustion for heating, burning biomass fuel
2 contributed to the large increase in the concentrations of carbonaceous aerosol in major haze
3 regions, except in PRD, in winter. No obvious changes were found for the proportions of each
4 chemical components of PM₁₀ from 2006 to 2013. Among all of the emissions recorded in chemical
5 compositions in 2013, coal-combustion was still the largest anthropogenic source of aerosol
6 pollution in various areas in China, with higher sulphate proportion of PM₁₀ in most areas of China.
7 OC normally ranked the third. PM₁₀ concentration increased by approximately 25% in January of
8 2013 relative to 2012 that caused persistent haze-fog events in HBP; emission also reduced by
9 approximately 35% in Beijing and its vicinity (BIV) in late fall of 2014, thereby producing “APEC”
10 blue; thus one can expect that the persistent haze-fog events would be reduced significantly in the
11 BIV, if ~ one-third of the 2013 winter emission could be reduced, which can also be viewed as the
12 upper limit of atmospheric aerosol pollution capacity in this area.

13

14 **Author Keywords: aerosol chemical component, change, metrological contribution, emission-**
15 **cutting, different haze regions, China**

1. Introduction

From satellite-based aerosol optical depth, ambient fine particulate matter concentrations were found to have a high loading area with China as major body in the world (Donkelaar and Villeneuve, 2010). Globally, mass concentrations of six major types of chemical components in aerosol particles in China were also found to be just lower than those in urban S. Asian area but far higher than those in Europe and N. America (Zhang et al., 2012a), with large variation in time and space (Zhang et al., 2008;He et al., 2001;Hu et al., 2002;Yao et al., 2002;Ye et al., 2003;Zhang et al., 1993;Zhang et al., 2002;Li et al., 2014;Xu et al., 2014;Yin et al., 2012). Moreover, approximately 37.5 billion tons of standard coal are consumed as energy source in China; approximately 66% of the produced energy was attributed to coal consumption in 2013 (NBS-China, 2014). Because the aerosol particles and cloud (fog) droplet can influence atmospheric visibility (Watson, 2002); and in the ambient atmosphere, no cloud (fog) can be formed if no hygroscopic aerosols can be activated to cloud condensation nuclei (CCN) or ice nuclei (IN) (Twomey, 1977;Seinfeld and Pandis, 1997), high loadings of aerosols not only affect climate change (Forster et al., 2007;Boucher et al., 2013), but also adversely influence weather (Wang et al., 2010;Pérez et al., 2006) and contribute to the occurrence of haze and fog events; both of them can be considered as types of aerosol pollution in present day China (Zhang et al., 2013). Since individuals experienced persistent haze-fog events in January 2013 in central-eastern China, the change of aerosol particles and their chemical component are attracting special attentions in this rapid economic growth and high population density area (Wang et al., 2014c;Huang et al., 2014;Zhang et al., 2013;Guo et al., 2014;Wang et al., 2014a;Wang et al., 2014b;Wang et al., 2015;Sun et al., 2014). However, questions were raised about what changes happened to the major chemical components of aerosol in different haze areas in China during recently year? Why a big difference existed in 2013 and an adjacent year in the case of no significant changes in emission? What extent of meteorological factors contributed to the change?

China can be classified into nine typical regions with similar visibility changes in each

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1 (Zhang et al., 2012a); four of these regions have experienced the largest loss of visibility in recent
2 decades, particularly (1) Hua Bei Plain in North China and Guanzhong Plain. This region also
3 includes “Jing-Jin-Ji” or called “Beijing-Tianjin-Hebei (BTH) region with the rapid economic
4 development; this area is also considered as Haze Region II in China; (2) East China with the main
5 body in Yangtze River Delta area (Haze Region III); (3) South China comprising Guangdong and
6 Pearl River Delta area (Haze Region V); (4) Si Chuan Basin in Southwest China (Haze Region VI)
7 (Figure 1). Changes in major chemical components of aerosol in these different haze areas also
8 remain unknown. These changes are also important to explore the reasons of the occurrence of
9 severe haze-fogs in China in recent years.

10 Various meteorological factors, including wind speed, wind direction, air pressure,
11 temperature, humidity, precipitation, and atmosphere stability, are possibly related to aerosol
12 pollution, but each meteorological factor cannot completely and quantitatively indicate the
13 integrated situation of meteorological conditions that may aggravate aerosol pollution (Sui et al.,
14 2007;Pang et al., 2009). However, mechanisms by which these meteorological impacts can be
15 quantified and by which these data can be used to diagnose aerosol pollution based on a longer time
16 scale of emission changes than meteorological factors (Wang et al., 2012;Yang, 2009).

17 Long-term daily-based aerosol chemical components were determined here for aerosol
18 particles with diameter less than 10 μm (PM_{10}) from regionally representative measurement
19 networks (China Atmosphere Watch network-CAWNET) from 2006 to 2013. The parameterized
20 index (PLAM) (Wang et al., 2012; Yang, 2009) was also used in this study to evaluate specific
21 meteorological conditions and their connections with severe aerosol pollution. This study
22 investigates the changes and the extent of these changes by analyzing chemical component changes
23 and meteorological factors; this study also determined the relative contribution of specific
24 meteorological conditions in winter. These chemical component data, especially in 2012 and 2013,
25 can also be used as a basis to evaluate various control measures that have been used. After 2013, the
26 Chinese government promoted ten prevention and countermeasures for aerosol pollution control

1 called “Atmospheric Pollution Prevention and Control of the Ten Measures of China.” The
2 government also released the Second Atmospheric Pollution Control Special Plan. All these have
3 gained increasing attention among researchers to reduce emission caused by aerosol with an
4 emphasis on coal combustion and industrial manufacturing processes, mainly in steel mills,
5 chemical plants, glass, and cement plants. The long-term chemical characterization of aerosols in
6 China is also essential to assess the effect of aerosols in the atmosphere and climate, and the results
7 can be used to evaluate and improve existing haze-fog forecasting systems.

8 **2. Sample Collection and Analyses**

9 **2.1. Sampling Description**

10 24-hr aerosol filter samples were collected at 13 CAWNET stations on a one day in every three
11 day basis from 2006 to 2013. These CAWNET stations are operated by the China Meteorological
12 Administration (CMA), as shown in Figure 1 and the details of these stations have been reported in
13 previous studies (Zhang et al., 2012a; Zhang et al., 2008). Aerosol samples were collected by using
14 MiniVol™ air sampler (Airmetrics, Oregon USA) operated at an ambient air flow rate of 5 l/min
15 for 24 hours from 9:00 AM to 9:00 AM (BST) the following day. The filtration media were 47 mm
16 Whatman quartz microfibre filters (QM/A) that were cleaned by heating at 800°C for 3 hours
17 before use.

18 *Insert [Figure 1] here*

19 **2.2. Aerosol chemical component analyses**

20 The elemental concentrations were analyzed directly via X-Ray Fluorescence (XRF) method
21 using X-Lab 2000 (SPECTRO, Germany) at the Key Laboratory for Atmospheric Chemistry (LAC),
22 Chinese Academy of Meteorological Sciences (CAMS). Eighteen elements, namely, As, Br, Ca, Cr,
23 Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Se, Ti, V, Zn and Zr were analyzed using a Multi-Channel
24 Analyzer that was calibrated using a standard plastic sample to check the signal energy and the

1 multi-channel twice a month. The XRF spectrometer includes a high-tech detector using a silicon
2 lithium drifted crystal cooled at a low temperature (-90°C). This crystal is able to discriminate
3 between X-ray photons of different energies, i.e. energy dispersion. Four different targets (Mo, Co,
4 Al₂O₃, and Highly Oriented Pyrolytic Graphite (HOPG)) with different energy are employed to
5 identify different elements. For the Mo target, the energy range is 25 keV, which is suitable for Cr,
6 Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Pb and Zr. The Al₂O₃ target with a working energy of 50 keV is
7 deal for Cd, Sb and Ba while the Co target has an energy range of 12.5 keV for the analysis of K,
8 Ca, Ti, V, Cr, Mn. The HOPG target's working tube voltage is 12.5keV, which is good for Na, Mg,
9 Al, P, S and Cl. Eighteen elements, i.e. As, Br, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Se, Ti, V,
10 Zn and Zr, were analyzed by the Multi-Channel Analyzer. A standard glass sample (Spectro Corp.
11 Germany) was used to check the signal energy and the multi-channel twice a month. The standard
12 calibration curve between the intensity of signal and the elemental concentration is determined by
13 single-element Mylar filters. Seven blank quartz filters were analyzed with Mylar matrices method.
14 The averaged background of blank filters was subtracted during spectral processing. The detailed
15 procedures at (LAC, CAMS) can be found in previous studies (Zhang et al., 2012a).

16 After XRF analysis, a portion of the filter samples was extracted with 25 ml of double-
17 deionized water (DDI) using a 3" x 5" clean-room Poly bag (Clean Room Products, In.,
18 Ronkonkoma, NY). The resulting extracts were analyzed for SO₄²⁻, NO₃⁻, NH₄⁺ and other ionic
19 species, including Na⁺, K⁺, Ca²⁺, Mg²⁺, F⁻ and Cl⁻ by ion chromatography (Dionex JCS 3000) with a
20 OmniPac Pax-500 column, 25 mM H₂SO₄ autoregenerant, gradient elution (from 5 to 28.75 mM
21 NaOH/5% methanol) at the Key Laboratory of Atmospheric Chemistry, CMA. The detailed
22 protocol can be found in a previous study (Zhang et al., 2002).

23 Thermal/optical reflectance carbon (TOR) analysis method for element carbon (EC) and
24 organic carbon (OC) content was performed following the Interagency Monitoring of Protected
25 Visual Environments (IMPROVE) protocol (Chow et al., 1993;Chow et al., 2004). The sample
26 filter was heated stepwise at temperatures of 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C

1 (OC4) in a non-oxidizing (He) atmosphere, and at 550°C (EC1), 700°C (EC2), and 800°C (EC3) in
2 an oxidizing atmosphere of 2% oxygen and 98% He. Evolved carbon is oxidized to CO₂, and then
3 reduced to CH₄ for detection by FID. The pyrolyzed or charred OC is monitored by reflectance at
4 $\lambda = 633$ nm. The portion of EC1 until the laser signal returns to its initial value is assigned to
5 pyrolyzed organic carbon (OP). The OC is defined by the sum of OC1, OC2, OC3, OC4, and OP
6 while the EC is defined by EC1+EC2+EC3-OP. The detailed procedures at (LAC, CAMS) can be
7 found in previous studies (Zhang et al., 2008).

8 **2.3. Parameterized a index (PLAM) for evaluating specific meteorological condition that** 9 **resulted in severe aerosol pollution**

10 In this study, we used a parameterized index, namely, Parameter Linking Aerosol Pollution
11 and Meteorological Elements (PLAM), which was derived from a relationship of PM₁₀ and key
12 meteorological parameters from 2000 to 2007 from various region of China by our group. The
13 PLAM index has been used to evaluate the contribution of meteorological factors to changes in
14 atmospheric composition and optical properties over Beijing during the 2008 Olympic Games
15 (Zhang et al., 2009), and to identify the contribution of specific meteorological factors to the ten-
16 day haze-fog event in 2013 (Zhang et al., 2013). Based on a set of weather sensitive parameters, an
17 integrated index “PLAM” was parameterized (Wang et al., 2012; Yang, 2009). Among these factors,
18 high temperature, high humidity, moderate wind, and high stability were the most relevant to the
19 poor air-quality in China. The PLAM was thus established as a function of the following
20 parameters::

$$22 \quad \text{PLAM} (F) \in f(p, t, w, \text{rh}, e, s, c', \dots) \quad (1)$$

23
24 where p , t , w , rh , e , s , and c' represent air pressure, air temperature, winds, relative humidity,
25 evaporability, stability, and effective parameter associated with the contribution of air pollution

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1 $\beta(c')$, respectively.

2 A stable summer weather with high air temperature, high relative humidity, moderate winds,
3 and stability might create a microenvironment for high PM₁₀ concentrations in August over Beijing
4 (Yang, 2009), and this climate corresponds to static dynamic forcing (baroclinicity) and thermal
5 forcing (equivalent potential temperature (θ_e) gradient) in moist adiabatic processes in the
6 atmosphere (Gao et al., 2004). Part of the temperature profile is between the adiabatic lapse rate
7 (neutral stability) and the isothermal lapse rate (Johnson and Baker, 1997). Condensation is also a
8 key factor that contributes to intense pollution at given weather conditions in the moist adiabatic
9 processes in the atmosphere. Apparently, the final PLAM can be attributed to two major separate
10 factors: (1) initial meteorological conditions $\alpha(m)$ associated with the atmospheric condensation
11 processes and (2) a dynamic effective parameter associated with the initial contribution of air
12 pollution $\beta(c)$ such as:

$$14 \quad \text{PLAM} = \alpha(m) \times \beta(c). \quad (2)$$

15
16 The details have been described in the reference (Wang et al., 2012; Yang, 2009).

17 3. Results and Discussion

18 3.1. Spatial distribution of chemical components

19 The CAWNET observational network covers all areas of China with 30 ground-based stations
20 that have been operating since 2006. The concentrations of SO₄²⁻, OC, NO₃⁻, NH₄⁺, EC, and mineral
21 aerosol were measured in this paper by using PM₁₀ filter samples collected from 13 stations, which
22 are located in Haze Region I (Dalian), Haze Region II (Gucheng, Zhengzhou and XiAn), Haze
23 Region III (LinAn, Jinsha and Change), Haze Region V (Panyu and Nanjing), Haze Region VI
24 (Chengdu), Haze Region VIII (Lasha, but data in this study were just from 2006 to 2010), and Haze
25 Region IX (Gaolanshan and Dunhung) (Figure 1, and (Zhang et al., 2012a)). Mineral aerosol was

1 the largest component in almost all stations based on the five-year average data from 2006 to 2010
2 (Figure 2a). Thus, high “dust” is a character in aerosol pollution in China. In general, a high mineral
3 concentration was observed in northwest China, thereby indicating the influence of dust from
4 natural Asian dust sources. However, in the southern margin of the Loess Plateau in XiAn, the
5 mineral level exceeded those in stations closer to natural dust sources (Dunhuang, Galanshan etc).
6 Thus, urban fly coal ash and fugitive dust sources were also observed to affect the mineral levels in
7 these areas. Based on the measurement results of non-crustal Ca in coarse particle fractions,
8 especially during non-spring seasons (with fewer occurrences of Asian sand and dust storm (SDS)),
9 part of the mineral dust is hypothesized to originate from construction activities and coal ash
10 (Zhang et al., 2002). As such, even in the southern part of China, where the influence of Asian dust
11 is low, the concentrations of these minerals are still significant. Mineral dust was characterized by
12 using the surrogate concentration of Fe, which is around 4% in the Chinese mineral dust ~~mass. This~~
13 ~~approach has been used in our previous papers in various ambient conditions and areas in China,~~
14 ~~and has been proved to be able to estimate mineral dust content properly~~ (Zhang et al., 1993; Zhang
15 et al., 2003; ~~Zhang et al., ACP, 2012a~~), although the uncertainties are still present. ~~We didn't use~~
16 ~~the oxides of Al, Si, Fe, Ca, Mg, Ti to estimate mineral aerosol concentration, mainly because we~~
17 ~~found, in our previous work, that we can get similar concentration of mineral aerosol by using this~~
18 ~~simple method (just on the basis of Fe) and by using oxides of various element, which will probably~~
19 ~~bring the extra uncertainties due to limitation of elemental analysis; another reason is that we can~~
20 ~~not measure Si, Al in relative higher accuracy by using Whatman quartz microfibre filters as the~~
21 ~~filtration media for simultaneously measuring water-soluble constituents, carbonaceous species and~~
22 ~~mineral aerosol.~~
23 ~~It is hard to separated the relative contributions of coal-ash and other sources to mineral~~
24 ~~aerosol mass by only using Fe, but the contribution of coal ash to mineral aerosol do existed in~~
25 ~~China. However, the contribution of this part from incomplete coal-combustion, tended to be~~
26 ~~ignored in the previous source apportionment, which desert to pay a further attention.~~

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1 The highest mean concentrations of SO_4^{2-} in aerosol particles from 2006 to 2010 were larger
2 than $33 \mu\text{g m}^{-3}$ at the urban stations of XiAn, Zhengzhou in Haze Region II, and at Chengdu of
3 Haze Region VI. This result indicates that the effect of coal combustion emission was high in these
4 areas (Figure 2a). The lowest concentrations ($<6 \mu\text{g m}^{-3}$) were observed in the western desert area
5 (Dunhuang) and the Tibetan Plateau (Lasha). Thus, the effect of coal combustion is low. The spatial
6 patterns of total inorganic ammonia ions (NH_4^+) in China are fairly similar to those of SO_4^{2-} and
7 NO_3^- . Aside from XiAn, Zhengzhou, and Chengdu, stations with high NO_3^- concentrations also
8 include those further north of China (Gucheng and Dalian) with concentrations $>11 \mu\text{g m}^{-3}$, even at
9 Panyu in Pearl River Delta area of the Haze Region V, mainly because of the influences from both
10 motor vehicle and coal-combustion as well as natural gas burning (reason discussed later).

11 The concentrations of OC and EC are similar to the distribution of SO_4^{2-} , and the highest
12 concentrations of OC ($20 \mu\text{g m}^{-3}$ to $30 \mu\text{g m}^{-3}$) and EC ($7 \mu\text{g m}^{-3}$ to $10 \mu\text{g m}^{-3}$) at XiAn, Zhengzhou,
13 Gucheng, and Chengdu, in Haze Region II and Haze Region VI in southwestern China, and the
14 lowest concentrations were observed in rural northwest China and at the Tibetan Plateau. These
15 higher levels are typically observed in regions with a high population density and are associated
16 with emissions from biomass burning, traffic, and power generation (Zhang et al., 2012a).

17 *Insert [Figure 2a;b] here*

18 **3.2. Chemical proportions of PM_{10} and their changes from 2006 to 2013**

19 From Figure 2b, the highest concentrations of PM_{10} during 2013 were observed at urban
20 stations of XiAn ($\sim 320 \mu\text{g m}^{-3}$), followed by $200 \mu\text{g m}^{-3}$ to $240 \mu\text{g m}^{-3}$ at Gucheng and Zhengzhou.
21 These stations are all located in Haze Region II (the HBP area), which is considered as the most
22 seriously polluted region in China in terms of aerosol pollution. This result is similar with those
23 obtained from 2006 to 2007 (Zhang et al., 2012a). In rural northwest China (Gaolanshan and
24 Dunhuang station), the PM_{10} levels ($240 \mu\text{g m}^{-3}$ to $250 \mu\text{g m}^{-3}$) remain high, but chemical
25 compositions are different with higher mineral fractions. In the Yangtze River Delta area in central

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1 | eastern China (LinAn, Jinsha and Changde) of the Haze Region III, the PM_{10} levels ($70 \mu g m^{-3}$ to
2 | $90 \mu g m^{-3}$) were 3 times lower than those in the HBP, but the stations in Haze Region III are located
3 | in rural areas and those in the HBP are in urban areas. In the Chengdu urban station located in Haze
4 | Region VI, which is also called Si Chuan Basin (SCB) area in southwestern China, the PM_{10} level
5 | went up to $\sim 160 \mu g m^{-3}$, and this value is between the level of Gucheng ($200 \mu g m^{-3}$) and Dalian in
6 | N. E. China in Haze Region I ($90 \mu g m^{-3}$). Thus, SCB is considered to be another polluted region in
7 | China, followed by N. E. China. The urban PM level in Haze Region V (PRD areas), with values of
8 | $\sim 90 \mu g m^{-3}$ at Panyu and Nanning, were similar to those in rural areas in Haze Region III, thereby
9 | showing that the area has a relatively low aerosol pollution in 2013.

10 | During 2013, mineral dust was still the dominant fraction over various regions with a relatively
11 | high proportion, especially in rural northwest China (Gaolanshan and Dunhuang). Mineral dust
12 | accounted for about 75% to 85% of PM_{10} . In other areas, the percentage was between 25% and
13 | 50%.

14 | In most of areas of China except rural northwest China, sulphate contributed the second, and
15 | the first large anthropogenic, mass fraction to the atmospheric aerosol with a range of 12% to 25%.
16 | In other three stations (Gucheng, XiAn and Panyu), the sulphate fraction were bit lower than OC
17 | and ranked the third with a range of about 9%-16% (Figure 2b). As such, coal combustion was still
18 | the largest anthropogenic source of aerosol pollution in various areas of China during 2013. These
19 | sulfate proportions and related conclusions are quite similar to those from our previous study, where
20 | we mainly focused on the classification of sources of aerosol in various regions in China from 2006
21 | to 2007 (Zhang, 2014; Zhang et al., 2013), and from 2007 to 2008 in urban Beijing (Zhang et al.,
22 | 2012b). Table 1 shows the proportion change of each chemical component of PM_{10} at Haze Region
23 | II (Gucheng). No evident changes were observed from 2006 to 2013, again indicating that the
24 | sources of aerosol particles did not significantly change from 2006 to 2013. This result was also
25 | observed in other major haze regions in China, but that in northwest China (Gaolanshan and
26 | Dunhuang) is slightly different.

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1 In Figure 2b, OC normally ranked the third and accounted for about 7%–19% in terms of mass,
2 with high proportions in Gucheng (19%) and Panyu (16%) in 2013. This value is also similar to that
3 from 2006 to 2007 (Zhang et al., 2013). In the rural northwest China, OC accounted ~8%. In the
4 urban and rural areas of China, about 55% and 60% of OC can be attributed to secondary organic
5 carbon (SOC) formed from volatile organic gases (VOCs), which mainly originate from chemical
6 plants, paint and coatings, motor vehicle (including leaks during fuel), and vegetation from natural
7 sources (Zhang et al., 2012a). The other half of OC is primary organic carbons (POCs) originating
8 from coal combustion. Based on the emission inventory of Beijing and its vicinity (BIV) (Cao et al.,
9 2010), about 55% of POC emission can be attributed to coal combustion, and POC from coal
10 combustion was estimated to account for 12% of the total PM₁ mass (Zhang et al., 2012b; Zhang et
11 al., 2013). Still from Beijing urban area, the primary organic aerosol (POA) from coal-combustion
12 was also found to be most important fraction of total POA, and accounted ~33% of total organic
13 aerosol (Sun et al., 2014). Biomass burning and motor vehicle are the two other major sources for
14 POC (Cao et al., 2010; Lu et al., 2011), and their contribution to OC will be discussed in Section
15 3.4.

16 The mass fractions of nitrate and ammonium normally were around 5% to 10% and 3% to 7%,
17 respectively. The mass fraction of nitrate was less than 5% in rural northwest China (Gaolanshan
18 and Dunhung) and that of ammonium was less than 3% in rural northwest China, urban Haze
19 Region V (Panyu), and urban Haze Region I (Dalian) (Figure 2b). The percentage of nitrate and
20 ammonium in 2013 had no significant differences with those in 2006 and 2007 (Zhang et al., 2013).
21 Comparing the nitrate mass in PM₁₀ among the stations within Haze Region II in 2013 (Table 2),
22 the concentrations in urban Beijing (~20 µg/m³, from 2009 data because no data was obtained in
23 2013) were not higher than those in other stations (19 µg/m³ to 22 µg/m³ for Zhengzhou, Gucheng,
24 and XiAn). However, the contribution from motor vehicle emission is the largest in BIV (NBS-
25 Beijing, 2013). This result shows that nitrate over the region does not only originate from motor
26 vehicle emission but also from coal combustion. Even in BIV, about 28% of the emission amount

1 of NO_x can still be attributed to coal combustion. In other areas in China, about 50% of nitrate mass
2 can be attributed to coal combustion (Cao et al., 2010). Globally, NO_x is mainly derived from
3 natural sources. However, in urban areas, NO_x mainly comes from anthropogenic activities such as
4 oil and coal combustion. Given the rapid development of China's economy in recent years, the
5 amount of gasoline and diesel oil consumption has significantly increased over the past few years
6 (Lu et al., 2011), even if the Chinese government started promoting the “low nitrogen combustion
7 technology” for denaturalization in power generation since 2012. The installation capacity reached
8 only around 70% until the middle of 2013, except in BIV (meeting communication), which can
9 probably explain the high nitrate concentration in HBP.

10 In most areas in China (Figure 2b), EC normally accounts for 3% to 4% of aerosol mass, with
11 less than 2% in rural northwest China (Figure 2b); this result is also similar to the data obtained
12 from 2006 to 2007 (Zhang et al., 2013). The EC has similar sources with POC (Cao et al., 2010),
13 and is not a major chemical fraction in aerosol particles over China.

14 Almost similar concentrations were found for each chemical component in aerosol particle
15 with diameters less than 10 μm (PM₁₀) and less than 2.5 μm (PM_{2.5}) were observed in urban
16 Beijing, respectively (Table 2). These results provide further evidence that the secondary aerosol
17 particle (sulfate, nitrate, ammonium, and SOC) and particles from combustion processes (EC and
18 POC) are present in particles with a diameter of <2.5 μm.

19 3.3. Changes of annual mean concentration of chemical components

20 Table 2 provides the annual averaged daily concentrations for PM₁₀ of major chemical
21 components in six major haze areas of China from 2012 to 2013. In the Gucheng station (Haze
22 Region II), the annual mean concentrations of most chemical components had no significant
23 difference between 2013 and 2012, except OC with an increase of ~10 μg m⁻³ in 2013. This result
24 indicates that no significant difference was observed in emission between the two years. About 37.5
25 and 36.2 billion tons of standard coal were used for energy consumption in 2013 and 2012 (NBS-

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1 China, 2014) , respectively, and the difference is not that high. The mass of mineral aerosol in 2013
2 was even bit lower than that in 2012, resulting in a relatively lower yearly mean PM10
3 concentration in 2013 but was unexpectedly associated with the occurrence of persistent heavy
4 haze-fog events in the winter of 2013. This event did not occur in 2012. As such, this difference
5 was the subject of studies because no significant changes were observed in the emission. Gucheng
6 station is located in a rapidly urbanized area of Baoding city, Hebei province, which is the closest
7 city to Beijing (about 140 km southwest). Zhengzhou, XiAn, and Beijing are all within the Haze
8 Region II. The annual concentration levels of chemical components were not significantly different
9 between 2013 and 2012.

10 *Insert [Table 2] here*

11 A similar situation was also observed in stations such as LinAn, Jinsha, and Changde in Haze
12 Region III (YRD area), Panyu in Haze Region V (PRD area), Chengdu in Haze Region VI (SCB
13 area), Dalian in Haze Region I (N. E. China), and Gaolianshan and Dunhuang in Haze Region IX
14 (N. W. China) (Table 2). As such, no evident annual concentration differences were observed in
15 2012 and 2013 in terms of the major chemical components, especially those associated with fine
16 particles such as SO_4^{2-} , OC, NO_3^- , NH_4^+ , and EC.

17 Comparing the annual averaged concentrations, the annual mean of most chemical components
18 in 2013 are even lower than those from 2006 to 2007 (Zhang et al., 2012a). A survey of the main
19 aerosol chemical components shows a wide spatial variability and higher concentrations for all
20 aerosol components in aerosol mass concentration in the same stations from 2006 and 2007. For
21 these annual mean concentrations, large decreases were observed in 2013 relative to the values from
22 2006 to 2007 in Gucheng station for various major chemical species, especially for SO_4^{2-} , NH_4^+ ,
23 and NO_3^- with 2006 to 2007 to 2013 ratios of 1.5, 1.5, and 1.2, respectively. The only component
24 whose concentration increased in 2013 was OC. The reason will be discussed in the next section.
25 For EC and mineral aerosol, their concentrations exhibited no evident changes. The same result was
26 observed for stations (Zhengzhou, XiAn) within the same haze region (II), where the concentrations

1 of most chemical components, except for OC and mineral aerosol, were all lower in 2013 relative to
2 those from 2006 to 2007. Moreover, the final PM₁₀ concentration in 2013 was also lower than that
3 from 2006 to 2007.

4 **3.4. Occurrence of haze-fog event in Jan. of 2013 as opposed to 2012 in Gucheng in Haze** 5 **Region II as an example**

6 **3.4.1. Winter concentration and year-long aerosol pollution**

7 The typical seasonal patterns in various aerosol components in China are summarized by
8 (Zhang et al., 2012a), where the maximum concentrations of most aerosol chemical components
9 were observed in winter, whereas that of mineral aerosol was observed in spring. In addition to the
10 regular seasonal maximum, secondary peaks were found for sulfate and ammonium during the
11 summer and for OC and EC during May and June. The general changing patterns of various
12 chemical components were also true in Gucheng at this study (Figure 3-left panel). The OC
13 concentration from late autumn to winter season was normally 2 to 4 times higher than those in
14 summer, and the concentration during winter continuously declined from 2006 to 2009 and then
15 increased from 2010 to 2013. This result can also be seen in the linear trend of wintertime
16 concentration from 2010 to 2013 in Figure 3. The averaged OC concentration in January of 2013
17 even reached $\sim 145 \mu\text{g m}^{-3}$, which is a ~ 2.2 time higher than that in 2010. A similar situation was
18 also observed for EC, SO_4^{2-} , NO_3^- , NH_4^+ , and PM₁₀.

19 *Insert [Figure 3] here*

20 Although the annual mean concentration had no evident changes, the winter concentration of
21 PM₁₀ was higher by at least 25% in 2013 than in the winter of 2012, whereas the winter
22 concentrations of SO_4^{2-} and NH_4^+ in 2013 even increased by a factor of 1 or near 1 relative to that in
23 to 2012, and the OC concentration increased by $\sim 50\%$. All these increases resulted in the heavy and
24 persistent haze-fog event in January of 2013.

25 Based on the OC concentration histogram in Figure 3 (right panel), the OC concentration is

1 usually $15 \mu\text{g m}^{-3}$, which can be considered as the regularly-observed background concentration in
2 Haze Region II. A peak concentration of $55 \mu\text{g m}^{-3}$ can be considered as the maximum wintertime
3 mass of OC. As discussed in Section 3.2, the increased value of OC concentration during the winter
4 can be partially attributed to scattered and central centralized coal combustion during the heating
5 season. Aside from this, the increased OC concentration during the winter was also highly
6 correlated with biomass fuel burning in Gucheng, Baoding city, Hebei province in the south of
7 Beijing during the winter. This is mainly inferred from the OC/EC ratio speculation, although the
8 uncertainties do existed. The OC/EC ratio was 4.6 for Gucheng in the winter of 2013 and ranged
9 from 4.1 to 4.5 during wintertime in other years. This group “Gucheng” ratio (4.1 to 4.6) is between
10 the ratio of biomass fuel combustion (3.3) and open biomass burning (8.9 in winter, 8.0 in spring,
11 5.6 in summer, and 5.9 in autumn) based on the emission inventory (Cao et al., 2006;Cao et al.,
12 2010), but is much higher than the ratio of coal combustion (2.0), gasoline (1.4), and diesel oil (3.0),
13 as well as the normal value of 3.1 to 3.9 for ambient aerosol in urban areas in China (Zhang et al.,
14 2008a). Thus, biomass fuel burning was identified to be another main source for the increase in OC
15 concentration during winter in these areas in the past few years. Baoding (Gucheng station located)
16 is the nearest city in Hebei province to Beijing and has a population of about 11 million, in which
17 ~80% are rural dwellers living in more than 600 villages of 27 counties. Even in urban areas with
18 more than 2 million inhabitants, the proportion of central heating during winter in Baoding is less
19 than 40%. In the village and country, large amounts of biomass and scattered coal were burned
20 during winter for heating. During summer, the OC/EC ratios ranged from 1.6 to 3.0 from 2008 to
21 2012 and 2.6 to 3.4 from 2006 to 2007 (Zhang et al., 2008). As such, the contribution of gasoline
22 and diesel combustion during summer to the OC concentration is high, which is evidently different
23 during the winter.

24 The change in EC is similar to that in OC, and its background concentration is around $5 \mu\text{g m}^{-3}$.
25 In winter of 2012, the value is about $21 \mu\text{g m}^{-3}$.

26 In Figure 2b, sulfate, similar to OC, accounted for a large fraction (~12%) of PM_{10} in 2013 in

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1 Gucheng, and its seasonal variation pattern is similar to the general trend in other areas of China
2 (Zhang et al., 2012a) with the maximum concentrations found during winter, and secondary peaks
3 during summer (Figure 3-left panel). The histogram analysis for sulfate (Figure 3-right panel) also
4 shows two peak values of 43 and 33 $\mu\text{g m}^{-3}$, which may represent the peak concentrations in winter
5 and summer, respectively. Another peak at 21 $\mu\text{g m}^{-3}$ may represent the background value. Based on
6 the winter sulfate concentration from 2010 to 2013, a slight increase in SO_4^{2-} concentration was
7 observed from linear fitting of SO_4^{2-} in Figure 3 (left panel), particularly in January of 2013. A peak
8 at 56 $\mu\text{g m}^{-3}$ was observed, thereby indicating that the sulfate probably originated from scattered
9 coal combustion and central heating involving the use of coal in Gucheng because the major
10 emission sources for SO_2 , i.e., coal power plant and industrial manufacturing processes, would be
11 no extra increase during winter. In China, half of coal is used for power generation. About three
12 quarters of another half are used in industrial manufacturing processes, mainly in steel mills,
13 chemical plants, and glass and cement plants, and a quarter of this half can be attributed to scattered
14 coal combustion for winter heating (Cao et al., 2010). Only this part caused the increase during
15 winter. The emissions of scattered coal combustion were those from smaller heating boilers (less
16 than 40 tons) and those of coal burning were from scattered residential households. All sulfate data
17 fitting (not just based on wintertime data) still shows the decreasing trend from 2010 to 2013 (-0.07
18 slope for linear fitting, data omitted), Thus, desulphurization processes in power plant, which have
19 been carried out 2000 in China, might cause these decreases.

20 Similar to sulfate, nitrate concentration was also higher in winter relative to other seasons, and
21 an increasing trend during winter was observed from 2010 to 2013 with less significant seasonal
22 variations relative to OC and EC (Figure 3-left panel). Given that the main sources of NO_x emission,
23 i.e., coal combustion from coal power plants, industrial manufacturing processes, fuel burning from
24 motor-vehicle, and natural gas burning (Göke et al., 2014), are relatively the same for all four
25 seasons, the contribution of scattered coal heating or central heating boilers without denitrification
26 devices to the increase of NO_3^- concentration during winter cannot be ignored. The lower height of

1 | the planetary boundary layer during the winter is another reason for the high concentration during
2 | winter. If one just compares the winter data, the effect would be eliminated. This is, of course, an
3 | important aspect to determine the impact of meteorological factors on pollution and will be
4 | discussed in the next section by using PLAM. Based on the NO_3^- histogram result (Figure 3-right
5 | panel), the regional background and winter peak concentrations are around 12 and $28 \mu\text{g m}^{-3}$,
6 | respectively. Unlike in sulfate, the linear fit by using all nitrate data still showed an increasing trend
7 | for NO_3^- (Figure 3-left panel), thereby showing that the denitrification in power plants since 2012
8 | had no obvious effect in the increase in NO_3^- concentration.

9 | Of the anions, SO_4^{2-} and NO_3^- are dominant species contributing to aerosol acidities, both of
10 | which are highly correlated with NH_4^+ in Gucheng (Zhang et al., 2012a). The median ratio of the
11 | observed mole number of NH_4^+ and capable molecules for neutralizing this substance from SO_4^{2-}
12 | and NO_3^- was approximately 0.70 from 2006 to 2013, thereby suggesting that excess overbalanced
13 | anion can sufficiently neutralize NH_4^+ in Haze Region II. The change in NH_4^+ concentration since
14 | 2010 was similar to that of NO_3^- , with the same tendency to increase during winter (Figure 3-left
15 | panel). The frequency distribution was also similar to that of NO_3^- but different with that of SO_4^{2-}
16 | (Figure 3-right panel). The frequency distribution analyses of NH_4^+ concentration also showed that
17 | the background and winter concentrations were 7.5 and $23 \mu\text{g m}^{-3}$, respectively (Figure 3-right
18 | panel). Both values are much higher in the HBP area than in other regions, which imply that the
19 | major sources of NH_4^+ are located in the HBP. Waste and coal consumption account for $\sim 67\%$ to
20 | 85% of the total NH_3 emissions, of which human and poultry wastes as well as coal combustion
21 | from industry, commercial, and residential usage are the major contributors in urban areas (Cao et
22 | al., 2010). In rural areas, another source of ammonia emission is agricultural activities, which
23 | account for $\sim 14\%$ to 28% of the total NH_3 emission, with nitrogen fertilizer as the major
24 | contributor (Cao et al., 2010).

25 | In Figure 3-left panel, the linear trend of winter mineral aerosol concentration shows almost no
26 | change from 2010 to 2013, thereby indicating that the change in PM_{10} in these years was mainly

1 attributed to the changes in fine aerosol particle concentrations. The histogram analysis of the
2 mineral suggests that a high regional background loading of $90 \mu\text{g m}^{-3}$ was observed in the Haze
3 Region II, which not only caused by sand-dust-storm dust, urban fugitive dust, but also coal ash that
4 is highly related with the large amount of coal combustion activities in this area. The winter
5 concentration of mineral aerosol is around $130 \mu\text{g m}^{-3}$ (Figure 2-right panel).

6 3.4.2. Contribution of specific meteorological condition to the wintertime PM_{10} changes

7 The PM_{10} concentration increased by about 25% in January of 2013 compared with that in
8 2012. The specific meteorological conditions that are highly related with aerosol pollution
9 (parameterized as an index called “PLAM”) also increased by ~15% at the same period. Given that
10 the pollutant emissions did not significantly change from 2012 to 2013 (NBS-China, 2014), which
11 was not enough to cause a significant increase of 25%, about 60% of this 25% increase in PM_{10}
12 concentration can thus be considered as the contribution of worsening meteorological conditions
13 because PLAM has been confirmed to be linearly related with PM_{10} concentration (Wang et al.,
14 2012).

15 The comparison of averaged PM_{10} concentration between January 2013 and January 2010 also
16 showed that the mean value in 2013 was 1.2 times higher than that in 2010, whereas the PLAM
17 index increased to about 35% in 2013 compared with that in 2010. Given the linear relation
18 between PLAM and PM_{10} (Wang et al., 2012), about 28% of the 1.2 times increase in PM_{10} can be
19 approximately regarded as the contribution from worsening meteorological conditions since 2010.
20 Based on the changes in mean mass of various chemical components between January 2010 and
21 January 2013 and by multiplying these by the proportion of each component of PM_{10} in 2013
22 (Figure 2b), about 20%, 41%, 18%, 16%, 2.0%, and -5.0% of the increase in PM_{10} in 2013 relative
23 to 2010 can be attributed to SO_4^{2-} , OC, NO_3^- , NH_4^+ , EC, and mineral, respectively. The other
24 components accounted for about ~9% of this increase in PM_{10} concentration between 2010 and
25 2013. OC contributed the largest percent of the increase in PM_{10} concentration from 2010 to 2013.

1 3.5. Changes in the chemical components of PM₁₀ in other major haze areas in China

2 3.5.1. Haze Region III (Yangtze River Delta (YRD) area) in China

3 Although the winter concentrations of particular aerosol chemical components, such as OC,
4 NO₃⁻, and NH₄⁺, continuously increased since 2010 in Haze Region III (LinAn) (Figure 4-left
5 panel), the increase in amplitude was much smaller than that of HBP. The winter concentration of
6 EC and dust slightly decreased and that of sulfate did not significantly change from 2010 to 2013.
7 Thus, PM₁₀ concentration remained unchanged since 2010, which was very similar to the change in
8 wintertime PLAM since 2010 in the same area. This result implies the important effect of
9 meteorological condition on aerosol pollution. In general, the pollution-meteorological condition
10 worsened from 2006 to 2010 in Haze Region III (LinAn) and remained almost unchanged from
11 2010 to 2013 with a slight decrease in 2011 (Figure 4-left panel-upper part).

12 *Insert [Figure 4] here*

13 The regional background concentrations of SO₄²⁻, OC, NO₃⁻, NH₄⁺, EC, and mineral dust are
14 normally 17, 11, 6, 6, 3, and 25 μg m⁻³, respectively, which are about 60% to 80% of the HPB level
15 (Figure 4-right panel). The corresponding winter values are normally 33, 22, 15, 10, 5, and 65 μg m⁻³,
16 respectively. The winter values were still more than 1 times higher than the annual background
17 concentration, but the concentrations are much smaller than in HBP, thereby suggesting the weak
18 influence of winter heating in the YRD area. Winter heating is not legally imposed in the southern
19 parts of China. However, coal-fired heating during winter is still practiced in this area, which can
20 increase the mineral content to 65 μg m⁻³ during winter from the normal value of 25 μg m⁻³. The
21 increased wintertime mineral concentration is most likely caused by coal ash, whereas other
22 fugitive dust, such as dust from sand and dust storm events, construction sites, and unpaved roads,
23 would cause a significant increase during winter. Unlike in HBP, the proportion of sulfate (~19% of
24 PM₁₀) is much higher than the OC fraction (13% of PM₁₀).

25 The winter OC/EC ratio was 3.7 with a range of 2.7 to 5.3 from 2006 to 2013 in Haze Region

1 III (LinAn), and a high value of ~4.0 was observed from 2012 to 2013. These values are similar
2 those from biomass fuel combustion (Cao et al., 2010), thereby suggesting that the influence of
3 biomass burning for heating was also observed in the YRD area during winter.

4 **3.5.2. Haze Region V (Pearl River Delta (PRD) area) in China**

5 The pollution-meteorological conditions during wintertime were much better in Haze Region
6 V (Panyu) in the PRD area than that in the HBP, with PLAM values ranging from 60 to 90 from
7 2010 to 2013 (corresponding values of 110 to 150 in HPB; ~120 to 125 in YRD) and are associated
8 with a declining trend (Figure 5-left panel-upper part). This decrease in PLAM was very similar to
9 the decreased trend of PM₁₀, thereby implying the effect of meteorological factors on the change in
10 PM. In Figure 5, almost all chemical components presented a decreasing since 2010, except for
11 nitrate. In addition to the reduced emission in YRD with emphasis on coal combustion sources, the
12 decrease in the concentrations of major chemical components and PM₁₀ can also be partially
13 attributed to improved meteorological conditions since 2010. The proportion of coal in primary
14 energy consumption decreased to 49% in 2013 in Guangzhou. The corresponding number is 60% in
15 2004 (meeting communication).

16 *Insert [Figure 5] here*

17 The regional background concentrations of SO₄²⁻, OC, NO₃⁻, NH₄⁺, EC, and mineral dust in
18 this region are 17, 13, 9, 7, 3.5, and 25 μg m⁻³, respectively, which are similar to the values in YRD.
19 The corresponding winter values are 33, 22, 15, 9, 6.7, and 70 μg m⁻³ for SO₄²⁻, OC, NO₃⁻, NH₄⁺,
20 EC, and mineral, respectively. The difference between the winter and background concentrations in
21 other season in the PRD area is very similar to those in the YRD area.

22 The winter OC/EC ratio in Haze Region V (Panyu) is 0.79 with a range of 0.25 to 2.9 from
23 2006 to 2013, which is close to the value of 1.4 for gasoline (Cao et al., 2010). Thus, different
24 sources were noted in the HBP area for OC and EC with less biomass burning contribution. In
25 January of 2006, 2008, and 2009, the OC/EC ratios were within the range of 2.4 to 2.9, which were

1 very similar to the fossil fuel combustion (2.0) and diesel oil (3.0) (Cao et al., 2010). As such,
2 emission had an evident effect in reducing the contribution of coal combustion and diesel vehicles
3 in Guangzhou. After 2010, the winter ratio of OC and EC were within 0.3 to 0.5.

4 **3.5.3. Haze Region VI (Si Chuan Basin (SCB) area) in China**

5 Based on the monthly changes in the various chemical components and PM₁₀ in Haze Region
6 VI (Chengdu) (Figure 5-left panel), the wintertime mass of various chemical components generally
7 had peak values from 2006 to 2013. However, in particular years, this kind of situation was not
8 particularly evident. These results suggest that the wintertime heating season had an effect on the
9 chemical composition in the SCB area. Specifically, the mass of mineral aerosol was found to have
10 an evident peak in winter, which is different from other areas. As such, the influences of coal-ash
11 contribution were observed. The significant increase in the concentration during winter was not
12 evident for sulfate relative to other chemical species, such as EC and nitrate, especially after 2010,
13 because another period had existed in the summer where the values were at their maximum.
14 Moreover, the decreasing trend of sulfate in January from 2010 to 2013 shows the effect of
15 desulfurization in this area. The opposite behavior was observed for nitrate during the same period,
16 showing no obvious denitrification effect of power generation plants. During winter, PLAM
17 decreased from 2006 to 2009 and remained at a similar level at ~130 from 2010 to 2013. However,
18 the value was low in 2011, thereby showing that the effect of bad weather on aerosol pollution is
19 medium in the SCB area (Figure 5-left panel-upper part).

20 *Insert [Figure 6] here*

21 The background concentrations of SO₄²⁻, OC, NO₃⁻, NH₄⁺, EC, and mineral dust in this region
22 are 23, 22, 9, 7, 5, and 65 μg m⁻³, respectively, which are similar to the HBP value, with slightly
23 higher masses for SO₄²⁻ and OC and slightly lower values for NO₃⁻ and mineral dust. The
24 corresponding winter values are 43, 47, 23, 18, 14, and 145 μg m⁻³. The difference between the
25 winter and background concentrations in the SCB area is very similar to that in the HBP area,


1 thereby showing the relatively polluted condition in this area.

2 In general, two values of OC/EC were obtained: ~3.1 in December to January and ~0.41 in
3 February. The higher OC/EC ratio is quite similar to biomass fuel combustion (3.3), and the lower
4 value is close to gasoline (1.4) (Cao et al., 2010). These results suggest the contributions of biomass
5 burning for heating during winter in the SCB area, and the contribution from motor vehicle was
6 also observed. The low OC/EC ratio during winter is also similar to most values of OC/EC during
7 other seasons, thereby showing the strong influences of motor vehicle to OC and EC in this area.

8 4. Summary

9 On the basis of mass concentration of sulfate, OC, nitrate, ammonium, EC, and mineral dust
10 from 24-hr aerosol particle (PM₁₀) collected from various CAWNET stations from 2006 to 2013,
11 the change in these major water-soluble constituents, carbonaceous species, mineral aerosol and
12 PM₁₀ since 2006 and the contribution of meteorological condition were investigated in this study.
13 The mass concentration and comparison of the chemical components in major haze regions of
14 China were also provided with details for 2012 and 2013 in particular, in hope to strengthen the
15 understanding of the growing haze-fog over the years in China. Moreover, this study can also serve
16 as a basis in chemical composition aspect for further evaluation the effect of implementation of
17 various pollution control countermeasures after 2013, called "atmospheric pollution prevention and
18 control of the ten measures of China" by Chinese government. This investigation also provides the
19 inputs and validation of haze-fog forecasting system that used a lot of near-real time (NRT) data.

20 The major findings of this study can be summarized as follows:

21  During 2013, the mineral aerosol was found still to be the largest component of PM₁₀ in
22 almost all stations in different haze areas, thereby showing the high "dust" characteristics in aerosol
23 pollution of China, in which the contribution of coal-ash should not be ignored. Thus, a high
24 mineral concentration was observed even at southern part of the urban areas in China. The high
25 regional background loading of 90 μg m⁻³ in mineral aerosol was observed in the Haze Region II,

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1 which not only caused by sand-dust-storm dust, urban fugitive dust, but also coal ash that is highly
2 related with the large amount of coal combustion activities in this area. The increased coal ash
3 during winter, which were mainly from the increased coal-combustion for heating, can be the
4 reason for higher mass concentration of mineral dust in winter, which about 1.5 times higher
5 concentration of mineral aerosol in winter relative to normal background mean at HBP area (~130
6 µg m⁻³) (Table 3). This is also true for other haze regions in China with 2 to 3 factors higher mineral
7 dust mass in winter (Table 3).

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8 ● Sulphate contributed the second and the first large anthropogenic, mass fraction to the
9 atmospheric aerosol (i.e., 12% to 25%) in most of areas of China except rural northwest China in
10 2013. OC normally ranked the third and accounted for about 7% to 19% by mass, with high
11 proportions in Gucheng and Panyu. The mass fractions of nitrate and ammonium were normally
12 around 5% to 10% and 3% to 7%, while in most areas of China, elemental carbon represented 2%
13 to 4%. All these percentage are similar with the results of 2006 and 2007 (Zhang et al., 2012a).

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删除的内容: The winter concentration of mineral aerosol is around 130 µg m⁻³.

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删除的内容: At stations of Gucheng, XiAn and Panyu, the sulphate fraction were bit lower than OC and ranked the third, but still with a percentages of 9% to 16%.

14 ● More than 50% of primary OC and 28% to 50% nitrate mass were attributed to coal-
15 combustion in 2013. In the stations of Gucheng, Zhengzhou and XiAn in HBP, the nitrate
16 concentrations are all higher than or close to that in Beijing that has the largest number of motor
17 vehicles within the Haze Region II. The result suggests that coal-combustion also has an important
18 contribution to the increased nitrate concentration in this area. NH₄⁺ concentration are much higher
19 in HBP than in other regions, with the background and winter concentrations of 7.5 and 23 µg m⁻³,
20 respectively, which imply that the major sources of NH₄⁺ are located in the HBP. Agricultural
21 activity is the most important source of ammonium.

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22 ● Excessive amount of unclean energy-consumption was the most fundamental reason for the
23 increased severity of haze and fog events in China, in which coal-combustion was still the largest
24 anthropogenic source for aerosol pollution in various areas of China in 2013. The proportion of
25 each chemical component of PM₁₀ had no evident changes from 2006 to 2013, which also shows
26 that the sources for aerosol particles did not significantly change from 2006 to 2013.

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● Wintertime mass concentrations of aerosol chemical components and PM₁₀ are more important than annual mean value in evaluating of aerosol pollution for a year. In the HBP area, the winter concentrations were usually about 2-4 factors higher than the normal regional background masses (Table 3), and the concentrations in winter for various components normally exhibited a decline during 2006 to 2010 (considered as the first phase for the pollution change during 2006-2013), and then rose till 2013 (called second phase).

● Given the ~25% increase in PM₁₀ concentration in January of 2013, relative to 2012 in the HBP area, while the winter values of SO₄²⁻ and NH₄⁺ concentrations in 2013 even increased by 1 or near 1 factor in 2013, relative to 2012. The OC concentration increased by ~50%. All these resulted in persistent haze-fog event in Jan. of 2013, which did not happen in the winter of 2012. About ~60% of this increment can be attributable to worsening meteorological conditions. The APEC summit period (8-10 November 2014) was associated with bad meteorological conditions with ~100 to 120 of PLAM at Beijing, ~35% reduction of pollutant emission in the BIV area by various control measures. This ~35% cut resulted in good air quality, and was called "APEC blue" in media (all the details will be introduced in a companioned paper separately). From the fact of increment of ~25% pollutants in the HBP area resulted in persistent haze-fog event in winter 2013, and ~35% cutting derived in APEC Blue in 2014 winter, one could approximately estimates that there will be no frequent persistent haze-fog event induced by aerosol pollution if ~one third of pollutant emission can be reduced on the basis of winter emission level of 2013 in BIV. The ~one-third reduction of 2013 winter emission might be considered as the upper limit of capacity of aerosol pollution in this area.

● OC contributed the largest in the increase in PM₁₀ concentration during winter from 2010 to 2013 in the HBP area, in which the contribution from biomass fuel burning for heating was identified in addition to the contribution from the scattered and central coal-combustion for heating. The phenomenon was also found in YRD area and SCB but not in PRD area, where the contribution from the coal-combustion to various chemical components was noted before 2009, but after 2010,

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1 the contributions from motor vehicle increased.

2 ● All sulfate data fitting from 2010 to 2013 shows a decreasing trend in the HBP area that is
3 opposite of the fitting when only wintertime data are used, thereby reflecting the effect of power
4 plant desulphurization since 2002 in China. This is also true for PRD and SCB areas, but almost no
5 change in the YRD area. Unlike in sulfate, the linear fit using all season nitrate data in the four
6 major haze regions still showed an increasing trend from 2010 to 2013, thereby partially showing
7 the lack of effect of power plant denitrification. Since large-scale caring on power plant
8 denitrification started in 2012 in China, the effect of desulphurization is not yet fully expressed. Of
9 course the increased number of motor vehicle and the burning of more natural gas also contributed
10 to the increase in nitrate concentration over these years.

11 ● In Haze Region III (YRD area), although there were some changes in different chemical
12 components between 2010-2013, the PM₁₀ concentrations in winter season remained **less change**
13 and is associated with similar changes in PLAM. The regional background concentrations of SO₄²⁻,
14 OC, NO₃⁻, NH₄⁺, EC and mineral dust are normally **2 to 2.6 factors less than** winter high values for
15 each of them **(Table 3)**. The weak influence of winter heating was identified in this area.

16 ● In Haze Region V (PRD area), the pollution-meteorological conditions during winter were
17 much better than that in the HBP, and continually getting better from 2010 to 2013. This
18 improvement is associated with a declining in almost all chemical components and PM₁₀ during
19 winter, with less change for nitrate. This trend is the opposite of that in HBP. Within the same Haze
20 Region V, nitrate mass was a factor higher in Panyu of Guangdong province than in Nanjing of
21 Guangxi province, thereby showing a relatively larger influence of motor vehicle and natural gas
22 burning on nitrate concentration in Panyu compared with that in Nanjing. Similar to the mass and
23 difference between winter and normal conditions in the YRD area, the regularly-observed
24 background concentrations of SO₄²⁻, OC, NO₃⁻, NH₄⁺ and EC are normally **1-3 factors lower than**
25 winter **higher** values for each of them **(Table 3)**.

26 ● In Haze Region VI (SCB area), the background and higher concentrations of chemical

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1 components and PM₁₀ in winter were all similar to those of the HBP, with background masses 2-3
2 factors lower than winter concentrations for SO₄²⁻, OC, NO₃⁻, NH₄⁺, EC and mineral dust (Table 3).
3 During winter, the contributions of biomass fuel burning from heating to OC and EC were also
4 identified in this area, and the contribution from motor vehicles also observed in other part of
5 wintertime and other season. The change in chemical components in January and the associated
6 changes in PLAM in the SCB area were similar to those in the YRD area, with a slight change in
7 winter, 130 of PLAM, for aerosol pollution from 2010 to 2013.

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8 ● Evidence of comparisons for the chemical components in PM₁₀ and PM_{2.5} in Beijing
9 suggests that the secondary aerosol particle (sulfate, nitrate, ammonium, SOC), and particles from
10 combustion (EC and POA) are almost associated with the particles with diameters smaller than 2.5
11 μm. The measurement of PM₁₀ from monitoring or filter analysis can provide information that
12 covers all kinds of information related to chemical components of PM_{2.5} and also includes
13 information about mineral dust, especially those with diameters between 2.5 and 10 μm, which can
14 fully reflect the problems of aerosol pollution in China.

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3 **Table 1. Proportion change in major chemical components of PM₁₀ at Gucheng**

	2006	2007	2008	2009	2010	2011	2012	2013
NO ₃ ⁻	0.10	0.07	0.04	0.07	0.06	0.06	0.09	0.10
SO ₄ ²⁻	0.16	0.14	0.09	0.12	0.13	0.13	0.10	0.12
NH ₄ ⁺	0.07	0.05	0.04	0.04	0.04	0.04	0.05	0.06
Mineral	0.32	0.36	0.42	0.48	0.52	0.32	0.44	0.40
OC	0.14	0.14	0.11	0.13	0.16	0.16	0.17	0.19
EC	0.05	0.04	0.03	0.04	0.04	0.04	0.04	0.04
Others	0.17	0.23	0.28	0.13	0.05	0.25	0.12	0.08

1 **Table 2. Annual averaged daily concentrations ($\mu\text{g m}^{-3}$) for PM_{10} , chemical components in various regions of China during 2013 and 2012**

Stations	Type	Region	PM_{10}	Mineral	SO_4^{2-}	OC	NO_3^-	NH_4^+	EC	No.
<i>Haze Region II (HBP)</i> ¶										
Gucheng (GC)-2013	semi-urban	Province south of Beijing	196	74	21	45	17	10	10	52
	2012-GC		203	84	20	36	17	10	8.1	101
Zhengzhou (ZZ)-2013	urban	Province south of Beijing	235	110	35	26	20	13	6.6	103
	2012-ZZ		221	107	34	24	21	13	7.0	105
XiAn (XA)-2013	urban	Guanzhong Plain	293	138	31	34	20	11	11	81
	2011-XA‡		268	123	28	26	16	6.2	9.9	74
Beijing (BJ)-2009- PM_{10}	urban	Haidian District of Beijing	174	nd	19	19	20	7.6	4.8	155
	2009- $\text{PM}_{2.5}$		126	nd	17	16	16	8.0	4.1	153
<i>Haze Region III (YRD)</i>										
LinAn (LA)-2013	rural	Yangtze River Delta regions	88	38	16	12	7.3	5.0	2.5	100
	2012-LA		94	32	16	11	8.4	5.4	3.3	102
Jinsha (JS) -2013	rural	Lower reach of Yangtze River	78	28	19	8.5	5.8	5.4	2.2	52
	2012-JS		86	33	21	8.7	6.5	5.7	2.2	52
Changde (TYS)- 2013	rural	Dongting and Buoyan lakes basin	72	16	18	10	6.1	6.1	2.0	82
	2012-TYS		87	16	21	11	7.0	7.1	1.9	86
<i>Haze Region V (PRD)</i>										
Panyu (PY) -2013	urban	Pearl River Delta region	97	40	16	18	11	4.2	3.9	37
	2012-PY		97	39	16	14	10	4.9	4.0	33
Nanning (NJ) -2013	urban	Pearl River Delta region	90	30	17	14	5.2	4.6	3.4	103
	2010-NJ‡		91	44	18	14	4.3	4.1	3.3	111
<i>Haze Region VI (SCB)</i>										
Chengdu (CD) -2013	urban	Si Chuan Basin	166	79	24	25	14	11	6.6	94
	2012-CD		141	64	23	21	12	9.0	5.7	100
<i>Haze Region I (N. E. China)</i>										
Dalian (DL) -2013	urban	Southern tip of Liaodong peninsula	101	58	13	11	8.5	4.0	3.2	69
	2012-DL		89	52	14	10	8.8	4.2	2.8	89
<i>Haze Region IX (N. W. China)</i>										
Gaolanshan (GLS) -2013	rural	Gansu province	247	184	16	17	8.9	4.0	3.2	103
	2012-GLS		157	102	15	15	7.3	3.9	2.4	99
Dunhuang (DH) -2013	rural	North margin of Kumutage Desert	240	201	9.1	24	2.5	0.65	2.5	68
	2012-DH		198	162	6.6	20	2.5	0.81	2.3	70

2 ¶ Classification of major haze regions referred from (Zhang et al., 2012a); ‡ At XiAn and Nanjing here used are data in 2011 and 2010, respectively, for comparing with
3 2013 results; | Beijing are 2009 data for PM_{10} and $\text{PM}_{2.5}$; Lasha data omitted because of no data of 2012 and 2013 for this station

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Table 3. Comparisons between normal regional background and winter concentrations ($\mu\text{g m}^{-3}$) for major chemical components of aerosol particles in major haze regions of China.

Regions	Conditions	SO_2^{2-}	OC	NO_3^-	NH_4^+	EC	Mineral aerosol
HBP	Regional background conc.	20	15	12	7.5	5	90
	Winter conc.	43	55	28	23	21	130
YRD	Regional background conc.	17	11	6	6	3	25
	Winter conc.	33	22	15	10	5	65
PRD	Regional background conc.	17	13	9	7	3.5	25
	Winter conc.	33	22	15	9	6.7	70
SCB	Regional background conc.	23	22	9	7	5	65
	Winter conc.	43	47	23	18	14	145

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1 **Figure Captions:**

2 Figure 1: Locations of thirteen CAWNET stations and nine similar visibility changing regions in China (Zhang et
3 al., 2012a)

4 Figure 2a: Averaged mass concentrations ($\mu\text{g m}^{-3}$) of major chemical components in thirteen stations during 2006-
5 2010

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6 Figure 2b: Chemical proportions of PM_{10} in 2013

7 Figure 3: Left panel: Change of monthly median concentrations of major chemical components, PM_{10} , and
8 January PLAM at Gucheng in Haze Region II, one of major haze region in the Hua Bei Plain (HPB) area in
9 China. Wintertime data were used in linear trend fitting from 2010 to 2013; Right panel: Histogram analysis
10 for various chemical components.

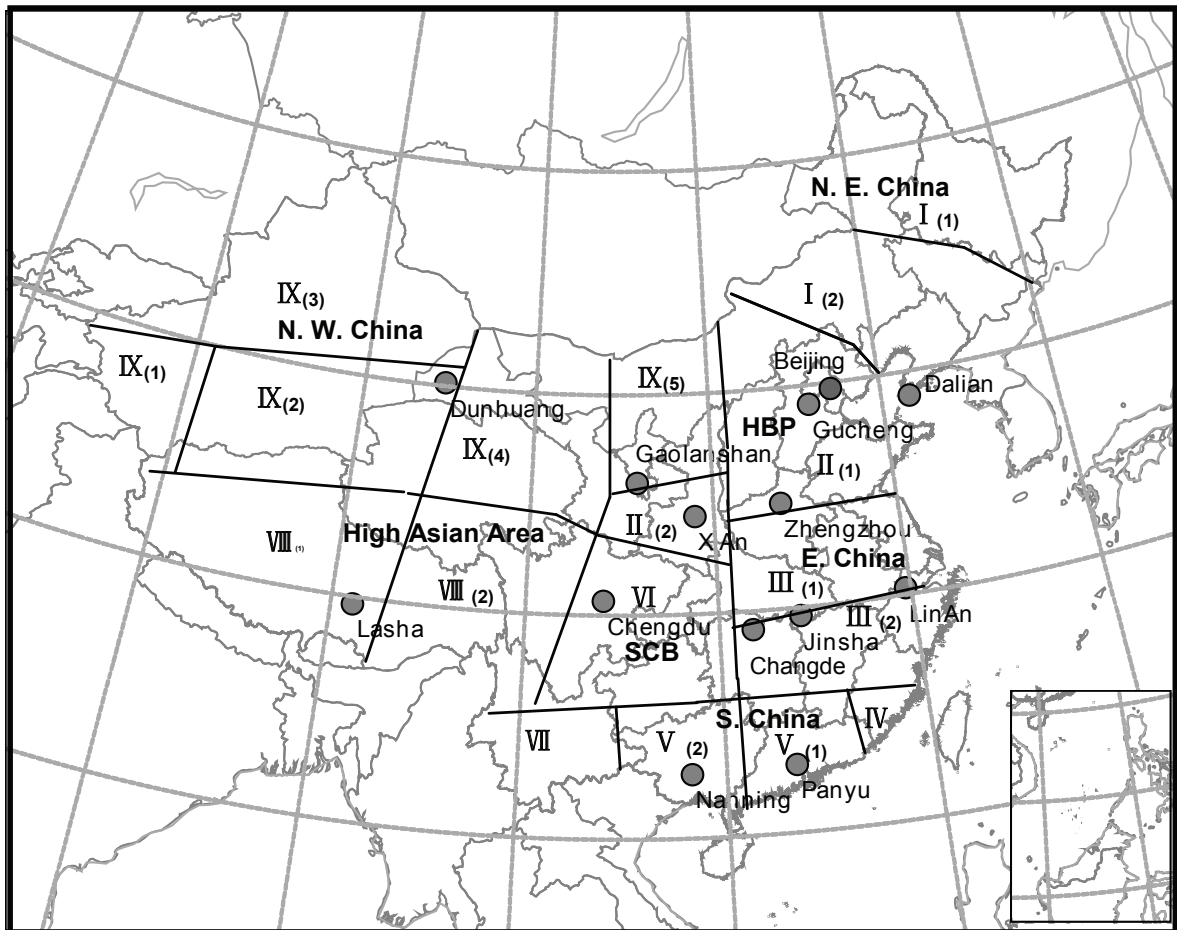
11 Figure 4: Left panel: Change of monthly median concentrations of major chemical components, PM_{10} , and
12 January PLAM at LinAn in Haze Region III, one of major haze region in the Yangtze River Delta (YRD)
13 area in China. Wintertime data were used in linear trend fitting from 2010 to 2013; Right panel: Histogram
14 analysis result for various chemical components.

15 Figure 5: Left panel: Change of monthly median concentrations of major chemical components, PM_{10} , and
16 January PLAM at Panyu in Haze Region V, one of major haze region in the Pearl River Delta (YRD) area in
17 China. Wintertime data were used in linear trend fitting from 2010 to 2013; Right panel: Histogram analysis
18 result for various chemical components.

19 Figure 6: Left panel: Change of monthly median concentrations of major chemical components, PM_{10} , and
20 January PLAM at Chengdu in Haze Region VI, one of major haze region in the Si Chuan Basin (SCB) area in
21 China. Wintertime data were used in linear trend fitting from 2010 to 2013; Right panel: Histogram analysis
22 result for various chemical components.

The winter concentrations were usually around 43, 55, 28, 23, 21 and 130 $\mu\text{g m}^{-3}$ for SO_4^{2-} , OC, NO_3^- , NH_4^+ , EC and mineral dust, respectively, which were about 2-4 factors higher than the background masses, with corresponding values of 20, 15, 12, 7.5, 5 and 90 $\mu\text{g m}^{-3}$ in the HBP area.

Figure 1



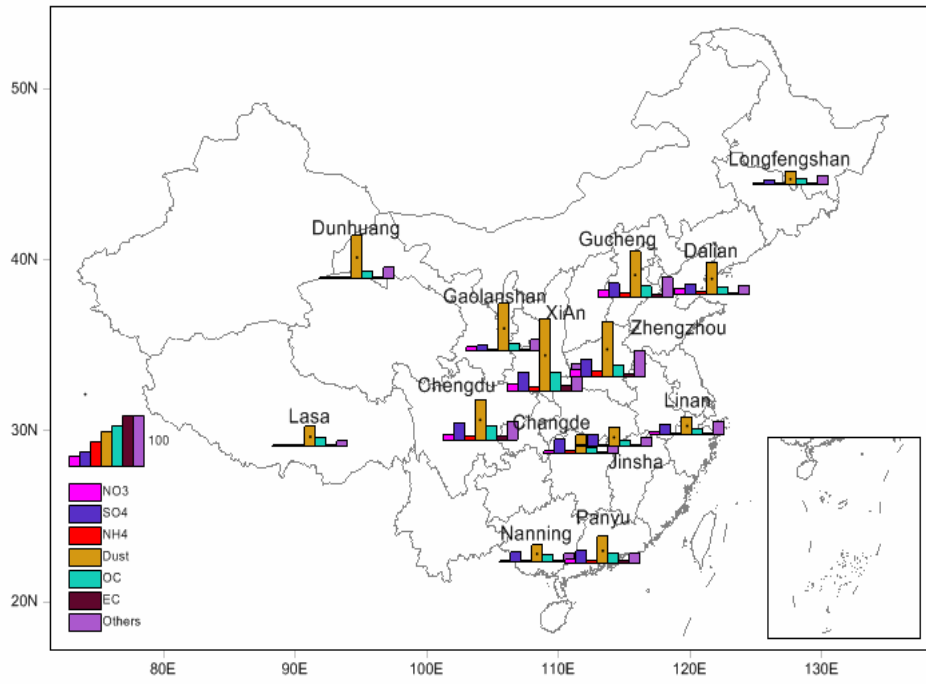


Figure 2a

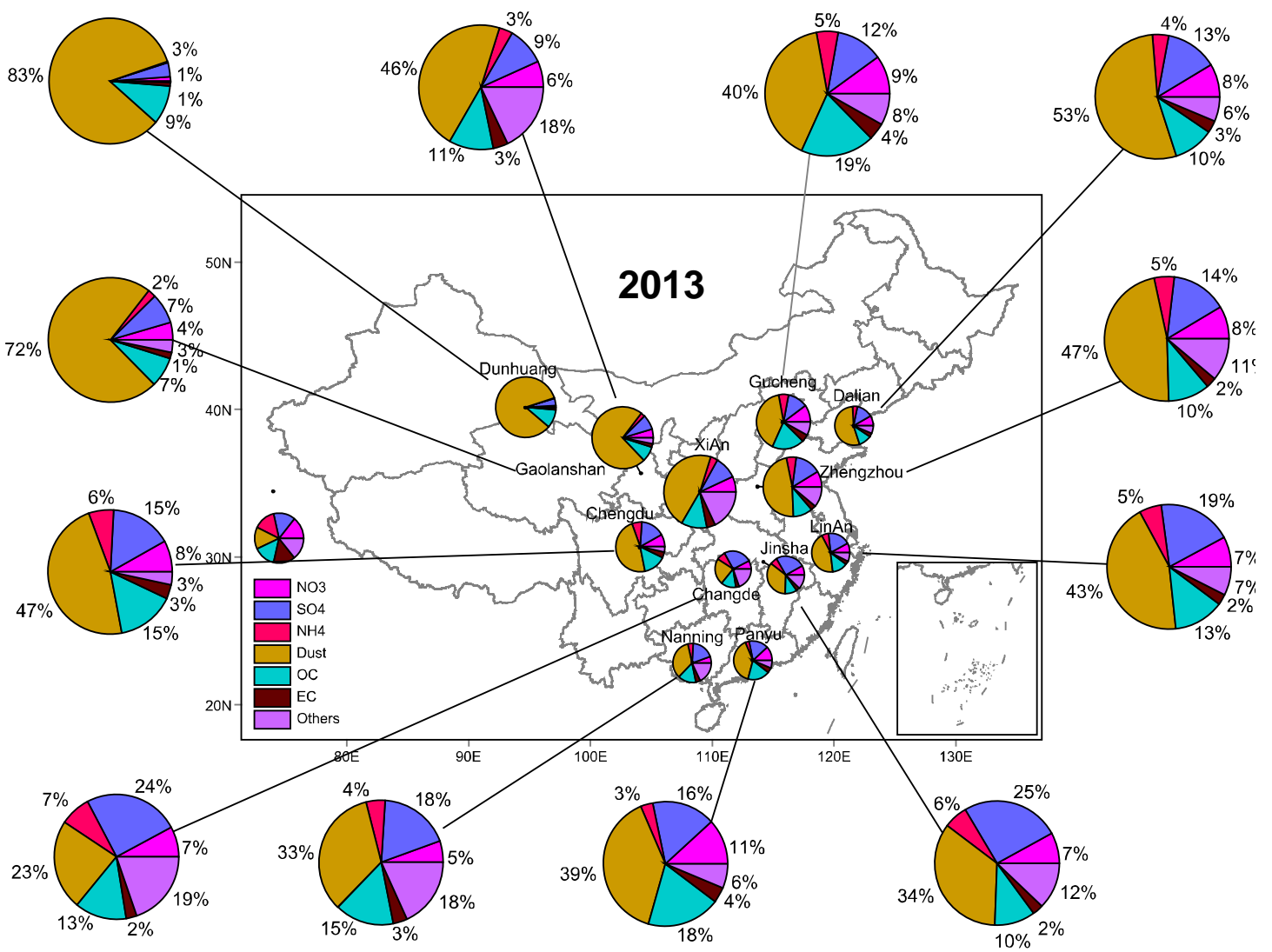


Figure 2b

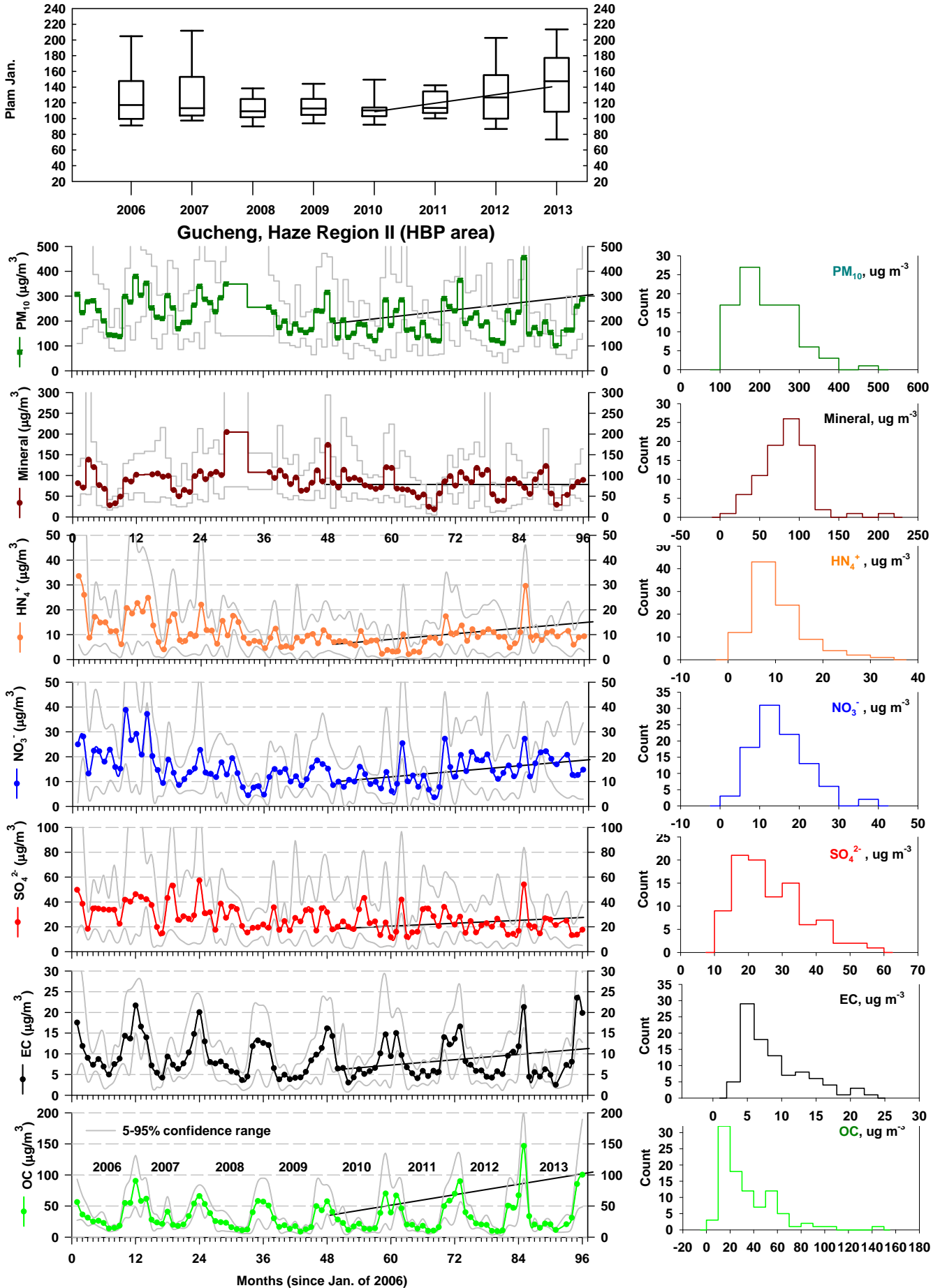


Figure 3

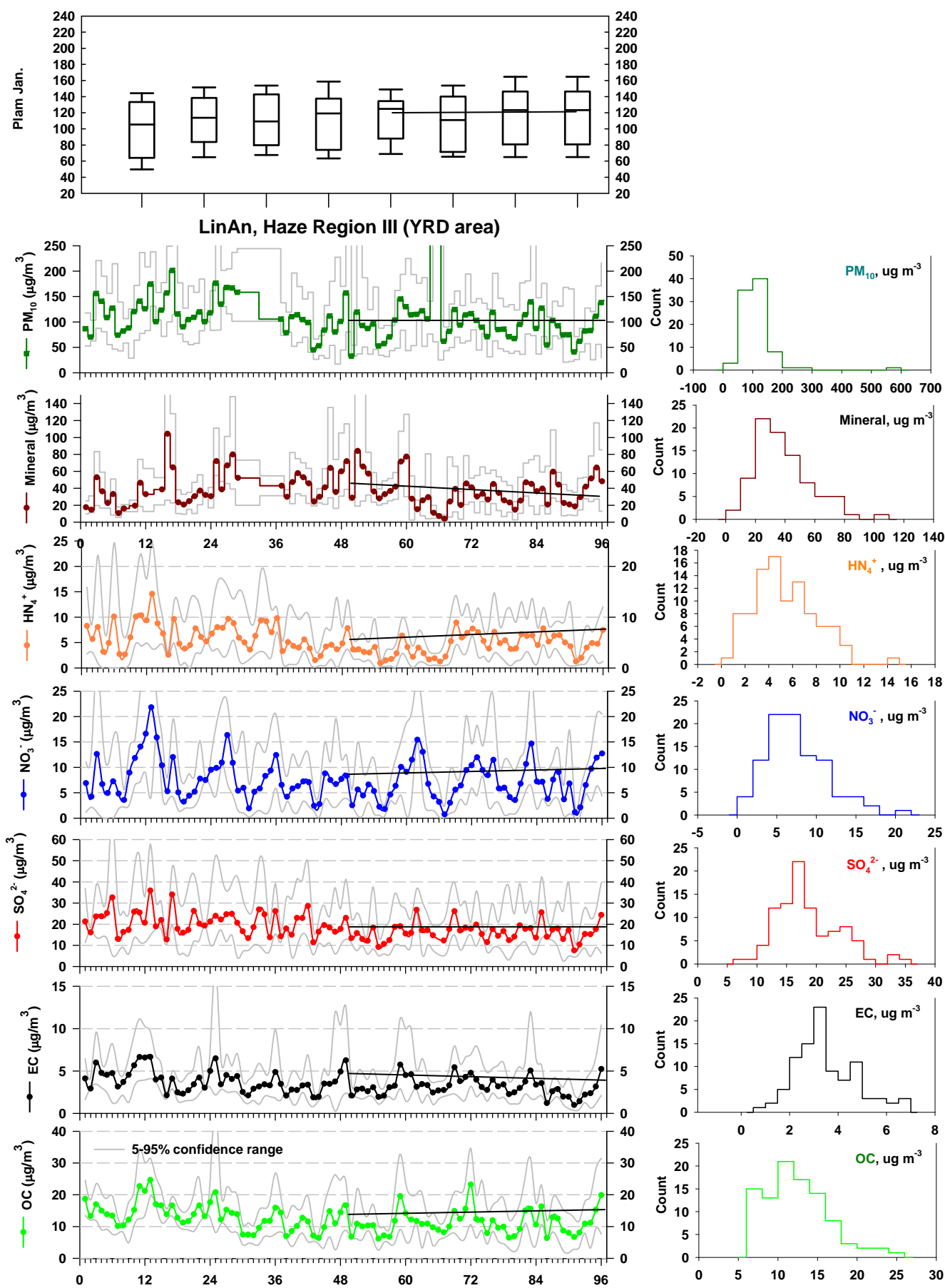


Figure 4

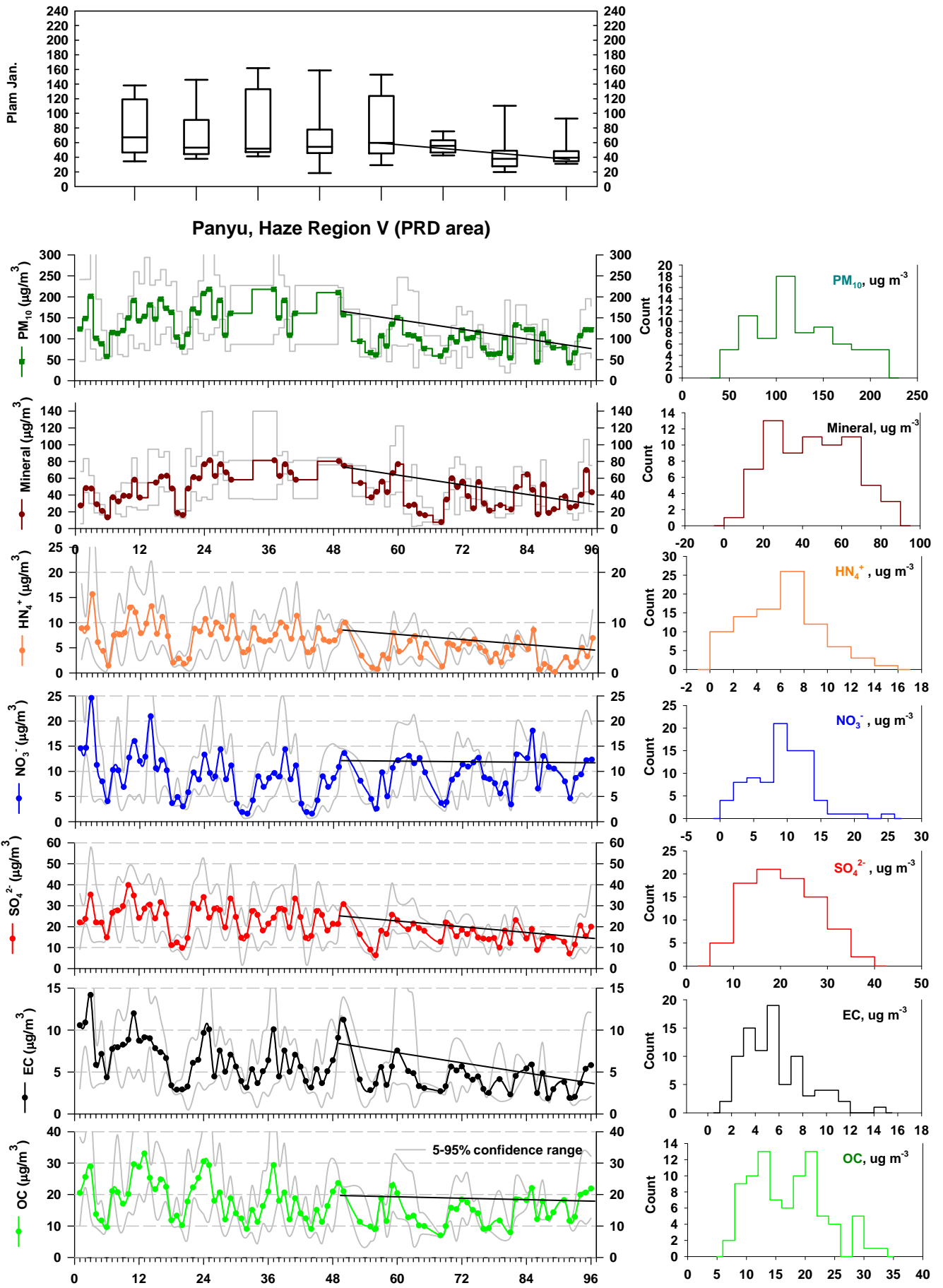


Figure 5

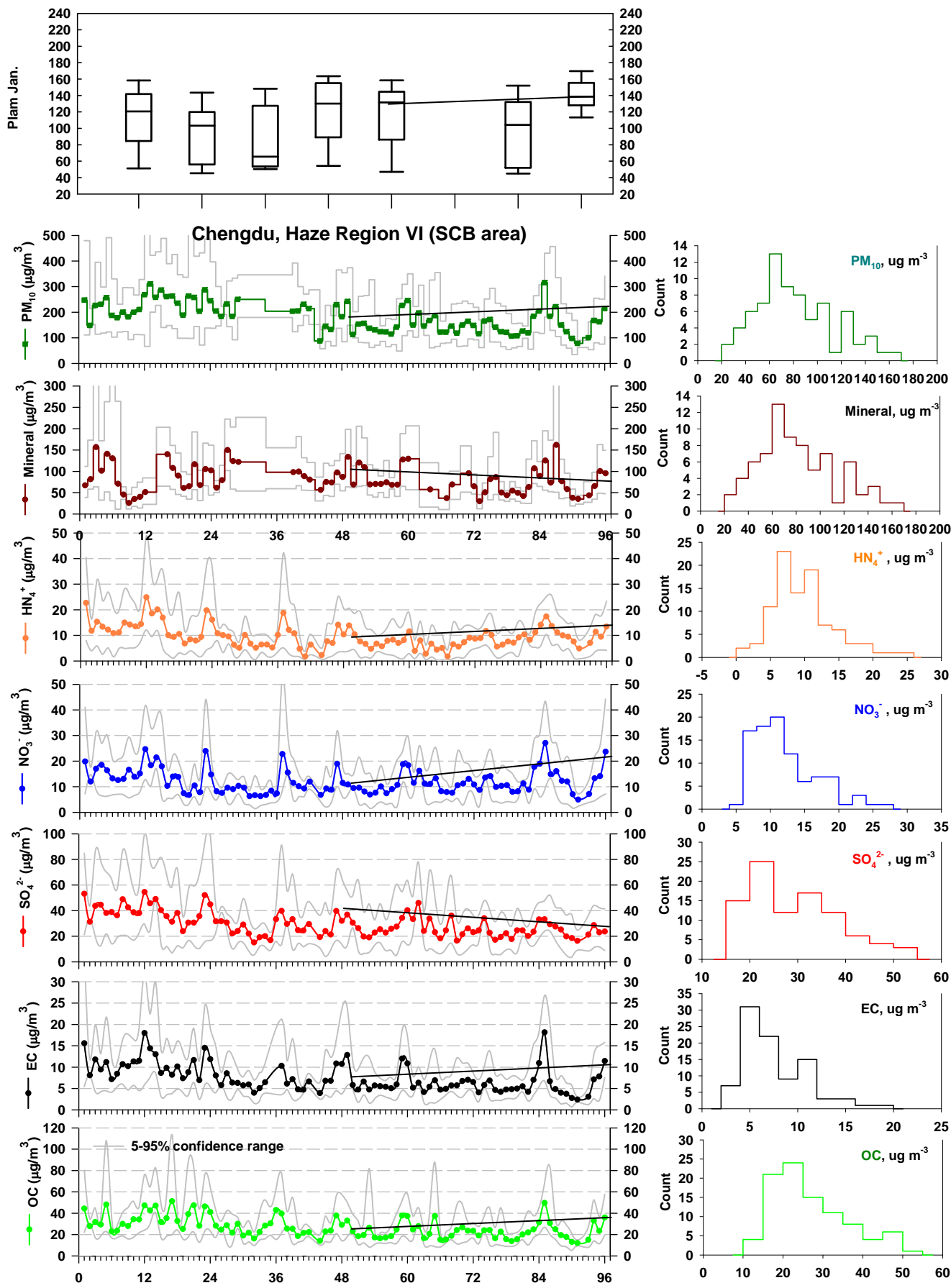


Figure 6