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A Preliminary Assessment of the Impacts of Multiple Temporal-scale Variations in Particulate Matter on its Source Apportionment

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Abstract. Time series of pollutant concentrations consist of variations at different time scales that are attributable to many processes/sources (data noise, source intensities, meteorological conditions, climate, etc.). Improving the knowledge of the impact of multiple temporal-scale components on pollutant variations and pollution levels can provide useful information for suitable mitigation strategies for pollutant control during a high pollution episode. To investigate the source factors driving these variations, the Kolmogorov-Zurbenko (KZ) filter was used to decompose the time series of $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) and chemical species into intra-day, diurnal, synoptic, and baseline temporal-scale components (TS components). The synoptic TS component has the largest amplitude and relative contributions (about 50%) to the total variance of SO_4^{2-}, NH_4^+, and OC concentrations. The diurnal TS component has the largest relative contributions to the total variance of $PM_{2.5}$, NO_3^-, EC, Ca, and Fe concentrations, ranging from 32% to 47%. To investigate the source impacts on $PM_{2.5}$ from different TS components, four datasets RI (intra-day removed), RD (diurnal removed), RS (synoptic removed), and RBL (baseline removed) were created by respectively removing the intra-day, diurnal, synoptic, and baseline TS component from the original datasets. Multilinear Engine 2 (ME-2) and/or principal component analysis was applied to these four datasets as well as the original datasets for source apportionment. ME-2 solutions using the original and RI dataset identify crustal dust contributions. For the solutions from original, RI, RD, and RS datasets, the total primary source impacts are close, ranging from 35.1 to 40.4 μg m^{-3} during the entire sampling period. For the secondary source impacts, solutions from the original,

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RI and RD dataset give similar source impacts (about 30 μg m^{-3}), which were higher than the impacts derived from the RS datasets (21.2 μg m^{-3}).

Key words: Multilinear Engine 2, Kolmogorov–Zurbenko filter, particulate matter, temporal-scale components, source impact.

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1 Introduction

Aerosol pollutants have become a major problem in recent years (Huang et al., 2014; van Donkelaar et al., 2015), due to its negative influences on visibility, climate change and human health (Langridge et al., 2012; Cheng et al., 2015; Butt et al., 2016; Ding et al., 2017). Variations in aerosol concentrations and chemical species reflect influences from multiple factors, such as local emissions sources and weather conditions, etc. (Keim et al., 2005). Observed concentrations of pollutants, in general, have characteristic variations, which are influenced by data noise, source intensities, short-term fluctuations, source seasonal variation, meteorological condition, climate, policy, and economic conditions (Milanchus et al., 1998; Wise and Comrie, 2005).

Online instruments can provide high time resolution data of particulate matter (PM) and chemical species, and these instruments have been widely applied in the detection of pollutants (Tchepel et al., 2010; Du et al., 2011; Zheng et al., 2015; Gao et al., 2016). More and more studies on aerosol pollution have become dependent on high temporal resolution observations due to their capabilities in revealing multiple temporal-scale fluctuations of the aerosol concentrations that tend to arise from different physical, chemical and dynamical processes. For example, during a high pollution period, pollutant concentrations increase rapidly by several times over a short time period, and such an increase tends to result from changing meteorological conditions. Hogrefe et al. (2000) suggested that the time series of pollutant concentrations can be decomposed into four components. The first component is the intra-day component with periods less

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than 12 h and is typically linked to fast-acting, local emission sources and local-level processes (Tchepel et al., 2010). The second is the diurnal component dominated by 12-48 h periodicity. The third is the synoptic component mainly driven by 2-21 day fluctuations in weather patterns and short-term fluctuations in emissions. The last baseline component is related to the low-frequency fluctuations with periods greater than 21 days, which might including seasonal or long-term scale variation in emissions, climate, policy, etc. (Rao et al., 1997; Wise and Comrie, 2005).

Pollution sources are the key drivers of aerosol pollution. Understanding source impacts on aerosols is important for the control of air pollution (Zhao et al., 2017). Factor analysis models are widely used for estimating source impacts. These models include principal component analysis/multiple linear regression (PCA/MLR), Unmix, positive matrix factorization (PMF), and Multilinear Engine (ME-2) (Thurston and Spengler, 1985; Paatero and Tapper, 1994; Henry and Christensen, 2010; Yin et al., 2015; Zong et al., 2016). Among these, ME-2 is a particularly useful tool and has been widely used in source apportionment studies (Paatero, 1999; Amato et al., 2009; Peng et al., 2016). Factor analysis models depend on the variation of chemical species in aerosols (which reflects the temporal variation of sources) to extract source categories and calculate their contributions. Therefore, multiple temporal-scale variations in the raw online datasets associated with various factors (e.g., data noise and weather fluctuations) can have significant impacts on the source apportionment results using factor analysis models. This is the main motivation behind our analysis, i.e., to decompose the raw online datasets into multiple temporal-scale components and then

to estimate the influences of inclusion/exclusion of a specific temporal component on the final apportionment results.

The Kolmogorov–Zurbenko (KZ) filter used in our study for extraction of a specific temporal-scale component (TS component hereafter) is a low-pass filter that has been widely used for decomposing temporal variations in O_3, PM, and chemical species (Rao et al., 1997; Hogrefe et al., 2000, 2006; Wise and Comrie, 2005; Tchepel et al., 2010). Hogrefe et al. (2006) reported that the synoptic component associated with synoptic scale weather fluctuations has the largest relative contribution to the total variance of hourly $PM_{2.5}$ concentrations, and the relative contributions of other components to total $PM_{2.5}$ mass concentrations varies by chemical species in $PM_{2.5}$. In addition, the noise of data might impact the analysis, and efforts have been made to remove the noise (Kuebler et al., 2001; Tchepel et al., 2010; Henneman et al., 2015). Our earlier studies demonstrated that the time resolution of the data could influence the source apportionment results (Peng et al., 2016). Tchepel et al, (2010) used the KZ filter to remove noise in the PM data, fed filtered PM data into air quality models and showed that the model performance improved. In this study, we make a preliminary assessment of the impacts of multiple temporal-scale variations in PM data on source apportionment with $PM_{2.5}$ (PM with an aerodynamic diameter less than 2.5 μm) and its chemical species observed in Beijing, China. Wavelet analysis was first used to evaluate the periodicities of the PM and chemical species concentrations. The time series data of the PM and chemical species were then decomposed into multiple TS components using the KZ filter. Several new datasets were created by removing individual TS

components from the original receptor datasets. ME-2 or PCA analysis was conducted on the original and new datasets to assess the impacts of excluding a specific TS component on the final source apportionment results. We aim to determine what processes/sources are responsible for the main variation characteristics and overall pollution levels in this specific dataset. We also aim to determine what the implications of our results are for source apportionment analyses conducted with data from different geographical locations and under various weather/climate conditions.

2 Methods

2.1 Sampling

Ambient particles were collected in Beijing from 22 July 2014 to 12 August 2014 at CRAES (Chinese Research Academy of Environmental Sciences) in this research. And concentrations of $PM_{2.5}$, inorganic ions, OC/EC and heavy metals were measured by β-ray monitor, model ADI 2080 online analyzer (MARGA, Applikon Analytical B.V., The Netherlands), OC/EC analyzer (Sunset Laboratory Inc, USA) and the Xact 625 automated multi-metals monitor (Copper USA), respectively, at 1 h time resolution. Twenty-three chemical species were selected for analysis, including NH_4^+, Na^+, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Ag, Cd, Ba, Hg, Pb, OC and EC. The principles of these instruments and QA/QC are described in detail by Gao et al. (2016).

2.2 Source Impact Model

ME-2, a general factor analysis model developed by Paatero (1999), was applied to

estimate the impacts of source categories at a location of interest. It is a general solver of widely different multilinear and quasi-multilinear problems (Ramadan et al., 2003) with the ability to deal with models consisting of a sum of products of unknowns. Instead of being restricted to a specific structure, ME-2 is defined in a "script file" that is written in a special-purpose programming language. It has efficient performance as it runs in DOS, which made it faster than those models with graphical interfaces (Ramadan et al., 2003). ME-2 decomposes original matrix $X_{(m\times n)}$ into source impact matrix $G_{(m\times p)}$ and source chemical species (source profile) matrix $F_{(p\times n)}$, as follow:

$$X_{(m\times n)} = G_{(m\times p)}F_{(p\times n)} + E_{(m\times n)} \quad (1)$$

Variable $X_{(m\times n)}$ is the chemical species concentrations (unit: μg m^{-3}) in $PM_{2.5}$ that are observed at the receptor site; $E_{(m\times n)}$ is the residual matrix; m and n are the sample size and chemical species number, respectively; and p is the number of sources. The basic principle of ME-2 also can be expressed as follow:

$$x_{ij} = \sum_{k=1}^{p} g_{ik}f_{kj} + e_{ij} \quad \text{i} = 1,2,\dots,\text{m} \quad \text{j} = 1,2,\dots,\text{n} \quad (2)$$

where x_{ij} is the element in matrix $X_{(m\times n)}$, which is the measured concentration of the j^{th} specie in the i^{th} sample (μg m^{-3}); g_{ik} is the element in matrix $G_{(m\times p)}$ and is the impact of the k^{th} source on the i^{th} sample; f_{kj} is the element of matrix of $F_{(p\times n)}$ and is the concentration of the j^{th} specie in the k^{th} source (source profile); and e_{ij} is the element in the residual matrix (Hopke, 2003).

In ME-2, a priori information (e.g. chemical profiles and ratios) can be incorporated as a target to be approximately accomplished. The prior information must

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be handled in form of auxiliary equations (Paatero, 1999). Auxiliary equations are included as additional terms Q_{aux} in an enhanced object function Q_{enh} (Amato et al., 2009; Amato and Hopke, 2012), the equation can be written as follows:

$$Q_{enh} = Q_{main} + Q_{aux} \quad (3)$$

The term Q_{main} is described as follows:

$$Q_{main} = \sum_{i=1}^{m} \sum_{j=1}^{n} (e_{ij}/\sigma_{ij})^2 \quad (4)$$

where σ_{ij} is the uncertainty in the j^{th} species for the i^{th} sample; e_{ij} has the same meaning as is described in Eq.(2).

One of the simplest forms of the auxiliary equation is the "pulling equation" (Paatero and Hopke, 2009), consisting of pulling f_{kj} (for instance) toward the specific target value a_{kj}:

$$Q_{aux} = \frac{(f_{kj} - a_{kj})^2}{\sigma_{kj}^{aux2}} \quad (5)$$

where σ_{kj}^{aux} is the uncertainty connected to the pulling equation or softness of the pull; and f_{kj} is the element of factor loading. The task of ME-2 is to calculate a minimum Q_{enh} value or balance the minimization of the values Q_{main} and Q_{aux} in the iterative process (Paatero and Hopke, 2009).

For ME-2, it requires that every element in the input dataset (matrix X) be a non-negative value. Some datasets removing TS component in this work have negative values and were analyzed using PCA instead of ME-2 due to this non-negative requirement. PCA is a useful method to qualitatively identify the pollutant sources. It reduces the number of original variables and generates a set of new variables (or called principal components) that are ordered by the contribution to the total variance in the

original data.

2.3 Temporal Scale Analysis

The KZ filter is a widely applied filtering technique due to its powerful separation characteristics, simplicity, and ability to handle missing data (Rao et al., 1997; Hogrefe et al., 2006). The principle of KZ filter is described as follow:

$$y_t = \frac{1}{m}\sum_{s=-(m-1)/2}^{(m-1)/2} x_{(t+s)} \quad (6)$$

m is the length of the moving average window, which is an odd number; $x_{(t+s)}$ is the $(t+s)^{th}$ original value, y_t is the average value. Then the y_t as the input data and calculate according to Eq. (6). After k times (number of iterations) calculation, $y_t^{(k)}$ is expressed as:

$$y_t^{(k)} = KZ_{m,k}(X) \quad (7)$$

$y_t^{(k)}$ is removed the variations that frequency lower than w (cutoff frequency). k is the number of iterations. Before conducting the KZ filter, the data is log transformed for variance stabilization (Hogrefe et al., 2000). The separation point w, between the high-frequency and low-frequency component, is a function of the filter parameters m and k (Rao et al., 1997). The equation can be written as follows:

$$w \approx \frac{\sqrt{6}}{\pi}\sqrt{\frac{1-(1/2)^{1/2k}}{m^2-(1/2)^{1/2k}}} \quad (8)$$

Selecting proper filter parameters m and k could remove the temporal component at a specific frequency from the original dataset.

To select the appropriate parameters for the KZ filter, the wavelet analysis method analyzed the $PM_{2.5}$ and chemical species' periodicities before decomposing their

concentrations time series. The results of wavelet analysis suggested that the periodicities of $PM_{2.5}$ and chemical species are mainly 4-8 h (<12 h), 16-32 h, and 128-256 h (6-10 day) (Figure S1, see the Supporting Information), which was similar to the results reported by Hogrefe et al. (2000). This work referred to the KZ filter parameters reported by the Hogrefe et al. (2000) study, and decomposed the $PM_{2.5}$ and chemical species hourly concentrations into intra-day (time period less than 12 h), diurnal (12-24 h), and synoptic (2-21 days) TS components to evaluate the influence of TS components on their temporal variability. The formulas of the different TS components are as follow:

$$X_{(intra-day)} = X_{(Original)} - e^{KZ_{3,3}\{ln[X_{(Original)}]\}} \quad (9)$$

$$X_{(diurnal)} = e^{\mathrm{KZ}_{3,3}\{ln[X_{(Original)}]\}} - e^{\mathrm{KZ}_{13,5}\{ln[X_{(Original)}]\}} \quad (10)$$

$$X_{(synoptic)} = e^{\mathrm{KZ}_{13,5}\{ln[X_{(Original)}]\}} - e^{\mathrm{KZ}_{103,5}\{ln[X_{(Original)}]\}} \quad (11)$$

$$X_{(baseline)} = X_{(Original)} - X_{(intra-day)} - X_{(diurnal)} - X_{(synoptic)} \quad (12)$$

$X_{(Original)}$ (original dataset) is the measured concentrations dataset including $PM_{2.5}$ and chemical species (μg m^{-3}); $X_{(intra-day)}$, $X_{(diurnal)}$, $X_{(synoptic)}$, and $X_{(baseline)}$ are concentration datasets of the intra-day, diurnal, synoptic and baseline components, respectively (μg m^{-3}). The subscript numbers of KZ are descriptive parameters. For example, the first "3" in $KZ_{3,3}$ is the length of the moving average window, and the second "3" is the iteration time.

2.4 TS Component Removed Datasets

To exam the impact of the four TS components on the source impacts, datasets without

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the TS component influence were created. Four datasets were created by respectively removing the intra-day, diurnal, synoptic, and baseline TS component from the original datasets, as follow:

$$X_{(intra-day\ removed)} = e^{\mathrm{KZ}_{3,3}\{ln[X_{(Original)}]\}} \quad (13)$$

$$X_{(diurnal\ removed)} = X_{(Original)} - X_{(diurnal)} \quad (14)$$

$$X_{(synoptic\ removed)} = X_{(Original)} - X_{(synoptic)} \quad (15)$$

$$X_{(baseline\ removed)} = X_{(Original)} - X_{(baseline)} \quad (16)$$

$X_{(intra-day\ removed)}$ (RI dataset) is the concentration dataset with the intra-day TS component removed from the original dataset (μg m^{-3}) and it contains the diurnal, synoptic, and baseline TS components. $X_{(diurnal\ removed)}$ (RD dataset), $X_{(synoptic\ removed)}$(RS dataset), and $X_{(baseline\ removed)}$ (RBL dataset) are the datasets with the diurnal, synoptic, and baseline TS components singly removed from the original dataset, respectively. As there were many negative values in the RBL dataset, these data were analyzed by PCA to qualitatively identify the sources of $PM_{2.5}$. The original, RI, RD, and RS datasets were run by ME-2 for the source apportionment, and their results were compared. Also, few negative values (very low count) were replaced with a value equal to half of the detection limits. The average absolute error (AAE, see the SI) and correlation analysis were employed to compare the differences in the source impacts between original dataset and datasets with removed TS components. AAE was employed and is calculated as follows (Javitz et al., 1988):

$$AAE_k = \frac{1}{n} \times \sum_{i=1}^{n} \frac{|E_{ik} - T_{ik}|}{T_{ik}} \times 100 \quad (17)$$

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where, AAE_k is the AAE value for the k^{th} species and n is the number of samples. E_{ik} is the concentration (μg m^{-3}) of the k^{th} species for the i^{th} sample from the RI, RD, or RS datasets. T_{ik} is the concentration (μg m^{-3}) of the k^{th} species for the i^{th} sample from the original dataset. The larger AAE value and the lower correlation coefficients (r) indicate a larger difference in source impacts between the original dataset and modified datasets, suggesting that the corresponding TS component has a larger influence on the observed concentrations.

3 Result and discussion

3.1 TS Component Influence on Concentrations

The influence of each TS component on the pollutant concentration variation and the concentration levels were investigated. The original dataset was decomposed into intra-day, diurnal, synoptic, and baseline TS components by using the KZ filter (Figure 1). The variation analysis was then employed to study each TS component contribution to the total variance of $PM_{2.5}$ and the chemical species concentrations (Table 1). We placed emphasis on investigating $PM_{2.5}$ and the source markers (e.g. SO_4^{2-}, Ca, OC, etc.), because the variation of those markers can reflect the source emission pattern to some extent.

The sample size of the four TS components was less than original dataset, because the KZ filter was iterated with a moving average with a specified length and resulted in missing head and tail data of the original data. The same period (from 24 July 2014 to 10 August 2014) of the original datasets with the same size were selected for

comparison and analysis. Among all the species, $PM_{2.5}$ and NO_3^- had similar trends: the diurnal and synoptic TS components had larger amplitudes and higher relative contributions to the total variance of $PM_{2.5}$ (diurnal: 36%, synoptic: 32%) and NO_3^- (diurnal: 36%, synoptic: 32%) than the intra-day and baseline TS components. SO_4^{2-} and NH_4^+ showed similar variability: synoptic TS component had the largest amplitude and had the largest relative contributions to the total variance of SO_4^{2-} (48%) and NH_4^+ (54%) concentrations, followed by the baseline, diurnal and intra-day TS components. OC was relatively different from the species mentioned above. For OC, the relative contribution of the synoptic TS component was the largest (56%), followed by diurnal (23%), baseline (12%) and intra-day TS components (9%). Species from primary emission sources (such as EC, Ca, Fe, etc.) showed different patterns, compared with the secondary species (NO_3^-, SO_4^{2-}, NH_4^+) discussed above. For EC and Ca, the diurnal TS component had the largest relative contribution to the total variance of concentrations, accounting for 47% and 45%, respectively. The synoptic (28%) and intra-day (40%) TS component was the second largest contributor to the total variance of EC and Ca concentrations, respectively. For Fe, diurnal and synoptic TS components had larger amplitudes and higher relative contributions to the total variance than intra-day and baseline TS components. For other elements, diurnal or intra-day TS components had the largest amplitudes and were the larger contributors to the total variance of the concentrations. Secondary organic carbon (SOC) also has been estimated using the OC/EC ratio (see Supporting Information), and the influence of TS component on the SOC was investigated (Table 1). The average concentration of SOC

was 5.7 ± 3.1 μg m^{-3} in this work. For SOC, the diurnal and synoptic TS components had larger amplitudes (Figure S2) and higher relative contributions to the total variance of $PM_{2.5}$ (diurnal: 20%, synoptic: 62%). For species showing different TS component contributions, the cause was external influencing factors. For example, variability in primary species (such as Ca, EC) concentrations was mainly caused by local emission patterns and meteorological diffusion(van Pinxteren et al., 2009); secondary species were mainly influenced by chemical reaction (photochemical, liquid phase or heterogeneous reaction) and meteorological conditions (Buzcu et al., 2006; Jung et al., 2010, Martin et al., 2014). Therefore, species with similar TS component contributions trends may have similar sources or influencing factors.

To investigate the influence of the TS components on concentration levels, partial statistical analysis and AAE analysis were performed on the $PM_{2.5}$ and source markers (NO_3^-, SO_4^{2-}, NH_4^+, Ca, Fe, OC, and EC) from five ambient datasets (including the original, RI, RD, RS, and RBL datasets). The results are shown in Figure 2 and Table S1. For ions, elements, OC/EC and $PM_{2.5}$, the larger gap in AAE value between the concentrations of RBL and original dataset means a larger difference between them, suggesting that the baseline TS component was the largest contributor to the average concentrations of $PM_{2.5}$ and chemical species. The synoptic TS component also had a relatively high contribution to the average concentrations of NO_3^-, SO_4^{2-}, and NH_4^+. The average concentrations of the three ions of the RS dataset were obviously lower and had large AAE values, compared with the results of the original dataset. For $PM_{2.5}$ and seven species, the correlation coefficients for the original dataset and RI, RD, RS,

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and RBL datasets are displayed in Table S2. The lowest correlation coefficients were obtained for the RBL TS components and the original data.

Overall, baseline TS components dominating the average concentrations of $PM_{2.5}$ and chemical species might imply that pollutant emissions and other long-term fluctuation factors mainly determined the pollutants level in Beijing, from 22 July 2014 to 12 August 2014. When synoptic, diurnal, and intra-day TS components mainly influenced the variation of $PM_{2.5}$ and chemical species, this suggests that the short-term fluctuation (e.g. noise, weather etc.) dominantly determined the variation of pollutants.

3.2 Source Impacts on $PM_{2.5}$ Concentrations

Four datasets, including the original, RI, RD and RS datasets, were respectively introduced into ME-2 to identify the sources of $PM_{2.5}$. The RBL was analyzed by PCA, as several negative values were in this dataset (the ME-2 model only allows nonnegative input values). The source apportionment results were explored, including source profiles and source impacts, to investigate the source impacts on the $PM_{2.5}$ concentrations under the influence of different TS components.

For all four datasets, 3 to 7 factors were tested to determine the optimal number of factors (source categories). There are some criteria for choosing the appropriate number of factors, including the Q values, physical meaningfulness of the factor profiles, the reasonableness of source impacts, and goodness of fit for $PM_{2.5}$ and chemical species concentrations. After testing, four source categories were identified using ME-2 from the original, RD, and RS datasets; five sources were obtained from the RI dataset. When

328 the calculated Q value close to the theoretical Q (Q_{the}), the corresponding results might
329 be acceptable (Hopke, 2003). The Q values of each solution calculated by ME-2 are
330 displayed in Table S3 and were close to the theoretical Q, further suggesting that the
331 results are acceptable.

332 Performance of ME-2 was evaluated by analyzing the goodness of fit for the
333 modeled and measured $PM_{2.5}$ and chemical species mass concentrations (slope, r).
334 Figure S3 illustrates the slope and r results, respectively. For $PM_{2.5}$, the slopes (ranging
335 from 1.0 to 1.1) and r (ranging from 0.8 to 1) were close to 1, suggesting the good
336 performance of ME-2 obtained for the five runs. For original dataset run, 13 out of 23
337 chemical species (e.g. SO_4^{2-}, OC, EC, Fe,) obtained slop values ranged from 0.80 to
338 1.20, and r of the corresponding species were varied from 0.60 to 0.96. Other species
339 (e.g. As, Cr, Se) obtained high slop values (larger than 1.20) and relative low r (ranged
340 0.01 to 0.84), indicating the poor precision of modeled results for those species.
341 Performance of solutions from RI and RD datasets are better than the solution from
342 original dataset, due to more species obtained good slops and r values (close to 1). For
343 RS run, slop values of chemical species range from 0.94 to 1.45, and values of six
344 chemical species larger than 1.20. The correlation coefficients are ranged from -0.06 to
345 0.95, which are similar with the results from the original dataset. The precision of
346 results from BL dataset is the best than the other four runs, because slop and r values
347 (larger than 0.89) of all species are close to 1. Summarily, receptor data filtering by KZ
348 filter approach can improve the performance of model results obtained by ME-2.

349 For the original dataset, four factor profiles were obtained (Figure 3). Factor 1 was

characterized by Ca and Fe, which is linked to crustal dust (Pant and Harrison, 2012). Factor 2 had OC and EC, which are markers of vehicle emissions (Ramadan et al., 2003). Factor 3 was identified as coal combustion due to high loadings of OC, EC and Ca (Ramadan et al., 2003). Factor 4 was secondary formation due to elevated SO_4^{2-}, NO_3^- and NH_4^+ (Pant and Harrison, 2012). According to the previous studies (Yu et al., 2013), coal combustion, secondary formation, vehicle emissions and crustal dust were the dominating sources of $PM_{2.5}$ in Beijing. Five sources were obtained from the RI dataset, including coal combustion, crustal dust, secondary formation, secondary nitrate and vehicle emissions (Figure 3). For the RD and RS datasets, coal combustion, secondary formation, secondary nitrate and vehicle emissions were identified (Figure 3), and crustal dust was not identified and was mixed with vehicle emissions from the two datasets. It was an expected result that ME-2 failed to identify the crustal dust source for the RD dataset. Because ME-2 extracts factors based on the chemical species variation pattern (the marker species variation can reflect the source emission pattern over the time), crustal dust markers (Ca and Fe) lost much variance and could not reflect the expected pattern after removing the diurnal TS component (the largest contributor to the total variance of Ca and Fe) (Table 1). As for the solution for RS dataset, the sulfate source (not the secondary formation) and the nitrate source were distinguished as different factors (Figure 3). For the solutions of the original, RI, and RD datasets, secondary formation of sulfate and nitrate source were mixed together and extracted as one factor. We found that after removing the similar part of the variance (the information filtered by KZ filter) of sulfate and nitrate, the difference between sulfate

and nitrate variation trend was more obvious, so these two sources can be distinguished by ME-2. It can be confirmed that the correlation coefficient between NO_3^- and SO_4^{2-} was highest (0.86) for the synoptic TS component compared with other TS components (0.41, 0.28, and 0.82 for intra-day, diurnal, and baseline TS components, respectively). The correlation was lowest (0.49) for the RS dataset compared with other datasets (0.68, 0.72, and 0.85 in the original, RI, and RD datasets, respectively).

The PCA results of the RBL dataset are listed in Table S4. Seven factors were extracted and accounted for 80.9% of the total variance, which had corresponding eigenvalues larger than 1 (can be considered as the potential sources). Factor 1 (19.6% of the variance) had high loadings for heavy metals, such as As, Se, Pb, etc. Factor 2 had high loadings for Ca and Ba, and relatively high loadings for Mn, Fe, and EC. This factor might be associated with crustal dust and had a 14.3% contribution to the variance (Pant and Harrison, 2012). High loadings were observed for SO_4^{2-}, NO_3^-, and NH_4^+ in factor 3, which is associated with secondary formation (Pant and Harrison, 2012). Factor 4 had relatively high loadings for Cu and Cl^-, and factor 5 and 6 were characterized by heavy metals. After removing the baseline dataset, heavy metals and crustal dust were the dominant sources of $PM_{2.5}$. According to the results of the RBL dataset, we found the evidence that intra-day and diurnal TS components had larger relative contributions to the total variance of element (heavy metals) concentrations, as these elements are mainly emitted from primary sources.

Because there were different sample sizes for the four datasets, we selected the same period of results (from 24 July 2014 to 10 August 2014) to study the influence of

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TS components on the source variation (Figure 4). The time series of source impacts from the RI, RD, and RS datasets were respectively used for correlation analysis with the corresponding results from the original dataset (Table S5). Vehicle emissions solutions from the RI (r = 0.45) and RD (r = 0.51) datasets had a higher correlation than the RS dataset (r = 0.25), suggesting that intra-day and diurnal TS components had stronger influences on the source pattern (variation) of vehicle emissions. For coal combustion, results from the RI, RD, and RS datasets had similar correlation coefficients (ranging from 0.74 to 0.82). The sulfate source was identified from the RS dataset (Figure 3), however, the sulfate source had the lowest correlation with secondary formation (Table S5) solutions from the original dataset. The correlation analysis of the nitrate source produced similar results, where the lowest correlation coefficient occurred between solutions from the RS dataset and original dataset, suggesting that secondary source impact variation is dominantly affected by synoptic scale influences.

To further investigate source impacts on $PM_{2.5}$ from different TS components, we discussed the average impacts of individual source categories on $PM_{2.5}$ from the datasets with removed TS components (Table 2).

Vehicle emissions, crustal dust, and coal combustion were combined together for the analysis (called as TPS: total primary sources), because crustal dust was mixed with vehicle emissions and coal dust for the RD and RS datasets, as mentioned above. Secondary formation and nitrate source were also plus together for the discussion (called as TSS: total secondary sources). To better explore the influence of TS

components, source impacts during the entire sampling period and pollution period were investigated separately. For the entire sampling period, the impacts of TPS obtained from the original, RI, RD, and RS datasets were similar to each other, ranging from 35.1 to 40.4 μg m^{-3}. This was an expected result because the intra-day, diurnal, and synoptic TS components had small influence on the concentrations levels of primary source markers (OC, EC, elements), as shown in Figure 2. The TSS solutions from the original, RI, and RD datasets exhibited similar source impacts, accounting for about 30 μg m^{-3}, which was higher than the solution from the RS dataset (21.2 μg m^{-3}). The synoptic TS component had impact on the SO_4^{2-}, NO_3^- and NH_4^+ concentrations, and removing this TS component may have resulted in lower impacts of the secondary sources.

During the pollution period (from 30 July to 4 August 2014, gray shadow shown in Figure 1), the highest concentration of $PM_{2.5}$ was up to 183.7 μg m^{-3} at 1:00 am on 31 July 2014, with an average concentration of 85.5 μg m^{-3}. The TPS impacts derived from the original, RI, RD, and RS datasets were relatively stable, ranging from 30.3 μg m^{-3} to 37.4 μg m^{-3} (Table 2). The TSS impacts from the RS dataset (29.3 μg m^{-3}) were lower than the solutions from the original, RI, and RD runs (about 51 μg m^{-3}). The synoptic TS component increased the NO_3^-, SO_4^{2-}, and NH_4^+ concentrations (Figure 1), accounting for 58%, 57%, and 50% of their original average concentrations, respectively. This implies that the synoptic TS component had a larger impact on the secondary source than the primary source during the pollution period. Liu et al. (2017) reported that some haze episodes in North China Plain (including Tianjin) resulted from

438 elevated relative humidity (RH) and stagnant weather conditions. The study proposed
439 an inorganic aerosol formation mechanism for which the elevated RH and the inorganic
440 fraction increased the aerosol liquid water content (LWC), then the liquid particles
441 would uptake pollutants to form the aerosols. In this work, elevated RH and reduced
442 wind speeds have been observed during the pollution period (Figure S4). To further
443 confirm the assumption, the aerosol LWC was estimated using ISORROPIA II model
444 (Guo et al., 2015). The LWC and total ions (NO_3^-+SO_4^{2-}+NH_4^+) depending on RH are
445 shown in Figure S5. Under similar RH conditions, the total ions (ranged from 93 to 121
446 μg m^{-3}) and LWC concentrations (ranged from 48 to 513 μg m^{-3}) during the pollution
447 period were higher than the corresponding values (total ions concentrations: 22 to 38
448 μg m^{-3}; LWC: concentrations 12 to 108 μg m^{-3}) during the non-pollution, suggesting
449 high total ion and LWC concentrations. When the RH lower than 90% during the
450 pollution period, the total ions concentrations remained relatively stable (about 100μg
451 m^{-3}), while the LWC concentrations increased. When the RH was higher than 90%, the
452 total ions and LWC concentrations increased to 120 and 513 μg m^{-3} during the pollution
453 period, respectively, suggesting the drastically increasing in LWC concentrations may
454 have led to the elevated ions concentrations. Therefore, the stagnant weather conditions
455 and the elevated RH may increase the inorganic concentrations during the pollution
456 period in this work.

457 Overall, removing the different TS components had little influence on primary
458 source impact levels, suggesting that primary source impact levels were mainly
459 influenced by the source emissions. The secondary source impact levels were mainly

influenced by synoptic influences and source emissions.

The BL dataset may be linked with source emissions, source seasonal variance, and long-term meteorological fluctuations. To study the source impacts from the baseline TS component, ME-2 was applied to the baseline dataset. Four sources were identified, including the nitrate source, secondary formation, coal combustion, and vehicle emissions (Figure S6). During the entire sampling period (Table 3), the average TPS and TSS impacts on $PM_{2.5}$ mass concentrations were 29.9 μg m^{-3} (57%) and 22.8 μg m^{-3} (43%) respectively. The average impacts of TPS and TSS during the pollution period were higher than the corresponding average impacts during the entire sampling period, which were 35.6 μg m^{-3} and 26.0 μg m^{-3}, respectively (Table 3). TPS and TSS obtained same impact percentages from the entire period and pollution period, accounting for 58% and 42% of $PM_{2.5}$ mass concentrations, respectively. The time series of TPS, TSS, and $PM_{2.5}$ are shown in Figure S7 and suggest that the periodicities of TPS and TSS were not synchronized. In this work, the peak of the BL TS component of $PM_{2.5}$ was obtained when the both the TPS and the TSS impact levels were high.

4 Conclusions

In this work, KZ filter was applied to decompose the time series of $PM_{2.5}$ and chemical species concentrations collected in Beijing into intra-day, diurnal, synoptic, and baseline temporal-scale (TS) components. This work investigated the factors driving these variations, and influencing factors were found to vary with species. The intra-day and diurnal TS components mainly influence the fluctuation of elements concentrations

(e.g. Ca, Cr, Mn, etc); diurnal and synoptic TS components mainly impacted the fluctuation of $PM_{2.5}$, NO_3^-, EC, and OC concentrations; baseline and synoptic TS components were the main factors contributing to SO_4^{2-} and NH_4^+ variance. For the $PM_{2.5}$ and all chemical species concentration levels, the baseline TS component was the dominant factor.

To study the influence of different TS components on the source impacts on $PM_{2.5}$, four datasets (RI, RD, RS, and RB) were created by removing one individual TS component from the original dataset each time. The original and the four modified datasets were analyzed by ME-2 and/or PCA, and the source apportionment results were compared. We found that removing some TS components affected the source identification. Four sources were obtained from the original and RI analyses, including crustal dust, vehicle emissions, coal combustion, and secondary formation. Crustal dust was not identified by ME-2 from the RD, RS, and BL datasets, possibly due to the fact that much of the information regarding the markers of crustal dust (e.g. Ca) was lost after removing the corresponding TS components. This suggests that the diurnal and synoptic TS components of chemical species were important for identifying the crustal dust source.

For the solutions from the original, RI, RD, and RS datasets, TPS (including crustal dust, vehicle emissions, and coal combustion) were similar to each other, implying that intra-day, diurnal or synoptic TS components had little influence on the TPS impact levels. The TSS (secondary formation and nitrate source) from the original, RI, and RD datasets obtained similar source impact levels; while TSS impact from the

RS dataset was lower than other three results, suggesting that TSS was mainly influenced by the synoptic TS component and source emissions. Performance of four ME-2 runs was evaluated by analyzing the goodness of fit for the modeled and measured $PM_{2.5}$ and chemical species mass concentrations (slope, r). Receptor data filtering intra-day TS components by KZ filter approach can improve the performance of the model and produce reasonable source impact results, suggesting that filtering noise from the instrument is useful to data analysis.

The major findings of this work are that during the whole sampling period and pollution period, TPS impact levels were mainly influenced by source emissions, and TSS impact levels were mainly influenced by synoptic scale weather fluctuations and source emissions. The future work will focus on the mechanism through which synoptic scale weather disturbances modulate the secondary species and sources.

Data availability. The data used in this study are available from the corresponding author upon request (**nksgl@nankai.edu.cn; fengyc@nankai.edu.cn**).

Competing interests. The authors declare that they have no conflict of interest.

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682 ## Tables

683 **Table 1.** Relative contributions (%) of the different TS components to the total variance of $PM_{2.5}$

684 and chemical species concentrations.

	NO_3^-	SO_4^{2-}	NH_4^+	OC	EC	Ca	Fe	SOC	$PM_{2.5}$
Intra-day (%)	5	4	4	9	17	**40**	20	9	9
Diurnal (%)	**36**	18	17	23	**47**	**45**	**32**	**20**	**36**
Synoptic (%)	**32**	**48**	**54**	**56**	28	10	**32**	**62**	**32**
Baseline (%)	27	31	26	12	8	5	16	9	24

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686 **Table 2.** Average source contributions to $PM_{2.5}$ (μg m^{-3}) estimated by ME-2 from Beijing for the

687 original, RI, RD, and RS datasets during the entire sampling period.

		Crustal dust	Vehicle emission	Coal combustion	TPS[a]	Secondary formation	Nitrate source	TSS[b]
During the entire sampling period	Original	14.2 (20%)	15.2 (22%)	11 (16%)	**40.4 (58%)**	29.4 (42%)		**29.4 (42%)**
	RI	8.6 (13%)	12.7 (19%)	18.5 (27%)	**39.9 (58%)**	26.3 (38%)	2.3 (3%)	**28.7 (42%)**
	RD		14.4 (22%)	20.8 (32%)	**35.1 (54%)**	26.2 (41%)	3.2 (5%)	**29.4 (46%)**
	RS		19.2 (32%)	19.8 (33%)	**39 (65%)**	6.8 (11%)	14.4 (24%)	**21.2 (35%)**
Pollution period	Original	13.5 (16%)	12.3 (14%)	7.7 (9%)	**33.5 (39%)**	52.1 (61%)		**52.1 (61%)**
	RI	6 (7%)	10.1 (12%)	17.9 (21%)	**34 (40%)**	50.3 (59%)	1.0 (1%)	**51.2 (60%)**
	RD		14.8 (18%)	15.5 (19%)	**30.3 (37%)**	48.9 (60%)	2.5 (3%)	**51.4 (63%)**
	RS		24.4 (37%)	13.1 (20%)	**37.4 (56%)**	10.8 (16%)	18.5 (28%)	**29.3 (44%)**

688 [a]TPS is the total contributions of crustal dust, vehicle emissions, and coal combustion. [b]TSS is the

689 total contributions of secondary formation and nitrate source.

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690 **Table 3.** Average source contributions to $PM_{2.5}$ (μg m^{-3}) estimated by ME-2 from the BL datasets.

	Vehicle emission	Coal combustion	TPS[a]	Secondary formation	Nitrate source	TSS[b]
During the entire sampling period	15.4 (29%)	14.5 (28%)	**29.9 (57%)**	12.0 (23%)	10.8 (20%)	**22.8 (43%)**
Pollution period	17.6 (29%)	17.9 (29%)	**35.6 (58%)**	22.4 (36%)	3.6 (6%)	**26.0 (42%)**

691 [a]TPS is the total contributions of crustal dust, vehicle emissions, and coal combustion. [b]TSS is the

692 total contributions of secondary formation and nitrate source.

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Figures

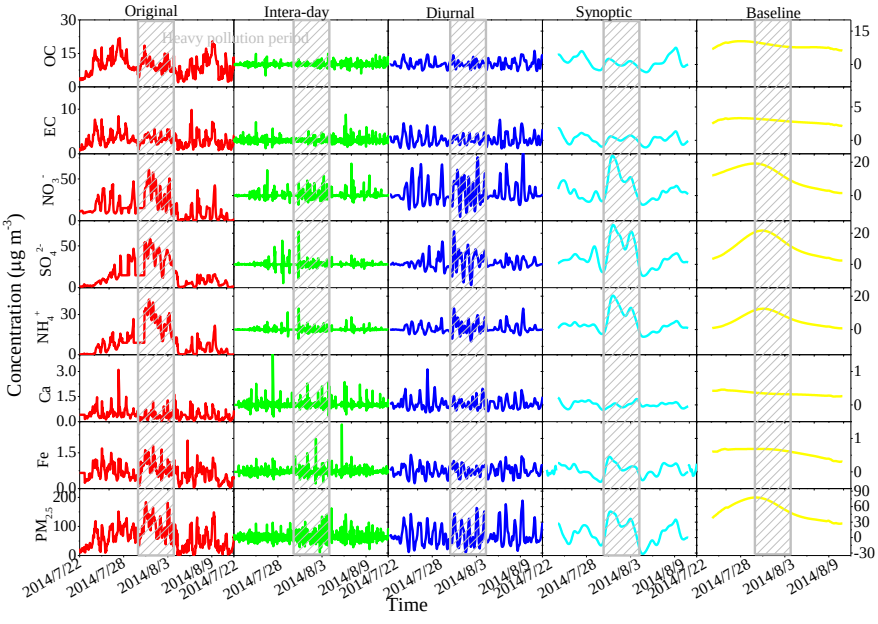

Figure 1. Variance of $PM_{2.5}$ and chemical species concentrations influenced by intra-day (time period less than 12 h), diurnal (12-24 h), synoptic (2-21 days), and baseline (greater than 21 days) temporal-scale (TS) components, for the period of 22 July 2014 to 13 Aug 2014 at Beijing, China. The variation of species that originated from primary sources mainly were influenced by diurnal TS components. The variation of ions and OC (partly from secondary formation) that originated from secondary formation mainly were influenced by synoptic TS component. The vertical gray lines demarcate the heavy pollution period.

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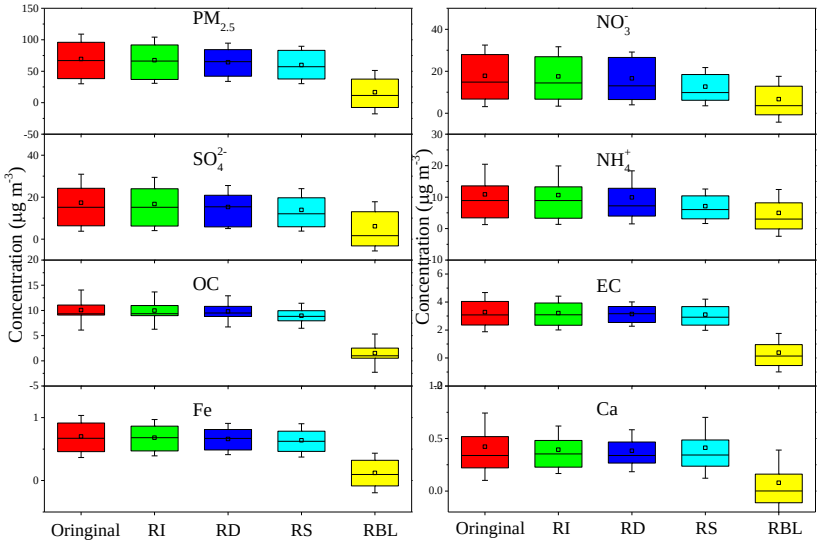

Figure 2. The influence of different TS components on the average concentrations of $PM_{2.5}$ and chemical species. The baseline TS component dominated the $PM_{2.5}$ and chemical species average concentrations. Presented are box plots of individual chemical species from the original, RI, RD, RS, and RBL datasets. Cubes denote the average and dashes denote the median concentration. The whiskers are the standard deviation. (RI: intra-day removed dataset, RD: diurnal removed dataset, RS: synoptic removed dataset, RBL: baseline removed dataset).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-997
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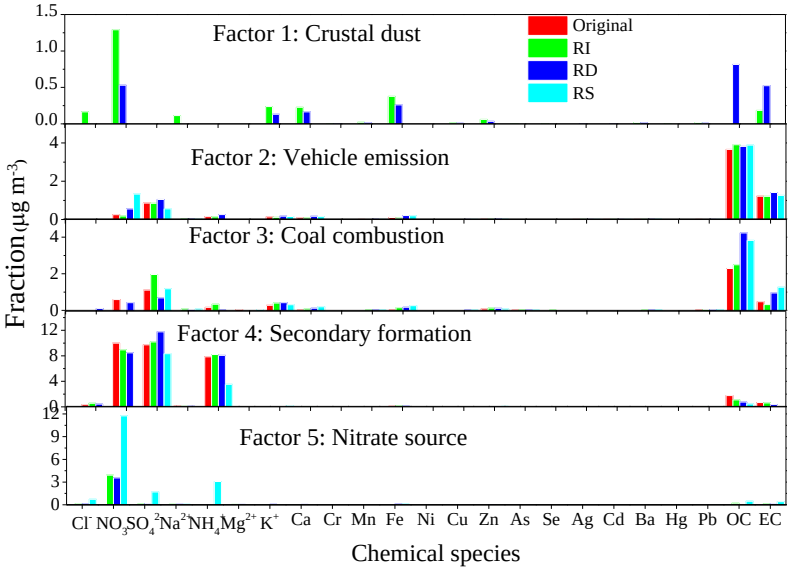

Figure 3. The influence of different TS components on source determination. Crustal dust was not identified from the RD and RS datasets. Nitrate source and sulfate source were identified from the RS dataset. Note: The factor 4 solution was generated from removing the synoptic dataset and represents the sulfate source.

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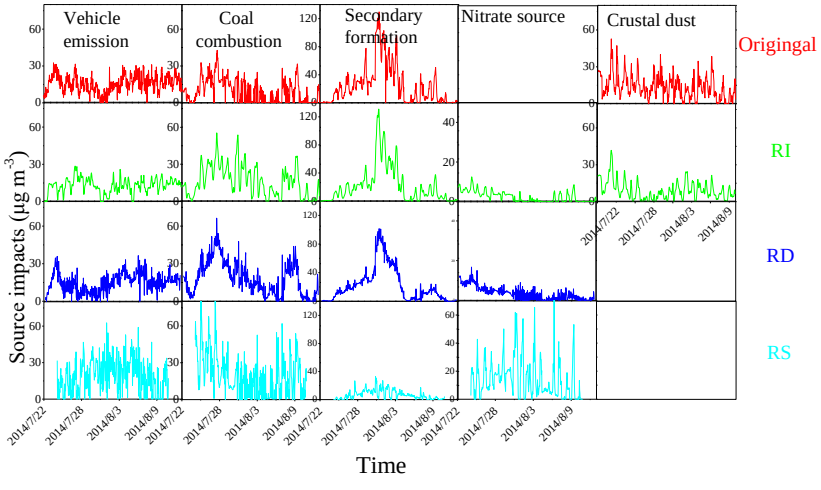

Figure 4. Source contributions to $PM_{2.5}$ for each source (vertical columns) and each TS component (horizontal rows). The blanks mean that the source has not been identified.