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Molecular distributions of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in $PM_{2.5}$ collected at Mt. Tai, in North China in 2014

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Abstract.

Daytime and nighttime fine particulate matter ($PM_{2.5}$) samples collected at Mt. Tai in the North China Plain (NCP) during summer 2014 were analyzed for dicarboxylic acids and related compounds (oxocarboxylic acids and α-dicarbonyls). The total concentrations of dicarboxylic acids and related compounds were 1050 ± 580 ng m^{-3} and 1040 ± 490 ng m^{-3} during the day and night time, respectively. Although these concentrations were about 2 times lower than similar measurements in 2006, the concentrations reported here were about 1-13 times higher than previous measurements in other major cities in the world. Molecular distributions of dicarboxylic acids and related compounds revealed that oxalic acid (C_2) was the dominant species (50%), followed by succinic acid (C_4) (16%) and malonic acid (C_3) (12%). WRF modeling revealed that long range transport was a major factor governing the distributions of the measure compounds at Mt. Tai. A majority of the samples (79%) had comparable concentrations during the daytime and nighttime, with their day-night concentration ratios between 0.9-1.1. Correlation analyses of dicarboxylic acids and related compounds and their gas precursor- volatile organic compounds (VOCs) (day: R^2 = 0.19; night: R^2 = 0.24) and between C_2 and sulfate (day: R^2 = 0.28; night: R^2 = 0.64) indicated that precursor emissions and aqueous phase oxidations during long range transport likely play an important role, especially during the nighttime. Source identification indicated that anthropogenic activities including fossil fuel and biomass/fuel combustion accounted for about 60% of the total variance and was the dominant source at Mt. Tai. However, biomass burning was only a significant source during the first half of the sampling period. Measurements of potassium (K^+), dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls were about 2 times higher than those from the second half of the measurement period. While the levoglucosan concentration, a biomass burning tracer, has decreased by about 80% between 2006 and 2014, indicating that biomass burning is obviously decreased between 2006 and 2014.

1 Introduction

Fine particulate matter ($PM_{2.5}$) is an atmospheric pollutant of particular concern due to its contribution to visibility degradation (Ghim et al., 2005; Watson, 2002), exacerbation of respiratory diseases (Davidson et al., 2005), and modification of climate (Sloane et al., 1991). In recent years, haze frequently occurred in China and has received increasing attention due to its serious impact on air quality and human health (Mu and Zhang 2013; Guo et al., 2014; Huang et al., 2014; Wang et al., 2014).

Previous studies have demonstrated that $PM_{2.5}$ is a major pollutant causing haze, particularly its secondary component (Huang et al., 2014). Dicarboxylic acids and related compounds (oxocarboxylic acids and α-dicarbonyls) are significant constituents in $PM_{2.5}$, and mainly produced by secondary processes (Kawamura and Sakaguchi, 1999; Kawamura and Yasui, 2005; Pavuluri et al., 2010a). Highly water-soluble, dicarboxylic acids and related compounds can significantly contribute to $PM_{2.5}$ impact on air quality (van Pinxteren et al., 2009; Kundu et al., 2010b; Kawamura and Bikkina, 2016). However, the studies associated with dicarboxylic acids and related compounds in the world are mostly on total suspended particles (TSP) (Aggarwal and Kawamura, 2008; Hegde and Kawamura, 2012; Kawamura et al., 2013; Bikkina et al., 2015); there are few studies on $PM_{2.5}$.

The North China Plain (NCP) is one of the most heavily polluted regions in China, and possibly in the world (Ohara et al., 2007). The region is characterized by high loading of dicarboxylic acids and related compounds due to its high emissions of primary (incomplete combustion of fossil fuel and biomass burning) and secondary (atmospheric oxidations of biogenic and anthropogenic VOCs) sources of dicarboxylic acids and related compounds (Ho et al., 2006; Kundu et al., 2010a; Sempéré and Kawamura, 2003; Mkoma et al., 2013). The previous studies have reported that the NCP is an important coal consumer (Xu, 2001), one of the major fire impacted areas (Zhu et al., 2016) and one of the highest VOCs emission regions in China (Zhang et al., 2009). In order to comprehensively understand the atmospheric formation and processing of dicarboxylic acids and related compounds in the NCP, knowledge of their characteristics over remote background areas is necessary. Moreover, understanding aerosol pollution characteristics over remote background regions is central to identifying source regions and the impact of long-range transport.

In this study, we collected $PM_{2.5}$ samples at the summit of Mt. Tai in the NCP during the agriculture burning season (June-July). As the highest mountain in the NCP, Mt. Tai provides an ideal site to investigate long-range transport and secondary oxidation. The objectives of this study were: (1) to identify the impact of long range transport by WRF modeling and back-trajectory analysis, (2) to investigate the measured concentrations and compositional trends of dicarboxylic acids and related compounds, (3) to compare our measurements with previous studies at Mt. Tai and other locations, (4) to study the diurnal trend of the compounds, (5) to characterize the biomass burning impact on temporal variations of dicarboxylic acids and related compounds, and (6) to identify potential sources of dicarboxylic acids and related compounds using principal component analysis (PCA).

2 Experimental methods

2.1 Sampling site for $PM_{2.5}$

$PM_{2.5}$ sampling was conducted at the summit of Mt. Tai (36.25N, 117.10E, ~1532.7 m a.s.l.). Mt. Tai is located in the Shandong province in the NCP in a deciduous forest zone and is surrounded by urban and industrialized regions (Gao et al., 2005; Richter et al., 2005). During sampling period, average values of temperatures, relative humidity (RH) and winds were 17 ℃, 87% and 2.1 m/s. The detailed description can be found in Zhu et al. (2017).

The $PM_{2.5}$ sampler was placed at the Air Force Hotel in the Houshiwu area. The region is not typically frequented by tourist and is not near any temples. Using a TH-16A Intelligent $PM_{2.5}$ sampler (Wuhan Tianhong Corporation, China) and quartz fiber filters, $PM_{2.5}$ was sampled at 100 L min^{-1} between 06:00-18:00 (n = 32) and 18:00-06:00 local time (n = 27) from 4 June to 4 July 2014 on rain-free days. Before each sample the filters were pre-heated at 600 ℃ for 4 h. Blank samples were collected in the same manner as the samples, but without pumping. After the sample were collected, loaded filters and blanks samples were stored in plastic petri dishes and transported to the laboratory, where they were stored at -20 ℃.

2.2 VOCs sampling

VOCs samples were collected by stainless steel canisters from 04 June to 04 July on rain-free days. They were instantaneously sampled and the sampling times were 8:00, 14:00, and 0:00. A total of 70 VOCs samples were collected. After sampling, the canisters were shipped to the University of California, Irvine for further analysis. VOC samples were identified and quantified by gas chromatography equipped with electron capture detection (ECD), flame ionization detection (FID), and mass spectrometer detection (MSD). Detailed descriptions about the chemical analysis have been presented in Blake et al. (1994) and Simpson et al. (2010).

2.3 WRF Model

The boundary layer heights around Mt. Tai during the campaign were calculated using Weather Research and Forecasting Model (WRF V3.5.1) (Skamarock et al., 2005; Wang et al., 2007). In this study, the Yonsei University (YSU) boundary layer scheme (Hong et al., 2006) was used, which can reasonably represent the daytime boundary layer structure (Hu et al., 2013). Although the model may have lower confidence about the nighttime boundary layer height estimation (Hu et al., 2013), this insignificantly influenced our analysis and conclusion because the nighttime boundary layer was always well below the measurement site. Previous studies also reported that the WRF model can capture the boundary layer structure and local circulation over the NCP mountainous regions during summer (Chen et al., 2009). More details of the model configurations were given in Chen et al. (2016).

2.4 Analytical procedures

Aliquots of the aerosol filter samples were extracted by Milli Q water under ultrasonications. The extracts were concentrated by a rotary evaporator under vacuum. The concentrates were reacted with 14% BF_3/n-butanol to convert to dibutyl esters and butoxy acetals. The derivatives were dissolved in n-hexane and analyzed by an Agilent 6890 gas chromatograph (GC) installed with a split/splitless injector (250 ℃), fused silica capillary column (HP-5, 0.2 mm × 25 m, film thickness 0.5 μm), and a flame ionization detector (FID). Identification of each compound was based on a comparison of retention times of GC peaks with those of authentic standards and confirmed by GC/mass spectrometry. Recoveries were 77% for oxalic acid and > 86% for malonic, succinic, and adipic acids. Kawamura and Yasui (2005) reported recoveries of glyoxylic acid, pyruvic acid, and methylglyoxal of about 88, 72, and 47%, respectively. Kunwar and Kawamura (2014) reported recovery of glyoxal of about 91%. Although field blanks revealed peaks of oxalic acid and phthalic acid, the concentrations were below 5% of the real sample concentrations. The data reported in this study has been corrected for the field blanks. The analytical errors based on duplicate analysis were below 10% for the major species. A more detailed description of the analytical method can be found in previous reports (Kawamura and Ikushima, 1993; Hegde and Kawamura, 2012).

Additionally, organic carbon (OC) and elemental carbon (EC) were detected by a Sunset Laboratory carbon analyzer with the thermal-optical transmittance method. Detailed descriptions of this methodology have been presented in Cui et al., (2016). Water-soluble ions were measured using an ion chromatography system (Dionex ICs-90, Dionex Corporation, USA). Analyses of the ionic components were presented in Zhu et al. (2015).

2.5 Back-trajectory analysis

72 h back trajectories were calculated using Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, version 4.9) (Draxler and Rolph, 2003) and Global Data Assimilation System (GDAS) meteorological data from the NOAA Air Resources Laboratory's web server. Three-dimensional (latitude, longitude, and height) backward trajectories were computed every 1 hour from 04 June to 04 July 2014. A total of 744 trajectories were obtained and classified the trajectories into four different groups. Detailed descriptions about cluster analysis have given in our previous publication (Yuan et al., 2014).

3 Results and discussion

3.1 Air-mass back trajectory analysis

To identify the impact of regional transport, we calculated back trajectories using the HYSPLIT model (Draxler and Rolph, 2003). Clusters 2 and 4 accounted for 79%

of the trajectories. The mean transport pathway and corresponding total concentration of dicarboxylic acids and related compounds for every cluster are displayed in Figure 1. The total concentrations of dicarboxylic acids and related compounds were the greatest in clusters 2 and 4. The source regions of the air in clusters 2 and 4 were characterized by large emissions of VOCs, which are important precursors of dicarboxylic acids and related compounds (Zhang et al., 2009). As a result, clusters 2 and 4 had higher concentration of dicarboxylic acids and related compounds. The two clusters contributed 73% of the total concentration of dicarboxylic acids and related compounds. Clusters 1 and 3 originated from cleaner areas (i.e., the ocean and Siberia, respectively), so the total concentration of dicarboxylic acids and related compounds was lower compared with clusters 2 and 4. Using WRF modeling, the boundary layer heights (BLH) at Mt. Tai (Figure S1) were calculated. The results revealed that the daytime BLH were higher than the site elevation for only 7% of cluster 2 and 9% of cluster 4 trajectories, while nighttime BLH were all lower than the site elevation. Therefore, our measurements generally represent concentrations in the free troposphere, which suggests that pollutant concentrations at Mt. Tai were largely controlled by long range transport.

3.2 Measured concentrations of dicarboxylic acids and related compounds and their compositional trends

Homologous series of dicarboxylic acids (C_2-C_{12}), oxocarboxylic acids (C_2-C_9 except C_6), and α-dicarbonyls (C_2-C_3) were detected in $PM_{2.5}$ samples during daytime and nighttime at Mt. Tai (Table 1). The concentration of all detected dicarboxylic acids and related compounds was 1050 ± 580 ng m^{-3} during the daytime and 1040 ± 490 ng m^{-3} during the nighttime. Dicarboxylic acids were the major contributors (i.e., 85% during the daytime and 86% during the nighttime). The dicarboxylic acids-C, oxocarboxylic acids-C, and α-dicarbonyls-C at Mt. Tai in 2014 accounted for 2.65, 0.46 and 0.11% of OC, respectively.

As shown in Table 1, the dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls trends were comparable during the daytime and nighttime. Oxalic acid

(C_2) represented the greatest contribution to the total concentration of dicarboxylic acids (57% during the daytime and 60% during the nighttime), followed by with succinic acid (C_4, 14% and 14%, respectively) and malonic acid (C_3, 10% and 9%, respectively). These results were consistent with the previous 2006 study at Mt. Tai (Wang et al., 2009; Kawamura et al., 2013). Phthalic acid (Ph, 4% and 3%, respectively), glutaric acid (C_5, 3% and 3%, respectively), and azelaic acid (C_9, 2% and 2%, respectively) also exhibited significant contributions. The other dicarboxylic acid species contributed less than 2%. Among the oxocarboxylic acids, glyoxylic acid (ωC_2) was the most abundant (43% and 46%, respectively), followed by pyruvic acid (Pyr, 18% and 16%) and 4-oxobutanoic acid (ωC_4, 13% and 13%, respectively). Additionally, two α-dicarbonyls were identified (glyoxal (Gly) and methylglyoxal (MGly)). During daytime, they had similar concentration, but MGly exhibited higher concentrations than Gly during the nighttime.

3.3 Comparison with previous aerosol studies at Mt. Tai in 2006 and other urban sites in the world

In Table 2 the concentrations of dicarboxylic acids and related compounds at Mt. Tai in 2014 and from other previous measurements are presented. Using the ratio of $PM_{2.5}/TSP = 0.91$ (Deng et al., 2011) and concentrations of dicarboxylic acids and related compounds in TSP at Mt. Tai in 2006 (Kawamura et al., 2013), we estimated the corresponding concentrations of dicarboxylic acids and related compounds in $PM_{2.5}$ at Mt. Tai in 2006 (dicarboxylic acids: 1550 ng m^{-3}, oxocarboxylic acids: 220 ng m^{-3}, α-dicarbonyls: 62 ng m^{-3}). Compared with the results with this study, the levels of dicarboxylic acids and related compounds in 2014 at Mt. Tai were about two times lower. Different meteorology conditions in 2006 and 2014 may partially explain the decreased concentrations, as well as the implementation of regulatory controls of biomass burning by the Chinese government. In 2014, the levoglucosan concentration was 70.4 ng m^{-3} in $PM_{2.5}$ (Zhu et al., 2017), which is substantially lower than the 2006 estimated value of 387 ng m^{-3} (Fu et al., 2008; Deng et al., 2011). Therefore, from 2006 to 2014, biomass burning decreased by about 80%.

Compared with the Chinese megacities, such as Guangzhou (Ho et al., 2011) and Beijing (Ho et al., 2010), the dicarboxylic acids and related compounds 2014 Mt. Tai concentrations were about 1-2 times higher. The concentrations of dicarboxylic acids at Mt. Tai in 2014 were similar to the concentrations reported in the 14 Chinese cities study (Ho et al., 2007), while oxocarboxylic acids and α-dicarbonyls were more than three times higher. Compared with other Asian urban sites, the results reported here were about 1-2 times higher than those reported in Chennai, India (Pavuluri et al., 2010b), Tokyo, Japan (Kawamura and Yasui, 2005), and Sapporo, Japan (Aggarwal and Kawamura, 2008), but lower than those reported in Raipur, India in $PM_{2.1}$ (Deshmukh et al., 2016). Furthermore, the Mt. Tai dicarboxylic acids and related compounds concentrations were approximately 5-13 times higher compared with those in Europe and USA urban aerosols, such as in Leipzig, Germany (van Pinxteren et al., 2014), Zurich, Switzerland (Fisseha et al., 2006), and Houston, USA (Yue and Fraser, 2004). The high concentrations of dicarboxylic acids and related compounds at Mt. Tai likely resulted from the substantial emissions of VOCs in Mt. Tai's surrounding areas, which are some of the most heavily polluted regions in China.

C_2 was found to be the most abundant species at Mt. Tai in 2014, and the concentration of C_4 was larger than C_3. This trend was consistent with measurements at several urban sites, where local anthropogenic emissions were significant sources, such as in the 14 Chinese cities study (Ho et al., 2007) and Tokyo, Japan (Kawamura and Yasui, 2005). Ph which can be utilized as a tracer for anthropogenic source (Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005), was the fourth most abundant species at Mt. Tai in 2014. The trend was dissimilar to Beijing, Guangzhou, and to the 14 Chinese cities studies, where Ph was the second most abundant species. This is likely due to photochemical aging during long range transport from source regions to Mt. Tai.

Although concentration of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls notably decreased from 2006 to 2014, they were still greater when compared to other urban sites in the world. Due to photochemical aging during long-range transport, the compositional trends of dicarboxylic acids and related compounds was distinct from previously studied Chinese sites.

3.4 Comparisons of day and night measurements of dicarboxylic acids and related compounds

As shown in Table 1, the daytime total concentrations of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls were similar to the nighttime total concentrations. 79% of the day-night concentration ratios ranged between 0.9 and 1.1.

The boundary layer height was higher during the daytime, peaking near noontime. The boundary layer occasionally extended high enough during the daytime to approach the sampling site (Figure S1). However, the maximum of boundary layer height was only ~ 600 m during the nighttime, which was much lower than the sampling site height. This suggests that mountain/valley breezes may bring ground level pollutants to the summit of Mt. Tai during the daytime when the boundary layer height was above the sampling site height. A similar transport process was observed over the Taihang Mountains in the Beijing region (Chen et al., 2009). However, this transport mechanism did not occur during the night. Therefore, the similar day and night average concentrations of dicarboxylic acids and related compounds cannot be explained by the changes in the boundary layer heights. As shown in Figure 2, dicarboxylic acids and related compounds exhibited correlations with their gas phase precursors-VOCs (Zhu et al., 2017). These result suggests that the difference in the day and night measurements was possibly dependent on the amount of precursor emissions.

In addition, the daytime concentrations might have been enhanced by photochemical reactions, and the nighttime concentration might have been enhanced by effective aqueous oxidation and less effective loss. The RH was generally high during the nighttime (86.8% ± 15.2% on average, up to 100 %), indicating that dicarboxylic acids and related compounds may have been produced through aqueous phase oxidation. Correlations between C_2 and SO_4^{2-} and the corresponding linear regression slopes were used to evaluate whether C_2 might have been related to aqueous phase oxidation (Yu et al., 2005; Sullivan and Prather, 2007). As shown in

Figure 3, C_2 and SO_4^{2-} exhibited a significantly higher correlation during the nighttime ($R^2 = 0.64$) than that during the daytime ($R^2 = 0.28$), and the linear regression slope during the nighttime (0.028) was also higher than that during the daytime (0.016). Assuming aqueous phase formation of sulfate was the dominant process (Yu et al., 2005), these results indicate that a considerable amount of C_2 may have been produced via aqueous-phase oxidation during the nighttime. In addition, photolysis of iron-oxalate complexes is an important sink of C_2 in the aqueous phase; therefore, the removal of C_2 was lower during the nighttime than during the daytime (Ervens et al., 2003; Tilgner and Herrmann 2010; Pavuluri and Kawamura, 2012).

Details of the multiphase formation pathways, removal mechanisms, and major precursor contributions will be further investigated using the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM, Wolke et al. 2005) together with chemical aqueous-phase radical mechanism (CAPRAM, Tilgner et al. 2013) in an upcoming study.

3.5 Impact of biomass burning on the temporal variations of dicarboxylic acids and related compounds

The temporal variations of dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and K^+ are presented in Figure 4. Concentration maxima of dicarboxylic acids were observed during the first half of the observational period (4-19 June), and then they decreased during the second half (20 June-4 July). Dicarboxylic acids and K^+ exhibited a strong correlation during the first half, while during the second half, dicarboxylic acids and K^+ exhibited no correlations (Figure 5). The peaks of dicarboxylic acids and K^+ appeared almost simultaneously (Figure 4). It was also clear that when the K^+ concentrations increased, dicarboxylic acids correspondingly increased during the first half (Figure 5). These results indicate that biomass burning was a significant contributor to dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls during the first half of the measurement period. Emission hotspots reported by the Ministry of Environment Protection of the People's Republic of China further supported this conclusion.

Concentrations of C_2 declined from the first half to the second half (Figure S2). C_3, C_4 and longer-chain dicarboxylic acids (C_5-C_9) also exhibited similar trends, with much higher concentrations during the first half. However, iC_4 and iC_6 were generally constant throughout the whole period. This result suggests that biomass burning was an insignificant source for these two species. M, F, mM, Ph, iPh, tPh, kC_3, and kC_7 had higher concentrations during the first half, suggesting that the anthropogenic components, such as vehicle emissions, fossil combustion, and plastic burning (Kawamura and Sakaguchi, 1999; Kawamura and Kaplan, 1987; Simoneit et al., 2005), were probably transported to the Mt. Tai site concurrently with biomass burning plumes.

Oxocarboxylic acids and α-dicarbonyls exhibited similar temporal trends when compared to dicarboxylic acids. On average, oxocarboxylic acids and α-dicarbonyls were more abundant during the first half (158 ± 101 ng m^{-3} and 32.9 ± 25.5 ng m^{-3}, respectively) than during the second half (89.2 ± 25.1 ng m^{-3} and 16.8 ± 8.82 ng m^{-3}, respectively). ωC_2, ωC_3, ωC_4, ωC_5, ωC_9, Pyr, Gly, and MGly also displayed similar trends as C_2, with higher concentrations during the first half.

Ph is a photo-degradation product of anthropogenic aromatic hydrocarbons, and C_9 is a photo-oxidation product of biogenic unsaturated fatty acids (Schauer et al., 2002; Kawamura and Ikushima, 1993). As a result, the Ph/C_9 ratio can be used to evaluate the source strength of anthropogenic versus biogenic emissions (Kawamura and Yasui, 2005). In this study, the Ph/C_9 ratios ranged between 0.32 and 8.64 (average: 3.20) and were mostly higher than 1 (Figure 6), which is comparable to those from the 14 Chinese cities study (average in the summer: 3.37) (Ho et al., 2007) but much higher than in Nanjing, China (average in summer: 1.98) (Wang et al., 2002) and Chennai, India (average in summer: 0.69) (Pavuluri et al. 2010b). These comparisons suggest that anthropogenic sources contributed more significantly than biogenic sources at Mt. Tai. Moreover, the Ph/C_9 ratios were higher during the daytime (range: 0.32-8.64, average: 3.75) compared to those during the nighttime (range: 0.54-7.09, average: 2.53). In addition, the Ph/C_9 ratios were higher during the second half when almost no biomass burning was observed.

3.6 Source identification of dicarboxylic acids and related compounds

Principal component analysis (PCA) is a multivariate analytical tool and that can be employed to reduce the dimensionality of original variables and extract the principal components (PCs) in order to study the relationships among the observed variables. Only factors with eigenvalues greater than 1 were extracted based on Kaiser-Meyer-Olkin (KMO) and the Bartlett's test of sphericity. Then the factors were rotated by the Varimax method (Malinowski, 1991). In this study, PCA was used with particulate concentrations of 25 variables for daytime and nighttime samples by using IBM SPSS Statistics 21.0. If the compound concentrations were below the detection limit, the data was replaced by a value half of the corresponding detection limit. The factor-loading matrix after Varimax rotation is shown in Table 3 and Table 4. Weighting factors |x| < 0.2 were considered insignificant and not listed, while |x| > 0.6 were considered high loading and are depicted in bold.

From the daytime samples, five PCs were extracted, and PC1, PC2, PC3, PC4, and PC5 explained 64, 9, 7, 6, and 4%, respectively, of the total variance (90% in total). As shown in Table 3, PC1 was dominated by high loadings of C_2-C_6, iC_5, F, hC_4, Ph, kC_3, Pyr, ωC_2, ωC_4, Gly, MGly, OC, and K^+, which was most associated with anthropogenic activities such as fossil fuel and biomass/fuel combustion, followed by photochemical aging during long range transport. NH_4^+, NO_3^-, and SO_4^{2-} were positively related with PC2, indicating they were derived from secondary sources, including gas and aqueous phase chemistry. Fine mode SO_4^{2-} is formed through aqueous-phase oxidation of SO_2 on aerosols and cloud droplets (Seinfeld and Pandis, 1998). PC3 was enriched in M, F, and EC and was assumed to represent fuel combustion (Puxbaum et al., 2007; Zhang et al., 2008; Jung et al., 2010). In PC4, C_9 and Na^+ were dominant, suggesting that the photooxidation of unsaturated fatty acids emitted from the sea surface (such as sea salt particles) was an important factor. For PC5, tPh was dominant, indicating significant contributions by solid wastes/plastic polymers burning.

During the nighttime period, four PCs were extracted. PC1, PC2, PC3, and PC4 explained 56, 14, 13, and 6%, respectively, of the total variance (89% in total). Nighttime sources for dicarboxylic acids and related compounds were similar to the daytime, but there were distinctions between the contribution orders. As shown in Table 4, C_2, C_6, hC_4, Ph, Pyr, ωC_2, ωC_4, Gly, OC, and K^+ strongly correlated with PC1, which was attributed to anthropogenic activities followed by photochemical aging. In contrast, C_3-C_5, iC_5, M, F, kC_3, and EC displayed strong correlations with PC2. As a result, PC2 was attributed to emissions from fuel combustion and photochemical reactions. For PC3, MGly, NH_4^+, NO_3^-, and SO_4^{2-} dominated, suggesting that gas and aqueous phase secondary processing was a significant factor. Moreover, the variance of the sources was higher during the nighttime (13%) than that during the daytime (9%), suggesting that secondary processes were more important during the nighttime. PC4 was characterized by high loadings of C_9, tPh, OC, and Na^+ suggesting a mixed aerosol related to the photooxidation of unsaturated fatty acids emitted from sea surfaces and anthropogenic emissions from burning of solid wastes/plastic polymers.

Conclusions

Dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls were quantified in $PM_{2.5}$ filter samples collected between 04 June and 04 July 2014 at Mt. Tai in the North China Plain. Concentrations of dicarboxylic acids and related compounds were higher than those reported in urban sites in the world but lower than previous measurements at Mt. Tai. WRF modeling and backward trajectory analyses suggested that long range transport of pollutants was a major factor governing the distributions of dicarboxylic acids and related compounds at Mt. Tai. PCA results revealed that anthropogenic activities were the major sources for dicarboxylic acids and related compounds at Mt. Tai. However, biomass burning only had a significant impact during the first half of the sampling period (4-19 June).

Campaign-averaged dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls concentrations had similar averages during the daytime and nighttime. In our study, boundary layer dynamics did not explain this trend. Based on the correlation analyses between dicarboxylic acids and related compounds and their gas precursors-VOCs and the correlations between C_2 and sulfate, the day-night ratios were probably dependent on precursor emissions and aqueous oxidation. Further interpretations of the complex Mt. Tai dataset using a detailed multiphase chemistry air parcel model, including chemical source and sink analyses, will be completed in a follow-up study.

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Table 1. Measured concentrations of dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, OC, and EC in $PM_{2.5}$ aerosols collected at Mt. Tai from 4 June to 4 July 2014.

	Daytime (n = 32)				Nighttime (n = 27)				Day-Night Ratio
Components, abbreviation	Min.[a]	Max.[b]	Mean	SD [c]	Min.	Max.	Mean	SD	Mean
I. Dicarboxylic acids (ng m^{-3})									
Oxalic, C_2	122	1790	512	304	151	1280	534	272	1.0
Malonic, C_3	23.7	195	86.2	33.8	17.9	141	78.4	32.6	1.1
Succinic, C_4	25.8	485	126	81.1	62.3	227	121	53.7	1.0
Glutaric, C_5	6.88	99.3	26.3	15.9	10.5	53.7	24.9	11.3	1.1
Adipic, C_6	4.69	46.4	12.6	7.46	3.97	31.8	12.7	7.45	1.0
Pimelic, C_7	0.69	22.6	4.14	4.32	BDL	19.1	4.38	4.12	0.9
Suberic, C_8	BDL[d]	2.85	0.34	0.71	BDL	1.85	0.36	0.48	0.9
Azelaic, C_9	3.42	95.1	16.2	20.6	2.30	68.1	19.4	17.6	0.8
Sebabic, C_{10}	BDL	8.95	1.18	2.14	BDL	13.2	1.84	3.01	0.6
Undecanedioic, C_{11}	BDL	5.99	1.67	1.91	BDL	7.56	1.73	1.99	1.0
Dodecanedioc, C_{12}	BDL	1.33	0.20	0.33	BDL	1.83	0.29	0.46	0.7
Methylmalonic, iC_4	BDL	7.92	3.43	1.56	0.66	7.59	3.33	1.54	1.0
Methylsuccinic, iC_5	2.85	32.7	8.03	5.47	3.01	18.3	7.98	4.53	1.0
2-methylglutaric, iC_6	BDL	6.78	1.82	1.17	BDL	4.23	1.64	1.09	1.1
Maleic, M	BDL	25.7	7.44	7.23	2.19	23.7	6.56	5.03	1.1
Fumaric, F	0.99	15.1	3.90	2.73	BDL	7.13	3.15	1.85	1.2
Methylmaleic, mM	1.25	13.1	3.52	2.53	1.05	6.42	2.90	1.40	1.2
Malic, hC_4	0.08	5.15	1.19	1.04	0.29	3.27	1.37	0.75	0.9
Phthalic, Ph	19.3	99.4	36.8	16.1	16.3	53.9	29.3	10.2	1.3
Isophthalic, iPh	BDL	13.8	1.78	2.55	BDL	9.06	1.57	2.22	1.1
Terephthalic, tPh	0.88	130	13.6	24.9	0.58	155	12.9	32.2	1.1
Oxomalonic, kC_3	3.66	31.5	12.6	7.04	2.06	29.5	11.3	6.83	1.1
4-oxopimelic, kC_7	2.93	29.3	11.6	6.56	2.12	27.8	11.6	5.71	1.0

Subtotal	239	2954	893	479	358	1973	892	402	1.0
II. Oxocarboxylic acids (ng m^{-3})									
Pyruvic, Pyr	6.34	124	23.6	22.9	7.07	54.8	19.7	11.0	1.2
Glyoxylic, ωC_2	8.84	241	54.7	45.2	11.9	166	55.9	41.4	1.0
3-oxopropanoic, ωC_3	1.99	24.3	8.85	4.99	1.60	24.6	8.31	4.93	1.1
4-oxobutanoic, ωC_4	5.54	52.4	16.0	10.1	5.48	54.2	15.3	10.6	1.0
5-oxopentanoic, ωC_5	1.03	12.2	3.78	2.21	1.29	10.7	3.53	2.08	1.1
7-oxoheptanoic, ωC_7	2.09	17.8	7.31	3.33	1.93	13.7	6.67	2.95	1.1
8-oxooctanoic, ωC_8	1.13	29.9	9.40	5.66	0.86	18.3	8.78	4.43	1.1
9-oxononanoic, ωC_9	BDL	10.8	3.93	2.96	BDL	13.2	3.64	3.69	1.1
Subtotal	26.9	496	128	88.9	49.0	344	122	73.6	1.0
III.α-dicarbonyls (ng m^{-3})									
Glyoxal, Gly	1.82	59.6	12.3	10.3	3.20	39.3	12.4	9.68	1.0
Methylglyoxal, MGly	BDL	45.2	12.1	11.2	BDL	59.9	13.6	13.1	0.9
Subtotal	5.07	105	24.4	20.5	8.04	94.9	25.9	21.6	0.9
Total (all detected organics)	271	3550	1050	580	429	2380	1040	490	1.0
IV. Carbonaceous aerosols (μg m^{-3})									
OC	4.42	30.7	11.6	5.77	4.02	32.9	11.7	7.75	1.0
EC	0.46	3.31	1.34	0.67	0.40	4.69	1.50	0.90	0.9

[a] Minimum. [b] Maximum. [c] Standard deviation. [d] BDL: Below detection limit.

Table 2. Concentrations of dicarboxylic acids and related compounds reported in this study and literature data from the previous measurements at Mt. Tai in 2006 and other urban sites in the world (unit: ng m^{-3}).

Location	Type	Season	Size	Total dicarboxylic acids	Total oxocarboxylic acids	Total α-dicarbonyls	Major Species
This study (day)	mountain	summer	$PM_{2.5}$	893 ± 479	128 ± 88.9	24.4 ± 20.5	$C_2 > C_4 > C_3 > \mathrm{Ph}$
This study (night)	mountain	summer	$PM_{2.5}$	892 ± 402	122 ± 73.6	25.9 ± 21.6	$C_2 > C_4 > C_3 > \mathrm{Ph}$
Mt. Tai, China [a]	mountain	summer	TSP	1702 ± 1385	242 ± 210	68.3 ± 64.1	$C_2 > C_4 > C_3 > \omega C_2$
14 Chinese cities [b]	urban	summer	$PM_{2.5}$	892 ± 457	36.7 ± 23.7	5.17 ± 4.14	$C_2 > \mathrm{Ph} > C_4 > C_3$
Guangzhou, China [c]	urban	summer	$PM_{2.5}$	523 ± 134	19.5 ± 9.59	5.11 ± 2.13	$C_2 > \mathrm{Ph} > \mathrm{tPh} > C_3$
Beijing, China [d]	urban	autumn	$PM_{2.5}$	760 ± 369	44.7 ± 26.6	9.05 ± 4.90	$C_2 > \mathrm{Ph} > C_4 > C_9$
Chennai, India [e]	urban	summer	PM_{10}	502.9 ± 117.9	31.7 ± 11.2	7.1 ± 2.0	$C_2 > \mathrm{tPh} > C_3 > C_9$
Raipur, India [f]	urban	winter	$PM_{2.1}$	1072	90.9	30.2	$C_2 > C_4 > C_9 > \mathrm{Ph}$
Tokyo, Japan [g]	urban	summer	TSP	726 ± 636	117 ± 95	46 ± 39	$C_2 > C_4 > C_3 > \mathrm{Pyr}$
Sapporo, Japan [h]	urban	summer	TSP	406	35	9.7	$C_2 > C_3 > C_4 > \omega C_2$
Leipzig, Germany [i]	urban	summer/ winter	PM_{10}	175 [l]			$C_2 > C_3 > C_5 > \mathrm{h}C_4$
Zurich, Switzerland [j]	urban	summer	TSP	66.9 [l]			$C_2 > C_3 > \mathrm{h}C_4 > C_4$
Houston, USA [k]	urban	summer	$PM_{2.5}$	67.7 [l]			$C_4 > C_3 = C_9 > C_5$

[a] Kawamura et al. (2013).

[b] Ho et al. (2007).

[c] Ho et al. (2011).

[d] Ho et al. (2010).

[e] Pavuluri et al. (2010b).

[f] Deshmukh et al. (2016).

[g] Kawamura and Yasui (2005).

[h] Aggarwal and Kawamura (2008).

[i] van Pinxteren et al. (2014).

[j] Fisseha et al. (2006).

[k] Yue and Fraser (2004).

[l] did not include all dicarboxylic acid species.

Table 3. PCA analysis result for daytime dicarboxylic acids and related compounds in $PM_{2.5}$ aerosols collected at Mt. Tai in 2014.

Compounds	PC1	PC2	PC3	PC4	PC5
C_2	**0.861**	0.382	0.203		
C_3	**0.851**	0.277			
C_4	**0.788**	0.353	0.407		
C_5	**0.837**	0.267	0.437		
C_6	**0.877**	0.222	0.322		
C_9		-0.256	0.294	**0.756**	0.389
iC_5	**0.762**		0.523		
M			**0.927**		
F	**0.630**	0.288	**0.635**		
hC_4	**0.884**	0.205			
Ph	**0.793**		0.431		0.313
tPh					**0.904**
kC_3	**0.716**		0.285		-0.202
Pyr	**0.823**	0.353	0.218		
ωC_2	**0.874**	0.406			
ωC_4	**0.961**				
Gly	**0.834**	0.396	0.248		
MGly	**0.687**	0.540			
OC	**0.787**			0.559	
EC	0.411	0.226	**0.632**		-0.337
Na^+	0.241	0.314		**0.862**	

NH_4^+	0.315	**0.938**			
K^+	**0.875**	0.289		0.293	
NO_3^-	0.355	**0.814**	0.302		
SO_4^{2-}	0.279	**0.895**			
Variance (%)	64%	9%	7%	6%	4%

Extraction method: Principal component analysis.

Rotation method: varimax with Kaiser normalization.

Table 4. PCA analysis result for nighttime dicarboxylic acids and related compounds in $PM_{2.5}$ aerosols collected at Mt. Tai in 2014.

Compounds	PC1	PC2	PC3	PC4
C_2	**0.684**	0.504	0.464	
C_3	0.341	**0.728**	0.436	
C_4	0.356	**0.714**	0.506	
C_5	0.578	**0.699**	0.285	
C_6	**0.661**	0.400		0.516
C_9		0.531		**0.726**
iC_5	0.407	**0.657**		0.585
M		**0.870**		0.239
F	0.538	**0.642**	0.334	
hC_4	**0.735**		0.364	
Ph	**0.610**	0.478	0.305	0.467
tPh				**0.953**
kC_3	0.514	**0.779**		
Pyr	**0.834**	0.293	0.356	
ωC_2	**0.823**	0.312	0.435	
ωC_4	**0.893**	0.261		0.283

Gly	**0.819**	0.352	0.378	
MGly	0.568		**0.671**	
OC	**0.674**	0.223		**0.660**
EC		**0.770**		
Na^+	0.374			**0.865**
NH_4^+	0.273		**0.921**	
K^+	**0.894**	0.248		
NO_3^-	0.540	-0.206	**0.684**	
SO_4^{2-}		0.365	**0.887**	
Variance (%)	56%	14%	13%	6%

Extraction method: Principal component analysis.

Rotation method: varimax with Kaiser normalization.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-1240
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 25 January 2018

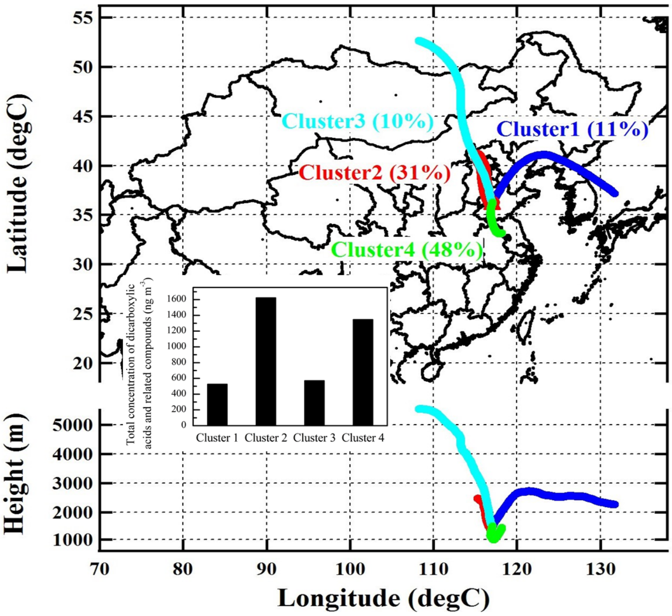


Figure 1. Three-day backward trajectories for Mt. Tai during the study period. (Since cluster 2 was covered by cluster 3, the width of the cluster 2 trajectory has been increased.)

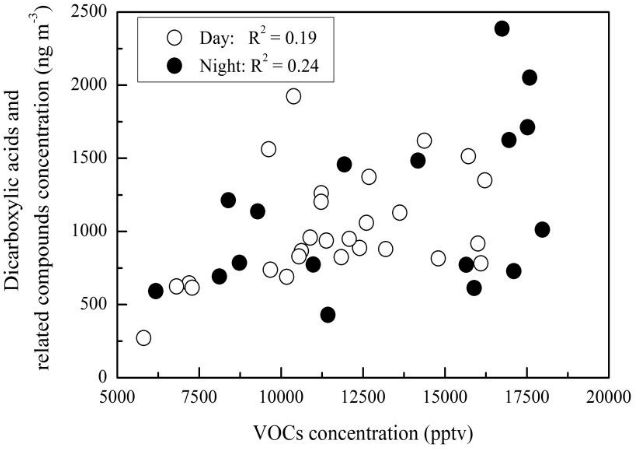


Figure 2. Scatter plot of the daytime and nighttime concentrations of VOCs and dicarboxylic acids and related compounds concentration, where the VOCs concentration is the sum of alkanes, alkenes, alkynes, and aromatics (Zhu et al. 2017).

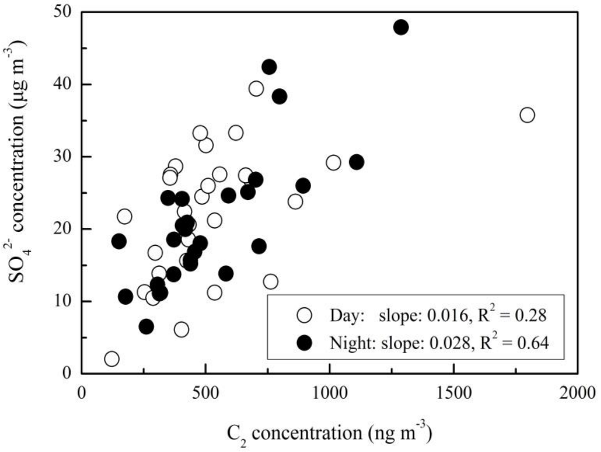
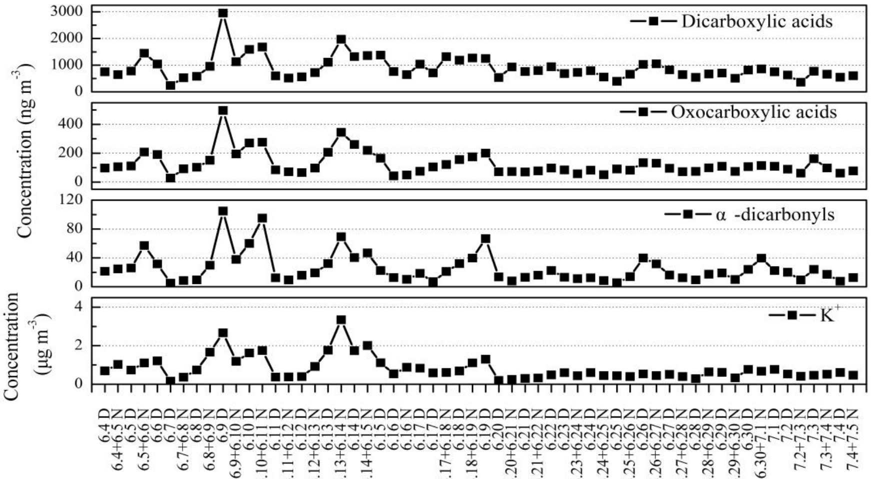


Figure 3. Daytime and nighttime scatter plots between C_2 and SO_4^{2-}.



5 **Figure 4.** Temporal variations of dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and K^+ in $PM_{2.5}$ aerosol collected at Mt. Tai during daytime (D) and nighttime (N) in 2014.

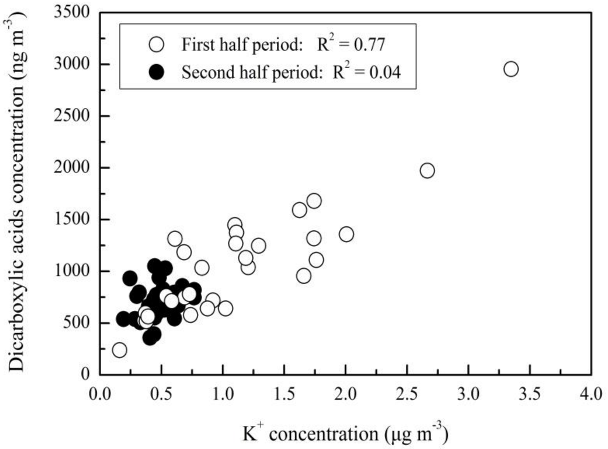


Figure 5. Scatter plots of K^+ and the total dicarboxylic acids concentration during the first half and second half of the campaign.

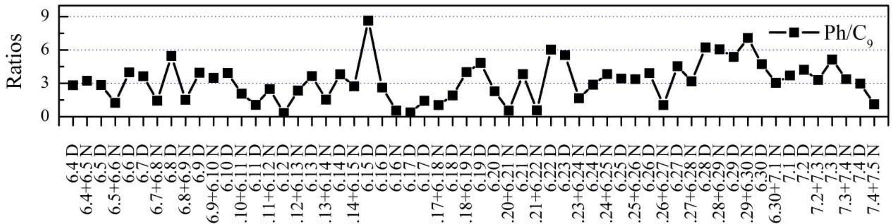


Figure 6. Time series of the Ph/C_9 ratio (D : daytime, N: nighttime).