Characteristics of carbonate carbon in $PM_{2.5}$ in a typical semi-arid area of Northeastern China

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ABSTRACT

Daily concentrations of carbonate carbon (CC) in $PM_{2.5}$ collected in semi-arid area in Northeast China (Tongyu) were quantified by acidification that measures carbon dioxide (CO_2) gas evolved using DRI Model 2001 Thermal Optical reflectance (TOR) Carbon Analyzer. The concentrations of CC during Asian dust storm (DS) and non-dust storm (NDS) periods during 14 April to 21 June, 2006 were determined and the transport pathways and possible sources for the CO_3^{2-} aerosols were identified. Concentrations of CC in $PM_{2.5}$ collected from 14 April to 23 June, 2006 in Tongyu are ranged from 0.1 to 7.5 µgC m^{-3} with an average of 1.3 µgC m^{-3}. The average CC concentration during DS events was 2.6 ± 1.7 µg m^{-3}, which was almost 4 times the daily average concentration of 0.6 ± 0.5 µg m^{-3} during non-dust storm (NDS) period. Carbonate carbon accounted for 10% and 4% of total carbon in Tongyu during DS and NDS period, respectively. Carbonate concentrations were also derived by calculating the difference between cations and anions (ionic balance method). And good correlation is observed for the carbonate measured to the values for carbonate calculated from the ionic balance difference ($R^2 = 0.90$). Higher correlations were observed between Ca with selected water-soluble ions (sulfate, nitrate or chloride) and elemental carbon in DS than in NDS periods. This is consistent with previous studies that more calcium salts (sulfate, nitrate or chloride) were formed during atmospheric transport during DS period. During the DS in spring 2006, three groups (A to C) of air mass trajectories were identified that passed over Tongyu. In general, when the air mass came from northwest, and south or southwest to Tongyu, high concentrations of carbonate were observed.

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1. Introduction

Carbonaceous aerosol in atmosphere exists in three forms: organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC). Even though the CC levels are generally low in ambient atmosphere (Mader et al., 2002; Watson et al., 2005; Huang et al., 2006), they may be measured as either OC or EC depending on the chemical nature of the carbonates and their thermal decomposition temperatures (Schauer et al., 2003; Hitzenberger et al., 2006). Within the past decade, there has been increasing interest in airborne carbonate (CO_3^{2-}) in suspended dust because of its important roles in atmospheric chemistry, global climate, and radiative forcing (Sequeira, 1993; Buseck and Posfai, 1999; Oba and Pedersen, 1999; Li et al., 2000), presenting "carbonate mysteries" in the global climatic system (Elderfield, 2002). However, only few carbonate measurements for analysis of ambient particulate samples have been described. In spite of many Asian dust studies, information about CO_3^{2-} in the atmosphere near Asian dust source regions is scarce. Soil derived CO_3^{2-} from Asia is of interest for a better understanding of alkaline matter contribution to climatic and environmental effects at local, regional, and global scales (Dentener et al., 1996).

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Dust aerosol emitted from the wind erosion process in arid and semi-arid regions is an important driving factor on climate change and has received increasing attention in recent years. Asian dust storms (ADS) originate in hyper-arid, arid and semi-arid lands located in Northwest and North China, South Mongolia, and East Russia (Yuan et al., 2004; Shen et al., 2005; Zhou and Zhang, 2003). Due to human activity, desert areas in China have expanded to 1.61×10^6 km^2, accounting for 16.7% of the total land mass (Yuan et al., 2006). Annually, ~800 Tg of the Chinese desert dust is injected into the atmosphere, and 70% is transported eastward and deposited (Zhang et al., 1997). Calcium carbonate (CaCO$_3$) is a prominent alkaline component of source materials in Asian dust source regions (Liu, 1985; Andronova et al., 1993; Gomes and Gillette, 1993). Even though many have studied the physical and chemical properties of dust aerosols from the arid and semi-arid source regions in North and Northwest China and their character-ization of spatial and temporal variation in remote marine regions (Huebert et al., 2003; Iwasaka et al., 2003; Zhang et al., 2003; Arimoto et al., 2004; Cao et al., 2005; Cheng et al., 2005; Shen et al., 2006a,b), the research on the chemical characteristics of soil dust from Northeast China is still limited. Previous studies defined Ca as an indicator for CO$_3^{2-}$ (Gomes and Gillette, 1993; Sequeira, 1993); however, both calcium oxide (CaO) and calcium hydroxide (Ca(OH)$_2$) can contribute to the ambient Ca levels.

Here we present the 24-hour integrated PM$_{2.5}$ observations associated with CO$_3^{2-}$ species at a typical site over semi-arid region in the Northern China during 2006 spring. The objectives of this study are to investigate the concentrations of CC and CO$_3^{2-}$ during Asian dust storm (DS) and non-dust storm (NDS) periods at a typical semi-arid area of Northeastern China and to identify the transport pathways and possible sources for the CO$_3^{2-}$ aerosols.

2. Sampling and analysis

2.1. Sampling sites and sample collection

Tongyu station (44°25′N, 122°52′E, 184 m above sea level) was selected as sampling location to represent semi-arid area in Northeastern China, which is located at Xinhua downtown, Tongyu County, Jilin Province (Liu et al., 2008; Zhang et al., 2008). There are no major industrial activities surrounding the sampling location and it is situated over the grassland, about 3 m above the ground level. A frmOmni Ambient Air Sampler (BGI Incorporated, Wal-tham, MA, USA) was used to collect PM$_{2.5}$ samples with a flow rate of 5 l min^{-1}. The sampler is equipped with a solar power battery to avoid power failure. Daily samples were collected from 14 April to 23 June 2006 and each was conducted from 08:00 in the morning to 08:00 next day morning. A total of 53 aerosol samples were collected during spring time in 2006.

PM$_{2.5}$ samples were collected on 47 mm Whatman quartz microfibre filters (QM/A). The filters were pre-heated at 800 °C for 3 h before sampling. The exposed filters were stored in a refrigerator at <4 °C until chemical analysis to prevent the evaporation of volatile components. Field blank filters were also collected to subtract any positive artifacts due to adsorption of gas-phase organic components onto the filter during and/or after sampling. However, negative artifacts due to volatilization of particle-phase organics from particle sample were not investigated in this study as limited resources. During the sampling period, meteorological data, including ambient temperature, pressure, relative humidity (RH), wind speed, and wind direction were also recorded at Tongyu Meteorological station. In weather observations made by the China Meteorological Administra-tion (CMA), dust events are classified into four categories: dust in suspension, blowing dust, a dust storm, or a severe dust storm. These categories are defined on the basis of horizontal visibility, that is,

the horizontal visibilities for dust in suspension, blowing dust, dust storm and severe dust storm are less than 10 km, 1 to 10 km, 500 to 1000 m and less than 500 m, respectively.

2.2. Mass analysis

The aerosol mass concentrations were determined gravimetri-cally using a Sartorius MC5 electronic microbalance with 1 µg sensitivity (Sartorius, Göttingen, Germany) at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS). Before weighing, the quartz filter samples were equilibrated for 24 h at a constant temperature at 23 °C and RH between 35% and 45%. Each filter was weighted at least three times before and after sampling by a 24 h equilibration. The mean net mass for each filter was obtained by the average post-weight data subtracting the pre-weight. The precisions of the weighing were <10 µg for blank filters and <20 µg for filter samples.

2.3. Carbonate carbon analysis

The method used to quantify the carbonate concentrations in the samples has been reported elsewhere (Ho et al., submitted for publication). Three aliquots of filter punches (each of 0.5 cm^2) from a parent sample were transferred into the empty reaction vial. One milliliter of 20% H$_3$PO$_4$ was injected into the vial through the acid introduction tube from the vial cap. The amount of acids is sufficient to neutralize 619 µg of carbonate on the filter punches. As soon as the acid was added, the sonication started and the program began to acquire the data. The CO$_2$ evolved from the acid-ification was entrained into the carrier gas stream, reduced to CH$_4$ by nickel catalyst, and finally detected by FID. An aliquot 1 ml of cali-bration gas (5% CH$_4$ by volume in He) was automatically introduced into the line once the FID signal returned to its baseline. The inte-grated peak area was divided by the calibration peak area and multiplied by an instrument-specific calibration slope and y-inter-cept to obtain µg C per sample. After each analysis, the used vial with filter sample and acid solution was replaced by an empty vial. The minimum detection limit (MDL) is obtained as the minimum amount of the carbonate that generates the minimum distinguishable analytical signal S_m. S_m is taken as the sum of mean blank signal S_{b1} plus three times the standard deviation of the blank signal σ_{b1}, i.e., $S_m = S_{b1} + 3\sigma_{b1}$ (Skoog et al., 1998; Meier and Zünd, 2002). The MDL is calculated as $(S_m - b)/k$, where b and k are the calibration curve intercept and slope respectively. The concentrations of the blank filter punches ranged from 0.01 to 0.03 µg C cm^{-2}, with an average of 0.02 µg C cm^{-2}. The MDL for CC is thus calculated as 0.02 µg C cm^{-2} (Note: atomic mass of C = 12) and for carbonate is 0.10 µg cm^{-2} (Note: molecular weight of CO$_3^{2-}$ = 60). The MDL for carbonate can be also translated to 0.14 µg m^{-3} for a sampling volume of 7.2 m^3 when three filter punches (each of 0.5 cm^2) were used in each analysis (Note: the entire 47 mm quartz-fiber filter size = 14.7 cm^2). If the sampled air volume or flow increased, the MDLs would be propor-tionally lower. The concentrations of carbonate in both DS and NDS samples were above the MDL (0.14 µg m^{-3}). Each blank or field blank was analyzed by taking three punches (the same numbers of punches used for the real sample analysis) from the parent filter. The samples were then acidified with 1 ml of 20% H$_3$PO$_4$ as the same analytical procedures described above. A total of two field blanks were collected. No significant contribution of carbonate (<MDL) was observed on the field blanks.

2.4. Water-soluble inorganic ions analysis

One-fourth of each filter sample was used to determine the ion mass concentrations. Six anions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, F$^-$, Br$^-$ and NO$_2^-$)

and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in aqueous extracts of the sample filters were determined by an ion chromatography (IC) (Dionex 500, Dionex Corp, Sunnyvale, CA). To extract the water-soluble species from the quartz filters, each filter was put into a separate 20 mL vial containing 10 ml distilled-deionized water (a resistivity of 18 MΩ), and then shaken first by an ultrasonic instrument for 60 min and then by mechanical shaker for 1 h for complete extraction the water-soluble compounds. The extracts were stored at 4 °C in a clean tube before analysis. Cation concentrations were determined with the use of a CS12A column (Dionex Corp.) with 20 mM MSA eluent. Anions were separated by an AS11-HC column (Dionex Corp.), using 20 mM KOH as the eluent. The limits of detection were less than 0.05 mg l^{-1} for anions and cations. Standard Reference Materials produced by the National Research Center for Certified Reference Materials, China were analyzed for quality assurance purposes. Blank values were subtracted from sample concentrations. Replicate analyses were performed at the rate of one per group of 10 samples for quality control.

2.5. Elemental analysis

The elemental concentrations of $PM_{2.5}$ samples were analyzed directly by a proton induced X-ray emission (PIXE) method using the 2.5 MeV protons with a 50 nA beam at the Institute of Low Energy Nuclear Physics, Beijing Normal University (Zhang et al., 2005; Zhu and Wang, 1998). All concentrations were corrected for backgrounds from blank filters. Eighteen elements for each sample were quantified, which include S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr and Pb.

3. Composition of carbonate carbon

3.1. Concentrations of carbonate carbon

Daily $PM_{2.5}$ mass and CC concentrations from 14 April to 21 June at Tongyu site were shown in Fig. 1. The average mass concentration

of $PM_{2.5}$ at Tongyu station was 261 μg m^{-3}, ranging from 24.4 to 1630 μg m^{-3} while the average concentration of CC was 1.30 μg m^{-3}, ranging from 0.05 to 7.47 μg m^{-3}. The $PM_{2.5}$ mass and CC concentrations in the DS samples increased because of the large contribution of crustal matter. During the observation period, nine DS events were observed at Tongyu station on 21–23 April (DS1), 28–29 April (DS2), 4–5 May (DS3), 8 May (DS4), 11 May (DS5), 15–19 May (DS6), 22 May (DS7), 29 May (DS8), and 5–7 June (DS9) (Zhang et al., 2008), with CC loadings of 1.56, 4.58, 3.39, 2.12, 1.36, 3.63, 1.95, 0.55 and 1.41 μg m^{-3}, respectively, mostly higher than the spring mean value (1.30 μg m^{-3}). The average CC concentration during the nine DS events was 2.59 ± 1.69 μg m^{-3}, which was almost 4 times higher than the mean concentration of 0.59 ± 0.50 μg m^{-3} during the NDS period. This was a heavy dust storm and lasted for 5 days on 15–19 May with maximum daily $PM_{2.5}$ concentrations of 1630 μg m^{-3} on 17 May. The peak concentration of daily average CC also reached 7.47 μg m^{-3} on 17 May, twelve times of the average CC concentration during the NDS period (Table 1). Observation at Kosan (126°100′E, 33°170′N) supersite of ACE-Asia in Korea (Kawamura et al., 2004) showed that the average concentration of CC in 2002 was 6.3 μg m^{-3} for TSP. The comparison reveals that the fine dust pollution is very serious in North China, even in arid and semi-arid regions.

Limited data for PM CO_3^{2-} concentrations were available (Table 2). Compared with other studies, the average $PM_{2.5}$ CO_3^{2-} in Tongyu during NDS periods was generally higher than those reported in Table 2, except in Xi'an. While CO_3^{2-} levels during DS were also higher than those reported, except in Xi'an. CO_3^{2-} on average accounted for 2.4% of $PM_{2.5}$ during DS and 2.6% of $PM_{2.5}$ under NDS conditions. Most of the dust storm events at Tongyu were associated with high wind speed and low RH. It implies that the occurrences of dust storms at Tongyu are usually associated with dry air, high wind speed weather conditions.

The maximum possible CC was estimated as 0.3 times the calcium ion (Ca^{2+}) concentration and 0.49 times the magnesium ion (Mg^{2+}), which is an upper limit for actual CO_3^{2-} level, since Ca^{2+} and Mg^{2+} in surface soils are often present in oxide form such as
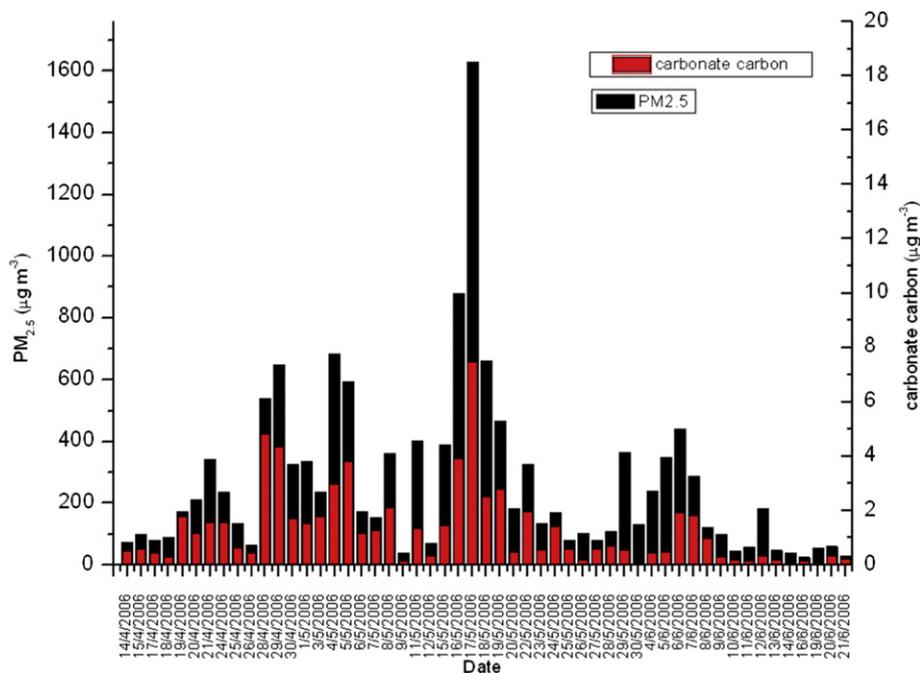

Fig. 1. Time series of $PM_{2.5}$, and carbonate carbon (CC) in the spring at Tongyu.

Table 1
Concentrations of carbonate carbon, carbonate and PM$_{2.5}$during DS period and NDS period.

	Concentration (μg m^{-3})		
	PM$_{2.5}$	Carbonate carbon (CC)	carbonate
Average	261 ± 277	1.30 ± 1.44	6.51 ± 7.22
DS (19)	528 ± 311	2.59 ± 1.69	12.9 ± 8.44
NDS (34)	112 ± 63.7	0.59 ± 0.50	2.93 ± 2.51

CaO and magnesium oxide (MgO). Good correlations (Ca^{2+}: $R^2 = 0.87$; Mg^{2+}: $R^2 = 0.81$) show that elevated Ca^{2+} or Mg^{2+} concentrations are associated with elevated CC concentrations. In average, measured CC is about half of the CC calculated from Ca^{2+} and Mg^{2+} (assuming, soluble Ca and Mg are present in the form of their carbonates), consistent with Ca^{2+} and Mg^{2+} being present mostly in CO$_3^{2-}$ minerals.

3.2. Comparison of results for carbonate in PM$_{2.5}$ by modified acid addition method and ionic balance

The major cations in aerosol are Na$^+$, NH$_4^+$, K$^+$, Mg^{2+} and Ca^{2+}, while the major anions are CO$_3^{2-}$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and (COO)$_2^{2-}$ (e.g. Puxbaum et al., 2004), with small amounts of other organic acid anions (Limbeck and Puxbaum, 1999) and metal cations. Ionic balance is commonly used to evaluate the acid–base balance of aerosol particles. Almost all of these species except carbonate can be determined in solution by routine ion chromatography (IC), the carbonate could then be determined by calculating the difference between cations and anions. Acid aerosols were common and attracted attention recently in China (e.g. Shen et al., 2009). Previous studies (Ocskay et al., 2006; Kocak et al., 2007) found that the fine fraction of the aerosol ($<$2 mm) is slightly acidic or neutral, while the coarse particles (2–10 mm) are alkaline. Carbonate cannot be determined in the aqueous extracts from the filters by the applied method. However, the other major anions can be quantified by IC and thus the concentration of carbonate can be derived from the ionic balance. The results can be compared with the values obtained from the direct measurement method. The concentrations obtained from the IC analyses are converted to milli-equivalents,

$$C\,(\text{cation microequivalents}) = \text{Na}^+/23 + \text{NH}_4^+/18 + \text{K}^+/39$$
$$+ \text{Mg}^{2+}/12 + \text{Ca}^{2+}/20 \quad (1)$$

$$A\,(\text{anion microequivalents}) = \text{F}^-/19 + \text{Cl}^-/35.5 + \text{NO}_3^-/62$$
$$+ \text{SO}_4^{2-}/48 \quad (2)$$

and the difference ($C - A$) gives the estimate for carbonate in the solid sample. Table 3 shows results for the carbonate calculated

from Ca^{2+} and Mg^{2+} (assuming, soluble Ca and Mg are present in the form of their carbonates), from the ionic balance difference and from the analytical method used in this study. As the two methods (Ca + Mg and IB) used for carbonate estimation are based on other inorganic species and assumption, e.g. Ca + Mg: carbonated calculated from Ca and Mg content; IB: carbonate calculated by ionic balance difference. Therefore, large differences of carbonate concentrations were observed from direct measurement.

Comparisons among carbonate measured in this study, calculated from Ca^{2+} and Mg^{2+} and calculated from the ionic balance difference are shown in Fig. 2. The correlation between the two calculation methods is excellent ($R^2 = 0.94$), and good correlations are observed for the carbonate measured by our modified method to the values for carbonate calculated form Ca^{2+} and Mg^{2+} ($R^2 = 0.86$) and the ionic balance difference ($R^2 = 0.90$) (Fig. 1). The slopes of determination show the best fit for the ionic balance difference with the measured carbonate − a slope of 1.022 and correlation of 0.90. However, the uncertainty in the method of ionic balance difference derives from other ions which have not been determined, and from measurement errors. Undetermined cations are the "main" trace metals, while the undetermined anions are mainly organic acids. The main organic acid in atmospheric aerosol is oxalic acid (e.g. Limbeck and Puxbaum, 1999), which is considered for ambient air samples in the ionic balance here. During DS, ionic balance difference is underestimated (slope = 0.80) because the existence of insoluble Ca or metals were non-determined during high dust loading period. During NDS, ionic balance difference is overestimated (slope = 1.20) because the existence of organic acids were undetermined.

3.3. Correlation analysis of selected species

Calcium carbonate (CaCO$_3$, Calcite) is regarded as the most chemically reactive mineral component in aeolian dust particles (Laskin et al., 2005; Tang et al., 2004; Usher et al., 2003). Its strong alkaline nature causes it to react readily with acidic gases during atmospheric transport or on the filter, such as reactions with SO$_2$(g) to produce sulphate, HCl(g) producing condensed-phase chloride, and nitrogen oxides such as NO$_2$(g), HNO$_3$(g), and N$_2$O$_5$(g) to produce nitrate compounds (Krueger et al., 2004; Sullivan et al., 2007a,b; Usher et al., 2003). The conversion of insoluble calcium carbonate particles to deliquescent calcium nitrate through reaction with nitric acid vapour was first demonstrated in laboratory experiments by Krueger et al. (2003, 2004) and has also been observed in recent field studies (Laskin et al., 2005; Matsuki et al., 2005; Shi et al., 2008). That means more acidic gases will be converted to calcium salts such as calcium sulfate, calcium nitrate and calcium chloride during DS periods.

Table 4 shows the correlation coefficients of Ca^{2+} with selected water-soluble ions (sulfate, nitrate or chloride) during DS and NDS periods. Higher correlations were observed in DS than in NDS

Table 2
Comparison of dicarboxylic acid concentrations (ng m^{-3}) in fine particles from different cities.

Site/type	Season	Size	Method	Carbonate	Ref.
Kosan, Korea/rural area	Spring/2002 (Peak)	TSP	Subtraction after acid addition	0.58	Kawamura et al., 2004
				6.3	
Xi'an, China/urban city	Spring/2002 (Peak)	PM$_{2.5}$	Acid addition method	1.9	Cao et al., 2005
				15.8	
Texas, USA/National Park		PM$_{2.5}$	Acid addition method	0.42	Chow and Watson, 2002
Vienna, Austria/urban roadside		PM$_{10}$	Ionic Balance	1.37	Jankowski et al., 2008
			Thermo treatment	1.95	
Tongliao, China/sand land	Spring/2005 (DS)	PM$_{2.5}$	Acid addition method	8.5	Shen et al., 2007
Tongyu, China	Spring/2006 (DS)	PM$_{2.5}$	Modified acid addition method	6.5	This Study
				13.0	

Table 3
Comparison of carbonate concentration determined by different methods.

	Mean	Range
Ca + Mg	11.5 ± 9.64	$0.81–45.1$
IB	10.3 ± 7.82	$0.98–36.2$
Carbonate	6.51 ± 7.22	$0.27–37.4$

Ca + Mg: CC calculated from Ca and Mg content; IB: CC calculated by ionic balance difference.

periods. The good correlation coefficients of Ca with SO_4^{2-} and NO_3^- during DS may be due to atmospheric chemical reaction during long range transport or from a semi-arid source region which may contain salt minerals. Moreover, higher correlations were observed between elemental carbon (analyzed by DRI Model 2001

Table 4
Correlation coefficients of Ca^{2+} with selected water-soluble ions (sulfate, nitrate or chloride) during DS and NDS periods.

	Ca^{2+}	SO_4^{2-}	NO_3^-	Cl^-	EC
DS period/R^2					
Ca^{2+}	1.00	0.70	0.54	0.30	0.45
SO_4^{2-}		1.00	0.79	0.42	0.60
NO_3^-			1.00	0.40	0.49
Cl^-				1.00	0.38
EC					1.00
NDS period/R^2					
Ca^{2+}	1.00	0.02	0.02	0.22	0.13
SO_4^{2-}		1.00	0.46	0.01	0.03
NO_3^-			1.00	0.04	0.02
Cl^-				1.00	0.27
EC					1.00

Thermal/Optical Carbon Analyzer using IMPROVE_A protocol) and SO_4^{2-} or NO_3^- in DS than in NDS periods (Table 4). This can be used to further explain the sources of SO_4^{2-} or NO_3^- was mainly from the combustion source rather than from the salt mineral of semi-arid region during DS period. This is consistent with previous studies that more sulfate and nitrate might be formed during atmospheric transport during DS period. There are several important changes in the physicochemical properties of the particles upon conversion of carbonate to sulfate or nitrate salts, including increased hygroscopicity. The cloud condensation nuclei (CCN) activity of the particle will increase with increasing hygroscopicity. Enhanced water uptake by atmospherically aged $CaCO_3$ can also increase the mineral dust single scattering albedo (Vlasenko et al., 2005), a key variable in assessing the impact of mineral dust on climate. Moreover, high correlations were observed between Ca^{2+} and crustal elements (Fe, Mn and Ti).

3.4. Impact of meteorological factor

Since carbonate is predominately emitted from mineral dust, it has often been used as a tracer of dust storm. The standard meteorological parameters including wind speed and direction, air
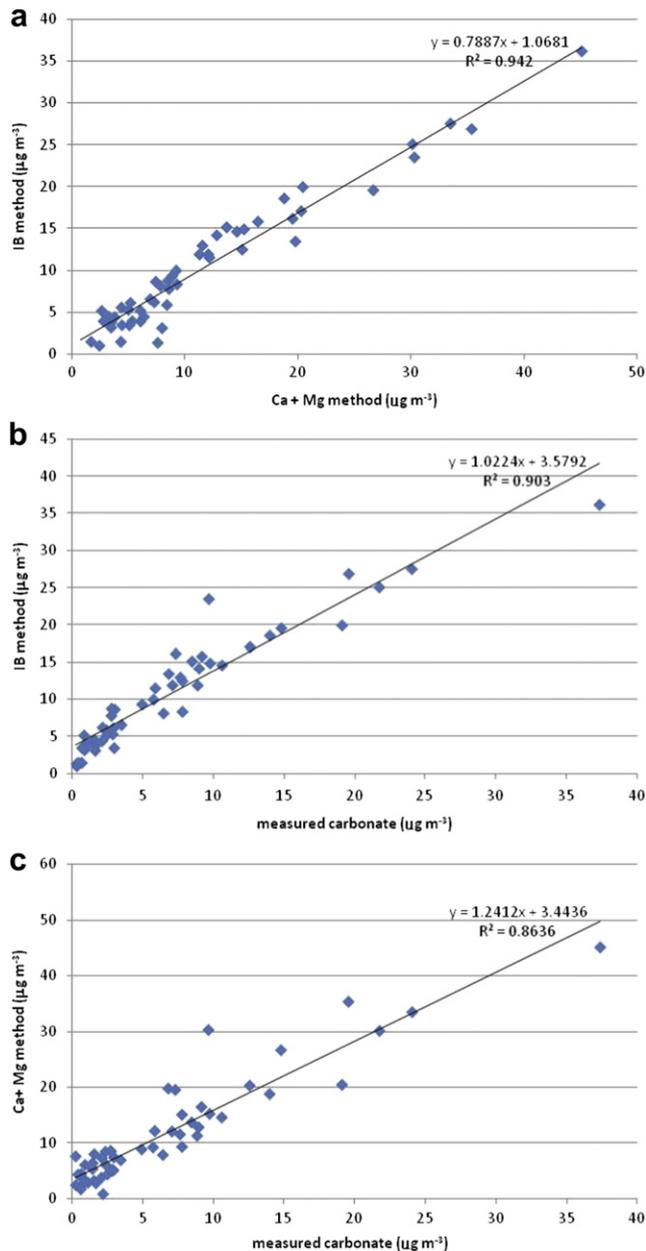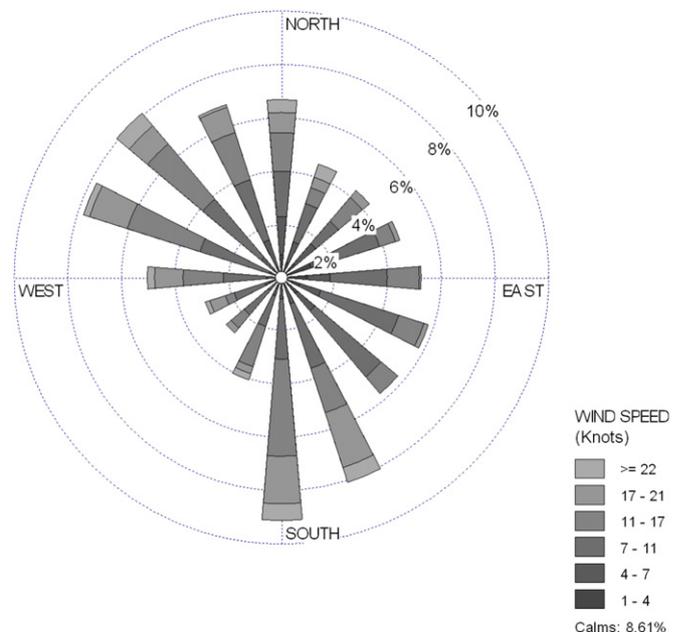

Fig. 2. Correlations of carbonate concentrations determined between a) Ca and Mg method and the ionic balance difference method; b) measured carbonate and the ionic balance difference method; c) measured carbonate and Ca and Mg method.

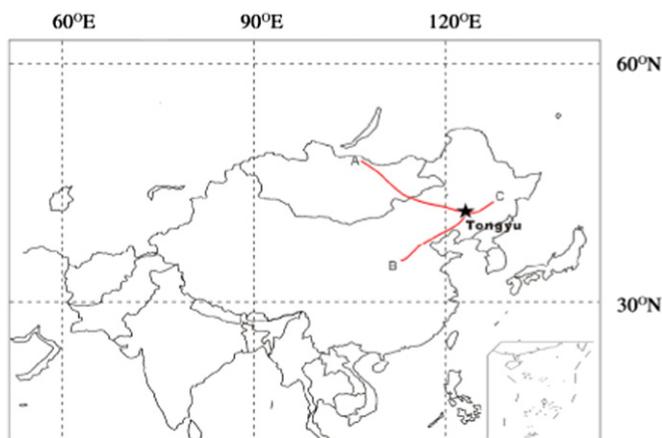**Fig. 3.** Wind rose diagram during the sampling period in Tongyu.

Fig. 4. Three groups (A to C) of air mass trajectories were identified by the NOAA HYSPLIT 4 trajectory model.

temperature and relative humidity were routinely measured. Fig. 3 presents the wind rose diagram measured at the 20 m level of the meteorological tower. The wind was mainly from the south, southeast or northwest sector during the sampling period. 24-hour mass back trajectories arriving at 1000 m above ground level (at 06 UTC) were calculated for Tongyu station using the NOAA HYSPLIT 4 trajectory model to investigate the transport pathways and origin. During the DS in spring 2006, three groups (A to C) of air mass trajectories were identified that passed over Tongyu (Fig. 4).

Group A represents the air mass arriving at Tongyu from northwest, passing through Gobi of Northern China, desert regions of Mongolia and Hunshan Dake sandland (12 mg m^{-3} of carbonate). Group B shows the pathway from south and southwest to Tongyu (18 mg m^{-3} of carbonate). Group C is from north and northeast to Tongyu (9 mg m^{-3} of carbonate). In general, when the air mass came from Group A and B, high concentrations of carbonate were observed (dust emission from loess). On the contrary, when the air masses came from Group C, relatively low carbonate concentrations were found. Southwest part of Tongyu is relatively urbanized than northwest and south part of Tongyu. High emission of mineral dust from western part of Tongyu was the major course for the dusty day.

4. Conclusion

Aerosol chemistry studies generally comprise the measurement of OC and elemental carbon (EC). A further constituent of carbonaceous material, CC is often not considered as the concentration levels of CC in atmospheric aerosol are generally low, and hence often negligible. Carbonate can affect atmospheric chemistry and aerosol characteristics because its alkalinity favors the uptake of acidic gases and the conversion to sulfate and nitrate on the surface. Daily concentrations of CC in PM$_{2.5}$ collected during 14 April to 23 June, 2006 in semi-arid area in Tongyu were determined. During the observation period, nine dust storm events (DS) were observed at Tongyu station. CC concentrations in the samples increased because of the large contribution of crustal matter during DS period. The average CC concentration during DS events was 2.6 μgC m^{-3}, which was more than 6 times the daily average concentration of 0.4 μgC m^{-3} during non dust storm (NDS) period. PM CO$_3^{2-}$ has not been measured very often and when compared with other measurements, the average airborne CO$_3^{2-}$ in Tongyu during NDS periods was slightly higher than those reported in other cities, except in Xi'an.

Carbonate concentrations were also calculated from Ca^{2+} and Mg^{2+} and from the ionic balance difference (ionic balance method).

Good correlations were observed between the measured carbonate concentrations to the values calculated form Ca^{2+} and Mg^{2+} ($R^2 = 0.86$) and the ionic balance difference ($R^2 = 0.90$). However, there are still some uncertainties in the method of calculation which have not been determined.

During DS period, more calcium carbonate was observed. These processes will increase hygroscopicity of particles. Enhanced water uptake by atmospherically aged CaCO$_3$ can also increase the mineral dust single scattering albedo, a key variable in assessing the impact of mineral dust on climate. In general, when the air mass came from northwest, and south or southwest to Tongyu, high concentrations of carbonate were observed. High emission of mineral dust from western part of Tongyu was the major course for the dusty day.

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