

Answer to the referees comments

Anonymous Referee #1

We thank reviewer #1 for these helpful comments and have made a lot reversion about the manuscript following the suggestion.

This paper describes the multi-analysis of ambient particles collected during a dust storm in Beijing. Asian dust storms are widely known to have large effects on the region's atmospheric chemistry and radiation budget, with resulting climate impacts.

This topic has been extensively reported on and is of interest to the Atmospheric Chemistry & Physics readership. As such a vast number of papers characterizing Asian dust storm particles have been published over the last three decades; I feel strongly that successive papers on this topic must present significant new findings and understanding to warrant publication in leading journals such as ACP. Unfortunately this manuscript is severely hampered by inappropriate sample collection and handling methods. This creates great difficulties in accurately and reliably interpreting the results from the subsequent particle analysis. The discussion and interpretation of the analysis is incomplete. Furthermore no new significant reliable findings are reported here. Therefore I cannot recommend this manuscript for publication in ACP.

Response: Many attentions have been paid to the heterogeneous reaction between SO₂ and mineral dust which indicated mineral dust can play an important role in the chemistry of sulfur dioxide. However, there still exists some uncertainty of the interaction between SO₂ and Asian dust. "Several observation-based studies have reported that although East Asian dust particles have long contact times with sulfate and nitrate precursors, they contain only small amounts (typically, less than 10-50%) of sulfate and nitrate (Maxwell-Meier et al. 2004; Ro et al. 2005; Zhang, D. Z., and Iwasaka, Y., 1999;). Field measurement during a dust period also revealed low conversion rate of SO₂ to sulfate during dust storm period (Xie et al., 2005). A recent modeling result (Manktelow et al., 2010) also suggested that the sulfate species on Asian dust may mainly derivate from the uptake of H₂SO₄ rather than reaction of SO₂ on the dust surface." (These sentences are added the revised manuscript) Therefore, it needs further laboratory study for the reactivity of authentic Asian dust particles to SO₂. In this study, we investigated the uptake coefficient of SO₂ on authentic Asian dust particles and the effect of reaction with SO₂ on hygroscopicity. It demonstrated that authentic dust particle, even containing reactive components such as aluminosilicate and carbonate, showed low reactivity to SO₂. It suggested that the mixture and reaction with organic and NO_x species reduced the reactivity of dust to SO₂.

Since the main focus in this study is the reactivity of Asian dust to SO₂, characterization of the dust particle was performed for interpreting the low reactivity. So, detailed characterization of dust, such as individual analysis and size segregation, were not conducted. However, from the comments of reviewers, we recognized some deficient of this paper and the title was changed to "A case study of Asian dust storm particles: chemical composition,

reactivity to SO₂, and the hygroscopic property”

A major concern results from the sample collection methods. Particles were collected “in a clean jar on the roof of a building”. This is not an appropriate way to collect aerosol samples for analysis. Even for TSP measurements particles should be collected on a filter or other substrate. The jar impedes any sort of particle size cut and likely favors the collection of larger particles. There will also be substantial mixing of the particles together, and continued chemical processing as the particles remain exposed to the atmosphere. Furthermore, no details as to how long the sample was collected, the meteorological conditions that prevailed, or the extent of the dust storm (e.g. particle mass loadings) were provided.

Response: It is our mistake to give the details about the collection process. The following sentences are added “The dust episode originated from Mongolia and reached Beijing at 16th April. The dust particles were collected during a dust storm period for 24 h where the ambient condition was in dust storm atmosphere. By a particle collection jar, both coarse particles and fine particles were collected without segregation of size. The collected particles were sealed in a Teflon package before analysis and experiments.”

It is not a traditional particle collection method for particles characterization. However, the particles collected by this way also represent dust particles and it provided an effective way to collect enough particles for laboratory reaction study since the major focus in this study was the reactivity of authentic Asian dust particles to SO₂. Mixing and chemical processing during the collection was still considered as atmospheric processing.

As there was no size or other particle segregation during collection it cannot be assumed that only dust particles were collected and analyzed here. Even though collection occurred during a dust storm mixing with other particles and gases from the regions high urban pollution levels will have occurred. Therefore the observations of various components mixed with the dust particles can't simply be assumed to have occurred through reactive uptake or condensation on the particles, as the authors appear to assume here.

Response: All the particles collected in this study were wind-blown particles during dust storm event which could be considered as representative of dust particles. The mixing with other species during the collection process in urban region was inevitable which was still considered as atmospheric processing. Reactive uptake and condensation of other species on particles as two major ways of various components mixed were assumed for the observations of various components.

There is no description of how the samples were stored or handled before analysis. Serious sampling and storage artifacts can occur if precautions are not taken to prevent the uptake of gaseous components, or evaporation from the sample, for example.

Response: The particles were sealed in a Teflon package to avoid the contact with ambient air which can prevent the uptake of gaseous or evaporation from the samples.

The particles were then diluted in water with ultrasonic dispersion before SEM/EDX analysis. This will alter the chemistry of the particles, removing and redistributing any material that dissolves, and potentially altering properties such as hygroscopicity (Herich et al., 2009; Koehler et al., 2009; Sullivan et al., 2009). Grinding the particles before DRIFTS analysis will also distort the original particle physicochemical properties. Alcohol was also used to disperse particles for the Knudsen cell experiments; this can also change particle composition and related properties.

Response: The preparation way for SEM/EDX analysis may be not suitable because the soluble components were destroyed. We also made element analysis with XPS which does not change the state of particles, as shown in the revised manuscript. The XPS analysis showed similar results as EDX with high fraction of C and no detection of S (as added in the revised manuscript). Grinding the particles before DRIFTS has little effect on the DRIFTS results when the ungrounded particles show similar spectra with weaker signal-to-noise ratio. Disperse particles with alcohol and pretreatment in vacuum condition may have some influence on the properties of particle; however it was unavoidable and always neglected in laboratory uptake experiments.

The SEM, FT-IR, and other analyses were all performed on bulk particle samples. Much more valuable information can be derived from individual particle analysis (Falkovich et al., 2001; Jeong, 2008; Laskin et al., 2006; Ro et al., 2005; Russell et al., 2002; Shi et al., 2008; Sullivan et al., 2007a). Why was this not performed?

Response: We thank the reviewer for the constructive suggestion of individual particle analysis. It provides more valuable information for characterizing particles. However, results of individual particle analysis vary with particles and give statistic information. Since the major focus of this study was the reactivity of authentic dust particles to SO₂, as mentioned in point 1, we only performed the bulk particle analysis to get integrated information for interpreting the low reactivity.

Since bulk samples with no size segregation were analyzed, these will be strongly biased by the larger dust particles present due to their much larger mass. However large dust particles experience different and often relatively less atmospheric processing than the more abundant (by number) smaller dust particles (Ro et al., 2005; Song and Carmichael, 1999; Sullivan et al., 2007a). This is an important factor to consider but is never mentioned here. I note the large 10 micron scale of the congested SEM image in Fig. 1.

Response: We thank the reviewer to bring these reported researches to our attention and

hereby give us the valuable suggestion. Large fraction of coarse particles is now added as a probable factor for the low reactivity.

How were the particles treated, if at all, before the TPD and FTIR experiments? Can you be certain that the sample did not absorb water and other gases after collection but before analysis?

Response: The particles were sealed in a Teflon package before TPD and FTIR experiments. During the experiments processes, the particles were in contact with air which may induce physical adsorption of H₂O and CO₂. However, before the TPD or FTIR experiments, the samples were purged with dry Ar(99.999%) or N₂ (99.999%) for 1 h to remove these physisorbed surface species.

Similarly, how were the particles treated before water adsorption isotherms were determined? Often samples are heated to remove pre-existing water to compare with unheated samples.

Response: Before water adsorption experiment, the sample was flushed with dry N₂(99.999%) for 1 h to remove the physisorbed water.

P. 8906, line 22: Why do you assume that carbonaceous components only coated the particles? If the particles are being heated until they char, these compounds could also be released from the particle core.

Response: Since individual particles analysis was not conducted, the mixture state assumed was not suitable in this study. Therefore, the interpretation of C sources was changed to “The unexpected higher fraction of C was possibly due to the mixture of carbonaceous aerosols during the dust event.” in the revised manuscript.

P. 8907, line 2: No evidence is presented to establish the process by which nitrate became mixed with the particles. Condensation of HNO₃ and reaction with alkaline components are just two possibilities. Coagulation with nitrate-containing particles and condensation of ammonium nitrate are others. Individual particle size and compositional analysis could help resolve this.

Response: We appreciate the reviewer for the valuable comments. The assumption of “These processed resulted in the nitrate coated on dust” was removed.

Little significance can be taken away from the small uptake value for SO₂ on the ambient aerosol sample as this was conducted dry and without oxidant. As the authors point out, adsorbed water and an oxidant are required to convert S(IV) to S(VI) via heterogeneous

processes. The ambient particles may have contained secondary material deposited through atmospheric processing which could have impeded the uptake of SO₂ in the Knudsen cell or DRIFTS experiments, unfortunately this was not addressed here. The dry requirement in Knudsen cell experiments represents a serious limitation and is an important reason why this technique has seen decreasing application in recent years to study atmospheric heterogeneous reactions.

Response: Uptake coefficient determined from Knudsen cell has been considered as the critical parameter for characterizing the reaction possibility between gas and solid particles. Low uptake coefficient means that the first step of gas reacted with solid hardly occur. Since oxidants are required to convert S(IV) to S(VI), the reversibility of SO₂ uptake on dust particles makes the reaction possibility among SO₂, oxidants and dust particles very small. Therefore, uptake coefficient of SO₂ on authentic dust should be determined. Besides Knudsen cell, DRIFTS study of the reaction between SO₂ and dust under both dry and humid conditions were also performed in this study. No IR peaks of sulfur species was observed in DRIFTS spectra. For authentic atmospheric particles, atmospheric processing induced the deposition of secondary materials which could impede the uptake of SO₂. It was considered as an important reason for the low reactivity of dust particles to SO₂ (page 8912, line 3-4).

It is most surprising that sulfate was not detected. As SO₂ emissions are high in China, and several other papers have detected sulfur compounds in Asian dust storm particles (Ro et al., 2005; Shi et al., 2008; Song and Carmichael, 1999; Sullivan et al., 2007a; Zhang and Iwasaka, 1999), this deserves discussion and explanation.

Response: We thank the reviewer to bring these reported researches to our attention and further discussions are added. "The unexpected low amount of sulfur species disagrees with some previous researches where sulfur species were always detected in Asian dust storm particles (Ro et al., 2005; Shi et al., 2008; Song and Carmichael, 1999; Sullivan et al., 2007a; Zhang and Iwasaka, 1999). However, EDX analysis of individual dust storm particle also implied that almost no sulfate is formed on the surface of dust storm particles during their transport from source areas to Beijing (Zhang and Iwasaka, 1999). In addition, it was reported that more than 90% of Asian Dust particles collected in Qingdao, China during three Asian Dust events in the spring of 2001 were not disturbed by sulfate, nitrate, and/or sea-salts (Zhang et al., 2000). It seems the dust storm particle has low reactivity to SO₂ since SO₂ emissions are high in China."

Similarly, since sulfate was not detected in the particles, why did you choose to expose them to only SO₂(g). Why not also expose them to NO_x/NO_y(g), since nitrate was observed in the particles.

Response: It is a valuable suggestion and exposure to NO_x/NO_y(g) would be studied in the future. Since SO₂ emissions are high in China and sulfate was not detected which was different from other reported results, therefore reactivity to SO₂ of dust particles was investigated in this study.

You detect chlorine in the dust particles, but this is not discussed. Dust particles can react with HCl(g) to accumulate chloride (Sullivan et al., 2007b; Zhang and Iwasaka, 2001).

Response: Thank for the suggestion. The following sentence is added “High concentration of Cl was also possibly from the polyvinylchloride plastic in the trash-burning and coal burning (Sun et al., 2004a) or the chemical process between HCl and dust particles (Sullivan et al., 2007b; Zhang and Iwasaka, 2001).”

P. 8905, 1st Para: The possible uptake of organic vapors by dust (or other) particles seems to be ignored here (Falkovich et al., 2004; Prince et al., 2008; Russell et al., 2002; Sullivan and Prather, 2007). I do not know what to conclude about the origin of various components detected by the SEM/EDX analysis.

Response: Thank for the suggestion. The following sentence is added “Another source of C may be due to the uptake of organic vapors by dust particles (Falkovich et al., 2004; Prince et al., 2008; Russell et al., 2002; Sullivan and Prather, 2007).” As mentioned above, analysis of dust particle was intent to explain the low reactivity to SO₂ and the origin of various components detected was not the main purposes of this study.

The Reference list was notably lacking several important related papers. Some suggestions are listed below. The lack of papers from the comprehensive studies of Asian dust storms during the ACE-Asia, TRACE-P, and PACDEX studies was particularly surprising.

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Response: We appreciate the reviewer very much for the valuable recommendation. The related references were added which help us interpret the results in this study.