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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Elevated nitrogen-containing particles observed in Asian dust aerosol samples collected at the marine boundary layer of the Bohai Sea and the Yellow Sea" *by* H. Geng et al.

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We thank Anonymous Referee #1 for his/her valuable comments on our manuscript, which help to improve the quality of our manuscript. Our response to the reviewer's comments is given below:

1. General comments: "... it may be misleading to use the term 'fine fraction' throughout the paper for aerosols in the size range 1.0-2.5 micron. ... I would suggest that the

authors should use a somewhat less deceptive term for this rather specific intermediate size range."

Response: In the manuscript, we clearly defined what "fine fraction" and "coarse fraction" terms are. However, we agree that the more specific description is better, so that we will change the words "coarse fraction" and "fine fraction" into "PM2.5-10 fraction" and "PM1.0-2.5 fraction", respectively.

2. Specific comments:

(1) Page 13663 line 5: more oxygen in fine particles: could structural or crystal water be still present in some solid particles?

Response: On page 13663, the first paragraph describes that for fine (PM1.0-2.5) alminosilicate particles in Asian dust samples, there are more oxygen contents than those in normal day samples, implying that a fraction of oxygen should come from secondary sulfates or nitrates that have been adsorbed on or adhered to the alminosilicate particles since atmospheric "secondary acids" can react or mix with primary mineral or soil-derived particles, as being discussed in the section of "3.2.1" (page 13667). It doesn't mean that structural or crystal water could be still present in some solid particles.

(2) Page 13663 line 23: how could reacted sea salt be internally mixed with soil derived particles? Is resuspension of deposited particles trapped in the sea surface microlayer possible by bubble bursting?

Response: Andreae et al. and Fan et al. reported that "a lot of Sahara dust particles were also mixed internally with sea salt over the Atlantic Ocean.", "about 20% of all the aerosol particles in the sample collected in Nagasaki (Japan) are sea-salt particles which are present externally with minerals, and 60% of the mineral particles collected at Nagasaki is internally mixed with sea salt.", and "a large fraction of dust particles was found to be internally mixed with sea salt over the Equatorial Pacific Ocean.", indicating

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that sea-salt particles can be abundantly internally mixed with mineral or soil-derived particles in the marine boundary layer (MBL). Two mechanisms can explain the presence of the internally mixed sea-salt/mineral aerosol: one is the reinjection of mineral particles during sea-spray formation that have previously settled onto the sea surface; the other is the collision of sea-salt and mineral particles in the atmosphere (Andreae et al., 1986). Thus, the reacted sea salt (formed by the process that genuine sea salt particles react with nitrogen and sulfur oxides species in the atmosphere) would be internally mixed with soil-derived particles by the above mechanisms. Alternatively, the internally mixed particles of reacted sea salts with mineral are produced by cloud processes through droplet coalescence (Fan et al., 1996). When the continental air enters the marine boundary layer in which genuine/reacted sea salt particles are abundantly present, both dust and sea-salt particles would act as cloud condensation nuclei (CCN). It is easy to form cloud droplets individually on dust and sea-salt particles in clouds. Coalescence of these droplets will occur and internal mixture of dust particles with sea salt will then be formed upon the evaporation of the cloud droplets (Fan et al., 1996). Based on the above discussion, we will add a sentence at the end of the line 23 (on page 13663): "They can be formed by two possible mechanisms, i.e., (a) collisions of reacted sea-salt and soil-derived particles in the atmosphere (Andreae et al., 1986); (b) cloud processes through droplet coalescence (Fan et al., 1996)." The reference of Andreae et al. will be added on page 13675, line 8.

(A) Andreae, M. O., Charlson, R. J., Bruynseels, F., Storms, H., van Grieken, R. E., and Maenhaut, W.: Internal mixture of sea salt, silicates and excess sulfate in marine aerosols, Science, 232, 1620-1623, 1986.

(B) Fan, X.; Okada, K.; Nimura, N.; Kai, K.; Arao, K.; Shi, G.Y.; Qin, Y.; Mitsuta, Y. Mineral particles collected in China and Japan during the same Asian dust-storm event, Atmospheric Environment, 1996, 30(2): 347-351

(3) Page 13664 line 14-15: The lack of soot particles attached to larger particles is surprising and may deserve additional comment.

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Response: Using SEM/EDX, it is difficult to identify soot particles attached to larger particles, because soot particles will lose their characteristic agglomerated morphology when attached to the large particles. Therefore, we will change the sentence "..., no soot agglomerates and tar balls were encountered," (Page 13664 line 14-15) to ""..., no identifiable, separated particles of soot agglomerate and tar ball were encountered.", to be more specific.

(4) Page 13665 line 19: how a hygroscopic compound can absorb seawater droplets?

Response: Thank the reviewer for the keen comment. The word "absorb" is not a correct expression here and causes misleading. We will replace it by "mix". So, the sentence "...are hygroscopic, they can readily absorb seawater droplets containing Na and Mg..."(page 13665 line 19) will be changed into "...are hygroscopic, they can be readily mixed with seawater droplets containing Na and Mg...".

(5) Page 13665 line 20: the sentence suggests that ammonia and nitric acid vapors can nucleate, which is not true: the entire paragraph needs careful reconsideration.

Response: Many previous papers said that nitric acid in the atmosphere is produced from NOx by gas-phase oxidation reactions, ammonium nitrate is a major component of atmospheric aerosols, and secondary NH4NO3 particles are from the reaction of gaseous HNO3 with NH3 in the atmosphere. Some references are:

Hitomi Kobara, Koji Takeuchi, and Takashi Ibusuki (2007). Effect of Relative Humidity on Aerosol Generation through Experiments at Low Concentrations of Gaseous Nitric Acid and Ammonia. Aerosol and Air Quality Research, Vol. 7, No. 2, pp. 193-204.

Barthelmie, R.J. and Pryor, S.C. (1998). Implications of Ammonia Emissions for Fine Aerosol Formation and Visibility Impairment: A 10 Case Study from the Lower Fraser Valley, British Columbia. Atmos. Environ. 32, 3: 345-352.

Makar, P.A., Wiebe, H.A., Staebler, R.M., Li, S.M. and Anlauf, K. (1998). Measurement and Modeling of Particle Nitrate Formation. J. Geophys. Res. 103, D11: 13095-13110.

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(6) Page 13666 line 2: as it is understood now, HULIS mostly come from biomass burning: (see Lukacs et al., JGR 2007, Feczko et al., JGR 2007).

Response: Indeed, in the literature, "Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe" (written by Lukacs et al., and published in JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, D23S18, doi:10.1029/2006JD008151, 2007) and "Determination of water and alkaline extractable atmospheric humic-like substances with the TU Vienna HULIS analyzer in samples from six background sites in Europe" (written by Feczko et al. and published in JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, D23S10, doi:10.1029/2006JD008331, 2007), it was reported that humic-like substances (HULIS) are omnipresent in rural, urban and biomass burning aerosol . . .ïijŇand biomass burning is a probable primary source of HULIS. However, HULIS were reported to commonly exist from the clean marine air to the heavily polluted winter urban atmosphere (Krivacsy, Z., Kiss, G., Ceburnis, D., Jennings G., Maenhaut, W., Salma, I., and Shooter, D.: Study of water-soluble atmospheric humic matter in urban and marine environments, Atmos. Res., 87, 1–12, 2008.). Also they are reported to be present even in fog water and seawater (E. R. Graber and Y. Rudich. Atmospheric HULIS: How humic-like are they? A comprehensive and critical review, Atmos. Chem. Phys., 6, 729–753, 2006). The sentence ". . . HULIS are of biogenic origin and have high contents of carbon and oxygen. . ." (page 13666 line 2) will be changed to ". . .HULIS, which mostly come from biomass burning or are of biogenic origin, have high contents of carbon and oxygen. . .".

(7) Page 13667 line 10: it is trivial that the lower the particle size, the larger the effective specific surface area (see Warneck, 2001).

Response: Indeed, "it is trivial that the lower the particle size, the larger the effective specific surface area". However, herein (line 3-11 on page 13667), our statistical results (based on data from Table 5) indicate that the smaller soil-derived particles in the atmosphere should be more prone to reacting or mixing with air pollutants or "secondary

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acids" than the larger ones, which can be worth while just to mention it.

(8) Page 13668 line 15: HNO3 is far more abundant in the gas phase than H2SO4 due to its much higher vapor pressure, so in terms of atmospheric processing (ageing) primarily not the precursors (NOx and SO2) are interesting in themselves but photochemistry, sink processes and a number of other factors play a more important role.

Response: The reviewer's comment is right. We will add a sentence, "In addition, photochemistry, sink processes, and a number of other factors also play important roles in the formation/decomposition process of nitrate- or sulfate-containing particles.", before "The decreasing trend for the. . ." on page 13668 line 16.

(9) Page 13669 line 25: '. . .elevated sea salt. . .': add 'concentrations'

Response: The sentence ". . .resulting in the elevation of reacted sea salts (& mixture)" will be changed to ". . .resulting in the elevation of reacted sea salt (& mixture) concentrations". Thank the reviewer for the correction.

(10) Page 13670 line 19: part of N may come from the reaction of nitric acid with NaCl and MgCl2 also present in the droplets.

Response: The comment might be right, however, it is not clear enough to say that in the text.

(11) Page 13670 line 26: it is reasonable that in the dust storm in that size range ammonium sulfate formation is suppressed since sulfuric acid was taken up by mineral particles.

Response: The comment is reasonable, so that a sentence, "or the formation of ammonium sulfate/bisufate might be suppressed as sulfuric acid was taken up by mineral particles (Zhang et al., 1999; 2003)),", following the word "event" and before "and that, on the other hand, . . ."on page 13670 line 28 (the last line).

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13655, 2009.