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Interactive comment on “Evolution of aerosol chemistry in Xi’an, inland China during the dust storm period of 2013 – Part 1: Sources, chemical forms and formation mechanisms of nitrate and sulfate” by G. H. Wang et al.

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Anonymous Referee #2 General comments This study focused on aerosol chemistry in inland China and discussed the possible chemical mechanisms of nitrate and sulfate. The authors designed the research during one Asian dust storm. The hourly dust samples were collected to understand the chemical changes from early stage of dust storm to end. Through comparisons chemical compositions of different dust samples at different stages of dust storm and size resolved aerosol sampling, the authors obtained

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the chemical forms and formation mechanisms of nitrate and sulfate. The study is good presentation for the research results. However, the paper needs to be one minor revision. Response: We thank the reviewer's comments, and have revised the paper. See the details below.

Comments: 1) 17441 L2 deleted in the current work./ Total suspended particulate (TSP) samples were Response: Suggestion taken. See page 2, line 37.

Comments: 2) L17, biomass burning emitted Cl⁻. The author should provide any evidence. Response: Suggestion taken. There are many literatures showing that aerosols derived from biomass burning are enriched with Na⁺, K⁺ and Cl⁻, which largely stay in fine particles (Andreae et al., 1998; Shen et al., 2008). In addition, K⁺ in fine particles is often taken as a key tracer of biomass burning (Agarwal et al., 2010; Shen et al., 2008). We have added some references into the text to prove that biomass burning emission is an important source of fine particulate Cl⁻ in Xi'an city during our observation period. Related discussions are modified. See page 12-13, line 304-315.

Comments: 3) L12-21, the author need to consider why NH₄⁺ and NO₃⁻ were mixed with mineral dust particles in coarse mode instead of the externally mixed with dust particles although the good linear from NH₄⁺ and NO₃⁻. Response: As we have stated in the manuscript, Cl⁻, SO₄²⁻ and NO₃⁻ are the major anions and Na⁺, Ca²⁺ and NH₄⁺ are the major cations in the TSP samples, among which Cl⁻ and SO₄²⁻ strongly linearly correlated with Na⁺ and Ca²⁺ rather than NH₄⁺. Instead, NH₄⁺ only well correlated with NO₃⁻ and no correlation was found between NO₃⁻ and other cations. Moreover, linear fit regression showed that NH₄⁺ and NO₃⁻ linearly correlated each other with a molar ratio of 1:1. The above results clearly indicate that NH₄⁺ and NO₃⁻ were mixed with mineral dust particles as the chemical form of NH₄NO₃. Therefore, during the observation periods both ions displayed an identical temporal variation pattern and presented same size distribution patterns in the dust and non-dust periods. See the related discussions in page 10, line 254-257, page 13, line 325-330, and page 14-15, line 358-365.

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Comments: 4) L23 CaSO₄ particles are minor hygroscopic materials. The Na₂SO₄, CaSO₄ and NaCl have high deliquescence relative humidity but during the dust period the relative humidity is quite low. My question is any evidence to prove these particles absorb water to form aqueous phase. Response: We agree with the reviewer that CaSO₄ is minor hygroscopic, and Na₂SO₄ and NaCl have high deliquescence relative humidity points, which are $84.2 \pm 0.4\%$ (RH) and $75.3 \pm 0.1\%$ at 25°C, respectively (Tang, 1980; Tang, and Munkelwitz, 1993). Under these high RH conditions Na₂SO₄ and NaCl particles can deliquesce and become water droplets. However, this is not the case in the current work. Actually, in this paper we have talked about the formation of liquid phase on the dust surface, which can occur under very low RH conditions. For examples, a liquid phase formed on dust particle surface during Asian dust storm event has been reported by Li and Shao (2009). They used transmission electron microscopy (TEM) to observe mineral particles collected during a dust storm event and found visible coatings on the dust particle surface, which contain Na, Ca, O and N. During this dust storm event RH was 20–45%. Laboratory study by Goodman et al (2000) showed that even under RH < 20% conditions a liquid phase can quickly form on the calcite surface via water vapor uptake of Ca(NO₃)₂ that is produced by heterogeneous reaction of HNO₃(g) with CaCO₃. Andreae and Rosenfeld (2008) also pointed out that dust is insoluble but wettable. In the current work, we do not have any direct evidence to prove that these particles absorb water to form aqueous phase. However, we have measured the hygroscopicity of the ambient aerosols during the whole campaign by determining the hygroscopic growth factor of the water-soluble fraction of the TSP samples (Huang and Wang, 2014). The results showed that κ value of the water-soluble fraction of dust particles ranged from 0.20–0.38 (0.30 ± 0.04) (Huang and Wang, 2014), indicating a wettable nature of the dust particles (Andreae and Rosenfeld, 2008). The above field observation and laboratory measurements demonstrated that a liquid phase can be formed on the dust surface under a low RH condition, which can be ascribed to the hygroscopic salts (e.g., NaCl and Na₂SO₄) in dust particles. We have added the above related discussions into the text. See page 15, line 368–372. We agree with the

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reviewer that CaSO₄ is minor hygroscopic, thus we deleted CaSO₄ from the related discussions and modified our statement. See page 2, line 56.

Comments: 5) 17444. L27, hygroscopic salts include NaCl, Na₂SO₄ not CaSO₄? I am worried about the CaSO₄ here. Response: We removed CaSO₄ from the sentence and modified the statement. See page 6, line 141-142.

Comments: 6) 17448 L6, PM_{2.5} mass concentration Response: Suggestion taken. See page 9, line 218.

Comments: 7) 17449 L17-19, sulfate concentration, ammonium concentration Response: Suggestion taken. See page 10, lines 254 and 255.

Comments: 8) 17451 L4 NaCl- should be NaCl Response: We have corrected this mistake. See page 12, line 293.

Comments: 9) 17452, Na₂SO₄ and CaSO₄. Again my question is L23 Response: In the surface soil of north China like Inner Mongolia and Qinghai Province, Na₂SO₄ and CaSO₄ exists as the hydrated salts, i.e., mirabilite(Na₂SO₄·10H₂O) and gypsum (CaSO₄·2H₂O), both co-exist together and are water-soluble (Zheng, 1991). These salts, along with NaCl, can absorb water vapor, forming a liquid phase on the dust surface. Please see our response above.

Comments: 10) 17453, L25-26, need reference or evidence. Response: For the evidence to prove that a liquid phase can be formed on the dust particle surface. See our response to the 2nd reviewer's above comment point (4) and page 15, line 368-372.

Reference: Agarwal, S., S. G. Aggarwal, K. Okuzawa, and K. Kawamura: Size distributions of dicarboxylic acids, ketoacids, α -dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over Northern Japan: implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols, Atmos. Chem. Phys., 10(13), 5839-5858, 2010.

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