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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Summertime $PM_{2.5}$ ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere" *by* Ravi Kant Pathak et al.

Ravi Kant Pathak et al.

Received and published: 7 November 2008

Response to Reviewers

We thank the three reviewers for their helpful comments and suggestions which have helped improving the original paper. Below are our itemized responses.

Anonymous Referee #2 Received and published: 3 August 2008

This manuscript discussed the PM2.5 ionic composition and the nitrate formation at four sites in China. The idea was good and the theoretical methodology was encouraged. However, several basic issues were not appropriate in the sampling and analysis, which may bias the results and conclusion. Major concerns are listed as follows.

1. Sampling site. The authors used different types sampling sites like urban, suburban, rural microenvironments for the comparison of formation mechanisms of nitrate. Do these microenvironments have potential impact for the comparison? Tai Cang site located in Tai Cang Meteorological Station, which should be mirrored to the more influence from local emission due to Tai Cang is an active industrial town rather than the impact from Shanghai pollutants. As such, the Wan Qing Sha site should reflected the impact not only from Guangzhou pollutants but also the emissions from the adjacent counties like Zhuhai and Zhongshan cities especially in summer time. In the third paragraph of introduction, the authors described the four cities situated in northern, eastern, southern, and central regions of China. However, no one think Lanzhou represent the central regions of China.

Response: The measurements sites were in a suburban or rural area near four major cities of China. The locations of these sites were selected to investigate the impact of emissions from the adjacent urban centers. Although Tai Cang was influenced to a larger extent by local emissions compared to the other sites, it is downwind of Shanghai during the summer under the prevailing south-east winds. For Wan Qing Sha, it is reasonable to expect that the cities south of the site may affect the measurements, as the referee has pointed out. An examination of air-pollution and wind data, however, indicated that the highest levels of pollution were observed when the winds came from north (i.e., from Guangzhou), and the lowest with the winds from the south. This suggests small impact of southern cites on the measurements during the study period due in part to a stronger vertical mixing under the Asian Monsoon.

This study focuses on secondary aerosols of sulfate and nitrate, which are less influenced by local emissions. We believe that the data are representative of the respective study areas despite the difference in proximity of the sites to emission sources in these regions.

Geographically Lanzhou is in the central part of China. Considering that the Chinese people generally think the city is in the west or northwestern region of the country, we

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will change its location to north-western in the revised paper.

2. Sampling time. Since the monsoon climate in China, May should belong to spring time. It is not appropriate to compare the properties of spring aerosol with summer aerosol.

Response: Subtropical Southern China has a shorter spring and a longer summer compared to mid-latitude regions. Our study was conducted from the later half of May until end of the June; we think this period can be treated as early summer.

3. Author should be careful in discussing the formation of NO3- because there are a lot of nitrate losses when sampling with Teflon filters in summer time. This loss should not be neglected because it has great impact on the discussion of nitrate formation.

Response: We agree on the concern of sampling artifacts. Artifacts of nitrate occur due to evaporation of semivolatile NH4NO3 (NH4NO3(s) <-> NH3 (g) + HNO3(g)) from the particles collected on the filter due to fluctuations in temperature and RH and/or pressure drop across the filter, which perturb the gas-particle equilibrium. Nitrate evaporations are also possible due to the mixing of acidic (H2SO4) and alkaline particles (Ca(NO3)2, NaNO3, KNO3 etc.) on the filter (e.g. Ca(NO3)2 + H2SO4 -> 2HNO3(g) + CaSO4). The above two processes cause negative bias of the filter data. Positive artifacts of nitrate can occur when HNO3 is absorbed on the sea salt (or dust) particles collected on the filter (e.g. NaCl + HNO3(g) -> NaNO3+HCl(g)). Generally, the evaporations of semivolatile NH4NO3 under dry sampling conditions are the major cause for nitrate artifacts.

In our study, except for Lanzhou, samples in Beijing, Shanghai, and Guangzhou were collected in humid conditions and particles were deliquesced all the time. Previous studies (Pathak and Chan, 2005) have shown that nitrate artifacts from the deliquesced particles collected on the filter can be estimated using the following empirical correlations:

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For ammonium rich samples: Nitrate loss (%) = 30*[Ln([NH4+]/[NO3-]) - 1.2]

For ammonium poor samples: Nitrate loss (%) = 30*[Ln([H+]/[NO3-]) - 1.2]

In this present study, we have used the above methods to estimate the nitrate artifacts for the four city samples. The results show that the average nitrate artifacts were not significant for samples taken in Beijing (3%), Shanghai (10%), and Guangzhou (2%). The smaller artifacts in Beijing and Shanghai can be attributed to the high acidity, little alkaline and sea salt particles and lack of NH4NO3 in the collected aerosols. For Lanzhou, due to its dry conditions, the estimated evaporated loss of 10% should be viewed as a lower limit. In this study we have corrected these sampling artifacts in the dataset. We will clarify these points in the revised paper.

4. The PM2.5 filters after sampling should keep in cool container in order to prevent the loess of ammonium. How do the authors keep the filters in cool environment at four cities during two years& sampling? Ammonium in the Teflon filter is sensitive to the temperature change.

Response: Filters after sampling were stored at 4oC at the sampling site and during the transportation as well as in the laboratory until chemical analysis was performed.

Anonymous Referee #3 Received and published: 8 October 2008

This paper presents some unusual observations in which significant amounts of NO3- are observed in particles which have low NH4+/SO42- ratios. While these interesting measurements are compared to a substantial amount of data from other sites, the weakness of the paper is that it does not identify what sets these high nitrate measurements from Beijing and Shanghai apart from other sites.

Response: We believe that the high levels of nitrates observed at the Beijing and Shanghai sites were likely due to the presence of highly acidic and abundant aerosols which promoted the formation of nitrate via N2O5 hydrolysis under humid summer weather conditions. We have presented some evidence; nonetheless more studies are

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needed to confirm this hypothesis.

Is it simply the magnitude of the particulate sulphate concentrations or is there some other aerosol constituent or property that is key?

Response: We have shown that the acidity [H+]total and pH of aerosol phase, aerosol water content, and aerosol surface area are the parameters that appear to have influenced the nitrate formation in this study. The discussion on these properties and parameters has been provided in the paper (see section 3.3)

Because these measurements are so unusual, and because the 24 hour sampling scheme offers many opportunities for bias, I think a better assessment of potential biases and artefacts is warranted.

Response: We agree on the concern of sampling artifacts. Artifacts of nitrate occur due to evaporation of semivolatile NH4NO3 (NH4NO3(s)<-> NH3 (g) + HNO3(g)) from the particles collected on the filter due to fluctuations in temperature and RH and/or pressure drop across the filter, which perturb the gas-particle equilibrium. Nitrate evaporations are also possible due to the mixing of acidic (H2SO4) and alkaline particles (Ca(NO3)2, NaNO3, KNO3 etc.) on the filter (e.g. Ca(NO3)2 + H2SO4 -> 2HNO3(g) + CaSO4). The above two processes cause negative bias of the filter data. Positive artifacts of nitrate can occur when HNO3 is absorbed on the sea salt (or dust) particles collected on the filter (e.g. NaCl + HNO3(g) -> NaNO3+HCl(g)). Generally, the evaporations of semivolatile NH4NO3 under dry sampling conditions are the major cause for nitrate artifacts.

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No mention is made of the organic content of the aerosol, yet that has been shown to have an influence over N2O5 hydrolysis rate.

Response: Organic carbon in the aerosol may play a role. However laboratory study by [Antilla et al. 2006] suggests that the presence of organics in the aerosol phase tends to suppress the heterogeneous hydrolysis rate of N2O5 on aerosol surfaces.

There is no explanation given for why the nitrate that is formed by heterogeneous processing would remain in the acidic aerosol, rather than re-entering the gas phase as HNO3. It would be helpful if the authors could demonstrate what other chemical or physical properties or conditions are unique in Beijing and Shanghai and whether we would expect to encounter them in other parts of the atmosphere.

Response: As discussed, the samples with high concentrations of nitrates were collected during humid and hazy weather; the nitrate formed via hydrolysis might have favored its partitioning in the aerosol phase. A discussion on the unique conditions prevailing in Beijing and will be included in the paper.

P 11489 line 17 - is it really just at low NH3 that neutralization of sulphate is favoured? I think it's more strictly correct that it's always favoured, but it's only evident when there's

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a limited amount of NH3 around.

Response: We agree. We will correct this in the revised paper.

P11489 line 25 - The contribution to the formation of nitrate in PM2.5 is relatively less known - the contribution of what ? do you mean the relative contributions of gas phase and heterogeneous chemistry?

Response: We will modify the sentence as The contributions of various pathways of nitrate formation to PM2.5 mass is relatively less known compared to the formation of sulfate, which is dominated by cloud/fog processes.

P3 line 12 - why nevertheless? It seems like the preceding sentence supports rather than contradicts your claim.

Response: Corrections will be made as suggested.

P11493 line 15 - is this artefact in sulphate 7-11% of the ammonium, of the measured sulphate or of the SO2? Please explain why

Response: These artifacts refers to the positive artifacts of sulfate in the ammonium rich samples. The sentence in the revised paper will be modified to - The positive artifacts of sulfate have been estimated to be about 7% and 11% in ammonium-rich samples of PM2.5 and PM10, respectively. The positive artifacts of sulfate are caused by absorption of the SO2 into the ammonium rich sulfate particles collected on the filter while sampling, which is consequently oxidized to form sulfate within the collected particles. We will incorporate the above changes in the revised paper.

P 11494 Line 4 - why would there be no evaporation of HNO3 from particles just because ammonium wasn't present? Over 24 hours the relative humidity could certainly change and you might expect evaporative losses from an acidic particle.

Response: RH fluctuations can affect the equilibrium and thus can cause artifacts. However, major loss of nitrate are expected mainly at low RH, but is not significant at

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high RH when particles are already deliquesced. Since our high-nitrate samples were collected at high RH (>75% as shown in Figure 6) and the particles were deliquesced all the time, we do not expect a major loss of nitrate from our samples due to RH fluctuations as described above.

P11494 Line 28- here you say aerosol total acidity [H]tot was measured in the aqueous extract, then later on the next page, you say it was estimated from the sulphate, nitrate and ammonium concentration. It's not clear whether the value is actually measured, or simply calculated from other measured values using the equation given Section 2.4 should be re-ordered to be clear about which values were measured, and which were calculated according to the equations given

Response: [H+]total was not measured, but estimated using the equation given. Corrections will be made as suggested.

P11496 - line 13, were organic acids or amines measured?

Response: No.

P11498 line 21 what does released mean in this sentence?

Response: The word - released- means freed. [H+] ion was freed from H2SO4 or HSO4- molecules in the presence of water as in-situ [H+]. The meaning will be clarified in the paper.

P11499 - lines 6-9, this sentence is confusing; do you mean that the amount of nitrate is unusual for an ammonium-deficient particle?

Response: We will rephrase the sentence as - One important finding of this study is the high concentrations of nitrate found in the ammonium-deficient samples, which is different from previous studies indicating that significant amount of PM2.5 nitrate was normally observed in an ammonia-rich environment.

P11499 : line 17, why is excess ammonium that above which the molar ratio of

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[NH4]/[SO4] = 1.5, shouldn't this ratio have to equal 2 for the neutralization of sulphate?

Response: Previous studies have shown that at [NH4+]/[SO42-] = 1.5, nitrate formation via gas-phase reaction NH3+HNO3 <-> NH4NO3 becomes evident in the NH3 - H+ - SO42- - H2O system in aerosol (Pathak et al., 2004a; 2005). This is also illustrated by data complied in Figure 4 and 5. Therefore, in this study the excess ammonium is defined as the amount of ammonium in excess of that required for [NH4+]/[SO42-] =1.5 (i.e., excess [NH4+] = ([NH4+]/[SO42-] - 1.5)* SO42-]). In other words, when the excess ammonium is $>$ 0, homogenous gas-phase formation of nitrate will be significant, as shown in Figure 5. We will modify the text to clarify this point.

P11499 line 27 - is the solid line based on your own fit to the pooled data from other studies?

Response: Yes. We will add a sentence in the revised text.

P11501 line 5 - haven't studies (see refs) also shown that N2O5 hydrolysis is inhibited or turned off when the particle contains significant nitrate? How can this be reconciled with the large amounts of nitrate that are present, and possibly accumulating in the aerosol?

Response: This is a good point. The nitrate inhibiting effect can be seen in Figure 8 which shows leveling off concentrations of nitrate at higher nitrate loading despite high acidity, surface areas etc that act to promote hydrolysis. We will add some discussions in the revised paper.

P11501 line 27 - NOy is said to include aerosol nitrate, yet Figure 7 includes points with 42 ug/m3 of NO3 (equivalent to 16 ppb NOy) and only 14 ppb of total NOy? how is this possible?

Response: There was an error in the Figure 7. For the Beijing data, the plotted X-axis values for NOy is (NOy - NO3-). Corrections will be incorporated in the revised paper.

P11502 line 5 - anticipation is the wrong word in this context

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Response: Corrections will be incorporated in the revised paper.

P11502 line 13 - I don't find this formulation very convincing. Why would it only hold in Beijing and Shanghai? It would be more useful to identify the difference between the conditions where these data were collected and all of the acidic aerosol from other studies in Figure 4 that does not show substantial amounts of nitrate. Is it the total amount of sulphate that matters?

Response: The formulation indicates that nitrate formation was linked to the parameters that are believed to be important to heterogeneous chemistry. It holds for the Beijing and Shanghai samples. It may be applicable to the other sites too. However, it is difficult for us to test it for other sites due to the unavailability of detailed composition data from these studies. High pollution levels observed at the Beijing and Shanghai sites were striking. As shown in the paper, the humid weather coupled with high loadings of acidic aerosols and NOx at Beijing and Shanghai sites is believed to favor more hydrolysis in the formation of nitrate compared to data from other places. Sulfate is important because higher sulfate leads to higher acidity (in ammonium deficient atmosphere), lower pH, higher aerosol surface area, and higher aerosol water content, which are believed to promote the heterogeneous hydrolysis.

Figure 1 -it is quite difficult to read the font on the bars; please enlarge

Response: The suggestions will be incorporated in the revised paper.

Figure 4 - many of the points from this graph are from the same cities in China ; what Makes the data collected in your study so different?

Response: As shown in Fig. 2, previous studies in the Beijing and Shanghai show comparable levels of ammonia to the present study. But the sulfate and nitrate are much higher in our study, which suggests a highly NH3-decifcient situation. We will mention this point in the revised paper.

Figure 6 - make the symbols smaller so we can see more of the points

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Response: The suggestions will be incorporated in the revised paper.

1. M. Hallquist, D. J. Stewart, S. K. Stephenson, R. A. Cox, Phys. Chem. Chem. Phys. 5, 3453 (2003) 2. T. F. Mentel, M. Sohn, A. Wahner, Phys. Chem. Chem.Phys. 1, 5451 (1999). Interactive comment on Atmos. Chem. Phys. Discuss., 8, 11487, 2008.

P. Bhave bhave.prakash@epa.gov Received and published: 6 August 2008

The authors present ionic composition measurements of inorganic PM2.5 collected during the summer near 4 major cities in China. Their analysis focuses largely on the observations of abnormally high concentrations of particulate nitrate in the ammonium poor samples collected near Beijing and Shanghai.

This is a very interesting finding and certainly worthy of publication and further investigation. As additional motivation for this analysis, the authors may be interested to know that numerical air quality models consistently under predict the concentrations of particulate nitrate during Summer in the eastern United States because the observed levels of nitrate (though lower than the concentrations reported in this study) are consistently greater than those predicted by conventional thermodynamic gas/particle partitioning modules (e.g., ISORROPIA, EQUISOLV, etc.) embedded within the numerical models. The models predict essentially zero nitrate due to high sulfate and moderate ammonium concentrations found in the eastern U.S. during Summer.

The authors suggest that the high nitrate near Beijing and Shanghai was most probably formed via the heterogeneous hydrolysis of N2O5. This raises a couple of questions.

1. Is there any reason to expect that nitrate formed via N2O5 hydrolysis should behave differently (from a thermodynamic standpoint) than nitric acid formed by gas-phase oxidation of NOx? In other words, why wouldn't the nitrate formed by N2O5 hydrolysis partition back to the gas phase and maintain thermodynamic equilibrium within the SO4/NO3/NH4/H2O system?

Response: Nitrate formed via N2O5 hydrolysis should also partition into gas phase. In

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our study the high nitrate samples were collected on humid/foggy days, as a result the equilibrium should have favored the partitioning of nitrate into the particulate phase. We will add a sentence to clarify this point.

2. Did the authors consider the possibility that a sizeable portion of the nitrate near Beijing and Shanghai may be present in the form of organic nitrates?

Response: To our knowledge, there have not been reports to show that organic nitrates contributed to a significant fraction of nitrates in atmospheric PM2.5.We believe that most of nitrate measured in Beijing and Shanghai was the inorganic nitrate.

A final question that may be of minor importance to the overall findings: given that the authors measured the concentrations of sodium, calcium, magnesium, potassium, chloride, and nitrite ions, why aren't those values included when estimating [H+]total on Line 10 of page 11495?

Response: We did not include these species for the following reasons: 1) Their influence on the acidity ([H+]total) would be insignificant 2) Chloride at the Lanzhou site was exceptionally high that may be due to presence of organics from local emissions. Therefore, inclusion of chloride might have misled the [H+]total estimations. Hence, for consistency, all the ionic species of minor significance were not included.

If the authors can address these questions (especially the first 2) in their final paper, it may provide more valuable insights for future air quality model development.

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