

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.

Anonymous Referee #3

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This paper presents some unusual observations in which significant amounts of NO_3^- are observed in particles which have low $\text{NH}_4^+/\text{SO}_4^{2-}$ 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. Is it simply the magnitude of the particulate sulphate concentrations or is there some other aerosol constituent or property that is key? 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. No mention is made of the organic content of the aerosol, yet that has been shown to have an influence over N_2O_5

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hydrolysis rate. 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 HNO_3 . 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.

P 11489 line 17 – is it really just at low NH_3 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 a limited amount of NH_3 around.

P11489 line 25 – “The contribution to the formation of nitrate in $\text{PM}_{2.5}$ is relatively less known” – the contribution of what – do you mean the relative contributions of gas phase and heterogeneous chemistry?

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

P11493 line 15 – is this artefact in sulphate 7-11% of the ammonium, of the measured sulphate or of the SO_2 ? Please explain why

P 11494 Line 4 – why would there be no evaporation of HNO_3 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.

P11494 Line 28- here you say aerosol total acidity $[\text{H}]_{tot}$ 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

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

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P11498 line 21 what does 'released' mean in this sentence?

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

P11499 – line 17, why is excess ammonium that above which the molar ratio of $[\text{NH}_4]/[\text{SO}_4] = 1.5$, shouldn't this ratio have to equal 2 for the neutralization of sulphate?

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

P11501 line 5 – haven't studies (see refs) also shown that N_2O_5 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?

P11501 line 27 - NO_y is said to include aerosol nitrate, yet Figure 7 includes points with $42 \mu\text{g}/\text{m}^3$ of NO_3 (equivalent to 16 ppb NO_y) and only 14 ppb of total NO_y – how is this possible?

P11502 line 5 – 'anticipation' is the wrong word in this context

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?

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

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?

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

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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).

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