

Interactive comment on “Acid gases and aerosol measurements in the UK (1999–2015): regional distributions and trends” by Y. Sim Tang et al.

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Received and published: 29 June 2018

Reviewer's comments on ACP-2018-489 manuscript "Acid gases and aerosol measurements in the UK (1999-2015): regional distributions and trends" by Tang et al.

General Comments

The manuscript describes the results of a long term (15-year) national-scale monitoring network for atmospheric acid gases and aerosols in the UK. Trends in concentrations since ca 2000 are analysed alongside reported changes in emissions, showing non-linearities between emission and concentration changes, caused by shifts in gas/aerosol partitioning. The dataset is fairly unique worldwide and well worth publishing in ACP. The paper is well written, with an abundance of detail and perhaps too

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many figures, with the same data sometimes shown twice in different places. A little streamlining could improve the readability of the paper, as one tends to get swamped by the large number of figures and tables. I would recommend some minor changes before final publication (see below).

The mean weakness in the quality of the dataset is likely the large uncertainty in HNO₃ caused by interferences by other NO_y compounds on potassium carbonate coated denuders. This is mentioned in the methods but not referred to later on in the discussion in relation to trends in measured HNO₃ and reported NO_x emissions. With a flat and constant correction factor of 0.45 for HNO₃ measured from K₂CO₃ coated denuders (meaning that 55% of the raw concentration is subtracted to provide a corrected number), one can wonder whether the apparent decrease in HNO₃ since 2000 is significant, or if the slope of the apparent decrease has any meaning. With large changes in NO_x emissions and in the general pollution climate of the UK over the last 20 years, and therefore with possibly large changes in the ratios of HNO₃ to the interfering NO_y gases (NO₂, HONO, PAN, etc), it is risky to assume a constant 0.45 correction factor for the whole period, and also across the whole country, given the large differences in pollution profiles between the sites of the network.

Specific Comments

p6, l4, '...sampling rate of 0.2-0.4 l/min...' Please mention at this stage, or just below in the paragraph describing the aerosol collection system, what the particle size cut-off is for the DELTA sampler (mentioned later on p10, l3). It is important to know what the size spectrum of collected aerosols is, and that some (coarse) particles are not sampled, eg dust, large marine aerosols.

p7, l6-7, change of analytical labs from Harwell to CEH Lancaster in 2009: was there a transitional period of overlapping parallel measurements by the two labs, to make sure no bias was introduced in the long term time series by the change of laboratory?

p7, l26, '...flagging up occurrences of poorly coated denuders and/or sampling issues...'

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Another possibility is that concentrations are so large that the first denuder saturates and thus much is collected by the second denuder. This can happen for NH₃ at agricultural sites after fertilisation; it is much less likely for acid gases due to lower concentrations, unless perhaps at some polluted urban stations?

p8, I15, the term 'bias' is used in relation to the 0.45 correction factor for HNO₃, in the title of 2.6 and also other parts of the text. This is perhaps misleading as a bias suggests an offset, while the multiplicative correction applied acts on the span.

Further, in the Tang et al 2015 report, the authors write that '... It is recommended that a correction factor of 0.45 be applied to the historic HNO₃ measurements. The range of ratios was 0.44 ± 0.15 ($\pm 2SD$), i.e. 0.29-0.59, therefore it is reasonably likely that the value lies between 0.4 and 0.5. Therefore a correction factor of 0.45 should be applied...' It is quite clear that the percentage of non-HNO₃ NO_y compounds that is measured after extracting K₂CO₃-coated denuders depends on the relative abundances of these gases compared with HNO₃, as well as their collection efficiencies on K₂CO₃ and their oxidation/reaction rate following adsorption. I would expect large seasonal changes, and large spatial/geographical variations, in these concentrations and the associated chemical processes, as reflected in the observed 0.29-0.59 range. Applying the same correction factor at all sites of the network, that range from remote to coastal to rural to sub-urban and urban, does not seem to be adequate. This is hinted at in the Eskdalemuir example of Fig. 3, where applying the large 0.45 multiplier makes the DELTA TIN values diverge from the EMEP filter pack measurements, ie at this rural background site the need for such a large correction is not warranted.

The correction factor should account for the differences in pollution climates between sites, and also for changes over the 20-year period. Could an empirical correction be derived from chemical transport modelling (eg EMEP4UK), whereby the ratios of modelled HNO₃ to NO₂, HONO, PAN, etc, are used to construct a geographically- and temporally-varying index to drive the correction function? The HNO₃ data reported in Tang et al (2015) for NaCl vs K₂CO₃ coating, with measurements made in contrasted

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situations (rural, urban, remote, see Table 1 in that report), may be used for calibrating such a function.

p8-11, section 2.7 Performance of the DELTA method: strictly speaking, this section describes measurement results from intercomparison experiments or even long term datasets (Bush, Eskdalemuir) does not belong in Methods, and should be moved to the beginning of Section 3- Results

p10, I12: Ca⁺⁺ and Mg⁺⁺ concentrations were near detection limits because they are mostly in the coarse fraction, with particle sizes near or above the DELTA cut-off. How much of the NaCl is similarly not collected by the DELTA system?

Also, in relation to the DELTA v. ADS intercomparison, the loss of NO₃, Na and Cl on the surface of the cyclone is put forward as an explanation for the lower ADS aerosols concentrations (compared with DELTA) (p10, I10), but why in that case is SO₄= 23% larger in the ADS?

p13, I2: the highest HCl concentrations are in the SE and SW of England, but also in the Midlands

p13, I5: '...Further away from the coast and influence of marine aerosol, the smallest concentrations of Cl and Na⁺ are measured in the west of the country (Lough Navar in Northern Ireland...' Lough Navar is very near the coast (10km) and yet NaCl concentrations are very low (similar to concentrations in the Midlands), compared with all other western sites in the network (Fig. 5); what could be the reason?

p13, I5: For Cl⁻ and Na⁺, '...largest concentrations at coastal sites in the south (Barcombe Mills) and west (Yarner Wood)...'; actually the highest concentrations are at Goonhilly at the SW tip of Cornwall.

p13, I9-10, '...There is however no clear spatial pattern for Ca²⁺, with concentrations that are mostly at or below LOD...' For both Ca and Mg, which are mostly in the coarse fraction, it may be argued that the DELTA system does not allow a realistic assessment

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of the total concentration, because a large share of coarse particles are not collected. Please comment.

Further, our own tests with DELTA systems at INRA indicated very substantial losses for Mg and Ca in all the non-filter parts of the sampling train (particularly the 6-mm diameter LDPE elbow connecting the 2nd acid denuder to the first NH₃ denuder, Fig. S1), which are therefore not measured on the filter. We analysed the loss fraction LDPE / (LDPE + den + filter) for all compounds; for NH₄⁺ and NO₃⁻ this was less than 5%; for Cl⁻ and Na⁺ this was 5-10%; for SO₄⁼ and Mg₂⁺ this was 10-15%; while for Ca₂⁺ this was 30-40%. Beyond the question of coarse aerosols that were not sampled at all (did not enter the sampling train), there is the question of those coarse aerosols that 'did not make it' to the filter pack. Did the authors carry out similar tests, and could the results be shown in the supplement? It may be that the new straight design for the DELTA sampling train allowed a reduction of these losses ? Please comment.

p15, l1: This section 3.4 is mostly about sub-annual (seasonal) variations, so could be re-named 'Seasonal variations in acid gases and aerosols', as opposed to long term trends of Sections 3.5-3.6

p15, l9-10: '...In spring, the peak in HNO₃ and NO₃...' Fig.7 does not actually show any spring peak for HNO₃; the late winter (Feb-Mar) concentrations are only marginally higher (but not significantly different according to the error bars) than the rest of the year? The opening sentence of the paragraph should read '...maximum in late winter and early spring...'

p15, l22, '...this contributes to the winter minimum in NH₄NO₃...' : the minimum NO₃- actually occurs in July?

p16, l9-13: how far should seasonal cycles for Mg and especially Ca be discussed, given the low collection efficiency (and thus high uncertainty) of filter data (see my comment above on aerosol size cut-off and losses in sampling train for these large aerosols)?

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p17 and beyond, general comment on sections 3.5-3.6: a linear regression is fitted to all datasets from 1999 through 2015, but looking closely at the 15-yr time series for the 12 sites (eg Fig. 12-13), for HNO₃, NO₃⁻, SO₄⁼, NH₄⁺, NH₃, it appears that concentrations were rather stable (with some interannual variability but no trend) in the period 2000-2007, and then only started declining after 2007. The only exception is SO₂ with a continuous decline all the way. Fitting a linear trend is helpful to quantify a multi-annual rate of decrease (which is what you do), but is not an accurate representation of the time course of concentrations. Can you think of any plausible explanation for a change of course around the year 2007: change or implementation of pollution control policies? Decadal change in weather patterns? It might be useful to show (in the supplement) a summary of weather patterns for all sites of the network, the 15-yr time course of temperature, rainfall, wind speed etc.

p18, l6: '...The long-term time series in annually averaged concentrations of the gas and aerosol components are shown in Figure 12a and Figure 12b...': would it be possible to show, alongside the measured DELTA time series, the modelled NO/NO₂ time series (from a CTM, eg EMEP4UK) for the same sites? In a way this would account for both NO_x emission changes as well as climatic variability over the period.

p18, l12 '...The exceptions are Na⁺ and Cl⁻ that have higher mean concentrations...' : Na⁺ is not shown in Fig.12.

Figures 13, 14: use only one type of regression to simplify the figures (LR and MK give almost identical results)

p20, l24-25 '...the reduction in SO₂ emission and measured concentration is accompanied by a smaller negative trend in particulate SO₄⁼...', and l27, '...The smaller decrease in particulate SO₄⁼ compared with its gaseous precursor, SO₂, is similar to that observed at Eskdalemuir...'. Question: Is the smaller reduction rate in SO₄⁼ (compared with SO₂) a reflection of the fact that increasingly in the UK, total sulphate includes a larger and larger fraction of marine sulphate, such that the decrease in anthropogenic

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SO₄= (resulting from SO₂ abatement) has an increasingly small effect on total sulphate? Is it possible to re-calculate the SO₄= trend separately for coastal and inland (eg Midland/London) sites?

p21, l5-22: The argument about the NH₃/SO₂ ratio impacting the dry deposition velocities of SO₂ and NH₃ was developed in the 1980s and early 1990s, when SO₂ concentrations were still very large in W. Europe. It is no longer sufficient to consider the NH₃/SO₂ ratio alone, since SO₂ no longer massively dominates the acid load in W. European atmospheres. Instead, the ratio NH₃/(2*SO₂ + HNO₃ + HCl) should be computed to analyse long term trends, as shown in Fowler et al. (Atmospheric Environment 43 (2009) 5193–5267, see Fig. 4.5). It is the combined effects of all acids and NH₃ that determines the pH of ecosystem/vegetation surfaces and hence their sink strength for water-soluble pollutants.

p21, l30: '...The increase in ratio of HNO₃:NO₃- is similar to changes in upward trend in gas-aerosol partitioning between NH₃ and NH₄+ over time...': what do you call similar? For HNO₃/NO₃-, the ratio increases by ~20%, while for NH₃/NH₄+, the ratio increases by 100% (according to Fig. 18) ?

p22, l11-12, '...a change in the particulate phase from (NH₄)₂SO₄ to NH₄NO₃. This change is expected to increase residence times of NH₃ and HNO₃ in the atmosphere...' I am not convinced the shift from ammonium sulphate to ammonium nitrate should increase the residence time, since NH₃ and HNO₃ will deposit faster (higher deposition velocities) than either aerosol form?

p22, l12 '...expected to increase residence times of NH₃ and HNO₃ in the atmosphere...' and p22, l15 '...NH₃ and NO_x emitted will deposit more locally with a smaller footprint...': these two statements appear to contradict each other?

p22, l12: perhaps another way to analyse this trend is to calculate the (changing) linear regression slopes of NO₃- vs NH₄+ and SO₄= vs NH₄+, for each year of the 2000-2015 period (as in Fig. 6b), and examine how the two slopes change over time,

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as an indicator of the fraction of the total NH₄+ that neutralizes NO₃- and SO₄= and its trend over time.

p24, l14 '...Higher concentrations of the NH₃ and HNO₃ in the atmosphere will deposit more locally...' But then, NH₃ and HNO₃ concentrations are actually decreasing; they are not higher than before?

Technical Corrections

Units: different units are used. They should either be harmonized, or else each figure should state explicitly what the unit is, especially for the difference between element (N,S) based or molecule (HNO₃, SO₂) based. For example, mean HNO₃ at the Bush site is reported as 0.55 μg m⁻³ in Fig.2 (average of 0.54 and 0.56 for samplers A and B), while the color code on the concentration map (Fig. 5) indicates a concentration in the range 0.15-0.25, from which I infer that Fig.2 is μg HNO₃ m⁻³, while Fig.5 is μg N m⁻³ ?

Similarly, p12, l16, is the Cromwell site HNO₃ concentration 1.3 μg HNO₃ m⁻³, or 1.3 μg HNO₃-N m⁻³? From Figure 5 I expect it is the latter (N, not HNO₃ as written in the text). Further below, are the SO₂ concentrations at Sutton Bonington given as μg SO₂ m⁻³, or in fact μg SO₂-S m⁻³ ? Given that the map in Fig. 5 gives numbers in μg N or μS per m³, it would be good to use the same units. Thus I would recommend to check carefully throughout the text in this paragraph and in the whole paper and make the necessary text changes to eliminate the ambiguity in units.

p4, l26-27, delete '...that is also deployed at some CASTnet sites (Rumsey and Walker, 2016).' (already mentioned same page, l14)

p4, l32, suggest change 'temporal' to 'seasonal'

p5, l9-12: this mostly repeats what was said in the introduction p4, l20-25

p7, l20, please provide the equation for the calculation of the denuder capture efficiency

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p35: Figure 2 contains scatter plots and a statistical summary table for the Bush DELTA intercomparison (parallel sampling). It would be good to adapt the same or similar style of display for the other intercomparisons (scatter plots + stats table). Thus for the comparison with ADS (2.7.2), take Fig. S2 out of the supplement and stack it above the statistics given in Table 2. Similarly for the intercomparisons of DELTA vs EMEP TIA/TIN (add statistical table), as is already also done for DELTA vs Bubble/FP Eskdalemuir (Fig 4).

p11, sections 2.8 and 3.6: throughout the time series trend analysis, both linear regressions and non-parametric MK tests are used, but as far as I can see, there is essentially no difference between the slopes for any of the pollutant time series. To improve readability and reduce unnecessary redundant information, I would suggest to stick to just one of the methods; it would suffice to say in the methods that both regressions were used and no significant differences were found, and thus henceforth only one regression is displayed.

p12, l22, '...A peak MONTHLY concentration of...'

p12, l28, '...expected to be more SPATIALLY homogeneous...'

p15, l19 '...in summer promotes AEROSOL dissociation...'

p17, l12 change to '...are available SINCE 1989...'

p18, l31, '...To QUANTIFY changes...'

p18, l32, the unit for the annual trend is $\mu\text{g HNO}_3\text{-N m}^{-3} \text{ y}^{-1}$

p19, l3: '...The LR % annual trends for each time series...' Delete 'annual', since the % reduction are not expressed per year, but over the whole period? Note that if the concentration reduction were a constant percentage every year, say -10% per year, then the overall time course over 15 years would not look linear, but exponential: if $\text{yr}1=100$, then $\text{yr}2=90$, $\text{yr}3=81$, $\text{yr}4=72.9$, $\text{yr}5=65.6$, ... $\text{yr}15=20.6$

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p19, l6: same as above, delete 'annual'

p21, l17-18 '...The dry deposition... IS known to be enhanced...'

p23, l9, delete 'from coal combustion'

p24, l1, '... modest reductionS in HNO₃...' (plural)

p24, l12, '...smaller THAN emission trends...'

All figures: when the units displayed on axes or legends are given in $\mu\text{g m}^{-3}$, please specify whether this is on an element basis (NH₃-N, HNO₃-N, SO₂-S) or molecule basis (NH₃, HNO₃, SO₂)

Figure 8: "...Average annual cycles in the ratios of gas:aerosol component concentrations ($\mu\text{g m}^{-3}$)..." The unit for the ratio is not $\mu\text{g m}^{-3}$, it must be dimensionless, or mol mol⁻¹?

Figures 13-14: keep only one of the two trend lines (LR or MK); and delete Fig.14 but add the n=30 datapoints to Fig. 13 as a different symbol shape or color

Figure 18: the left-hand side panels show the same data as Figs. 13-14 and should therefore not be repeated here.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-489>, 2018.

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