Anonymous Referee #2
Received: 13th October 2017

RESPONSE TO REVIEWER

1) "The current version of the manuscript is lack of solid evidences and full of speculation and arguments.

Author Response: We have addressed comments raised by both reviewers and revised the manuscript accordingly. Reviewer 1 was satisfied with latest version of the manuscript. We have carefully considered further comments raised by reviewer 2 in the following pages. Please refer to the specific responses.

2) "What the authors selected the statistical analysis tool appears to be quietly at will, at least to this reviewer. The authors failed to demonstrate why the selected statistical analysis tool can allow addressing the scientific questions associated with their specific data sets."

Author Response: To reiterate, the long-term continuous monthly measurement data of atmospheric NH_3 and NH_4^+ from the UK National Ammonia Monitoring Network was used in the manuscript to establish whether, and the extent to which, concentrations of these air pollutants have changed in relation to the estimated decrease in NH_3 emissions over the time period where data is available. With a long data record, trend analysis represents the best approach to evaluate gradual change in air pollutant concentrations resulting from UK-wide emission changes with time. The two basic types of trends that can be statistically analyzed are monotonic and step trends (see e.g. Hirsch et al., 1991). Monotonic trends are generally gradual changes that are either increasing or decreasing with no reversal of direction. Step trends are where there is an abrupt shift at a specific point in time.

Monotonic trend assessment on annual mean data was conducted since:

1) UK emissions data are annual. Annual trends in air pollutant data was thus investigated in relation to annual trends in emissions data,
2) UK-wide changes in NH_3 emissions over time has been gradual with no abrupt changes. Plotting the long-term data show either none or gradual changes that are either increasing or decreasing with no reversal of direction.

Parametric (e.g. linear regression) and non-parametric (e.g. Mann-Kendall) tests are commonly used for monotonic trend assessment in environmental data.

See also our response (excerpt copied below) to your previous comment *"The trend analysis in this study is superficial and does not meet a criteria for publishing in a high-impacted journals such as ACP."*
"The objective of the statistical trend analysis presented in our research paper was to identify trends in the long-term datasets (univariate monotonic, see e.g. Hirsch et al., 1991), estimate the rate of change and to address the question of whether trends in NH_3 and NH_4^+ concentrations (if any) are consistent with the changes in estimated UK annual NH_3 emissions (data downloaded from: http://naei.beis.gov.uk/data/data-selector-results?q=101505)?" The dataset is sufficiently long-term (i.e. gaseous NH_3: 17 years and particulate NH_4^+: 16 years) and collected by consistent methods, to allow for effective statistical trend analyses to be carried out.

To address the concerns of reviewer 2 regarding the selection of statistical analysis tools, additional text (highlighted) has been added in <section 2.2.5. Trend Analyses> below:

Statistical trend analysis was conducted on the long-term dataset from the UK NAMN to identify trends in the long-term datasets (univariate monotonic, see e.g. Hirsch et al., 1991), estimate the rate of change and to address the question of whether trends in NH_3 and NH_4^+ concentrations (if any) are consistent with the changes in estimated UK annual NH_3 emissions (data downloaded from: http://naei.beis.gov.uk/data/data-selector-results?q=101505)? The dataset is sufficiently long-term (i.e. gaseous NH_3: 17 years and particulate NH_4^+: 16 years) and collected by consistent methods, to allow for effective statistical trend analyses to be carried out.

Trend analyses were carried out using (i) linear regression (LR), (ii) Mann-Kendall (MK) test (Gilbert, 1987) on annually averaged and monthly mean data, and (iii) Seasonal Mann-Kendall (SMK) test (Hirsch et al., 1982) on monthly data only. Mann-Kendall tests were performed using the 'Kendall' package (McLeod, 2015) in the R software. Computation of the Sen's slope and confidence interval (for non-seasonal Sen's slope only) of the linear trend were performed using the R 'Trend' package (Pohlert, 2016).

Since concentrations of NH_3 show strong seasonality, the SMK test was applied to identify the months that are driving the long-term trends in data. The SMK test (Hirsch et al., 1982) takes into account a 12 month seasonality in the time series data by computing the MK test on each of monthly 'seasons' separately, and then combining the results. So for monthly 'seasons', January data are compared only with January, February only with February, etc. No comparisons are made across season boundaries. The Sen's slope is the fitted median slope of a linear regression joining all pairs of observations. For the SMK, an estimate of the seasonal Sen's trend slope over time is computed as the median of all slopes between data pairs within the same season (i.e. January compared only with January etc.). Therefore no cross-season slopes contribute to the overall estimate of the SMK trend slope.

Parametric LR analysis are simple and straightforward to use and interpret monotonic trend assessment in environmental data (e.g. Kindzierski et al., 2009; Meals et al., 2011), but they require assumptions about normality of data and homogeneity of variance of data. The MK approach on the other hand are widely used in environmental time series assessments, e.g. long-term trends in precipitation (Serrano et al. 1999) and long-term trends in European air quality (Colette et al., 2016; Torseth et al., 2012). The main advantages, as discussed in the literature of the MK approach over linear regression for trend assessments are that (i) it does not require normally distributed data, (ii) it is not affected by outliers, and (iii) it removes the effect of temporal auto-correlation in the data (e.g., Gurreiro et al., 2014, Li et al., 2016, Torseth et al., 2012., Yao et al., 2016). Trend assessment using the LR approach have however been used in UK air quality monitoring network reports (e.g. Conolly et al., 2016); therefore both LR and MK approaches were used in this paper primarily as a quality assurance check.

References:

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Hirsch, R.M., Slack, J.R. and Smith, R.A.: Techniques of trend analysis for monthly water quality data. Water resources research, 18(1), 107-121, 1982.

Li, C., Martin, R. V., Boys, B. L., van Donkelaar, A., and Ruzzante, S.: Evaluation and application of multi-decadal visibility data for trend analysis of atmospheric haze, Atmos. Chem. Phys., 16, 2435-2457, https://doi.org/10.5194/acp-16-2435-2016, 2016.

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Serrano, A., Mateos, V.L.and Garcia, J.A.: Trend analysis of monthly precipitation over the iberian peninsula for the period 1921–1995, Physics and Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere, 24(1), 85-90, 10.1016/S1464-1909(98)00016-1, 1999.

Kindzierski W,B., Chelme-Ayala, P & Gamal El-Din, M. Ambient Air Quality Data Summary and Trend analysis, Part I Main Report for Wood Buffalo Environmental Association, Fort McMurray, Alberta. December 2009. Available online at *https://www.ceaa-acee.gc.ca/050/documents_staticpost/59540/82534/Ambient_Air_Quality_Studies.pdf*. 2009.

3) *"The modeling results were not fully used while the authors presented a bunch of non-evidence supported arguments."*

Author Response: This is a non-specific comment to which we are unable to provide response. This paper is an analysis of a substantial spatially and temporally-resolved dataset of measurements. We have provided responses below to the individual instances where the reviewer feels that statements in our paper are insufficiently evidenced.

4) *"The analysis of formation of particulate NH4+ is also not convincing."*

Author Response: additional text (highlighted) has been added in <section 3.5.6: Changing chemical climate and effects on long-term trends in NH_3 and NH_4^+ > - see below:

The interpretation of the NH_3 and NH_4^+ measurement data can further be aided by comparison with particulate nitrate (NO_3^-) and sulphate (SO_4^{2-}) data from the UK AGANet that are made concurrently with the NAMN NH_3 and NH_4^+ measurements at 30 sites (see Sect. 2.2). There is close agreement between the aerosol components, with a near 1:1 relationship between NH_4^+ and the sum of NO_3^- and SO_4^{2-}, lending support that particulate NH_4^+ in the UK is mainly derived from NH_3 and acidic gases such as SO_2 and NO_x to form $(NH_4)_2SO_4$ and NH_4NO_3, respectively (Conolly et al., 2016).

5) *"Page 1, Line 37, "associated with a slower formation of particulate NH4+ in the atmosphere from gas-phase NH3." Formation rate of particulate NH4+ in the atmosphere highly varies, depending on formation pathways. Gas-particle condensation is only one, but not necessary to be the major one. Did the authors verify the importance of formation of particulate NH4+ via the route?"*

Author Response: This was a typo error identified by reviewer 1 also. "slower" should read "lower" and was already corrected for the revised manuscript. We have also corrected the typo error in the last line of the abstract in the latest revision.

The authors also concur with the reviewer that there are a number of formation pathways, of which gas-particle condensation is only one. Other routes for the presence of NH_4^+ in particulate matter are as a primary ion in sea salt and degradation of organics and amines, and primary suspension of dust and soil particles. However, given UK aerosol is frequently dominated by ammonium nitrate (e.g. see Malley et al., 2016 and Twigg et al., 2016) and ammonia gas is present in excess, then gas-particle transfer of ammonia to ammonium is the dominant pathway for forming ammonium in PM.

References:

Malley, C. S., Heal, M. R., Braban, C,F ., Kentisbeer, J., Leeson, S. R., Malcolm, H., Lingard, J. J. N., Ritchie, S., Maggs, R., Beccaceci, S., Quincey, P., Brown, R. J. C., and Twigg, M. M.: The contributions to long-term health-relevant particulate matter at the UK EMEP supersites between 2010 and 2013: Quantifying the mitigation challenge. Environment International, 95, 98-111, doi: 10.1016/j.envint.2016.08.005, 2016.

Twigg, M. M., Ilyinskaya, E., Beccaceci, S., Green, D. C., Jones, M. R., Langford, B., Leeson, S. R., Lingard, J. J. N., Pereira, G. M., Carter, H., Poskitt, J., Richter, A., Ritchie, S., Simmons, I., Smith, R. I., Tang, Y. S., Van Dijk, N., Vincent, K., Nemitz, E., Vieno, M., and Braban, C. F.: Impacts of the 2014–2015 Holuhraun eruption on the UK atmosphere, Atmospheric Chemistry and Physics, 16, 11415-11431, doi: 10.5194/acp-16-11415-2016, 2016.

6) *"Page 2, lines 32-34, "While it is clear that reductions in NH3 emissions will lead to reductions in overall NH4+ concentrations, the relative changes in gaseous NH3 and NH4+ particles remains poorly quantified" It is only true for the NH3-limited formation of ammonium salts. The reference is thereby needed to demonstrate when and where."*

Author Response: additional text and references (highlighted) has been added – see below.

Since UK particulate NH_4^+ is generally dominated by NH_4NO_3 and $(NH_4)_2SO_4$ (see e,g. Twigg et al., 2016 and Malley et al., 2016) and NH_3 gas is present in excess, then gas-particle transfer of NH3 to NH_4^+ is the dominant pathway for forming NH_4^+ in PM. While it is clear that reductions in NH_3 emissions will lead to reductions in overall NH_4^+ concentrations (Vieno et al., 2016), the relative changes in gaseous NH_3 and particulate NH_4^+ remains poorly quantified.

References:

Vieno, M., Heal, M. R., Williams, M. L., Carnell, E. J., Nemitz, E., Stedman, J. R., and Reis, S.: The sensitivities of emissions reductions for the mitigation of UK PM2:5. Atmospheric Chemistry and Physics, 16, 265–276, doi:10.5194/acp-16-265-2016, 2016.

7) *"Page 8, lines 31-32 "The observed variability is consistent with the large regional variability in NH3 emissions and sources (Figure 4c & d)." At least to this reviewer, it is hard to find this."*

Author Response: The authors have already responded to a similar comment raised by Reviewer 1 previously. To reiterate, the measured annual concentrations of NH_3 and NH_4^+ were shown as coloured dots on the map to illustrate the spatial variability across the UK. Interpolated concentration maps have not been used since the interpolation of the discrete measurement points (e.g. using bilinear interpolation) will give the reader a false sense of the spatial variability of air concentrations from the limited number of measurement locations.

The authors feel that these figures are relatively easily to compare by eye, but have added the sentence (highlighted) in the Figure 4 caption below to help draw the reader's eye:

Figure 4: Measured annual mean concentrations from the UK National Ammonia Monitoring Network (NAMN) for 2005 for (a) NH_3 and (b) particulate NH_4^+, and maps at 5 km by 5 km grid resolution for 2005 of (c) the estimated annual NH_3 emissions (Dragosits et al. 2005) and (d) the dominant NH_3 emission source category (based on Hellsten et al., 2008), indicating the relationships between measured air concentrations and spatial variability in NH_3 sources emissions. The measurements show a broad pattern of small air concentrations across NW Scotland. Conversely, the largest concentrations occur in areas with intensive cattle, pig and poultry farming with high NH_3 emissions e.g. East Anglia in SE England.

8) *"Page 9, lines 7-9 "The limited variation across the UK for the annual average NH4+ concentrations can be attributed to the atmospheric formation process (providing a diffuse source) and its longer atmospheric lifetime" This is very speculative, although the argument is one of potential causes."*

Author Response: The authors have replaced the above sentence with **"**Particulate NH_4^+ is a slowly formed secondary product with a longer residence time in the atmosphere and is thus expected to show less spatial variation than NH_3. This is confirmed in the measurement data."

9) *"Page 10, line 10, why use "for an example year of 2012s" but not 2005 as used early?"*

Author Response: The 2012 comparison (modelled vs monitored) updates an earlier inter-comparison assessment carried out for the year 2002 by Dore et al. (2007).

In section 3.1, the 2005 dominant sources map was used to classify NAMN sites according to one of seven dominant emission source categories. 2005 annual mean concentrations from the NAMN were therefore shown alongside annual NH_3 emissions and the dominant NH_3 emission source category for 2005 in Figure 4.

10) *“Page 10, lines 13-15 “The scatter may be explained by the large local spatial variability of NH3, related primarily to rapid decreases of NH3 concentrations with distance from a source (see e.g. Pitcairn et al., 1998; Dragosits et al., 2002),” How come the references in ten year ago can support the interpretation of the difference in 2012? Is it still true and any evidence to say this?*

Author Response: The two early references were quoted for the following reasons:

Pitcairn et al., (1998) is an early reference that measured the gradient in NH_3 concentrations downwind of an emission source. Concentrations close to the livestock buildings (within 300 m) were found to be very large, with concentrations reaching background concentrations at distances of about 1 – 2 km from source.

Dragosits et al., (2002) presented a detailed assessment of the sub-grid spatial variability in NH_3 concentrations and deposition within a 5 km x 5 km case study site.

Large spatial variability of NH_3 at local, regional and regional scales is widely described in the literature, e.g. Li et al., 2017.

Li, Y., Thompson, T, M., Van Damme, M., Chen, X., Benedict, K. B., Shao, Y., Day, D., Boris, A., Sullivan, A. P., Ham, J., Whitburn, S., Clarisse, L., Coheur, P-F., and Collett Jr, J.L.: Temporal and spatial variability of ammonia in urban and agricultural regions of northern Colorado, United States. Atmospheric Chemistry and Physics, 17, 6197–6213, doi:10.5194/acp-17-6197-2017, 2017.

11) *“Page 10, lines 10-29, the agreement is of course more important than the correlation and should be discussed.“*

Author Response: We think the reviewer is referring to the two paragraphs below (Page 10, lines 10-29): “Comparison of measurements with modelled NH_3 concentrations from the FRAME model for an example year of 2012 showed significant scatter when considering the full network of sites ($n = 85$, $R^2 = 0.62$) (Figure 5a). In this graph, each point is colour-coded according to the estimated dominant NH_3 emission source category for the 5 km by 5 km grid square. This updates a similar comparison from Sutton et al. (2001b) for the year 2000. The scatter may be explained by the large local spatial variability of NH_3, related primarily to rapid decreases of NH_3 concentrations with distance from a source (see e.g. Pitcairn et al., 1998; Dragosits et al., 2002), with the result that a single site measurement only gives an approximate indication of concentrations across the model grid square it is located in. At many of the sites where the model overestimates concentrations, the measurements are in fact carried out in nature reserves, or in clearings inside forests. The monitoring sites in these sink areas are typically well away from local sources. Conversely, some of the outliers where measurements are larger than the model predictions show indications of being affected by nearby emission sources, as was established by investigations during site visits.

Figure 6 considers measured NH_3 concentrations at a subset of sites (44 out of the full 85 sites) that are located away from nearby local sources, in forest or semi-natural areas, following the site classification and assessment by Hallsworth et al. (2010). For this restricted set of sites, $R^2 = 0.76$ for 2012 which is higher than the correlation for the overall UK network. The improvement in correlation between measured and modelled NH_3 concentrations for this subset of sites can be explained by the monitoring locations typically being further away from sources, so that uncertainties in local emissions estimates are to some extent averaged out. This observation is also consistent with the findings of Vieno et al. (2009).”

The authors have revised the two paragraphs to include more explanatory details and discussion – see below:

"The comparison of NAMN NH_3 and NH_4^+ measurements with modelled NH_3 concentrations from the FRAME model in this paper is made for an example year of 2012. This updates an earlier inter-comparison assessment carried out by Dore et al. (2007) for the year 2002, In the comparison of the FRAME model estimates (based on 2012 UK AENEID NH_3 emission data) with the NAMN measurement results for 2012 (Figure 5), the network annual mean concentrations for each site is compared against the model estimate for the 5-km grid square in which it occurs. Each point is also colour-coded according to the estimated dominant NH_3 emission source category for the 5 km by 5 km grid square, following the methodology described in a similar comparison from Sutton et al. (2001b) for the year 2000.

For NH_3, both the model estimates and the measurement agree that background and sheep sites are characterised by small NH_3 concentrations (< 1 µg NH_3 m^{-3} annual mean), while agricultural areas, particularly areas with intensive pig and poultry areas, are associated with large NH_3 concentrations (up to 8 µg NH_3 m^{-3} annual mean). Overall, the comparison suggests a fairly good fit with regard to both the magnitude and spatial variability of NH_3 concentrations at a national scale ($n = 85$), with an R^2 value of 0.6 (**Error! Reference source not found.**5a). UK NH_3 emissions with a 5×5 km grid-square resolution is used as input in the FRAME model and the accuracy of the emissions data is critical to the model performance. The broad agreement between measurement and FRAME estimates broadly support the predictions of the FRAME model, lending support to the AENEID model outputs. There are however significant scatter in the comparison, with some systematic differences in the comparison of FRAME and the measurements, depending on the air concentration and dominant source.

NH_3 is known to exhibit large sub-grid variability (e.g. Dragosits et al. 2002), influenced by proximity to emission source strength and type. In the vicinity of emission sources, NH_3 concentrations generally decay exponentially with distance away from source due to dispersion and dilution (e.g. Pitcairn et al., 1998). As it is a highly reactive gas, a significant fraction of the NH_3 emitted is also rapidly deposited within 1 km radius of the source, so that concentrations reach background concentrations at distances of about 1 – 2 km from source (Fowler et al., 1998). This effect is particularly important in areas with high local variability in NH_3 emissions, such as intensive agricultural areas. The observed scatter in the comparison may therefore be due to the spatial location of the sampling site relative to the distribution of sources. For example, at many of the sites where the model overestimates concentrations, the measurements are in fact made in nature reserves, or in clearings inside forests. The monitoring sites in these sink areas are typically well away from local sources and which would on average be more distant from sources than assumed in the FRAME 5 km average estimates, thereby underestimating concentrations, Conversely, some of the outliers where measurements are larger than the model predictions show indications of being affected by nearby emission sources, as was established by investigations during site visits. This effect is particularly important in areas with high local variability in ammonia emissions, such as intensive agricultural areas and illustrates the importance of having a large number of sites for comparison.

Figure 6 considers measured NH_3 concentrations at a subset of sites (44 out of the full 85 sites) that are located away from nearby local sources, in forest or semi-natural areas, following the site classification and assessment by Hallsworth et al. (2010). For this restricted set of sites, $R^2 = 0.76$ for 2012 which is higher than the correlation for the overall UK network. The improvement in correlation between measured and modelled NH_3 concentrations for this subset of sites can be explained by the monitoring locations typically being further away from sources, so that uncertainties in local emissions estimates are to some extent averaged out. This observation is also consistent with the findings of Vieno et al. (2009)."

Dore, A. J., Vieno, M., Tang, Y. S., Dragosits, U., Dosio, A., Weston, K. J., & Sutton, M. A. (2007). Modelling the atmospheric transport and deposition of sulphur and nitrogen over the United Kingdom and

assessment of the influence of SO 2 emissions from international shipping. *Atmospheric Environment*, *41*(11), 2355-2367.

Dore, A. J., Carslaw, D. C., Braban, C., Cain, M., Chemel, C., Conolly, C. & Lawrence, S. (2015). Evaluation of the performance of different atmospheric chemical transport models and inter-comparison of nitrogen and sulphur deposition estimates for the UK. *Atmospheric Environment*, *119*, 131-143.

Sutton, M. A., Tang, Y. S., Dragosits, U., Fournier, N., Dore, A. J., Smith, R. I., Weston, K. J., and Fowler, D.: A spatial analysis of atmospheric ammonia and ammonium in the U.K, ScientificWorldJournal, 1 Suppl 2, 275-286, 10.1100/tsw.2001.313, 2001b.

12) *"Page 10, lines 39-41 "This suggests either too low a formation rate for NH4+ in the model at cleaner sites, or too high a removal rate for NH4+, or a combination of both. The presence of higher measured NH4+ concentrations in remote areas than shown by the model may also indicate that NH4+ has a longer residence time than treated in the model." This is very speculative. Under prediction of particulate NH4+ by air quality models is very common in the remote clean atmosphere due to those simple assumptions. "*

Author Response: We agree that models may underestimate particulate NH_4^+ due to simplistic assumptions. The models uses simple chemistry schemes and deposition velocities from the literature. Our text already includes the implication that the model treatment may have shortcomings.

13) *"Page 11, lines 19-24, all arguments are absolutely correct, but then what? In other words, how these directly explain the seasonal variation?"*

Author Response: The authors feel that the seasonal variations in NH_3 and NH_4^+ have been fully explained and discussed fully in <Section 3.3. Seasonal variability in measured UK NH_3 and NH_4^+ concentrations>, and that there is nothing more usefully to add to this section.

14) *"Page 11, lines 28-29 "A smaller peak in NH3 can also be seen annually in April, which indicates potential longer range influences of manure spreading in spring, even at this remote location (Figure 8b)." The argument is also very speculative. Solid evidence is needed."*

Author Response: The application of manure and fertilizers in the UK occurs predominantly during spring, but to a lesser extent in autumn farmlands and agriculture. Peak NH_3 concentrations are often measured in April at sites within agricultural landscapes. It is thus perfectly plausible that manure spreading activities within or outside the 5 km x 5 km grid square containing the background site shows up as a small April peak, depending on which way the wind is blowing.

15) *"Page 12, lines 5-6, "Interestingly, the dip in concentrations in June matches a period when crops will be actively growing with possible uptake and removal of NH3 from the atmosphere." Evidence but not just arguments!"*

Author Response: Additional text and references (highlighted) added – see below:

"Interestingly, the dip in concentrations in June matches a period when crops will be actively growing with possible uptake and removal of NH_3 from the atmosphere. Vegetation can be a source or a sink of atmospheric NH_3 and uptake of NH_3 can occur when the relative concentration of NH_3 in the atmosphere is higher than inside the plant stoma (e.g. Sutton et al.,1995, Massad et al., 2010; Flechard et al., 2013).

Flechard, C. R., Massad, R. S., Loubet, B., Personne, E., Simpson, D., Bash, J. O., Cooter, E. J., Nemitz, E., and Sutton, M. A.: Advances in understanding, models and parameterizations of biosphere-atmosphere ammonia exchange, Biogeosciences, 10, 5183-5225, 10.5194/bg-10-5183-2013, 2013.

Massad, R-S., Nemitz, E. and Sutton, M.A.: Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere, Atmospheric Chemistry and Physics, 10, 10359–10386, doi:10.5194/acp-10-10359-2010, 2010

Sutton, M. A., Schjoerring, J. K., and Wyers, G. P.: Plant-atmosphere exchange of ammonia, Philos. T. Roy. Soc. S-A, 351,261–278, 1995.

16) *"Page 12, lines 10-13 "Although the formation of particulate NH4+ primarily depends on the occurrence of NH3 in the atmosphere, synoptic meteorology and long range transboundary transport from continental Europe are important drivers influencing the seasonal variations of NH4+ across the UK, due to its' longer lifetime." The part is totally confused and which studies support these?"*

Author Response: the references which supports the statement quoted is added at the end of the statement – see below:

"Although the formation of particulate NH_4^+ primarily depends on the occurrence of NH_3 in the atmosphere, synoptic meteorology and long range transboundary transport from continental Europe are important drivers influencing the seasonal variations of NH_4^+ across the UK, due to its longer lifetime (Vieno et al., 2014, 2016)."

Vieno, M., Heal, M. R., Hallsworth, S., Famulari, D., Doherty, R. M., Dore, A. J., Tang, Y. S., Braban, C. F., Leaver, D., Sutton, M. A., and Reis, S.: The role of long-range transport and domestic emissions in determining atmospheric secondary inorganic particle concentrations across the UK, Atmospheric Chemistry and Physics, 14, 8435-8447, 10.5194/acp-14-8435-2014, 2014.

Vieno, M., Heal, M. R.,Williams, M.L., Carnell, E.J., Nemitz, E., Stedman, J.R., and Reis, S.: The sensitivities of emissions reductions for the mitigation of UK $PM_{2.5}$, Atmospheric Chemistry and Physics, 16, 265-276, doi: 10.5194/acp-16-265-2016, 2016.

17) *“Page 12, lines 10-35, it is odd. Why not use modeling results,.e.g., processing analysis, to interpret? It is very straight forward by comparing with current arguments.”*

Author Response: The authors think the reviewer is referring to the text below. In which case the authors are not entirely clear what the reviewer is asking. We reiterate that this paper is an analysis of what can be learnt from trends and patterns in measurement data. As has already been noted above, it is accepted that modelling of these processes can have limitations.

“For particulate NH_4^+, as expected for a secondary pollutant, concentrations are more decoupled from the dominant NH_3 source sectors in the vicinity of a site. Although the formation of particulate NH_4^+ primarily depends on the occurrence of NH_3 in the atmosphere, synoptic meteorology and long range transboundary transport from continental Europe are important drivers influencing the seasonal variations of NH_4^+ across the UK, due to its’ longer lifetime. The seasonal trends in particulate NH_4^+ are seen to be broadly similar for the four different emission source sectors (Figure 7b), with the magnitude of the NH_4^+ concentrations reflecting NH_3 concentrations at a regional level. In the atmosphere, particulate NH_4^+ are primarily in the form of $(NH_4)_2SO_4$ and NH_4NO_3, formed when the acid gases HNO_3 and H_2SO_4.in the atmosphere are neutralised by NH_3 (Putaud et al., 2010). NH_3 preferentially neutralizes H_2SO_4 due to its low saturation vapour pressure (forming NH_4HSO_4 then $(NH_4)_2SO_4$), while NH_4NO_3 is formed when abundant NH_3 is available, In contrast to $(NH_4)_2SO_4$, NH_4NO_3 is a semi-volatile component (Stelson & Seinfeid, 1982). Long-term data from the UK Acid Gas and Aerosol Network (AGANet, Conolly et al., 2016) shows a change in the particulate phase of NH_4^+ from $(NH_4)_2SO_4$ to NH_4NO_3, with particulate nitrate concentrations exceeding that of particulate sulphate approximately three-fold (on a molar basis) (Fig. 18a). This suggests that the thermodynamic equilibrium between the gas phase NH_3 and HNO_3 and the aerosol phase NH_4NO_3 will have a much greater effect on the seasonal concentrations of NH_4^+ than $(NH_4)_2SO_4$. The formation and dissociation of NH_4NO_3 depend strongly on ambient temperature and humidity (Stelson and Seinfeld, 1982). Warm, dry weather in summer promotes dissociation, decreasing particulate phase NH_4NO_3 relative to gas phase NH_3 and HNO_3. During the winter months, low temperature and high humidity favour the formation of NH_4NO_3 from the gas phase NH_3 and HNO_3. By contrast, the spring peak in NH_4^+ concentrations may be attributed to photochemical processes (elevated ozone) leading to enhanced formation of HNO_3 during this period (Pope et al., 2016) and also to import of particulate NO_3^- through long-range transboundary transport, e.g. from continental Europe, as discussed in Vieno et al. (2014). Nevertheless, it is notable that the winter minima for NH_4^+ aerosol concentrations at sheep and background sites are more pronounced than that for pig, poultry and cattle dominated sites. This may be a result of a combination of smaller NH_3 emissions in winter in these areas (as indicated by Figure 7a) and differences in long-range transport to the more remote areas in winter conditions.”

18) *“The analysis in Section 3.5.1 does not sound scientific when analytic errors were considered. The same concern is applicable for Section 3.5.4.”*

Author Response: It is not clear what the reviewer means by “,,,*does not sound scientific when analytic errors were considered* “

<*Section 3.5.1.* Mann-Kendall non-parametric time series analysis> The MK approach was applied to the long-term dataset using the methodology described. It is a commonly used approach, as acknowledged by the reviewer.

<Section 3.5.4. Influence of climate> An exponential model (using R) was used to fit the data (NH3 vs temperature/rainfall) and to determine the significance of the regression.

19) *"Section 3.5.6, a bunch of arguments are redundant.Technically, the study is informative and valuable. However, this reviewer believes that a few cavities are still there. It should be improved to better service research community."*

Author Response: <Section 3.5.6. Changing chemical climate and effects on long-term trends in NH_3 and NH_4^+> We feel that sufficient evidence have been presented to support the findings in this section. As the reviewer has not specified which arguments they find redundant, the authors have to disagree with the reviewer and look to the editor to adjudicate.

Previous communication regarding reviewer 2 comments:

Author query: ” the reviewer does not discuss what was wrong with our response to the first review in any quantitative way, while re-iterating some of the same unsubstantiated issues from the first review, e.g. "authors failed to demonstrate why the selected statistical analysis too can address..." where we fully referenced the methods we used.”

Reviewer response: “The reviewer’s second round comments are based on the revised version, which no track changes or highlights can be found for revision.

Author response: The track changes version was uploaded and is available in the manuscript management page.

Reviewer response: A bunch of statistical analysis tools are available for trend analysis, but the reviewer cannot find any scientific reason in the revised version for the authors’ selection. The reviewer fully agrees that the authors employed popular ones which have been widely used in literature. If the authors really want to emphasize so-called “standard” (the reviewer would like to believe the “standard” should be updated with improving knowledge), their description and citation technically sound. However, it does not mean the selected tools are scientifically applicable for their specific datasets, at least to this reviewer and his experience on applying these tools.

Author response: Given that reviewer 2 acknowledges that the methods used are popular in the peer review literature i.e. are a proven method for trend analysis scientifically, it is not inappropriate to use them. There may be many other statistical methods available, we are not sure which one is the Reviewer’s preferred method, however all data in this paper are available for others to analysis with whichever statistical analysis they wish. We do not think we need to re-analyse for this paper as we have used valid techniques.

Reviewer response: The justification for choosing the tools by the authors, particularly for studying the long-term trend in atmospheric ammonia, is very important and helpful for potential readers. I hope that the authors can agree and lead a way on this issue.

Author response: We added in the revised manuscript already the justification of the two methods both scientifically plus noting that the UK and European assessments use these tools so we are consistent.

Author query 2: the reviewer writes " A few comments are listed, but not just limited these." I would rather the reviewer detail all their queries so that they can be addressed rather than iterate through the review process again.

Reviewer response: Those minor issues haven’t been listed. The reviewer fully believes that the authors can find technically. Again, the reviewer has no intention to delay the study for publishing if these cavities listed can be properly fixed.

Author query 3: The reviewer is very vague in some of the comments, e.g. "Section 3.5.6, a bunch of arguments are redundant": I am not sure we can respond to such a non-specific comment.

Reviewer response: The reviewer believes that the authors have provided sufficient evidences at the last few paragraphs in Section 3.5.6. A bunch of redundant arguments could set a bad example for young students. I hope that the authors can agree on this.

Author response: As the reviewer themselves states, we have provided sufficient evidence, rather than having redundant arguments, and we fully believe the paper is an example of discussing the facts and issues and scientific questions. As the reviewer has not specified which arguments they find redundant, the authors just have to disagree with the reviewer and look to the editor to adjudicate.

To note, we responded in detail to Reviewer 1 and they were happy with the revision we provided.

Reviewer response: all scientists have to be forced by the so-called "standard", the reviewer concerns where new science comes from.

Author response: Reviewer 1 provided a detailed and thorough review. New science can only come through clear communication, which Reviewer 2 is not providing a good example of. Before we respond to Reviewer 2, which we are happy to do scientifically, could you check to see if the standard of the review are up to ACPD standards and advise.

Reviewer response: Again, the reviewer fully believes the study can be improved better.

Revised manuscript with all track changes (including revision 1 after first review):

Drivers for spatial, temporal and long-term trends in atmospheric ammonia and ammonium in the UK

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Abstract. A unique long-term dataset from the UK National Ammonia Monitoring Network (NAMN) is used here to assess spatial, seasonal and long-term variability in atmospheric ammonia (NH_3: 1998-2014) and particulate ammonium (NH_4^+: 1999-2014) across the UK. Extensive spatial heterogeneity in NH_3 concentrations is observed, with lowest annual mean concentrations at remote sites (< 0.2 µg m^{-3}) and highest in the areas with intensive agriculture (up to 22 µg m^{-3}), while NH_4^+ concentrations show less spatial variability (e.g. range of 0.14 to 1.8 µg m^{-3} annual mean in 2005). Temporally, NH_3 concentrations are influenced by environmental conditions and local emission sources. In particular, peak NH_3 concentrations are observed in summer at background sites (defined by 5 km grid average NH_3 emissions <1 kg N ha^{-1} y^{-1}) and in areas dominated by sheep farming, driven by increased volatilization of NH_3 in warmer summer temperatures. In areas where cattle, pig and poultry farming is dominant, the

largest NH_3 concentrations are in spring and autumn, matching periods of manure application to fields. By contrast, peak concentrations of NH_4^+ aerosol occur in spring, associated with long-range transboundary sources. An estimated decrease in NH_3 emissions by 16 % between 1998 and 2014 was reported by the UK National Atmospheric Emissions Inventory. Annually averaged NH_3 data from NAMN sites operational over the same period ($n = 59$) show an indicative downward trend, although the reduction in NH_3 concentrations is smaller and non-significant (–6.3 % (Mann-Kendall, MK); –3.1 % (linear regression, LR)). In areas dominated by pig and poultry farming, a significant reduction in NH_3 concentrations between 1998 and 2014 (–22 % (MK); –21 % (LR): annually averaged NH_3) is consistent with, but not as large as the decrease in estimated NH_3 emissions from this sector over the same period (–39 %). By contrast, in cattle-dominated areas there is a slight upward trend (non-significant) in NH_3 concentrations (+12%, (MK); +3.6% (LR): annually averaged NH_3), despite the estimated decline in NH_3 emissions from this sector since 1998 (–11%). At background and sheep dominated sites, NH_3 concentrations increased over the monitoring period. These increases (non-significant) at background (+17 % (MK); +13 % (LR): annually averaged data) and sheep dominated sites (+15 % (MK); +19 % (LR): annually averaged data) would be consistent with the concomitant reduction in SO_2 emissions over the same period, leading to a longer atmospheric lifetime of NH_3, thereby increasing NH_3 concentrations in remote areas. The observations for NH_3 concentrations not decreasing as fast as estimated emission trends are consistent with a larger downward trend in annual particulate NH_4^+ concentrations (1999-2014: –47 % (MK); –49 % (LR), $p < 0.01$, $n = 23$), associated with a slower formation of particulate NH_4^+ in the atmosphere from gas-phase NH_3.

1 Introduction

Atmospheric ammonia (NH_3) gas is assuming increasing importance in the global pollution climate, with effects on local to international (transboundary) scales (Fowler et al., 2016). While substantial reductions in SO_2 emissions and limited reductions in NO_x emissions have been achieved in Europe and North America following legislation designed to improve air quality, NH_3 emissions, primarily from the agricultural sectors (94 % of total NH_3 emissions in Europe in 2014) have seen much smaller reductions (EEA, 2016). In the period 2000-2014, NH_3 emissions are estimated to have decreased in the EU-28 (28 member states of the European Union) by only 8 % from 4.3 to 3.9 million tonnes, with the UK contributing 7.2 % in 2014 (EEA, 2016). SO_2 emission are estimated to have declined by 69 % and NO_x by 39 % across the EU-28 over the same period.

NH_3 is known to contribute significantly to total nitrogen (N) deposition to the environment, and causes harmful effects through eutrophication and acidification of land and freshwaters. This can lead to a reduction in both soil and water quality, loss of biodiversity and ecosystem change (e.g. Pitcairn et al., 1998; Sheppard et al., 2011). In the atmosphere, NH_3 is the major base for neutralization of atmospheric acid gases, such as SO_2 and NO_x emitted from combustion processes (vehicular and industrial) and from natural sources, to form ammonium-containing particulate matter (PM): primarily ammonium sulphate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3). This secondary PM is mainly in the 'fine' mode with diameters of less than 2.5 µm (i.e. $PM_{2.5}$ fraction) (Vieno et al., 2014). The effects of PM on atmospheric visibility, radiative scattering, cloud formation (and resultant climate effects) and on human health (bronchitis, asthma, coughing) are well documented (e.g. Kim et al., 2015; Brunekreef et al., 2015). Inputs of NH_3 and NH_4^+ (collectively termed NH_x) are the dominant drivers of ecological effects of deposited N, compared with wet deposited NH_4^+ in rain (UNECE, 2016) and the importance of NH_x can be expected to increase further, relative to oxidised N, as NO_x emissions have been decreasing faster than NH_3 emissions (Reis et al., 2012; EEA, 2016; EU, 2016).

In gaseous form, NH_3 has a short atmospheric lifetime of about 24 hours (Wichink Kruit et al., 2012). It is primarily emitted at ground level in the rural environment, and is associated with large dry deposition velocities to vegetation (Sutton and Fowler, 2002). High NH_3 concentrations can lead to acute problems at a local scale to, for example, nature reserves located in intensive agricultural landscapes (Sutton et al., 1998; Cape et al., 2009a; Hallsworth et al., 2010; Vogt et al., 2013). The NH_3 remaining in the atmosphere generally partitions to PM where the NH_4^+ can have a lifetime of several days (Vieno et al., 2014). Although NH_4^+ dry deposits at the surface, the primary removal mechanism for NH_4^+ is thought to be through scavenging of PM by cloud and rain, leading to wet deposition of NH_4^+ (Smith et al., 2000). Characterising the relationship between NH_3 emissions and the formation of PM is, however, not straight forward; an increase in NH_3 emissions does not automatically translate to a proportionate increase in NH_4^+ (Bleeker et al., 2009). The relationship depends on climate and meteorology as well as the concentration of other precursors to PM formation such as SO_2 and NO_x (Fowler et al., 2009). Since UK particulate NH4+ is generally dominated by NH_4NO_3 and $(NH_4)_2SO_4$ (see e,g. Twigg et al., 2016 and

Malley et al., 2016) and NH_3 gas is present in excess, then gas-particle transfer of NH_3 to NH_4^+ is the dominant pathway for forming NH4+ in PM. While it is clear that reductions in NH_3 emissions will lead to reductions in overall NH_4^+ concentrations(Vieno et al., 2016), the relative changes in gaseous NH_3 and NH_4^+ particles remains poorly quantified.

International targets have been agreed to reduce NH_3 emissions to move towards protection against its harmful effects. These include the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) Gothenburg Protocol and the recently revised EU National Emission Ceilings Directive (NECD 2016/2284) (EU, 2016). The 1999 UNECE Gothenburg Protocol is a multi-pollutant protocol to reduce acidification, eutrophication and ground-level ozone by setting emissions ceilings for sulphur dioxide, nitrogen oxides, volatile organic compounds and ammonia, which are to be met by 2020. Revised in 2012, the protocol requires national parties to jointly reduce emissions of NH_3, in the case of the EU-28 by 6 % between 2005 and 2020 (Reis et al., 2012). Under the revised NECD (EU, 2016), the EU is also committed to reductions of 6% for NH_3, but by a later date of 2029, as well as an additional 13% reduction in NH_3 emission beyond 2030 compared with a 2005 baseline.

Although this demonstrates that there is currently no strong commitment to reduce NH_3 emissions compared with SO_2 and NO_x, other supporting measures should also be noted including the Industrial Emissions Directive **2010/75/EU** (IED), which requires pig and poultry farms (above stated size thresholds) to reduce emissions using Best Available Techniques. The IED applies to around 70 % of the European poultry industry and around 25 % of the pigs industry (UNECE, 2010). In tandem, revised UNECE 'Critical Levels' (CLe) of NH_3 concentrations to protect sensitive vegetation and ecosystems were adopted in 2007 (UNECE, 2007). These set limits of NH_3 concentrations to 1 µg NH_3 m^{-3} and 3 µg NH_3 m^{-3} annual mean for the protection of lichens-bryophytes and other vegetation, respectively (Cape et al., 2009b). The new CLes replaced the previous single value of 8 µg NH_3 m^{-3} (annual mean) and have since been adopted as part of the revised Gothenburg Protocol. Such CLes for NH_3 are widely exceeded, including over the areas designated as Special Areas of Conservation (SAC) under the Habitats Directive, and indicates a significant threat to the Natura 2000 network established by that directive (Bleeker et al., 2009; Hallsworth et al., 2010; van Zanten et al., 2017).

Few countries have established systematic networks to measure NH_3 across their domains. In the Netherlands, a continuous wet annular denuder method (AMOR, replaced by the DOAS (Differential Optical Absorption Spectroscopy) device in 2015) has been used at 8 stations in the Dutch National Air Quality Monitoring Network (Van Pul et al., 2004; van Zanten et al., 2017). The Ammonia in Nature (MAN) network established in 2005 in the Netherlands monitors NH_3 with passive diffusion tubes in Natura 2000 areas (Lolkema et al., 2015). In the USA, the Ambient Ammonia Monitoring Network (AMoN) uses passive (Radiello) samplers at 50 sites since Oct 2010 (Puchalski et al., 2011). Hungary (Horvath et al., 2009), Belgium (den Bril et al., 2011), Switzerland (Thöni et al., 2004), West Africa

(Senegal and Mali under the Pollution of African Capitals program; Adon et al., 2016) and China (Xu et al., 2016) also have long-term NH_3 measurements (see review by Bleeker et al., 2009).

In the UK, the National Ammonia Monitoring Network (NAMN) was established in September 1996 with the aim of establishing long-term continuous monthly measurements of atmospheric NH_3 gas (Sutton et al., 2001a). Particulate NH_4^+ measurements were added in 1999, since this was expected to exhibit different spatial patterns and temporal trends to gaseous NH_3 (Sutton et al., 2001b). The NAMN thus provides a unique and important long-term record for examining responses to changing agricultural practice and allows assessment of the compliance of NH_3 emissions with targets established by international policies on emissions abatement. Measurements of NH_3 and NH_4^+ in the NAMN also address spatial patterns, covering both source and sink areas to test performance of atmospheric transport models, to support estimation of dry deposition of NH_x, to improve estimation of the UK NH_x budget (Fowler et al., 1998; Smith et al., 2000; Sutton et al., 2001b) and to assist with the assessment of exceedance of critical loads and critical levels (UNECE, 2007).

This paper provides an analysis on the state of atmospheric concentrations of NH_3 and NH_4^+ in the UK from 1998 to 2014 and their spatial and temporal trends. Overall, 17 years of continuous long-term NH_3 measurement data and 16 years of continuous long-term NH_4^+ measurement data from the NAMN are analysed to assess trends in concentrations in relation to estimated changes in emissions. The long-term measurement dataset is also used to explore spatial and temporal patterns in NH_3 and NH_4^+ across the UK in relation to regional variability in emission source sectors.

2 Material and Methods

2.1 Network structure and site requirements

The design strategy for NAMN was to sample at a large number of sites (>70) using low-frequency (monthly) sampling for cost-efficient assessment of temporal patterns and long-term trends. The network covers a wide distribution of monitoring sites with measurements in both agricultural and semi-natural areas. Monitoring locations are sited away from point sources (> 150 m) such as farm buildings, which avoids overestimating NH_3 concentrations compared with the grid square, since the aim is to provide meso-scale and regional patterns. In addition, where sampling is carried out in woodland areas, it is made in clearings. It was also recognised that the location of the network sites needed to consider the extent of sub-grid variability and the representativeness of sampling points. Spatially detailed local-scale NH_3 monitoring was therefore also carried out at a sub-1 km level to assess the extent to which a monitoring location is representative (Tang et al., 2001b). The NAMN started with 70 sites. Over time, new sites were added to fill gaps in the map, some sites were closed following reviews and some sites had to be relocated due to local reasons, for example land ownership changes or site re-development.

The number of sites peaked at 93 in 2000, but since 2009 has been stable at 85 sites. The locations of the NAMN sites for NH_3 and NH_4^+ in 2012 are shown in Figure 1a & b.

<INSERT FIGURE 1>

The selection of NAMN sites to provide a representative concentration field across the UK was aided by the availability of an estimated UK NH_3 concentration field at a 5 km by 5 km grid resolution provided by the Fine Resolution Atmospheric Multi-pollutant Exchange (FRAME) model (Singles et al., 1998; Fournier et al., 2002). A comparison of FRAME modelled NH_3 concentrations for NAMN sites with FRAME modelled concentrations for the whole of the UK shows that the network has a good representation in the middle air concentration classes of 0.5 – 1.5 µg m^{-3} (33 % of NAMN sites, compared with 29 % of all FRAME 5 km x 5 km grid squares) and 1.5 - 3 µg m^{-3} (32 % of NAMN sites, compared with 39 % of all FRAME 5km x 5 km grid squares), but with an over-representation at high concentrations and under-representation at low concentrations (Figure 1c). Since air concentrations are more variable in high concentration areas, a larger number of monitoring sites were located in these areas than in remote low concentration areas where air concentrations are more homogeneous. Similarly, the monitoring sites were strategically selected to cover source areas of expected high concentrations and variability on the basis of the FRAME model NH_3 concentration estimates (Figure 1a & b), and this approach was expected to provide additional evidence to test the performance of atmospheric dispersion models (Fournier et al., 2005; Dore et al., 2015). When compared with other atmospheric chemistry transport models, FRAME was found to correlate well with measured NH_3 concentrations (Dore et al. 2015). The NAMN sites were also similarly checked for representativeness of particulate NH_4^+ by comparing FRAME modelled NH_4^+ concentrations at NAMN sites with modelled concentrations for the whole of the UK, which demonstrates a good representation across the range of expected concentrations (Figure 1d).

2.2 Atmospheric NH_3 and NH_4^+ measurements

Monthly time-integrated measurements of atmospheric NH_3 are made in the NAMN using a combination of passive samplers (Sutton et al., 2001a; Tang et al., 2001a) and an active diffusion denuder method referred to as the DEnuder for Long Term Atmospheric (DELTA) sampler (Sutton et al., 2001a &c). In terms of passive samplers, membrane diffusion tubes (3.5 cm long) with a limit of detection (LOD) around 1 µg NH_3 m^{-3} (Sutton et al., 2001a) were used in the first 4 years (September 1996 – April 2000). These were replaced in May 2000 with the more sensitive Adapted Low-cost, Passive High Absorption (ALPHA, LOD = 0.03 µg NH_3 m^{-3}) diffusive samplers (Tang et al., 2001a; Tang and Sutton, 2003), following a period of parallel testing (Sutton et al., 2001c).

Particulate NH_4^+ measurement was added to the NAMN in 1999 at all DELTA sites (50) in the first two years (1999 and 2000). Following this initial period, the sampling density was reduced during early 2001 to 37 sites and has been stable at 30 sites since 2006. Although not presented in this paper, the DELTA samplers additionally provide concentrations of acid gases (HNO_3, SO_2, HCl) and aerosols (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}) for the UK Acid Gas and Aerosol monitoring network (AGANet) at a subset of NAMN DELTA sites (Tang et al., 2015; Conolly et al., 2016). Measurement data from the AGANet are used to aid interpretation of NH_3 and NH_4^+ results in Sect. 0.

2.2.1 DELTA method

The DELTA method uses a small pump to sample air (0.2 to 0.4 L min^{-1}) in combination with a high-sensitivity gas meter to record sampled volume (Sutton et al., 2001c). Two citric acid coated denuders (10 cm long borosilicate glass tubes) in series are used to collect NH_3 gas and to check the collection efficiency. A collection efficiency correction is applied to the measurement (Sutton et al., 2001d). The corrected air concentration (χ_a (corrected)) is determined as in Equation 1:

$$\chi_a\ (\text{corrected}) = \chi_a\ (\text{Denuder 1}) * \frac{1}{1-\chi_a\left[\frac{\chi_a(\text{Denuder 2})}{\chi_a(\text{Denuder 1})}\right]} \qquad (1)$$

Typically, denuder collection efficiency is better than 90% (Conolly et al., 2016). At 90 % collection efficiency, the correction represents < 1 % of the corrected air concentration. Individual measurements with collection efficiency < 75 % (correction amounts to 11 % of the total at 75%) are flagged as valid, but less certain (Tang and Sutton, 2003). Where less than 60 % of the total capture is recorded in the first denuder, the correction factor amounts to greater than 50 % and is not applied. The air concentration of (χ_a) of NH_3 is then determined as the sum of NH_3 in denuders 1 and 2 (Equation 2):

$$\chi_a = \chi_a\ (\text{Denuder 1}) + \chi_a\ (\text{Denuder 2}) \qquad (2)$$

At sites where particulate NH_4^+ is also sampled, a 25 mm filter pack with a citric acid impregnated cellulose filter is added after the denuders to capture the NH_4^+. The calculated air concentrations (Y_a) of NH_4^+ is corrected for incomplete capture of NH_3 by the double denuder. The corrected air concentrations (Y_a (corrected)) of NH_4^+ is determined as in Equation 3:

$$Y_a\ (\text{corrected } NH_4^+) = Y_a\ (NH_4^+) - [((\chi_a\ (\text{corrected } NH_3) - [(\chi_a\ (\text{Denuder 1 } NH_3) + \chi_a\ (\text{Denuder 2 } NH_3)])* (18/17)] \qquad (3)$$

For NH_4^+ sampling, loss of NH_3 due to volatilisation of NH_4^+ from the acid impregnated filter has been investigated, by adding a third citric acid coated denuder after the filter pack which was found to be negligible. At DELTA sites where additional simultaneous sampling of acid gases and particulate phase components are made for AGANet, ion balance checks between anions and cations in the particulate phase are performed to provide an indication of the quality of the particulate measurements. For the acid and base particulate components, close coupling is expected between NH_4^+ and the sum of NO_3^- and SO_4^{2-}, as NH_3 is neutralised by HNO_3 and H_2SO_4 to form NH_4NO_3 and $(NH_4)_2SO_4$, respectively (Conolly et al., 2016).

At the Bush OTC site in Scotland (UK-AIR ID = UKA00128), duplicate DELTA measurements are made to assess the reproducibility of the method. For continuous monthly measurements between 1999 and 2014, the R^2 between the duplicate systems was 0.96 for both NH_3 and NH_4^+ (supp. Figure S1).

2.2.2 Passive methods

The NH_3 membrane diffusion tubes deployed in the NAMN from 1996 to 2000 are hollow cylindrical tubes (FEP, 3.5 cm long). A cap at the top end holds in place two stainless steel grids coated with sulphuric acid. The lower air-inlet end of the tube is capped with a gas-permeable membrane (Sutton et al., 2001a; Tang et al., 2001a; Thijsse, 1996). In comparison, the ALPHA passive sampler is a badge-type high sensitivity sampler with an uptake rate that is ~20 times faster than the diffusion tube. It consists of a cylindrical low-density polyethylene body. An internal ridge supports a cellulose filter coated with citric acid, which is held in place with a polyethylene ring. The open end is capped with a PTFE membrane, providing a diffusion path length of 6 mm between the membrane and absorbent surface (Tang et al., 2001a).

Triplicate passive samplers are deployed for every measurement in the NAMN. Where the % coefficient of variation (CV) of the triplicate samplers is greater than 30% for the diffusion tubes or greater than 15% for the ALPHA samplers, the sample run is classed as failing the quality control test. Large discrepancies are most likely due to contamination of samples and data from contaminated samples are excluded from the assessment in this paper.

The passive methods are calibrated against the DELTA method in the NAMN by ongoing comparison at several sites representing a wide range of ambient NH_3 concentrations (see Sect. 2.2.4). Since 2009, the number of inter-comparison sites has been nine. These are Auchencorth (UKA00451), Bush OTC (UKA00128), Glensaugh (UKA00348), Lagganlia (UKA00290), Llynclys Common (UKA00270), Moorhouse (UKA00357), Rothamsted (UKA00275), Sourhope (UKA00347) and Stoke Ferry (UKA00317). The inter-comparison is used to establish a regression between the active and passive methods, with the DELTA samplers as the reference system, since the air volume sampled is accurately measured with high sensitivity gas meters. The calibration is necessary to account for the fact that the sampling path length in the passive samplers is longer than the distance between the membrane and adsorbent, due to the additional resistance to molecular diffusion imposed by the turbulence damping membrane at the inlet and the presence of a laminar boundary layer of air on the outside of the sampler (Tang et al., 2001a). In addition, parallel measurements were made at a high NH_3 concentration farm site (1998-2007) to extend the calibration range, and to ascertain linearity of response to high concentrations. To ensure that no bias is introduced in the sampling and to maintain the validity of long-term trends, the calibration is evaluated on an annual basis (Tang and Sutton, 2003; Conolly et al., 2016).

For the period up to 2000 when the diffusion tubes were implemented in the NAMN, their calibration (at 10 µg m^{-3}) amounts to an average of 1.5 % compared with the DELTA system. The mean ALPHA sampler calibration (at 10 µg m^{-3}), compared with the DELTA system, amounts to a correction of 10 % (ALP1: prototype 1, 1998-2000), 15 % (ALP2: injection mould 1, 2001-2005), 17 % (ALP3: injection mould 2, 2006), 34 % (ALP4: injection mould 2 + new membrane, 2007-2008) and 40 % (ALP5: injection mould 2 + new membrane + new lab/instrument FloRRia, 2010-2014), respectively. The new PTFE membrane (5 µm pore size) is supported on a regular polypropylene grid and is thicker (305 µm) than the earlier PTFE membrane (also 5 µm pore size, but 265 µm thickness) used which was supported instead on a randomly arranged polypropylene support material. The difference in calibration was therefore due to the extra resistance to gas diffusion imposed by the new thicker membrane. The annual calibration of the methods shows both high precision and constancy between years (Figure 2), which is important to support the detection of temporal trends in NH_3 concentrations. There is no systematic trend over time in either of the passive method calibrations.

<INSERT FIGURE 2>

The comparison of monthly measurement data between the DELTA and calibrated passive measurements demonstrated a close agreement (Figure 3). The correlation (R^2) between DELTA and calibrated diffusion tubes was 0.91 (Figure 3a), while the correlation between DELTA and calibrated ALPHA samplers was 0.92 (Figure 3b). From the calibrated results, the intercept for the diffusion tubes was 0.10 µg NH_3 m^{-3}, while that for the ALPHA samplers was 0.03 µg NH_3 m^{-3}, demonstrating the improvement in sensitivity with the ALPHA samplers compared with the diffusion tubes (Figure 3). In the present case the value of the intercepts, even for diffusion tubes, is much less than typical NH_3 air concentrations (see Sect. 3). However, this cannot be assumed to be the case in other implementations of the same methods. Experience from other studies using the lower sensitivity diffusion tubes indicates a tendency to overestimate NH_3 concentrations under clean conditions (RGAR, 1990; Thijsse et al., 1996; Tang et al., 2001a; Lolkema et al., 2015). This observation points to the need for any application of NH_3 passive sampling for ambient monitoring to be accompanied by testing and calibration against a verified active sampling method. In independent assessments, for example in the USA (Puchalski et al., 2011), the ALPHA samplers performed well against a reference annular denuder method with a median relative percent difference of −2.4%.

<INSERT FIGURE 3>

2.2.3 Chemical analysis

NH_3 gas captured on the acid coating of the denuder (DELTA), grid (diffusion tubes) or filter paper (ALPHA), and particulate NH_4^+ captured on the DELTA aerosol filter, are extracted into deionised water and analysed for NH_4^+ on an ammonia flow injection analysis system. The analytical instrument has changed over the network's operational period from the AMFIA (ECN, NL) to the FloRRIA (Mechatronics, NL), an updated model based on AMFIA (Conolly et al., 2016). The principles of operation of both instruments are the same and are based on selective diffusion of NH_4^+ across a PTFE membrane at *c*. pH 13 into a counter-flow of deionized water, allowing selective detection of NH_4^+ by conductivity (Wyers et al., 1993). The extracted samples were analysed for NH_4^+ against a series of NH_4^+ standards and quality controls. Parallel analysis of laboratory and field blank (unexposed) samples were used to determine the amounts of NH_4^+ derived from NH_3 and NH_4^+ in the atmosphere during transport and storage. The limit of detection (LOD) calculation of the ALPHA and DELTA methodologies are determined as three times the standard deviations of the laboratory blanks. For the DELTA method, the LODs were 0.01 µg m^{-3} for gaseous NH_3 and 0.02 µg m^{-3} for particulate NH_4^+. For the ALPHA method, the LOD was determined as 0.03 µg m^{-3}.

2.2.4 Data Quality Control

Measurement data are checked and screened, based on the quality management system applied in the UK air monitoring networks (Tang and Sutton, 2003). Data quality is assessed against the following set quality control criteria: a) DELTA system: monitoring of the air flow rate and the use of two denuders in every sample to assess capture efficiency for $NH_{3,}$ and b) passive samplers: use of triplicate samplers for monitoring NH_3 concentrations at every site, to allow an assessment of sampling precision, and c) ongoing calibration of passive samplers against the DELTA. Data flags are applied to the dataset; a full list of these is available from the EMEP website (http://www.nilu.no/projects/ccc/flags/index.html). Following the quality control checks and data flagging on the collected dataset, the annually ratified data from the NAMN are made publically available on the Department for Environment, Food & Rural Affairs (Defra) UK-AIR website (https://uk-air.defra.gov.uk/) and are also in the process of being made available on the EMEP website (http://ebas.nilu.no/).

An intercomparison of NH_3 measurements by the RIVM AMOR system (hourly, Wyers et al., 1993) and the DELTA sampling system (monthly) have been carried out at the Zegweld site (ID 633) in the Dutch National Air Quality Monitoring Network (van Zanten et al., 2017) since July 2003. Since September 2012, ALPHA measurements have also been included. To compare results, monthly mean concentrations were derived from the average of hourly AMOR data for the corresponding DELTA and ALPHA monthly sampling periods with good agreement (supp. Figure S6).

2.2.5 Trend Analyses

Statistical trend analysis was conducted on the long-term dataset from the UK NAMN to identify trends in the long-term datasets (univariate monotonic, see e.g. Hirsch et al., 1991), estimate the rate of change and to address the question of whether trends in NH3 and NH4+ concentrations (if any) are consistent with the changes in estimated UK annual NH3 emissions (data downloaded from: http://naei.beis.gov.uk/data/data-selector-results?q=101505)? The dataset is sufficiently long-term (i.e. gaseous NH3: 17 years and particulate NH4+: 16 years) and collected by consistent methods, to allow for effective statistical trend analyses to be carried out. Trend analyses were carried out using (i) linear regression (LR), (ii) Mann-Kendall (MK) test (Gilbert, 1987) on annually averaged and monthly mean data, and (iii) Seasonal Mann-Kendall (SMK) test (Hirsch et al., 1982) on monthly data only. Mann-Kendall tests were performed using the 'Kendall' package (McLeod, 2015) in the R software. Computation of the Sen's slope and confidence interval (for non-seasonal Sen's slope only) of the linear trend were performed using the R 'Trend' package (Pohlert, 2016). Since concentrations of NH3 show strong seasonality, the SMK test was applied to identify the months that are driving the long-term trends in data. The SMK test (Hirsch et al., 1982) takes into account a 12 month seasonality in the time series data by computing the MK test on each of monthly 'seasons' separately, and then combining the results. So for monthly 'seasons', January data are compared only with January, February only with February, etc. No comparisons are made across season boundaries.

The Sen's slope is the fitted median slope of a linear regression joining all pairs of observations. For the SMK, an estimate of the seasonal Sen's trend slope over time is computed as the median of all slopes between data pairs within the same season (i.e. January compared only with January etc.). Therefore no cross-season slopes contribute to the overall estimate of the SMK trend slope. Parametric LR analysis are simple and straightforward to use and interpret monotonic trend assessment in environmental data (e.g. Kindzierski et al., 2009; Meals et al., 2011), but they require assumptions about normality of data and homogeneity of variance of data. The MK approach on the other hand are widely used in environmental time series assessments, e.g. long-term trends in precipitation (Serrano et al. 1999) and long-term trends in European air quality (Colette et al., 2016; Torseth et al., 2012). The main advantages, as discussed in the literature of the MK approach over linear regression for trend assessments are that (i) it does not require normally distributed data, (ii) it is not affected by outliers, and (iii) it removes the effect of temporal auto-correlation in the data. The MK approach are widely used in environmental time series assessments, e.g. long-term trends in precipitation (Serrano et al. 1999) and long-term trends in European air quality (Colette et al., 2016; Torseth et al., 2012). However linear trend assessment have been used in UK air quality monitoring network reports (e.g. Conolly et al., 2016), therefore both approaches were used in this paper primarily as a quality assurance check.

3 Results and discussion

In order to summarise and discuss the NAMN dataset, the spatial patterns in the measurements of NH_3 and NH_4^+ are considered in Sect. 3.1 (comparison with emission estimates) and Sect. 3.2 (comparison with modelled concentration estimates), seasonal patterns are discussed in Sect. 0, and long-term trends across the UK in Sect. 3.4.

3.1 Spatial variability in NH_3 and NH_4^+ concentrations in relation to estimated emissions

As a primary pollutant emitted from ground-level sources, NH_3 exhibits high spatial variability in concentrations (Sutton et al., 2001b; Hellsten et al., 2008; Vogt et al., 2013), confirmed by NH_3 data from the NAMN (e.g. range of 0.06 – 8.8 µg m^{-3} annual mean in 2005) (

In section 3.1a). The observed variability is consistent with the large regional variability in NH_3 emissions and sources (

In section 3.1c & d). With agriculture being the main source of NH_3 emissions,

In section 3.1a shows the largest concentrations of measured NH_3 in parts of the UK with the highest livestock emissions, such as eastern England (East Anglia), north-west England (Eden Valley, Cumbria) and the border area between England and Wales (Shropshire) (

In section 3.1d). By contrast, the lowest NH_3 measured concentrations are found in the north-west Scottish Highlands (< 0.2 µg m^{-3}), which is consistent with the emissions map (

In section 3.1c). The 2005 data show exceedance of the Critical Levels for annual mean NH_3 concentrations of 1 and 3 µg NH_3 m^{-3} for the protection of lichens-bryophytes and vegetation, respectively (UNECE, 2007) at many of the sites (53 % > 1 µg NH_3 $m^{-3}$and 13 % > 3 µg NH_3 m^{-3}). In 2014, exceedance of the 1 and 3 µg NH_3 m^{-3} CLe increased to 60 % and 16 %, respectively. The widespread exceedance of the CLe for NH_3 concentrations across the UK thus represents an ongoing threat to the integrity of sites designated under the Habitats Directive, as well as nationally designated Sites of Special Scientific Interest (SSSI) and other sensitive habitats.

Concentrations of NH_4^+ are less spatially heterogeneous than those of NH_3, based on data from 30 sites (e.g. range of 0.14 to 1.8 µg m^{-3} annual mean in 2005) with a more coherent pattern of variation across the country, reflecting regional differences in NH_3 concentrations (

In section 3.1b). Thus there is a general decreasing gradient from the south-east to the north-west of the UK, due to both NH_3 sources in England and import of particulate matter from Europe (Vieno et al., 2014; Dore et al., 2015). The limited variation across the UK for the annual average NH_4^+ concentrations can be attributed to the atmospheric formation process (providing a diffuse source) and its longer atmospheric lifetime.

<INSERT FIGURE 4>

A similar picture is reported by the Dutch National Air Quality Monitoring Network (van Zanten et al., 2017), with large spatial variability of NH_3 concentrations (2 – 20 µg NH_3 m^{-3}) across the country and a more homogeneous distribution of particulate NH_4^+ (1-2 µg NH_4^+ m^{-3} in 2014), although the number of Dutch monitoring sites reported there is much smaller with only 8 stations providing continuous measurements. Both NH_3 and NH_4^+ concentrations were correlated with emission density, but the correlation was smaller for NH_4^+ than for NH_3 because of the larger contribution to NH_4^+ concentrations from long-range transport in the Netherlands.

The UK NH_3 emissions inventory is calculated and spatially distributed annually. Agricultural sources at a 5 km by 5 km grid resolution are combined with a large number of non-agricultural sources (Sutton et al., 2000; Tsagatakis et al., 2016) at a 1 or 5 km resolution to produce the annual NH_3 emissions data, and maps at a 1 km by 1 km grid resolution are reported by the official UK National Atmospheric Emissions Inventory (NAEI; http://naei.defra.gov.uk/data/mapping). In the UK, agriculture accounts for > 80% of total NH_3 emissions and is estimated by the National Ammonia Reduction Strategy Evaluation System (NARSES) model (Webb & Misselbrook 2004; Misselbrook et al., 2015). For the agricultural NH_3 emission maps, parish statistics on livestock numbers and crop areas are combined with satellite-based land cover data to model emissions at a 1 km resolution, using the AENEID model (Dragosits et al., 1998; Hellsten et al., 2007). For reasons of data confidentiality, the 1 km data need to be aggregated to produce annual agricultural NH_3 emissions maps at a 5 km by 5 km grid resolution. National emission estimates for NH_3 are submitted to both the European Commission under the NECD (2001/81/EC) and the United Nations Economic Commission for Europe (UN/ECE) under the Convention on Long-Range Transboundary Air Pollution (CLRTAP).

The AENEID approach (Dragosits et al. 1998) can further be used to classify each 5 km by 5 km grid square in the UK into dominant NH_3 emission source categories (

In section 3.1d), following the method of Hellsten et al. (2008), where grid squares with >45% from a given category are referred to as dominated by that source. The seven categories are: cattle, pigs & poultry (combined for data disclosivity reasons), sheep, fertilizer application to crops and grassland, non-agricultural sources, as well as a mixed category where no single source dominates, and background. Background grid squares are defined by very low NH_3 emissions of <1 kg N ha^{-1} y^{-1}.

Using the dominant emission sources map, each site in the NAMN is classified to one of the seven categories just described. This provides information of the main emission source type expected in the 5 km by 5 km grid square containing the monitoring site and is useful for assessing whether the network has a good representation of key emission source categories (Supp. Figure S2a & b). Over the period since the NAMN was established, from 1996 to present, there have been substantial changes in emissions estimated for the different source sectors. For analysis in this paper, the dominant sources map for 2005 emission year was used as representing the mid-point of the data series (1998-2014) and compared with the classification from other years for consistency. This categorization of sites is used further in the interpretation of the monitored NH_3 and NH_4^+ concentrations and their long-term trends in the next sections.

<INSERT FIGURE 5>

3.2 Spatial variability in NH_3 and NH_4^+ concentrations in relation to modelled concentrations

Comparison of measurements with modelled NH_3 concentrations from the FRAME model for an example year of 2012 showed significant scatter when considering the full network of sites ($n = 85$, $R^2 = 0.62$) (Figure 5a). In this graph, each point is colour-coded according to the estimated dominant NH_3 emission source category for the 5 km by 5 km grid square. This updates a similar comparison from Sutton et al. (2001b) for the year 2000. The scatter may be explained by the large local spatial variability of NH_3, related primarily to rapid decreases of NH_3 concentrations with distance from a source (see e.g. Pitcairn et al., 1998; Dragosits et al., 2002), with the result that a single site measurement only gives an approximate indication of concentrations across the model grid square it is located in. At many of the sites where the model overestimates concentrations, the measurements are in fact carried out in nature reserves, or in clearings inside forests. The monitoring sites in these sink areas are typically well away from local sources. Conversely, some of the outliers where measurements are larger than the model predictions show indications of being affected by nearby emission sources, as was established by investigations during site visits.

<INSERT FIGURE 6>

Figure 6 considers measured NH_3 concentrations at a subset of sites (44 out of the full 85 sites) that are located away from nearby local sources, in forest or semi-natural areas, following the site classification and assessment by Hallsworth et al. (2010). For this restricted set of sites, $R^2 = 0.76$ for 2012 which is higher than the correlation for the overall UK network. The improvement in correlation between measured and modelled NH_3 concentrations for this subset of sites can be explained by the monitoring locations typically being further away from sources, so that uncertainties in local emissions estimates are to some extent averaged out. This observation is also consistent with the findings of Vieno et al. (2009).

In contrast to NH_3, the correlation between NAMN measurements and FRAME model output is stronger for particulate NH_4^+ concentrations ($R^2 = 0.87$). However, measured concentrations are generally larger than the modelled ones (slope 1.1, intercept –0.16 µg m^{-3} (Figure 5b). One reason for the better agreement for NH_4^+ is the more slowly changing spatial patterns in concentrations, which are not expected to vary on a finer scale than the model's 5 km by km grid, improving the representativeness of site-based measurements. The 2012 comparison shown here updates an earlier inter-comparison assessment carried out by Dore et al. (2007) for the year 2002 and demonstrates that the FRAME model is performing well in describing the spatial distribution of NH_4^+. However, for the 2012 inter-comparison, the FRAME model appears to underestimate NH_4^+ at sites with concentrations < 0.6 µg NH_4^+ m^{-3}, with better agreement at concentrations above 0.6 µg NH_4^+ m^{-3}. This suggests either too low a formation rate for NH_4^+ in the model at cleaner sites, or too high a removal rate for NH_4^+, or a combination of both. The presence of higher measured NH_4^+ concentrations in remote areas than shown by the model may also indicate that NH_4^+ has a longer residence time than treated in the model. Similar regressions between NAMN and FRAME NH_4^+ aerosol concentrations were observed for other years. For example, for 2008 the FRAME model underestimated NH_4^+ at concentrations < 0.7 µg NH_4^+ m^{-3} (slope 1.2, intercept –0.26 $µg^{-3}$; $R^2 = 0.89$, range = 0.2 – 1.4 µg m^{-3}). Changes in the chemical climate, such as reduced emissions of SO_2 in the UK, are postulated to affect conversion rates of NH_3 into NH_4^+, as well as the dry deposition rates, leading to more NH_3 remaining in the atmosphere (van Zanten et al., 2017). This is discussed further in Sect. 0.

3.3 Seasonal variability in measured UK NH_3 and NH_4^+ concentrations

A comprehensive account of the seasonal variability of NH_3 and NH_4^+ for different regions across the UK is provided by the NAMN. In Figure 7, the average seasonal cycles of grouped sites from four different emission source categories are compared for NH_3 and NH_4^+.

<INSERT FIGURE 7>

In addition to substantial differences in the overall magnitude of NH_3 concentrations, where the largest concentrations in the network are found at sites dominated by pig and poultry farming, followed by areas where cattle farming predominates, it is clear that the seasonal patterns of NH_3 also vary depending on the dominant source type (Figure 7a). For background sites (defined as located in grid squares with NH_3 emissions <1 kg N ha^{-1} y^{-1}), a clear summer maximum in NH_3 concentrations can be observed, with minimum concentrations occurring in winter. The summer peak is probably related to increased land surface NH_3 emissions in warm, dry summer conditions, both from the presence of low-density grazing livestock and wildlife. It is also related to surface factors such as the compensation point for vegetation, which is defined as the concentration below which growing plants start to emit NH_3 into the atmosphere (Sutton et al., 1995). The interaction between atmospheric NH_3 concentrations and vegetation is complex, leading to both emission and deposition fluxes, depending on relative differences in concentrations. However, it is well established that warm, dry conditions promote NH_3 emission from vegetation (e.g. Massad et al., 2010; Flechard et al., 2013). It is therefore possible that bi-directional exchange with vegetation is at least partly controlling NH_3 concentrations at remote sites distant from intensive livestock farming.

The possibility for such interactions can be considered further using the example of Inverpolly (UKA00457), a remote background site in the NW Scottish Highlands. This site shows a very clear seasonal cycle with peak concentrations in July when warmer, drier conditions prevail, while lowest concentrations occur during the cooler and wetter winter months (Figure 8a & b). A smaller peak in NH_3 can also be seen annually in April, which indicates potential longer range influences of manure spreading in spring, even at this remote location (Figure 8b). Although there is substantial scatter, Figure 9 shows that there is significant correlation between monthly NH_3 concentrations and both temperature ($R^2 = 0.33$, $n = 231$, $p < 0.05$) and precipitation ($R^2 = 0.19$, $n = 231$, $p < 0.05$). The influence of temperature and rainfall on NH_3 emission and concentrations is well characterised (e.g. see Sutton et al., 2013; van Zanten et al., 2017).

<INSERT FIGURE 8>

<INSERT FIGURE 9>

For sites dominated by emissions from sheep farming, the seasonal profile in NH_3 concentrations is similar to that for background sites, although the summer maximum in NH_3 is larger than background sites, because grazing emissions are larger (Hellsten et al., 2008). It is notable that the peak NH_3 concentration occurs later in the year for background areas (July-September) than for sheep areas (June-August). This may be related to the seasonal presence of lambs, which are often only present for the first part of the summer. In areas with more intensive livestock farming, where emissions comes from either cattle or from pig & poultry farming, the largest concentrations are observed in spring and autumn, corresponding to periods of manure application to land. The spring peak in March is larger than the autumn peak in September, which coincides with the main period for manure application being in spring, before the sowing of arable crops or early on in the grass-growing period (Hellsten et al., 2007). Ammonia concentrations in these areas are also larger in summer than winter, due to warmer conditions promoting volatilization. Interestingly, the dip in concentrations in June matches a period when crops will be actively growing with possible uptake and removal of NH_3 from the atmosphere. Vegetation can be a source or a sink of atmospheric NH_3 and uptake of NH_3 can occur when the relative concentration of NH_3 in the atmosphere is higher than inside the plant stoma (e.g. Sutton et al.,1995, Massad et al., 2010; Flechard et al., 2013).

For particulate NH_4^+, as expected for a secondary pollutant, concentrations are more decoupled from the dominant NH_3 source sectors in the vicinity of a site. Although the formation of particulate NH_4^+ primarily depends on the occurrence of NH_3 in the atmosphere, synoptic meteorology and long range transboundary transport from continental Europe are important drivers influencing the seasonal variations of NH_4^+ across the UK, due to its' longer lifetime. (Vieno et al., 2014, 2016). The seasonal trends in particulate NH_4^+ are seen to be broadly similar for the four different emission source sectors (Figure 7b), with the magnitude of the NH_4^+ concentrations reflecting NH_3 concentrations at a regional level. In the atmosphere, particulate NH_4^+ are primarily in the form of $(NH_4)_2SO_4$ and NH_4NO_3, formed when the acid gases HNO_3 and H_2SO_4.in the atmosphere are neutralised by NH_3 (Putaud et al., 2010). NH_3 preferentially neutralizes H_2SO_4 due to its low saturation vapour pressure (forming NH_4HSO_4 then $(NH_4)_2SO_4$), while NH_4NO_3 is formed when abundant NH_3 is available, In contrast to $(NH_4)_2SO_4$, NH_4NO_3 is a semi-volatile component (Stelson & Seinfeid, 1982). Long-term data from the UK Acid Gas and Aerosol Network (AGANet, Conolly et al., 2016) shows a change in the particulate phase of NH_4^+ from $(NH_4)_2SO_4$ to $NH_4NO_{3,}$ with particulate nitrate concentrations exceeding that of particulate sulphate approximately three-fold (on a molar basis) (Fig. 18a). This suggests that the thermodynamic equilibrium between the gas phase NH_3 and HNO_3 and the aerosol phase NH_4NO_3 will have a much greater effect on the seasonal concentrations of NH_4^+ than $(NH_4)_2SO_4$. The formation and dissociation of NH_4NO_3 depend strongly on ambient temperature and humidity (Stelson and Seinfeld, 1982). Warm, dry weather in summer promotes dissociation, decreasing particulate phase NH_4NO_3 relative to gas phase NH_3 and HNO_3. During the winter months, low temperature and high humidity favour the formation of NH_4NO_3 from the gas phase NH_3 and $HNO_{3.}$ By contrast, the spring peak in NH_4^+ concentrations may be attributed to photochemical processes (elevated ozone) leading to enhanced formation of HNO_3 during this period (Pope et al., 2016) and also to import of particulate NO_3^- through long-range transboundary transport, e.g. from continental Europe, as discussed in Vieno et al. (2014). Nevertheless, it is notable that the winter minima for NH_4^+ aerosol concentrations at sheep and background sites are more pronounced than that for pig, poultry and cattle dominated sites. This may be a result of a combination of smaller NH_3 emissions in winter in these areas (as indicated by Figure 7a) and differences in long-range transport to the more remote areas in winter conditions.

Overall, the seasonal distributions show that NH_3 concentrations are mostly governed by local emission sources and by changes in environmental conditions, with warm, dry weather favouring increased volatilisation. By contrast, particulate NH_4^+ concentrations are largely determined by more distant sources through long-range transport and synoptic meteorology.

3.4 Long-term trends in estimated UK NH_3 emissions

UK NH_3 emissions are estimated to have fallen by 16 % between 1998 and 2014, from 336 to 281 kt (Figure 10a) (http://naei.defra.gov.uk/). The most significant cause of the estimated reductions has been decreasing cattle, pig and poultry numbers in the UK over this period. Between 2013 and 2014, the decreasing trend in UK NH_3 emissions was however reversed with an increase of 3.3 % from 272 to 281 kt NH_3 due to an increase in emissions from the agricultural sector from 224 kt in 2013 to 234 kt in 2014. This is attributed to an increase in dairy cow numbers (and dairy cow N excretion) and increase in fertiliser N use (particularly urea, which is associated with a higher emission factor than other fertilisers types used in the UK) (Misselbrook et al. 2015; http://naei.defra.gov.uk/).

<INSERT FIGURE 10>

Although the UK met the 2010 emission ceilings target of 297 kt NH_3 emission per year set out under the Gothenburg Protocol and NEC Directive, it is committed to a further emission reduction by 2020 of 8 % from the 2005 total under the 2012 revised Gothenburg Protocol, and by 17% after 2030 under the revised 2016 NEC Directive (EU, 2016). The revised 2020 target of 282 kt NH_3 (8% reduction of the baseline figure of 307 kt NH_3 emissions total in 2005) may require emission strategies to be implemented, rather than relying on decreasing livestock populations as during the recent decades.

Agricultural emissions are by far the largest NH_3 sources in the UK's emission inventory, accounting for 86 % and 83 % of the total NH_3 emissions in 1998 and 2014, respectively. The primary source of agricultural emissions is livestock manure management, in particular from cattle which make up approximately 46 % of the total agricultural emissions, followed by pigs and poultry contributing another 18 % in 2014 (Defra, 2015; Misselbrook et al., 2015) (Figure 10b). Over the period 1998 to 2014, NH_3 emissions from cattle are estimated to have decreased by 11 % (from 144 to 128 kt), with emissions estimated to have remained relatively stable since 2008, followed by a modest 2 % increase between 2013 and 2014 from 125 kt to 128 kt (Figure 10a; Figure 16). Emissions from pigs and poultry showed a large downward trend between 1998 and 2014, with a decrease of 39 % (from 82.7 kt to 50.3kt) (Figure 10a; Figure 16), although the decreasing trend was reversed between 2012 and 2014, with an increase of 6 % from 46.7 kt to 50.3 kt, The sheep sector is a minor source, contributing 3.6 % to the total agricultural emissions. NH_3 emissions from this sector are estimated to have decreased by 24 % in 2014 relative to 1998 (from 13.3 to 10.1 kt).

3.5 Long-term trends in measured NH_3 concentrations

The UK NAMN dataset was analysed to compare levels and trends against the NH_3 emission inventory. To avoid bias due to changes in the number and locations of sites over the duration of the network, sites with incomplete data runs over selected periods for analysis are excluded. Based on these exclusion criteria, the number of sites with complete data runs was 59 for the period 1998 to 2014, 66 sites for

1999 to 2014, and 75 sites for the period 2000 to 2014. To ensure consistency in the trend analysis, several combinations of the available data were used:

1a. 1998 – 2014 (59 sites): annually averaged data

1b. 1998 – 2014 (59 sites): monthly mean data

2a. 1999 - 2014 (66 sites): annually averaged data

2b. 1999 - 2014 (66 sites): monthly mean data

3a. 2000 - 2014 (75 sites): annually averaged data

3b. 2000 – 2014 (75 sites): monthly mean data

A visualization of the time series according to dataset 1a is summarized in Figure 11. This shows the mean UK monitored annual NH_3 concentrations of 59 sites with complete data runs from 1998 (first complete year of monitoring) to 2014, summarised in a boxplot, together with annual mean UK rainfall and temperature data and compared with NH_3 emissions trends over the same period. The interquartile ranges and the spread of the NH_3 concentrations can be seen to be variable from year to year, demonstrating both substantial inter- and intra-annual variability.

<INSERT FIGURE 11>

3.5.1 Mann-Kendall non-parametric time series analysis

To detect trends and to indicate the significance level of the trends in the long-term NAMN data, the non-parametric Mann-Kendall (MK) approach was used combined with the Sen's slope method for estimating the trend and confidence interval of the linear trend (see Sect. 2)). The classic MK test was used on the annually averaged data (datasets 1b, 2b, 3b), while both the classic MK and seasonal Mann-Kendall (SMK) tests were applied to the monthly averaged data (datasets 1a, 2a, 3a).

Results of the Mann-Kendall tests are summarised in Table 1. For each time series, the median annual trend (in units of µg NH_3^{-1} y^{-1}) is estimated from the Sen's slope and intercept of the MK linear trend. To assess the relative change over time, the % relative median change was calculated from the estimated NH_3 concentration at the start (y_0) and at the end (y_i) of the selected time period ($100*[(y_i-y_0)/y_0]$) computed from the Sen's slope and intercept. This approach was adopted instead of a direct comparison of actual observed NH_3 concentrations at the start (y_0) and at the end (y_i) of the time series, since there is substantial inter-annual variability in the data (Figure 10, Figure 16). Using the estimated concentrations at the start and end from the fitted Sen's slope allows using a reference that is less sensitive to inter-annual variability than the actual observed concentrations.

<INSERT TABLE 1>

For the annually averaged NH_3 concentrations across the UK, dataset 1a (1998-2014, 59 sites) show a small, but non-significant decreasing trend (relative median change = –6.3 %), while datasets 2a (1999-2014, 66 sites) and 3a (2000-2014, 75 sites) show no discernible trends (median relative change = 0.0 % for both) (Table 1). Results from the analysis of monthly data from all three different data groupings (1b, 2b, 3b) (relative median change = –4.2 to –8.2 %) are similar to results for dataset 1a, based on analysis of annual data (Table 1). In the SMK tests on monthly data, two monthly "seasons" (January and April) in dataset 1b (1998-2014, 59 sites) are significant ($p < 0.05$) with a third monthly "season" (August) near-significant at $p = 0.06$. For datasets 2b (1999-2014, 66 sites) and 3b (2000-2014, 75 sites), August is the only monthly "season" in either time series to be close to significance at $p = 0.06$. Trends in individual monthly "seasons" are therefore weak and results between the MK and seasonal MK tests on monthly data are similar (Table 1).

3.5.2 Linear regression parametric time series analysis

<INSERT TABLE 2>

The parametric linear regression time series trend analysis was also performed on the different data groupings. Results of the linear regression tests are summarised in Table 2, and a comparison of trends from the Mann-Kendall with the linear regression approach is provided in Figure 12 for annual datasets 1a, 2a, 3a, and Figure 13 for monthly datasets 1b, 2b, 3b. A similar approach to the Mann-Kendall was taken to assess the relative change, by calculating the % relative change from the estimated NH_3 concentration at the start (y_0) and at the end (y_i) of the time series ($100*[(y_i-y_0)/y_0]$) computed from the linear regression slope and intercept. The different data groupings all show small, but non-significant decreasing trends (relative change = –2.4 % to –5.3 %), similar to the trends and % relative median change from the MK and SMK analysis (Figure 12, Figure 13). This suggests that the the errors in the NAMN data are normally distributed and that no or few outliers are present, since the results from the non-parametric Mann-Kendall are very similar to the parametric least squares linear regression.

<INSERT FIGURE 12>

<INSERT FIGURE 13>

3.5.3 Trends in NH_3 concentrations *vs* trends in NH_3 emissions

Overall, the long-term NH_3 concentration data from the UK NAMN suggests evidence of a small, but non-significant decreasing trend (Figure 12, Figure 13). The level of reduction observed in the datasets is however less than the 16.3 %, 15.6 % and 13.1 % reduction in estimated UK NH_3 emissions over the periods 1998-2014, 1999-2014 and 2000-2014, respectively (Tables 1,2). Inventories have inherent uncertainties such as uncertainties in activity data and emission factors, or may be missing emission sources. In terms of measurement data, it has already been shown in Sects. 3.1 and 0 that the annually averaged data mask considerable spatial and seasonal variability in NH_3 concentrations. Drivers contributing to this variability include the influence of climate on emissions, variations in management practice for a particular emission source, and influence of local emission sources and interactions on concentrations at a site. In addition, once emissions have taken place, the resulting atmospheric NH_3 concentrations are influenced by local deposition, which is in turn affected by receptor surfaces and by concentrations of interacting chemical species that affect atmospheric lifetime and transport distance of NH_3 and physical dispersion (e.g. Bleeker et al., 2009; Sutton et al., 2013). In the following sections, we consider the possibility of interactions with climate, emission source type and chemical interactions as this may affect long term trends in NH_3 concentrations.

3.5.4 Influence of climate

UK temperature and rainfall varied from year to year over the period 1998 to 2014 (Figure 11), with no clear relationship with NH_3 easily visible in the graph. Plotting the annual mean NH_3 concentrations against the average temperature and rainfall however does show indicatively that elevated annual mean NH_3 concentrations are observed in warmer years, and reduced annual mean NH_3 concentrations are observed in wetter years (Supp. Figure S3). This analysis for the full network is therefore consistent with the observation at a remote site (Inverpolly, Figure 9). The thermodynamic equilibrium shifts NH_3 from the aqueous (or particulate) phase to the gas phase with increased temperature, hence emissions from animal manures, soils and vegetation increase with increasing temperature (Asman et al., 1998; Sutton et al., 1993). Conversely, increases in precipitation decrease NH_3 emissions because rain events dilute the available NH_3 pool, while having the potential to wash urea and NH_x in solution from the surface. As NH_3 is soluble and washed out of the atmosphere by rainfall, this should also contribute to reduced NH_3 concentrations during wet periods.

An exception to this relationship can occur where N is excreted as uric acid from birds (e.g. poultry). In this case, sufficient water is needed to allow hydrolysis to form NH_3 (Riddick et al., 2014). In this situation, the arrival of rain promoted uric acid hydrolysis from seabird guano surfaces, which was limited in the absence of soil moisture. It is possible that this interaction could lead to NH_3 emissions from field spreading of poultry litter to be larger in wetter years. In a recent trend analysis of NH_3 concentrations from the Dutch Air Quality Monitoring Network, an attempt was also made to correct for meteorological (temperature and rainfall) influences for the eight monitoring stations, which broadly produced similar results with slightly enhanced statistical significance for the trends (van Zanten et al., 2017).

3.5.5 Influence of local emission sources

<INSERT FIGURE 14>

<INSERT FIGURE 15>

The inter- and intra-annual variability is also expected to be linked to influences from local emission source and activities. It has already been shown in Sect. 3.1 that the concentrations of NH_3 in air are greatest in parts of the country with a large presence of livestock farming, particularly in areas of pig, poultry and cattle farming. Using the classification of NAMN sites according to dominant emission source sectors described in Sect. 3.1, the long-term change in NH_3 concentrations at sites grouped into four different emission source sectors: background, sheep, cattle, and pigs and poultry are compared in Figure 14 (annual mean data) and Figure 15 (monthly mean data). Results of the Mann-Kendall time series trend analysis are summarised in Table 3 and results of linear regression analysis are summarised in Table 4. A comparison of trends in measured NH_3 concentrations with trends in NH_3 emissions for the different source types then provided indicative evidence to support and inform the national emission inventory compilation. In Figure 16, the relative changes in UK emissions between 1998 and 2014 are compared with relative changes in mean measured NH_3 concentrations for all NAMN sites, and for grouped sites classified as dominated by cattle, pigs & poultry, and sheep.

<INSERT TABLE 3>

<INSERT TABLE 4>

For the 17 sites in cattle dominated areas, there is an increasing, but non-significant trend. Overall, based on MK analysis of annual data, the relative change from 1998 to 2014 is a 12 % increase (Table 3, Figure 14), compared with a smaller increase of 4 % from linear regression (Table 4, Figure 14). With the monthly data, there is no discernible trend (–0.9 % (MK); 1.4 % (LR)). In the seasonal MK test on monthly data (% relative median change = 3.9 %), no monthly "seasons" are significant, with only January approaching significance at $p = 0.07$. The near-significant trend for January is likely to be due to unusually high NH_3 concentrations recorded in January at some sites in the first few months of the time series, attributed to manure spreading activities taking place in the winter months when the ground was frozen (confirmed by local observations), in direct contravention of good farming practice.

In terms of UK cattle NH_3 emission, this has a decreasing trend with an estimated 11% decrease since 1998 (Figure 16, Table 5), and is therefore clearly in contrast to the non-discernible or small increasing trend (non-significant) in NH_3 concentrations from cattle sites. In principle, a signal related to substantial livestock changes associated with the 2000 outbreak of Foot and Mouth Disease might have been expected. However, this outbreak was actually rather localized in north-west England and south-west England, and was followed by substantial restocking from 2001 (Sutton et al., 2006) and there was no detectable signal of FMD in the average for cattle-dominated areas.

<INSERT FIGURE 16>

<INSERT TABLE 5>

By contrast, in pig and poultry dominated areas (9 sites) there is a decreasing trend with significant reduction in measured NH_3 concentrations between 1998 and 2014 (–22 % (MK), $p = 0.02$, Table 3; –21 % (LR), $p = 0.06$, Table 4) from analysis of annual data (Figure 14). For the monthly data, the overall change based on linear regression is also a 22 % decrease ($p = 0.02$) (Table 4, Figure 15), compared with a larger level of decrease based on MK analysis (–32 %, $p = 0.01$) (Table 3, Figure 15). The SMK test also show a significant decreasing trend (–11 %, overall $p < 0.001$), with 6 of the 12 monthly "seasons" showing significant trends (Feb, Jun, Nov, Dec: $p <0.05$, Oct: $p < 0.01$, Jan: $p < 0.001$). A decrease in emissions from pig and poultry of 39 % between 1998 and 2014 (Figure 16, Table 5) is therefore broadly supported, although not matched by a similar decrease in measured NH_3 concentrations.

For sheep dominated sites (4 sites), there is an increasing trend in NH_3 (MK: +16 %, $p = 0.17$, Table 3; LR: 20 %, $p = 0.09$, Table 4) between 1998 and 2014 in the annual data (Figure 14). The monthly data also show a similar upward trend (Figure 14) with relative change in concentrations of +19% based on MK ($p = 0.10$) (Table 3) and +17% based on LR ($p = 0.14$) (Table 4). The increasing trend at sheep sites is therefore in contrast to the estimated 24 % decrease in NH_3 emissions from this sector since 1998 (Figure 16, Table 5). For the SMK test, no individual monthly "seasons" were significant, although 3 of the monthly "seasons" approached the significance level (Apr, Dec: $p = 0.08$, Oct: $p = 0.09$). Overall, the increasing trend from the SMK test is significant at $p < 0.01$. While the Sen's trend slope from both MK and SMK tests were comparable, at 0.0036 and 0.0033 µg NH_3 y^{-1}, respectively, the % relative median change results computed from them are very different (MK = 16 % *cf* SMK = 210 %), because the intercepts of the fitted Sen's trend slopes are different (MK = 0.289 µg NH_3 m^{-3} *cf* SMK = –0.0267 µg NH_3 m^{-3}). Caution therefore needs to be exercised when interpreting the % relative change results, especially at sites with low NH_3 concentrations, which must be examined together with the fitted trends.

At background sites (5 sites where total NH_3 emissions for the respective 5 km grid squares are estimated at <1 kg N ha^{-1} y^{-1}), NH_3 concentrations also appear to have increased (non-significant). Based on the MK analysis for the period 1998 to 2014, NH_3 concentrations increased overall by 18 % and 13 % from the analysis of annual and monthly data, respectively (Table 3). Results from linear regression were similar, with an overall increase of 13 % and 12 % from analysis of the annual and monthly data, respectively (Table 4). Similar to sheep sites, the % relative median change estimated from the seasonal MK Sen's slope and intercept (+ 49%) is larger than from the classic MK Sen's slope (+13%) due to differences in the intercepts of the fitted trend lines (MK = 0.1528 µg NH_3 m^{-3} *cf* SMK = 0.0388 µg NH_3 m^{-3}) since the trend slopes are the same (0.0012 µg NH_3 y^{-1}). Overall, the SMK test show a significant increasing trend in the monthly data ($p = 0.05$). No individual monthly "seasons" were significant, with March, April and November monthly "seasons" approaching the significance level ($p = 0.09$).

As with the annual UK-wide long-term datasets (Sect. 3.5), it is useful to consider the significance of the NH_3 trends for the groupings of sites according to dominant emission source sectors. Table 3 and Table 4 shows that neither the annual nor the monthly time series showed a significant change in NH_3 concentrations for the cattle dominated sites. In the case of pig and poultry dominated sites, the decrease in measured NH_3 concentrations was significant for both the annual and monthly datasets. For sheep dominated and backgrounds sites, the estimated increase in NH_3 concentrations was not significant based on the MK and linear regression tests on the annual and monthly data, but was significant based on the SMK test of the monthly data. Overall, these statistics confirm significant differences between NH_3 trends for sites dominated by different source types, with concentrations decreasing at pig and poultry dominated sites, concentrations increasing at sheep dominated and background sites, and no significant trend at cattle dominated sites (Table 5).

3.5.6 Changing chemical climate and effects on long-term trends in NH_3 and NH_4^+

Other pollutants that affect NH_3 concentrations in the atmosphere include SO_2 and NO_x emissions, which determine rates of secondary inorganic aerosol formation and therefore the lifetime of NH_3 in the atmosphere. UK emissions of SO_2 are estimated to have declined significantly by 81 % from 1.6 million tonnes in 1998 to 0.3 million tonnes in 2014 (Defra, 2015). Similarly, NO_x emissions over the same period are estimated to have fallen by 50 % from 2 million tonnes to 1 million tonnes (Defra, 2015). The reaction of NH_3 with H_2SO_4 to form $(NH_4)_2SO_4$ is effectively irreversible (in the absence of in-cloud reprocessing), whereas an equilibrium exists between gaseous NH_3 and particulate NH_4NO_3 and NH_4Cl components which are appreciably volatile at ambient temperatures. A change in the particulate phase from $(NH_4)_2SO_4$ to NH_4NO_3 suggests that NH_3 will remain longer in the atmosphere, since NH_4NO_3 is volatile and releases NH_3 in warm weather.

Elsewhere, a mismatch between reported trends in emissions and measurement data have similarly been investigated. The question of the ‘Ammonia Gap’ in the Netherlands was debated over a number of years. There, the estimated reduction in emissions due to mitigation measures was not matched by expected decreases in measured NH_3 concentrations in air and/or NH_4^+ in precipitation (Erisman et al., 2001; Bleeker et al., 2009; van Zanten et al., 2017). Similarly in Hungary, monitored NH_3 concentrations from long-term measurements did not match the estimated reduction in NH_3 emissions following the decline in agricultural livestock population and fertiliser usage after political changes in 1989 (Horvath and Sutton, 1998). This was subsequently attributed to a reduction in SO_2 emissions over the same period, increasing the atmospheric lifetime of NH_3 (Horvath et al., 2009).

Dry deposition of SO_2 and NH_3 are enhanced in the presence of both gases, an interaction referred to as “co-deposition” (Fowler et al., 2001). The acid-base neutralization by each of the gases provides an efficient sink for dry deposition on leaf surfaces and deposition enhancement for each gas depends on the relative air concentrations of NH_3 and SO_2. For SO_2, the dry deposition process has been shown to be strongly influenced by ambient concentrations of NH_3 because the surface resistance is regulated mainly by uptake in moisture on foliar surfaces, which, in turn, is strongly influenced by the presence of NH_3. The large reduction in SO_2 emissions and ambient concentrations, compared with the relative stagnation in NH_3 emissions and concentrations over the same period has meant that the SO_2/NH_3 ratio has decreased dramatically. This has led to a systematic decrease in canopy resistance to uptake of SO_2 on surfaces, increasing dry deposition of SO_2 in the UK (ROTAP 2012). The underlying cause of the decrease in surface resistance is that the ambient NH_3 is sufficient to neutralize acidity from the solution and oxidation of deposited SO_2, maintaining large rates of deposition.

Similar interactions are seen to be occurring in the UK based on the NAMN data, where the concurrent reduction in SO_2 and NO_x emissions over the same period (Figure 18b) should theoretically lead to a longer atmospheric lifetime of NH_3, thereby increasing NH_3 concentrations in the UK, especially in remote areas. The interpretation of the NH_3 and NH_4^+ measurement data can further be aided by comparison with particulate nitrate (NO_3^-) and sulphate (SO_4^{2-}) data from the UK AGANet that are made concurrently with the NAMN NH_3 and NH_4^+ measurements at 30 sites (see Sect. 2.2). There is close agreement between the aerosol components, with a near 1:1 relationship between NH_4^+ and the sum of NO_3^- and SO_4^{2-}, lending support that particulate NH_4^+ in the UK is mainly derived from NH_3 and acidic gases such as SO_2 and NO_x to form $(NH_4)_2SO_4$ and NH_4NO_3, respectively (Conolly et al., 2016). For particulate NH_4^+, it has already been shown in Sect. 0 that this regional species has less of a relationship to the dominant NH_3 source sectors; trend analysis was therefore undertaken using all NH_4^+ site data combined. As with the NH_3 time series analysis, sites with incomplete data runs for particulate NH_4^+ due to reduced density of NH_4^+ measurements and site changes occurring from 2001-2006 were excluded (see Sect. 2.2.1).

<INSERT TABLE 6>

Two data series for NAMN NH_4^+ data were selected for analysis, i) 23 sites with complete NH_4^+ time series from 1999 to 2014, and ii) 30 sites with complete NH_4^+ time series from 2006 to 2014. Both time series show a large significant downward trend in NH_4^+ ($p < 0.01$) (Table 6, Supp. Figure S4). Overall, MK and LR tests show a significant decrease in NH_4^+ concentrations by 47 % and 49 %, respectively, between 1999 and 2014 and by 44 % and 43 %, respectively, between 2006 and 2014 (Table 6, Supp. Figure S4). By contrast, concurrent NH_3 data from the same sites over the same time periods showed a much smaller, non-significant downward trend between 1999 and 2014 (–17 % (MK); –18 % (LR)), and no discernible trend between 2006 and 2014 (+ 3 % (MK and LR)) (Table 6). This reduction in particulate NH_4^+ can be seen to be closely associated with parallel decreases in particulate SO_4^{2-} and NO_3^- concentrations from AGANet (Table 7, Figure 18a), which are themselves associated with reductions in SO_2 and NO_x emissions (Table 7, Figure 18b).

<INSERT FIGURE 17>

<INSERT FIGURE 18>

<INSERT TABLE 7>

The comparisons above therefore suggest that reductions in SO_2 and NO_x emissions over the period have led to a lower formation of particulate NH_4^+ in the atmosphere. Further evidence in support of this is indicated by plotting the ratio of NH_3/NH_4^+ (Figure 17b), which has increased from 1.8 in 1999 to 2.8 in 2014. This demonstrates how a larger fraction of the reduced N is staying in the gas phase as NH_3, increasing its atmospheric residence time and maintaining NH_3 concentrations at a higher level than solely based on NH_3 emission trends. Although the overall changes in NH_3 concentrations in the UK dataset are small and in many cases not significant for particular data groupings, they are consistent with similar phenomena observed in Hungary, the Netherlands and Denmark (Horvath et al., 2009; Erisman et al., 2001; Sutton et al., 2003; Bleeker et al., 2009).

4. CONCLUSIONS

Spatial and temporal trends in NH_3 are found to be related to variability in emission source types across the UK and also to be influenced by changes in environmental conditions. Extensive spatial heterogeneity in NH_3 concentrations was observed, with lowest annual mean concentrations at remote sites (< 0.2 µg m^{-3}) and highest in the areas with intensive agriculture (up to 22 µg m^{-3}). NH_4^+ concentrations show less spatial variability (e.g. range of 0.14 to 1.8 µg m^{-3} annual mean in 2005) with a general decreasing gradient from the south-east to the north-west of the UK, due to both regional differences in NH_3 concentrations and import of particulate matter into south-east England from Europe.

Peak NH_3 concentrations are observed in summer at background sites (defined by 5 km grid average NH_3 emissions <1 kg N ha^{-1} y^{-1}) and in areas dominated by sheep farming, driven by increased volatilization of NH_3 in warmer summer temperatures. In areas where cattle, pig and poultry farming is dominant, the largest NH_3 concentrations are in spring and autumn, matching periods of manure application to fields. By contrast, peak concentrations of NH_4^+ aerosol occur in spring from long-range transboundary sources. The spatial and seasonal patterns established for sites influenced by different emission source sectors are important for providing a foundation to understanding NH_3 exchange processes, impacts and the UK NH_3 budget, and to inform abatement strategies.

Official published estimates of UK NH_3 emissions are estimated to have declined by 16.3 % between 1998 and 2014. The long-term NH_3 concentration data from the UK NAMN suggests evidence of a smaller, but non-significant decreasing trend (–6.3 % (MK); –3.1 % (LR)), based on analysis of annually averaged data ($n = 59$) over the same period (Table 2). Analysis of annually averaged data for different groupings of the NAMN dataset for the time periods 1999-2014 ($n = 66$) and 2000-2014 ($n = 75$) also gave similar results. In each case, the level of reduction observed in the datasets (1999-2014: 0.0 % (MK) *vs* –3.0 % (LR); 2000-2014: 0.0 % (MK) *vs* –2.8 % (LR)) is less than the 15.6 % and 13.1 % reduction in estimated UK NH_3 emissions over the periods 1999-2014 and 2000-2014, respectively (Table 2).

In areas with intensive pig and poultry farming, there is a significant downward trend in NH_3 concentrations from the analysis of annually averaged data (–22 % (MK), $p = 0.02$; –21 % (LR), $p = 0.06$) that is consistent with, but not as large as the decrease in estimated NH_3 emissions from this sector over the same period (–39 %) (Table 5). By contrast, in cattle-dominated areas, there is evidence of a small increasing, but non-significant trend in NH_3 concentrations (+12 % (MK); +3.6 % (LR): annually averaged data), despite the decline in NH_3 emissions from this sector since 1998 (–11%) (Table 5). At background and sheep dominated sites, NH_3 concentrations increased (non-significant) over the monitoring period

(Table 5). These increases in NH_3 concentrations at background (+17 % (MK); +13 % (LR): annually averaged data) and sheep dominated sites (+15 % (MK); +19 % (LR): annually averaged data) are consistent with decreasing SO_2 emissions (and to a lesser extent NO_x emissions) associated with a change in the PM from $(NH_4)_2SO_4$ to NH_4NO_3, the latter being volatile and releasing NH_3 in warm weather.

Particulate NH_4^+ represents a secondary pollutant formed from NH_3 and oxidation products of acidic gases such as SO_2 and NO_x. As the emissions of these acidic gases have reduced over the past years, the ratio between NH_3 and NH_4^+ has increased from 1.8 to 2.8 between 1999 and 2014. These changes are consistent with observed decreases in particulate SO_4^{2-} and NO_3^- concentrations that are associated with decline in SO_2 and NO_x emissions over the same period. This effect appears to be of sufficient magnitude to explain the lack of overall decrease in NH_3 concentrations, where the decrease in NH_4^+ is larger than for NH_3 at corresponding sites. Overall, UK annual particulate NH_4^+ concentrations decreased by –47 % (MK) and –49 % (LR) for period 1999 -2014, associated with a slower formation of particulate NH_4^+ in the atmosphere from gas-phase NH_3. The findings are consistent with a parallel change in partitioning from particulate NH_4^+ to gaseous NH_3 as also detected in Hungary, the Netherlands and Denmark.

Until now, only a modest commitment has been agreed to reduce European NH_3 emissions. By contrast, SO_2 and NO_x emissions have decreased over Europe over the past decades, and are projected to decrease further under the revised Gothenburg Protocol and revised NECD. As a result, the importance of NH_3 relative to oxidised N and SO_2 emissions is expected to continue to increase over the next decades, playing a significant role in the formation of fine PM and contributing to ecosystem effects through N deposition. With longer atmospheric lifetimes of gaseous NH_3 and little commitment to reduce emissions, combined with climate warming effects tending to increase NH_3 emissions, there is a substantial risk that exceedance of the NH_3 critical levels may increase in the future, exacerbating the threat to the most sensitive semi-natural habitats. The growing relative importance of reduced nitrogen to total acidic and total nitrogen deposition indicates that future strategies to tackle acidification and eutrophication will need to include measures to abate emissions of NH_3.

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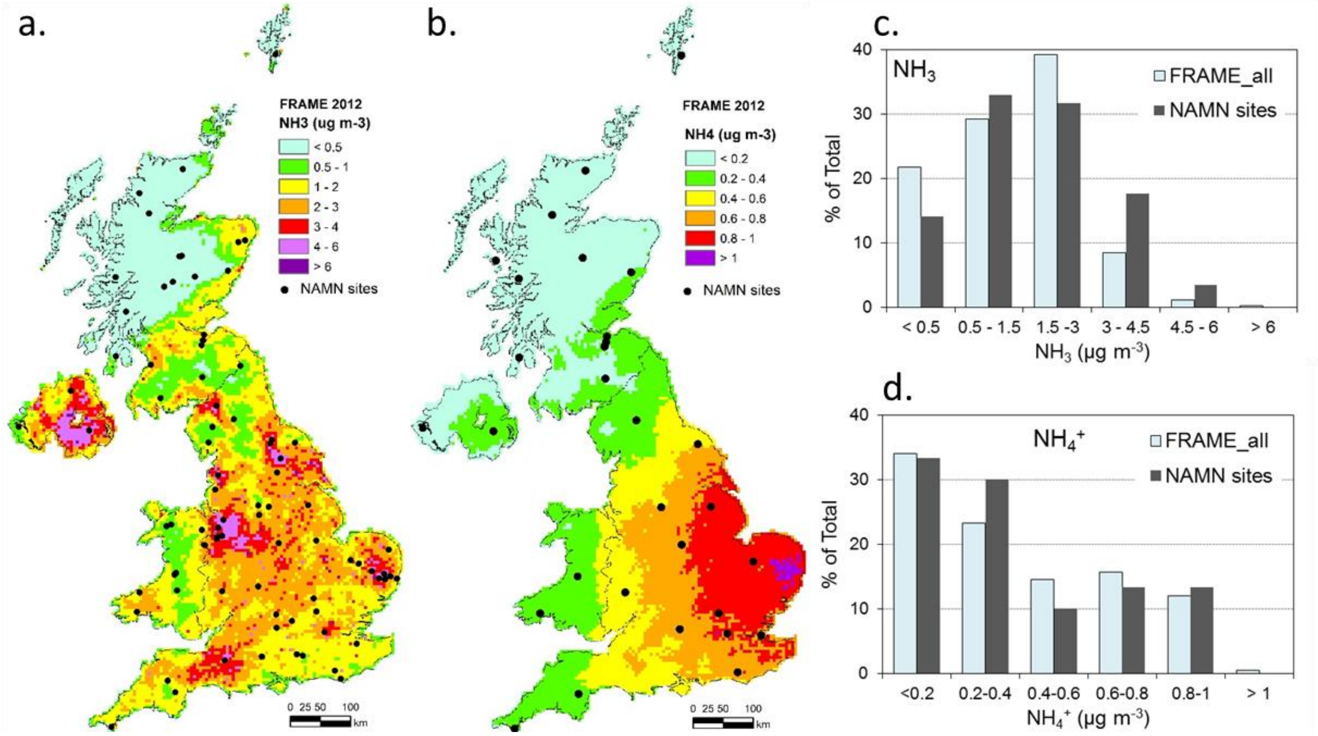


Figure 1: Maps of modelled annual mean concentrations of (a) NH_3 and (b) NH_4^+ at 5 km × 5 km grid resolution from the FRAME atmospheric transport model using 2012 UK emissions data, based on Dore et al. (2008), overlaid with the National Ammonia Monitoring Network (NAMN) measurement sites, and frequency distributions of the modelled concentrations of (c) NH_3 and (d) NH_4^+ for the FRAME 5 km grid squares containing a NAMN site (85 and 30 sites, respectively, in 2012) and for all model grid squares over the UK.

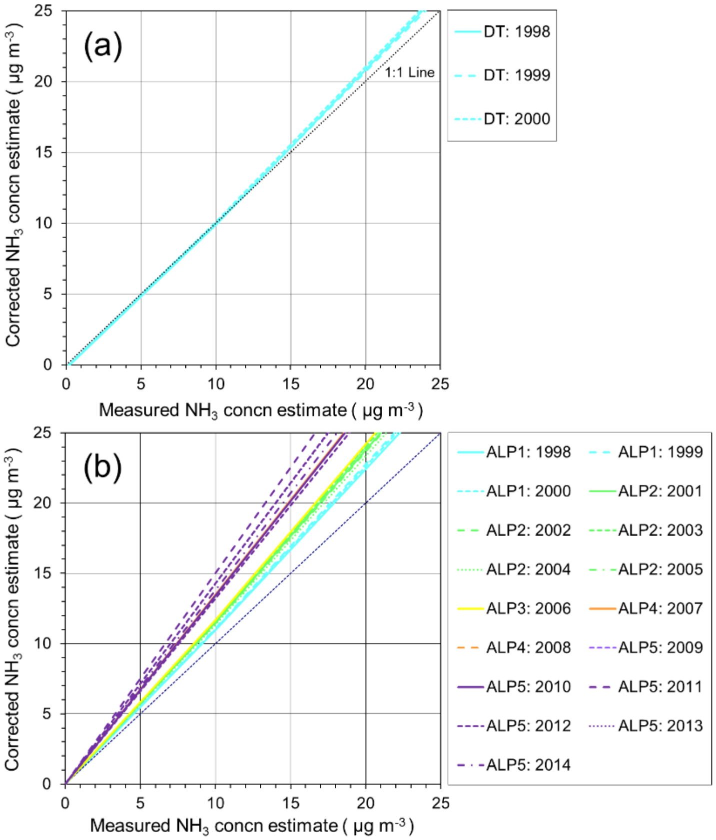


Figure 2: Comparison of annual empirical calibration curves for the passive samplers against the reference estimates from DELTA sampling at > 8 sites in the UK National Ammonia Monitoring Network (NAMN). (a) DT = Diffusion Tubes. (b) ALP = ALPHA samplers, ALP1 is prototype 1 (1998-2000), ALP2 (2001-2005) and ALP3-ALP5 were manufactured from injection moulds 1 and 2, respectively. ALP4 and ALP 5 = new inlet PTFE membrane (Swiftlab 07-OPM-027: 305 µm, regular polypropylene grid support material) that replaced the previous TE38 PTFE membrane (265 µm, randomly arranged polypropylene support material). ALP5 = new laboratory with analysis on FloRRia (previously on AMFIA).

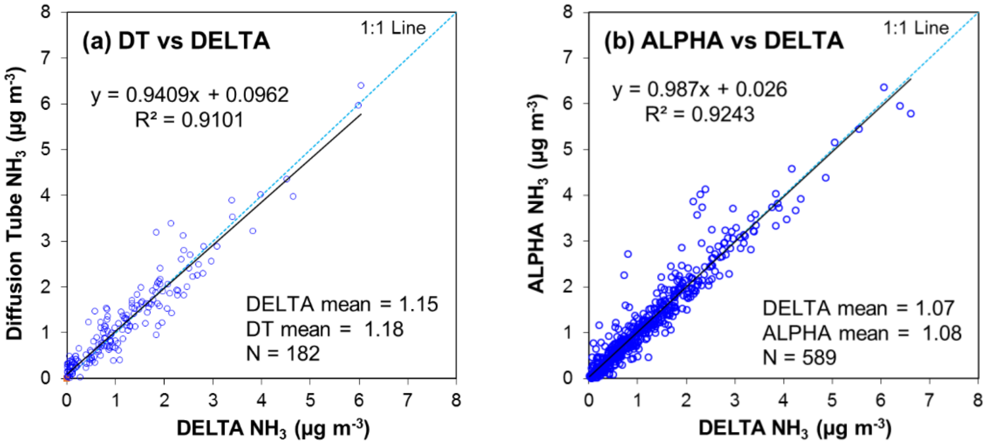


Figure 3: Regression of passive samplers vs DELTA measurements at >8 sites in the UK National Ammonia Monitoring Network (NAMN), showing results for (a) diffusion tubes (DT), used during the early years of the network (1998-2000), and (b) for ALPHA samplers (results shown are for 2009-2014 where all analyses were carried out at a new laboratory). All passive data shown are the monthly measured concentrations for each site using the calibrated data for the respective passive methods.

(a) (b) (c) (d)

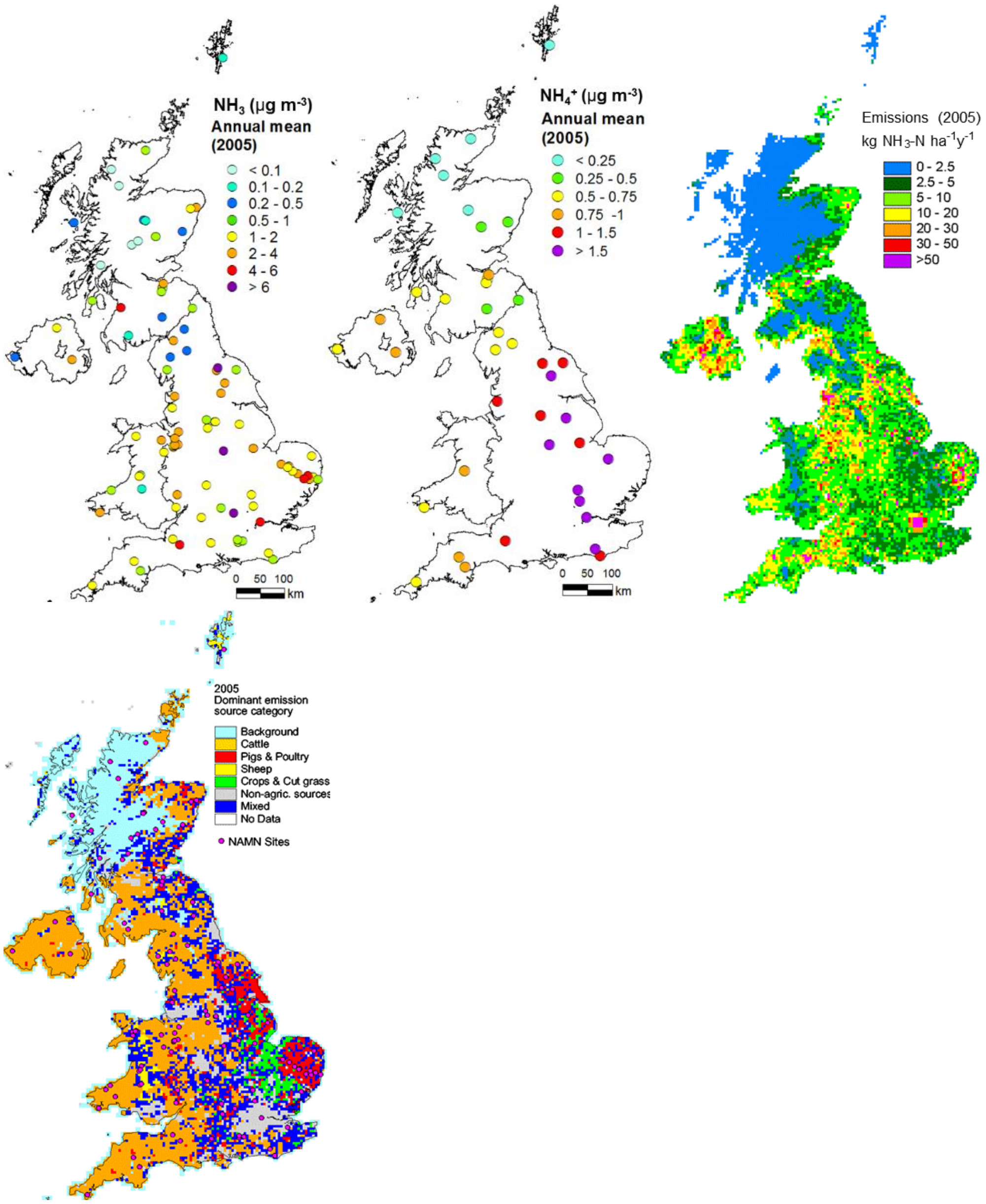


Figure 4: Measured annual mean concentrations from the UK National Ammonia Monitoring Network (NAMN) for 2005 for (a) NH_3 and (b) particulate NH_4^+, and maps at 5 km by 5 km grid resolution for 2005 of (c) the estimated annual NH_3 emissions (Dragosits et al. 2005) and (d) the dominant NH_3 emission source category (based on Hellsten et al., 2008), indicating the relationships between measured air concentrations and spatial variability in NH_3 sources emissions. The measurements show a broad pattern of small air concentrations across NW Scotland. Conversely, the largest concentrations occur in areas with intensive cattle, pig and poultry farming with high NH_3 emissions e.g. East Anglia in SE England.

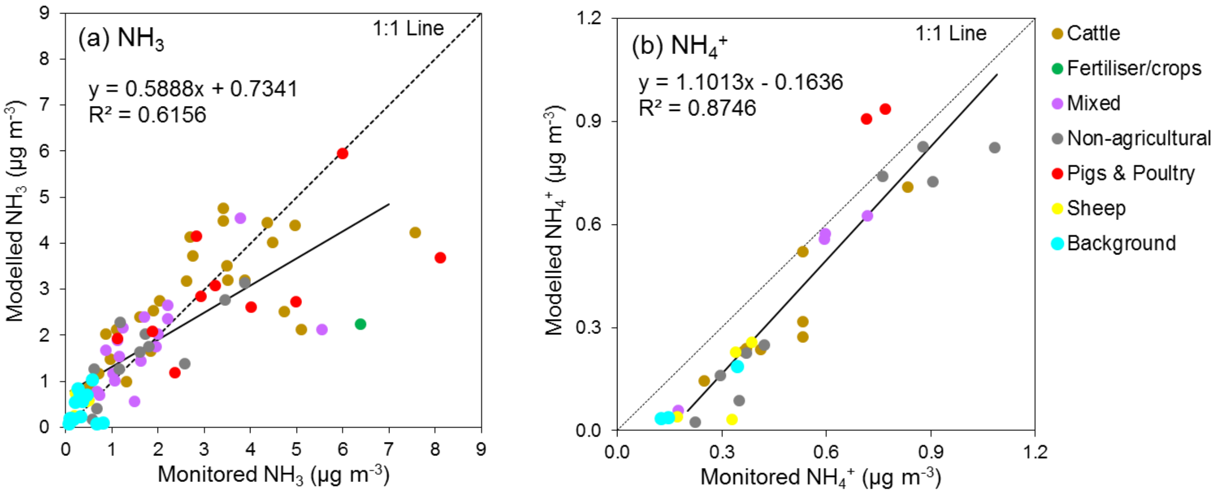


Figure 5: Comparison of 2012 annual mean concentrations of (a) NH_3 and (b) NH_4^+ modelled using the FRAME atmospheric model with 2012 measurements from the UK National Ammonia Monitoring Network (NAMN) for all sites according to dominant emission source classification.

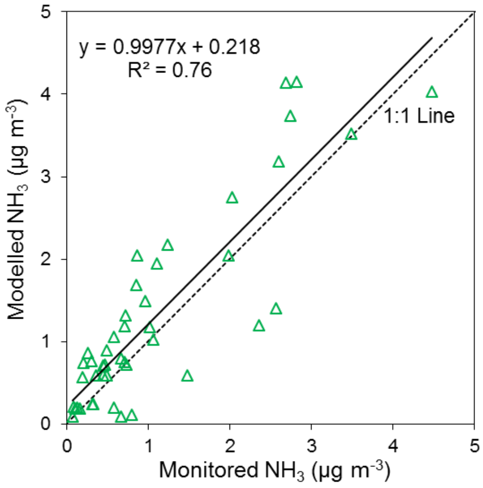


Figure 6: Comparison of 2012 annual mean concentrations of NH_3 from output of the FRAME atmospheric model with measurements from the UK National Ammonia Monitoring Network (NAMN) for a subset of sites classified as located in semi-natural or forest locations.

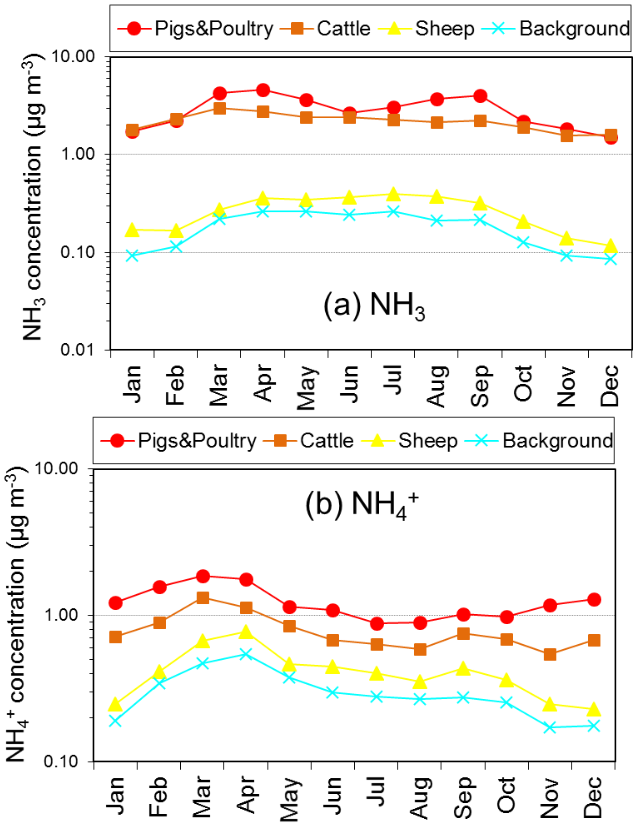


Figure 7: Seasonal trends in (a) NH$_3$ (mean monthly data for 1998-2014) and (b) NH$_4^+$ (mean monthly data for 1999-2014) concentrations of sites in the UK National Ammonia Monitoring Network (NAMN) classified according to four key emission source categories: cattle, sheep, pigs & poultry and background (based on 2005 dominant emission source classification). The concentrations are plotted on a log scale for better visualisation of the low concentration background and sheep profiles.

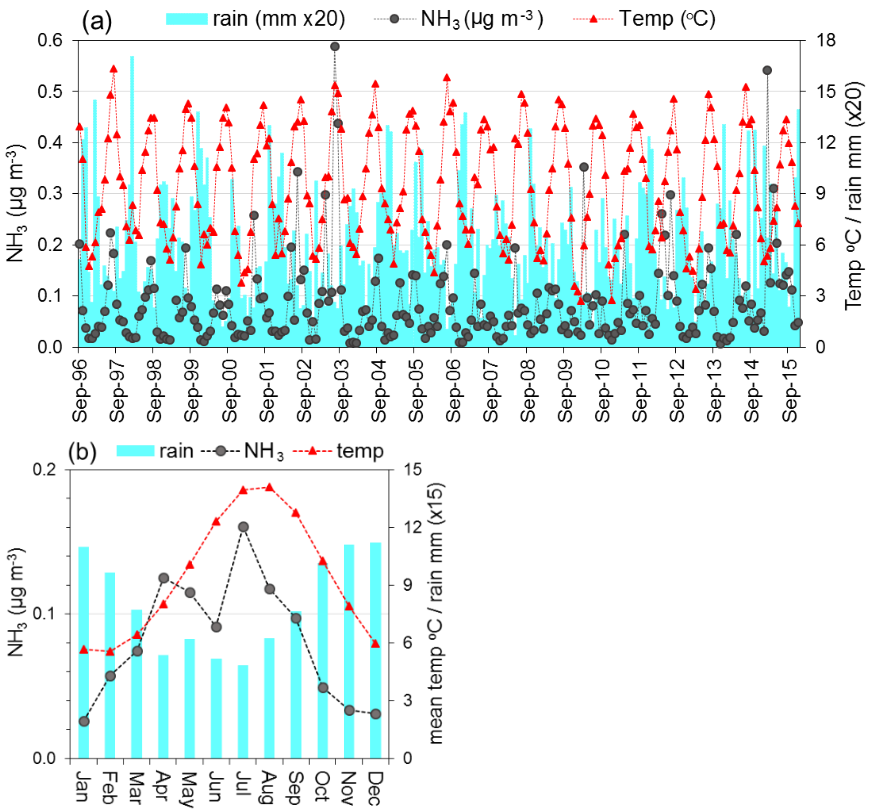


Figure 8: (a) Long-term trends in measured monthly-mean NH_3 concentrations at the remote background Inverpolly site in NW Scotland (UKA00457), demonstrating strong intra- and inter-annual variability, from the UK National Ammonia Monitoring Network (NAMN). Also plotted for comparison are monthly rainfall and temperature data from the nearby Aultbea meteorological station (ID no. 52; MetOffice, 2016). (b) Comparison of seasonal trends in NH_3 concentrations with temperature and rainfall at Inverpolly. Data shown are averaged over the period 1996 – 2015. Peak concentrations of NH_3 can be seen to coincide with summer maxima in the temperature profile, while the lowest concentration occur in winter when the temperature is lowest and also when rainfall is generally highest.

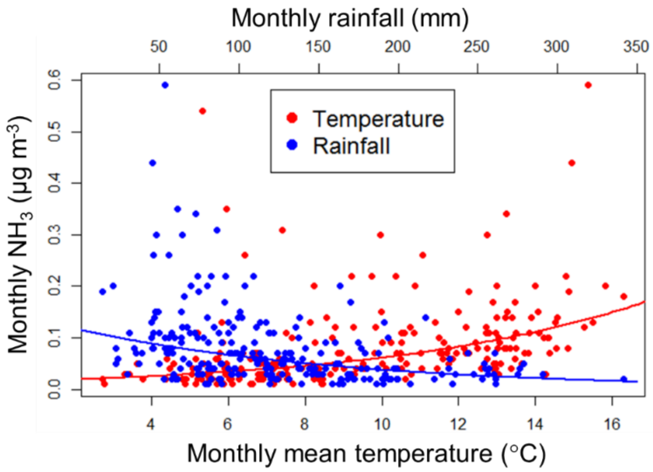


Figure 9. Relationships between measured monthly-mean NH_3 concentrations from the UK National Ammonia Monitoring Network (NAMN) and mean monthly temperature and rainfall at Inverpolly (UKA00457). NH_3 was negatively correlated with rainfall (blue line: $\mathrm{Log}(NH_3) = -0.0059*\mathrm{Log}(rain) – 2.1612$, $R^2 = 0.19$, $n = 231$, $p < 0.05$) and positively correlated with temperature (red line: $\mathrm{Log}(NH_3) = 0.1482*\mathrm{Log}(temp) – 4.2708$ $R^2 = 0.33$, $n = 231$, $p < 0.05$). Rain and temperature data are from the nearby Aultbea meteorological station (ID no. 52; MetOffice, 2016).

(a)

(b)

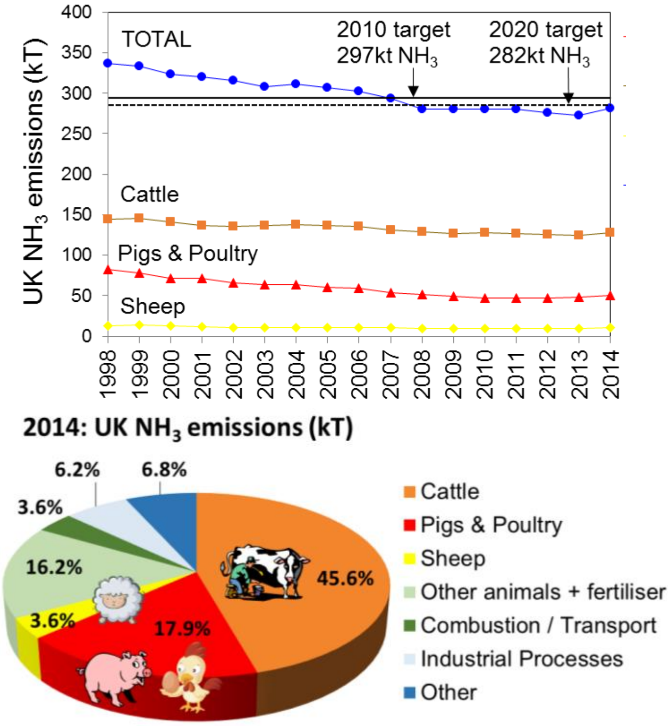


Figure 10: (a) Trends between 1998 and 2014 in the UK National Atmospheric Emission Inventory (NAEI) for total UK NH_3 emissions and selected sub-sources: cattle, pigs & poultry and sheep. The 2010 NH_3 national emissions ceilings target of 297 kt (Gothenburg protocol and NECD) and the 2020 target of 282 kt (revised Gothenburg protocol) area are also shown for comparison. (b) UK NH_3 emission sources in 2014. Data from *http://naei.defra.gov.uk/* and Misselbrook et al. 2015.

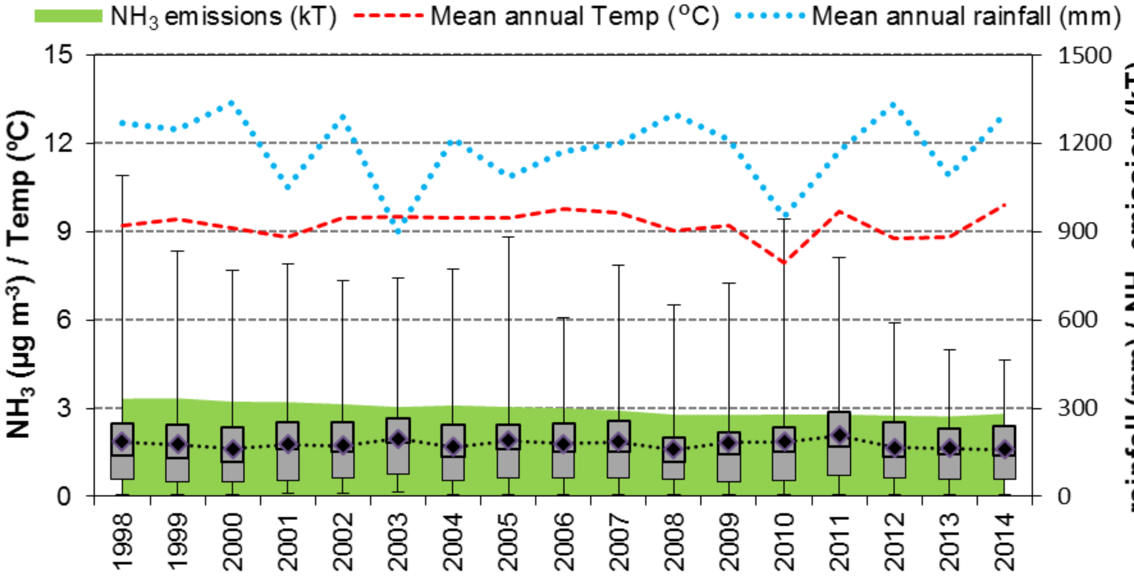


Figure 11: Changes in annual mean atmospheric NH_3 concentrations averaged over all sites in the National Ammonia Monitoring Network (NAMN) operational between 1998 and 2014 (59 sites). The diamonds show the mean NH_3 concentration, with the grey box indicating the median and interquartile range, while the error bars show the range (minimum and maximum) of measured mean concentrations. Annual mean UK meteorological data (source *http://www.metoffice.gov.uk/*) are also plotted for comparison over the same period. 2010 was an unusual year, characterised by a considerably lower than average mean annual temperature of 7.9 °C due to exceptionally cold winters, with Dec 2010 recorded as the coldest for over 100 years (*cf.* mean = 9.2 °C for 1998 to 2014) and lower than average rainfall of 950 mm (*cf* mean = 1190 mm for 1998 to 2014).

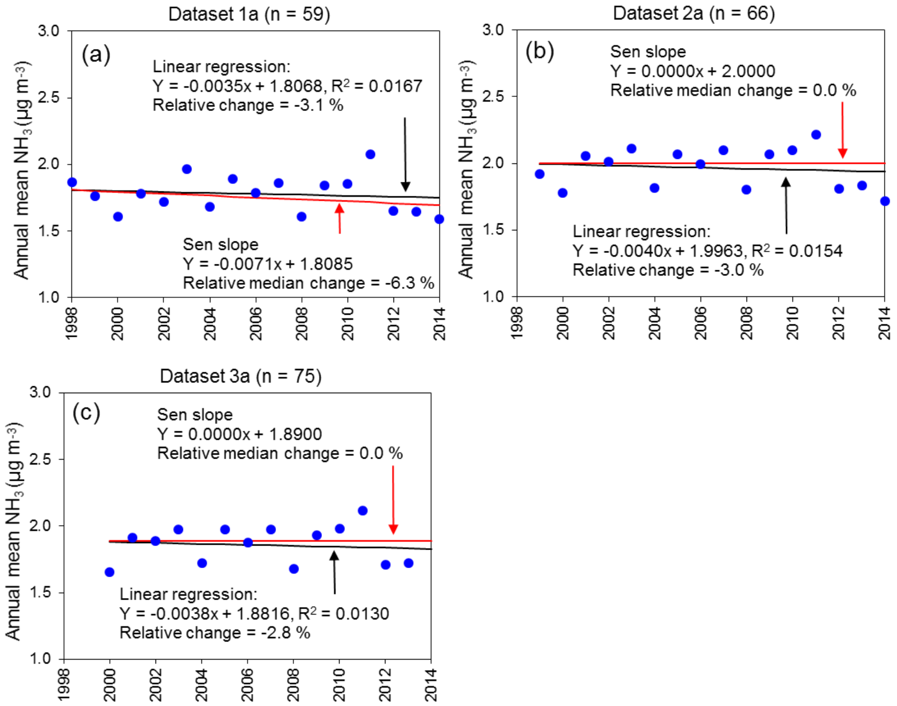


Figure 12: Time series trend analysis by non-parametric Mann-Kendall Sen slope *vs* parametric linear regression on annually averaged NH_3 concentrations from the UK National Ammonia Monitoring Network (NAMN) for a) dataset 1a (1998-2014, *n*=59), b) dataset 2a (1999-2014, *n*= 66) and c) dataset 3a (2000-2014, *n*=75). Individual data points are annually averaged NH_3 concentrations.

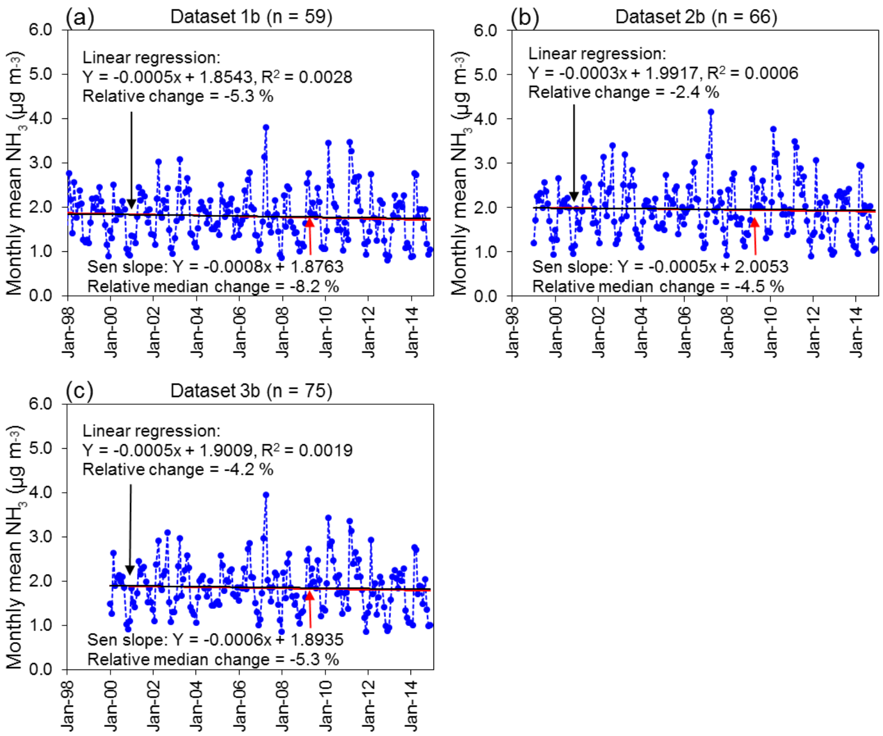


Figure 13: Time series trend analysis by non-parametric Mann-Kendall Sen slope *vs* parametric linear regression on monthly mean NH_3 concentrations from the UK National Ammonia Monitoring Network (NAMN) for a) dataset 1b (1998-2014, *n*=59), b) dataset 2b (1999-2014, *n*= 66) and c) dataset 3b (2000-2014, *n*=75). Individual data points are monthly mean NH_3 concentrations.

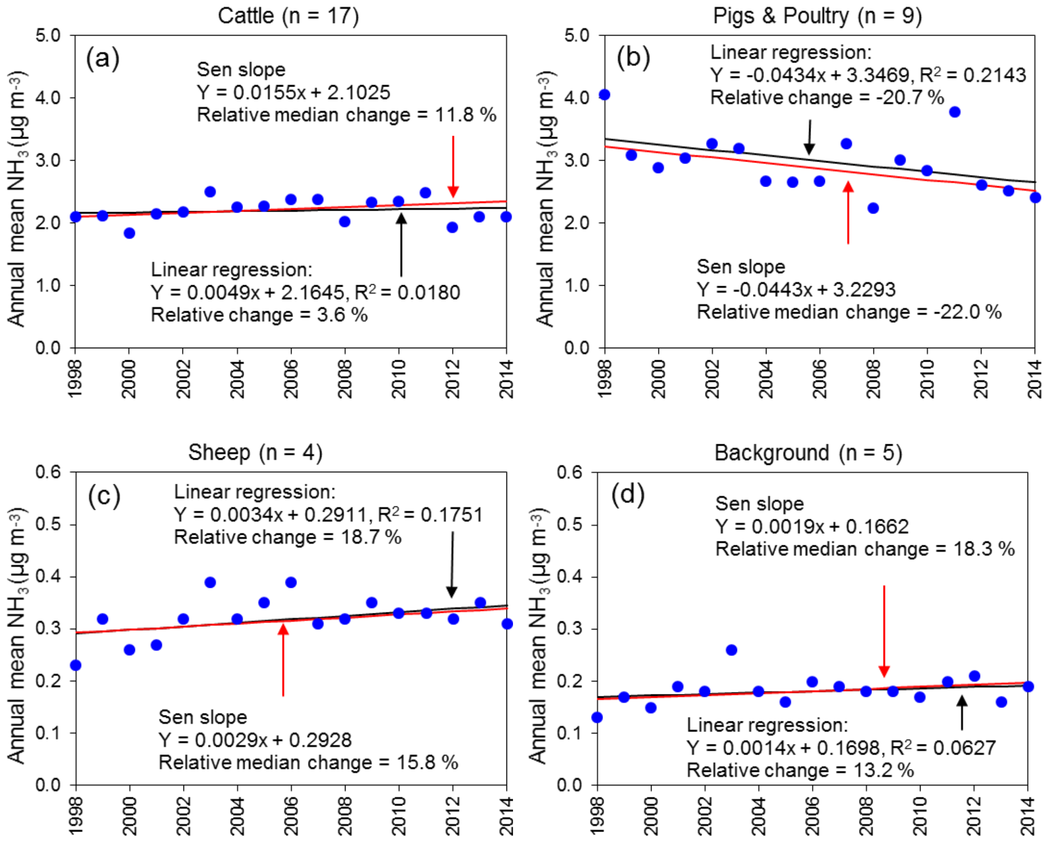
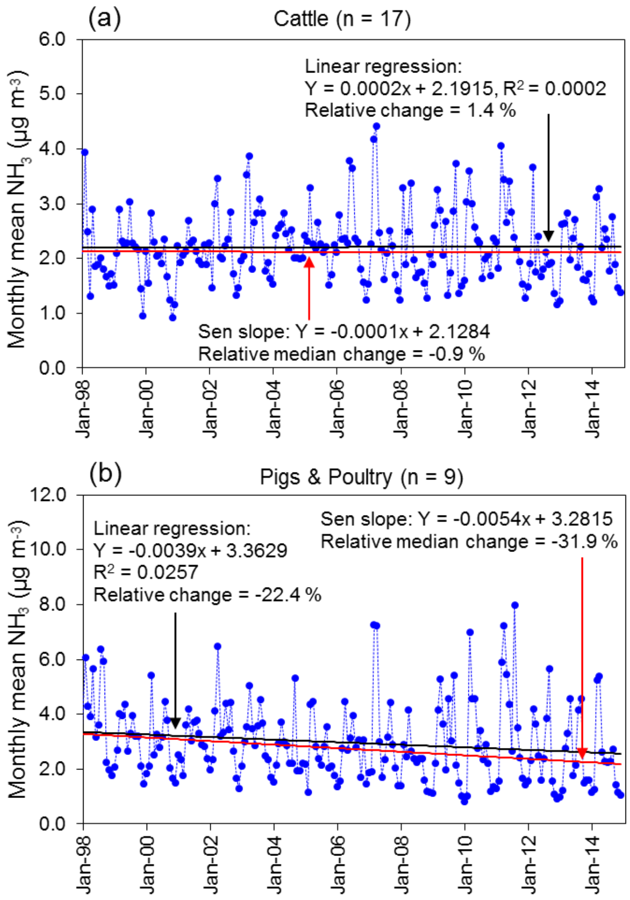


Figure 14: Time series trend analysis by non-parametric Mann-Kendall Sen slope *vs* parametric linear regression on annually averaged NH_3 concentrations from the UK National Ammonia Monitoring Network (NAMN) for sites in 5 km grid squares classed as dominated by (a) cattle (> 45 % of total NH_3 emissions from this category in a grid square); (b) pigs & poultry (> 45 % of total NH_3 emissions from this category in a grid square); (c) sheep (> 45 % of total NH_3 emissions from sheep in a grid square); (d) NAMN sites in grid squares classed as background (defined as grid squares with average NH_3 emissions <1 kg N ha^{-1} y^{-1}). Individual data points are annually averaged NH_3 concentrations.


(a)
Cattle (n = 17)
Monthly mean NH_3 (µg m^{-3})
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Linear regression:
Y = 0.0002x + 2.1915, R^2 = 0.0002
Relative change = 1.4 %
Sen slope: Y = -0.0001x + 2.1284
Relative median change = -0.9 %
Jan-98
Jan-00
Jan-02
Jan-04
Jan-06
Jan-08
Jan-10
Jan-12
Jan-14
(b)
Pigs & Poultry (n = 9)
Monthly mean NH_3 (µg m^{-3})
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Linear regression:
Y = -0.0039x + 3.3629
R^2 = 0.0257
Relative change = -22.4 %
Sen slope: Y = -0.0054x + 3.2815
Relative median change = -31.9 %
Jan-98
Jan-00
Jan-02
Jan-04
Jan-06
Jan-08
Jan-10
Jan-12
Jan-14

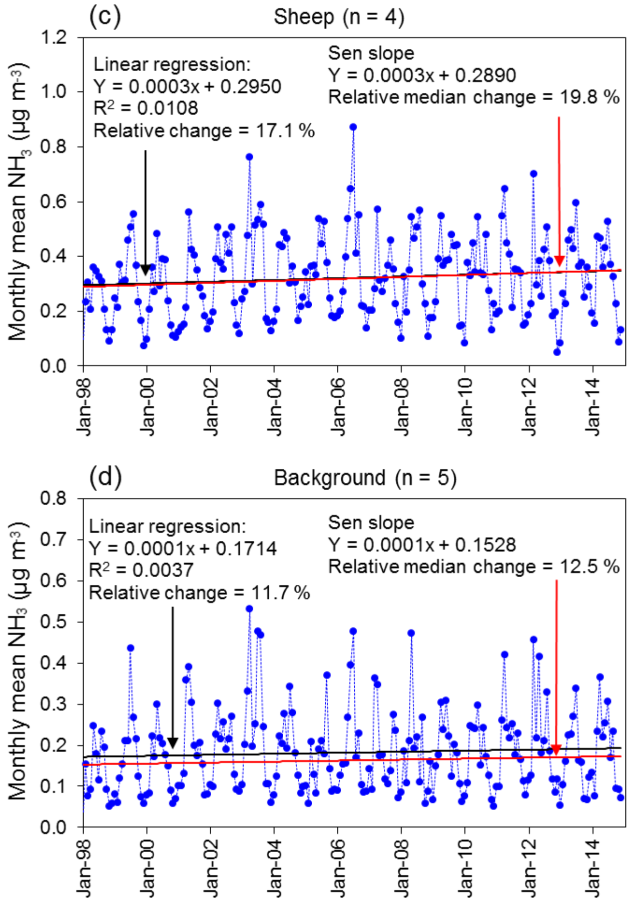


Figure 15: Time series trend analysis by non-parametric Mann-Kendall Sen slope *vs* parametric least squares linear regression on annually averaged NH_3 concentrations from the UK National Ammonia Monitoring Network (NAMN) for sites in 5 km grid squares classed as dominated by (a) cattle (> 45 % of total NH_3 emissions from this category in a grid square); (b) pigs & poultry (> 45 % of total NH_3 emissions from this category in a grid square); (c) sheep (> 45 % of total NH_3 emissions from sheep in a grid square); (d) NAMN sites in grid squares classed as background (defined as grid squares with average NH_3 emissions <1 kg N ha^{-1} y^{-1}). Individual data points are monthly mean NH_3 concentrations.

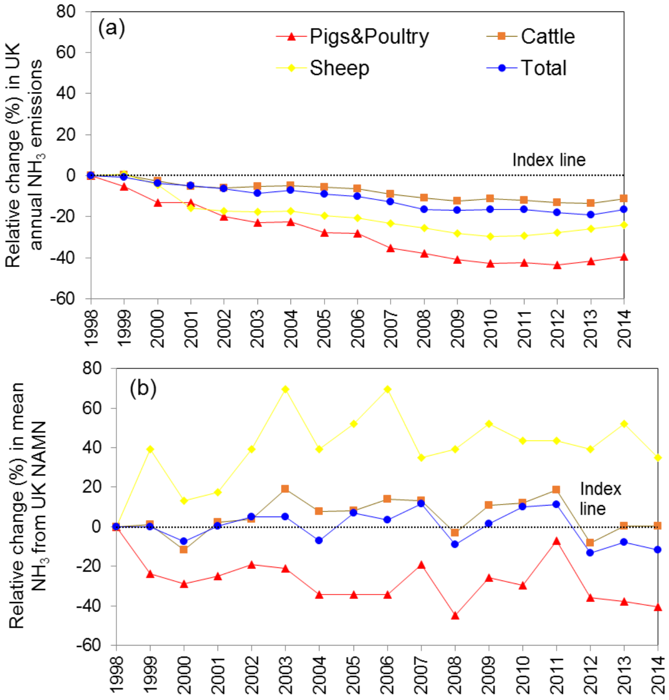


Figure 16: (a) Relative trends between 1998 and 2014 in NH_3 emissions from the UK National Atmospheric Emission Inventory (NAEI) for total emissions (all NH_3 sources) and emissions from cattle, pigs & poultry, and sheep separately (data from*:* *http://naei.defra.gov.uk/* and Misselbrook et al, 2015). (b) Relative trends between 1998 and 2014 in measured annual mean NH_3 concentrations (µg NH_3 m^{-3}) for all UK National Ammonia Monitoring Network (NAMN) sites, and for grouped sites classified as dominated by cattle, pigs & poultry, and sheep. Both figures are plotted with the same scale to allow direct comparison of the relative magnitudes in trends.

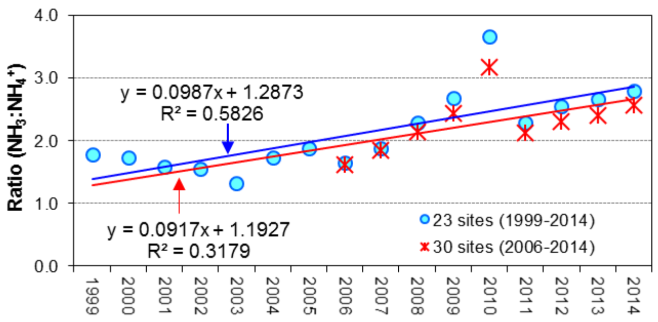


Figure 17: Long-term trends in ratio of NH_3:NH_4^+, indicating an increase in this ratio with time. The comparisons shown is for datasets i) 23 sites with complete NH_4^+ time series from 1999 to 2014, and ii) 30 sites with complete NH_4^+ time series from 2006 to 2014.

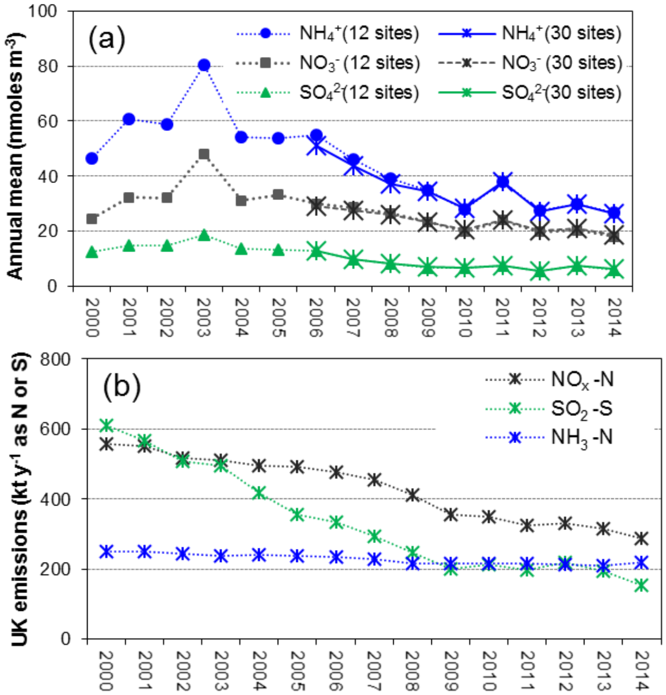


Figure 18**: (a) Long-term trends in particulate NH_4^+ from the UK National Ammonia Monitoring Network (NAMN) compared with particulate NO_3^- and SO_4^{2-} concentrations from the UK Acid Gas and Aerosol Network (AGANet; Connolly et al. 2016) measured at the same time. Each data point represents the averaged monthly measurements from all AGANet sites (increased from 12 to 30 sites since Jan 2006) and also the original l2 AGANet sites in the network (1999 data were excluded as measurements started in September 1999). (b) Trends in total UK emissions of NH_3, NO_x and SO_2 over the same period (2000-2014). Data from the National Atmospheric Emission Inventory (NAEI, *http://naei.defra.gov.uk/).***

Table 1: Summary of Mann-Kendall (MK) and Seasonal Mann-Kendall (SMK) time series trend analysis on NH_3 data (annually averaged datasets 1a, 2a, 3a and monthly mean datasets 1b, 2b, 3b) from the UK National Ammonia Monitoring Network (NAMN). The following are shown: the *p*-value, median annual trend (Sen's slope, in µg NH_3 y^{-1}) and the relative median change over the selected time period (in %). For the MK tests, the 95% confidence interval (CI) for the trend and relative change are also estimated. For comparison, the reduction in estimated UK NH_3 emissions over the periods 1998-2014, 1999-2014 and 2000-2014 are 16.3 %, 15.6 % and 13.1 % respectively.

Dataset	Time series	[a]Number of sites	*p-value*	Significant trend ($p<0.05$)	[b]Median annual trend & [95% CI] (µg NH_3 y^{-1})	[c]Relative median change over the period & [95% CI] (%)
1a: annual (MK)	1998-2014	59	0.46	no	-0.0071 [-0.0200, 0.0125]	-6.3 [-16, 12]
1b: monthly (MK)	1998-2014	59	0.22	no	-0.0096 [-0.0264, 0.0060]	-8.2 [-21, 5.5]
1b: monthly (SMK)	1998-2014	59	0.10	no	-0.0100	-5.8
2a: annual (MK)	1999-2014	66	1.00	no	0.0000 [-0.0227, 0.0200]	0.0 [-16, 16]
2b: monthly (MK)	1999-2014	66	0.51	no	-0.0060 [-0.0252, 0.0132]	-4.5 [-18, 11]
2b: monthly (SMK)	1999-2014	66	0.25	no	-0.0073	-4.2
3a: annual (MK)	2000-2014	75	1.00	no	0.0000 [-0.0283, 0.0175]	0.0 [-19, 14]
3b: monthly (MK)	2000-2014	75	0.43	no	-0.0072 [-0.0264, 0.0120]	-5.3 [-18, 9.5]
3b: monthly (SMK)	2000-2014	75	0.15	no	-0.0079	-4.5

[a] Number of sites providing complete data runs over the time period.

[b] Median annual trend = fitted Sen's slope of Mann-Kendall linear trend (unit = µg NH_3 y^{-1})

[c] Relative median change calculated based on the NH_3 concentration at the start (y_0) and at the end (y_i) of time series computed from the Sen's slope and intercept ($=100*[(yi-y_0)/y_0]$).

Table 2: Summary of linear regression time series trend analysis on NH_3 data (annually averaged datasets 1a, 2a, 3a and monthly mean datasets 1b, 2b, 3b) from the UK National Ammonia Monitoring Network (NAMN). The following are shown: the *p*-value, annual trend (fitted slope, in µg NH_3 y^{-1}), R^2, and the relative change over the selected time period (in %). For comparison, the reduction in estimated UK NH_3 emissions over the periods 1998-2014, 1999-2014 and 2000-2014 are 16.3 %, 15.6 % and 13.1 % respectively.

Dataset	Time series	[a]Number of sites	*p-value*	Significant trend ($p<0.05$)	[b]Annual Trend (µg NH_3 y^{-1})	R^2	[c]Relative change over the period (%)
1a: annual	1998-2014	59	0.62	no	-0.0035	0.0167	-3.1
1b: monthly	1998-2014	59	0.45	no	-0.0062	0.0028	-5.3
2a: annual	1999-2014	66	0.65	no	-0.0040	0.0154	-3.0
2b: monthly	1999-2014	66	0.74	no	-0.0031	0.0006	-2.4
3a: annual	2000-2014	75	0.69	no	-0.0038	0.0130	-2.8
3b: monthly	2000-2014	75	0.56	no	-0.0057	0.0019	-4.2

[a] Number of sites providing complete data runs over the time period.

[b] Annual trend = fitted slope of linear regression (unit = µg NH_3 y^{-1})

[c] Relative change calculated based on the estimated annual NH_3 concentration at the start (y_0) and at the end (y_i) of time series (=100*[(yi-y_0) /y_0]) computed from the slope and intercept (=100*[(yi-y_0) /y_0]).

Table 3: Summary of Mann-Kendall (MK) and Seasonal Mann-Kendall (SMK) time series trend analysis on grouped NH_3 concentration data (annually averaged and monthly mean data) from the UK National Ammonia Monitoring Network (NAMN) for four different emission source sectors. The following are shown: the *p*-value, median annual trend (Sen's slope, in µg NH_3 y^{-1}) and the relative median change over the selected time period (in %). For the MK tests, the 95% confidence interval (CI) for the trend and relative change are also estimated.

Source sector	Time series (1998-2014)	[a]Number of sites	*p-value*	Significant trend ($p<0.05$)	[b]Median annual trend & [95% CI] (µg NH_3 y^{-1})	[c]Relative median change over the period & [95% CI] (%)
Cattle	Annual (MK)	17	0.46	no	0.0155 [-0.0150, 0.0300]	12 [-10, 24]
Cattle	Monthly (MK)	17	0.90	no	-0.0012 [-0.0192, 0.0168]	-0.9 [-14, 13]
Cattle	Monthly (SMK)	17	0.51	no	0.0043	3.9
Pigs&Poultry	Annual (MK)	9	0.02	yes	-0.0043 [-0.1008,-0.0071]	-22 [-42, -3.9]
Pigs&Poultry	Monthly (MK)	9	< 0.001	yes	-0.0648 [-0.0984,-0.0300]	-32 [-46, -16]
Pigs&Poultry	Monthly (SMK)	9	< 0.001	yes	-0.0588	-11
Sheep	Annual (MK)	4	0.17	no	0.0029 [0.0000, 0.0069]	16 [0.0, 46]
Sheep	Monthly (MK)	4	0.10	no	0.0036 [0.0000, 0.0072]	20 [0.0, 45]
Sheep	Monthly (SMK)	4	< 0.01	yes	0.0033	210
Background	Annual (MK)	5	0.20	no	0.0019 [-0.0012, 0.0038]	18 [-10, 41]
Background	Monthly (MK)	5	0.23	no	0.0012 [-0.0012, 0.0036]	13 [-11, 42]
Background	Monthly (SMK)	5	0.05	yes	0.0012	49

[a] Number of sites providing complete data runs over the period 1998 to 2014.

[b] Median annual trend = fitted Sen's slope of Mann-Kendall linear trend (unit = µg NH_3 y^{-1})

[c] Relative median change calculated based on the annual NH_3 concentration at the start (y_0) and at the end (y_i) of time series computed from the Sen's slope and intercept ($=100*[(y_i-y_0)/y_0]$).

Cattle sites: Bickerton Hill (UKA00297), Brown Moss (UKA00369), Castle Cary (UKA00328), Cwmystwyth (UKA00325), Fenn's Moss (UKA00291), High Muffles (UKA00169), Hillsborough (UKA00293), Little Budworth (UKA00298), Llynclys Common (UKA00270), Lough Navar (UKA00166), Myerscough (UKA00356), Northallerton (UKA00316), North Wyke (UKA00269), Penallt (UKA00324), Wardlow Hay Cop (UKA00119), Wem Moss (UKA00299), Yarner Wood (UKA00168).

Pig & Poultry sites: Bedlingfield (UKA00334), Dennington (UKA00331), Dunwich Heath (UKA00308), Fressingfield (UKA00335), Mere Sands Wood (UKA00280), Redgrave + Lopham (UKA00311), Sibton (UKA00012), Stoke Ferry (UKA00317), Stanford (UKA00476).

Sheep sites: Glensaugh (UKA00348; 2005 classification = background, but 1km radius is predominantly sheep from local landuse information), Moorhouse (UKA00357) and Sourhope (UKA00347) (2015 classification = cattle, but 1km radius around site is sheep from local landuse information), (Shetland UKA00486).

Background sites: Allt a Mharcaidh (UKA00086), Dumfries (UKA00368), Eskdalemuir (UKA00130), Inverpolly (UKA00457), Strathvaich (UKA00162).

Table 4: Summary of linear regression time series trend analysis on grouped NH_3 concentration data (annually averaged data and also monthly mean data) from the UK National Ammonia Monitoring Network (NAMN) for four different emission source sectors. The following are shown: the *p*-value, annual trend (fitted slope, in µg NH_3 y^{-1}), R^2, and the relative change over the selected time period (in %).

Source sector	Time series (1998-2014)	[a]Number of sites	*p-value*	Significant trend ($p<0.05$)	[b]Annual Trend (µg NH_3 y^{-1})	R^2	[b] Relative change over the period [%]
Cattle	annual	17	0.61	no	0.0049	0.0180	3.6
Cattle	monthly	17	0.84	no	0.0019	0.0002	1.4
Pigs&Poultry	annual	9	0.06	no	-0.0434	0.2143	-21
Pigs&Poultry	monthly	9	0.02	yes	-0.0466	0.0257	-22
Sheep	annual	4	0.09	no	0.0034	0.1751	19
Sheep	monthly	4	0.14	no	0.0032	0.0108	17
Background	annual	5	0.33	no	0.0014	0.0627	13
Background	monthly	5	0.39	no	0.0013	0.0037	12

[a]Number of sites providing complete data runs over the specified time period in analysis

[b]Annual trend = fitted slope of linear regression (unit = µg NH_3 y^{-1})

[c]Relative change calculated based on the estimated annual NH_3 concentration at the start (y_0) and at the end (y_i) of time series ($=100*[(yi-y_0)/y_0]$) computed from the slope and intercept ($=100*[(yi-y_0)/y_0]$).

Cattle sites: Bickerton Hill (UKA00297), Brown Moss (UKA00369), Castle Cary (UKA00328), Cwmystwyth (UKA00325), Fenn's Moss (UKA00291), High Muffles (UKA00169), Hillsborough (UKA00293), Little Budworth (UKA00298), Llynclys Common (UKA00270), Lough Navar (UKA00166), Myerscough (UKA00356), Northallerton (UKA00316), North Wyke (UKA00269), Penallt (UKA00324), Wardlow Hay Cop (UKA00119), Wem Moss (UKA00299), Yarner Wood (UKA00168).

Pig & Poultry sites: Bedlingfield (UKA00334), Dennington (UKA00331), Dunwich Heath (UKA00308), Fressingfield (UKA00335), Mere Sands Wood (UKA00280), Redgrave + Lopham (UKA00311), Sibton (UKA00012), Stoke Ferry (UKA00317), Stanford (UKA00476).

Sheep sites: Glensaugh (UKA00348; 2005 classification = background, but 1km radius is predominantly sheep from local landuse information), Moorhouse (UKA00357) and Sourhope (UKA00347) (2015 classification = cattle, but 1km radius around site is sheep from local landuse information), (Shetland UKA00486).

Background sites: Allt a Mharcaidh (UKA00086), Dumfries (UKA00368), Eskdalemuir (UKA00130), Inverpolly (UKA00457), Strathvaich (UKA00162).

Table 5: Comparison of % change in estimated UK NH_3 emissions reported by the National Atmospheric Emission Inventory (NAEI) (data from*:* [*http://naei.defra.gov.uk/)*](http://naei.defra.gov.uk/) with % change between 1998 and 2014 in annually averaged NH_3 concentration data from the UK National Ammonia Monitoring Network (NAMN) for all NAMN sites (dataset 1a) and for grouped sites in four different emission source sectors.

Comparison period: 1998 - 2014	All sites (dataset 1a: n = 59)	Cattle (n=17)	Pigs & Poultry (n=9)	Sheep (n=4)	Background (n=5)
UK NH_3 emissions: % change relative to 1998	-16	-11	-39	-24	no data
UK NAMN NH_3: % relative median change estimated from MK Sen's slope and intercept	-6.3 (see Table 1)	12 (see Table 3)	-22* (see Table 3)	15 (see Table 3)	17 (see Table 3)
UK NAMN NH_3: % relative change estimated from linear regression slope and intercept	-3.1 (see Table 2)	3.6 (see Table 4)	-21^{Δ} (see Table 4)	19 (see Table 4)	13 (see table 4)

Significance: *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$, $^{\Delta}p = 0.06$.

Table 6: Comparison of % change in UK NH_3, SO_2 and NO_x emissions reported by the National Atmospheric Emission Inventory (NAEI) (data from*:* [*http://naei.defra.gov.uk/)*](http://naei.defra.gov.uk/) with % change in annually averaged NH_4^+ and NH_3 concentration data from the UK National Ammonia Monitoring Network (NAMN) for sites with complete data runs of both NH_4^+ and NH_3 over the specified time periods.

	NH_4^+ (23 sites) (1999-2014)	NH_3 (23 sites) (1999-2014)	NH_4^+ (30 sites) (2006-2014)	NH_3 (30 sites) (2006-2014)
UK emissions: % change over the time period	-16 (NH_3), -75 (SO_2), -53 (NO_x)		-7 (NH_3), -54 (SO_2), -39 (NO_x)	
UK NAMN: % relative median change estimated from MK Sen's slope and intercept	-47**	3.0	-44**	-17
UK NAMN: % relative change estimated from linear regression slope and intercept	-49**	3.0	-43**	-18^{Δ}

Significance: *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$, $^{\Delta}p = 0.06$.

Table 7: Comparison of % change in UK NH_3, SO_2 and NO_x emissions reported by the National Atmospheric Emission Inventory (NAEI) (data from: *http://naei.defra.gov.uk/)* with % change in annually averaged NH_4^+ concentration data from the UK National Ammonia Monitoring Network (NAMN) and SO_4^{2-} and NO_3^- concentration data from the UK Acid Gas and Aerosol Network (AGANet) for sites with complete concurrent data runs over the specified time periods.

	NH_4^+ (12 sites) (2000-2014)	$SO4^{2-}$ (12 sites) (2000-2014)	NO_3^- (12 sites) (2000-2014)	NH_4^+ (30 sites) (2006-2014)	$SO4^{2-}$ (30 sites) (2006-2014)	NO_3^- (30 sites) (2006-2014)
UK emissions: % change over the time period	-16 (NH_3)	-75 (SO_2)	-53 (NO_x)	-7 (NH_3)	-54 (SO_2)	-39 (NO_x)
UK NAMN: % relative median change estimated from MK Sen's slope and intercept	-56**	-63***	-46***	-44**	-45*	-35**
UK NAMN: % relative change estimated from linear regression slope and intercept	-58**	-65***	-45**	-43**	-46**	-33***

Significance: $^*p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$.