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Acid gases and aerosol measurements in the UK (1999-2015): regional distributions and trends

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Abstract. The UK Acid Gases and Aerosol Monitoring Network (AGANet) was established in 1999 (12 sites, increased to 30 sites from 2006), to provide long-term national monitoring of acid gases (HNO_3, SO_2, HCl) and aerosol components (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}). An extension of a low-cost denuder-filter pack system (DELTA) that is used to measure NH_3 and NH_4^+ in the UK National Ammonia Monitoring Network (NAMN) provides additional monthly speciated measurements for the AGANet. A comparison of the monthly DELTA measurement with averaged daily results from an annular denuder system showed close agreement, while the sum of HNO_3 and NO_3^- and the sum of NH_3 and NH_4^+ from the DELTA are also consistent with previous filter pack determination of total inorganic nitrogen and total inorganic ammonium, respectively. With the exception of SO_2 and SO_4^{2-}, the AGANet provides for the first time the UK concentration fields for each of the other measured species. The ranges in site-annual mean concentrations (nmol m^{-3}) in 2015 for the gases were: HNO_3: 0.7-17; HCl: 2.4-21; SO_2: 0.9-10, while those for aerosol were: NO_3^-: 6.3-53; Cl^-: 22-89; SO_4^{2-}: 2.2-11; Na^+: 20-74; Ca^{2+}: <lod-2.6; Mg^{2+}: 1.3-6.8. The largest concentrations of HNO_3, SO_2, and aerosol NO_3^- and SO_4^{2-} are found in south and east England and smallest in western Scotland and Northern Ireland. For HCl, highest concentrations are in the southeast and southwest, that may be attributed to dual contribution from anthropogenic (coal combustion) and marine sources (reaction of sea salt with acid gases to form HCl). The spatial distributions of Na^+ and Cl^- were similar, with largest concentrations at coastal sites in the south and west and at Shetland, reflecting a contribution from sea salt (NaCl) since a near 1:1 relationship was also observed in their concentrations. Temporally, peak concentrations in HNO_3 and NO_3^- occurred in late spring and early summer, due to photochemical processes and transboundary pollutant transport. The spring peak in SO_4^{2-} concentrations coincides with the peak in concentrations of NH_3 and NH_4^+, and are therefore likely attributable to formation of $(NH_4)_2SO_4$ from reaction with higher concentrations of NH_3 in spring. By contrast, peak concentrations of SO_2, Na^+ and Cl^- during winter are consistent with combustion sources for SO_2 and marine sources in winter for sea salt aerosol. Key pollutant events were captured by the AGANet. In 2003, a spring episode with elevated concentrations of HNO_3 and NO_3^- was driven by meteorology and transboundary transport of NH_4NO_3 from Europe. A second, but smaller episode occurred in September 2014, with elevated

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concentrations of SO_2, HNO_3, SO_4^{2-}, NO_3^- and NH_4^+ that was shown to be from the Icelandic Holuhraun volcanic eruptions. Since 1999, AGANet has shown substantial decrease in SO_2 concentrations relative to HNO_3 and NH_3, accompanied by large reductions also in the aerosol components, with concentrations of NO_3^- and NH_4^+ in molar excess over SO_4^{2-}. At the same time, a positive trend in HNO_3:NO_3^- and NH_3:NH_4^+ ratios, contrasting with a negative trend in SO_2:SO_4^{2-} ratio provides evidence of a change in the particulate phase from $(NH_4)_2SO_4$ to NH_4NO_3, with indications that atmospheric lifetime of HNO_3 and NH_3 has increased. Due to different removal rates of the component species by wet and dry deposition, this change is expected to affect spatial patterns of pollutant deposition with consequences for sensitive habitats with exceedance of critical loads of acidity and eutrophication. The changes are also relevant for human health effects assessment, particularly in urban areas as NH_4NO_3 constitutes a significant fraction of fine particulate matter (< 2.5 µm) that are linked to increased mortality from respiratory and cardiopulmonary diseases.

1 Introduction

Monitoring the atmospheric concentrations of acid gases and their aerosol reaction products is important for assessing their effects on human health, ecosystems, long-range transboundary transport and global radiative balance. Concentration data are necessary for quantifying long-term trends and spatial patterns, understanding gas-aerosol phase interactions, and estimating the contributions of different pollutants to dry deposition fluxes (ROTAP, 2012; AQEG, 2013a; Colette et al., 2016), as well as to provide data for testing the performance of atmospheric models (e.g. Chemel et al., 2010; Vieno et al. 2014, 2016). Acid gases in the atmosphere include sulphur dioxide (SO_2), nitrogen oxides (NO_x), nitric acid (HNO_3), hydrochloric acid (HCl) and nitrous acid (HONO). Secondary inorganic aerosols (SIA) include sulphate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-) and nitrite (NO_2^-) that are formed from reactions of SO_2 and NO_x (and HNO_3, a secondary product of NO_x) with ammonia (NH_3) in the atmosphere. These aerosols make an important contribution to concentrations of particulate matter (PM) in the UK (15 to 50 % of the mass of atmospheric PM) and constitute a significant fraction of fine particles that are less than 2.5 µm in diameter ($PM_{2.5}$) implicated in harming human health (AQEG, 2012; 2013b). In addition, base cations in aerosol are also of interest to estimate the extent to which acidity is neutralized and to estimate the contribution of marine influences (ROTAP, 2012; Werner et al., 2011).

Anthropogenic emissions of SO_2, NO_x, HCl and NH_3 in the UK declined by 81, 51, 87 and 13 %, respectively, over the period 1999 to 2015 (Defra, 2017; NAEI 2017). Despite the success in mitigating SO_2 emissions however, sulphur still remains a pollutant of national importance, because reduction in sulphur deposition in remote sensitive areas have been more modest than close to major sources (ROTAP, 2012). HCl was also recently identified as another important acidifying pollutant for sensitive habitats (Evans et al., 2014). Emissions of HCl (from coal burning in power stations) have however declined to very low levels (from 74 kt in 1999 to 9 kt in 2015), although it could still pose a threat to habitats close to sources. For NO_x, the more modest decrease in emissions reflects difficulties in their abatement, while for NH_3, the decrease to date is largely a result of changes in animal numbers (Defra 2017).

With the decline in SO_2 emissions and deposition, the large number of reactive nitrogen compounds in the atmosphere are assuming greater importance owing to the complexities of the global N cycle and associated challenges in their abatement. These include the gas phase components NH_3, with over 80% estimated from agricultural emissions (EEA, 2017) and nitrogen oxides (NO, NO_2) from combustion, the secondary gas phase reaction products HNO_3, HONO and PAN (peroxyacetyl nitrate) and particulate phase components ($(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3) formed by the reaction between NH_3 and acid gases. (AQEG, 2012). Ammonia and the N-containing aerosols are known to cause nitrogen enrichment and eutrophication, as well as contributing to acidification processes (Sutton et al., 2011). Oxidised nitrogen species (NO_x) are precursors to ground-level O_3 formation, while the production of acids (HNO_3, HONO) and PAN in the atmosphere affects air quality and is damaging both to human health and to vegetation (Cowling et al., 1998, Bobbink et al., 2010).

In Europe, air pollution policies regarding acidification and nitrogen eutrophication apply the “critical loads approach” (Bull, 1995; Gregor et al., 2001), which requires that atmospheric deposition inputs be mapped at an appropriate scale for the assessment of effects. In parallel, the “critical levels” of concentrations addresses the direct impacts of concentrations of nitrogen components in the atmosphere (Bull, 1991; Gregor et al., 2001; Cape et al., 2009). Quantifying the dry deposition of reactive nitrogen compounds is a major challenge and a key source of uncertainty for effects assessment (Dentener et al., 2006; Flechard et al., 2011; Schrader et al., 2018; Sutton et al., 2007). While deposition may be estimated using atmospheric transport and chemistry models (e.g. Dore et al., 2015; Flechard et al., 2011; Smith et al., 2000), air concentration data at sufficient spatial resolution are needed, both to assess the atmospheric models and provide input data for estimating deposition using inferential models.

In light of policies to reduce atmospheric emissions, e.g. the amended 2012 Gothenburg Protocol (UNECE, 2018) and the revised National Emissions Ceilings Directive (NECD, EU Directive 2016/2284) (EU, 2016), it is important to assess long-term trends in the measured pollutants, since this provides the only independent means to assess the effectiveness of any abatement policies. Both these international agreements set emissions reduction commitments for SO_2, NO_x and NH_3, of 59, 42, and 6 %, respectively, by 2020 (with 2005 as base year) and includes $PM_{2.5}$ for the very first time. Under the 2016 NECD, further reduction commitments of 79 % (SO_2), 63 % (NO_x) and 19 % (NH_3) are also set for the EU 28 countries from 2030. Since emissions of these gases comes from different sources, emissions controls require very different strategies, making it important to monitor and assess the the relative concentrations and deposition of nitrogen and sulphur components.

The spatial and temporal patterns of gases and particulate phases of these pollutants differ substantially. Although it is widely acknowledged that speciation between reactive gas and aerosol measurement is critical, there are few national long-term monitoring programmes dedicated to measuring separately their concentrations and dry depositions at high spatial resolution (Torseth et al., 2012). Across Europe, the European Monitoring and Evaluation Programme (EMEP, 2014) continues to recommend using a daily filter pack sampling method to measure oxidised nitrogen (total inorganic nitrate, TIN) and reduced nitrogen (total inorganic ammonia, TIA) (Torseth et al., 2012; Colette et al., 2016). The filter pack method is generally considered as robust for measuring SO_2 and SO_4^{2-} concentrations (EMEP, 2014; Hayman et al., 2006; Sickles et al., 1999). However, many papers have shown that there are potential artefacts in filter-pack sampling for HNO_3 and HCl, due to interactions with NH_3 and the volatility of NH_4NO_3 and NH_4Cl aerosol (Pio, 1992; Sickles et al., 1999; Cheng et al., 2012). Results from EMEP filter pack measurements are therefore reported as TIN and TIA, due to phase uncertainties in the method (Torseth et al., 2012). This has been complemented by daily measurements of HNO_3 and NO_3^- using annular denuders (Allegrini et al., 1987; EMEP, 2014) that are made at a restricted number of sites because of the resources required. In North America, filter pack sampling is also used in weekly measurements of sulphur and nitrogen species in the CASTnet (Clean Air Status Trends Network) national monitoring network of 95 sites across USA, Canada and Alaska (https://www.epa.gov/castnet). At a small number of CASTnet sites, hourly measurements of water-soluble gases and aerosols are made with the Monitor for AeRosols and GAses in ambient air (MARGA) system (Rumsey and Walker, 2016). In the UK, the MARGA approach is deployed for continuous hourly measurements at just two sites (Twigg et al., 2016).

High time-resolution measurements of gases and aerosols are useful at selected locations for detailed analysis and model testing, but the high costs and resources required for these measurements make them unsuitable for the assessment of long-term trends at many sites, particularly where spatial patterns are required. To achieve this, a larger number of sites operated at lower time-resolution is needed. In the UK, the Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network provides long-term measurements for the UK rural atmospheric concentrations and deposition of air pollutants that contribute to acidification and eutrophication processes (Conolly et al., 2016). UKEAP comprises of two EMEP supersites and four component networks: precipitation network (Precip-net), NO_2 diffusion tube network (NO_2-net), National Ammonia Monitoring Network (NAMN) and the Acid Gases and Aerosol Network (AGANet). At the two EMEP supersites (Auchencorth and Harwell – relocated to Chilbolton in 2016), semi-continuous hourly speciated measurements of reactive gases and aerosols are made with the MARGA system (Twigg et al., 2016) that is also deployed at some CASTnet sites (Rumsey and Walker, 2016). These measurements are contributing to the validation and improvement of atmospheric models, such as FRAME (Dore et al., 2015) and EMEP4UK (Vieno et al., 2014, 2016) that are used to develop and provide the evidence base for air quality policies, both nationally and internationally.

The long-term dataset of monthly speciated measurements from the AGANet (1999 – 2015) are analysed in this paper to provide a comprehensive assessment of the spatial, temporal and long-term trends in atmospheric concentrations of the acid gases HNO_3, SO_2, HCl and related aerosol components NO_3^-, SO_4^{2-} and Cl^- (and also base cations Na^+, Ca^{2+} and Mg^{2+}) across the UK, together with an assessment of the DELTA denuder-filter pack sampling method (Sutton et al., 2001b; Tang et al.,

2009) as compared with other sampling techniques. To aid interpretation of the relative changes and trends in the acid gases and aerosols, NH_3 and particulate NH_4^+ data from the NAMN (Tang et al., 2018) are included, since atmospheric NH_3 is a major interacting precursor gas in neutralisation reactions with the acid gases.

2 Methods

2.1 Acid Gases and Aerosol monitoring Network (AGANet)

The UK Acid Gases and Aerosol Network (AGANet), known previously as the nitric acid monitoring network, was started in September 1999 under the Acid Deposition Monitoring Network (ADMN, Hayman et al., 2007) to deliver for the very first time, long-term monthly speciated measurement data on gaseous HNO_3 and particulate NO_3^- across the UK. Other acid gases (SO_2, HCl) and aerosols (SO_4^{2-}, Cl^-, plus base cations Na^+, Ca^{2+}, Mg^{2+}) are also measured and reported. Since 2009, the AGANet, together with the NAMN (monthly NH_3 and NH_4^+), Precip-net (2-weekly wet deposition measurements) and NO_2-net (4-weekly NO_2 concentrations) were unified under the UKEAP network to provide long-term measurements of eutrophying and acidifying atmospheric pollutants (Conolly et al., 2016).

AGANet and NAMN are closely integrated, with AGANet established at a subset of NAMN sites to provide additional speciated measurements of the acid gases and aerosol components. To improve on national coverage, the number of sites in AGANet was increased in 2006 from 12 to 30 (Figure 1, Table 1). At the same time, the Rural Sulphur Dioxide Monitoring Program ceased, replaced by SO_2 and SO_4^{2-} measurements made under the expanded AGANet (Hayman et al., 2007). A broad spatial coverage of the UK is provided by the AGANet sites, with a focus on sites providing parallel information on other air pollutants (e.g., co-location with the Automatic Urban and Rural Network that provides compliance monitoring against the Ambient Air Quality Directives (https://uk-air.defra.gov.uk/networks/) and ecosystem assessments (e.g. Environmental Change Network, http://www.ecn.ac.uk/) (Monteith et al., 2016).

<INSERT Figure 1 HERE>
<INSERT Table 1 1HERE>

2.2 Extended DELTA methodology for sampling acid gases and aerosol in AGANet

A low-cost manual denuder-filter pack method, DELTA (DEnuder for Long-Term Air sampling) implemented in the NAMN for measurement of NH_3 gas and aerosol NH_4^+ (Sutton et al., 2001a,b; Tang et al., 2018) is extended to provide additional simultaneous monthly time-integrated average concentrations of acid gases (HNO_3, SO_2, HCl) and particulate phase NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+} and Mg^{2+} for the AGANet (Conolly et al., 2016; Tang et al., 2015).

The DELTA method used in AGANet has also been applied in an extensive European-scale network of 58 sites to deliver 4 years of atmospheric concentrations and deposition data for reactive trace gas and aerosols from 2006 to 2009 (Tang et al., 2009; Flechard et al., 2011). Detailed descriptions of the DELTA method are provided by Sutton et al. (2001b) and by Tang et al. (2009, 2015). In brief, a small air pump is used to provide low sampling rates of 0.2–0.4 L min^{-1}, and air volumes are measured by a high-sensitivity diaphragm gas meter. By sampling air slowly, the method is optimised for monthly measurements, with sufficient sensitivity to resolve low concentrations at clean background sites (e.g. LOD = 0.05 µg m^{-3} for HNO_3 for monthly sampling; see Supplement Tables S1, S2). In addition, the power requirement is very small, and low voltage versions (using 6 V and 12 V micro-air pumps) of the system powered by wind-solar energy operate at some remote sites.

An extended denuder-filter pack sampling train is used to provide speciated sampling of reactive gases and aerosols (Supplement Figure S1) (Tang et al., 2009, 2015). A Teflon inlet (2.8 cm long) at the front end ensures development of a laminar air stream (Table S3), followed by a first pair of K_2CO_3 and glycerol coated denuders to collect HNO_3, SO_2 and HCl , a second pair of citric acid coated denuders to collect NH_3 and a 2-stage filter pack at the end to collect aerosol components. Stage 1 of the filter pack is a cellulose filter impregnated with K_2CO_3 and glycerol to collect NO_3^-, SO_4^{2-}, Cl^-, Na^+, $Ca^{2+,}$ Mg^{2+}, with evolved aerosol NH_4^+ from this filter collected on the stage 2 citric acid impregnated filter. The separation of gases and aerosol is achieved by higher diffusivities of reactive gases to the denuder walls where they react with the chemical coating and are retained, whereas aerosol components pass through and are retained by post-denuder filters (Ferm, 1979). In this approach, potential artefacts caused by phase interactions associated with filter packs and bubblers are avoided (e.g. Sickles et al., 1999).

For the base coating, K_2CO_3 is used instead of Na_2CO_3 (Ferm et al., 1986) to sample acid gases so that the system can also measure aerosol Na^+ concentrations. Glycerol increases adhesion, stabilizes the base coating (Ferm, 1986; Finn et al., 2001), and is reported to minimise potential oxidation of nitrite that is also collected on the denuder to nitrate in the presence of atmospheric oxidants such as ozone (Allegrini et al., 1987; Perrino et al., 1990). The lengths of denuders (borosilicate glass tubes 10 cm and 15 cm long to capture > 95 % of NH_3 and acid gases, respectively) in the sampling train was calculated according to the procedures described by Sutton et al. (2001b), based on the calculations derived by Gormley and Kennedy (1948) and Ferm (1979) (see Table S3). All sites were set up as “outdoor” systems sampling directly from the atmosphere, avoiding potential adsorption losses (in particular $HNO_{3,}$ which is highly surface active) and artefacts in air inlet lines. The sampling train is installed inside a simple watertight housing (Figure S1), which is mounted on a steel post in the desired location. A low density polyethylene funnel (89 mm aperture) is placed at the inlet as a rain shelter, and sampling height is approx. 1.5 m.

2.3 Analytical methodology

2.3.1 Base coated denuders and filters

Base-coated denuders and aerosol filters are extracted into 5 mL of deionised H_2O for analysis. Anions (NO_3^-, SO_4^{2-} and Cl^-) in the denuder and filter extracts are analysed by Ion Chromatography (IC). Base cations Na^+, Mg^{2+} and Ca^{2+} from the filter extracts were analysed by IC between 1999 – Jun 2008 and by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES/ICP-AES) from Jul 2008. Up to June 2009, analyses were carried out at Harwell Laboratory (Hayman et al., 2007) and from July 2009 at CEH Lancaster (Conolly et al. 2016). The limit of detection (LOD) for the DELTA method for the different components are calculated by analysing a series of laboratory blanks. The mean and standard deviation of the results are calculated and the LOD is calculated as three times the standard deviation divided by 15 m^3, the typical volume of air sampled over a month by the DELTA system. Details of changes in laboratory, analytical methods and LODs for the gases and aerosols are summarised in Tables S1 and S2, respectively.

2.3.2 Acid coated denuders and filters

Acid coated denuders and filter papers are also extracted into deionised H_20 (3 mL and 4 mL, respectively), with analysis of NH_4^+ performed on a high sensitivity ammonia flow injection analysis system, as described in Tang et al., (2018).

2.4 Calculation of air concentrations

The air concentration (χ_a) of a gas or aerosol is calculated according to equation 1 (see Sutton et al., 2001b, Tang et al., 2018):

$$\chi a = \frac{Q}{V} \qquad (1)$$

where Q = amount of a gas or aerosol collected on a denuder or aerosol filter, and
V = volume of air sampled (from gas meter, typically 15 m^3 in a month)

The denuder capture efficiency for each of the gas is calculated by comparing the concentrations of the individual gases in the denuder pairs and are applied in an infinite series correction on the raw data to provide corrected air concentrations ($\chi_{a\,(\text{corrected})}$) according to equation 2 (see Sutton et al., 2001b, Tang et al., 2018):

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

Sutton et al. (2001b) and Tang et al. (2003) have shown that this procedure provides an important quality control, flagging up occurrences of poorly coated denuders and/or sampling issues. With denuder capture efficiency better than 90 %, the correction represents < 1 % of the corrected air concentration of the gas. Below 60 %, the correction is large (> 50 %) and is not applied, and the air concentration is then calculated as the sum of concentrations of the denuder pair. The amount of correction for gas not captured that is added to the corrected gas concentration, is subtracted from the estimated aerosol concentrations of matching anions and cations (see Tang et al., 2018).

2.5 Data Quality Control

The following data quality checks are applied to the network data, as part of the network quality management system (Tang and Sutton, 2003; Conolly et al., 2016):

i) Air flow rate (0.2 – 0.4 L min^{-1}): where this is below the expected range for a sampling period, the data is flagged as valid but failing the QC standard.

ii) Denuder capture efficiency: where this is less than 75% for a sample, the data is flagged as valid but less certain.

iii) Ion balance checks: close agreement expected between NH_4^+ and the sum of NO_3^- and $2\times SO_4^{2-}$, 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), and for Na^+ and Cl^-, as these are marine (sea salt) in origin.

iv) Screening the whole dataset for sampling anomalies and outliers, e.g. due to contamination or other issues.

2.6 Bias correction applied to HNO_3 data

Tang et al. (2009, 2015) have identified that HNO_3 concentrations (NO_3^- on denuders assumed to be from HNO_3) may be overestimated on carbonate coated denuders, due to partial co-collection of other oxidized nitrogen components such as nitrous acid (HONO). In the case of HONO, this collects on the denuder carbonate coating as nitrite (NO_2^-), but oxidizes to nitrate (NO_3^-) in the presence of oxidants such as ozone (Bytnerowicz et al., 2005) which can result in a bias in HNO_3 determination (Tang et al., 2009, 2015). Other oxidised nitrogen species present in the atmosphere such as peroxyacetyl nitrate (PAN) and nitrogen oxides (NO_x) can also potentially contribute to a further small interference (Allegrini et al., 1987; Bai et al., 2003). Based on the tests of Tang et al. (2015), raw HNO_3 data are corrected with an empirical factor of 0.45 which is estimated to be uncertain by ±30 %. Apart from where stated, all HNO_3 data reported in this study have the 0.45 correction factor applied.

2.7 Performance of the DELTA method

2.7.1 Measurement reproducibility

Replicated DELTA measurements are made at the Bush OTC site in Scotland (UKA00128). A comparison of the parallel measurements (Figure 2) showed good reproducibility in the method, with close agreement for all components (e.g. mean difference of < ± 3 % for all components and ± 6 % for HCl).

<INSERT Figure 2 HERE>

2.7.2 Comparison with daily annular denuder measurements

An assessment of the DELTA method for NH_3 has previously been reported by Sutton et al. (2001b). Following the extension to additionally sample acid gases and aerosols, the modified system was compared with independent daily measurements from an annular denuder system (ADS). The ADS (ChemspecTM model 2500 air sampling system, R&P Co. Inc.) was operated at Barcombe Mills in southern England (UKA00069) alongside the AGANet DELTA monthly measurements for a period of 18 months. Due to significant instrument and local site issues resulting in low data capture with the ADS, only 11 months of data were available for intercomparison. The sampling train used in the ADS consisted of 2 K_2CO_3 + glycerol-coated annular denuders (same coating as AGANet DELTA), 2 citric acid-coated annular denuders; a cyclone with 2.5 µm cut-off, followed by a 2-stage filter pack containing a 2 µm PALL Zefluor teflon membrane (collection NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, Ca^{2+}) and a 1 µm PALL Nylasorb nylon membrane (collection of evolved NO_3^-), with a sampling rate of 10 L min^{-1}. For comparison against the monthly DELTA measurements, daily ADS values were averaged to the corresponding monthly periods, with results summarised in Table 2 and Figure S2.

<INSERT Table 2 HERE>

For HNO_3, the DELTA (mean = 1.56 µg m^{-3}, n = 11) was on average 23 % higher than the ADS (mean = 1.31 µg m^{-3}, n = 11). Since both methods used the same carbonate coating on the denuders to sample acid gases, the HNO_3 data here have not been corrected with the bias adjustment factor described in Sect. 2.6. Nitrous acid (HONO) was found to be close to or below limit of detections for most of the DELTA measurements (mean = of 0.03 µg m^{-3}), compared with a significantly higher concentration (mean = 0.41 µg m^{-3}) from the ADS. Since the sampling period of the ADS is daily, any HONO collected as nitrite on the ADS is likely to remain as nitrite and not oxidised to nitrate. The very low HONO (nitrite on the denuders assumed to be from HONO) concentrations from the DELTA supports the hypothesis of the retention of HONO that is subsequently oxidised to nitrate, resulting in an artefact in HNO_3 determination (Possanzini et al., 1983; Allegrini et al., 1987; Tang et al., 2015). Further corroboration is provided by the improved agreement between both methods (line of fit closer to the 1:1 line) when comparing the sum of HNO_3 and HONO (see graph in supp. Figure S2). Agreement between the DELTA and ADS was within 19 % for SO_2 (mean DELTA = 1.75 µg m^{-3} *cf* mean ADS = 2.18 µg m^{-3}) and 4 % for HCl (mean DELTA = 0.40 µg m^{-3} *cf* mean ADS = 0.41 µg m^{-3}). Given the limited data available, it is not clear why SO_2 measured on the ADS is higher than the DELTA, since there was good agreement for HCl.

For the particle-phase components, NO_3^- measured by the DELTA method (mean = 2.59 µg NO_3^- m^{-3}) was on average 2-fold higher than the ADS method (mean = 1.32 µg NO_3^- m^{-3}), whereas SO_4^{2-} by the DELTA method was on average 23 % lower (DELTA = 2.10 vs ADS = 2.74 µg SO_4^{2-} m^{-3}) (Table 2). NO_3^- and SO_4^{2-} are both present as fine mode (< 1 µm) NH_4NO_3 and

$(NH_4)_2SO_4$ (Putaud et al., 2010). Some NO_3^- can also be present in the coarse mode (> 2.5 µm), likely as calcium nitrate ($Ca(NO_3)_2$) from a reaction between gas-phase HNO_3 (or its precursors) and soil dust particles (Putaud et al., 2010). For SO_4^{2-}, some will be coarse mode sea salt SO_4^{2-} (see section 3.3). A particle size cut-off of 4–5 µm was estimated for the DELTA air inlet) (Tang et al., 2015), which would suggest that the DELTA will also sample a small amount of coarse mode aerosols. An ion balance check of the ratio of µeq NH_4^+ to sum µeq (NO_3^- + SO_4^{2-}) yielded a near unity value, which confirms that NO_3^- and SO_4^{2-} collected by the DELTA aerosol filter are mainly fine mode NH_4NO_3 and $(NH_4)_2SO_4$. In comparison, the ADS has a 2.5 µm cyclone in front of the aerosol filters to collect aerosols < 2.5 µm on the aerosol filters. NH_4^+ was unfortunately not analysed in these tests, which would have allowed a similar ion balance check. Na^+ and Cl^- concentrations on the DELTA were also on average 331% and 444 % higher than on the ADS and the ion balance check of the ratio of Na^+:Cl^- was unity for both methods. In the absence of analytical errors, loss of NO_3^-, Na^+ and Cl^- on the surface of the cyclone, coupled to a small fraction of the aerosols > 2.5 µm that is collected (but not analysed) in the cyclone, could partly account for the observed lower concentrations of the aerosol components. Since Ca^{2+} and Mg^{2+} concentrations by both methods were at or below detection limits, comparisons of these are not meaningful and have not been made.

2.7.3 Comparisons with filter pack measurements: HNO_3/NO_3^- and NH_3/NH_4^+

The EMEP network (www.emep.int) measures atmospheric concentrations and depositions of a wide range of pollutants at rural background sites across Europe (Aas, 2014; Tørseth et al., 2012). For assessment of oxidised and reduced nitrogen species, the daily EMEP filter pack method are implemented at 39 sites across Europe (Colette et al., 2016; Tørseth et al., 2012), with results reported as Total Inorganic Nitrate (TIN: HNO_3 + NO_3^-) and Total Inorganic Ammonia (TIA: NH_3 + NH_4^+) (Torseth et al., 2012), as these are considered more reliable than reporting for the gas and aerosol components separately.

<INSERT Figure 3 HERE>

At the UK Eskdalemuir site (EMEP station code GB0002R; UKAIR ID UKA00130), a Scottish rural background site on the border between Scotland and England, daily filter pack measurements of TIN and TIA were made as part of the EMEP network from 1989 to 2000 (EMEP, 2017a). Following installation of the DELTA system in September 1999, both methods were operated in parallel for 14 months at Eskdalemuir, allowing a comparison to be made of TIN and TIA from both systems. Comparison results are shown in Figure 3 of parallel data from the AGANet (sum of HNO_3 and NO_3^-) and NAMN (sum of NH_3 and NH_4^+), demonstrating close agreement between the two independent measurements. The EMEP values shown are daily measurements of TIN and TIA averaged to corresponding monthly means for comparison with the DELTA data. For TIN, the regression between EMEP TIN and AGANet (sum of uncorrected HNO_3 + NO_3^-) is close to unity (slope = 0.984, R^2 = 0.94), which provided independent verification and support of the DELTA HNO_3 measurements at the start of the network. After applying a bias adjustment factor of 0.45 to the HNO_3 data (see Sect. 2.6), the AGANet values (sum of corrected HNO_3

+ NO_3^-) are smaller than the EMEP TIN (slope = 0.835, R^2 = 0.95). It is possible that the filter pack method may also be subject to similar artefacts in HNO_3 determination due to co-collection of other oxidised nitrogen species (Tang et al., 2015).

2.7.4 Comparisons with bubbler and filter pack measurements: SO_2 and SO_4^{2-}

Independent measurements of SO_2 and SO_4^{2-} with a daily bubbler and filter pack method, respectively, are also available for comparison with the DELTA method at the Eskdalemuir site. Daily SO_2 data with a bubbler method (Hayman, 2005) from Dec-77 to Dec-01 and daily SO_4^{2-} data with an EMEP filter pack method from Dec-77 to Apr-09 (Hayman, 2006) were downloaded from the EMEP website (EMEP, 2017b). A close agreement is found between the bubbler and DELTA method for SO_2 (slope = 0.86, R^2 = 0.82), while there is more scatter between the filter pack and DELTA method for SO_4^{2-} (slope = 0.67, R^2 = 0.66) (Figure 4). Concentrations of SO_2 for the 26 month overlap period were comparable (mean of bubbler method = 0.40 µg S m^{-3} *cf* mean of DELTA method = 0.44 µg S m^{-3}), whereas the filter pack SO_4^{2-} concentration (mean = 0.44 µg S m^{-3}, n = 87) is larger than the corresponding monthly DELTA measurement (mean = 0.28 µg S m^{-3}, n = 87) (Figure 4). An earlier detailed assessment of the DELTA system against filter pack with a focus on SO_2 and SO_4^{2-} in 1999 by Hayman et al. (2006) had shown close agreement between the methods. It is therefore unclear why the DELTA gives a reading lower than the filter pack SO_4^{2-} at Eskdalemuir in this assessment, since the dataset was a continuation of the original inter-comparison. Possible explanations include uncertainties associated with limit of detection of the daily filter pack method at the very low concentrations encountered at this site, or the sampling of coarser particles by this method (due to high flow rate and open-face sampling) with higher concentrations of sea salt sulphate. The DELTA methodology was unchanged for the duration of the AGANet dataset (1999 - 2015) in this manuscript, which allows a consistent assessment of overall trends in the SO_4^{2-} data.

<INSERT Figure 4 HERE>

2.8 Time series trend analyses

Statistical trend analyses using both parametric linear regression (LR) and non-parametric Mann-Kendall (MK) (Gilbert, 1987; Chatfield, 2016) tests were performed on annually averaged data from AGANet, and on a subset of annually averaged data from NAMN made at the same AGANet sites. The datasets are considered sufficiently long-term (>10 years) and produced by a consistent method for effective statistical trend analyses. Both the LR and MK approaches are widely adopted for trend analyses in long-term atmospheric data (e.g. Meals et al., 2011; Colette, 2016; Jones and Harrison, 2011; Marchetto et al., 2013; Hayman et al., 2007; Conolly et al., 2016), and were used in a recent trend assessment of atmospheric NH_3 and NH_4^+ data (1998 – 2014) from the NAMN (Tang et al., 2018). As described in Tang et al. (2018), LR tests were performed using R, and MK tests used the R 'Kendall' package (McLeod, 2015), with estimation of the MK Sen's slope (fitted median slope of a linear regression joining all pairs of observations) and confidence interval of the fitted trend using the R 'Trend' package (Pohlert, 2016). Results from both tests provides an indication of uncertainty associated with the choice of approach.

3 Results and Discussion

3.1 AGANet data

Annual data from the AGANet (and also from the NAMN) are submitted to the Department for Environment, Food & Rural Affairs (Defra) UK-AIR database (https://uk-air.defra.gov.uk/), in a format consistent with other UK Authority air quality networks and relevant reporting requirements. Every concentration value is labelled with a validity flag and an EMEP flag (see http://www.nilu.no/projects/ccc/flags/index.html). Ratified calendar year data are published from around June the year following collection. Currently, work is also in progress for the data to be made available from the EMEP database (http://ebas.nilu.no/). All data used in this paper (up to 2015), except where specified, are accessed from the UK-AIR website (Tang et al. 2017a, b).

3.2 Spatial patterns in relation to pollutant sources and transport

The spatial patterns for each of the gas and aerosol components measured are shown in the annual maps for the example year 2013 (Figure 5). A gradient in the concentrations of acid gases HNO_3 and SO_2, and related aerosols NO_3^- and SO_4^{2-} can be seen across the UK, highest in the south and east (combustion/vehicular sources and long-range transboundary pollutant transport from Europe) and lowest in the north and west of the UK (fewer sources, furthest from influence of Europe).

The largest HNO_3 concentrations were measured at the London Cromwell site (2013 site annual mean = 1.3 µg HNO_3 m^{-3} *cf* 2013 mean of 30 sites = 0.40 µg HNO_3 m^{-3}). London and Edinburgh are the only two urban sites in the AGANet, with the other 28 sites all in rural environments. HNO_3 concentrations in Edinburgh, the capital of Scotland with a population that is 18 times smaller than London (0.5 million *vs* 8.8 million), is about 2 times lower than London, but higher than the national average (2013 annual mean = 0.58 µg HNO_3 m^{-3}). For SO_2, the highest concentrations were recorded at Sutton Bonington due to close proximity to the 2000 MW capacity coal-fired Ratcliffe-on-Soar power station (2 km North). A peak concentration of 10.9 µg SO_2 m^{-3} was recorded in May 2000 at this site, with an annual mean concentrations of 5.9 µg SO_2 m^{-3} for that year that was also 3 times higher than the national average (mean of 12 sites = 1.9 SO_2 m^{-3} *cf.* mean of 11 sites (excl. Sutton Bonington) = 1.5 SO_2 m^{-3}). At remote sites further away from sources, concentrations of HNO_3 and SO_2 are smaller, e.g. Lough Navar in Northern Ireland (2013 annual mean: 0.15 µg HNO_3 m^{-3} and 0.21 µg SO_2) and Strathvaich Dam in northwest Scotland (2013 annual mean = 0.17 µg HNO_3 m^{-3} and 0.18 µg SO_2). NO_3^- and SO_4^{2-} as secondary aerosols have longer residence times in the atmosphere and are expected to be more homogeneous than their precursor gases. The spatial distribution in concentrations of particulate NO_3^- (0.33 – 3.1 µg m^{-3}) and SO_4^{2-} (0.35 – 1.2 µg m^{-3}) are however similar to that of HNO_3 (0.12 – 1.3 µg m^{-3}) and SO_2 (0.10 – 1.1 µg m^{-3}), with no clear differences in the main regional patterns from only 30 sites.

<INSERT Figure 5 HERE>

For HCl, the highest concentrations are in the southeast and southwest of England, that may be attributed to dual contribution from anthropogenic (coal combustion) and marine sources (reaction of sea salt with HNO_3 and H_2SO_4 to form HCl) (Roth and Okada 1998; Ianniello et al., 2011). The spatial distributions of Cl^- and Na^+ were similar, with largest concentrations at coastal sites in the south (Barcombe Mills) and west (Yarner Wood) and at Shetland, highlighting the importance of marine sources to the sea salt (NaCl) aerosol. Further away from the coast and influence of marine aerosol, the smallest concentrations of Cl^- and Na^+ are measured in the west of the country (Lough Navar in Northern Ireland and Cwmystwyth in mid-Wales) and most of Scotland (with the exception of Shetland). For Mg^{2+}, the range of concentrations at sites are small (0.03 – 0.19 µg m^{-3}), but the spatial distribution is similar to Na^+ and Cl^- and suggests that it may be in the form of $MgCl_2$. There is however no clear spatial pattern for Ca^{2+}, with concentrations that are mostly at or below LOD.

In the case of NH_3, the extensive spatial heterogeneity seen is related to large variation in emission sources at ground level across the UK (Tang et al., 2018). Aerosol NH_4^+, as expected for a secondary component, show a less variable concentration field. The spatial distribution of NH_4^+ is similar to SO_4^{2-} and NO_3^- over the UK (Figure 5), due to the close coupling between species from the formation of particle phase $(NH_4)_2SO_4$ and NH_4NO_3 (see next section).

3.3 Correlations between gas and aerosol species

Correlations between the gas and aerosol phases of the different components are summarised in Figure 6. The comparison of gas phase concentrations show that gaseous NH_3 is poorly correlated with either SO_2 or HNO_3, as might be expected since the emission sources of these pollutants are different. For HNO_3 and SO_2, there is a stronger correlation ($R^2 = 0.35$), which may be due to similarity in the regional distribution of their emissions. These comparisons show that there is on average 5 times more NH_3 than SO_2 and 13 times more NH_3 than HNO_3 at the AGANet sites (on a molar basis), and that SO_2 concentration is nearly 3 times larger than HNO_3 (on a molar basis).

<INSERT Figure 6 HERE>

For the aerosol components, there is very high correlation between NO_3^-, SO_4^{2-} and NH_4^+, and between Na^+ and Cl^-, but no discernible relationship between NH_4^+ and Cl^- (Figure 6). The near 1:1 relationship in the scatter plot of the sum of NO_3^- and SO_4^{2-} (µeq m^{-3}) *versus* NH_4^+ (µeq m^{-3}) (slope = 0.91, $R^2 = 0.93$), in the absence of any correlation between NH_4^+ and Cl^-, suggests that H_2SO_4 and HNO_3 in the atmosphere are fully neutralised by NH_3 to form $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 (Aneja et al. 2001). For Cl^-, the high correlation with Na^+ (slope = 1.04, $R^2 = 0.8$) lends support that the Cl^- measured in the DELTA are derived mainly from sea salt (NaCl). Similar to the relative concentrations of gases, NH_4^+ concentrations (on a molar basis) are larger than SO_4^{2-} and NO_3^-, but NO_3^- is in molar excess over SO_4^{2-}. The correlations between NH_4^+ and sum (NO_3^- + 2×SO_4^{2-}) and for Na^+ and Cl^- forms the basis of ion balance checks in data quality assessment, as discussed in section 2.5 and shows that robust data are obtained .

Sea salt aerosol, derived from sea spray has essentially the same composition as seawater (Keene et al., 1986). The marine aerosol comprises two distinct aerosol types: (1) primary sea salt aerosol produced by the mechanical disruption of the ocean surface and (2) secondary aerosol, primarily in the form of non-sea salt (nss) sulphate and organic species, formed by gas-to-particle conversion processes such as binary homogeneous nucleation, heterogeneous nucleation and condensation (O'Dowd and Leeuw, 2007). It has been shown that the ratio of the mass concentrations of SO_4^{2-} and Cl^- to the reference Na^+ species in seawater may be used to estimate mass concentrations of non-sea salt SO_4^{2-} (nss_SO4) and non-sea salt Cl- (nss_Cl) in aerosol, according to equations 3 and 4, respectively (Keene et al., 1986; O'Dowd and de Leeuw, 2007).

$$[\text{nss\_SO4}] = [SO_4^{2-}] - (0.25 \text{ x } [Na^+]) \qquad (3)$$

$$[\text{nss\_Cl}] = [Cl^-] - (1.80 \text{ x } [Na^+]) \qquad (4)$$

Applying Equation 3 to the SO_4^{2-} data in Figure 6, nss_SO4 is estimated to comprise on average 25 % (range = 3 – 83 %, n = 187) of the measured SO_4^{2-} aerosol. Regression of nss_SO_4 *vs* NH_4^+ (slope = 0.18, intercept = 0.47, R^2 = 0.71) (Figure S3) was not significantly different from the regression of total SO_4^{2-} *vs* NH_4^+ (slope = 0.18, intercept = 2.4, R^2 = 0.73) (Figure 6). Sources of nss_SO4 are (i) biological oxidation of dimethylsulphide and (ii) oxidation of SO_2 (O'Dowd and de Leeuw, 2007). This analysis demonstrates that sea salt SO_4^{2-} aerosol makes up a significant and variable fraction of the total SO_4^{2-} measured, consistent with observations of the contribution by sea salt SO_4^{2-} to the total SO_4^{2-} in precipitation in the UK (ROTAP 2012). The improved intercept from the nss_SO4 regression (Figure S3) suggests that nss_SO4 are mainly associated with NH_4^+.

For Cl^- (mean = 1.3 µg m^{-3}, n = 188), estimated nss_Cl concentrations according to Equation 4 were negligible (mean = –0.09 µg m^{-3}, n = 188). Studies have shown that part of the chloride of sea salt can be substituted by SO_4^{2-} and NO_3^- through a reaction with H_2SO_4 and HNO_3, known as the Cl^- deficit (Ayers et al., 1999). The close coupling between Cl^- and Na^+ (near 1:1 relationship) presented here suggests that the measured Cl^- in the aerosol are mostly sea salt in origin, with no evidence of depletion of Cl^- from sea salt aerosols.

3.4 Temporal trends in acid gases and aerosols

The average seasonal cycles for all gas and aerosol components derived from the mean of monthly data of all sites for the period 2000 to 2015 are compared in Figure 7. Clear differences are observed in these seasonal cycles, influenced by local to regional emissions, climate, meteorology and photochemical processes.

<INSERT Figure 7 HERE>

The seasonal cycle for HNO_3 and NO_3^- has a maximum in spring (Figure 7). HNO_3 is a secondary product of NO_x, but NO_x emissions are dominated by vehicular sources which are not expected to show large seasonal variations. Seasonal changes in chemistry and meteorology are therefore more likely to be a source of the observed variations in HNO_3 and NO_3^-. In spring, the peak in HNO_3 and NO_3^- concentrations are due to i) photochemical processes with elevated ozone in spring (AQEG 2009) leading to formation of HNO_3 during this period (Pope et al., 2016), and ii) long-range transboundary pollution from Europe, leading to regional enhancement across the UK (Vieno et al., 2014, 2016).

The ratio of the concentrations of HNO_3 and NO_3^- can also be seen to fluctuate throughout the year; largest in July and smallest in spring (Figure 8) which may be explained as follows. An equilibrium exists between gaseous HNO_3, NH_3 and particulate NH_4NO_3, the latter of which is appreciably volatile at ambient temperatures (Stelson and Seinfeld, 1982). The atmospheric residence times and therefore concentrations of HNO_3 and NH_3 are strongly dependent on their partitioning between the gas and aerosol phase. HNO_3 and NH_3 that are not removed by deposition may react together in the atmosphere to form NH_4NO_3 aerosol, when the concentration product $[NH_3].[HNO_3]$ exceeds equilibrium values. The formation and dissociation in turn are strongly influenced by ambient temperature and humidity. Warm, dry conditions in summer promotes dissociation, increasing gas-phase HNO_3 relative to particulate-phase NH_4NO_3 (Figure 8). In winter, low temperature and high humidity shifts the equilibrium to formation of NH_4NO_3 from the gas-phase HNO_3 and NH_3. Since NH_3 concentrations are also lowest in winter, this contributes to the winter minimum in NH_4NO_3. The low HNO_3:NO_3^- ratio in spring-time on the other hand is a result of higher NO_3^-, from higher concentrations of the precursor gases HNO_3 and NH_3, and from long-range transboundary transport of particulate NO_3^- e.g. from continental Europe into the UK, as discussed in Vieno et al. (2014, 2016).

<INSERT Figure 8 HERE>

For SO_2, the temporal profile shows highest concentrations in the winter, with concentrations exceeding summer values on average by a factor of 2 (Figure 7). Higher emissions of SO_2 from combustion processes (heating) during the winter months, coupled to stable atmospheric conditions resulting in build-up of concentrations at ground level contributes to the winter maximum. Since the reaction of SO_2 with NH_3 to form $(NH_4)_2SO_4$ is effectively irreversible (Bower et al., 1997), the ratio of the concentrations of SO_2 and SO_4^{2-} (Figure 8) is largely governed by the availability of SO_2 and NH_3 to form $(NH_4)_2SO_4$. The temporal profile of SO_4^{2-} has a peak in concentrations in spring, although not as pronounced as the NO_3^- peak (Figure 7). This may be attributed to enhanced formation of $(NH_4)_2SO_4$, since peaks in concentrations of NH_3 and NH_4^+ also occur in spring (Figure 7) and from the import of particulates from long-range transboundary transport.

Na^+ and Cl^- also have highest concentrations during winter, highlighting the importance of marine sources (more stormy weather) in winter for sea salt aerosol. The seasonal trends in Mg^{2+} is similar to Na^+, with maxima during winter and minima in summer (Figure 7). While sea salt aerosols comprise mainly of NaCl, other chemical ions are also common in seawater, such as K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} (Keene et al., 1986). Some of the sea salt aerosol may therefore be in the form of $MgCl_2$. Magnesium is however also a crustal element, and so it is not as good as sodium as a tracer for sea salt. Similarly, calcium is also a rock-derived element and its presence in the atmosphere is thought to come from chemical weathering of carbonate minerals (Schmitt & Stille, 2005). The seasonal cycle of Ca^{2+} is similar to, but less pronounced than Na^+ and Mg^{2+}. Measured concentrations of Ca^{2+} were mostly at or below the method LOD which makes interpretation uncertain, but the higher concentrations of Ca^{2+} in the winter months is likely to be both crustal dust and sea salt in origin.

<INSERT Figure 9 HERE>

Large inter- and intra-annual variability are also observed in the long-term mean monthly concentrations of gas and aerosol components, as illustrated in Figure 9. In 2003, elevated concentrations of HNO_3 and NO_3^- (and also NH_4^+) were observed between February to April that were more pronounced than the normal peak in concentrations that occur in Spring. The large spike in concentrations was of a sufficient magnitude to elevate the annual mean concentrations for 2003 of HNO_3 (0.54 µg m^{-3} *cf* 0.39 and 0.36 µg m^{-3} for 2002 and 2004, respectively), particulate NO_3^- (2.98 µg m^{-3} *cf* 1.99 and 1.93 µg m^{-3} for 2002 and 2004, respectively) and NH_4^+ (1.45 µg m^{-3} *cf* 1.06 and 0.97 µg m^{-3} for 2002 and 2004, respectively). In comparison, a much smaller spike in elevated SO_4^{2-} concentrations resulted in a slight increase in annual average SO_4^{2-} (1.79 µg m^{-3} *cf* 1.41 and 1.31 µg m^{-3} for 2002 and 2004, respectively) (Figure 9). Meteorological back trajectory analysis of the period showed air masses coming across the UK from Europe, and the pollution episode was attributed to the formation and transport of NH_4NO_3 from Europe, since other gases (SO_2, HCl and NH_3) and particulate Cl^- were not affected (Vieno et al., 2014). At the same time, stable atmospheric conditions due to a persistent high pressure system over the UK led to an accumulation of pollutant concentrations from both local and import sources. A similar pollution episode, but of shorter duration occurred in Spring 2014. At the time, the observed elevated PM was blamed on a Saharan dust plume, but which in fact was then shown to be from long-range transport of NH_4NO_3 (Vieno et al., 2016). Although the 2014 episode was not sufficiently large to be captured in the monthly AGANet data, it reaffirms the substantial contribution of long-range transport into the UK of NH_4NO_3, with precursor gas emissions from outside of the UK presenting a major driver (Vieno et al., 2016).

A second, but smaller pollutant episode that was captured by the AGANet occurred in September 2014, with elevated concentrations of SO_2, HNO_3, SO_4^{2-}, NO_3^- and NH_4^+ that came from the Icelandic Holuhraun volcanic eruptions (Twigg et al., 2016). The elevated SO_2 concentration in September 2014 led to a modest increase in annual concentrations in SO_2 for 2014 (0.58 µg m^{-3}, *cf* annual mean = 0.54 and 0.27 µg m^{-3} for 2013 and 2015, respectively). For the other components (HNO_3, particulate SO_4^{2}, NO_3^- and NH_4^+), the spikes in concentrations were smaller than for SO_2 and did not noticeably elevate their annual mean concentrations for that year. These pollution events together illustrate very clearly how short pollutant episodes can have a major influence on the measured annual concentrations in the UK, and that changes in meteorological conditions, coupled with long-range transboundary import can have a large effect on the UK concentration field.

3.5 Long-term trends at Eskdalemuir

At the Eskdalemuir rural background site, EMEP filter pack data in TIN (sum of HNO_3 and NO_3^-) and TIA (sum of NH_3 and NH_4^+) are available going back to 1989 (Sect. 2.7.3). In Figure 10, the EMEP filter pack TIN and TIA time series (Apr-89 to Dec-00) is extended with AGANet (HNO_3 and NO_3^-) and NAMN (NH_3 and NH_4^+) DELTA data (Sep-99 to Dec-15), with an overalpping period of 14 months. The combined time series shows that the annual concentrations of TIN has halved in 26 years between 1990 to 2015, from 0.36 to 0.16 µg N m^{-3}, compared with a 3-fold reduction in NO_x emissions (from 889 to 280 kt NO_2-N) (defra, 2017) over the same period. For TIA, the 52 % decrease between 1990 to 2015 (from 0.93 to 0.45 µg N m^{-3}) is larger than the corresponding 10 % reduction in NH_3 emissions (from 268 to 241 kt NH_3-N) (defra, 2017). Speciated NH_3 and NH_4^+ data from NAMN over the period 2000 – 2015 shows that the decrease in TIA is mainly driven by NH_4^+, which decreased by 59 % between 2000 (annual mean = 0.62 µg NH_4^+ m^{-3}) and 2015 (annual mean = 0.25 µg NH_4^+ m^{-3}), compared with no change in NH_3 (annual mean 0.32 µg NH_3 m^{-3} in 2000, unchanged in 2015). This is consistent with findings by Tang et al. (2018) that contrary to the reported decrease in UK NH_3 emissions, NH_3 concentrations at background sites (defined by 5 km grid average NH_3 emissions <1 kg N ha^{-1} y^{-1}) are showing an indicative increasing trend, while at the same time, a large downward trend in particulate NH_4^+ is observed. Together, the AGAnet and NAMN are thus providing an important long-term dataset that distinguishes between the gas and aerosol phase, allowing gas:aerosol phase interactions to be explored.

<INSERT Figure 10 HERE>

An extended time series illustrating the continued decline in SO_2 and SO_4^{2-} has also been constructed by combining historic SO_2 and SO_4^{2-} measurement data at the Eskdalemuir site going back to December 1977 (see Sect. 2.7.4) with AGANet SO_2 and SO_4^{2-} data (Sep-99 to Dec-15) (Figure 11). A substantial decline in SO_2 is observed, falling by 98 % from 4.5 µg S m^{-3} in 1978 to 0.07 µg S m^{-3} in 2015, in good agreement with similarly large reduction in UK SO_2 emissions over the same period of 95 % (from 2530 to 120 kt SO_2-S). The decrease in SO_4^{2-} is of a smaller magnitude, declining by 88 % from an annual mean concentration of 0.89 µg S m^{-3} in 1978 to 0.11 µg S m^{-3} in 2015, highlighting the non-linearity in relationship between the atmospheric gas and aerosol phase of sulphur at this background site.

<INSERT Figure 11 HERE>

3.6 Assessment of trends in relation to UK emissions

The long-term time series in annually averaged concentrations of the gas and aerosol components are shown in Figure 12a and Figure 12b, respectively. Annually averaged data from the original 12 sites for the period 2000 – 2015 (1999 data excluded since AGANet started in September 1999) and from the full network (30 sites) for the period 2006 – 2015 are plotted alongside each other for comparison. From 2006 – 2015, the decreasing trends for all gas and aerosol components from the expanded 30 sites are seen to be similar to those from the original 12 sites. The annual mean concentrations in gas and aerosol components derived from the expanded 30 sites (2006 – 2015) or from the original 12 sites over the same period are also in general comparable (Table 4). The exceptions are Na^+ and Cl^- that have higher mean concentrations from the 30 sites than the original 12 sites, due to the addition of two coastal sites (Shetland and Rum), with larger contribution from sea salt. Larger HNO_3 concentrations are due to two urban sites, London and Edinburgh (higher NO_x emissions from vehicular traffic). The addition of three sites in high NH_3 emission (agricultural) areas (Rosemaund in England, Narberth in Wales and Hillsborough in Northern Ireland) also elevated measured annual mean NH_3 concentrations. The comparisons here thus illustrates very clearly the need to consider the effect of site changes in a national network and the importance of maintaining consistency and site continuity for assessing long-term trends.

<INSERT Figure 12 HERE>

<INSERT Table 4 HERE>

Since there was a change in the number of sites during the operation of the AGANet, statistical trend analyses for HNO_3, SO_2, HCl and particulate NO_3^-, SO_4^{2-}, Cl^- were performed on annually averaged mean concentrations from two time series: i) the original 12 AGANet sites for the 16 year period from 2000 to 2015, and ii) the expanded 30 AGANet sites for the 10 year period from 2006 to 2015. NH_3 and NH_4^+ concentrations from the NAMN that were measured at the same time at the AGANet sites were also included for comparison and to aid interpretation of the acid gas and aerosol data. This approach avoids introducing bias as a result of changes in the sites and ensures site continuity for the long-term trend assessment.

Results of the Linear Regression (LR) and Mann-Kendall (MK) tests (Section 2.8) are summarised in Figure 13 and Table 5 for the original 12 sites (2000 – 2015), and in Figure 14 and Table 6 for the expanded 30 sites (2006 – 2015). To assess changes in measured concentrations over time, annual trends (e.g. µg HNO_3^{-1} y^{-1}) were estimated from the regression results of the LR and MK tests. This is considered to provide a more reliable estimate of trend than comparing measured annual concentrations at the beginning and end of the time series, which is subject to bias due to substantial variability in annual concentrations between years (Tang et al., 2018). The LR % annual trends for each time series are estimated from the LR's slope and intercept, while the MK % median annual trends are estimated from the MK Sen's slope and intercept (equation 5).

$$\%\text{ annual change } = 100\,.\frac{[Yi-Yo)}{Yo} \qquad [5]$$

where (y_0) and (y_i) = estimated annual mean concentrations at the start and end of the selected time period, estimated from the slope and intercept of the LR or MK tests.

The long-term trends in the gas and aerosol components, based on statistical analysis of monthly mean measurement data, are also shown for comparison in Figure S4 (mean monthly data of 12 sites for period 2000-2015) and Figure S5 (mean monthly data of 12 sites for period 2006-2015). Results of the trend analysis on monthly data (Tables S4, S5) were similar to trend analysis results of the annual data (Table 5; Table 6). While not discussed further here, since assessment of long-term trends in this paper focusses on trends in annual mean concentrations for comparison with trends in estimated annual emissions, the monthly plots serves to illustrate the large intra-annual variability of concentrations in gases and aerosols.

<INSERT Figure 13 HERE>
<INSERT Table 5 HERE>
<INSERT Figure 14 HERE>
<INSERT Table 6 HERE>

Measured concentrations of HNO_3 and particulate NO_3^- from the AGANet show a clear significant decreasing trend, although less substantial than for SO_2 and SO_4^{2-} (Figure 12). Between 2000 and 2015, HNO_3 decreased by 45 % (MK, LR = –42 %), compared with a 2-fold higher reduction of 81% (MK, LR = –84 %) in SO_2 concentrations (Table 5). The decrease in HNO_3 between 2006 and 2015 from the expanded 30 sites network (–36 % MK, –30 % LR) is similarly half that of SO_2 (–60 % MK / LR) over the same period (Table 6). The decrease in HNO_3 is accompanied by a slightly larger decrease in particulate NO_3^- (2000-2015: MK = –52 %, LR = –51 %, 2006–2015: MK = –43 %, LR = –39 %) (Table 7). By contrast, the decline in particulate SO_4^{2-} (2000-2015: MK = –69 %, LR = –70 %, 2006–2015: MK = –54 %, LR = –53 %) is smaller than its precursor SO_2 and larger than the decrease in NO_3^- (Table 7).

The formation of both NO_3^- and SO_4^{2-} requires NH_4^+ as a counter-ion, which decreased by 62 % (MK, –64 % LR) over the period 2000 - 2015 (Table 5) and by 49 % (MK, –48 % LR) between 2006 and 2015 (Table 6). The decrease in NH_4^+ is 2-fold higher than the decline in its precursor NH_3 gas (2000-2015 = –30 % MK / LR, 2006-2015 = –18 % MK / –21% LR), and intermediate between that of NO_3^- and SO_4^{2-} (Table 7). For HCl and Cl-, there is a decreasing trend in HCl (2000-2015: MK

= –28 %, LR = –26 %, 2006–2015: MK = –24 %, LR = –21 %), but overall there is no detectable trend in particulate Cl^- (Table 5, Table 6).

<INSERT Table 7 HERE>
<INSERT Figure 15 HERE>

Large decreasing trends in estimated emissions for NO_x, and in particular for SO_2 continued since monitoring in AGANet began in 1999. NO_x emissions decreased by 58 % between 2000 and 2015, followed closely by a similar reduction in measured HNO_3 (–45 % MK / –42 % LR) and NO_3^- concentrations (–52 % MK / –51 % LR) over the same period (Figure 15a; Table 7). Results from the trend analysis of 30 AGANet sites between 2006 and 2015 (HNO_3 = –36 % MK / -30 % LR, NO_3^- = –43 % MK / –39 % LR) are also consistent with the 41 % decline in NO_x emissions over this period, in agreement with the emissions inventory (Figure 15b; Table 7). HNO_3, as a secondary product of NO_x, provides an important measure of the fraction of NO_x emissions that is oxidised within the country and signals any long-term changes in the atmospheric processing timescales of NO_x over the country. Since the decreasing trends in estimated NO_x emissions and measured HNO_3 are similar, there appears to have been no change in the oxidation and processing of NO_x in the atmosphere.

<INSERT Figure 16 HERE>

For SO_2, there has been a more significant decline, both in emissions and measured concentrations during this period (Figure 16). The network annual mean concentration decreased from 1.9 µg SO_2 m^{-3} in 2000 to 0.25 µg SO_2 m^{-3} in 2015 (mean of 12 sites), continuing the long-term decline in SO_2 concentrations observed at the background Eskdalemuir site (Sect. 3.5) and across the UK (ROTAP 2012). From the trend analysis, the decrease in annual mean SO_2 concentrations of –81 % (MK, LR = –84 %) between 2000–2015 (Table 5), and –60 % (MK and LR) between 2006 – 2015 (Table 6) are consistent with the substantial reduction of –80 % and –64 % in SO_2 emissions over the two overlapping periods, respectively (Figure 16; Table 7). At the same time, the reduction in SO_2 emission and measured concentration is accompanied by a smaller negative trend in particulate SO_4^{2-} (2000-2015: –69 % MK/ -70 % LR; 2006-2015: –54 % MK / –53 % LR) (Table 5; Table 7), with concentrations falling 3-fold from an annual mean of 1.2 µg SO_4^{2-} m^{-3} in 2000 to 0.42 µg SO_4^{2-} m^{-3} in 2015. The smaller decrease in particulate SO_4^{2-}compared with its gaseous precursor, SO_2, is similar to that observed at Eskdalemuir (Sect. 3.5).

<INSERT Figure 17 HERE>

By contrast, a smaller 30 % decrease is seen in the annually averaged NH_3 concentrations at the 12 AGANet sites (2000-2015: –30 % MK/LR) (Figure 13; Table 5). This decrease is larger than the decrease in NH_3 emissions of 10 % over the same period (Table 7). A recent assessment by Tang et al. (2018) showed that NH_3 trends are highly dependent on site selection and a more comprehensive analysis of a larger number of sites shows smaller reductions over time. By contrast, a significant decreasing trend in NH_3 concentrations was observed in the grouped analysis of sites in areas classed as dominated by pig and poultry emissions, against an upward (non-significant) trend for sites in cattle-dominated areas. Therefore there is a large degree of uncertainty in interpreting the trends in NH_3 concentrations from a subset of just 12 sites. What the NH_3 data from the 12 sites does show, however, is that there is a shift from air being dominated by SO_2 towards it being dominated by NH_3, with a rapidly changing chemical climate in terms of relative concentrations of NH_3 and SO_2. The ratio of annual mean concentrations of NH_3 (80 nmol m^{-3}) to SO_2 (29 nmol m^{-3}) was 2.7 in 2000 (Figure 18). By 2015, this ratio had increased to 15 (annual mean concentrations of NH_3 = 58 nmol m^{-3} and SO_2 = 4 nmol m^{-3}) (Figure 18). At the same time, there is a larger decrease in NH_4^+ concentrations (–62 % MK / –64 % LR), contrasting with a smaller decrease in NH_3 concentrations over the period 2010–2015 (–30 % MK / LR) (Table 7), with the NH_3:NH_4^+ ratio increasing with time (Figure 18). This provides evidence for a shift in partitioning from the particulate phase NH_4^+ to the gaseous phase NH_3 in the UK data, discussed in Tang et al. (2018). The change in partitioning from particulate NH_4^+ to gaseous NH_3 is also occurring in other parts of Europe, where decreases in NH_3 concentrations have been smaller than emission trends would suggest, due to large decreases in SO_2 emissions (Bleeker et al., 2009; Horvath et al., 2009).

Studies have shown that the increasing ratio of NH_3 to SO_2 in the atmosphere leads to increased dry deposition of SO_2, accelerating the decrease in atmospheric SO_2 concentrations than would be achieved by emissions reduction alone (Fowler et al., 2001; ROTAP 2012). The dry deposition of SO_2 and NH_3, by uptake of the gases in a liquid film on leave surfaces, are known to be enhanced when both gases are present in a process termed “co-deposition” (Fowler et al., 2001). Where ambient NH_3 concentrations exceed that of SO_2, there is enough NH_3 to neutralize acidity in the liquid film and oxidise deposited SO_2, and maintain large rates of deposition of SO_2. Supporting evidence for enhanced deposition of SO_2 in a NH_3-rich atmosphere is provided by the AGANet data that shows a more rapid decline in SO_2 concentrations than SO_4^{2-}, and the negative trend in the ratio of SO_2:SO_4^{2-}.

<INSERT Figure 18 HERE>

The substantial decrease in UK SO_2 emissions and concentrations, while UK NO_x emissions and concentrations remain relatively high in comparison, set against a much smaller decrease in NH_3 emissions and concentrations since 2000 is leading to changes in the respective particulate SO_4^{2-}, NO_3^- and NH_4^+ concentrations. Since the affinity of H_2SO_4 (oxidation product of SO_2) for NH_3 is much larger than that of HNO3 and HCl, available NH_3 is first taken up by H_2SO_4 to form ammonium sulphate compounds (NH_4HSO_4 and $(NH_4)_2SO_4$), with any excess NH_3 then available to react with HNO_3 and HCl to formNH_4NO_3 and NH_4Cl. The increase in ratio of HNO_3:NO_3^- is similar to changes in upward trend in gas-aerosol partitioning between NH_3 and NH_4^+ over time (Figure 18). The negative trend in ratio of SO_2:SO_4^{2-}, contrasting with the positive trend in ratio of HNO_3:NO_3^- (Figure 18) lends further support that reduction in SO_2 emissions is contributing to a more rapid decrease in particulate $(NH_4)_2SO_4$ concentrations, as more NH_3 becomes available to react with HNO_3 to form the NH_4NO_3, A change to an NH_4NO_3 rich atmosphere may account for the smaller negative trend in particulate NO_3^- observed here.

Currently, the critical loads of acidity (sulphur and nitrogen) are exceeded by 44 % of the area of sensitive habitats in the UK (based on mean deposition data for 2012-2014), whereas the figure for exceedance of eutrophication (nutrient nitrogen) is even larger, at 62 % (based on deposition data for 2012 – 2014) (Hall & Smith, 2016). Air quality policies have been very successful in abating SO_2 emissions (–80 % between 2000 – 2015) and moderately successful with NO_x emissions (–58 % between 2000 – 2015), with both on course to meet the emission reduction targets set out under the 2012 Gothenburg protocol and 2016 NECD. There remains however little political will to reduce emissions of NH_3. Since estimated emissions of NH_3 decreased by only 10 % over the same period, it is likely that abatement measures may be required to meet emission reduction targets. At the same time, results from the AGANet show a change in the particulate phase from $(NH_4)_2SO_4$ to NH_4NO_3. This change is expected to increase residence times of NH_3 and HNO_3 in the atmosphere, as the semi-volatile NH_4NO_3 will volatilise in warm weather to release HNO_3 and NH_3. A higher concentration of the gas-phase nitrogen species (HNO_3 and NH_3) may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in NO_x and NH_3. More of the NH_3 and NO_x emitted will deposit more locally with a smaller footprint within the UK. Based on the current emission trends and evidence from AGANet and NAMN long-term measurements, atmospheric N deposition from oxidised N (NO_x, HNO_3 and NO_3^-) and from reduced N (NH_3, NH_4^+) are likely to continue to exceed critical loads of N deposition over large areas of sensitive habitats, with implications for UK's commitment to maintain or restore natural habitats (e.g. Natura 2000 sites; Hallsworth et al., 2010) to a favourable conservation status under the EU Habitats Directive (Council Directive 92/43/EEC). The changes are also relevant for human health effects assessments, since NH_4NO_3 and $(NH_4)_2SO_4$ are mainly in the fine mode and constitute a significant fraction of $PM_{2.5}$ that are associated with acute and chronic human health problems. The change in partitioning from $(NH_4)_2SO_4$ to NH_4NO_3, coupled to import of NH_4NO_3 from long-range transport (driven by emissions of NH_3 and NO_x from outside the UK) poses policy challenges in protection of human health from effects of air pollution, particularly in urban areas where concentrations of the $PM_{2.5}$ precursor gases NO_x, SO_2 and NH_3 are higher.

4 Conclusions

The UK Acid Gases and Aerosol network (AGANet) is delivering, uniquely, a comprehensive UK long-term dataset of speciated acid gases (HNO_3, SO_2, HCl) and aerosol components (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}) and also of NH_3 and NH_4^+ measured within the National Ammonia Monitoring Network (NAMN). Speciated measurements are made with an established low-cost DELTA denuder-filter pack methodology, allowing assessment of atmospheric chemical composition and gas-aerosol phase interactions. Other manual denuder-filter implementations designed for high time-resolution measurements are useful at selected locations for detailed analysis and model testing, but they are resource intensive and expensive. The DELTA monthly measurements on the other hand are cost-efficient for estimating annual mean concentrations, providing sufficient resolution for analysis of temporal trends and which can be operated at a large number of sites in the network to provide long-term trends and temporal/spatial patterns.

Large regional patterns in concentrations are observed, with the largest concentrations of HNO_3, SO_2, and aerosol NO_3^- and SO_4^{2-} in south and east England, attributed to anthropogenic (combustion, vehicular) and long-range transboundary sources from Europe, and smallest in western Scotland and Northern Ireland. HCl concentrations are also largest in the southeast and southwest of England, attributed to dual contribution from anthropogenic (coal combustion) and marine sources (reaction of sea salt with HNO_3 and H_2SO_4 to form HCl) from coal combustion. For Cl^-, this has a similar spatial distribution as Na^+, with highest concentrations of at coastal sites, reflecting their origin from marine sources (sea salt).

Distinctive temporal trends are established for the different components, with the seasonal variability influenced by local to regional emissions, climate, meteorology and photochemistry. HNO_3 and NO_3^- have a maximum during late spring and early summer, due to photochemical production processes and from long-range transboundary pollutant transport. SO_4^{2-} concentrations also have a peak in spring-time, coinciding with the peak in concentrations of NH_3 and NH_4^+, and is therefore likely to be attributed to formation of $(NH_4)_2SO_4$ from reaction with a surplus of higher concentrations of NH_3 at that time of year. Conversely, peak concentrations of SO_2, Na^+ and Cl^- occur during winter, likely from combustion processes (heating) for SO_2 and marine sources in winter (more stormy weather) for sea salt generation. Magnesium and calcium are both crustal elements, but which are also present in sea salt aerosols. The seasonal trend in Mg^{2+} is similar to Na^+, with maxima during winter and minima in summer; therefore some of the sea salt aerosol may be in the form of $MgCl_2$. For Ca^{2+}, the winter maxima is much less pronounced and its seasonal variability is likely to be influenced by both crustal dust and sea salt.

Enhancement of local to regional concentrations of reactive gases and aerosols in the UK from long-range transboundary transport of pollutants into the UK is highlighted by two pollution events, captured in the long-term AGANet monthly measurements. In 2003, a spring episode with elevated concentrations of HNO_3 and NO_3^- was driven by meteorology, with easterly winds transporting NH_4NO_3 formed in Europe into the UK and a high pressure system over the UK (Feb-April) that led to a build-up of NH_4NO_3 and HNO_3 concentrations from both local and transboundary sources. A second, but smaller episode of elevated concentrations of SO_2 and HNO_3, as well as of particulate SO_4^{2}, NO_3^- and NH_4^+, in September 2014 was shown to be from transport of pollutant plume from the Icelandic Holuhraun volcanic eruptions at that time.

After more than 16 years of operation, the AGANet is also capturing important long-term changes in the concentrations and partitioning between gas and aerosol of the N and S components in the atmosphere. For SO_2, a significant decreasing trend in annual mean SO_2 concentrations of –81 % (MK, LR = –84 %) from 2000–2015 was in agreement with the estimated –80 % SO_2 emissions reductions, but larger than the accompanying decline in particulate SO_4^{2-} (–69 % MK/ -70 % LR). A more modest reduction in HNO_3 (–45 % MK / –42 % LR) and particulate NO_3^- (–52 % MK / –51 % LR) are consistent with the estimated 58 % decline in NO_x emissions over this same period. At the same time, NH_3 measurements made under NAMN shows a shift from air being dominated by SO_2 towards it being dominated by NH_3. For particulate NH_4^+, the decrease in concentrations (–62 % MK / –64 % LR) is larger than the precursor gas NH_3 (2000 – 2015 = –30 % MK / LR), and larger than the estimated decline in estimated NH_3 emissions of 10 %. However, it should be noted that NH_3 trends are highly dependent on site selection and a more comprehensive analysis of a larger number of sites shows smaller reductions over time.

The substantial decrease in UK SO_2 emissions and concentrations, while UK NO_x emissions and concentrations (HNO_3) remain relatively high in comparison, set against a much smaller decrease in NH_3 emissions and concentrations since 2000 is leaving more NH_3 available to react with HNO_3 to form the semi-volatile particulate NH_4NO_3. The change in partitioning from particulate NH_4^+ to gaseous NH_3 is also occurring in other parts of Europe, where decreases in NH_3 concentrations have been smaller then emission trends would suggest, due to successful mitigation in SO_2 emissions. At the same time, a change in the particulate phase from $(NH_4)_2SO_4$ to NH_4NO_3 would contribute to slowing down the negative trend in particulate NO_3^- observed here. Higher concentrations of the NH_3 and HNO_3 in the atmosphere will deposit more locally, exacerbating the effects of local N deposition loads over large areas of sensitive habitats, with implications for UK's commitment to maintain or restore natural habitats (e.g. Natura 2000 sites) to a favourable conservation status under the EU Habitats Directive (Council Directive 92/43/EEC). The changes are also important in terms of human effects assessment since NH_4NO_3 constitute a significant fraction of $PM_{2.5}$ that are implicated in acute and chronic human health effects and linked to increased mortality from respiratory and cardiopulmonary diseases.

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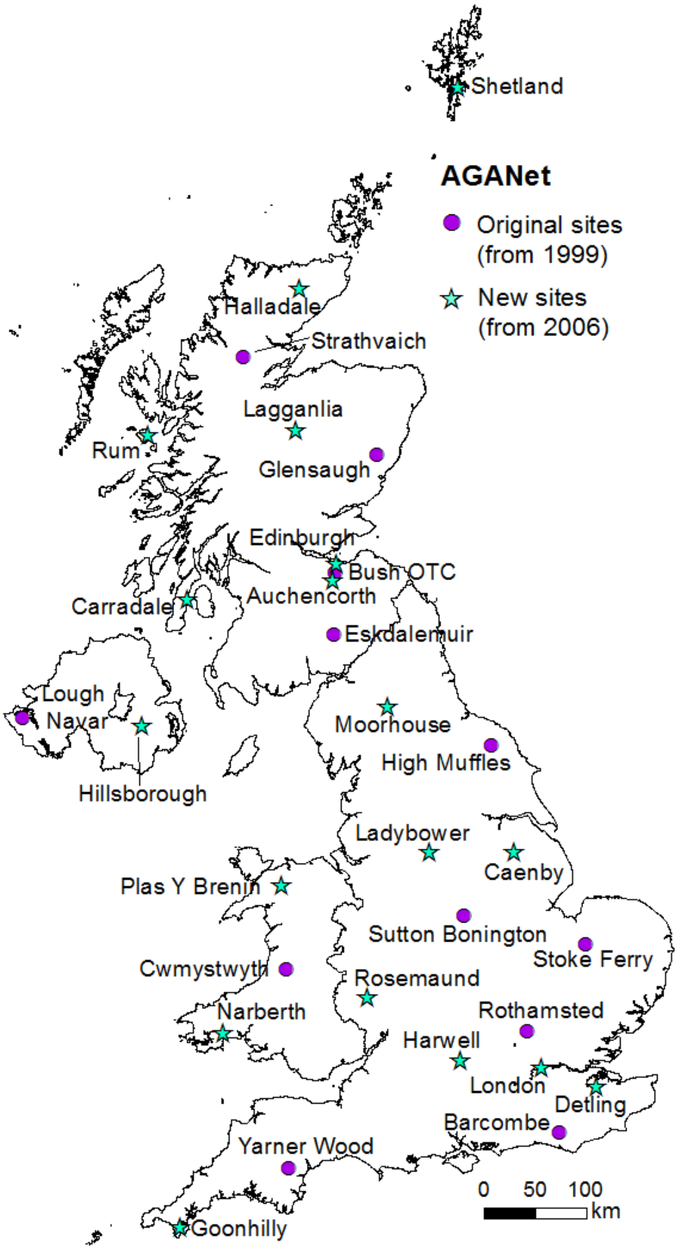

Figure 1: Site map of the UK Acid Gases and Aerosol Network (AGANet). The AGANet was established in September 1999 with 12 sites and expanded to 30 sites from January 2006 to improve national coverage. These sites also provide measurements of NH_3 and NH_4^+ for the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018). 5

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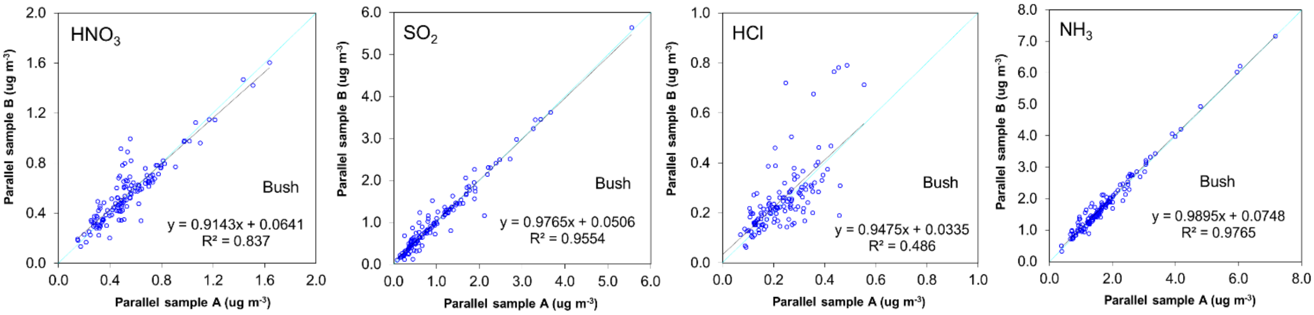
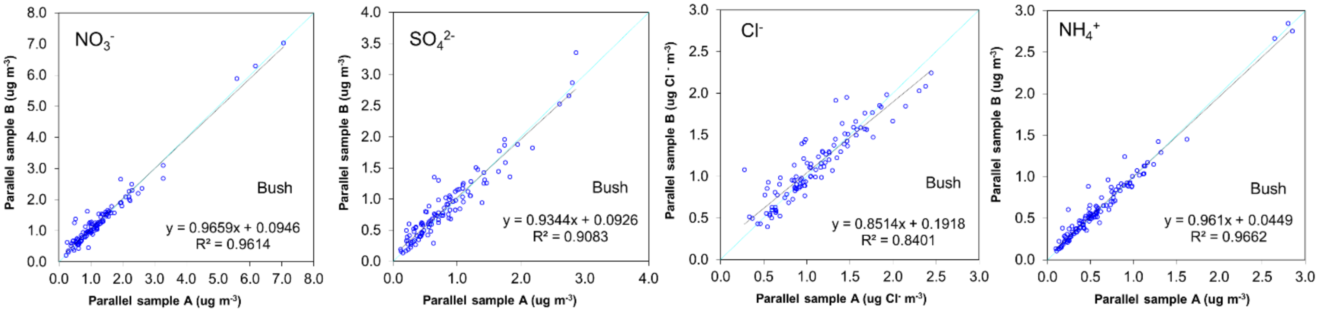
(a) Gases (HNO_3, SO_2, HCl, NH_3)



(b) Particulate (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+)



(c) Summary of regression analysis

	Gases				Particulates			
	HNO_3	SO_2	HCl	NH_3	NO_3^-	SO_4^{2-}	Cl^-	NH_4^+
R^2	0.837***	0.955***	0.486***	0.976***	0.961***	0.908***	0.840***	0.966***
slope	0.914*	0.976^{ns}	0.947^{ns}	0.989^{ns}	0.966^{ns}	0.934*	0.851***	0.961*
intercept	0.064**	0.051*	0.033^{ns}	0.075**	0.095**	0.093**	0.192***	0.045***
No. observations (*n*)	130	130	128	140	108	108	104	119
mean A (μg m^{-3})	0.54	1.02	0.23	1.75	1.29	0.84	1.09	0.61
mean B (μg m^{-3})	0.56	1.05	0.25	1.80	1.34	0.87	1.12	0.63

Significance level (slope different from 1, intercept = 0): * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. *ns* = not significant ($p > 0.05$)

Figure 2: Comparisons of parallel measurement of monthly (a) atmospheric reactive gases (HNO_3, SO_2, HCl and NH_3) and (b) particulate (NO_3^-, SO_4^{2-}, Cl^- and NH_4^+) concentrations from duplicate DELTA sampling at the UK Acid Gas and Aerosol Monitoring Network (AGANet) and National Ammonia Monitoring Network (NAMN) site Bush OTC (UKA00128) in Southern Scotland for the period 1999 to2015. (c) A summary of the regression analyses. Each point represents a comparison between the paired monthly DELTA measurements.

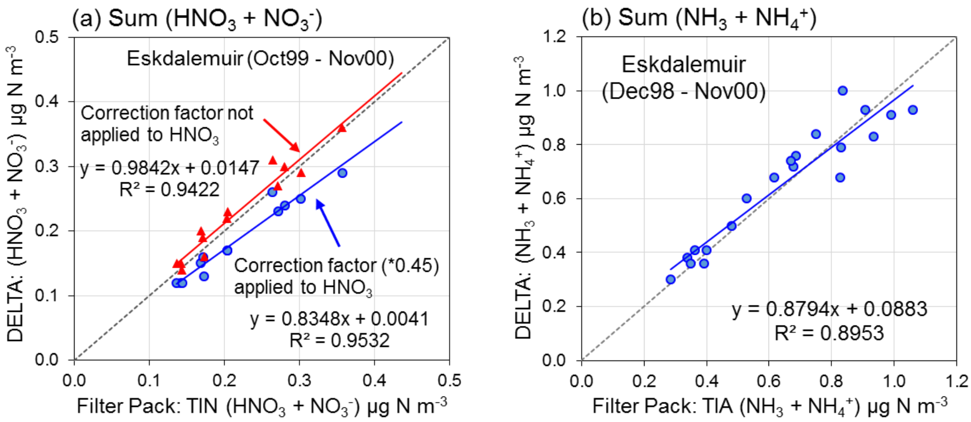
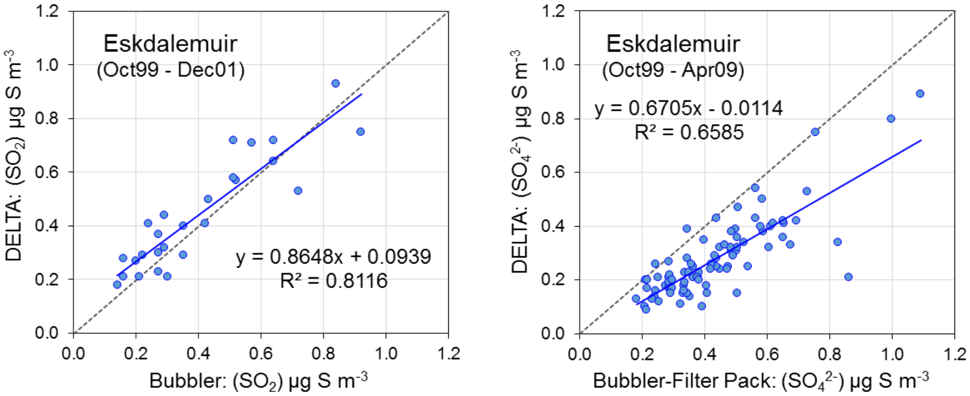


Figure 3: Comparison of (a) total inorganic nitrate, TIN (sum of HNO_3 + NO_3^-) and (b) total inorganic ammonium, TIA (sum of NH_3 + NH_4^+) concentrations at the Eskdalemuir monitoring station (EMEP station code = GB0002R; UK-AIR ID = UKA00130) measured under the EMEP program with concentrations of the corresponding gas and aerosol from the UK Acid Gases and Aerosol (AGANet, HNO_3 and NO_3^-) and UK National Ammonia Monitoring Network (NAMN, NH_3 and NH_4^+). EMEP values (data downloaded from http://ebas.nilu.no/) are means of daily measurements for TIN and TIA by the EMEP filter pack method, matched to the AGANet and NAMN sampling periods (monthly). Filter pack measurements at Eskdalemuir terminated in December 2000.



	AGANet DELTA: SO_2	Bubbler: SO_2	AGANet DELTA: SO_4^{2-}	Filter Pack: SO_4^{2-}
Linear regression: R^2	0.812***		0.658***	
slope	0.865*ns*		0.670***	
intercept	0.094*		0.011*ns*	
mean (µg S m^{-3})	0.44	0.40	0.28	0.44
No. of observations (*n*)	26	26	87	87

Significance level (slope different from 1, intercept = 0): * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. *ns* = not significant ($p > 0.05$)

Figure 4: Comparison of gaseous SO_2 and particulate SO_4^{2-} concentrations at the Eskdalemuir monitoring station (EMEP station code = GB0002R; UK-AIR ID = UKA00130) measured under the Acid Deposition Monitoring Program (ADMN, Hayman et al., 2007) with the corresponding gas and aerosol from the UK Acid Gases and Aerosol network (AGANet). ADMN values (data downloaded from http://ebas.nilu.no/) are means of daily measurements for SO_2 by the bubbler method and SO_4^{2-} by the EMEP filter pack method (Hayman et al., 2007), matched to the AGANet sampling periods (monthly). Bubbler and filter pack measurements at Eskdalemuir terminated in December 2001 and Apr 2009, respectively.

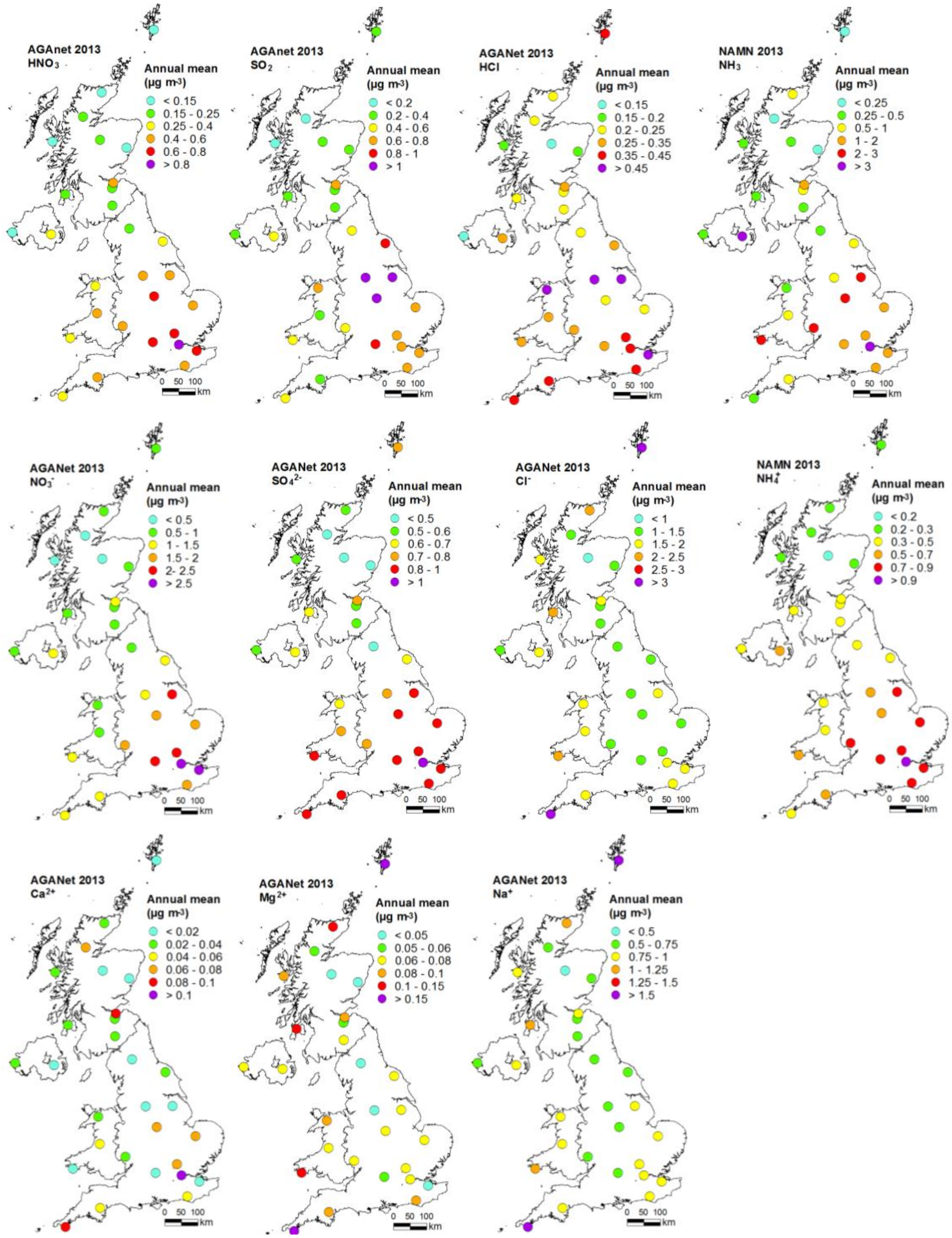
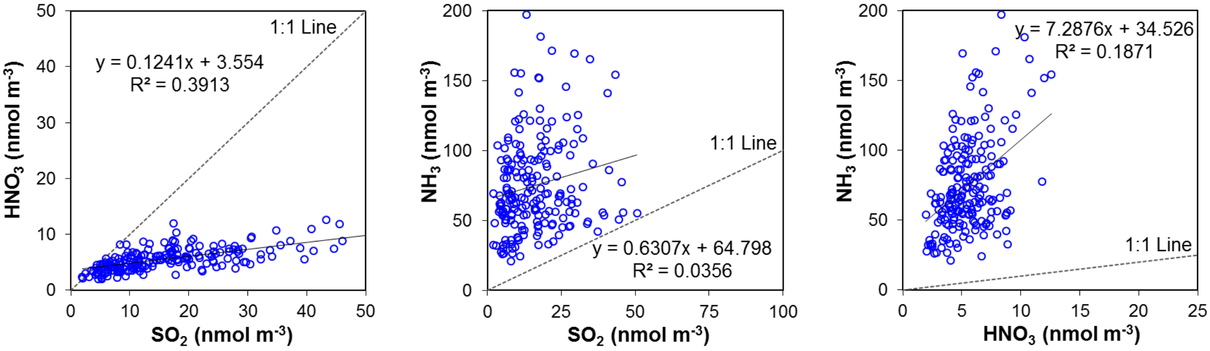


Figure 5: Annual mean monitored acid gas (HNO_3, SO_2, HCl) and aerosol (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}) concentrations from the UK Acid Gas and Aerosol Monitoring Network (AGANet) across the UK from annual averaged monthly measurements made in 2013. NH_3 and NH_4^+ measured at the same time from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown alongside for comparison.

(a) Gaseous components



(b) Particulate components

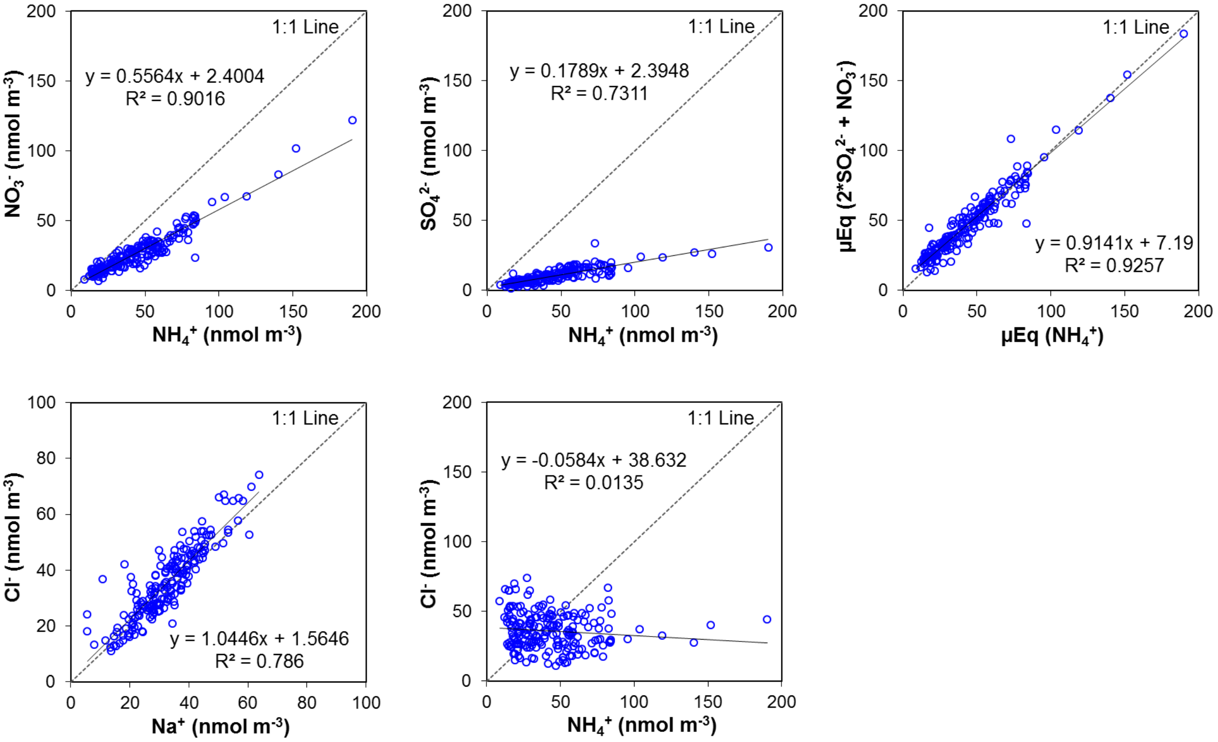


Figure 6: Scatter plots between concentrations of (a) gaseous species HNO_3, SO_2 and NH_3, and (b) particulate species NO_3^-, SO_4^{2-}, NH_4^+, Cl^- and Na^+ from mean monthly measurements (1999-2015) from the 12 sites in the UK Acid Gas and Aerosol Monitoring Network (AGANet) that were operational over the whole period. NH_3 and NH_4^+ data are from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) made at the same time. Each data point represents a single monthly DELTA measurement.

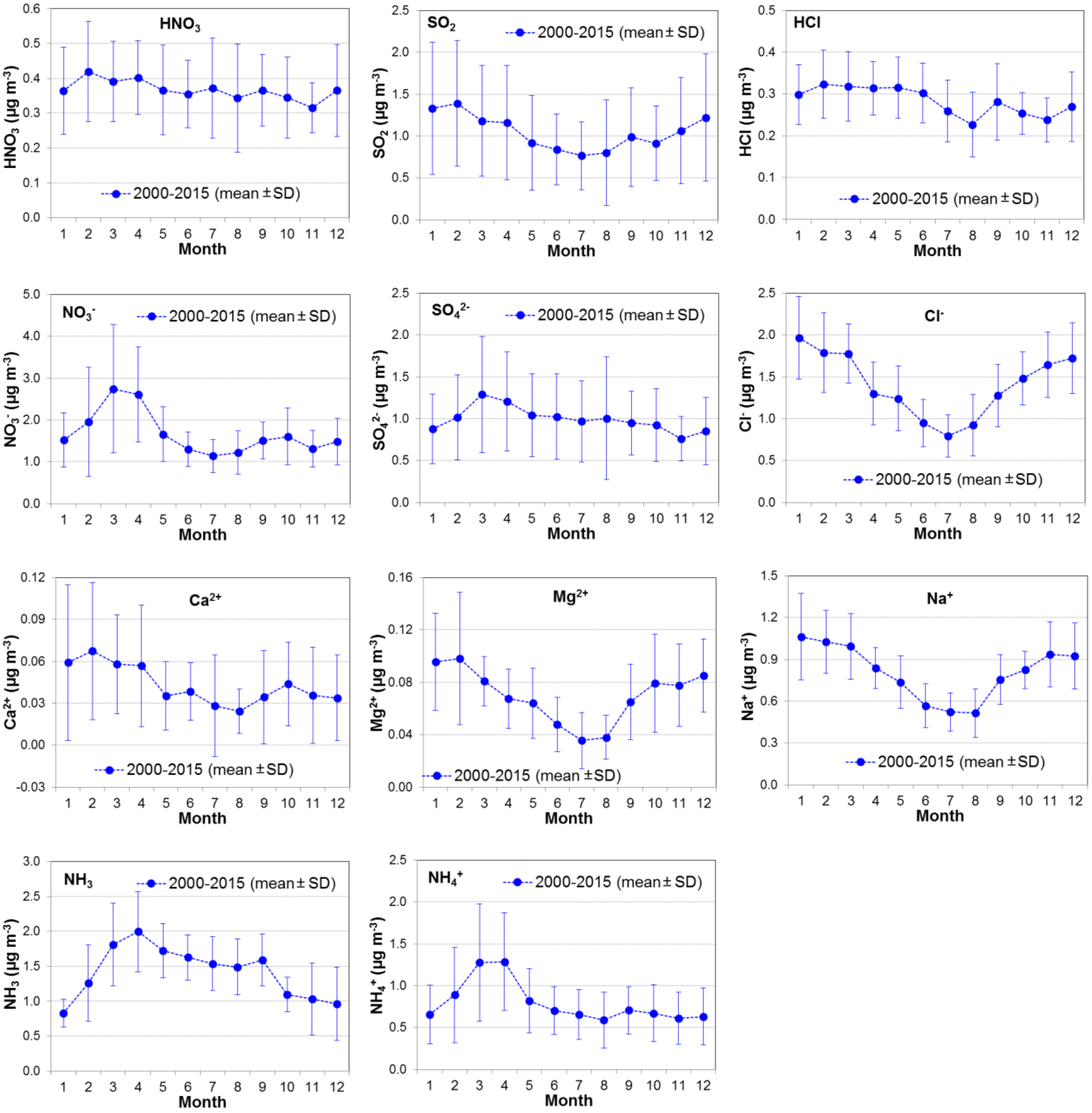


Figure 7: Average annual cycles for HNO_3, SO_2, HCl and aerosol NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+} and Mg^{2+} from the UK Acid Gases and Aerosol Monitoring Network (AGANet). The NH_3 and NH_4^+ concentrations measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown for comparison. Each data point in the graphs represents the mean ± SD of monthly measurements of all sites in the network.

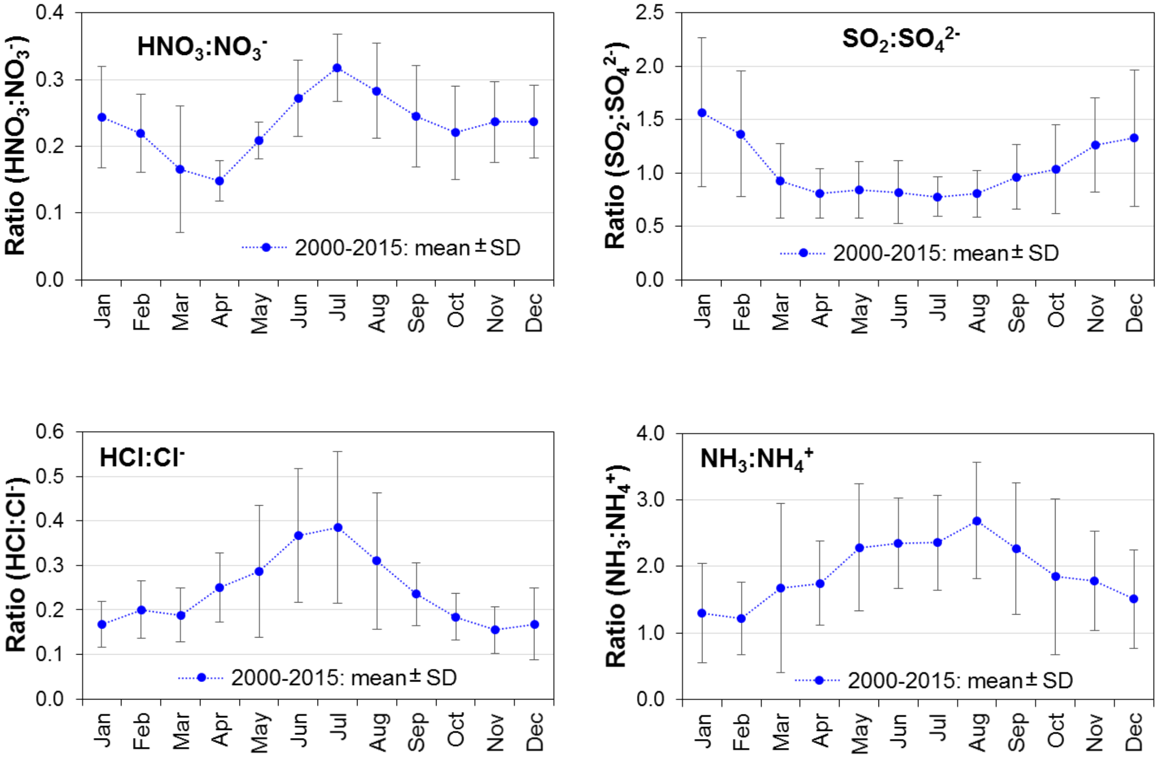


Figure 8: Average annual cycles in the ratios of gas:aerosol component concentrations (µg m^{-3}). HNO$_3$, SO$_2$, HCl and aerosol NO$_3^-$, SO$_4^{2-}$, Cl$^-$ data are from the UK Acid Gases and Aerosol Monitoring Network (AGANet). NH$_3$ and NH$_4^+$ concentrations (µg m^{-3}) that are measured at the same time for the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown for comparison. Each data point in the graphs represents the mean ± SD of monthly measurements of 12 sites operational in the network over the period 2000 to 2015.

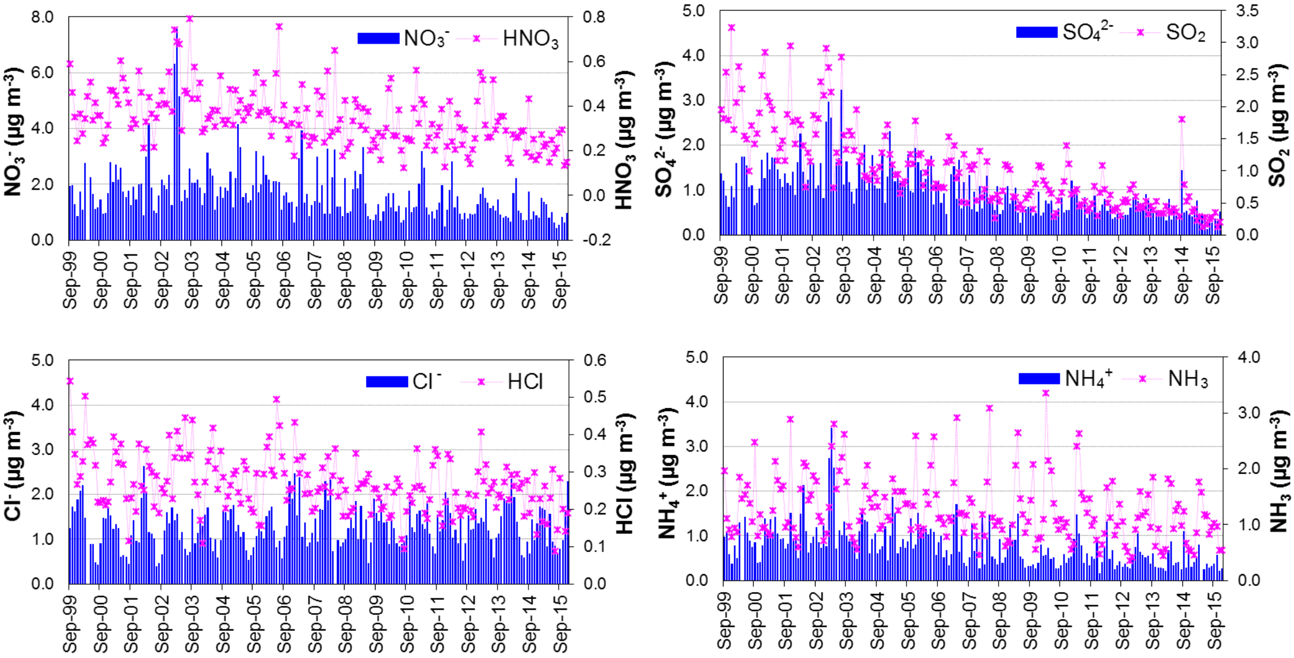


Figure 9: Monthly mean concentrations in gaseous HNO_3, SO_2, HCl and aerosol NO_3^-, SO_4^{2-}, Cl^- from the UK Acid Gases and Aerosol Monitoring Network (AGANet). Monthly mean concentrations of NH_3 and NH_4^+ that were measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown for comparison. Each data point in the graphs represents the mean of monthly measurements of 12 sites operational in the network over the period Sep 1999 to December 2015. The same plots for the full 30 site network from 2006 - 2015 are shown in Supp. Figure S6.

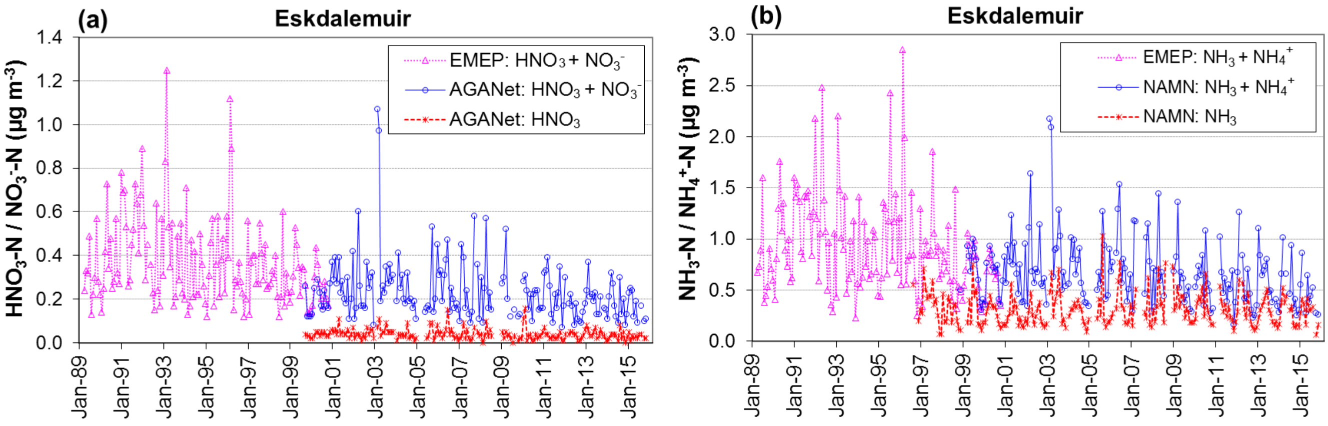


Figure 10: Long-term time series of (a) oxidised nitrogen (HNO_3 and NO_3^-) and (b) reduced nitrogen (NH_3 and NH_4^+) concentrations at Eskdalemuir (EMEP station code = GB0002R; UK-AIR ID = UKA00130). EMEP values (data downloaded from http://ebas.nilu.no/) are monthly means of daily measurements for total inorganic nitrogen, TIN (sum of HNO_3 and NO_3^-) and total inorganic nitrogen, TIA (sum of NH_3 and NH_4^+) by the EMEP filter pack method (Apr-89 – Nov-00), matched to the AGANet and NAMN sampling periods (monthly) where the measurements overlap. The AGANet and NAMN data are for gaseous HNO_3 and NH_3 and for the sum of (HNO_3 + NO_3^-) and sum of (NH_3 + NH_4^+), respectively, by the DELTA method. The AGANet HNO_3 values shown here includes the bias correction (Section 2.6).

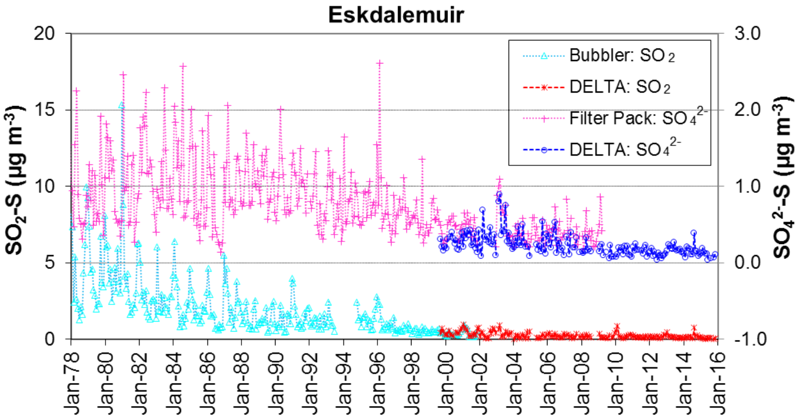


Figure 11: Long-term time series of SO_2 (Dec-77 – Jul-93) and SO_4^{2-} (Dec-77 – Dec-01) concentrations measured in the UK Acid Deposition Monitoring Network (ADMN) (Hayman et al., 2007) and the AGANet DELTA measurements (Oct-99 – Dec-15) at the Eskdalemuir monitoring station (EMEP station code = GB0002R; UK-AIR ID = UKA00130). ADMN values (data downloaded from http://ebas.nilu.no/) are monthly means of daily measurements for SO_2 and SO_4^{2-} by a daily bubbler and filter pack method, respectively, matched to the AGANet sampling periods (monthly) where the measurements overlap.

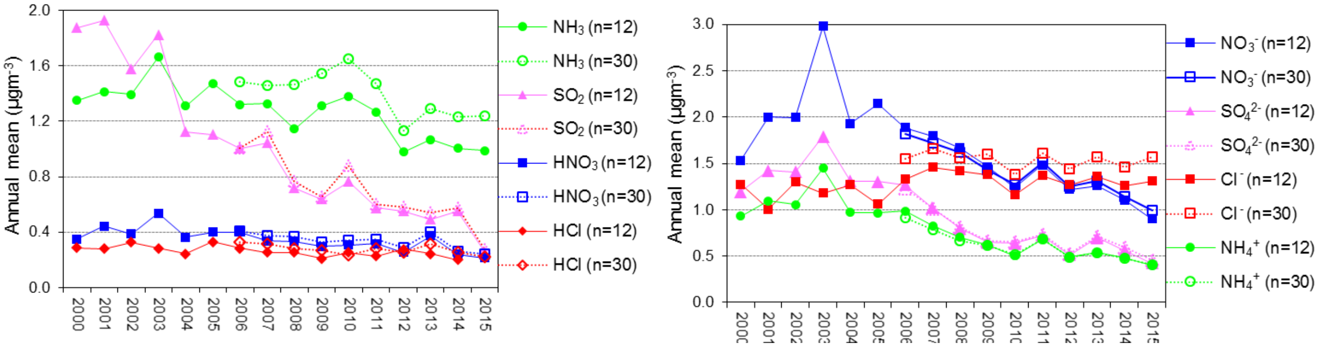


Figure 12: Long-term trends in (a) acid gases and (b) aerosol concentrations from the UK Acid Gases and Aerosol Network (AGANet). Each data point represents the annually averaged measurements from either the original 12 AGANet sites for the 16-year period from 2000 to 2015 or the expanded 30 AGANet sites for the 10-year period from 2006 to 2015. NH_3 and particulate NH_4^+ measured at the same time
5 in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison.

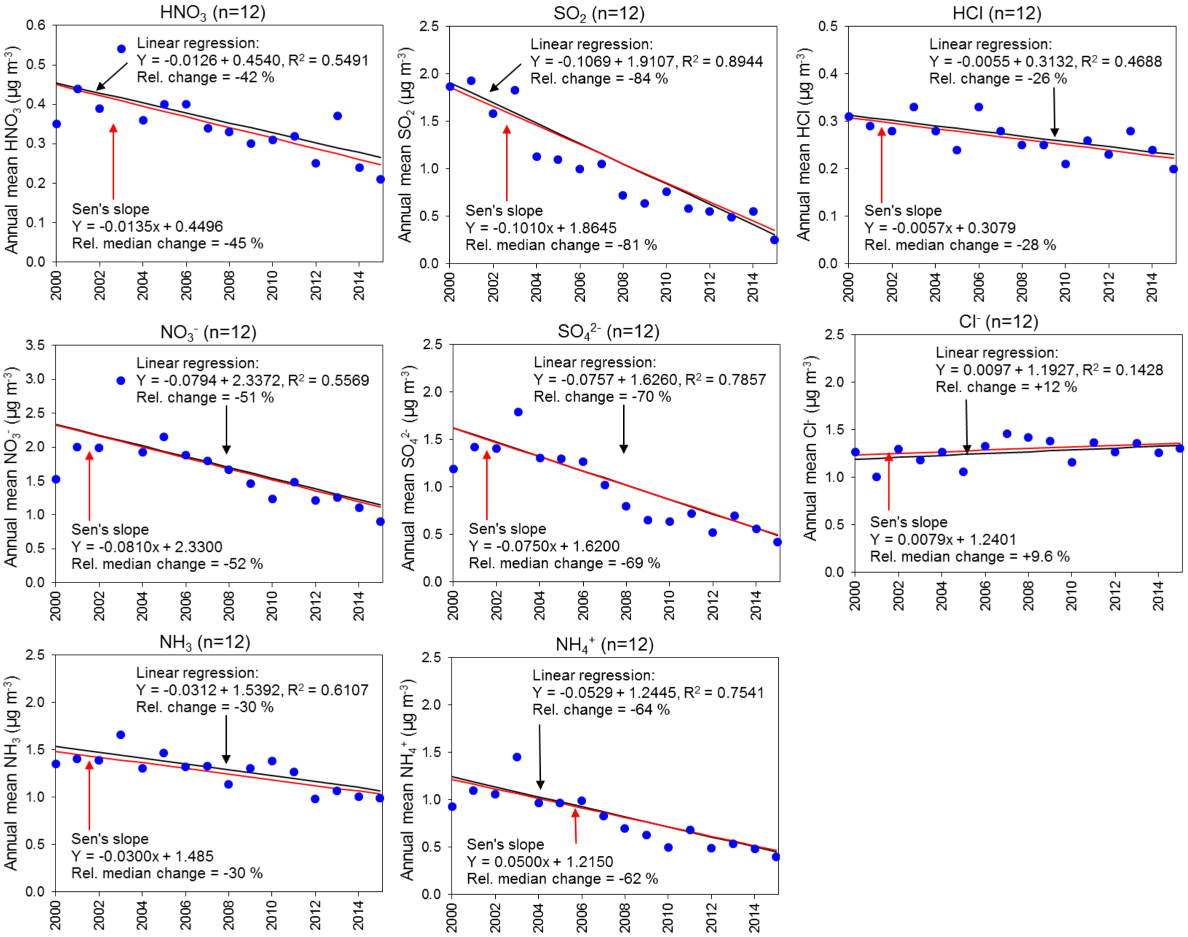


Figure 13: Time-series trend analysis by non-parametric Mann-Kendall Sen slope and by parametric linear regression on annually averaged gas and aerosol concentration data from the UK Acid Gases and Aerosol Monitoring Network (AGANet) of 12 sites that were operational over the period 2000 to 2015. NH_3 and NH_4^+ concentrations measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison.

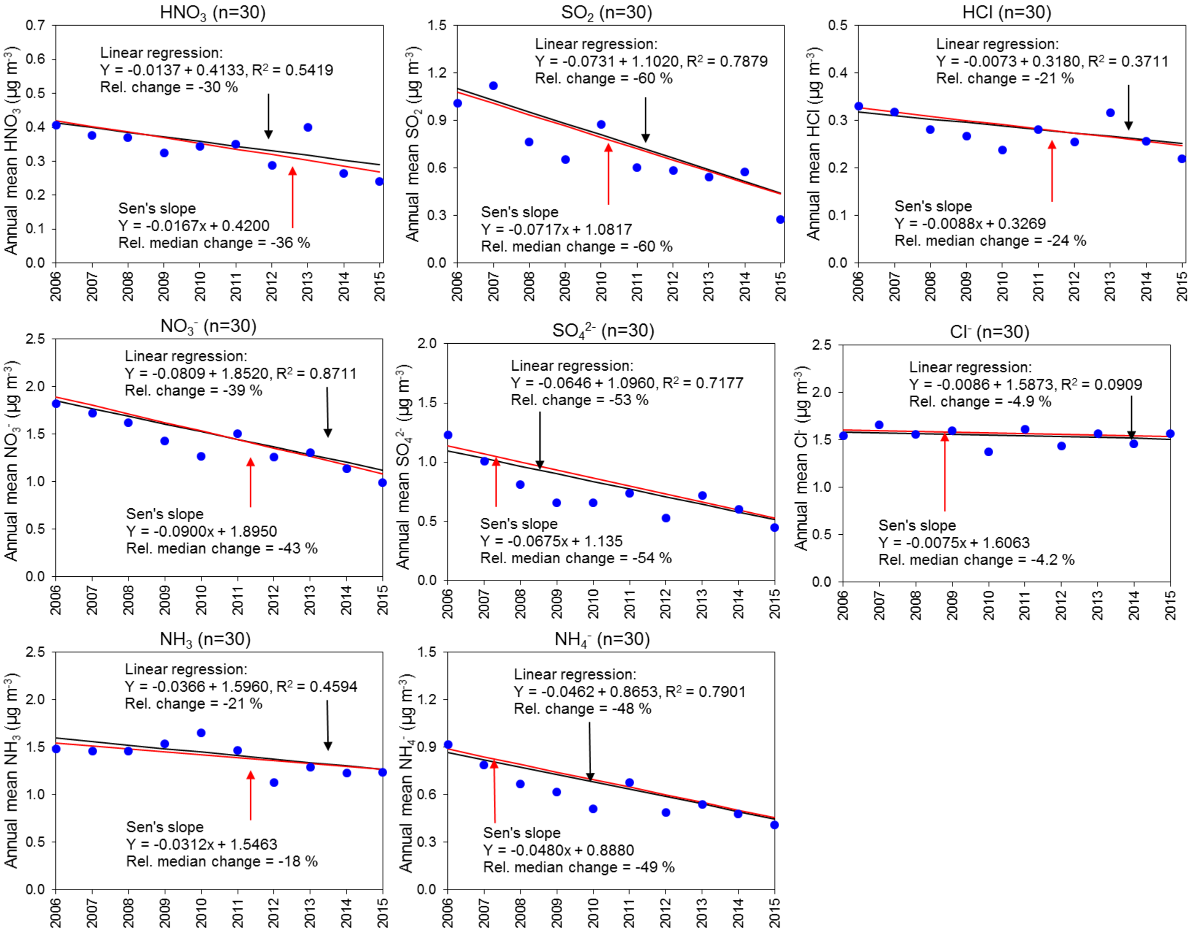


Figure 14: Time series trend analysis by non-parametric Mann-Kendall Sen slope and by parametric linear regression on annually averaged gas and aerosol concentration data from the UK Acid Gases and Aerosol Monitoring Network (AGANet) of 30 sites that were operational over the period 2006 to 2015. NH_3 and NH_4^+ concentrations data measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison.

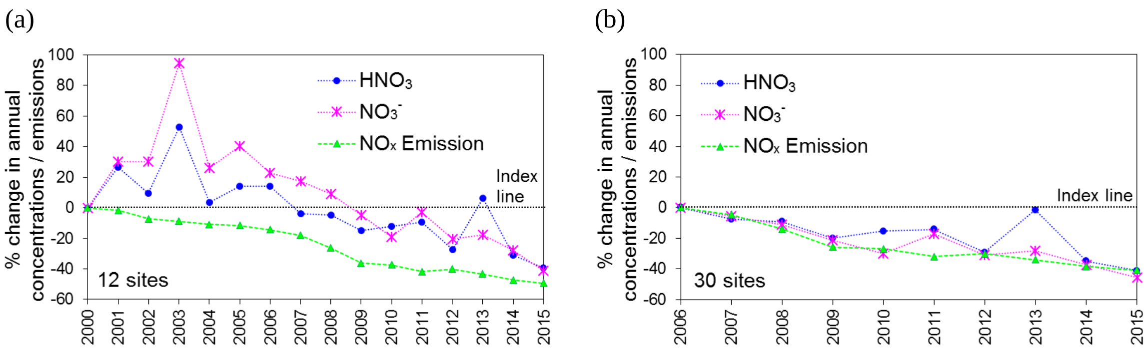


Figure 15: Relative trends in UK NO$_x$ emissions (Defra 2017) and in annually averaged HNO$_3$ and particulate NO$_3^-$ concentrations for (a) the original 12 AGANet sites for the 16 year period from 2000 to 2015, and (b) the expanded 30 AGANet sites for the 10 year period from 2006 to 2015.

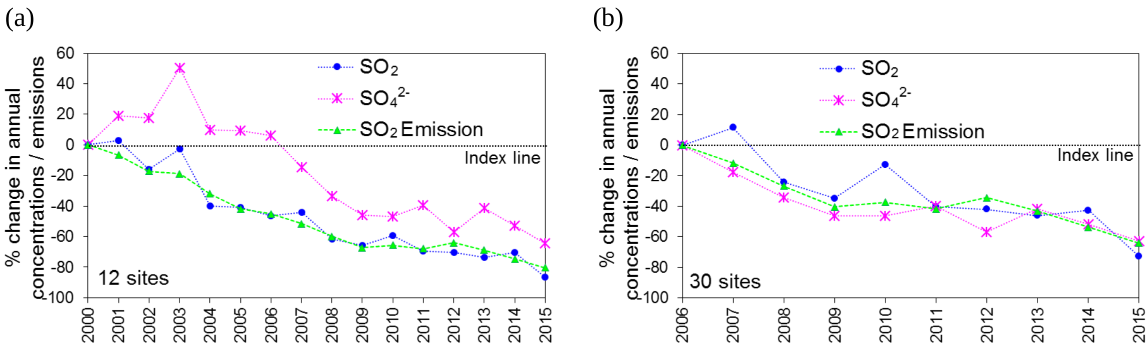


Figure 16: Relative trends in UK SO$_2$ emissions (Defra 2017) and in annually averaged SO$_2$ and particulate SO$_4^{2-}$ concentrations for (a) the original 12 AGANet sites for the 16 year period from 2000 to 2015 and (b) the expanded 30 AGANet sites for the 10 year period from 2006 to 2015.

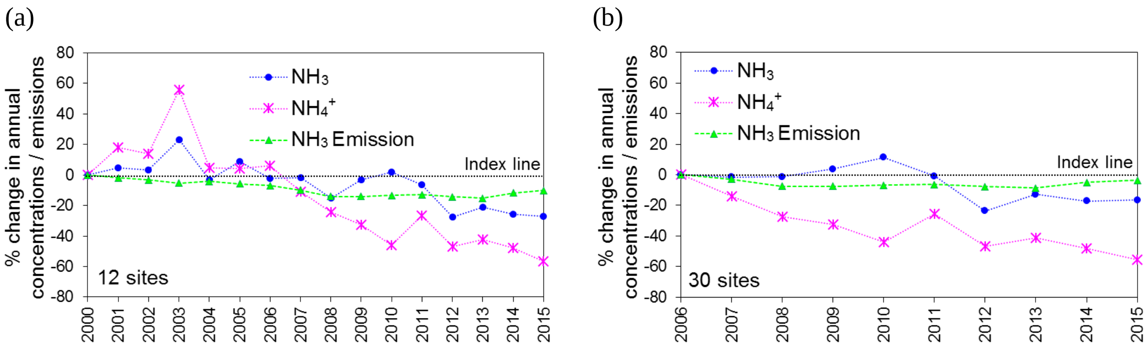


Figure 17: Relative trends in UK NH$_3$ emissions (Defra 2017) and in annually averaged NH$_3$ and particulate NH$_4^+$ concentrations from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) for (a) the original 12 AGANet sites for the 16 year period from 2000 to 2015 and (b) the expanded 30 AGANet sites for the 10 year period from 2006 to 2015.

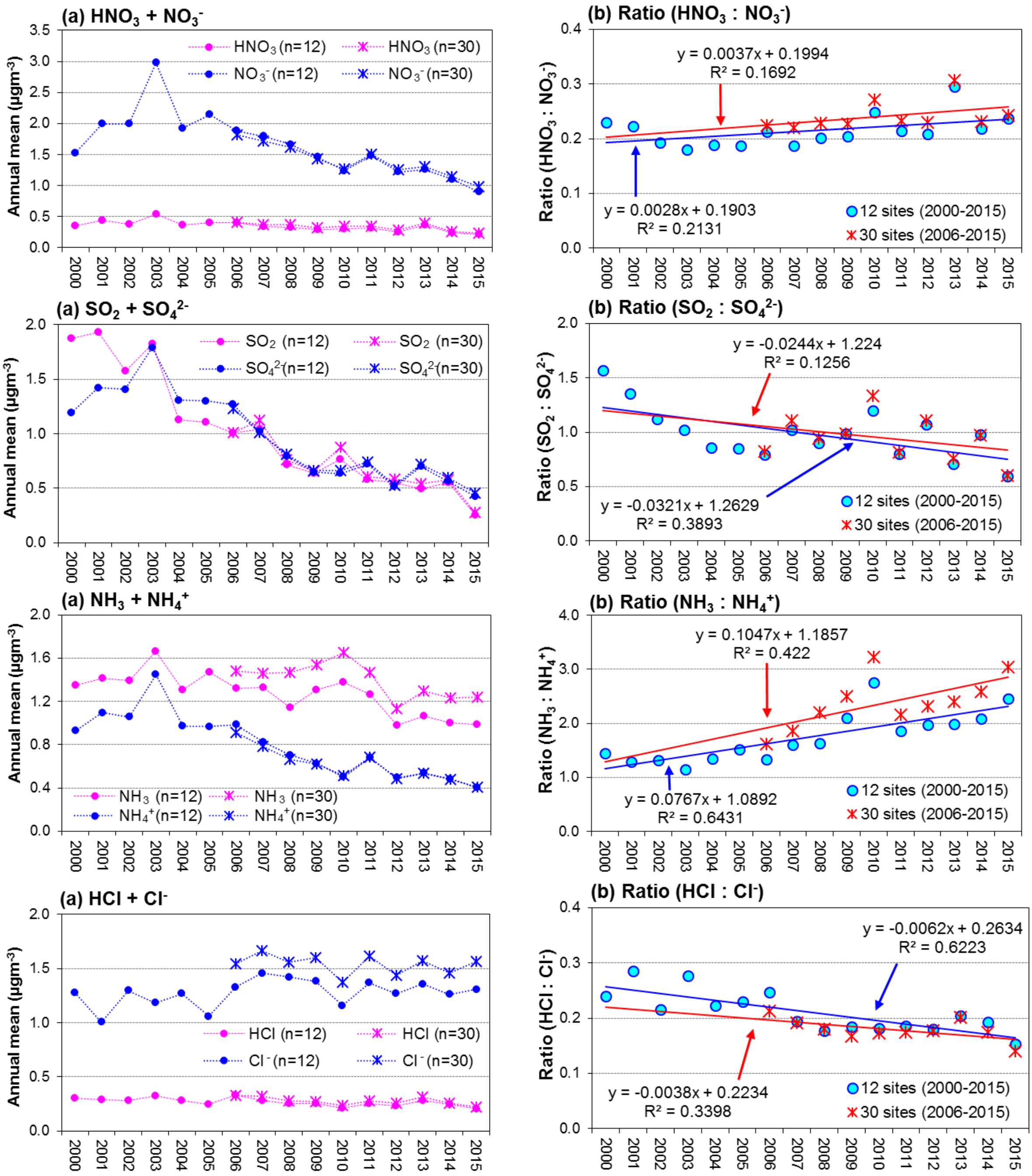


Figure 18: (a) Long-term trends in annual mean concentrations of acid gas and aerosol (HNO_3 / NO_3^- and SO_2 / SO_4^{2-}) from the UK Acid Gases and Aerosol Network (AGANet) and in reduced nitrogen (NH_3 / NH_4^+) from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) measured at the same time for comparison. Data are the annually averaged concentrations of 12 sites with complete time series from 2000 to 2015, and 30 sites with complete time series from 2006 to 2015. (b) Long-term trends in the gas:aerosol ratio, from the data in figure (a), indicating differences in direction of trends in this ratio with time.

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Table 1: List of sites in the UK Acid Gas and Aerosol Network (AGANet) with details of locations, start dates and UK-AIR ID (https://uk-air.defra.gov.uk/networks/network-info?view=aganet).

Site Name	UK-AIR ID	Latitude	Longitude	Start
Barcombe Mills	UKA00069	50.9191	0.0486	Apr '00
Bush OTC	UKA00128	55.8623	-3.2058	Sep '99
Cwmystwyth	UKA00325	52.3524	-3.8053	Sep '99
Eskdalemuir	UKA00130	55.3153	-3.2061	Sep '99
Glensaugh	UKA00348	56.9072	-2.5594	Sep '99
High Muffles	UKA00169	54.3349	-0.8086	Sep '99
Lough Navar	UKA00166	54.4395	-7.9003	Oct '99
Rothamsted	UKA00275	51.8065	-0.3604	Sep '99
Stoke Ferry	UKA00317	52.5599	0.5061	Sep '99
Strathvaich	UKA00162	57.7345	-4.7766	Sep '99
Sutton Bonington	UKA00312	52.8366	-1.2512	Sep '99
Yarner Wood	UKA00168	50.5976	-3.7165	Sep '99
New sites added from January 2006				
Auchencorth Moss	UKA00451	55.7922	-3.2429	Jan '06
Caenby	UKA00492	53.3979	-0.5074	Feb '06
Carradale	UKA00389	55.5825	-5.4962	Jan '06
Detling	UKA00481	51.3079	0.5827	Feb '06
Edinburgh St Leonards	UKA00454	55.9456	-3.1822	Jan '06
Goonhilly	UKA00056	50.0506	-5.1815	Jan '06
Halladale	UKA00314	58.4124	-3.8758	Jan '06
Harwell	UKA00047	51.5711	-1.3253	May '06
Hillsborough	UKA00293	54.4525	-6.0833	Jan '06
Ladybower	UKA00171	53.4034	-1.7520	Feb '06
Lagganlia	UKA00290	57.1110	-3.8921	Jan '06
Lerwick	UKA00486	60.1392	-1.1853	Jan '06
London Cromwell Road 2	UKA00370	51.4955	-0.1787	Jan '06
Moorhouse	UKA00357	54.6901	-2.3769	Jan '06
Narberth	UKA00323	51.7818	-4.6915	Mar '06
Plas Y Brenin	UKA00493	53.1018	-3.9179	May '06
Rosemaund	UKA00491	52.1214	-2.6363	Jan '06
Rum	UKA00276	57.0100	-6.2718	Feb '06

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Table 2: Comparison of HNO_3, HONO, SO_2, HCl and aerosol NO_3^-, SO_4^{2-}, Cl^- concentrations by the Acid Gases and Aerosol Network (AGANet) DELTA method with available measurements from the co-located ChemSpec Daily Annular Denuder system (ADS) at Barcombe Mills (UKA00069). Mean concentrations were derived from the average of daily ADS data for the corresponding DELTA sampling periods (monthly). HNO_3 values shown for DELTA and ADS are as calculated from the amount of NO_3^- collected on the denuders and have not been adjusted by a bias correction factor (see Sect. 2.6). Regression plots are shown in Supp. Figure S2.

	Gases				**Particulates**		
	HNO_3	**HONO**	**SO_2**	**HCl**	**NO_3^-**	**SO_4^{2-}**	**Cl^-**
Linear regression: R^2	0.813***	0.022^{ns}	0.840***	0.282^{ns}	0.570**	0.891***	0.168^{ns}
slope	0.974^{ns}	0.033***	0.880^{ns}	0.650^{ns}	0.570*	0.691**	2.339^{ns}
intercept	0.283^{ns}	0.014^{ns}	-0.163^{ns}	0.127^{ns}	1.809***	0.204^{ns}	0.540^{ns}
No. observations: *n*	11	11	11	10	11	11	11
mean DELTA (µg m^{-3})	1.56	0.03	1.75	0.40	2.59	2.10	1.24
mean ADS (µg m^{-3})	1.31	0.41	2.18	0.41	1.32	2.74	0.30

Significance level (slope different from 1, intercept = 0): * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. *ns* = not significant ($p > 0.05$)

Table 3: Correlation coefficients (R^2) for different species across the 30 measurement sites.

	HNO_3	**HCl**	**SO_2**	**NO_3^-**	**Cl^-**	**SO_4^{2-}**	**NH_4^+**	**Na^+**
HNO_3	1.00	0.25***	0.39***	0.45***	0.07***	0.54***	0.49***	0.02*
HCl	-	1.00	0.21***	0.14***	0.01^{ns}	0.24***	0.19***	0.04**
SO_2	-	-	1.00	0.30***	0.00^{ns}	0.47***	0.37***	0.01^{ns}
NO_3^-	-	-	-	1.00	0.00^{ns}	0.61***	0.90***	0.02^{ns}
Cl^-	-	-	-	-	1.00	0.04**	0.01^{ns}	0.79***
SO_4^{2-}	-	-	-	-	-	1.00	0.73***	0.00^{ns}
NH_4^+	-	-	-	-	-	-	1.00	0.00^{ns}
Na^+	-	-	-	-	-	-	-	1.00

Significance level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. *ns* = not significant ($p > 0.05$)

Table 4: Comparison of mean concentrations from the original 12 Acid gases and Aerosol Network (AGANet) sites *vs* the expanded 30 AGANet sites for the different gas and aerosol components. NH_3 and NH_4^+ measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. Each data point are the mean ± SD of annual mean concentrations over the period 2006 to 2015.

	Mean concentration (2006 – 2015), µg m^{-3}										
	HNO_3	**SO_2**	**HCl**	**NO_3^-**	**SO_4^{2-}**	**Cl^-**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**NH_3**	**NH_4^+**
12 sites (mean±SD)	0.31± *0.06*	0.66 ± *0.24*	0.25 ± *0.04*	1.40 ± *0.31*	0.73 ± *0.25*	1.33 ± *0.09*	0.75 ± *0.07*	0.04 ± *0.03*	0.06 ± *0.01*	1.18 ± *0.16*	0.62 ± *0.18*
30 sites (mean±SD)	0.34 ± *0.06*	0.70 ± *0.25*	0.28 ± *0.04*	1.41 ± *0.26*	0.74 ± *0.23*	1.54 ± *0.09*	0.84 ± *0.08*	0.04 ± *0.02*	0.07 ± *0.01*	1.40 ± *0.16*	0.61 ± *0.16*

Table 5: Summary of Mann-Kendall (MK) and Linear Regression (LR) time series trend analysis on annually averaged gas and aerosol concentrations from the UK Acid Gases and Aerosol Monitoring Network (AGANet) for the 12 sites that were operational over the period 2000 to 2015. NH_3 and NH_4^+ concentrations measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. For the MK tests, the 95% confidence interval (CI) for the median trend and relative change are also estimated.

2000 - 2015 (12 sites: annual data)	Mann-Kendall (MK)		Linear Regression (LR)		
	[a]Median annual trend & [95% CI] (µg y^{-1})	[b]Relative median change 2000-2015 & [95% CI] (%)	[c]Annual Trend (µg NH_3 y^{-1})	[d]Relative change 2000-2015 [%]	R^2
HNO_3	-0.0135 [-0.0067, -0.0180]	-45** [-26, -55]	-0.0126	-42**	0.549
SO_2	-0.1010 [-0.0729, -0.1250]	-81*** [-72, -91]	-0.1069	-84***	0.894
HCl	-0.0057 [-0.0020, -0.0100]	-28*** [-11, -42]	-0.0055	-26**	0.469
NH_3	-0.0300 [-0.0125, -0.0433]	-30** [-13, -39]	-0.0312	-30***	0.611
NO_3^-	-0.0810 [-0.0520, -0.1125]	-52** [-37, -63]	-0.0794	-51***	0.557
SO_4^{2-}	-0.0750 [-0.0450, -0.-0988]	-69** [-52, -82]	-0.0757	-70***	0.786
Cl^-	0.0079 [-0088, 0.0236]	9.6^{ns} [-9.5, 33]	0.0097	+12^{ns}	0.143
NH_4^+	-0.0500 [-0.0375, -0.0675]	-62** [-51, -74]	-0.0529	-64***	0.754

Significance level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, ^{ns} non-significant ($p > 0.05$)

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

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

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

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

Table 6: Summary of Mann-Kendall (MK) and Linear Regression (LR) time series trend analysis on annually averaged gas and aerosol concentrations from the UK Acid Gases and Aerosol Monitoring Network (AGANet) for the 30 sites that were operational over the period 2006 to 2015. NH_3 and NH_4^+ concentrations data measured at the same time from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. For the MK tests, the 95% confidence interval (CI) for the median trend and relative change are also estimated.

2006 - 2015 (30 sites: annual data)	Mann-Kendall (MK)		Linear Regression (LR)		
	[a]Median annual trend & [95% CI] (µg NH_3 y^{-1})	[b]Relative median change 2000-2015 & [95% CI] (%)	[c]Annual Trend (µg NH_3 y^{-1})	[d]Relative change 2000-2015 [%]	R^2
HNO_3	-0.0167 [-0.0075, -0.0200]	-36* [-18, -41]	-0.0137	-30*	0.542
SO_2	-0.0717 [-0.0300, -0.0108]	-60*** [-33, -73]	-0.0731	-60***	0.788
HCl	-0.0088 [0.0000, -0.0200]	-24* [0.0, -47]	-0.0073	-21^{ns}	0.371
NH_3	-0.0312 [0.0033, -0.0625]	-18^{ns} [+2.0, -31]	-0.0366	-21*	0.459
NO_3^-	-0.0900 [-0.0580, -0.1300]	-43*** [-30, -56]	-0.0809	-39***	0.871
SO_4^{2-}	-0.0675 [-0.0233, -0.1167]	-54** [-25, -78]	-0.0646	-53***	0.718
Cl^-	-0.0075 [+0.0167, -0.0300]	-4.2^{ns} [+12, -16]	-0.0086	-4.9^{ns}	0.091
NH_4^+	-0.0480 [0.0267, -0.0700]	-49** [-33, -64]	-0.0462	-48***	0.790

Significance level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, ^{ns} non-significant ($p > 0.05$)
[a]Median annual trend = fitted Sen's slope of Mann-Kendall linear trend (unit = µg y^{-1})
[b]Relative median change calculated based on the estimated annual 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])
[c]Annual trend = fitted slope of linear regression (unit = µg NH_3 y^{-1})
[d]Relative change calculated based on the estimated annual concentration at the start (y_0) and at the end (y_i) of time series computed from the slope and intercept (=100*[(yi-y_0) /y_0])

Table 7: Comparison of % change in estimated UK NO_x, SO_2 and NH_3 emissions reported by the National Atmospheric Emission Inventory (NAEI) (data from http://naei.defra.gov.uk/) with % change between 2000-2015 (12 sites with complete time series) and between 2006-2015 (30 sites with complete time series) in annually averaged HNO_3 / NO_3^- and SO_2 / SO_4^{2-} concentrations from the UK Acid Gas and Aerosol Monitoring Network (AGANet), and annually averaged NH_3 / NH_4^+ concentrations from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018).

Components	**2000 – 2015 (12 sites)**			**2006 – 2015 (30 sites)**		
	UK emissions % change	**MK Sen Slope** % relative median change[a]	**LR** % relative change[b]	**UK emissions** % change	**MK Sen slope** % relative median change[a]	**LR** % relative change[b]
Gas HNO_3	-58 (NO_x)	-45**	-42**	-41 (NO_x)	-36*	-43*
Particulate NO_3^-		-52***	-51***		-30**	-39***
Gas SO_2	-80 (SO_2)	-81***	-84***	-64 (SO_2)	-60***	-60***
Particulate SO_4^{2-}		-69***	-70***		-54**	-53***
Gas NH_3	-10 (NH_3)	-30**	-30***	-3.5 (NH_3)	-18^{ns}	-21*
Particulate NH_4^+		-62***	-64***		-49**	-48***

Significance level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, ^{ns} non-significant ($p > 0.05$)

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

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