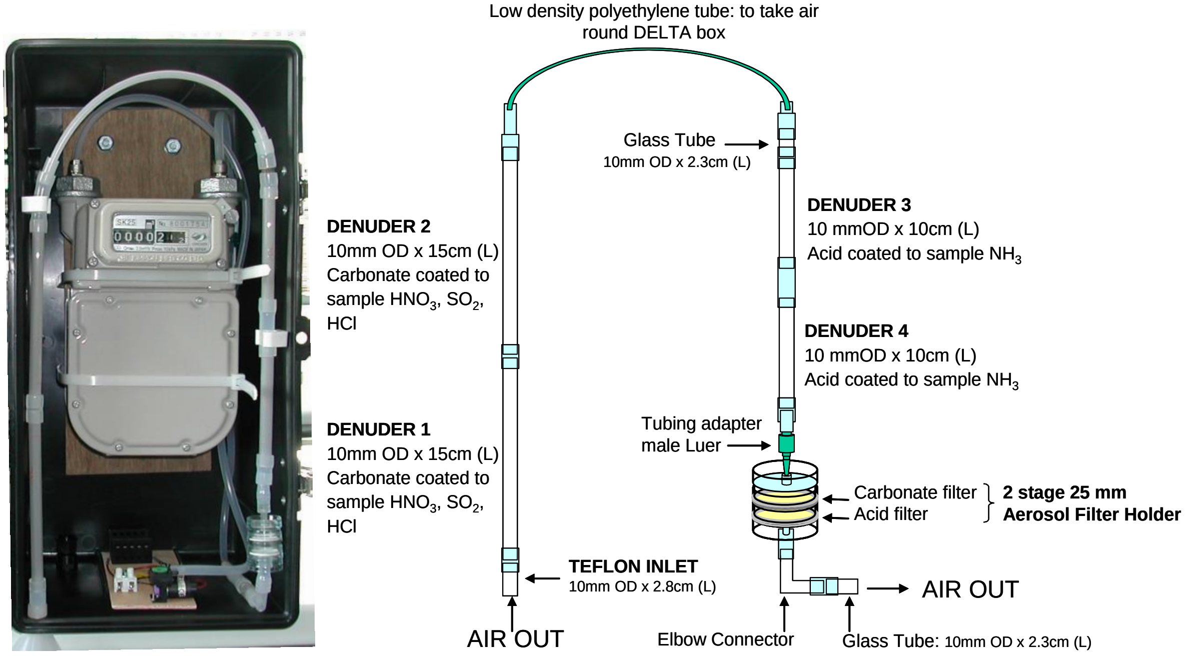
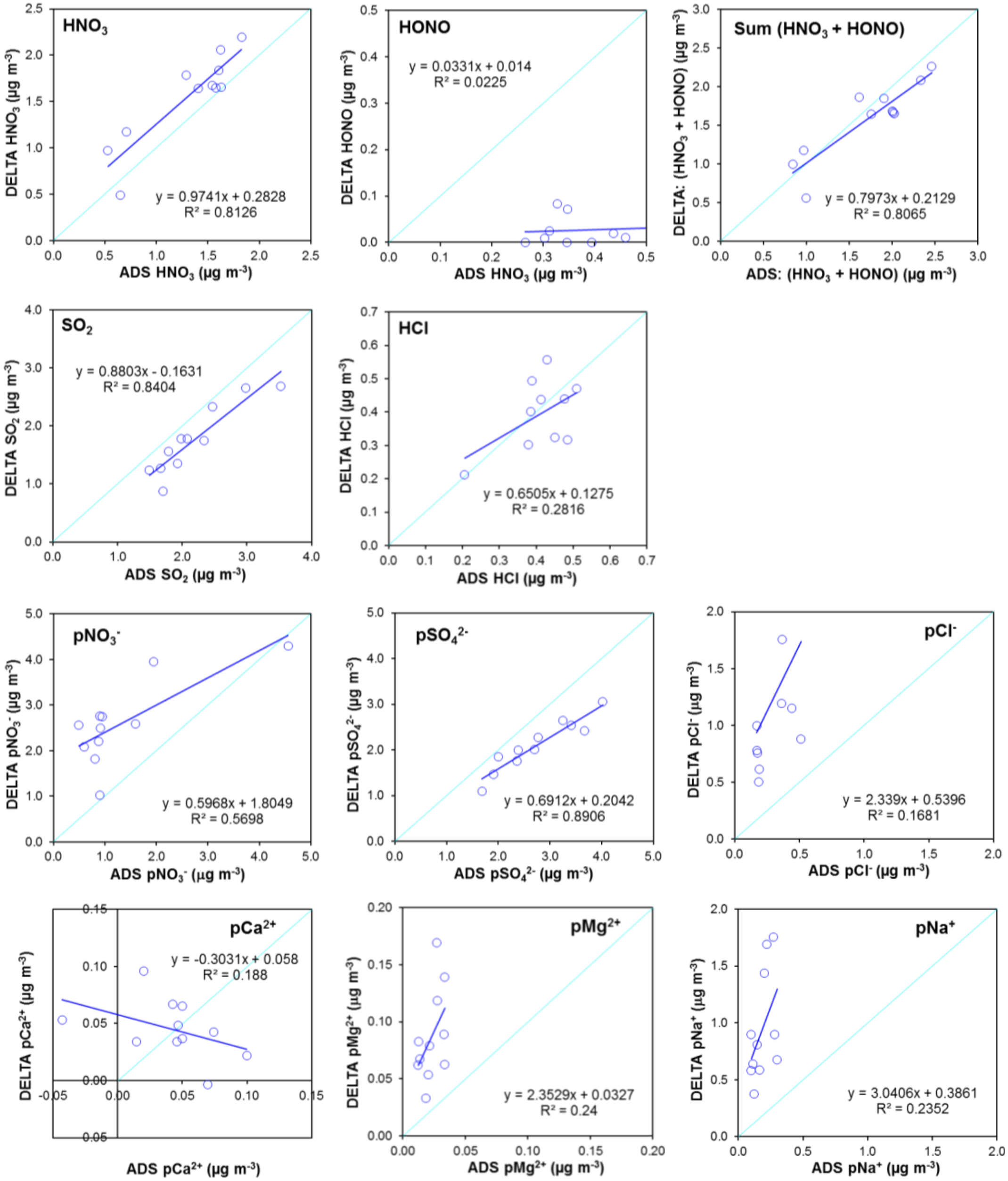
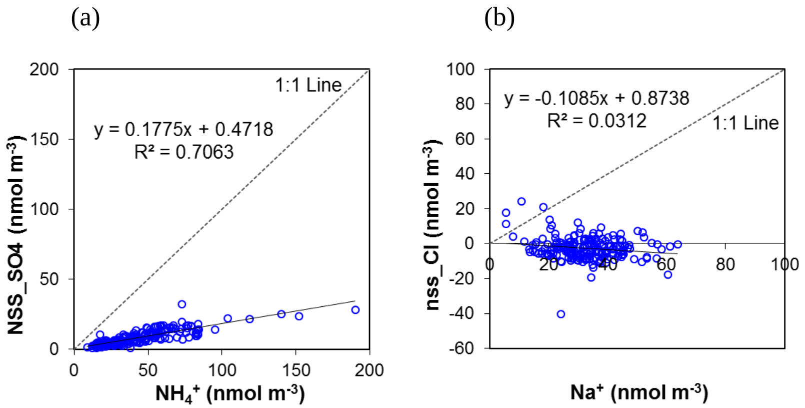
Supplementary material



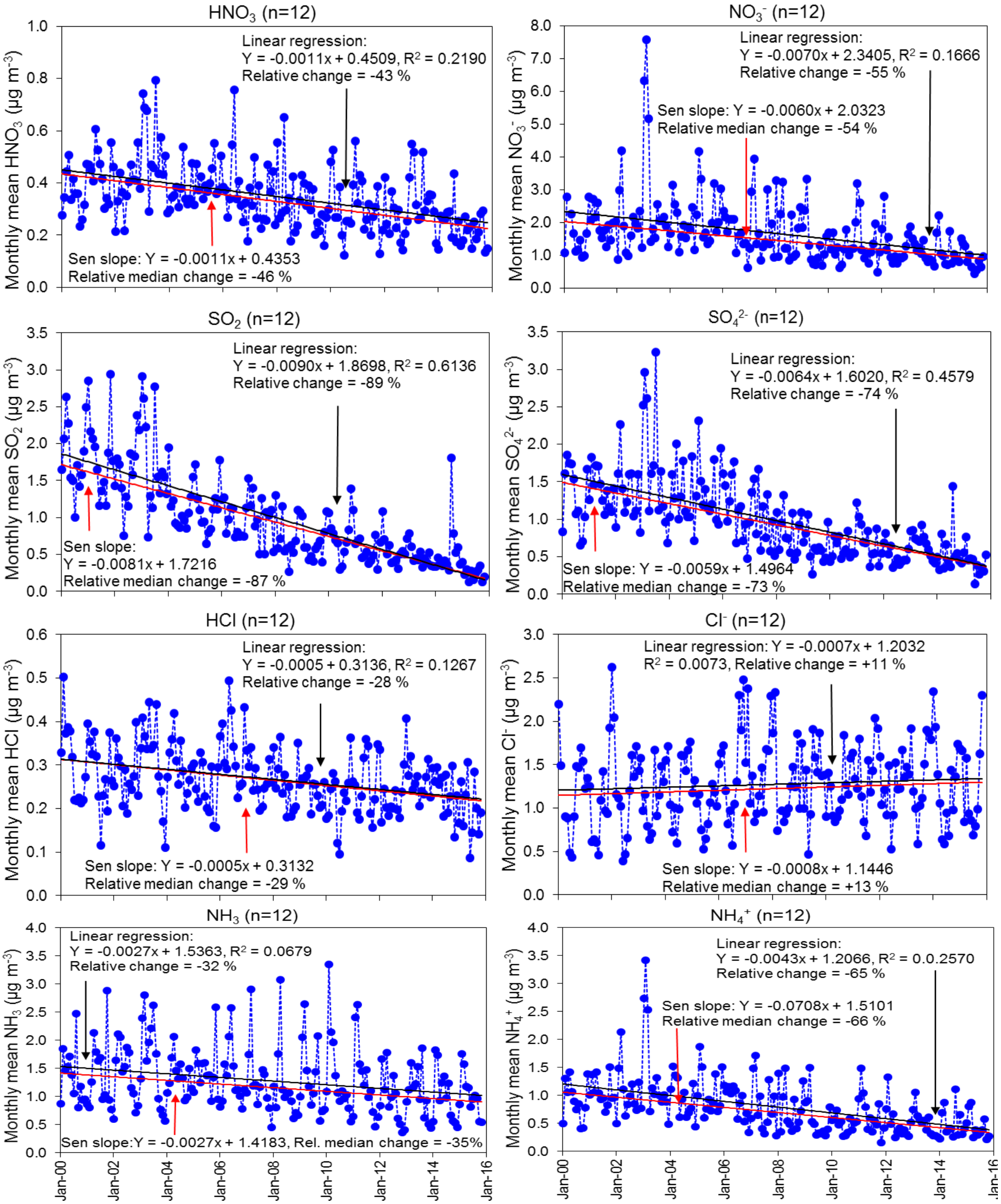
Supp. Figure S1: Left: DEnuder for Long-Term Atmospheric sampling (DELTA) as applied for the monthly measurements of reactive gases and particulate matter composition in the UK Acid Gases and Aerosol Network (AGANet), with sampling train *in situ*. Right: sampling train consisting of 2 x 15 cm long K_2CO_3 + glycerol coated denuders (determination of HNO_3, SO_2, HCl), 2 x 10 cm long acid coated denuders (determination of NH_3), carbonate coated filter (determination of NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}) and acid coated filter (determination of evolved NH_4^+).



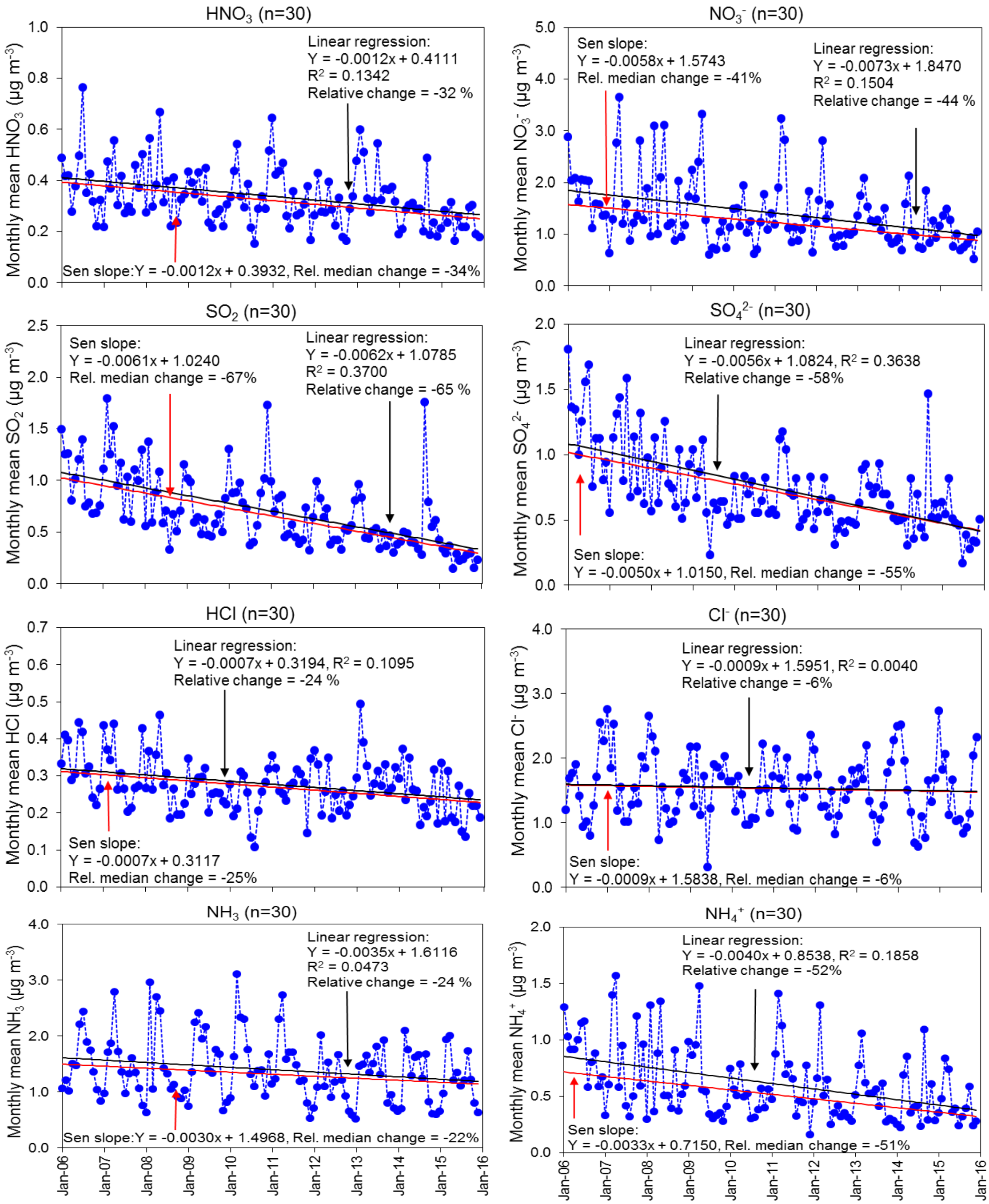
Supp. Figure S2: Comparison of HNO_3, HONO, sum (HNO_3+HONO), SO_2, HCl and aerosol NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+} concentrations by the Acid Gases and Aerosol Network (AGANet) DELTA method with available measurements from the co-located ChemSpec Daily Annular Denuder system (ADS) at Barcombe Mills (UKA00069). Mean concentrations were derived from the average of daily ADS data for the corresponding DELTA sampling periods (monthly). HNO_3 concentrations from both the DELTA and ADS are calculated from the amount of nitrate collected on the denuders and are shown here without any adjustment by the bias correction factor (see Sect. **Error! Reference source not found.**).



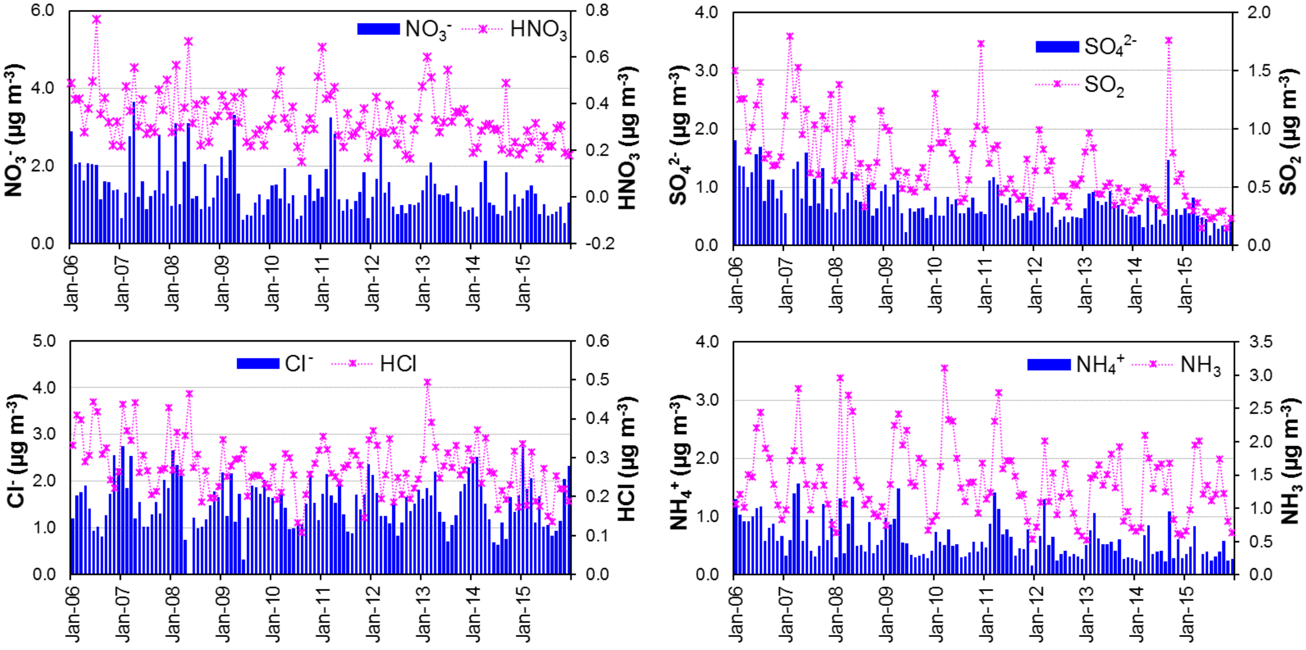
Supplement Figure S3: Scatter plots between concentrations of (a) non-sea salt sulphate (nss_SO4) vs NH_4^+, and (b) non-sea salt chloride (nss_Cl) *vs* Na^+ from mean monthly measurements (1999-2015) for the 12 sites in the UK Acid Gas and Aerosol Monitoring Network (AGANet) that were operational over 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.



Supp. Figure S4: Time series trend analysis by non-parametric Mann-Kendall Sen slope and by parametric linear regression on monthly mean gas and aerosol concentration data 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 data measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. Individual data points are monthly mean concentrations across 12 sites.



Supp. Figure S5: Time series trend analysis by non-parametric Mann-Kendall Sen slope and by parametric linear regression on monthly mean gas and aerosol concentration data 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 in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. Individual data points are monthly mean concentrations across 30 sites.



Supp. Figure S6: 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) over the period 2006 - 2016. 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 30 sites operational in the network over the period 2006 to 2015.

Supp. Table S1: Major ions measured in DELTA extracts and typical limits of detection (LOD).

Analytes (denuder aqueous extracts)	Harwell Laboratory (Sep99 – Jun09)		CEH Lancaster (from Jul09)	
	Analytical Method	Typical LOD (µg m^{-3})	Analytical Method	Typical LOD (µg m^{-3})
NO_3^-	IC	0.05 (HNO_3)	IC	0.05 (HNO_3)
NO_2^-	Colorimetry	0.05 (HONO)	IC	0.05 (HONO)
SO_4^{2-}	IC	0.05 (SO_2)	IC	0.05 (SO_2)
Cl^-	IC	0.05 (HCl)	IC	0.05 (HCl)

Supp. Table S2: Major ions measured in aerosol filter extracts and typical limits of detection (LOD).

Analytes (aerosol filter aqueous extracts)	Harwell Laboratory (Sep99 – Jun09)		CEH Lancaster (from Jul09)	
	Method	Typical LOD (µg m^{-3})	Method	Typical LOD (µg m^{-3})
NO_3^-	IC	0.05 (NO_3^-)	IC	0.06 (NO_3^-)
NO_2^-	Colorimetry	0.05 (NO_2^-)	IC	0.05 (NO_2^-)
SO_4^{2-}	IC	0.06 (SO_4^{2-})	IC	0.06 (SO_4^{2-})
Cl^-	IC	0.08 (Cl^-)	IC	0.16 (Cl^-)
Ca^{2+}	IC (Sep99-Jun08)	0.05	ICP-OES	0.09
Mg^{2+}	IC (Sep99-Jun08)	0.05	ICP-OES	0.05
Na^+	IC (Sep99-Jun08)	0.1	ICP-OES	0.16
Ca^{2+}	ICP-AES (Jul08-Jun09)	0.05		
Mg^{2+}	ICP-AES (Jul08-Jun09)	0.05		
Na^+	ICP-AES (Jul08-Jun09)	0.1		

Supp. Table S3: Calculated lengths of chemically impregnated denuders (borosilicate glass tubes, 10 mm o.d, 0.65 mm i.d) to capture 95 % of gas of interest at a flow rate of 0.4 LPM under laminar flow.

Reactive gas	HNO_3	SO_2	HCl	NH_3
Diffusion coefficient @ 10°C	1.15×10^{-5} m^2 s^{-1} (Massmana 1998)	1.22×10^{-5} m^2 s^{-1} (Durham & Stockburger 1986)	5.25×10^{-5} m^2 s^{-1} (Mumallah 1986)	2.01×10^{-5} m^2 s^{-1} (Hargreaves & Atkins, 1986)
L (cm): for 95 % capture efficiency at flow rate of 0.4 LPM	14	13	3	8

Note: 10 cm and 15 cm long denuders are used in the UK National Ammonia Monitoring Network (NAMN) and UK Acid Gases and Aerosol network (AGANet) to sample NH_3 and acid gases (HNO_3, SO_2, HCl), respectively.

Denuder theory:

The length of denuder required to obtain near complete capture of a reactive gas is a function of the diffusion rate of the reactive gas and the air sampling rate. For cylindrical tubes, with laminar flow and where the tube wall is a perfect sink for the gas of interest, Gormley & Kennedy (1949) and Ferm (1979) showed that the collection efficiency of a simple denuder for a reactive gas may be calculated using Equation 1.

$$\eta = 1 - \frac{\beta_1}{\beta_0} = 1 - 0.819 \cdot e^{-14.6272\delta} + 0.0976 \cdot e^{-89.22\delta_r} + 0.01896 \cdot e^{-212\delta_r} \tag{1}$$

where

η	is the collection efficiency of the denuder;
β_1	is the mass concentration of gas at the denuder outlet
β_0	is the mass concentration of gas at the denuder inlet

δ is described by Equation 2:

$$\delta = \frac{\pi DL}{4\phi} \tag{2}$$

where

D	is the molecular diffusion coefficient of reactive gas, in cm^2/s
L	is effective length of the denuder, in cm
ϕ	is the air flow rate through the denuder, in cm^3/s.

For collection efficiencies ≥ 95%, contributions from terms 2 and 3 in Equation 1 are insignificant (< 0.3 %) and only the first term is significant. Equation 1 may then be simplified to Equations 3 and 4:

$$\eta = 1 - \frac{\beta_1}{\beta_0} = 1 - 0.819 \cdot e^{-14.6272\left(\frac{\pi\ \mathrm{DL}}{4\phi}\right)} \tag{3}$$

$$\frac{\beta 1}{\beta o} = 0.819\ \mathrm{e}^{-14.6272\ \left(\frac{\pi DL}{4\phi}\right)} \quad , \frac{\beta 1}{\beta o} = 0.05 \text{ for 95 \% capture efficiency} \tag{4}$$

Laminar flow is achieved a short distance from the inlet. The minimum length of tube at inlet not coated with sorbent, $L_{\min}$ to fully develop laminar flow is given by Equation 5.

$$L_{\min} = 0.05.\mathrm{Re}.d \tag{5}$$

where

Re	is the Reynolds number
d	internal diameter of tube

An inlet length of 2.8 cm (uncoated Teflon tube: 10 mm o.d, 6.5 mm i.d) is used in the AGANet sampling train to develop laminar flow. Reynolds number must be <2000 for laminar flow. The Reynolds number for this is calculated to be 86 (at flow rate = 0.4 LPM and internal tube diameter = 6.5 mm).

Supp. Table S4: Summary of Mann-Kendall (MK) and Linear Regression (LR) time series trend analysis on monthly mean gas and aerosol concentration data 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: monthly 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	-0.0132 [-0.0096, -0.0156]	-46*** [-36, -52]	-0.0128	-43***	0.219 .
SO_2	-0.0972 [-0.0864, -0.1080]	-87*** [-82, -90]	-0.1078	-89***	0.614
HCl	-0.0060 [-0.0036, -0.0084]	-29*** [-19, -40]	-0.0058	-28***	0.127
NH_3	-0.0324 [-0.0168, -0.0468]	-35*** [-20, -46]	-0.0325	-32***	0.068
NO_3^-	-0.0720 [-0.0528, -0.0900]	-54*** [-44, -63]	-0.0839	-55***	0.167
SO_4^{2-}	-0.0708 [-0.0600, -0.0804]	-73*** [-66, -77]	-0.0770	-74***	0.458
Cl^-	0.0096 [-0.0048, 0.0252]	+13^{ns} [-5.7, +36]	+0.0085	+11^{ns}	0.007
NH_4^+	-0.0456 [-0.0360, -0.0552]	-66*** [-57, -74]	-0.0516	-65***	0.257

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])

Supp. Table S5: Summary of Mann-Kendall (MK) and Linear Regression (LR) time series trend analysis on monthly mean gas and aerosol concentration data 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 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.

2006 - 2015 (30 sites: monthly data)	Mann-Kendall (MK)		Linear Regression (LR)		
	[a] Median annual trend & [95% CI] (μg NH_3 y^{-1})	[b] Relative median change 2006-2015 & [95% CI] (%)	[c] Annual Trend (μg NH_3 y^{-1})	[d] Relative change 2006-2015 [%]	R^2
HNO_3	-0.0144 [-0.0072, -0.0204]	-34*** [-18, -44]	-0.0146	-32***	0.134
SO_2	-0.0732 [-0.0564, -0.0924]	-67*** [-59, -74]	-0.0749	-65***	0.370
HCl	-0.0084 [-0.0036, -0.0120]	-25** [-11, -33]	-0.0084	-24***	0.109
NH_3	-0.0360 [-0.0036, -0.0696]	-22* [-26, -39]	-0.0425	-24*	0.047
NO_3^-	-0.0696 [-0.0408, -0.0101]	-41*** [-26, -54]	-0.0875	-44***	0.150
SO_4^{2-}	-0.0600 [-0.0432, -0.0768]	-55*** [-44, -64]	-0.0674	-58***	0.364
Cl^-	-0.0108 [-0.0228, -0.0432]	-6^{ns} [-14, +23]	-0.0111	-6^{ns}	0.004
NH_4^+	-0.0396 [-0.0024, -0.0588]	-51*** [-35, -64]	-0.0480	-52***	0.186

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 ($=100*[(yi-y_0)/y_0]$)

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