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**Gaseous and particulate water-soluble organic and inorganic nitrogen in rural air in southern Scotland**

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**Key words**

Cofer sampler; Water soluble organic nitrogen; DON; reactive nitrogen

## Abstract

Simultaneous daily measurements of water-soluble organic nitrogen (WSON), ammonium and nitrate were made between July and November 2008 at a rural location in south-east Scotland, using a 'Cofer' nebulizing sampler for the gas phase and collection on an open-face PTFE membrane for the particle phase. Average concentrations of  $\text{NH}_3$  were  $82 \pm 17 \text{ nmol N m}^{-3}$  (error is s.d. of triplicate samples), while oxidised N concentrations in the gas phase (from trapping  $\text{NO}_2$  and  $\text{HNO}_3$ ) were smaller, at  $2.6 \pm 2.2 \text{ nmol N m}^{-3}$ , and gas-phase WSON concentrations were  $18 \pm 11 \text{ nmol N m}^{-3}$ . The estimated collection efficiency of the nebulizing samplers for the gas-phase was  $88 (\pm 8) \%$  for  $\text{NH}_3$ ,  $37 (\pm 16) \%$  for  $\text{NO}_2$  and  $57 (\pm 7) \%$  for WSON; reported average concentrations have not been corrected for sampling efficiency. Concentrations in the particle phase were smaller, except for nitrate, at  $21 \pm 9$ ,  $10 \pm 6$  and  $8 \pm 9 \text{ nmol N m}^{-3}$ , respectively. The absence of correlation in either phase between WSON and either  $(\text{NH}_3 + \text{NH}_4^+)$  or  $\text{NO}_3^-$  concentrations suggests atmospheric WSON has diverse sources. During wet days, concentrations of gas and particle-phase inorganic N were lower than on dry days, whereas the converse was true for WSON. These data represent the first reports of simultaneous measurements of gas and particle phase water-soluble nitrogen compounds in rural air on a daily basis, and show that WSON occurs in both phases, contributing 20-25% of the total water-soluble nitrogen in air, in good agreement with earlier data on the contribution of WSON to total dissolved N in rainfall in the UK.

## Introduction

Measurements of organic N compounds (amines, amino acids, urea, alkyl nitrates, peroxyacyl nitrates, nitrophenols etc.) in air have been made for many years, but there have been no reports of simultaneous total water-soluble organic N (WSON) in both the gas and particle phases. The peroxyacyl nitrates are probably the best-known class of gas-phase organic N compounds in terms of atmospheric measurements, and peroxyacetyl nitrate (PAN) has been quantified in many recent studies, e.g. (Lee, et al., 2008, McFadyen and Cape, 2005, Roberts, et al., 2007, Zhang, et al., 2009, Zhang, et al., 2005) as well as long-term studies over many years, e.g. (Bottenheim, et al., 1999, Grosjean, 2003), with attempts made to quantify the relative contribution to total airborne oxidised N ( $\text{NO}_y$ ). An early study in Pennsylvania estimated that PAN constituted 20-25% of total airborne oxidised reactive nitrogen, other organic nitrates contributed 1.5%, and 15% of total  $\text{NO}_y$  was unattributed, but behaved similarly to organic nitrates (Buhr, et al., 1990). However, subsequent research indicated that some of this 'unattributed' contribution to  $\text{NO}_y$  might have come from reduced N ( $\text{NH}_3$ ,  $\text{NH}_4^+$  and/or amines) (Harrison, et al., 1999). The low aqueous solubility of PAN (Kames, et al., 1991) and many other organic N compounds implies that their contribution to WSON might not, however, reflect their air concentrations.

The role of organic N in precipitation, and its large contribution to wet N deposition (Cornell, et al., 2003, Neff, et al., 2002), has focused attention on WSON, and individual components have been identified and quantified in the gas phase, aerosol phase and in precipitation, but no attempt has been made to quantify the total WSON present in air as gases or particles. Ultimately, the gas and particle WSON provides the dissolved organic N in precipitation, so an understanding of their air concentrations may provide an indication of potential sources. Moreover, measurements of WSON in precipitation (wet deposition) are often made with 'bulk'

precipitation collectors which are continuously exposed to the atmosphere. There is the likelihood of a sampling artefact caused by dry deposition of gaseous and particulate WSON on collector surfaces during dry periods prior to rainfall. A key finding from recent experimental work is that dry deposition of particles and gas on the funnel surface, rather than wet deposition, was the main contributor of N-containing species in bulk rain samples (between 53% and 84% of total N) (González Benítez, et al., 2009). Measurement of the contributory gas and aerosol phase concentrations in air is therefore important for estimating the possible contribution of WSON to 'bulk' deposition.

The contribution of WSON to total water-soluble N (WSN) in aerosols has been assessed in several studies, and appears to be on average around 30%, but variable with time of year and location. In coastal or marine air, overall concentrations of WSON in particles are low, but may still provide a large proportion of WSN: average 30% (up to 80%) in Hawaii (Cornell, et al., 2001), 26% in the eastern Mediterranean (Mace, et al., 2003c), 10% in Florida (Calderon, et al., 2007), 19-25% in Tasmania (Mace, et al., 2003b), 30% in Singapore (Karthikeyan, et al., 2009) and 10-24% in the East China Sea (Nakamura, et al., 2006), where the smaller proportion was observed in spring and the larger in autumn. Similar proportions of WSON in aerosol WSN are seen in continental areas: 30% in Beijing (Duan, et al., 2009) and 43-45% in Amazonia (Mace, et al., 2003a). Radiation fog acts as scavenger of WSN and so would be expected to reflect the combined contribution of both gas and aerosol phases; WSON contributed up to 16% of WSN in radiation fogs in California (Collett Jr, et al., 2008, Zhang and Anastasio, 2001).

The experiments described here were designed to measure daily atmospheric concentrations of the different water soluble nitrogen species in the boundary layer, in order to discriminate between what is in the gas phase and what is within particulate matter, the particle phase. They provide, to our knowledge, the first simultaneous measurement of gaseous and particulate WSON as a component of WSN.

## **Experimental**

### ***Study site and collection methods***

Atmospheric WSN components were sampled daily (usually for 24 h but with some samples between 4 and 48 h) from both the gas and particle phases over 4 months between July and November 2008. In the first phase of sampling (23<sup>rd</sup> July to 21<sup>st</sup> August), samples were collected in the grounds of the Centre for Ecology & Hydrology (3°12'19" W, 55°51'44" N) in a rural science park 15 km south west of Edinburgh and within 1 km of mixed farmland. In the main phase of sampling (26<sup>th</sup> August to 21<sup>st</sup> November), samples were collected at Easter Bush farm, less than 1 km to the north of the first site, in a grassland area mostly covered by perennial ryegrass (*Lolium perenne*) used for silage production and sheep grazing. Both sampling locations were 190 m above sea level.

Gaseous WSN species were collected in Cofer samplers (Figure 1) which operate by drawing air through a nebulizer to create a fine mist of droplets from an internal reservoir, into which the water-soluble gases partition (Cofer and Edahl, 1986, Sciare and Mihalopoulos, 2000, Spaulding, et al., 2002). Loss of mist droplets downstream of the sampler was prevented by use of a PTFE membrane filter that excluded liquid water. The initial volume of water used in the reservoir of the Cofer samplers in this

study was 10 mL, and the average air flow rate was ca. 5 L min<sup>-1</sup>, just sufficient to maintain nebulization in the chamber. The total volume of air sampled was measured using a dry gas meter. A flow rate of 3 L min<sup>-1</sup> was sufficient to provide efficient nebulization with the nebulizer geometry used, and for most sampling a flow rate of 5 L min<sup>-1</sup> was used as a compromise between minimizing evaporation of the sampling solution and maximising the volume of air sampled. Prior to sampling, all glassware was soaked overnight in 15% (v/v) dichlorodimethylsilane in toluene, then rinsed with toluene, methanol, and dichloromethane (three times each) and dried at 150°C (Spaulding, et al., 2002). The silanization procedure makes the glass surfaces hydrophobic, thereby improving the recirculation of nebulised droplets within the sampler.

Particle-phase WSN species were collected on upstream PTFE membrane filters (Whatman, 47 mm diameter, 1 µm pore size) which removed aerosol particles from the air stream prior to the nebulizer. Three samplers were used in this work: two had open-faced filter holders at their inlets, which gave more uniform surface coverage for aerosol capture but could be adversely affected by rain. The third had an enclosed filter holder, with 0.5 cm diameter 3 cm long inlet, which prevented rain ingress but may have provided less uniform surface area for particle filtration and possible loss of gaseous material (e.g. nitric acid) to the filter holder surface (Figure 1). Potential sampling artefacts caused by the inlet filter itself are discussed later.

At the CEH sampling site, the inlets of the Cofer samplers were placed 2 m above ground, facing north-east. The main objective for this sampling phase was to evaluate the collection efficiencies of the Cofer samplers and PTFE filters with respect to WSN components. To evaluate 'breakthrough,' two of the Cofer samplers were connected in series, with the third sampler co-located in parallel. Flow rates for the two samplers in series were less than for a single sampler, typically 3 L min<sup>-1</sup> in series and 5 L min<sup>-1</sup> for a single sampler. The lower flow rate was just sufficient to provide efficient nebulization. In the main sampling phase at Easter Bush, the three samplers were operated singly as replicates with their inlets 1 m above ground, facing south-west.

### ***Chemical analyses***

After sampling, the contents of the Cofer reservoir were collected via a syringe attached to the reservoir inlet. The sampler was then rinsed 3 times with a few mL of 18 MΩ cm water, to collect any water-soluble material retained on the internal surfaces, and the rinsings added to the main solution. Sample volume was determined by weighing the collected sample and washings in a pre-silanized glass vial. Water-soluble compounds in the particulate samples were extracted by immersing the PTFE filters in 10 mL of 18 MΩ cm water for two periods of 15 min in an ultrasonic bath (Duan, et al., 2009). Solutions were then filtered through a 0.2 µm pore-size inorganic membrane filter (Whatman, Anotop 10 IC). The same procedure was applied to 'blank' samples of unexposed PTFE filters. All solutions were stored at 4°C prior to analysis. No biocide was added as chemical analyses were always performed within a few days after sample collection.

Each sample was analysed for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> by ion chromatography and for total dissolved nitrogen (TDN) by high-temperature catalytic oxidation and chemiluminescence detection of the resulting nitric oxide (ANTEK 8060-M nitrogen-specific detector). The organic nitrogen component was calculated as the difference

between TDN and the sum of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Full experimental details of the analyses are given elsewhere (González Benítez, et al., 2009). Typical detection limits were  $0.5 \mu\text{M}$  for  $\text{NH}_4^+$  and  $0.4 \mu\text{M}$  for  $\text{NO}_3^-$  for a  $250 \mu\text{L}$  injection and  $1 \mu\text{M N}$  for TDN for a  $30 \mu\text{L}$  injection, the latter based on independent calibration with standard solutions of ammonium sulphate and sodium nitrate. Previous work has shown that the ANTEK system quantitatively combusts all but the most intransigent organic compounds (Cape, et al., 2001). The vast majority of analyses in this work were above their limits of detection. Final concentrations of all components were expressed as  $\text{nmol N m}^{-3}$  of air. Typical detection limits based on  $10 \text{ mL}$  solution and  $24 \text{ h}$  sampling at  $5 \text{ L min}^{-1}$  are  $0.7$ ,  $0.6$  and  $1.4 \text{ nmol N m}^{-3}$  for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN, respectively. The limit of detection for WSON is determined by a combination of the overall uncertainties in TDN and inorganic N analyses, and is best estimated from the precision of the replicate analyses from the three parallel samplers, as illustrated in Figure 2.

#### ***Gas-phase WSN species sampling efficiency***

Data from the first phase of sampling, 23<sup>rd</sup> July to 21<sup>st</sup> August 2008 at CEH, were used to evaluate sample collection methodology. Comparison of the concentrations captured by each of the two Cofer samplers in series showed that Cofer collection efficiency varied with WSN component measured. As expected, due to its high aqueous solubility, sampling of gas phase  $\text{NH}_3$  (determined as  $\text{NH}_4^+$ ) was very efficient, with average collection efficiency (% of total in both samplers) in the first sampler of  $88 (\pm 8) \%$  ( $n = 10$ ,  $\pm \text{sd}$ ), and with no correlation between concentrations measured in first and second samplers.

The collection efficiency of gas-phase oxidised nitrogen (measured as  $\text{NO}_3^-$ ) in the first Cofer sampler was lower, and harder to determine since  $\text{NO}_3^-$  concentrations were generally close to the analytical limits of detection but, on average,  $63 (\pm 16) \%$  of observed  $\text{NO}_3^-$  was in the first sampler, with again no correlation between concentrations in first and second samplers. The Cofer  $\text{NO}_3^-$  derives from two gas-phase components,  $\text{NO}_2$  and  $\text{HNO}_3$ , and also potentially from hydrolysis of organic nitrates. Nitric acid is highly soluble and expected to have close to 100% collection efficiency. On the other hand,  $\text{NO}_2$  has low Henry's Law solubility, although its transfer into the Cofer solution is enhanced by its hydrolysis into  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (Bambauer, et al., 1994), the  $\text{NO}_2^-$  subsequently reacting with dissolved oxidants (principally ozone) to yield  $\text{NO}_3^-$  also. If all the  $\text{NO}_3^-$  in the second sampler originates from  $\text{NO}_2$  the collection efficiency for  $\text{NO}_2$  would therefore be 37%. This calculation is consistent with the observation that at this sampling location the gas phase molar ratio of  $\text{NO}_2$  to  $\text{HNO}_3$  is  $\sim 20$ , on average (Tang, et al., 2009). However, the relatively large variability between sampling periods in the proportion of nitrate in the two Cofer samplers in series, although possibly reflecting fluctuations in the actual atmospheric ratio of  $\text{NO}_2$  to  $\text{HNO}_3$ , indicates the uncertainty in this calculation.

The average capture efficiency of gas-phase WSON in the first sampler was  $57 (\pm 7) \%$ , with much less variability in this proportion than for nitrate, but with a significant correlation ( $r^2 = 0.75$ ,  $n=10$ ) between concentrations in the first and second samplers. This correlation implies that WSON concentration is approaching saturation in the first sampler, with breakthrough of gas-phase material to the second sampler. As for collected nitrate, the WSON collected from the gas phase is likely to result from different components of differing solubility. The sampling rate was greater during the

main measurement period than when the Cofer samplers were operated in series, so that the estimated capture efficiency of 57% is likely to overestimate the sampling efficiency of a single sampler. The atmospheric concentration data reported in this paper have therefore not been adjusted for collection efficiency, but represent a lower limit, and could be a factor of 2 greater; the actual concentrations observed in precipitation and clouds presumably also reflect partitioning between the gaseous and aqueous phases, depending on the solubility of the individual components of WSON.

There was no evidence of significant loss of gaseous  $\text{HNO}_3$  to deposition on the additional surfaces of the sampler with a closed filter inlet (see Figure 1) compared with the two samplers with open-face filter inlet (paired t-tests on log-transformed Cofer nitrate concentrations from parallel samplers of each type during the Easter Bush campaign).

#### ***Particle-phase ion balance***

For the excess  $\text{NH}_3$  conditions generally prevailing at these sampling localities, the predominant sources of particle-phase  $\text{NH}_4^+$  are  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ , which are also the dominant source of particle-phase  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Determination of the latter ion was included in the IC analyses as an additional check, through ion balance, of particle-phase sample collection. Thus, for particle-phase samples, the sum  $[\text{NO}_3^- + 2 \cdot \text{SO}_4^{2-}]$  should equal, or exceed, particle  $[\text{NH}_4^+]$ . Figure 2 confirms significant linear correlation, and the gradient exceeding unity is consistent with an additional fraction of  $\text{SO}_4^{2-}$  of marine aerosol origin. The additional charge will be balanced by acidity or cations other than  $\text{NH}_4^+$ .

#### ***Artefacts from use of a pre-filter***

Operation of the Cofer sampler with a PTFE filter on the inlet might have led to potential artefacts. Any  $\text{NH}_4\text{NO}_3$  collected on the filter could have decomposed to give  $\text{NH}_3$  and  $\text{HNO}_3$  as air concentrations or temperature changed (Stelson and Seinfeld, 2007), so some of the WSN measured as 'gaseous' might have been originally particulate. The average proportions of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in the particle phase were 7:3 (on an ion equivalent basis), implying that only around 30% of the particulate  $\text{NH}_4^+$  was available as a potential source of 'artefact' gaseous data, as  $(\text{NH}_4)_2\text{SO}_4$  is not volatile. However, given the relatively large gas-phase  $\text{NH}_3$  concentrations, any effect of such particle decomposition on  $\text{NH}_3$  concentration is likely to be small. The effect on gas-phase  $\text{NO}_3^-$  concentration could have been significant, given the rather small overall  $\text{NO}_3^-$  concentrations from the gas-phase, but many of these data were close to the limit of detection and made an insignificant contribution to overall WSN concentrations. Based on average concentrations (Table 1) even if all the  $\text{NO}_3^-$  detected in the gas-phase had originally been present as particles, the loss of particulate  $\text{NO}_3^-$  would be ca. 20%, but in practice any contribution from  $\text{NO}_2$  and  $\text{HNO}_3$  to  $\text{NO}_3^-$  measured in the Cofer sampler would reduce this potential artefact. In practice, loss rates over 24h from PTFE are likely to be around 20% or less (Yu, et al., 2006). The low flow rates, and generally low temperature at the site, would also mitigate against such artefacts. Another source of uncertainty is the possibility that gaseous WSON molecules were adsorbed by the PTFE filter and thereby prevented from entering the Cofer sampler – this would lead to an apparently greater contribution of WSON in the particle phase. However, by their very nature, WSON species are likely to be polar molecules with little affinity for PTFE, so any artefact is likely to be small.

### ***Quality control criteria***

Sampling from the gas phase by Cofer sampler assumes that the mist remains a sink for water-soluble species and does not approach solution equilibrium. Depletion of the sampler reservoir by evaporation may cause the aqueous concentration of WSN species to become saturated, leading to inefficient removal or partitioning back into the gas phase. Evaporation from the single Cofer sampler was considerably greater than from Cofer samplers in series because of the greater flow rates with a single sampler, enabling investigation of the effect of reservoir evaporation on capture efficiency. For all sampling dates,  $\text{NH}_4^+$  concentration in the single sampler was, on average, 83% of the concentration in the first of the two samplers in series, but was 101% ( $R^2 = 0.98$ ) when only dates on which the single sampler had final reservoir volume greater than 3 mL were included. This volume was therefore chosen as the minimum volume required to be remaining in a Cofer sampler at the end of a sampling period for the sample to be regarded as valid. Applying this criterion resulted in 9 of 132 Cofer samples collected during the main sampling campaign being discarded.

For the particle-phase samples, there was no significant difference in concentrations of particle-phase total WSN species determined from parallel samplers with enclosed or open-face inlet PTFE filters (linear gradient 1.03,  $R^2 = 0.94$ ,  $n = 10$ ). Both types of filter sampler were therefore retained for the second phase of sampling at Easter Bush. To investigate the concern that particle-phase material on open-face filters may be subject to loss during rain events, total WSN concentrations derived from the two filter holders were compared separately for sampling dates with zero or light rain only and for dates with heavy rainfall. On the former dates, the linear gradient of total WSN from enclosed versus open-face filters was 0.94 ( $R^2 = 0.99$ ) while on the latter dates the gradient was 1.14 ( $R^2 = 0.97$ ). The difference in gradients was not statistically significant, although the trend is consistent with the hypothesis that the unprotected open-face filters may be prone to loss of water-soluble particle-phase material in wet weather. As a precaution against potential bias, 23 out of 168 filter samples collected in the main sampling campaign where open-face filter samples yielded lower total WSN air concentrations than the parallel enclosed sampler were discarded from the dataset.

Dates where the relative standard deviation of the measurements from the 3 parallel replicate Cofer or filter samples exceeded 100% were regarded as 'suspicious' and also removed. The final dataset for the main sampling campaign at Easter Bush site comprised 38 and 47 sets of 'valid' Cofer and filter samples, respectively.

### **Results**

Time series of the atmospheric concentrations of the measured gas and particle-phase WSN species at Easter Bush are shown in Figure 3. The time series are plotted as relative abundances of WSN species in each of the gas and particle phases in Figure 4. Concentrations differed substantially between species and were generally higher in the gas phase (except for oxidised inorganic nitrogen). Ammonia was the dominant WSN species overall, and  $\text{NH}_4^+$  was also the most abundant WSN species in the particle phase. Significant amounts of WSON were present in both phases.

On 28<sup>th</sup> August nitrogen fertilizer was applied to the field surrounding the sampling location at the rate of 35 kg N ha<sup>-1</sup> as urea. The gas-phase NH<sub>3</sub> concentration of 512 ± 8 nmol N m<sup>-3</sup> measured on this date was more than 6 times larger than the average concentration of 77 nmol N m<sup>-3</sup> for the other 36 dates with 3 valid replicates (after removal of data for 12<sup>th</sup> September also, see below). The WSON concentration was effectively zero, implying no direct loss of urea to the gas phase. This observation suggests that an important fraction of the urea applied to the soil was lost due to volatilization into the atmosphere as ammonia (Ball and Ryden, 1984, Fillery, et al., 1986). Given the clear causal factor to the ‘outlier’ data on this occasion, this date was not included in subsequent statistical summaries of general trends.

A large NH<sub>3</sub> concentration of 386 ± 61 nmol N m<sup>-3</sup> was also observed on 12<sup>th</sup> September, a value about 5 times the long-term average of the remaining dates. It is known that no fertilizer was applied at the sampling location at this date, although the possibility that fertilizer was applied on a field nearby cannot be excluded. However, given that the NH<sub>3</sub> value was so large, this date was also not included in subsequent statistical summaries.

Table 1 summarises the means and medians of the individual WSN concentrations, together with their average contributions to the total WSN measured in each phase, for the subset of 33 dates having valid data for both phases simultaneously. There was no substantive difference in summary statistics when using this subset of 33 dates (compared with the larger datasets of dates having valid data in each phase separately), and it provides a matched dataset across the two phases. Table 1 also includes the standard deviations of within-triplicate-sample variability and between-day variability, for each component in each phase, as apportioned using one-way ANOVA (see Table caption). The former statistic provides a measure of sampler and analytical replicability, whilst the latter is a measure of the species variability over the whole period of study. For the full dataset, between-day variability was always highly significantly larger than within-replicate-sample variability. Corresponding data for the variabilities in the relative proportions of each component in each phase area also presented.

The data in Table 1 quantify that substantially more WSN was present in the gas phase than in the particulate phase: the sums of the average concentrations of measured WSN components were 103 nmol N m<sup>-3</sup> in the gas-phase (range 27-275, sd 59) across the 33 dates, and 38 nmol N m<sup>-3</sup> (range 5-154, sd 34) in the particle phase. This difference was driven primarily by the dominance of NH<sub>3</sub> as a WSN species in the gas-phase (average concentration 82 nmol N m<sup>-3</sup>), but gas phase WSON species were also an important contributor with average concentration 18 nmol N m<sup>-3</sup>. The concentration of water-soluble gas-phase oxidised inorganic nitrogen, determined as NO<sub>3</sub><sup>-</sup> and presumed to derive from both HNO<sub>3</sub> and NO<sub>2</sub>, was <3 nmol N m<sup>-3</sup> on average (actual gas phase concentration of NO<sub>2</sub> will be higher since it has low aqueous solubility.) Using these campaign-average concentrations of each component gives contributions of NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and WSON to total measured gas-phase WSN of 80%, 2% and 18%, respectively. Alternatively, taking the average of the proportions on individual sampling dates gives contributions of NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and WSON to total gas-phase WSN of 77%, 3% and 20%, respectively. However, there was large day-to-day variation in individual species concentrations around these average values, as illustrated in Figure 3, and by the magnitude of the standard deviations in species

concentrations and their proportions within total WSN across sampling dates (Table 1). The ANOVA analysis provides estimated between-day standard deviations on the average daily proportions of  $77 \pm 11$ ,  $3 \pm 3$  and  $20 \pm 9\%$  for  $\text{NH}_3$ ,  $\text{NO}_3^-$  and WSON, respectively.

In the particle phase,  $\text{NH}_4^+$  was the dominant WSN species (average concentration  $21 \text{ nmol N m}^{-3}$ ), but less so than in the gas phase, whilst  $\text{NO}_3^-$  and WSON concentrations were comparable ( $10$  and  $8 \text{ nmol N m}^{-3}$ , on average, respectively). These campaign-average concentration values correspond to contributions to total measured particle-phase WSN of 54%, 26% and 20% for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and WSON respectively. Or, using the average of the daily sample proportions, relative contributions of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and WSON to particle-phase WSN comprised  $45 \pm 19\%$ ,  $25 \pm 12\%$  and  $30 \pm 22\%$ , respectively, where the quoted  $\pm$  values are again the estimated between-day standard deviations in daily contributions to WSN in that phase (Table 1). Overall, these summary analyses indicate that for this sampling campaign WSON contributed  $\sim 20\%$  on average to gas-phase WSN (with  $\text{NH}_3 \sim 77\%$ ,  $\text{NO}_3^- \sim 3\%$ ) and  $\sim 25\%$  on average to particle-phase WSN (with  $\text{NH}_4^+ \sim 50\%$ ,  $\text{NO}_3^- \sim 25\%$ ), with somewhat greater day-to-day variability in these proportions in the particle-phase than in the gas-phase.

Figure 5 shows the proportions of daily WSON and total WSN which were present in the gas phase during the sampling campaign. The averages ( $\pm 1$  sd) of the proportions in the gas phase across all valid sampling dates, for each of the measured WSN components, are shown in Figure 6 and were  $80 \pm 19\%$  for  $\text{NH}_3/\text{NH}_4^+$ ,  $30 \pm 22\%$  for  $\text{NO}_3^-$ ,  $67 \pm 15\%$  for WSON, and  $74 \pm 16\%$  for the sum of all the measured WSN components. The majority of water soluble oxidised inorganic nitrogen ( $\text{NO}_3^-$ ) was present in particles (as expected), whereas the majority of reduced inorganic nitrogen was present in the gas phase. WSON was also predominantly in the gas phase. However, as illustrated by the standard deviations and the individual sample data in Figure 5, the splits between the phases varied from day to day.

## Discussion

A single-plot summary of the concentrations of measured WSN species in the gas and particle phases for the subset of 33 days in the sampling period 26<sup>th</sup> August 2008 to 21<sup>st</sup> November 2008 at Easter Bush is shown in Figure 7, which illustrates the large differences in atmospheric concentrations between components and phases.

The concentrations of the water-soluble inorganic components measured at Easter Bush are compared in Table 2 with data from monthly samples collected by denuder at the CEH site as part of a long-term atmospheric sampling network (Tang, et al., 2009). Given the differences in sample collection periods between the two measurements noted in the table caption, the values agree very well. The agreement is better for particles than for the gases, as would be expected; particle concentrations tend to be less spatially variable because of long transport distances and slow dry deposition. Similar behaviour would be expected for  $\text{NO}_2$  and  $\text{HNO}_3$  unless there were major local sinks for the gases between the two sampling sites, either as rough vegetation or large  $\text{NH}_3$  sources. There was no major landscape sink for  $\text{NO}_2$  and  $\text{HNO}_3$  between the two sites, but emissions and concentrations of  $\text{NH}_3$  were likely to have been higher at the Easter Bush site, possibly leading to removal of  $\text{HNO}_3$  as  $\text{NH}_4\text{NO}_3$  particles. For  $\text{NH}_3$ , however, local variability can be very great, particularly in an agricultural landscape with multiple sources. The Easter Bush site is in the

middle of a fertilized and grazed grass field, which would be expected to sustain higher  $\text{NH}_3$  concentrations than the fallow field surrounding the long-term monitoring site; the observation of consistently lower  $\text{NH}_3$  concentrations at the latter is therefore not unexpected.

The generally lower concentrations of atmospheric WSN species apparent in Figure 3 for the period 2<sup>nd</sup> – 21<sup>st</sup> October did not appear to be related to sustained differences in temperature, rainfall or wind direction between this period and the rest of the sampling campaign. Instead, the likely explanation is the coincident removal of sheep from the grazing field immediately upwind (SW) of the sampling site between 24<sup>th</sup> September and 20<sup>th</sup> October inclusive.

The proportion of organic N within total WSN in the gas phase (~20%) was similar to that in the particle phase (~25%). The average contribution of organic N in rainfall at Bush measured in preceding years (González Benítez, et al., 2009) was 12-36% in wet deposition and up to 33% in dry deposition, from funnel washings. The sampling periods were at different times of year, making direct comparison difficult, but the larger relative contribution of organic N to 'dry deposition' implies that such material is less volatile than the major inorganic contributor ( $\text{NH}_3$ ) and is less likely to be revolatilised from surfaces after deposition.

The main components contributing to the Cofer solution  $\text{NO}_3^-$  are gas phase  $\text{NO}_2$  and  $\text{HNO}_3$ . These have very different sources to gas phase  $\text{NH}_3$ . The former are secondary atmospheric oxidation products derived from emissions of oxidised nitrogen (principally NO) from combustion sources, i.e. urban and traffic-related, whereas the overwhelming source of  $\text{NH}_3$  is primary emission in rural areas, from farms in particular, from decomposition and volatilization of animal wastes. At the rural Easter Bush sampling location, sources of  $\text{NH}_3$  are local, whereas  $\text{NO}_2$  and  $\text{HNO}_3$  are derived from more distant sources (the city of Edinburgh and longer range). The predominance of  $\text{NH}_3$  in the measured gas-phase WSN at this site indicates the influence of these local sources.

The source of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  within the particle-phase is  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ . These are secondary particulate matter components formed mainly by the reaction of nitric and sulphuric acids with  $\text{NH}_3$ . The  $\text{NO}_3^-$  measured in the particle phase was more than three times that in the gas phase indicating the favourable formation of condensed-phase inorganic material when  $\text{NH}_3$  is present in excess, as at this locality, with relatively low temperatures and high relative humidity. However, whilst some of the secondary inorganic components measured here may have formed locally and recently, accumulation mode particles can have a lifetime of several days so can also be transported over large distances.

WSON was an important fraction of both gas and particle-phase WSN at this location. Potential commonality of source was explored by examining correlations between daily concentrations of the measured WSN components in each phase (Table 3). There was highly significant correlation between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the particle phase, as expected given their common source of  $\text{NH}_4\text{NO}_3$  particles, but no other significant correlation. The absence of substantive correlation between WSON and  $(\text{NH}_3+\text{NH}_4^+)$  or oxidised inorganic nitrogen suggests that the WSON at this location is not strongly associated with either combustion or agricultural sources alone. Instead, the weakly

positive associations of WSON with both  $\text{NO}_3^-$  and  $\text{NH}_3$  possibly simply reflect common meteorological conditions that lead to correlations across all airborne species, but suggest it is likely that WSON comprises material emanating from a variety of sources, anthropogenic and non-anthropogenic, both local and further afield. These findings are consistent with the conclusion from a recent study of marine aerosols that WSON species contain both biogenic and anthropogenic components (Facchini, et al., 2008). In that study, WSON concentrations were higher in polluted air masses than in clean ones but the dimethyl- and diethylammonium salts within the WSON (taken to be of biogenic origin) were larger in the clean air masses.

The 33 sampling days with valid measurements for both the gas and particle phases were sub-divided according to whether the sampling day was dry (17 days) or had rain (16 days). The mean and median concentrations and proportions of each measured WSN component for the two weather categories separately are also included in Table 1. The concentrations of gas-phase  $\text{NH}_3$  and water-soluble oxidised inorganic nitrogen (sampled as  $\text{NO}_3^-$ ) were significantly lower on wet days than dry days ( $p = 0.012$  and  $0.028$ , respectively; ANOVA on log-transformed data). Mean  $\text{NH}_3$  concentrations were  $100$  and  $63 \text{ nmol N m}^{-3}$  on dry and wet days respectively, and mean  $\text{NO}_3^-$  concentrations were  $3.3$  and  $1.8 \text{ nmol N m}^{-3}$ . The depleted concentrations on wet days are not surprising since rain is expected to scrub highly water-soluble material from the boundary layer. Conversely, mean concentrations of gas-phase WSON were slightly greater on wet days ( $20 \text{ nmol N m}^{-3}$ ) than on dry days ( $16 \text{ nmol N m}^{-3}$ ), a difference just reaching statistical significance ( $p = 0.036$ ). As discussed above in relation to interpretation of the Cofer sampler carryover experiments, WSON includes species that are less water soluble than  $\text{NH}_3$  and  $\text{HNO}_3$ . This may account for the smaller differences between dry and wet days for WSON.

The concentration of particle-phase WSON was also significantly higher on wet sampling days than on dry days, with mean concentrations of  $11$  and  $5 \text{ nmol N m}^{-3}$ , respectively ( $p = 0.008$ , ANOVA on log-transformed data). Concentrations of particle-phase  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were not significantly different between wet and dry days.

There was no evidence for systematic differences in local wind direction (indicative of air-mass origin) between wet and dry days which might have indicated changes to contributing WSN sources to account for the enhancement of WSON on wet days. One possible explanation is that the wetting of the surrounding soil and/or vegetation (perennial ryegrass, *Lolium perenne*) by rainfall promotes release of volatile nitrogen-containing compounds. Similarly, the impact of rain droplets on leaves or soil may cause mechanical (re)suspension of particles back into the lower boundary layer. The scrubbing effect of rainfall would also still occur but the net effect of all these processes will depend on the intensity, duration and periodicity of rain events. This explanation is consistent with observations reported in previous studies (Calderon, et al., 2007), in which the poor rain scavenging of fine particles of  $\text{NH}_4^+$  and WSON (anticipated as the main contributors to particle-phase WSN at this sampling location) was attributed to low collision efficiencies, even in the presence of a high number of big droplets.

## Conclusions

Cofer samplers are effective and inexpensive samplers for water-soluble gases, easy to handle, to transport and to operate. Either open-face or enclosed membrane filters at the inlet to the sampler can be used to collect simultaneous samples of particulate matter.

In this study the total concentration of WSN was considerably higher in the gas phase than in the particle phase, the former dominated by  $\text{NH}_3$ . On average the sum of gas-phase  $\text{NH}_3$ , oxidised inorganic nitrogen (mainly  $\text{HNO}_3$ ) and WSON was  $103 \text{ nmol N m}^{-3}$ , apportioned ~77%, 3% and 20%, on average, whilst the sum of particle-phase  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and WSON was  $38 \text{ nmol N m}^{-3}$ , apportioned ~50%, 25% and 25%, on average. The fraction of each measured WSN component that was in the gas-phase (relative to the sum of gas and particle phase concentrations) was, on average,  $80 \pm 19\%$  for  $(\text{NH}_3+\text{NH}_4^+)$ ,  $30 \pm 22\%$  for  $\text{NO}_3^-$ , and  $67 \pm 15\%$  for WSON ( $\pm 1$  sd for 33 sampling days). These data summaries exclude days when nitrogen fertilizer was applied in the locality, when measured  $\text{NH}_3$  concentrations reached up to ~6 times the longer term average.

The WSON concentrations in the gas and particle-phase samples were only weakly correlated with reduced and oxidised inorganic nitrogen. This suggests that the WSON measured at this location was not primarily associated with just one or other of agricultural or combustion-related sources but likely has contributions from both anthropogenic and non-anthropogenic sources, both local and further afield. The gas and particle-phase WSON was also greater, on average, on wet days than on dry days (in contrast to WSIN), suggesting potential local release of WSON material from wetting and mechanical action of rain on surrounding soil and grassland.

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**Table 1:** Concentrations and relative proportions of  $\text{NO}_3^-$ ,  $(\text{NH}_3+\text{NH}_4^+)$  and WSON, in both gas and particle phases, for daily samples collected at Easter Bush between 26<sup>th</sup> August and 21<sup>st</sup> November 2008 where valid data were simultaneously available for both gas and particle phases. Standard deviation values were estimated via ANOVA separation of variance: within triplicate sd =  $\sqrt{(\text{within triplicate MS})}$ ; between day sd =  $\sqrt{((\text{between triplicate MS} - \text{within triplicate MS})/3)}$ . In all cases, except where marked with \*, estimated between-day variance was significantly greater than corresponding estimated within-triplicate variance, evaluated using log-transformed dataset.

		All days (n = 33)		Dry days (n = 17)		Wet days (n = 16)		
		Gas phase	Particle phase	Gas phase	Particle phase	Gas phase	Particle phase	
Median daily concentration / $\text{nmol N m}^{-3}$	$\text{NO}_3^-$	1.5	7.6	1.7	7.6	1.3	7.4	
	$\text{NH}_3+\text{NH}_4^+$	79.4	15.7	97.4	9.6	58.7	17.9	
	WSON	16.9	5.5	11.5	4.7	22.8	7.5	
Mean daily concentration / $\text{nmol N m}^{-3}$ (as % proportion of total WSN)	$\text{NO}_3^-$	2.6 (2.5%)	9.8 (25.6%)	3.3 (2.8%)	8.8 (29.2%)	1.8 (2.1%)	10.8 (23.1%)	
	$\text{NH}_3+\text{NH}_4^+$	82.4 (79.9%)	20.7 (54.2%)	100.4 (83.9%)	16.5 (54.8%)	63.3 (74.0%)	25.1 (53.8%)	
	WSON	18.1 (17.6%)	7.7 (20.2%)	15.9 (13.3%)	4.8 (16%)	20.4 (23.9%)	10.8 (23.1%)	
Standard deviations in concentration / $\text{nmol N m}^{-3}$ (also as RSD of dataset mean value)	Within triplicate sd	$\text{NO}_3^-$	2.2 (84%)	6.3 (64%)	2.9 (87%)	6.4 (73%)	1.0 (56%)	6.1 (56%)
		$\text{NH}_3+\text{NH}_4^+$	17.3 (21%)	9.4 (45%)	18.9 (19%)	7.9 (48%)	15.4 (24%)	10.7 (42%)
		WSON	11.5 (64%)	9.4 (122%)	12.5 (78%)	5.8 (122%)	10.4 (51%)	12.0 (111%)
	Between day sd	$\text{NO}_3^-$	2.1 (82%)	8.3 (85%)	2.6 (80%)	6.5 (74%)	1.1 (58%)	10.1 (93%)
		$\text{NH}_3+\text{NH}_4^+$	52.8 (64%)	23.1 (112%)	64.0 (64%)	21.3 (129%)	28.9 (45%)	24.8 (99%)
		WSON	9.5 (53%)	4.3 (56%)	11.2 (70%)	2.1 * (44%)	7.3 (36%)	4.1 * (38%)
Mean daily % proportion of WSN component	$\text{NO}_3^-$	3.1	25.4	3.7	29.0	2.6	21.7	
	$\text{NH}_3+\text{NH}_4^+$	76.9	44.9	80.5	44.5	73.0	45.3	
	WSON	20.0	29.7	15.8	26.5	24.4	33.0	
Standard deviations in % proportion of WSN component (also as RSD of dataset mean value)	Within triplicate sd	$\text{NO}_3^-$	2.4 (78%)	9.8 (38%)	3.1 (88%)	10.3 (36%)	1.3 (50%)	9.3 (42%)
		$\text{NH}_3+\text{NH}_4^+$	11.4 (15%)	14.3 (31%)	12.1 (15%)	15.1 (33%)	10.5 (14%)	13.5 (29%)
		WSON	11.1 (56%)	19.5 (68%)	11.9 (76%)	20.6 (80%)	10.1 (42%)	18.1 (58%)
	Between day sd	$\text{NO}_3^-$	2.6 (87%)	11.6 (46%)	3.2 (93%)	14.0 (49%)	1.8 (72%)	7.5 (32%)
		$\text{NH}_3+\text{NH}_4^+$	11.1 (14%)	19.1 (42%)	9.7 (12%)	20.7 (46%)	11.7 (16%)	18.0 (39%)
		WSON	9.2 (47%)	21.8 (76%)	6.4 * (40%)	24.8 (96%)	10.1 (42%)	18.7 (59%)

**Table 2:** Comparison of average concentrations, by month, of gas-phase ammonia and (nitric acid+NO<sub>2</sub>), and particle-phase ammonium and nitrate, from samples collected at Easter Bush as described in this work and by denuder sampler at CEH as part of the DELTA project (Tang *et al.*, 2009). The measurements are not directly comparable since the DELTA values are single monthly samples whereas the Easter Bush values are averages of an incomplete set of daily samples within the month (the number of contributing days are indicated in parentheses).

	Gas phase / nmol N m <sup>-3</sup>				Particle phase / nmol N m <sup>-3</sup>			
	NO <sub>2</sub> +HNO <sub>3</sub>		NH <sub>3</sub>		NO <sub>3</sub> <sup>-</sup>		NH <sub>4</sub> <sup>+</sup>	
	This work ( <i>n days</i> )	CEH DELTA (HNO <sub>3</sub> )	This work ( <i>n days</i> )	CEH DELTA	This work ( <i>n days</i> )	CEH DELTA	This work ( <i>n days</i> )	CEH DELTA
<b>September</b>	4.1 (12)	7.5	106 (12)	42	12 (19)	16	31 (19)	35
<b>October</b>	2.1 (15)	3.2	39 (15)	39	6.1 (14)	4.7	7.2 (14)	7.0
<b>November</b>	1.2 (8)	6.0	110 (8)	69	9.9 (9)	8.9	16 (9)	14

**Table 3:** Spearman rank correlation coefficients between WSN component concentrations for all days with valid measurements in (a) the gas phase, (b) the particle phase.

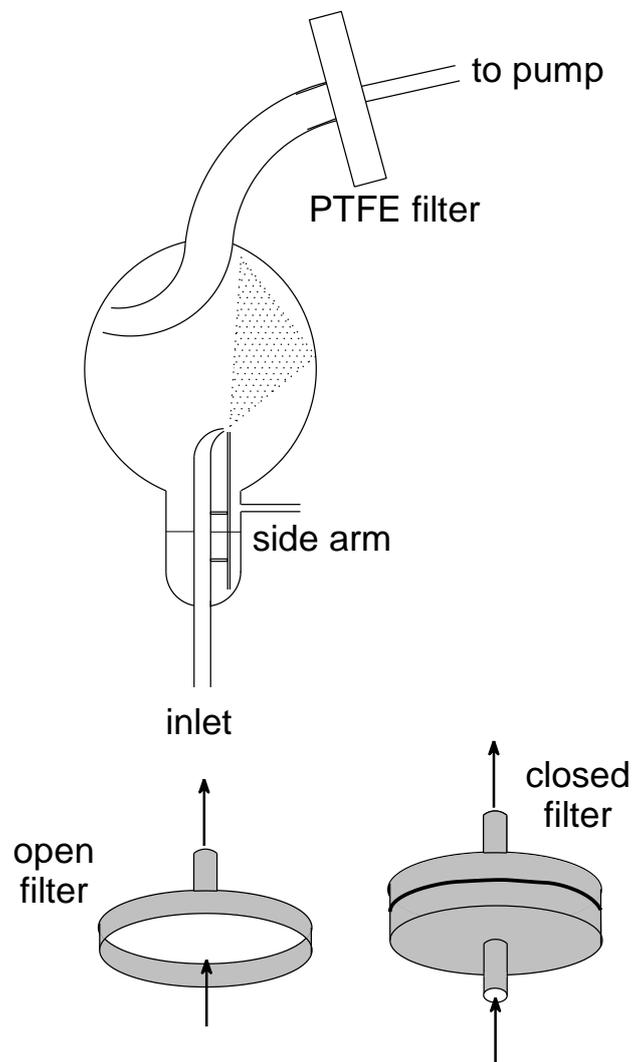
(a)

	Gas phase ( <i>n</i> = 36)	
	Oxidised WSIN	NH <sub>3</sub>
<b>NH<sub>3</sub></b>	0.077 ( <i>p</i> = 0.654)	
<b>WSIN</b>	0.242 ( <i>p</i> = 0.154)	0.236 ( <i>p</i> = 0.187)

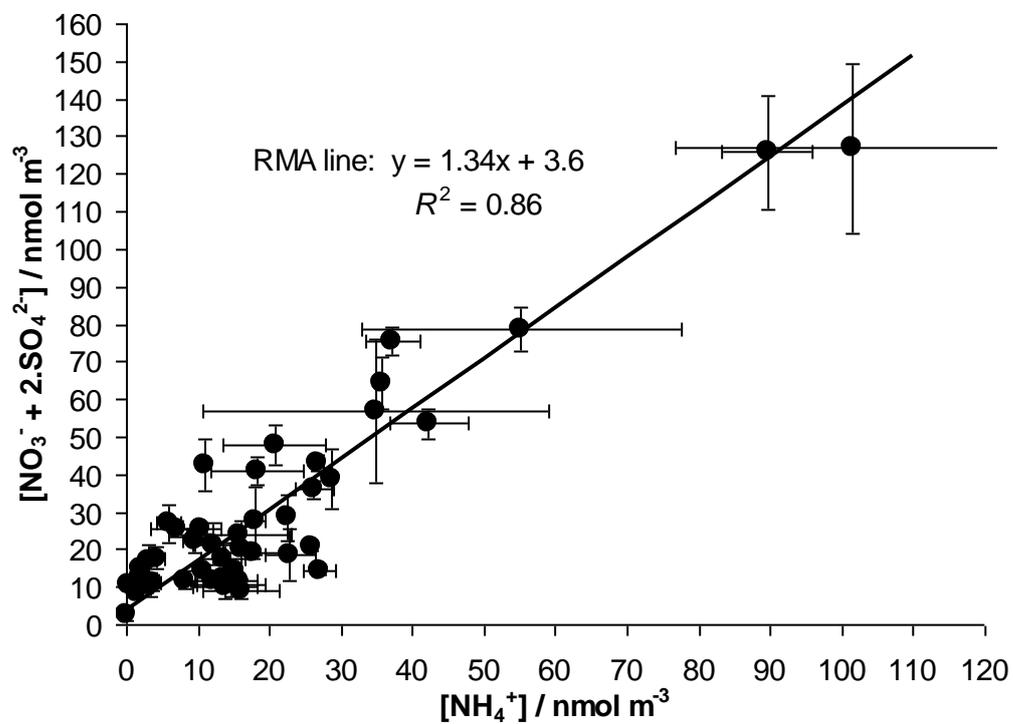
(b)

	Particle phase ( <i>n</i> = 45)	
	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
<b>NH<sub>4</sub><sup>+</sup></b>	0.674 ( <i>p</i> < 0.001)	
<b>WSIN</b>	0.126 ( <i>p</i> = 0.411)	0.252 ( <i>p</i> = 0.096)

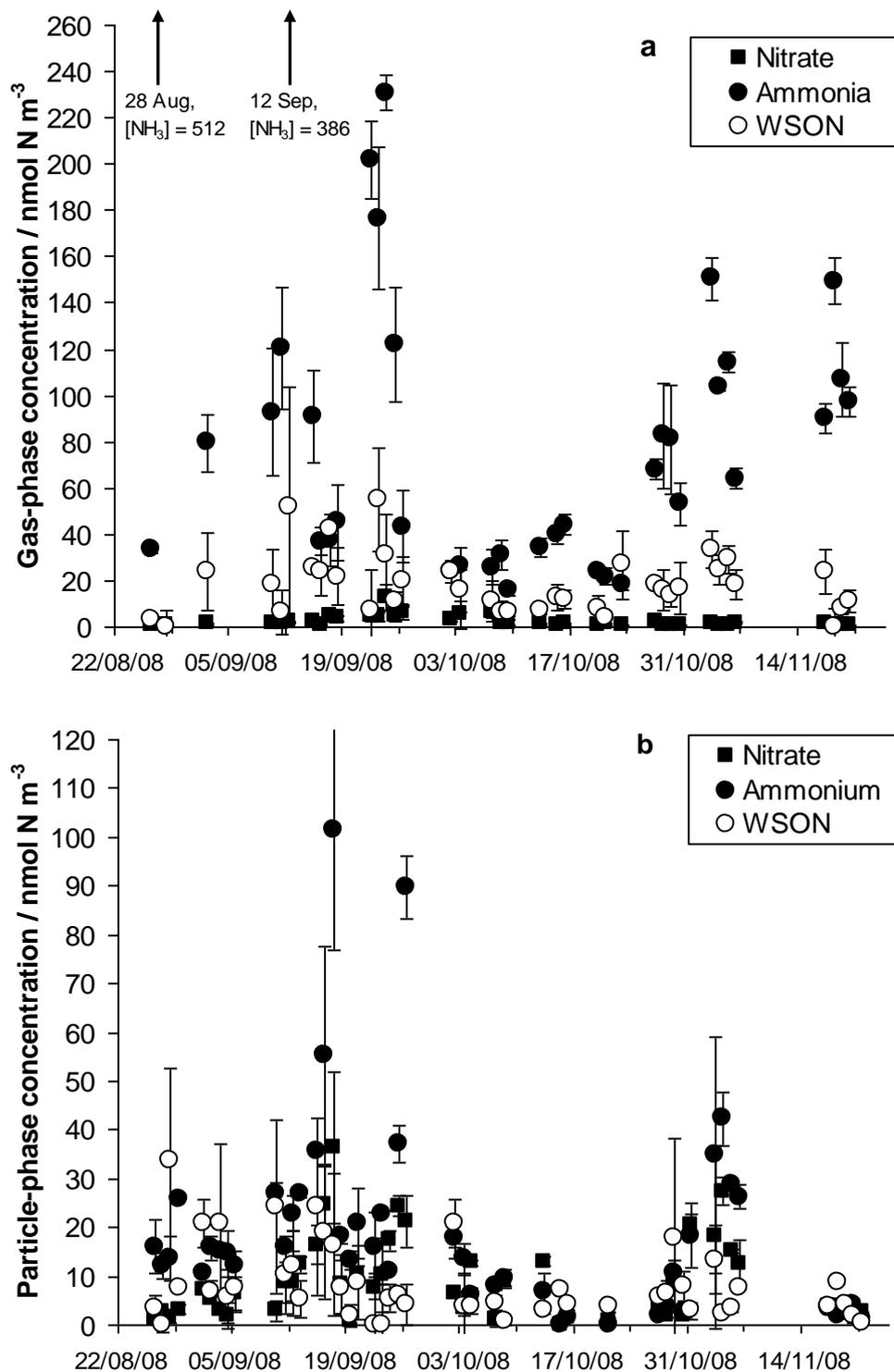
**Figure 1:** Schematic diagram of Cofer sampler used in this study. The 'open' and 'closed' filter holders are also shown.



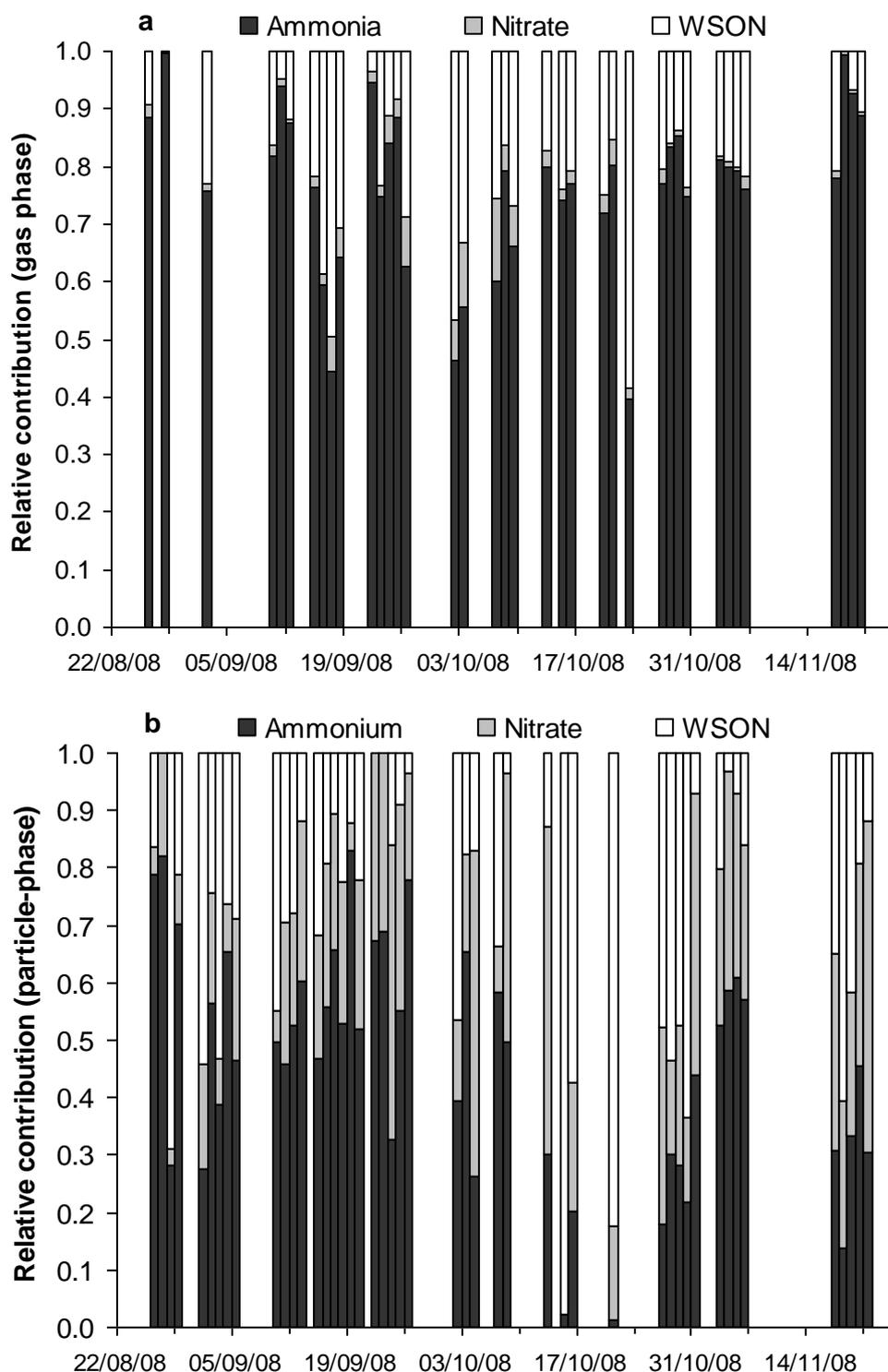
**Figure 2:** Ion balance comparison for particle-phase samples. Error bars are standard deviations of triplicate samplers.  $n = 47$  days with valid particle-phase triplicates.



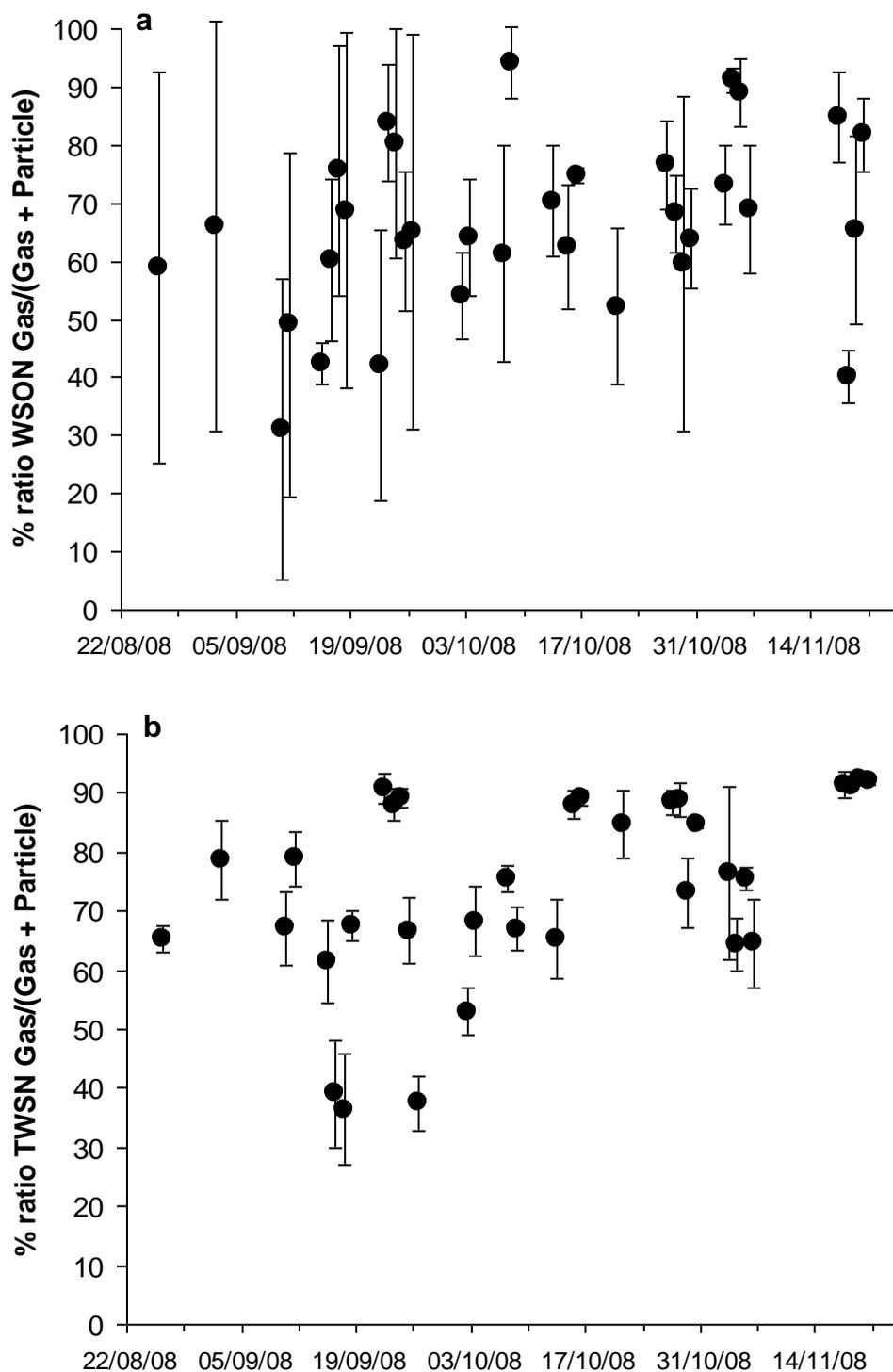
**Figure 3:** Time series of daily concentrations at Easter Bush of ammonia/ammonium, nitrate and water soluble organic nitrogen (WSON) in (a) the gas-phase, and (b) the particle-phase. Error bars are standard deviations of triplicate samplers ( $n = 38$  and 47 valid replicates for each phase, respectively).



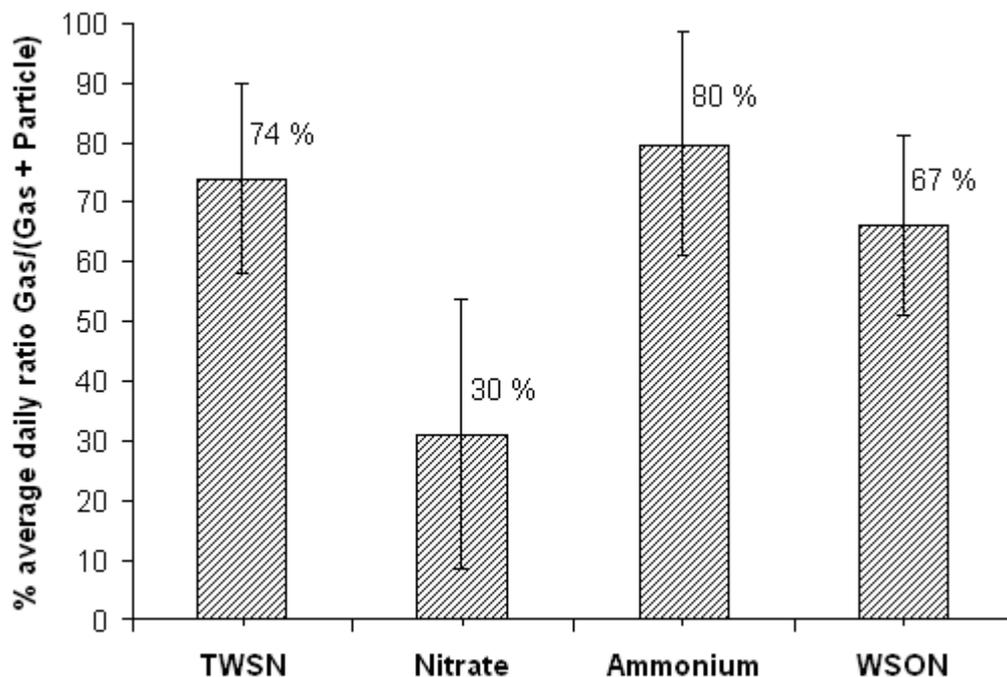
**Figure 4:** Time series of relative contributions at Easter Bush of (a) gas-phase  $\text{NH}_3$ , oxidised inorganic nitrogen ( $\text{NO}_2$  and  $\text{HNO}_3$ ) and WSON to total gas-phase WSN, and (b) of particle-phase  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and WSON to total particle-phase WSN. Each value is the mean from triplicate samplers ( $n = 38$  and 47 valid replicates for each phase, respectively).



**Figure 5:** Time series of the daily proportions in the gas phase (relative to the sum of gas and particle phase concentrations) for (a) WSON, and (b) TWSN, for 33 valid sets of daily samples collected at Easter Bush. Error bars are standard deviations from triplicate samplers.



**Figure 6:** Average daily % concentration ratio gas phase / (gas phase + particulate matter) for total measured WSN, nitrate, ammonia/ammonium and WSON for 33 valid sets of daily samples collected at Easter Bush between 26<sup>th</sup> August and 21<sup>st</sup> November 2008. Error bars are standard deviations across the 33 dates.



**Figure 7:** Summary of average concentrations of total measured WSN, nitrate, ammonia/ammonium and WSON in the gas and particle phases for 33 valid sets of daily samples collected at Easter Bush between 26<sup>th</sup> August and 21<sup>st</sup> November 2008.

