Development of a new model DELTA sampler and assessment of potential sampling artefacts in the UKEAP AGANet DELTA system

Summary and Technical Report

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Executive Summary

DELTA tests background

- The **DE**nuder for **L**ong-**T**erm **A**tmospheric sampling (DELTA) system is a sampler developed for low-cost measurements of:
    - acid gases: hydrochloric acid, sulphur dioxide, nitric acid and nitrous acid (HCl, SO_2, HNO_3, HONO respectively) on two potassium carbonate (K_2CO_3)-glycerol coated denuders
    - ammonia (NH_3) on two citric acid denuders
    - inorganic anions & cations (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, Ca^{2+}) on a K_2CO_3-glycerol impregnated filter
    - ammonium (NH_4^+) on a citric acid impregnated filter
- The DELTA sampler is currently deployed in the Acid Gas and Aerosol Network (AGANet) (part of the Defra AQ0647 UK Eutrophying and Acidifying Atmospheric Pollutants contract) across the UK at 30 sites for the purpose of measuring the UK-scale distribution of concentrations and the long-term trends.
- DELTA samplers were developed in the 1990s, being initially applied for ammonia and then extended for the other components. Tests in Defra project AC0103 have shown that the DELTAs sample the $PM_{4.5}$ fraction.
- Concerns were discussed regarding potential artefacts from NO_y species (NO_2, HONO, N_2O_5, PANs, $ClNO_2$ and other oxidised nitrogen species) collected on the K_2CO_3-glycerol denuders and biases in the methodology; therefore a series of test were initiated, prior to upgrading the DELTA samplers.
- Specifically these covered the following:
    - specificity of the HNO_3 measurement
    - loss of particulate to connecting tube in sampling train
    - performance of the filter pack configuration
    - further tests were carried out by NERC CEH to assess alternative coatings for the denuders

Key conclusions

Specificity of the HNO_3 measurement:

- the K_2CO_3-glycerol coated denuders have significant interferences in the HNO_3 measurement from other oxidised nitrogen species except NO_2. The interference dominating measured concentrations in the urban DELTA system
- Results from parallel sampling (NaCl denuders vs K_2CO_3-glycerol denuder) showed the following average ratios:
    - urban NaCl: K_2CO_3-glycerol denuder ratio = 0.21 (1 site, London Cromwell Road)
    - non-urban sites = 0.44±0.15 (4 sites)
- There are many unknowns for the interfering chemical species, including ambient concentration variation, deposition velocities and possible bi-directionalities in fluxes
- K_2CO_3-glycerol denuders are quantitative for SO_2 and HCl gas measurements
- NaCl and KF denuders were tested; NaCl is the most specific for HNO_3 but is not quantitative for SO_2 and HCl measurements are not possible. KF coating gave similar results as K_2CO_3-glycerol.
- Two NaCl denuders followed by a K_2CO_3-glycerol denuder captures HNO_3 quantitatively on the NaCl and other reactive-nitrate forming species on the K_2CO_3-glycerol, however this configuration is not suitable to measure HCl.

Loss of particulate to sampler connecting tube in sampling train:

- NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+} aerosol losses to LDPE connecting tube in sampling train are relatively small, on average being < 7% of the total aerosol ion concentration.
- Ca^{2+} measurements had a high uncertainty due to variability in LDPE blanks and low concentrations
- The new DELTA II design is linear, eliminating the use of the LDPE connecting tube.

Performance of the filter pack configuration:

- To test the particulate capture, all ions were analysed on both the K_2CO_3-glycerol and acidic filters plus a PTFE filter was introduced between the two filters to measure breakthrough from the first filter.
- Analysis of the K_2CO_3-glycerol coated filters showed that negligible amounts of NH_4^+ are retained.
- A sampling efficiency for the accumulation mode of about 71% for SO_4^{2-} and fine NO_3^- and of about 89% for NH_4^+ was measured, with close to quantitative measurement of Na^+, Cl^- and Mg^{2+} on the K_2CO_3-glycerol filter
- The 2μm porosity PTFE membrane quantitatively captures the SO_4^{2-} and NO_3^- PM components therefore this approach is suitable with an acid coated filter after the Teflon to capture NH_4

Future sampling recommendations

HNO_3/gas phase oxidised nitrogen measurement

Four possible options are discussed:

a. Continuation with the current configuration.
b. Change to a three stage denuder train: NaCl –NaCl – K_2CO_3-glycerol.
c. Continue with the current configuration but add a parallel (NaCl or K_2CO_3-glycerol) denuder at selected sites.
d. Assess alternative methods *e.g.* shift to on-line high resolution instrumentation.

Option (b) is recommended as the most cost-effect future sampling method. However HCl measurements will be discontinued with this option. NaCl denuders provided the best available quantitative measure of HNO_3 from the results found in the parallel experiments. Adding the final K_2CO_3-glycerol denuder allows quantitative measurement of SO_2, a key measurement of the DELTA samplers in AGANet and the "total nitrate" measurement to be maintained.

Connecting tube:

- No issue was found with the LDPE connecting tubing, apart from Ca.
- The new DELTA II is in a linear configuration, eliminating the use of the long LDPE connecting tube.

Filter pack configuration

It is proposed to change to a three-stage filter pack: PTFE-nylon-acid coated, which is the same configuration as used by the US EPA.

Implications for historic data

HNO_3/gas phase oxidised nitrogen measurement

- Discussions between the experimental team and pollutant deposition modellers were undertaken as to how to adjust for the over-reporting of HNO_3 concentrations.
- It is recommended that a correction factor of 0.45 be applied to the historic HNO_3 measurements. The range of ratios was 0.44±0.15 (±2SD), i.e. 0.29-0.59, therefore it is reasonably likely that the value lies between 0.4 and 0.5. Therefore a correction factor of 0.45 should be applied
- Historic measurements of SO_2 and HCl from K_2CO_3-glycerol coated denuders do not need correction.

Connecting tube

- No implications for historic data.

Filter pack configuration

- The sulphate and nitrate datasets should be historically corrected. However it is primarily important to correct appropriately. It is recommended that an assessment of the best method and any further specific tests for concentration effects be carried out before a historic data correction is applied.
- The dataset from the parallel measurements can be used to provide an interim correction.

Technical Summary

1. Introduction

The **DE**nuder for **L**ong-**T**erm **A**tmospheric sampling (DELTA) system is a sampler developed for low-cost measurements of acid gases: hydrochloric acid, sulphur dioxide, nitric acid and nitrous acid (HCl, SO_2, HNO_3, HONO), ammonia (NH_3), and inorganic aerosol components. The sampler is currently deployed in the Acid Gas and Aerosol Network (AGANet) (part of the Defra AQ0637 UK Eutrophying and Acidifying Atmospheric Pollutants contract) across the UK for the purpose of measuring the UK scale distribution of concentrations and the long-term trends. The method was developed by the Centre for Ecology and Hydrology in 1995, being initially applied for ammonia[1] and was then extended for the other components. First measurements in the UK National Nitric Acid Monitoring Network were made in September 1999 at 12 sites. Measurements were expanded by Defra to 30 sites in 2006 forming what is now called the Acid Gas and Aerosol Network (AGANet).

Measurement data from the AGANet are provided to the Defra modelling and mapping projects where annual concentration fields and deposition are calculated. In the **C**oncentration **B**ased **E**stimates of **D**eposition (CBED) procedure, oxidised nitrogen species currently included are HNO_3, NO_2 and aerosol nitrate (NO_3^-), with deposition velocities specified in the model. Deposition is estimated by calculating a UK concentration field and combining this with estimated deposition velocities.

The DELTA method[1] is based around the concept of a single cylindrical glass denuder for selective sampling of trace gases[2] followed by a filter pack to allow separate determination of gaseous and particulate components. A schematic of a DELTA sampler is shown below (Figure 1). When a laminar air stream passes through the denuder coated on the inside with a base coating, currently potassium carbonate and glycerol (K_2CO_3-glycerol), acid gases, such as HNO_3 are collected. Subsequently the air passes over denuders with a citric acid coating "acid denuders" (DA) and ammonia is captured by the acid coatings. Aerosols in the laminar flow should mostly pass through and are collected by aerosol filters placed downstream. The separation of aerosol from gaseous components is achieved due to the much more rapid diffusion of gaseous species to the tube wall compared with that of particles.

In 2010 a research plan (funded by Defra and CEH) was put in place in order to provide a quantitative assessment of the operation of the CEH developed **DE**nuder for **L**ong-**T**erm **A**tmospheric (DELTA) sampler. Concerns had been initially raised by Gehrig et al. at a conference in 2009[3] and in the UKEAP review[4] regarding the potential for the following:

1. Specificity of denuders, in particular the HONO and HNO_3 measurements
2. Deposition of aerosol on the low density polyethylene (LDPE) connecting tube in the DELTA sampling train.
3. Breakthrough in the aerosol sampler and potential artefacts

These topics were addressed by a series of experiments, which tested the configuration as it is currently deployed, and considered potential future configurations for the system and any corrections which might be required for the historical measurements. The experiments, results and conclusions for (1) – (3) are outlined below.
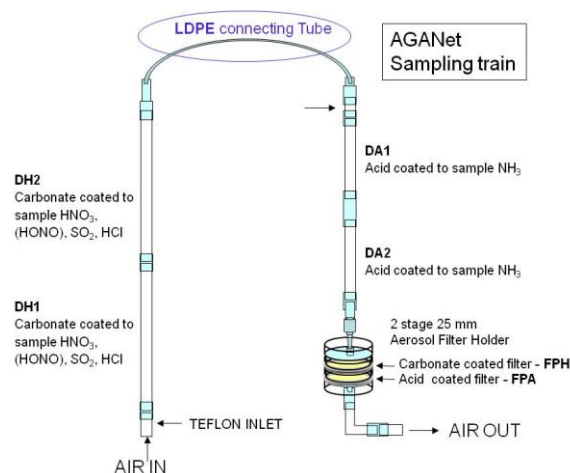
Figure 1 DELTA sampling train configuration. DH1 and DH2: K_2CO_3-glycerol coated denuders; low density polyethylene (LDPE) connecting tube; DA1 and DA2: citric acid coated denuders; FPH: K_2CO_3-glycerol impregnated filter paper; FPA: citric acid coated filter paper.

2.   Denuder testing: artefact assessment

2.1 Background

Oxidised nitrogen speciation in the atmosphere is complex, and both multiple gas phase compounds as well as heterogeneous processes may lead to more NO_y species to be sampled than first envisaged during the initial designs of the DELTA samplers and other HNO_3 analytical methods[5,6]. Oxidised nitrogen chemistry has become better understood in the past 5 years and while more continues to be learned there are still large gaps in both understanding atmospheric concentrations but also the detail chemical reactions, and biosphere-atmosphere interactions.[7] A schematic of some of the major oxidised nitrogen atmospheric species and interactions at the surface are summarised in Figure 2. Nitrous acid (HONO) has been known for decades to be a relevant atmospheric form of oxidised nitrogen, although its rates of atmospheric removal remain highly uncertain. More recently, HONO formation *via* heterogeneous reactions on surfaces (including atmospheric aerosol) and potential sources of HONO from the biosphere (e.g. as a by-product of nitrification in soils) have also been observed.[8,9] Other oxidised nitrogen species including PAN, $ClNO_2$ and N_2O_5 are also important reservoir species of oxidised nitrogen. The concentrations, interactions with surfaces, and their deposition velocities are either highly uncertain or unknown.

The K_2CO_3 coated denuders were originally selected due to tests showing quantitative capture of SO_2, HCl and what was considered in the late 1990s to be HNO_3 (compared against existing technology deployed at the time). The use of two denuders in series showed that typically 90% was captured in the first denuder for each of these components. Less attention was given to the role of HONO, which was thought to be captured and measured as nitrite (NO_2^-) when sampling was carried out with the addition of glycerol to the K_2CO_3 coating to impede oxidation.[10,11] Sodium chloride (NaCl) as a coating should be more specific to HNO_3 as the uptake is driven by an acid displacement reaction, therefore it has been proposed as a test to compare HNO_3 measurements on NaCl denuders against the K_2CO_3-glycerol denuders. Alternative coatings used or proposed in the literature included KF and therefore some tests were carried out with KF coated denuders too.

Given atmospheric composition and atmospheric chemistry is complex, it is important to understand what the DELTA sampler is measuring and investigate whether it can be made more specific. Such improvements are relevant as they may affect the UK deposition estimates of oxidised N by CBED and other models, which is a significant term in the total N deposition budget for the UK (Figure 3, from RoTaP report).
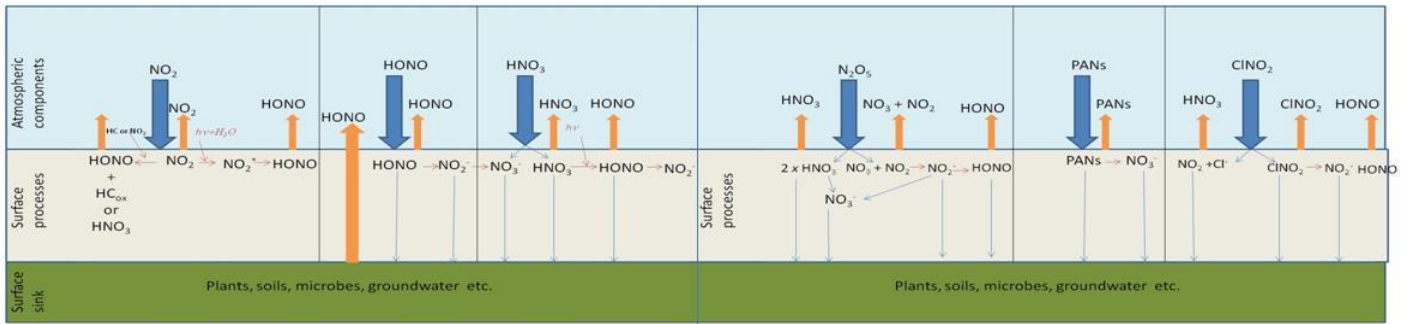
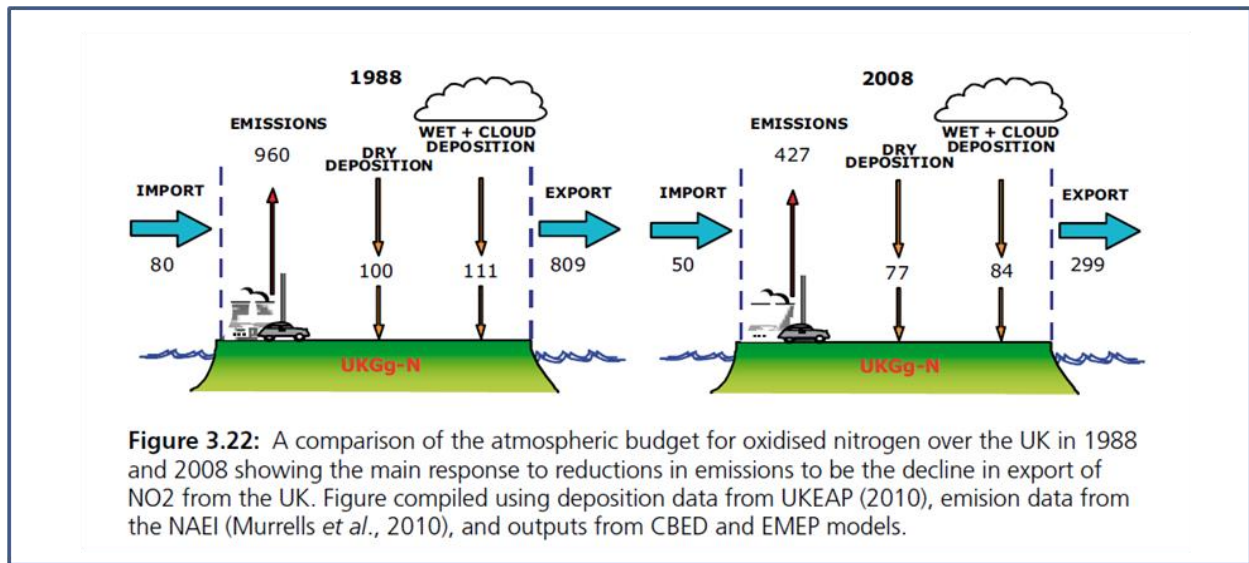Figure 2 Summary of major gas phase oxidised nitrogen species and potential ground-surface interactions

Figure 3.22: A comparison of the atmospheric budget for oxidised nitrogen over the UK in 1988 and 2008 showing the main response to reductions in emissions to be the decline in export of NO2 from the UK. Figure compiled using deposition data from UKEAP (2010), emission data from the NAEI (Murrells *et al.*, 2010), and outputs from CBED and EMEP models.

Figure 3 The oxidised nitrogen budget for the UK (From RoTaP, Fowler *et al.* 2012).

2.2 Experimental

The hypothesis to be tested was that the HNO_3 estimate as measured by nitrate capture on K_2CO_3-glycerol coated denuders in the DELTA sampling system includes a potentially significant interference by other reactive oxidised nitrogen species, i.e. HONO, PAN etc). Parallel DELTA systems were established at five of the UK AGANet DELTA Network to test the K_2CO_3-glycerol denuder against other denuder coatings in parallel with the network measurements. A denuder coating that that was un-reactive to HONO would reduce collection of NO_2^- and hence any subsequent NO_3^- contribution resulting from oxidation of the NO_2^-. The parallel measurements tested the coating the denuders with NaCl, which should be more specific to HNO_3 as the uptake is driven by an acid displacement reaction. The 5 sites selected spanned the range of concentrations observed in the UK from the "clean" rural/remote background at Auchencorth Moss to "polluted" at Cromwell Road, London. Further experiments were carried out by adding a third K_2CO_3-glycerol denuder subsequent to the two NaCl coated denuders to test the capture efficiency of the NaCl coated denuder. In addition, a KF denuder coating was also tested. The rationale for the KF coating was to allow continued measurement of HCl and Cl. The comparisons were applied for each of the components measured in AGANet to evaluate the implications of any sampler change on the performance for other gases and aerosols.

2.3 Results

This report summarises the results of the intercomparison experiment. A summary of the parallel DELTA measurements of analysed nitrate from the 5 sites is given in Table 1. Overall measured denuder nitrate is a factor 2-3 higher on the K_2CO_3-glycerol coating compared to the NaCl denuders. This confirms that the K_2CO_3-glycerol coated denuders do overestimate the HNO_3 concentrations compared with the NaCl coated denuders, and the overestimation is highest in the most "polluted" sites tested: London, Stoke Ferry and Harwell. Average chemical capture on the first NaCl denuder is 86% indicating the NaCl coated denuders adequately capture when using two in series. Some researchers subtract denuder 2 from denuder 1, assuming that interfering NOy species are captured to the extent on both NaCl denuders, to provide the "real HNO3" concentration. When a third K_2CO_3-glycerol denuder was placed after the two NaCl denuders the total nitrate was within error equal to the sum of the two nitrate denuders.

At the non-urban sites (Harwell, Stoke Ferry, Auchencorth, and Bush) the nitrate measurement previously reported as HNO_3 was a factor of 2 –3 larger than the NaCl denuder measurements with an average ratio for the four sites of 0.44±0.15. The urban site at Cromwell Road, London, was a factor of five higher on the K_2CO_3-glycerol denuder compared with the NaCl-coated denuder. The average ratio of NaCl/c K_2CO_3-glycerol nitrate for all the sites is 0.39. Both the rural and all site ratios show significant interference from other oxidised N species on the HNO_3 measurements with K_2CO_3-glycerol denuders.

SO_2 analysed as sulphate was also quantified on the NaCl denuders and on the K_2CO_3-glycerol denuders. Overall SO_2 was not quantitatively captured on the NaCl denuders compared to K_2CO_3-glycerol denuders (Table 2). When the third K_2CO_3-glycerol denuder was added the sulphate concentrations were within error quantitatively equivalent. Negligible NO_2^- was measured on both the K_2CO_3-glycerol and the NaCl denuders giving further weight to the hypothesis that HONO captured on either type of denuder is likely to be effectively converted from nitrite to NO_3^- by heterogeneous processes. It is not possible to make quantitative HCl measurement when using NaCl coated denuders, therefore when NaCl denuders are used this measurement is lost. In the configuration where a third K_2CO_3-glycerol denuder is used to analyse for HCl it is found that the HCl measured is higher than that observed with the standard K_2CO_3-glycerol denuders. This is likely to be due to evolution of HCl when HNO_3 chemically reacts with the NaCl coating to form $NaNO_3$.

Table 1: Summary of DELTA measurements of nitrate (expressed as estimated HNO_3) comparing K_2CO_3-glycerol and sodium chloride coated denuders. Note: the variability is driven by monthly variability of ambient concentrations rather than a high analytical uncertainty.

Site	Denuder HNO_3 ($\mu g\ m^{-3}$) (n = number of measurements) [mean % capture in first denuder]*		Ratio
	K_2CO_3-glycerol coating	NaCl coating	
Bush OTC (agricultural)	0.45 ± 0.14 (n=15) [90%]	0.21 ± 0.16 (n=15) [86%]	0.47
Auchencorth (remote)	0.36 ± 0.25 (n=27) [89%]	0.14 ± 0.16 (n=27) [84%]	0.40
London (urban)	3.28 ± 0.86 (n=23) [92%]	0.68 ± 0.95 (n=23) [90%]	0.21
Harwell (rural/sub-urban)	1.02 ± 0.50 (n=25) [92%]	0.53 ± 0.43 (n=25) [89%]	0.52
Stoke Ferry (rural)	0.95 ± 0.19 (n=11) [87%]	0.33 ± 0.19 (n=11) [85%]	0.35

Table 2 Comparison of SO$_2$ measured by K$_2$CO$_3$-glycerol -coated denuders (DH in Figure 1) *versus* NaCl coated denuders (DHNaCl in Figure 1). The concentration is sum of two denuders in series. The capture efficiency is for K$_2$CO$_3$-glycerol the first denuder divided by the sum of the two and for NaCl the sum of the two NaCl denuders divided by the sum of the NaCl denuders and the third K$_2$CO$_3$-glycerol denuder ("DH3" in Figure 1)

Site ID	SO$_2$ (µg m^{-3})		Ratio
	K$_2$CO$_3$-glycerol coating	NaCl coating	
Bush OTC (agricultural)	0.89 [96.7%]	0.45 [51.2%]	1.97
Auchencorth (remote)	0.70 [93.6%]	0.28 [40.5%]	2.52
London (urban)	1.33 [96.6%]	0.53 [47.9%]	2.50
Harwell (rural/sub-urban)	0.74 [97.7%]	0.23 [30.3%]	3.17
Stoke Ferry (rural)	0.83 [93.7%]	0.39 [48.9%]	2.11

2.4 Discussion

The intercomparison tests between the K$_2$CO$_3$-glycerol denuders and NaCl denuders show that the K$_2$CO$_3$-glycerol denuders do have significant interferences from other oxidised nitrogen species, with the interference dominating the measured concentration in the urban DELTA system. The UKEAP AGANet urban DELTA measurements (London and Edinburgh) are not used in the UK HNO$_3$ assessments (or the other atmospheric species) but the result has implications for the future use of DELTAs in urban environments and it would be a strong recommendation that this method is not generally useful for HNO$_3$ or NO$_y$ measurements in urban areas. The DELTA method is however not problematic for NH$_3$, SO$_2$ and HCl. Potential NO$_y$ interfering species are: NO$_2$, HONO, N$_2$O$_5$, PANs, ClNO$_2$ and other oxidised nitrogen species and as previously noted, there are many unknowns for many of these chemical species, not least the ambient concentration variation, deposition velocities and possible bi-directionalities in fluxes (recently shown to be potentially important for HONO[8,9]).

The ratio of HNO$_3$ measured on NaCl to K$_2$CO$_3$-glycerol denuders at the five sites presented in Table 1 can be qualitatively understood in the context of the theoretical capture efficiencies shown in Figure 4 and Figure 5 the theoretical chemical concentration of some of the NOy species. This theoretical assessment of the process occurring is shown in Figure 4 using indicative background concentrations of oxidised nitrogen gas phase species. The denuder efficiency is an assumed value, however there is significant evidence for a high HNO$_3$ denuder uptake efficiency, and laboratory measurements to support the low NO$_2$ capture efficiency of <1% (additionally given the high concentration of NO$_2$ relative to the other species it would dominate the concentrations measured in <u>both</u> denuders if captured efficiently). Figure 5 shows the same calculation for a set of NaCl denuders.

Overall, the more "polluted" the site, the higher the levels of interference. This may be due to higher concentrations of all NO$_y$ species at sub-urban and urban sites in the south of the UK. From Figure 2 it can be noted that if N$_2$O$_5$ is

present at significant concentrations then it will form two nitrates per molecule captured. The DELTA sampler denuder operation can be summarised as probably sampling a sum of HNO_3, HONO, N_2O_5, $ClNO_2$ and other simple oxidised nitrogen compounds, with very limited NO_2 interference. It potentially could be sampling the PANs and some organo-nitrate species however there is no experimental evidence for this currently. The NaCl denuders deployed measure significantly lower HNO_3 (as NO_3^-) concentrations and given the theoretical basis for chemical reaction of the HNO_3, the NaCl denuders are thought to provide a much more quantitative HNO_3 measurement. The HNO_3 capture on NaCl is *via* the chemical process of acid displacement with HCl being evolved in the chemical reaction.

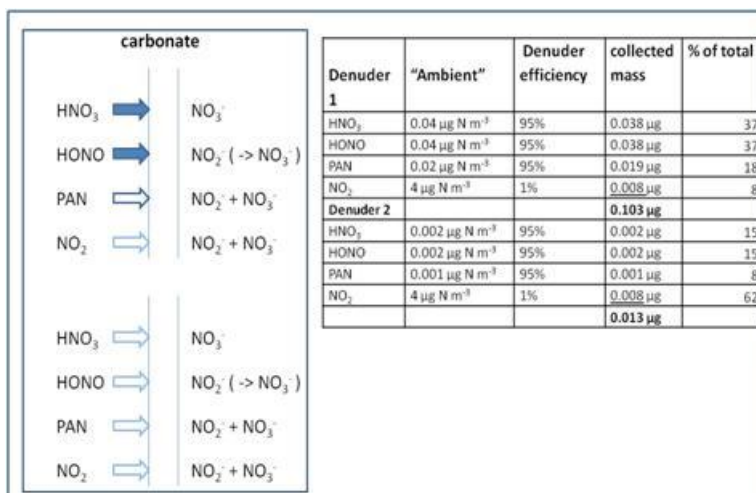**Figure 4 Theoretical processes on two K$_2$CO$_3$-glycerol denuders using indicative concentrations of gas phase NO$_\gamma$ species**
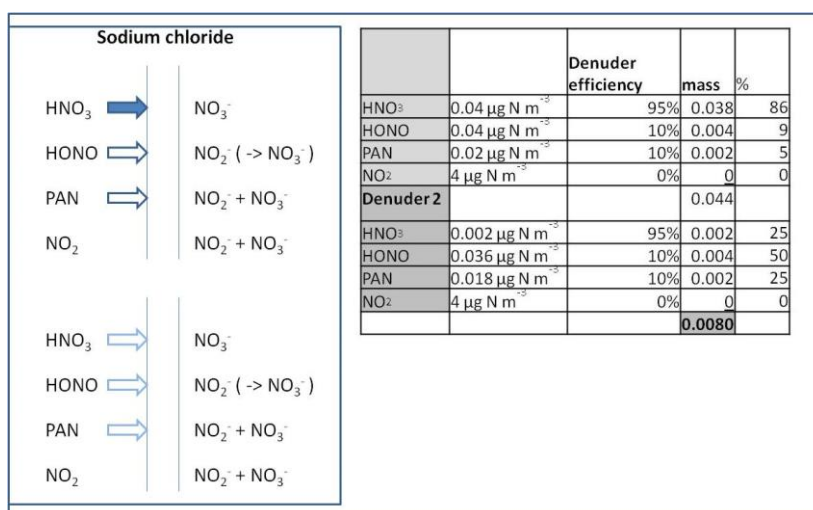

Figure 5: Theoretical process on two NaCl denuders using indicative concentrations of gas phase NO$_\gamma$ species

2.5 Future configuration of the DELTA system for gas phase measurements

The current configuration of DELTA sampling train in AGANet with two K_2CO_3-glycerol denuders has been shown to be quantitative for SO_2 and HCl but has a significant over-measurement of HNO_3 analysed as nitrate. This is due to the non-selectiveness of the K_2CO_3-glycerol denuders to HNO_3 due to either collection of other chemical species measured as nitrate (e.g. N_2O_5, PANs chlorine nitrate) and others which many be collected as nitrite but then heterogeneously oxidise to form nitrate. One clear consideration is that at the initial set-up of the measurements only the deposition of HNO_3 was considered whereas now the surface-atmosphere interactions of the other NOy species cannot completely be ignored. If all the chemical species collected as nitrate deposit to the surface as nitrate (with varying deposition velocities, these will all contribute to the N-deposition budget.

There are several potential ways forward, some of which are outlined in a-d below.

    a. Continuation with the current configuration
    b. Change to a three stage denuder train: NaCl –NaCl – K_2CO_3-glycerol
    c. Continuation with the current configuration but add a parallel (NaCl or K_2CO_3-glycerol) denuder at all or selected AGANet sites
    d. Assess alternative methods *e.g.* shift to on-line high resolution instrumentation

Option (a): if AGANet continued with the current configuration, there would be a significant overestimation of the HNO_3 concentration and hence HNO_3 dry deposition in the UK. The data from AGANet is used to calculate the HNO_3 deposition to the UK surface, by application of a HNO_3 deposition velocity, $v_{d,HNO3}$. $v_{d,HNO3}$ is a very high deposition velocity compared to many other atmospheric species and hence can be important in regions where wet deposition is low. Therefore it is not feasible to continue with the current configuration of the DELTA denuders.

Option (b): the HNO_3 measurement on the NaCl denuders would provide the best available quantitative measure of HNO_3 from the results found in the parallel experiments. Adding the final K_2CO_3-glycerol denuder allows quantitative measurement of SO_2, a key measurement of the DELTA samplers in AGANet and the "total nitrate" measurement to be maintained. Though as discussed above this measurement is not fully understood, if understanding of atmospheric composition and surface interactions improve the measurement may allow better interpretation of the total NO_y deposition budget.

One caveat is that NaCl denuders mean that HCl cannot be measured quantitatively. It is noted that HCl is currently measured hourly at the two UK Supersites. The importance of HCl deposition is an area in which there has not been a great deal of research however one recent study[12] considered HCl to be important ecologically. The final consideration for the three denuder configuration is that it has the benefit of measuring the "additional oxidised nitrogen", which in

the short term would allow an on-going assessment of the contribution of the other N species to test the validity of historical data corrections, which will be based on the five parallel sites. Also it will provide an ongoing assessment as to the magnitude of the oxidised N in the atmosphere. Further laboratory tests would allow capture efficiencies for chemical-specific contributions to be understood.

Option (c) where the network is maintained and either an additional NaCl or K_2CO_3-glycerol denuder in a DELTA would be run in parallel would allow HCl measurement to be preserved but would add significant extra logistical (and capital) costs to the network.

Option (d) would need some further assessment beyond the scope of this report. One option would be to upgrade the network to higher cost active instrumentation (e.g. aerosol chemical speciation monitors plus gas phase instrumentation (e.g. LOPAP for HONO). This also would be a large capital investment and a change in strategy for the UK and a shift in expertise required by Local site Operators.

Overall Option (b) is recommended as the most cost effective way of making the HNO₃ measurement quantitative with NaCl denuders while retaining the "total nitrate" for future assessment and making quantitative SO₂ measurements. However it is noted this change will stop HCl measurements in AGANet however hourly HCl measurements will still be made currently at the UK EMEP Supersites.

2.6 Back correction of the historic measurements

Given the magnitude of the over measurement of HNO_3, a back correction of historical data is necessary. In order to do this, the dataset from the parallel measurements which cover at least 1- 2 years, can be used to provide a correction. It is proposed that a discussion between the modellers and the experimental team led by Ron Smith and David Fowler propose a method to do this.

At the non-urban sites (Harwell, Stoke Ferry, Auchencorth, and Bush) the nitrate measurement previously reported as HNO_3 was a factor of 2 –3 larger than the NaCl denuder measurements with an average ratio for the four sites of 0.44±0.15, therefore it is recommended that a correction factor of 0.45 be applied to the historic HNO_3 measurements.

3. Potential adsorption loss to the LDPE connecting tube

The DELTA system which is shown in Figure 1 has the two denuder pairs connected by a ~ 30 cm long piece of low density polyethylene (LDPE) tubing. Due to the configuration of the sampler housing and connections for inlets and outlet the LDPE is held in a smooth curved shape. The length and material of the tubing were raised as a cause for concern as the connecting tube is a surface onto which deposition of aerosol could occur. The smaller the diameter of aerosol the more entrained in the air flow they are, so particle impacts with the LDPE will scale with particle size.

3.1 Experimental
During a period of 12 months the LDPE tubing at 8 sites across AGANet were rinsed with DI water and analysed along with the denuders as per the analytical protocol, in order to quantify the chemical composition of particulate which had been captured on the tubing. The methods and analytical techniques were identical to those used for the denuder analyses.

3.2 Results
The summary of the results obtained are summarised in Table 3. Overall the percentage of the main analytes (NO_3^-, NO_2^-, SO_4^{2-} Cl^-, Na^+, Mg^{2+}) measured on the LDPE was less than 10% of the total. The exception to this was Ca^{2+} which was significantly higher, however on a much lower absolute concentration, which is close to the LOD of the method (average of all measurements: 0.05 mg/L LOD = 0.05 mg/L Ca^{2+}), i.e. the high percentages relate more to a variation around a detection limit than a quantitative measurement. It is hypothesised that the small amounts of SO_4^{2-}, Cl^-, Na^+ and Mg^{2+} on the LDPE tubes are likely to be of sea salt origin, in the coarse fraction.

Table 3: Percentage of each analyte found in the LDPE tubes, relative to the K_2CO_3-glycerol denuders (1+2) and aerosol filter. Each data point represents the mean ± SD of 16 measurement periods from all 8 test sites between Jan 10 to Apr 11.

Loss to LDPE tube	NO_3^-	NO_2^-	SO_4^{2-}	Cl^-	Na^+	Mg^{2+}	* Ca^{2+}
% LDPE /[denuder 1+2+LDPE]	7.5 ± 2.4	8.3 ± 7.9	6.5 ± 2.8	21.0 ± 6.8			
% LDPE / [filter pack+LDPE]	3.4 ± 1.0	13.4 ± 15.9	8.7 ± 2.4	5.0 ± 1.9	6.8 ± 2.8	7.5 ± 3.6	45 ± 19
% LDPE / [denuder 1+2+aerosol filter+LDPE]	2.4 ± 0.8	5.4 ± 6.4	3.7 ± 0.9	4.2 ± 1.6			

* Note: where Ca^{2+} concentrations were negative after blank correction or were below method limit of detection (LOD), the Ca^{2+} concentrations were set to the analytical detection limit (0.05 mg/L Ca^{2+}).

3.3 Summary
- NO_3^-: loss to LDPE tube is negligible (2.4 ± 0.8 % (mean ± SD) across all sites for all available data).
- NO_2^-, SO_4^{2-} and Cl^-: losses to LDPE are small (< 6%).
- Base cations Na^+ and Mg^{2+}: losses to LDPE are slightly higher (<7%).
- Base cations Ca^{2+}: there is a large degree of uncertainty in the calcium assessment, due to 1) variability of Ca^{2+} in the blank LDPE tube extracts and 2) very low Ca^{2+} on LDPE tubes from sites, that were similar to blank values and close to the detection limit (LOD = 0.05 mg/L Ca^{2+}).

3.4 Recommendations
In the new design of DELTA a linear vertical sampling train has been adopted to eliminate any sampling uncertainties arising from the use of the LDPE connecting tube and for ease of transport of the sampling train for LSOs and laboratory staff. There is no historical correction required as losses to the LDPE tube were found to be small.

4. Performance of the filter pack: Potential filter breakthrough of aerosol nitrate

4.1 Background

The final stage of the DELTA system after the denuders is a filter pack on which aerosol components are collected. The filter pack consists of two coated 25 mm cellulose filter papers in a 2-stage filter pack at the end of the AGANet sampling train. The first filter is impregnated with K_2CO_3 and glycerol to sample aerosol NO_3^-, (NO_2^-), SO_4^{2-}, Cl^- plus the base cations: Na^+, Ca^{2+} and Mg^{2+}, followed by a citric acid coated paper to collect gaseous NH_3 liberated from NH_4^+ particles trapped on the alkaline filter, and measured on the acid impregnated paper as NH_4^+. The query arose that the filter pack may have issues with breakthrough due to re-volatilisation of HNO_3 and the configuration used in the UK network was different to that employed in other networks where a Teflon filter followed by a nylon filter and an acid-impregnated filter(for NH_3 capture) is used.

The low-cost DELTA sampler does not have a characterized size-cut inlet. The size-range that makes it to the filter membrane depends on the inlet characteristics and the potential for deposition in the denuders and connecting tubing. The size-fraction collected by the DELTA was evaluated in Defra project AC0103 with an Aerodynamic Particle Sizer (APS3021, TSI Inc.), which counts and sizes particles between 0.5 and 20 µm. This instrument alternately sampled the air that arrived at the filter pack of the standard sampling train and ambient air. The transmission efficiency of the DELTA sampling train was derived from the difference in concentration. Four DELTA sampling trains were used in parallel, so that the flow rate through each train matched that used in the field (0.35 to 0.4 lpm). The 50% size-cut was found to be around 4.5 µm and insensitive to wind speed. Thus, the DELTA train makes a measurement close to $PM_{4.5}$, which coincidentally is close to the inhalable fraction.

The combined sampling efficiency is shown in Figure 6 as a function of size, where it is compared with a typical chemical composition and size-distribution of an ambient aerosol.
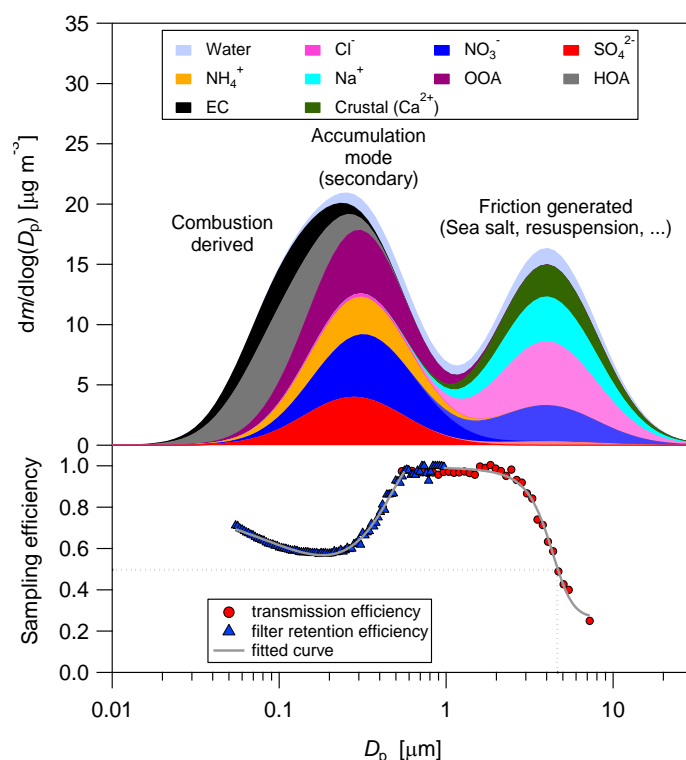

Figure 6 Retention and transmission efficiency of the DELTA sampling train as used in the AGANET network (from AC0103 Final report).

4.3 Experimental

Two approaches were adopted to investigate the processes occurring in the DELTA systems: Analyse the acid coated filters (FPA) for NO_3^-, SO_4^{2-} and Cl^- at 5 DELTA sites, to check for breakthrough and analyse the K_2CO_3-glycerol coated filters for ammonium to check for retention. Addition of a Teflon filter (PTFE) between the K_2CO_3-glycerol (FPH) and acid (FPA) filters to capture any particles, which tests whether this is a particle or gaseous breakthrough effect (Figure 7).
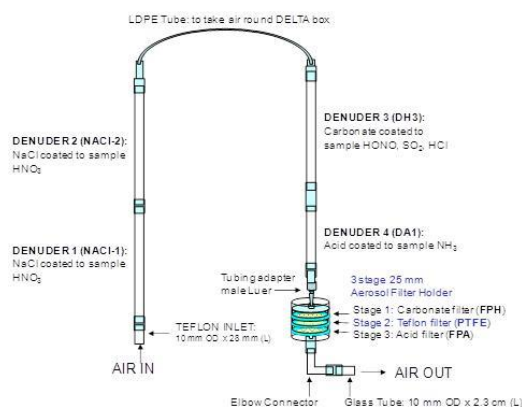

Figure 7: DELTA sampler with test 3 stage aerosol filter pack

4.4 Results

Citric acid coated aerosol filter (FPA) extracts proved to be very problematic due to the elution of the citrate peak very close to the NO_3^- peak. Due to this there are no results available for NO_3^- on the acid coated filters. The basic K_2CO_3-glycerol coated filter paper should release NH_4^+ aerosol as NH_3 gas, which is then captured on the acid coated filter. Additional tests were carried out in this study to check for potential adsorption loss of ammonium to the stage 1 K_2CO_3-glycerol coated aerosol filter (FPH), by analysing the K_2CO_3-glycerol coated filters also for ammonium at the 5 test sites. Analysis of the K_2CO_3-glycerol coated filters in the present study showed that negligible amounts of NH_4^+ are retained

Chemical analysis of the PTFE filter placed between the K_2CO_3-glycerol and acid coated filter papers are summarised in Table 4. Chloride breakthrough from FPH was found to be smallest (overall mean of 1.3 % loss from K_2CO_3-glycerol filter). On average for NO_3^-, SO_4^{2-} and NH_4^+ 11%, 37 % and 21% respectively of the total ion concentration were on the PTFE membrane. The molar ion balance of $[NO_3^- + 2*SO_4^{2-}]/NH_4^+$ on the K_2CO_3-glycerol filter, as well as the PTFE membrane, is equal to 1, which suggests a close coupling between acidic (NO_3^-, SO_4^{2-}) and basic (NH_4^+) aerosol components. The results suggest a small but systematic underestimation of particulate sulphate, nitrate and ammonium from the DELTA network. A measureable NO_2^- concentration was found on the PTFE membrane, which may be from neutral nitrites, and/or adsorption of NO_2, however absolute concentrations were low. With the base cations and in particular, Ca^{2+}, there is a large degree of uncertainty in the calcium assessment, due to 1) variability of Ca^{2+} in the blank K_2CO_3-glycerol and PTFE extracts, and 2) very low Ca^{2+} on site samples, that were similar to blank values and close to the detection limit (LOD = 0.05 mg/L Ca^{2+}).

Table 4: Percentage of each analyte on the PTFE membrane relative to the total analyte (mean± SD, n = # of samples)

Site ID	NO_3^-	NO_2^-	SO_4^{2-}	Cl^-	Na^+	Mg^{2+}	Ca^{2+}	NH_4^+
				PTFE / [PTFE + filters] %				
1	10.3 ± 8.5 (n=13)	85.2 ± 59.5 (n=13)	41.0 ± 16.8 (n=13)	3.8 ± 4.9 (n=13)	12.8 ± 7.0 (n=13)	17.2 ±14.0 (n=13)	103 ± 239 (n=13)	25.9 ± 4.8 (n=4)
18	13.1 ± 9.9 (n=10)	62.2 ± 45.2 (n=10)	40.1 ± 16.2 (n=10)	0.7 ± 1.1 (n=10)	12.4 ± 7.0 (n=10)	12.6 ± 5.0 (n=10)	13.7 ± 111 (n=10)	19.6 ± 10.2 (n=3)
36	6.7 ± 8.3 (n=11)	-0.43 ± 7.8 (n=11)	24.7 ± 16.6 (n=10)	0.9 ± 2.0 (n=11)	6.4 ± 5.8 (n=11)	8.5 ± 7.4 (n=11)	-1.4 ± 50.9 (n=11)	13.0 ± 5.6 (n=3)
98	10.4 ± 11.2 (n=14)	36.4 ± 55.7 (n=14)	35.6 ± 16.1 (n=14)	0.3 ± 1.6 (n=14)	7.8 ± 6.3 (n=14)	9.1 ± 5.9 (n=14)	102 ± 355 (n=14)	7.2 ± 5.6 (n=4)
33	12.3 ± 10.4 (n=10)	12.5 ± 57.8 (n=10)	43.1 ± 19.2 (n=10)	0.8 ± 1.2 (n=10)	14.9 ± 10.5 (n=10)	14.8 ± 9.9 (n=10)	92 ± 157 (n=10)	41.5 ± 8.8 (n=4)
Mean across sites	10.6 ± 2.9	39 ± 41	37 ± 7.3	1.3 ± 1.4	10.9 ± 3.6	12.4 ± 3.7	62 ± 51	21 ± 13

Grey shading indicates concentrations very low hence low confidence in quantitative or meaningful comparisons

4.5 Discussion and summary: Potential filter breakthrough

The results presented show the nitrate and sulphate aerosol are under-measured 11% and 37% respectively. Ammonium is slightly more complicated as although 21% is measured on the PTFE filter, it is designed not to be captured on the K_2CO_3-glycerol filter, but on the final acid-coated filter. Applying the sampling efficiencies of the DELTA to the 'typical' size distributions (Figure 8) implies a sampling efficiency for the accumulation mode of about 71% for SO_4^{2-} and fine NO_3^- and of about 89% for NH_4^+, which is captured with two filters. The report in Defra project AC0103 discussed that it is possible that NO_3^- reacts more efficiently with the K_2CO_3-glycerol on the first filter and that its collection efficiency is not a purely physical process. The $PM_{4.5}$ fraction contains about 63% of the coarse mode (sea salt & dust) and overall sampling efficiency for nitrate depends on the partitioning between the two modes. The breakthrough appears to differ across sites, with larger percentage capture by PTFE at lower concentrations. To retrospectively correct the data, this will need to be checked explicitly. The present study therefore shows that a significant amount of acidic sulphate, plus a small percentage of acidic nitrate in the fine mode is not retained by the K_2CO_3-glycerol coated cellulose filter paper, but is captured by a 2μm porosity PTFE membrane.

4.6 Recommendations: Filter system in new DELTA

In the new design of DELTA a three stage filter pack of a PTFE filter followed by a base and then an acidic impregnated filter pack is recommended. From the test results this should lead to a quantitative measurement of all the major inorganic species of interest, so long as all three filters are analyzed.

4.7 Back correction of historical measurements

In order to back-correct the data, it is primarily important to correct appropriately. It is recommended that an assessment of the best method to do this and any specific tests for concentration effects on the relative capture be carried out before the historic data is corrected, which was beyond the scope of this study. However the dataset from the parallel measurements can be used to provide an interim correction. A discussion between the deposition modellers and the experimental team should develop a method to do this. Subsequently, once the methodology has been switched over, a longer term correction factor can be assessed in comparison with the extrapolated correction from the 5-sites.

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