Responses to Reviews

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Authors response to interactive comment on "Water soluble aerosols and gases at a UK background site – Part 1: Controls of $PM_{2.5}$ and PM_{10} aerosol composition"

by M. M. Twigg et al.

The authors would like to thank the reviewers for the time spent reviewing the manuscript. We have revised the manuscript to implement the recommendations from the reviewers. Please find below in black the reviewer comments and in BLUE the authors response.

Anonymous Referee #1

Though the main ions have been measured from particles for decades (e.g. with the EMEP filter method) quite limited amount of shorter time-resolution data is available and therefore the 6.5 years MARGA data series from the UK EMEP Super Site Auchencorth Moss, Scotland is most valuable and worth publishing. This paper provides greater detail in the long term temporal variation of inorganic compounds in UK background air. Secondary inorganic aerosol (especially NH4+ and NO3-) were dominating in PM2.5 and sea salt was dominating in coarse fraction, especially in winter (with higher wind speed). Sea salt processing was discussed - considerable amounts of NO3- were occasionally found in coarse fraction with depletion of Cl-. Average seasonal ion balance was always basic (excess NH4+). The data was also used to study the influence of air masses from marine and anthropogenic sources. Furthermore, the data will be valuable to study long term trends in particulate matter composition in response to climate and policy drivers.

There was a very nice and detailed description of MARGA instrumentation in this paper. However, the data quality and processing should be described as well. There are some open questions like: Is there any estimation of detection limits (or quantitation limits) or/and measurement uncertainties available? Were the zero (or under the detection limit) values replaced somehow and were there any under the detection limit concentrations? Were the instrument blanks taken into account or were they negligible when compared to the measured values? Were the inlets cleaned / replaced regularly as well as the glassware?

RESPONSE: We concur with the reviewer's view that this is a valuable dataset and analysis of it. The authors acknowledge that the QA and QC processes were not well described as they could have been in this manuscript. The manuscript has been updated to address this by adding an additional section on QA/QC. Below is the updated text which can be found in the updated manuscript at the end of this document. A more detailed manuscript on the QA/QC protocols for the MARGA instrument will published in the near future, which includes points raised by the reviewer, therefore the points have been addressed below but not all have been included in the manuscript.

"***Quality analysis and quality Assurance***

As discussed previously the MARGA used in this work was one of the first to be field deployed. Processes were developed over the first several years which could be used to identify potential sources of error or contamination in the MARGA data. Firstly, periodic field blanks were carried out until 2011 by installing Whatman HEPA filters placed in front of the denuders and left on for ~24 hours. The filters removed aerosols but not the gas phase components from the air stream. The resultant change in PM concentrations allowed a blank value for the PM analytes to be assessed. Following the upgrade of the instrument in November 2011 (Table 2), automated monthly blanks were implemented in 2012, where the air pump and SJAC water supply and heaters were turned off, allowing for blanks for both aerosol and gas phase to be carried out. The blanks were not used to correct the data as they were usually below the detection limit (DL) of the instrument. Instead blanks were used to provide evidence of contamination in the system and to identify periods to be removed in the data ratification process. Prior to 2012 verification and instrument maintenance protocols has been experimental and the authors are in the process of finalising the protocols including calibration, which will be published separately. There was a step change in 2012, when the initial developmental protocols for maintenance were replaced by final protocols including quarterly replacement of inlets, cleaning of PM_{10} *head and* $PM_{2.5}$ *cyclone, monthly air flow calibrations and independent analysis of internal standards by a UKAS accredited laboratory.*

In the data ratification process values reported as 0 μg m^{-3} *were replaced with half the detection limit (DL). The method to determine the DL has changed over the 6 year period. From 2002 to 2011, the DL was taken as the average of the reported values below the manufacturers published DL. From 2012, the DL was calculated by the analysis of the logarithmic distribution of the measurements previously described by Kentisbeer et al. (2014), presented in table 3. The methodology for analysing the DL and calibrating this type of on-line IC instrument is an area of research in of itself and we plan to publish separately on this aspect of the MARGA operation.*

"

Is there any estimation of detection limits (or quantitation limits) or/and measurement uncertainties available?

Response: Please refer to QA/QC manuscript text on treatment of detection limits for the presented period. The calculated DLs have been reported to UKAir (http://uk-air.defra.gov.uk/data/) on a monthly basis from 2012 and only 1.4% of potential data were filled with ½ DL. From 2015, the protocol for calculating the DL will using 3σ of the measured concentration of low concentration external standard. It is expected that with the finalised protocol the reported DLs will be smaller and closer to the manufacturers listed DLs (see table below). No uncertainty analysis has been carried out yet but it is planned to be addressed in a future manuscript on the QA/QC of the MARGA.

List of detection limits using pre-concentration columns on the MARGA instrument given by the manufacturer.

Component	Manufacturers reported DL
	µg m^{-3}
Cl^-	0.001
NO_3^-	0.005
SO_4^{2-}	0.004
NH_4^+	0.005
Na^+	0.005
K^+	0.009
Mg^{2+}	0.006
Ca^{2+}	0.009

There are always risks for artifacts when using inlets: particles maybe lost in the inlet and there may be some gas-particle reactions inside the tubing, especially for NH4NO3 / NH3+ / NO3- .

RESPONSE: The authors agree that the use of an inlet can result in losses and potential interactions in the inlets. Within the MARGA community there is still no agreement on the best method to limit the interactions, including inlet material and if new or aged inlets are optimum. For the instrument presented periodic changing of the inlets and quarterly cleaning of both the PM_{10} head and the cyclone are carried out. Some experiments have been undertaken and more are planned in the future to compare the MARGA against species specific instruments to enable a clear understanding of the instrument performance

p. 3717. “It is not the first time that inorganic water soluble aerosols have been found to be major contributors to the total mass in Europe (Putaud et al., 2010). Aerosol components not resolved by the MARGA include inorganic aerosols, BC, water and crustal elements such as silicate. Organic aerosol often accounts for a larger fraction of the PM10 mass at central European background sites than the missing mass

at Auchencorth allows for . . .” I assume, you mean organic aerosol not resolved by MARGA instead of this: Aerosol components not resolved by the MARGA include inorganic aerosols. . .

RESPONSE: The referee is correct. The authors apologise for this mistake and have corrected the manuscript accordingly.

Table 2: I do not understand, why new type SJAC improved accuracy in maintaining the cut-off (17 Feb 2009).

RESPONSE: The authors have updated the text (see below) to give further description of the improved accuracy as a result of the new type of SJAC.

"The increase in diameter of the SJACs described in table 2, reduced the restriction in maintaining a flow rate, which was mass flow controlled at 1 m^3 hr^{-1} at standard temperature and pressure (STP) until November 2011, whereas thereafter it was controlled to keep the volumetric flow rate at ambient temperature and pressure through the size cuts constant."

Were blanks and external standard set-up remotely in practice and how often?

As the MARGA instrument presented was one of the first in production it is only recently that routine maintenance procedures have been put in place including monthly blanks, quarterly external standard checks and independent analysis by a UKAS accredited laboratory of the internal standard used in the instrument.

Did the solutions stay clean enough for that purpose?

Response: Blanks have demonstrated that the solution used is relatively clean. If contamination is suspected in the system, then additional blanks are run to confirm.

What was the external standard used for?

Response: The external standards are used to confirm the performance of the IC instrument from 2015, prior to this including the period presented standards were use only to identify peak positions.

Please, check that all abbreviations used are defined in the text, e.g. SPT (p. 3710) RH (%) and St (W m-2) in (Table 1), PILS..

Response: Corrections to the abbreviations in the manuscript have been carried out including a key in Table 1.

Figure 2: Check lines and font sizes.

Response: Both the line width and font size have been increased in figure 2.

Figure 3: Text far too small (especially seasons).

Response: The format including the font size in figure 3 has been modified.

Figure 5. Non-marine magnesium -1% and 0% could be replaced with < x %.

Response: The negative value and 0% has been replaced with a not detected (nd).

References: Check the formats. Sometimes there are commas in the author list (between authors) and sometimes not.

Response: The authors thank the referee for noticing this but it seems to be not related to the manuscript. We will check the proofs carefully to make sure the format is consistent.

p. 3722: Drewer: : : Penttila should be Penttilä.

Response: The spelling error has been corrected.

p. 3710: The performance of MARGA (e.g. tests of preconcentration colums) has been discussed also in: Makkonen et al. 2014: Semi-continuous gas and inorganic aerosol measurements at a boreal forest site: seasonal and diurnal cycles of NH3, HONO and HNO3. Boreal Env. Res. 19 (suppl. B): 311–328.

Response: The authors acknowledge the error in the manuscript and have corrected the text accordingly.

"The deployment of pre-concentration columns sets our MARGA instrument aside from the others, with the exception of Makkonen et al. (2014), allowing quantitative detection of the low concentrations encountered at this clean Scottish site."

Anonymous Referee #2

This article presents long-term measurements of aerosol composition at a background site in Scotland. Such long-term data sets of speciated chemistry are extremely valuable for understanding aerosol processes, pollution source apportionment, and model development and evaluation. The authors do a very good job at analyzing and presenting the data and the manuscript is well written.

The only shortcoming of the articleis the lack of detail regarding instrument performance and data quality control. In that regard, I have outlined several comments below which I believe the authors should be able to address.

Response: We acknowledge that the QA/QC of the instrumentation was not well described. As a result an additional section has been added to the manuscript, see response to Reviewer #1, which should address most of the questions highlighted by referee #2. We have however not discussed the reprocessing of chromatograms as it is beyond the scope of the manuscript. We are planning a publication which focusses on the challenges of QA/QC with an online IC instrument below is a summary in response to individual points on QA/QC which will be addressed in a future manuscript.

The authors note that the use of preconcentration columns sets this instrument apart from other descriptions of the MARGA instrument. For this reason, some detail regarding the basic characteristics of the analytical system is warranted. What are the detection limits for each analyte and how were they determined?

Response: Please refer to QA/QC manuscript text below. The calculated DLs have been reported to UKAir on a monthly basis from 2012.

"In the data ratification process 0 ug m^{-3} values were replaced with ½ detection limit (DL). The method to determine the DL has changed over the 6 year period. From 2002 to 2011, the DL was taken as the average of the reported values below the manufacturers reported DL. From 2012, the DL was calculated by the study of the logarithmic distribution of the measurements previously described by Kentisbeer et al. (2014), presented in table 3. The methodology for analysing the LOD and calibrating this type of on-line IC instrument is an area of research in of itself and we plan to publish separately on this aspect of the MARGA operation specifically."

How often were analytical blanks determined and did they vary over time?

Response: There was not a huge variability in the blanks, unless contamination was present in the system. Please refer to the updated manuscript text on QA/QC.

How often were external liquid standards analyzed?

Response: Only on small number of occasions have external solutions been analysed but it was not until 2012, following the instrument upgrade, could external standards be successfully run. Due to other operational issues this is only been implemented as a protocol on a quarterly basis in 2015, using certified standards of the major anions and cations. External standards however have occasionally been used to confirm the peaks on chromatograms.

Were multi-point liquid standards periodically evaluated?

Response: No multi-point standards have been run on the instrument. Li and Br are used for calibration of all anions and cations in the MARGA. The MARGA knows the concentration of the internal standard and measures the conductivity response as all components measured by the MARGA have a specific equivalent conductance value. The MARGA calculates with this values the sensitivity of all components. Using this tool a monthly time consuming multi-point external calibration is avoided.

How were the LiBr standards prepared and were they independently checked on another analytical system?

Response: The LiBr stock is prepared in house. The stock LiBr is used to produce a working solution for the instrument. Since 2012, where protocols were implemented an accredited laboratory has independently analysed both the stock and the working solutions on a quarterly basis.

How were potential biases between the two sample boxes evaluated? How often was the sample flow rate measured independently of the mass flow controlsystem (i.e., at the inlet with a calibrated flow meter)?

Response: Following the upgrade of the instrument in November 2011, the instrument boxes sample flow rate was measured by a calibrated mass flow controller and monthly 3 point calibrations were carried out on both MFCs. A summary description has been included in the text of the manuscript.

To what extent were the independently measured flows consistent with the flow reported by the mass flow controller?

Response: Following the upgrade, due to greater control of the MFCs the air flows were found to compare well with independent flow meters. Only on occasions did they differ after denuders or SJACs had been either moved or cleaned. As a result it is now procedure to recalibrate flows following any change in the sample boxes.

How often were the mass flow controllers calibrated?

Response: Mass flow controllers were monthly calibrated, using a 3 point calibration. If there was evidence of fluctuations in the flow, MFCs are sent to manufacturer for servicing. In addition, MFC were calibrated following any changes to position of either the denuder or SJAC in the sample box.

How often were the inlets cleaned?

Response: Following the implementation of the protocols in 2012, inlets are replaced quarterly, the PM_{10} head and $PM_{2.5}$ cyclone are cleaned too on a quarterly basis. This frequency increases if there is evidence of pollution events and visual dirt in the denuder or SJAC.

What was the process for reducing the raw hourly data? That is, how were blanks, external standards, and flow rate audits incorporated into the data reduction process?

Response: Blanks at present are only used to remove periods of contamination in the system. Due the frequency of flow rate audits, air concentration data is only corrected where there is evidence of drift in the MFC.

How were concentrations below detection limit treated?

Response: Concentrations below DL were flagged in both UK-Air and EMEP. Any reported 0 µg m^{-3} were replaced with ½ DL and flagged accordingly in the relevant databases. The treatment of 0µg m^{-3} has now been included into the text of the manuscript.

"In the data ratification process 0 ug m^{-3} values were replaced with ½ detection limit (DL). The method to determine the DL has changed over the 6 year period. From 2002 to 2011, the DL was taken as the average of the reported values below the manufacturers reported DL. From 2012, the DL was calculated by the study of the logarithmic distribution of the measurements previously described by Kentisbeer et al. (2014), presented in table 3. The methodology for analysing the LOD and calibrating this type of on-line IC instrument is an area of research in of itself and we plan to publish separately on this aspect of the MARGA operation specifically. "

Was there a need to reprocess any of the raw chromatograms?

Response: Raw chromatograms on occasions needed reprocessing either due to shifts in retention times or peaks which had not be integrated. Data which needed reprocessed were identified by either instrumentation flags, evaluation of time series and ion balance.

Additional comments:

Page 3705, line 26: Change "the exceeding the" to "exceeding the"

Response: Corrected

Page 3714, line 1: Why was 2012 chosen for the ion balance analysis?

Response: The ion balance was done for 2012 as it was the annual dataset with the highest data capture and the year we had greatest confidence in the results due to implementation of additional QA/QC protocols.

Page 3715, line 21: Change "that however," to "however,"

Response: Corrected.

Page 3717, line 9: “Aerosol components not resolved by the MARGA include inorganic aerosols,” Was this the intended statement?

Response: This was an error. Text updated

“Aerosol components not resolved by the MARGA include organic aerosols,”

Page 3717, lines 17-18: “Mass closure improved in 2012, probably in response to the improved flow control implemented in November 2011 on the MARGA (see above).” Can the authors give more detail on the flow control changes and how this improved mass closure?

Response: As stated earlier in the manuscript, prior to the instrument upgrade the flow rate was mass flow controlled to1m^3 h^{-1} at STP, whereas during 2012 was controlled to keep the volumetric flow rate at ambient temperature. Due to this there was greater accuracy in measured concentration of species. The manuscript text has been modified to make this more transparent.

“The increase in diameter of the SJACs described in table 2, reduced the restriction in maintaining a flow rate, which was mass flow controlled at 1 m^3 hr^{-1} at standard temperature and pressure (STP) until November 2011, whereas thereafter it was controlled to keep the volumetric flow rate at ambient temperature and pressure through the size cuts constant

Water soluble aerosols and gases at a UK background site. Part 1: Controls of PM$_{2.5}$ and PM$_{10}$ aerosol composition

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Abstract

There is limited availability of long-term, high temporal resolution, chemically speciated aerosol measurements, which can lead to further insight into the health and environmental impacts of particulate matter. The Monitor for AeRosols and Gases (MARGA, Applikon B.V, NL) allows characterisation of the inorganic components of PM$_{10}$ and PM$_{2.5}$ ((NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}) and inorganic reactive gases (NH_3, SO_2, HCl, HONO and HNO_3) at hourly resolution. The following study presents 6.5 years (June 2006 to December 2012) of quasi-continuous observations of PM$_{2.5}$ and PM$_{10}$ using the MARGA at the UK EMEP 'Supersite', Auchencorth Moss, SE Scotland. Auchencorth Moss was found to be representative of a remote European site with average total water soluble inorganic mass of PM$_{2.5}$ of 3.82 μg m^{-3}. Anthropogenically derived secondary inorganic aerosols (sum of NH_4^+, NO_3^- and nss-SO_4^{2-}), were the dominating species (63%) of PM$_{2.5}$. In terms of equivalent concentrations, NH_4^+ provided the single largest contribution to PM$_{2.5}$ fraction in all seasons. Sea salt was the main component (73%) of the PM$_{coarse}$ fraction (PM$_{10}$-PM$_{2.5}$), though NO_3^- was also found to make a relatively large contribution to the measured mass (17%) providing evidence of considerable processing of sea salt in the coarse mode. There was on occasions evidence of aerosol from combustion events being transported to the site in 2012 as high K^+ concentrations (deviating from the known ratio in sea salt) coincided with increases in black carbon at the site. Pollution events in PM$_{10}$ (defined as concentrations >12 μg m^{-3}) were on average dominated by NH_4^+ and

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NO_3^-, where as smaller loadings at the site tended to be dominated by sea salt. As with other Western European sites, the charge balance of the inorganic components resolved were biased towards cations, suggesting the aerosol was basic or more likely, that organic acids contributed to the charge balance. This study demonstrates the UK background atmospheric composition is primarily driven by meteorology with sea salt dominating air masses from the Atlantic Ocean and the Arctic, whereas secondary inorganic aerosols tended to dominate air masses from continental Europe.

1 Introduction

Gravimetric methods have long been used to monitor the long-term trends of the bulk aerosol mass contained in particulate matter (PM) with an aerodynamic diameter of less than 2.5µm or 10 µm (i.e. $PM_{2.5}$ and PM_{10}); however, these generally provide no information on the chemical speciation of the aerosol. Off-line chemical analysis after capture of aerosol on filters by high or low volume filter samplers (e.g. Partisol Sampler; Thermo Fisher Scientific, Inc.) is quite widely used but limited to daily or lower frequency measurements and therefore poorly captures diurnal patterns caused, e.g. by changes in emission and gas-aerosol partitioning. It is important to understand the composition and the role of aerosols as they can have a direct and indirect effect on climate. The current level of scientific understanding for aerosol properties in terms of their role in the climate system is low and recently it has been suggested that the major component of the uncertainty globally is with the biogenic fraction (Carslaw et al., 2013). As well as having an impact on climate, aerosols affect both environment and human health. Recent epidemiological research has suggested that health effects of aerosol may be less closely linked to the total mass of $PM_{2.5}$ or PM_{10} than to the physicochemical characteristic of the aerosol, however there is still much to be understood (Fuzzi and Gilardoni, 2013). Establishment of epidemiological links to individual aerosol chemical compounds is hampered by a lack of available measurements.

In addition, secondary aerosols and their precursor gases are required to be monitored to understand atmospheric processes and to validate chemical transport models, which are used to inform policy, such as the UNECE Convention for Long-range Transboundary Air Pollution (CLRTAP), and the revised European Air Quality Framework Directive (Directive 2008/50/EC) where the measurement of aerosol chemical composition is statutory. In addition, prior to 2008, EU member countries were fined for exceeding the total $PM_{2.5}$ and PM_{10} limits

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set in the directive, regardless whether the exceedance was due to anthropogenic or natural sources. In the current revised European Air Quality Framework Directive (Directive 2008/50/EC), countries are now allowed to subtract significant 'natural' contributions of aerosol from the total mass, if their contribution can clearly be quantified. This is important for large 'natural' pollution events, such as the long-range transport of Saharan dust which have been observed across Southern Europe and on occasions Northern Europe (Ansmann et al., 2003;Karanasiou et al., 2012). While many member countries have chosen to make daily filter measurements at a very few sites, the UK has opted for a strategy to combine a large number of sites that make monthly measurements (Tang et al., 2009) with a couple of 'supersites' that resolve hourly concentrations, as an optimum strategy for capturing the spatial and temporal variability.

Instrumentation has in the past decade become available for on-line monitoring of aerosol chemical composition, at varying levels of complexity. In particular, the wet chemistry MARGA instrument (Measurement of Aerosols and Reactive Gases Analyser, Metrohm Applikon B.V., NL) provides hourly measurements of water-soluble nitrate, chloride, sulphate, sodium, ammonium, potassium, magnesium and calcium (hereafter NO_3^-, Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} respectively) and in addition the gas phase basic and acid gases: ammonia, nitric acid, nitrous acid, hydrochloric acid and sulphur dioxide (hereafter NH_3, HNO_3, HONO, HCl, SO_2 respectively) (Makkonen et al., 2012;Rumsey et al., 2014;ten Brink et al., 2009), based on aerosol collection via a steam-jet aerosol collector (SJAC; (Khlystov et al., 1995)). Other similar IC based systems are available, including the Ambient Ion Monitor – Ion Chromatograph system (AIM- IC, URG Corp and Dionex Inc) (Markovic et al., 2012) as well as the Particle into Liquid Sampler with Ion Chromatography (PILS-IC, Metrohm AG, Herisau, Switzerland), and a range of custom-built wet-chemistry instruments based on the Particle Into Liquid Sampler (Weber et al., 2001).

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In parallel, there has been progress in developing monitoring instruments based on aerosol mass spectrometry. While there are now some studies using the standard Aerosol Mass Spectrometers (AMS; Aerodyne Research Inc, USA) for long-term measurements, a simplified version, the Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Inc), is being installed at supersites globally (Ng et al., 2011). Both AMS and ACSM currently measure an aerosol fraction that is close to PM_1 although work is in progress to extend this to $PM_{2.5}$. While SJAC and PILS based instruments measure water soluble aerosol components, similar to the filter-pack reference method, the mass spectrometer detects the aerosol components that volatilise efficiently at ≈ 600°C, which has the advantage of also characterising the organic fraction of the aerosol, whereas it does not efficiently quantify the refractory chemical components such as sea salt and crustal aerosol.

A dual MARGA system measuring both PM_{10} and $PM_{2.5}$ has been in operation at Auchencorth Moss, South East Scotland since June 2006 as part of measurements being made by the UK Department for Environment, Food and Rural Affairs (Defra) air quality monitoring network (http://uk-air.defra.gov.uk/). To our knowledge the Auchencorth Moss MARGA is the longest known quasi-continuous operation of a dual MARGA system to date. Auchencorth Moss has been developed as a Level II/III ‘supersite’ within the European Monitoring and Evaluation Program (EMEP) (Aas et al., 2012). EMEP monitoring sites feed into the EMEP database which serves to underpin the organisation’s modelling and policy role to provide governments information on the deposition and concentration of air pollutants, and long-range transport of air pollutants (Tørseth et al., 2012;UNECE, 2004).

The following study focuses on the first 6.5 years of data (1st June 2006 to 1st January 2013) from Auchencorth Moss, in conjunction with co-located measurements and air mass back trajectories. Daily, seasonal and annual variation of inorganic aerosol species and the influences of long-range transport for this remote rural site are discussed. The trace gases measured concurrently with the aerosol composition and gas/aerosol partitioning are described in a companion paper (Twigg et al., in preparation).

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2 Methodology

2.1 Field site description

Auchencorth Moss, South East Scotland (55°47’36” N, 3°14’41” W), is an ombotrophic mire with an extensive fetch at an elevation of 270 m, lying 18 km SSW of Edinburgh, and can be categorised as a transitional lowland raised bog. The moss is extensively grazed by sheep all year round with < 1 sheep ha^{-1}. Under the European Environment Agency classification scheme, the site is classed as a rural background site (Larssen et al., 1999). This has recently been confirmed by Malley et al. (2014) who demonstrated that the site was remote in the context of O_3 measurements at EMEP stations.

The meteorology is typical of a temperate system in the north of the UK. A summary of the meteorological conditions from June 2006 to the end of December 2012 can be found in Table 1. During 2010 atypical low rainfall was observed, however an additional 588 mm of precipitation fell as snow. Annual windroses for 2006 -2012 (Figure 1) show that the field site is dominated by a SW wind with a secondary NE flow occurring also.

Auchencorth Moss has been a long-term monitoring site for a number of trace gases including NH_3, SO_2 and CO_2 (Famulari et al., 2010;Drewer et al., 2010;Flechard and Fowler, 1998). The site belongs to a number of UK national networks including: UK Defra Automatic urban and rural network (AURN), UK Acid gas and aerosol network (AGANet), UK National Ammonia Monitoring Network (NAMN), UK Precip-Net (two-weekly bulk composition), UK PAH Network, UK Automatic Hydrocarbon Monitoring Network, UK Black Carbon Network and UK Toxic organic micropollutants (TOMPS) network. Details of the networks can be found on the Defra website (http://uk-air.defra.gov.uk/networks/site-info?site_id=ACTH). The site is also a European 'Supersite' within the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) (Tørseth et al., 2012), as well as one of 9 sites within the EU FP7 ÉCLAIRE project (http://www.eclaire-fp7.eu/) and a TransNational Access (TNA) site within the European FP7 Infrastructure Network ACTRIS (Aerosol, Clouds, and Trace gases Research InfraStructure Network). It was a Level 3 site within the EU FP6 NitroEurope IP (Sutton et al., 2007). In 2014, it became a World Meteorological Organisation Global Atmosphere Watch (WMO GAW) regional site.

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2.2 MARGA instrument

The MARGA 2S system (Metrohm Applikon B.V. Schiedam, NL) consists of two sampling boxes and utilises ion chromatography to analyze for a range of water soluble trace gases and aerosols. The MARGA 2S was set up to measure both PM_{10} and $PM_{2.5}$ aerosol. Air is first drawn through a common PM_{10} Teflon coated inlet (URG Corporation, Chapel Hill, NC, USA) at 3.55 m. above ground level into a 0.89 m long polyethylene (PE) 14 mm ID inlet line, which is housed in the centre of an 11 cm OD polyvinyl chloride (PVC) conduit. The conduit has an extractor fan at the base to draw air through based on the design used by Trebs et al. (2004) aimed at keeping the sample at the temperature of the measurement height for as long as possible. The PE tubing entering the air conditioned cabin (21°C) is split into two ¼" PE sample

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lines (0.4 m). The first line feeds directly into the first sampling box and the second sampling line goes through a further $PM_{2.5}$ cyclone (URG Coporation, Chapel Hill, NC, USA) before the second sampling box. The flow rate in each sampling box is regulated to a volumetric flow of 1 m^3 hr^{-1} using a mass flow controller downstream of the sampling box. In the sampling box air passes through a horizontal annular wet rotating denuder (WRD) (Keuken et al., 1988). The WRD is continuously coated with a thin film of solution which strips water soluble gases from the laminar air stream; the addition of 10 ppm H_2O_2 acts as a biocide and also promotes oxidation of SO_2 initially trapped as HSO_3^- through to SO_4^{2-}. Water soluble aerosols do not diffuse into the stripping solution due to their lower diffusion velocity. The air flow then enters a steam jet aerosol collector (SJAC). The steam in the SJAC promotes rapid growth of water soluble aerosols which are then separated out from the air flow mechanically in a cyclone. Details of the principles of the SJAC are described by Khlystov et al. (1995). The sampling solutions are continuously drawn from the WRDs and SJACs to the analyzer box at a rate of 25 ml hr^{-1} using syringe pumps. Samples are then analysed online by anion and cation chromatography (Metrohm AG, Herisau, Switzerland). The system is continuously calibrated by mixing the sample with a 325 mg/L internal standard of LiBr, prior to injection into the IC columns. Anions are concentrated on a Metrosep A PCC 1 HC IC Preconcentration column (2.29 ml) and then separated using a Metrosep A Supp 10-75 column (75 mm x 4.0 mm) using a 7 mmol l^{-1} Na_2CO_3 /8 mmol l^1 $NaHCO_3$ eluent. Cations are concentrated on a Metrosep C PCC1 HC IC Preconcentration column (3.21 ml) and separated using a Metrosep C4 (100mm x 4.0mm) cation column. A 3.5 mmol l^{-1} methanesulfonic acid (MSA) eluent was used for the cation column, rather than the recommended 3.2 mmol l^{-1} HNO_3 eluent used in other similar systems. This was in order to eliminate a potential NO_3^- artefact, which has been reported (ten Brink et al. (2009); Makkonen et al. (2012)). For the anion column a 1M H_3PO_4 solution was used for chemical suppression. Detection was by conductivity, where concentrations were calculated based on their specific conductivities relative to the internal standard ions (Li^+ and Br^-). These standard set-up conditions and all significant operational changes over the 6.5 years, which could be considered to have affected performance or data capture, are summarised in Table 2. The increase in diameter of the SJACs described in table 2, reduced the restriction in maintaining a flow rate, which was mass flow controlled at 1 m^3 hr^{-1} at standard temperature and pressure (STP) until November 2011, whereas thereafter it was controlled to keep the volumetric flow rate at ambient temperature and pressure through the size cuts constant.

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The performance of the MARGA has been further discussed by Rumsey et al. (2014);Makkonen et al. (2012);ten Brink et al. (2009);Cowen et al. (2011). The deployment of pre-concentration columns sets our MARGA instrument aside from the others, with the exception of Makkonen *et al.* (2014), allowing quantitative detection of the low concentrations encountered at this clean Scottish site.

Quality analysis and quality Assurance

As discussed previously the MARGA used in this work was one of the first to be field deployed. Processes were developed over the first several years which could be used to identify potential sources of error or contamination in the MARGA data. Firstly, periodic field blanks were carried out until 2011 by installing Whatman HEPA filters placed in front of the denuders and left on for ~24 hours. The filters removed aerosols but not the gas phase components from the air stream. The resultant change in PM concentrations allowed a blank value for the PM analytes to be assessed. Following the upgrade of the instrument in November 2011 (Table 2), automated monthly blanks were implemented in 2012, where the air pump and SJAC water supply and heaters were turned off, allowing for blanks for both aerosol and gas phase to be carried out. The blanks were not used to correct the data as they were usually below the detection limit (DL) of the instrument. Instead blanks were used to provide evidence of contamination in the system and to identify periods to be removed in the data ratification process. Prior to 2012 verification and instrument maintenance protocols has been experimental and the authors are in the process of finalising the protocols including calibration, which will be published separately. There was a step change in 2012, when the initial developmental protocols for maintenance were replaced by final protocols including quarterly replacement of inlets, cleaning of PM_{10} head and $PM_{2.5}$ cyclone, monthly air flow calibrations and independent analysis of internal standards by a UKAS accredited laboratory.

In the data ratification process values reported as 0 µg m^{-3} were replaced with half the detection limit (DL). The method to determine the DL has changed over the 6 year period. From 2002 to 2011, the DL was taken as the average of the reported values below the manufacturers published DL. From 2012, the DL was calculated by the analysis of the logarithmic distribution of the measurements previously described by Kentisbeer et al. (2014), presented in table 3. The methodology for analysing the DL and calibrating this type of on-line IC instrument is an area of research in of itself and we plan to publish separately on this aspect of the MARGA operation.

2.3 Back trajectories and associated analysis

To relate the aerosol species to air masses, back trajectory analysis was carried out. Four-day back trajectories at 3 hour intervals for Auchencorth Moss were obtained for the years 2007 to 2012 through the OpenAir software package (Carslaw, 2013), which calculates back trajectories with the HYSPLIT Trajectory Model (Hybrid Single Model Lagrangian Integrated Trajectory Model,(Draxler and Hess, 1997) using Global NOAA-NCEP/NCAR reanalysis data. A cluster analysis was then carried out using a routine in the OpenAir software, where data were clustered using a distance matrix, in this case according to the similarity of the angle from their origin. Further details of the calculations of the cluster analysis can be found in Carslaw (2013).

3 Results and Discussion

3.1 Overview

Table 4 summarises the annual data capture statistics for each compound. The Auchencorth MARGA was one of the first long-term field deployment of the MARGA instrument. Through troubleshooting and instrument improvements the data capture improved over the period reported with a highest data capture of 64% (average overall) in 2012. Though not reported here, data capture for 2013 is on average 83% for ratified data (http://uk-air.defra.gov.uk/). As seen in Table 4, Auchencorth Moss being a rural to remote site, the aerosol concentrations were low as there are no large local point pollution sources in the dominant SW wind direction.

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3.2 Concentration trends from June 2006 to December 2012

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The annual average concentrations from June 2006 to December 2012 are summarised in Table 4. Overall, the concentrations of individual species were generally low (< 1.5 µg m^{-3}). When compared with speciated PM$_{2.5}$ measurements from a background site in the Midlands, UK (Harrison and Yin, 2010), Cl$^-$ concentrations were higher at Auchencorth Moss based on annual averages (Table 4) but are in a similar range to other UK sites (Abdalmogith and Harrison, 2006). The average annual concentration of NO$_3^-$ and SO$_4^{2-}$ in the PM$_{10}$, on the other hand, were

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larger in other parts of the UK including the other rural EMEP supersite at Harwell (Harrison and Yin, 2010;Abdalmogith and Harrison, 2006). The maximum concentrations of the aerosol components, however, show that there were periods where large PM pollution events took place, which are hypothesised to have been due to long-range transport of polluted air masses. In both the $PM_{2.5}$ and PM_{10}, the largest concentrations of NH_4^+ and NO_3^- were recorded during 2012, SO_4^{2-} maximum concentrations were observed in 2007 and other species varied (Table 4). It is interesting that specific local events can be picked out from the data record, for example the maximum K^+ concentration in 2012 of 2.61 µg m^{-3} occurred at 00:00 GMT on the 06 November2012 - Guy Fawkes or "fireworks" night in the UK. The meteorological conditions that night were cool, with an average temperature of -0.1˚C at midnight and the wind direction was from the dominant wind sector (SW). An increase of K^+ is not unexpected as such an increase is reported to occur following firework events (Vecchi et al., 2008;Drewnick et al., 2006). This example illustrates the utility of the hourly composition measurements to understand specific atmospheric events.

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The monthly median concentrations for all 6.5 years are presented in Figure 2. There is a clear seasonal variation for Na^+ and Cl^- for all years, with the exception of 2009, with lower concentrations in the summer and higher concentrations in winter. This seasonality reflects higher average wind speeds in winter leading to more marine aerosol in the atmosphere, as previously observed at other sites in the UK, but for Cl^- is also consistent with increased NaCl reaction with HNO_3 which also peaks in summer. Of the secondary inorganic pollutants, NO_3^- shows individual peak concentrations only during the colder months, but not consistently while SO_4^{2-} and NH_4^+, do not have particularly strong annual variation. The largest monthly median concentration for NH_4^+ and NO_3^- was observed in March 2012. SO_4^{2-} on the other hand does not show the same feature; the maximum monthly concentrations were observed in July 2012.

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Comparing the average diurnal cycles for 2007 to 2012 (Figure 3) it is apparent that the contribution of PM_{coarse} is small compared with $PM_{2.5}$, where:

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$$PM_{coarse} = PM_{10} - PM_{2.5} \qquad (1)$$

PM_{coarse} is dominated by sea salt (Na^+ and Cl^-). In the fine fraction ($PM_{2.5}$) NH_4^+ aerosol dominates, as it is the major base in secondary inorganic aerosol (refer to Section 3.4). In the $PM_{2.5}$ there is a decrease of NO_3^- during the afternoon in all seasons, though this feature is strongest in winter. This behaviour is consistent with that previously reported from other North

European sites (Nemitz et al., in preparation) including Harwell (UK) (Revuelta et al., 2012), Cabauw (Netherlands) (Mensah et al., 2012), Melpitz (Germany) (Poulain et al., 2011) and SMEAR II (Finland) (Makkonen et al., 2012). It is assumed that the majority of fine NO_3^- will be in the form of NH_4NO_3 and that the relationship between the gas precursors, temperature, RH and chemical composition explain the observed cycle (see the discussion on gas concentrations at this site Twigg et al. (in preparation)). Timonen et al. (2011), who had also reported a decrease of daytime NO_3^- in Helsinki, explained the decrease to be the result of increased boundary layer mixing as the same feature was observed in black carbon. At Auchencorth Moss this behaviour of black carbon is not observed, instead the annual diurnal average shows an increase of black carbon during the day (Cape et al., 2012). It is therefore probable that diurnal variation in temperature and relative humidity exert a stronger influence on the $PM_{2.5}$ NO_3^- at this site than the depth of the mixing layer. $PM_{2.5}$ SO_4^{2-} at Auchencorth Moss, on the other hand, shows an increase in concentration during the day, with the feature strongest in the summer. The increase in SO_4^{2-} is interpreted to be the effect of stronger insolation in summer, which drives the oxidation of SO_2 to form sulphuric acid and finally SO_4^{2-}, due to the increase in OH radicals.

3.3 Ion Balance

The ion balance was calculated for $PM_{2.5}$ and PM_{coarse} for the year 2012. Figure 4a) and b) show the ion balance of the secondary inorganic species, while figs. 4c) and d) show the full ion balance of the measured species. In both the $PM_{2.5}$ and PM_{coarse} it is clear that though there is good correlation, there appears to be an excess of NH_4^+. This is not the first time excess NH_4^+ has been observed in aerosol measurements (Mensah et al., 2012). It is thought that water soluble organic acids such as oxalate may be the missing species to close the ion balance. Some of the Cl^- measured by the MARGA is likely to represent NH_4Cl which would affect the partial ion balance of Fig. 4a, but not the full ion balance of Fig. 4b. However, Aerosol Mass Spectrometer (AMS) measurements suggest that this contribution is negligible in S Scotland (Nemitz et al., in preparation). On the other hand, some of the NO_3^- in the partial ion balance is expected to represent $NaNO_3$, even in $PM_{2.5}$, and the excess NH_4^+ may be even larger than suggested by Figure 4a. Makkonen et al. (2012) observed that in Finland the ion balance was seasonal, with acidic aerosol in winter and a basic ion balance in spring. This seasonal trend was not observed at Auchencorth Moss, with the average seasonal ion balance always basic (i.e. excess NH_4^+) in character and is consistent with AMS measurements, that have

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demonstrated that in Europe acidic aerosol is only found in NE, E and S Europe, while there is always excess ammonia in NW and W Central Europe (Nemitz et al., in preparation;Morgan et al., 2010).

3.4 Sea salt and sea salt processing

An overview of the average inorganic $PM_{2.5}$ and PM_{coarse} composition based on mass is presented in Figure 5. Sea salt is presented as the individual species of measured Na^+, sea salt Cl^- ($ssCl^-$), sea salt SO_4^{2-} ($ssSO_4^{2-}$) sea salt Mg^{2+} ($ssMg^{2+}$), sea salt Ca^{2+} ($ssCa^{2+}$) and sea salt K^+ (ssK^+), which were calculated based on the known mass ratio to Na^+ in sea water (Seinfeld and Pandis, 2006):

$$[ssCl^-] = 1.8 \times [Na^+] \qquad (2)$$

$$[ssSO_4^{2-}] = 0.252 \times [Na^+] \qquad (3)$$

$$[ssMg^{2+}] = 0.12 \times [Na^+] \qquad (4)$$

$$[ssCa^{2+}] \text{ or } [ssK^+] = 0.04 \times [Na^+] \qquad (5)$$

As would be expected, the dominant fraction of the coarse aerosol at this site is from sea salt (73%); this is larger than reported at other European sites such as SMEAR III, near Helsinki (Makkonen et al., 2012), probably because of proximity to the ocean in all wind directions. There is also a large contribution from NO_3^- in the coarse fraction. This is not the first time that a large proportion of NO_3^- has been reported in the coarse mode; the same was observed in Melpitz, Germany and has been explained to be the result of chloride-nitrate exchange that takes place on coarse aerosol during long range transport of sea salt (Spindler et al., 2012;Dasgupta et al., 2007). This was further evident as the average non-sea salt Cl^- mass was -0.17 µg m^{-3} and -0.08 µg m^{-3} for $PM_{2.5}$ and PM_{coarse} respectively, where:

$$\text{Non-sea salt } Cl^- = [Cl^-]_{measured} - [ssCl^-]_{calculated} \qquad (6)$$

To investigate the process of sea salt substitution by reaction with HNO_3 further, the ratios of Na^+ and Cl^- were compared with NO_3^- in the coarse mode for the year 2012. In general, larger NO_3^- concentrations tended to be observed on occasions where a depletion of Cl^- was observed, though this was not true for all cases (Figure 6).It should be noted, however, that the concentrations of PM_{coarse} are calculated as differences (Eq. 1) and therefore subject to considerable uncertainty.

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$PM_{2.5}$ on the other hand is dominated by the secondary inorganic aerosol (SIA) (NH_4^+, NO_3^- and SO_4^{2-}) (Figure 5), with a total contribution of 63% to the total measured mass by the MARGA, which is to be anticipated. NO_3^- is the dominant mass of the SIA at Auchencorth Moss accounting for 26% for the total water soluble species detected by the MARGA. A similar comparison has been carried out by a MARGA operated at SMEAR III (near Helsinki, Finland) where SO_4^{2-} was the dominating mass responsible for 50.4% of the total inorganic $PM_{2.5}$ mass reported by the MARGA (Makkonen et al., 2012). This is not surprising as it has also been shown by Nemitz et al. (in preparation), from AMS studies, that in Finland PM_1 is dominated by SO_4^{2-}, whereas in the UK and the rest of NW Europe, NO_3^- is the dominant SIA. Sea salt, however, still makes a considerable contribution (35%) to the average measured $PM_{2.5}$ by the MARGA, bearing in mind that the cut-off might have been somewhat larger than 2.5 μm until November 2011 (see above). In 2012, sea salt still made a major contribution to the total mass of the $PM_{2.5}$ (30%), where there is the greatest confidence in the cut-off of the cyclone. There was a clear increase of $PM_{2.5}$ Na^+ with wind speed for 2012 (Figure 7) in the dominant wind sector (refer to Figure 1), suggesting that $PM_{2.5}$ Na^+ was related to sea salt and its presence at the site is driven by meteorology.

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Potassium (K^+) is present in sea salt and when the available 2012 $PM_{2.5}$ data was compared to the concentration of Na^+ it tended to follow the known ratio in sea water (Seinfeld and Pandis, 2006), Figure 8. The greatest deviation from this curve appears to be in periods of high black carbon (BC) concentrations. PM_{coarse} however had much scatter. High concentrations of black carbon are often associated with combustion processes, though K^+ can also occur as a product of other anthropogenic sources. There was clear evidence in the $PM_{2.5}$ that high concentrations of K^+ were associated with increased BC pointing to a contribution from combustion sources or biomass burning (Figure 8). The measured Mg^{2+} /Na^+ ratio in $PM_{2.5}$ followed the known ratio in sea water (Seinfeld and Pandis, 2006). The same comparison was done for PM_{coarse}, however there was much more scatter in the data.

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3.5 Comparison of total inorganic aerosol with TEOM-FDMS measurements

The total average water-soluble inorganic aerosol mass measured by the MARGA for the period January 2007 to December 2012 was 3.82 μg m^{-3} and 5.04 μg m^{-3} for $PM_{2.5}$ and PM_{10}, respectively. The measured mass by the MARGA was compared to the Tapered Element Oscillating Microbalance Filter Dynamic Measurement System (TEOM-FDMS) which measures the total aerosol mass; total mass data were obtained from the AURN network (http://uk-air.defra.gov.uk/networks/network-info?view=aurn) for the 6 years of interest (2007 to 2012). It was found that the PM_{10} mass measured by the MARGA accounted for 78% of total PM_{10} measured by the TEOM-FDMS, on average. It is not the first time that inorganic water soluble aerosols have been found to be major contributors to the total mass in Europe (Putaud et al., 2010). Aerosol components not resolved by the MARGA include organic aerosols, BC, water and crustal elements such as silicate. Organic aerosol often accounts for a larger fraction of the PM_{10} mass at central European background sites than the missing mass at Auchencorth allows for. This is consistent with AMS measurements in S.Scotland that also indicate relatively low contributions from organic aerosol (Nemitz et al., in preparation).

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Table 5 summarises the annual mass fraction that is accounted for by the MARGA instrument when compared with the TEOM-FDMS for both PM_{10} and $PM_{2.5}$. It is very clear that there are discrepancies between the measured $PM_{2.5}$ by the MARGA and that by TEOM-FDMS. Mass closure improved in 2012, probably in response to the improved flow control implemented in November 2011 on the MARGA (see above). An alternative explanation is that the PM concentrations at Auchencorth are close to the detection limits of the TEOM-FDMS, which is indicated by the large percentage of negative values reported by the instrument over the period January 2007 to December 2012 (26% and 10% respectively for $PM_{2.5}$ and PM_{10}), the annual variation of which can be found in Table 5. During the 6 years presented, the fraction of negative values for PM_{10} declined, while it stayed constant for $PM_{2.5}$. It therefore can be concluded that that the $PM_{2.5}$ TEOM-FDMS at Auchencorth Moss has an offset, as has previously been commented by Laxen et al. (2012). It is therefore not possible to comment on what the true contribution of the measured water soluble inorganic mass measured by the MARGA is to the total $PM_{2.5}$.

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3.6 Influence of air mass on aerosol composition

Due to the remote location of the site, the origin of air masses at the site influences the aerosol composition. Back trajectories, run over a 96 hour period, were obtained at 3-hour intervals for the years 2007 to 2012, which were then clustered, details of which can be found in Section 2.3. Figure 9 displays the mean trajectory for each of the 6 clusters assigned. The average concentration over the 6 year period for each cluster and the % species contribution to the total measured concentration by the MARGA are summarised in Figure 10. When calculating the average associated with each cluster, data were only used when all species were available. As

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would be expected, the air masses from the Atlantic Ocean and the Arctic (clusters 1, 2 and 4) are dominated by Na^+ and Cl^- aerosol in PM_{coarse}. In the $PM_{2.5}$, the same clusters show a large contribution from Na^+ and Cl^-, with the largest contribution in the Atlantic air mass (Cluster 1). Air masses which go over land tend to have the greatest contribution from secondary inorganic aerosols, as seen in clusters 5 and 6. Air masses, in particular from continental Europe (Cluster 6), have the largest average molar concentrations of NH_4^+ and NO_3^-, even in the coarse fraction. The dominance of NO_3^- compared to SO_4^{2-} from air trajectories from continental Europe has previously been highlighted by Abdalmogith and Harrison (2005), who explained this to be the result of high NO_x/SO_2 emissions ratios in Western Europe.

3.7 Aerosol composition during high pollution events

In order to optimise emission controls for the protection of human health against high concentration episodes, it is important to know which chemical components dominate when air concentrations are large. Figure 11 shows the average relative aerosol contribution as a function of total aerosol concentration for 2012 as an example, together with the histogram of the frequency with which different aerosol concentrations occur. The period with the highest concentrations recorded at the site by the MARGA are dominated by secondary inorganic aerosols, in particular by NH_4^+ and NO_3^-, with a smaller contribution from SO_4^{2-}. This is not the first time that NO_3^- has been found to be a dominating species during pollution events in the UK. Vieno et al. (2014) reported NO_3^- as a dominating fraction during pollution events at a site (Bush) approximately 10 km NE from the Auchencorth Moss field site. They show that the NO_3^- during pollution events at this site arise from a combination of emissions from the UK and continental Europe, but that the relative importance depends on synoptic conditions and differs greatly between episodes with the UK contribution ranging from 35% and 80% (Vieno et al., 2014). The Auchencorth measurements demonstrate the importance of controlling the emissions of NH_4NO_3 precursor gas concentrations (NH_3 and NO_x) in both the UK and the rest of Europe for controlling the high pollution episodes.

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The concentration dependence of the relative aerosol composition (Figure 11) also shows that sea salt dominates the aerosol composition at moderate aerosol loading (2 to 12 µg m^{-3}) while the relative contribution of K^+ and Ca^{2+} increases at very low concentrations (<2 µg m^{-3}). Even under very clean conditions, there is a basic concentration of crustal material.

4 Summary and conclusions

The first six and a half years of chemically speciated $PM_{2.5}$ and PM_{10} measurements from the MARGA at Auchencorth Moss have been analysed. This study has provided greater detail in the long term temporal variations of inorganic species in the UK background atmosphere and confirmed the status of the field site as a background site in the European context, where concentrations of the inorganic species were low over the 6.5 years. The dynamic changes between air masses dominated by anthropogenic and natural sources is clearly observable on an inter-annual scale and continuation of these long term measurements will be a valuable resource to understand long term trends in PM composition in response to climate and policy drivers.

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The average ion balance at this site was biased towards cations some of which would probably have been neutralised by organic acids such as oxalic acid. Additional studies to identify the missing water soluble species would therefore be beneficial at this site to close the ion balance. Comparison with the TEOM-FDMS bulk mass method found that the compounds resolved by the MARGA instrument accounted on average for 78% of the PM_{10} mass measured at Auchencorth Moss, with considerable uncertainty due to changes in the MARGA configuration over the period and the detection limits of the TEOM-FMDS and possible difference in the characteristics of the PM_{10} inlets. One recommendation is to add a continuous measurement of the organic aerosol mass at Auchencorth Moss to determine its contribution to the total mass, due to the regional importance of this site.

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Based on monthly median concentration, Na^+ and Cl^- generally were found to vary seasonally due to the meteorology of the site, with the highest concentrations in winter when the average wind speed was greatest. As expected NH_4^+ dominated the finer $PM_{2.5}$ aerosol in terms of µmol m^{-3}, as it is the major base for aerosol in the atmosphere and free ammonia is always available in NW Europe. The influence of long-range transport at this site is evident, with sea salt dominating air masses originating from the Arctic and Atlantic Ocean, whereas SIA dominate air masses that originate over land, with largest contributions from continental Europe. It therefore supports the importance of a transboundary co-operation, in controlling precursor gases such as NO_x and NH_3 as highlighted in this long term study, where NH_4^+ and NO_3^- tended to be the drivers of the (regional) pollution events observed at this background site. The dominance of NO_3^- compared to SO_4^{2-} was evident too in the diurnal cycles, with the exception of summer and provides evidence of a shift in recent decades from sulphur to nitrogen driven

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chemical climate. The air quality implications of the NH_4^+ and NO_3^- predominance during high PM loading events provide insight for future mitigation of PM impacts. Additional studies of gas-to-particle conversions at this field site will help to understand sulphur-nitrogen budget and atmospheric chemical processing to form PM (Twigg et al., in preparation).

5 Acknowledgements

Back trajectories were calculated on the NOAA ARL Ready Website using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model (Draxler, R. R. and Hess, G. D.,2003, NOAA Air Resources Laboratory, Silver Spring, MD, USA). The authors would like to thank the following for funding this work: the UK Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations, through the projects "Operation and Management of the EMEP Supersite project" (AQ0618) and the "UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) project" (AQ0647). Auchencorth Moss is supported by the EU FP7 Infrastructure Project "ACTRIS". Thanks go to Ms Margaret Anderson, Mr Ivan Simmons, Mr Frank Harvey, Dr Gavin J Phillips and Mr Robert Storeton-West for their assistance in the operation of the instrument.

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Table 1 Summary of metrological conditions for the period June 2006 to December 2012

Year	Total Rainfall (mm)	Air Temperature (°C)			Windspeed at 1 m (m s^{-1})		RH (%)	St (W m^{-2})
		Median	Min	Max	Median	Max	Mean	Mean
2006[a]	*740*	*11.2*	*-5.4*	*28.5*	*2.8*	*13.3*	*88.6*	*99.52*
2007	1124	7.8	-9.7	22.1	3.0	24.8	83.0	88.67
2008	1212	7.3	-8.4	23.2	2.9	24.3	84.4	84.91
2009	989	7.6	-9.0	27.5	3.0	12.2	84.8	92.92
2010	649	6.7	-12.0	24.6	2.7	11.6	83.9	92.39
2011	1101	8.4	-8.9	24.6	3.1	13.5	86.1	88.38
2012	1322	6.6	-8.3	23.3	2.8	16.8	88.1	83.63

[a] 2006 only includes data from the 01 June 2006 onwards. Key: RH- Relative Humidity, St – Total Solar Radiation.

Table 2 Summary of major operational changes which will have potentially affected the MARGA performance or data capture from June 2006 to December 2012

Date	Operation Change	Change to Performance
03/12/2008	Changed from Metrohm C2 column with 4 mM MSA eluent to Metrohm C4 column with a 3.5 mM MSA	Better separation of NH_4^+ and Na^+ peaks.
17/02/2009	SJACs were replaced with an increased internal diameter. Syringe valves increased from 0.6 mm to 0.8 mm i.d.	Improved accuracy in maintaining the cut-off for $PM_{2.5}$ and PM_{10}. Reduction in downtime due to blockages.
28/07/2009	Replaced glass fibre filters to PTFE Whatman Rezist 30 mm filter.	Glass fibre filters had a high Na^+ and SO_4^{2-} background and required rinsing prior to use.
29/07/2009	100 ppm H_2O_2 added to H_2O stripping solution	Prevents loss of NH_4^+ from bacteria by acting as a biocide. Converts HSO_3^- to SO_4^{2-}, resulting in better SO_2 recovery in the denuder.
09/02/2011	Reduced to 10 ppm H_2O_2 in stripping solution	Optimum concentration as a biocide, whilst preserving lifetime of the column.
17/11/2011	MARGA hardware and software upgrade.	Calibration of mass flow controllers can now be carried out in situ. Blanks and external standards can be set-up remotely.

Table 3 Annual average detection limits calculated using lograthimic profile for 2012

Component	DL
	µg m^{-3}
PM_{10}	
NH_4^+	0.062
Na^+	0.123
K^+	0.019
Ca^{2+}	0.016
Mg^{2+}	0.015
Cl^-	0.086
NO_3^-	0.105
SO_4^{2-}	0.349
$PM_{2.5}$	
NH_4^+	0.069
Na^+	0.106
K^+	0.014
Ca^{2+}	0.015
Mg^{2+}	0.007
Cl^-	0.053
NO_3^-	0.091
SO_4^{2-}	0.242

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Table 4 Annual concentrations of both PM_{10} and $PM_{2.5}$ species measured by the MARGA system at Auchencorth Moss from 1st June 2006 to 1st January 2013. (* 2006 data coverage: June – December 2006 only) Key: μ_A – arithmetic mean, μ_G – median, Max – maximum, σ_A – arithmetic standard deviation, DC – data capture (%).

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	2006*					2007					2008					2009					2010					2011					2012				
	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC
$PM_{2.5}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%
NH_4^+	0.93	0.36	6.86	1.23	18.08	0.72	0.21	8.30	1.21	35.99	0.61	0.20	12.35	1.23	36.15	0.77	0.36	12.90	1.24	49.10	0.79	0.36	9.14	1.08	46.02	0.64	0.28	6.81	0.95	25.58	0.89	0.35	14.66	1.46	63.90
Na^+	0.26	0.15	3.36	0.36	38.29	0.37	0.26	7.28	0.48	32.39	0.43	0.27	8.55	0.61	34.71	0.70	0.44	7.87	0.91	48.97	0.29	0.18	3.97	0.32	38.28	0.44	0.29	4.02	0.43	24.11	0.48	0.33	2.78	0.43	65.01
K^+	0.05	0.04	0.55	0.04	37.59	0.06	0.04	0.50	0.05	27.61	0.10	0.04	1.05	0.13	35.63	0.19	0.06	3.33	0.53	49.11	0.04	0.03	1.79	0.05	46.14	0.05	0.02	0.45	0.09	25.82	0.05	0.04	1.05	0.04	66.75
Ca^{2+}	0.07	0.03	0.73	0.11	37.11	0.09	0.08	1.61	0.07	36.38	0.11	0.09	1.39	0.08	37.42	0.12	0.07	3.70	0.21	49.09	0.06	0.05	1.84	0.06	46.18	0.05	0.03	0.49	0.05	25.91	0.05	0.04	0.54	0.03	66.55
Mg^{2+}	0.04	0.03	0.22	0.02	38.29	0.08	0.06	1.55	0.07	36.38	0.05	0.03	0.61	0.06	37.36	0.06	0.04	0.38	0.05	48.70	0.04	0.03	1.28	0.05	46.18	0.04	0.02	0.41	0.04	25.91	0.04	0.02	0.31	0.04	66.56
Cl^-	0.47	0.41	3.53	0.51	38.68	0.59	0.38	9.66	0.75	32.55	0.68	0.38	8.91	0.92	31.55	0.59	0.41	4.56	0.60	18.77	0.56	0.38	6.49	0.64	33.79	0.72	0.38	10.23	0.92	26.85	0.61	0.30	6.18	0.75	53.85
NO_3^-	1.32	0.79	12.05	1.63	22.81	1.20	0.36	16.12	2.12	37.72	0.98	0.30	20.60	2.11	38.73	1.11	0.35	29.31	2.88	39.93	1.18	0.37	20.18	2.19	38.05	0.91	0.40	15.02	1.61	28.52	1.54	0.43	32.75	3.20	59.23
SO_4^{2-}	1.46	0.74	15.87	2.05	39.19	0.81	0.44	34.27	1.09	37.73	1.01	0.56	18.63	1.40	38.88	1.22	0.89	15.36	1.31	39.89	0.97	0.66	10.53	1.00	38.11	1.11	0.76	7.75	1.05	28.53	1.21	0.77	11.39	1.25	59.22
PM_{10}																																			
NH_4^+	0.97	0.43	6.66	1.19	17.76	0.98	0.33	16.88	1.54	47.96	0.57	0.20	14.47	1.11	31.66	0.76	0.38	13.59	1.29	49.32	0.81	0.41	9.33	1.11	44.92	0.64	0.34	8.41	0.90	34.01	0.98	0.35	19.51	1.75	66.80
Na^+	0.48	0.32	8.05	0.57	43.71	0.62	0.36	9.58	0.76	45.81	0.62	0.36	13.88	0.95	31.57	0.90	0.64	14.17	0.88	48.90	0.55	0.35	11.14	0.70	39.01	0.57	0.37	4.94	0.62	32.61	0.84	0.63	4.98	0.74	67.96
K^+	0.04	0.03	0.36	0.03	43.09	0.06	0.05	0.54	0.05	40.19	0.07	0.04	0.95	0.09	32.70	0.16	0.08	2.67	0.32	49.27	0.05	0.04	2.29	0.06	45.08	0.04	0.02	2.17	0.06	34.09	0.07	0.06	2.61	0.07	70.33
Ca^{2+}	0.06	0.03	0.99	0.09	43.16	0.11	0.08	0.84	0.09	47.93	0.18	0.15	1.06	0.12	32.67	0.18	0.09	3.16	0.42	49.19	0.09	0.07	2.06	0.09	44.84	0.06	0.02	0.80	0.08	33.93	0.06	0.05	1.22	0.07	70.11
Mg^{2+}	0.04	0.03	0.50	0.04	43.71	0.10	0.07	2.14	0.10	48.30	0.07	0.05	0.78	0.07	32.70	0.10	0.07	0.71	0.11	47.77	0.06	0.05	1.59	0.07	44.57	0.05	0.02	0.54	0.07	34.09	0.06	0.04	0.52	0.07	70.14
Cl^-	0.70	0.49	7.40	0.86	42.35	0.95	0.55	11.57	1.17	44.14	1.08	0.59	12.65	1.44	33.20	0.97	0.60	7.32	1.06	20.21	1.05	0.67	8.46	1.20	34.51	1.04	0.51	10.25	1.31	35.92	1.11	0.54	8.87	1.38	55.73
NO_3^-	1.92	1.43	12.58	2.13	21.27	1.55	0.56	31.60	2.48	48.52	1.18	0.38	24.42	2.48	37.17	1.24	0.43	30.65	2.93	41.04	1.31	0.47	21.40	2.32	37.88	1.07	0.49	15.95	1.68	37.42	1.86	0.55	50.15	3.81	60.73
SO_4^{2-}	1.65	0.91	16.01	2.09	42.79	1.19	0.61	33.98	1.70	48.73	1.01	0.68	11.86	1.07	37.19	1.30	0.92	18.79	1.39	41.22	0.99	0.72	12.57	0.99	37.79	1.03	0.77	8.07	0.88	37.41	1.43	0.89	12.75	1.55	60.74

Table 5 Measured MARGA mass vs TEOM-FDMS mass and the percentage of time the TEOM FDMS reported values ≤ 0 µg m^{-3} for the years 2007 to 2012.

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Year	**PM_{10} unaccounted (%)**	**$PM_{2.5}$ unaccounted (%)**	**PM_{10} measured by TEOM-FDMS - Reported values ≤ 0 µg m^{-3} (%)**	**$PM_{2.5}$ measured by TEOM-FDMS - Reported values ≤ 0 µg m^{-3} (%)**
2007	21	-15	14	25
2008	23	-38	10	25
2009	29	-48	7	28
2010	28	-27	6	17
2011	32	-20	9	26
2012	18	-9	3	20

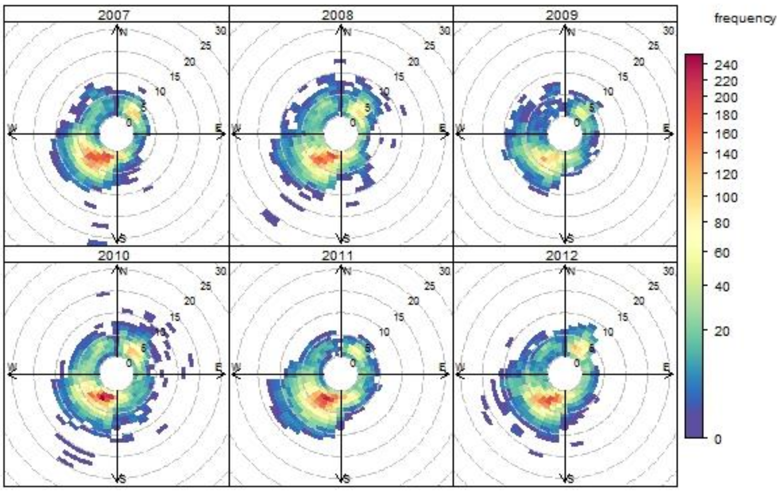

Figure 1 Frequency plots of wind direction and windspeed (m s^{-1}) averaged over an hour at Auchencorth Moss for the years 2007 to 2012. Windspeed scale is limited to 30 m s^{-1}. (Graphs produced using OpeAir;Carslaw and Ropkins (2012))

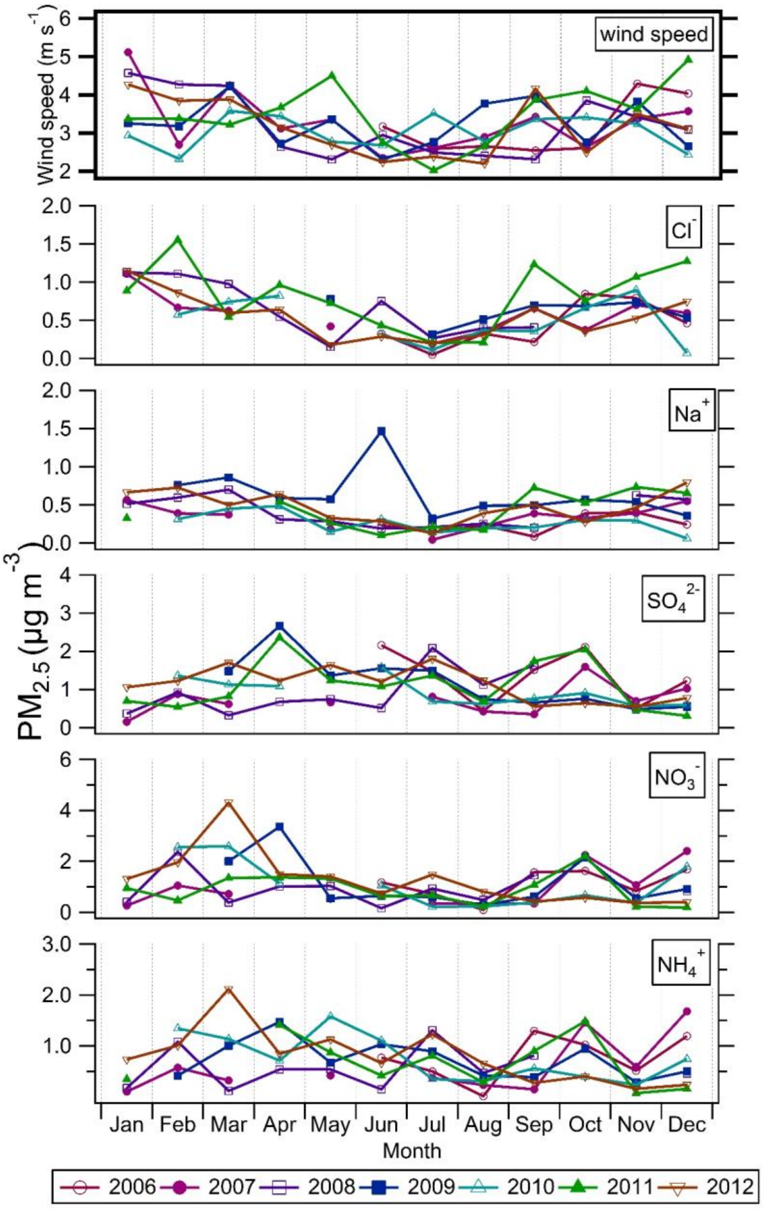

Figure 2 a) Median monthly mass concentrations of $PM_{2.5}$ species measured by the MARGA and median wind speed from June 2006 to December 2012

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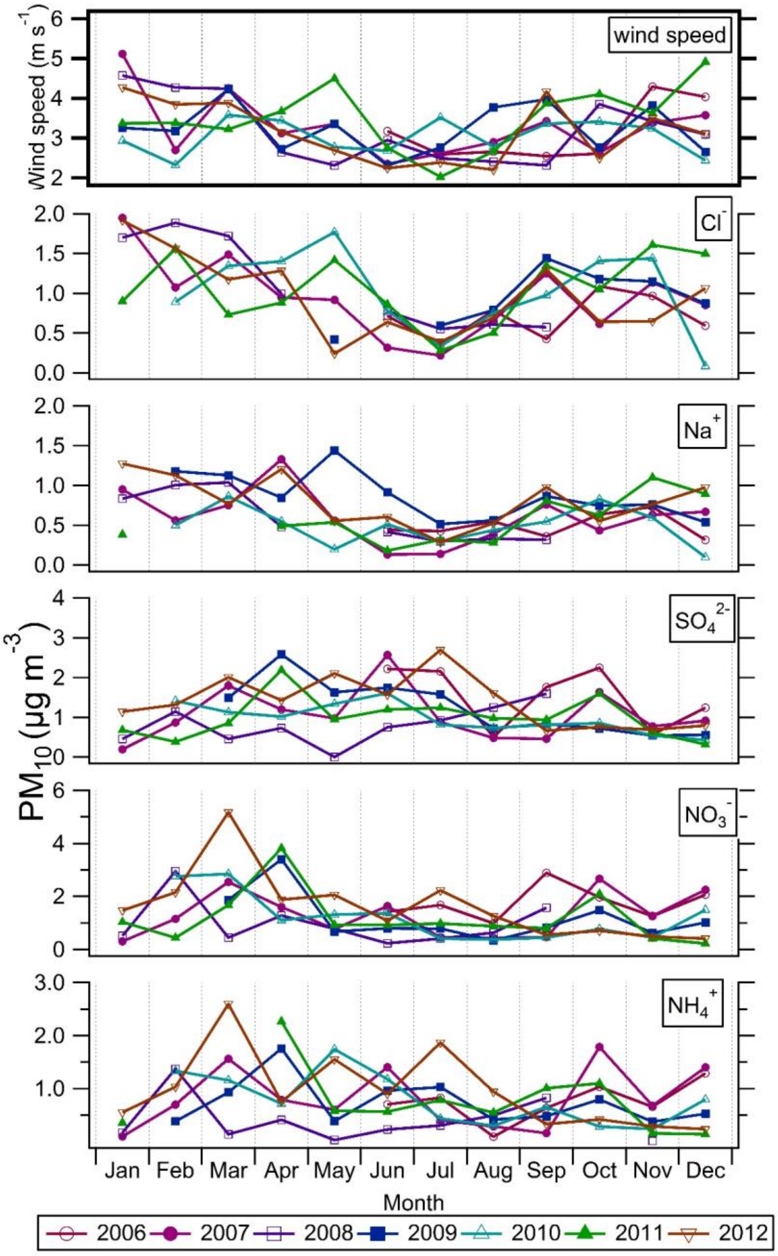

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2 Figure 2b) Median monthly mass concentrations of PM_{10} species measured by the MARGA
3 and median wind speed from June 2006 to December 2012

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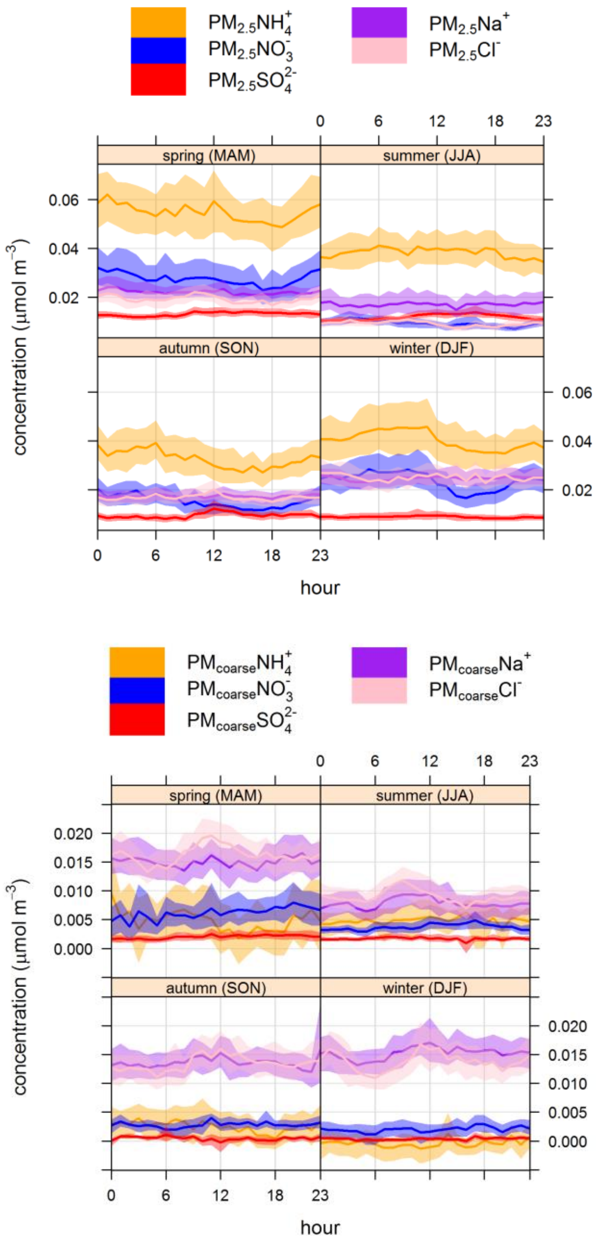

Figure 3 Median seasonal diurnal cycles of molar concentrations of $PM_{2.5}$ and PM_{coarse} NH_4^+, NO_3^-, SO_4^{2-} , Na^+ and Cl^- using data from January 2007 to December 2012, with the shading

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showing the 95% confidence level of the median. (Graphs produced using Open air; Carslaw and Ropkins (2012)).

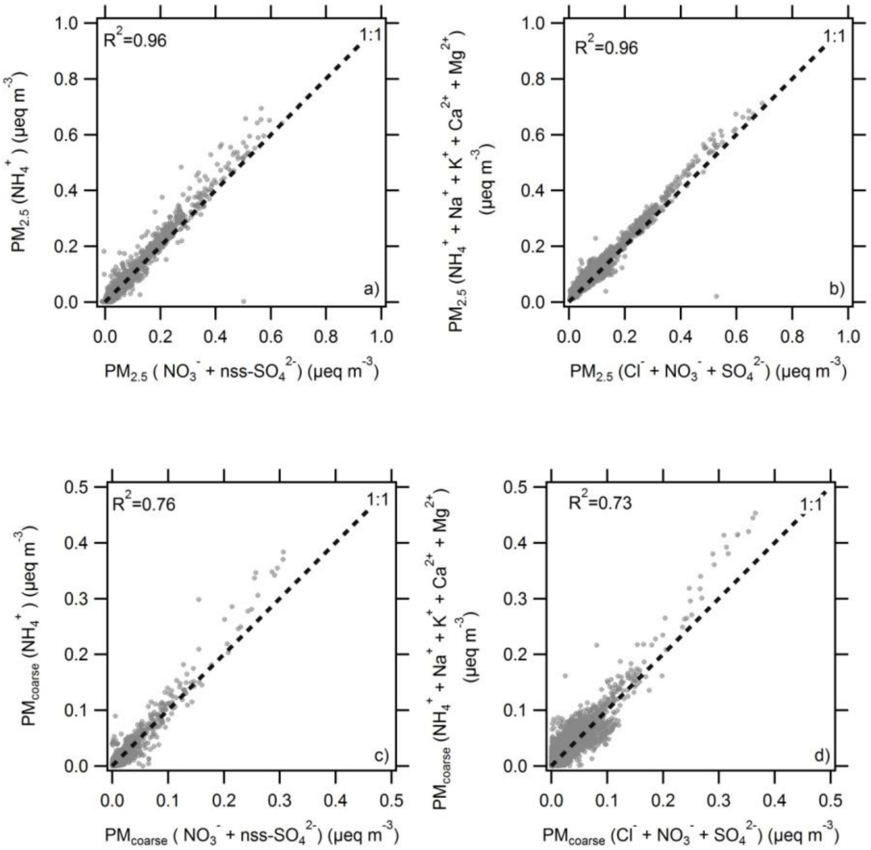

Figure 4. Measured ion balance for the year 2012 in microequivalents m^{-3}. a) Neutralisation of $PM_{2.5}$ NH_4^+ by $PM_{2.5}$ nss-SO_4^{2-} and $PM_{2.5}$ NO_3^-, b) Ion balance of measured $PM_{2.5}$ anions (Cl^-, NO_3^- and SO_4^{2-}) and measured $PM_{2.5}$ cations (NH_4^+, Na^+, K^+, $Ca^{2+}$and Mg^{2+}), c) Neturalisation of PM_{coarse} NH_4^+ by PM_{coarse} nss-SO_4^{2-} and PM_{coarse} NO_3^-, d) Ion balance of measured PM_{coarse} anions (Cl^-, NO_3^- and SO_4^{2-}) and measured PM_{coarse} cations (NH_4^+, Na^+, K^+, $Ca^{2+}$and Mg^{2+}).

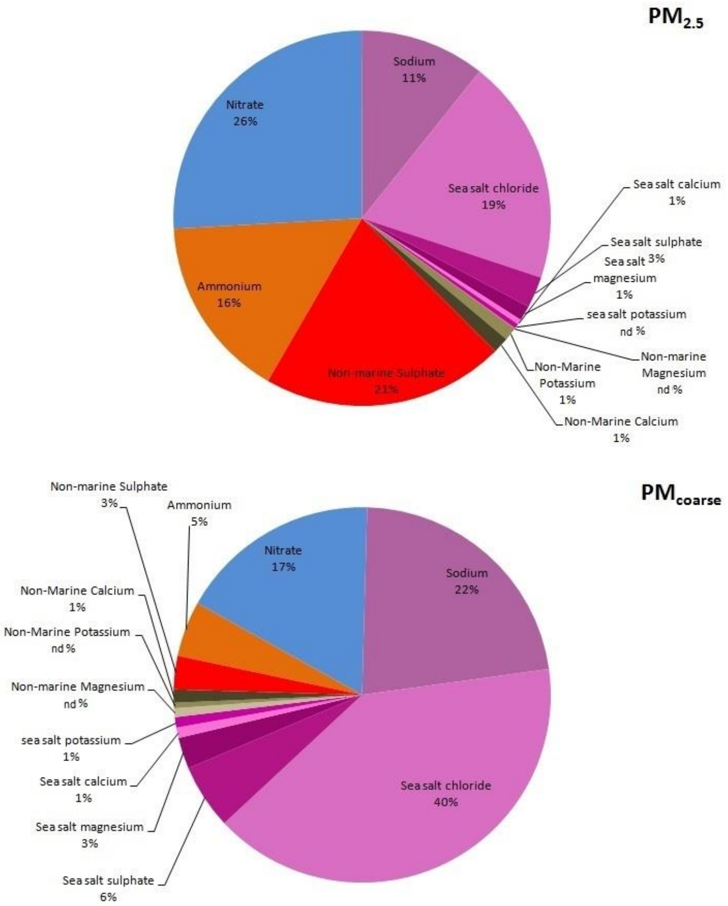

Figure 5 Average composition by mass of the water soluble inorganic aerosol fraction measured by the MARGA from January 2007 to December 2012 in both the PM$_{2.5}$ and PM$_{coarse}$. Sea salt chloride, sulphate, magnesium, calcium and potassium were derived based on the known mass ratios to Na$^+$ in sea water, refer to Eqs. 2 to 5. Key: nd – not detected.

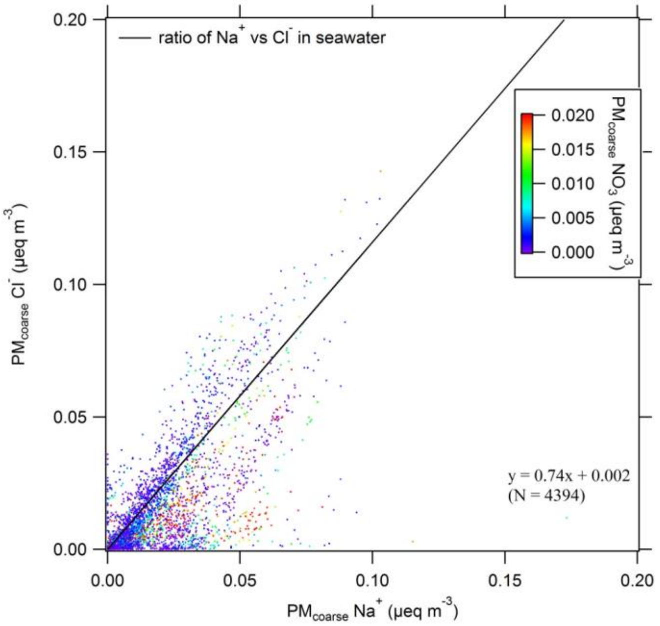

Figure 6. Demonstration of the depletion of Cl^- for the year 2012 as a result of Cl^- - NO_3^- interactions during long-range transport for coarse aerosol. The black line is the known ratio of Cl^- to Na^+ in seawater (Seinfeld and Pandis, 2006). Colour scale is set to 0 to >0.2 µeq m-3 NO_3^- to focus in on the depletion of Cl^- at high NO_3^- concentrations.

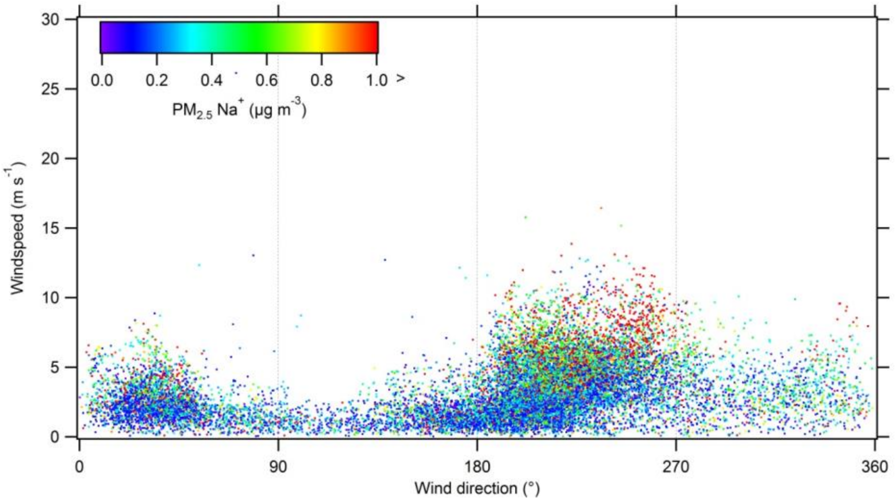

Figure 7 The influence of wind direction and wind speed on the concentration of $PM_{2.5}$ Na^+ at Auchencorth Moss from the 1 January 2007 to 1 January 2013.

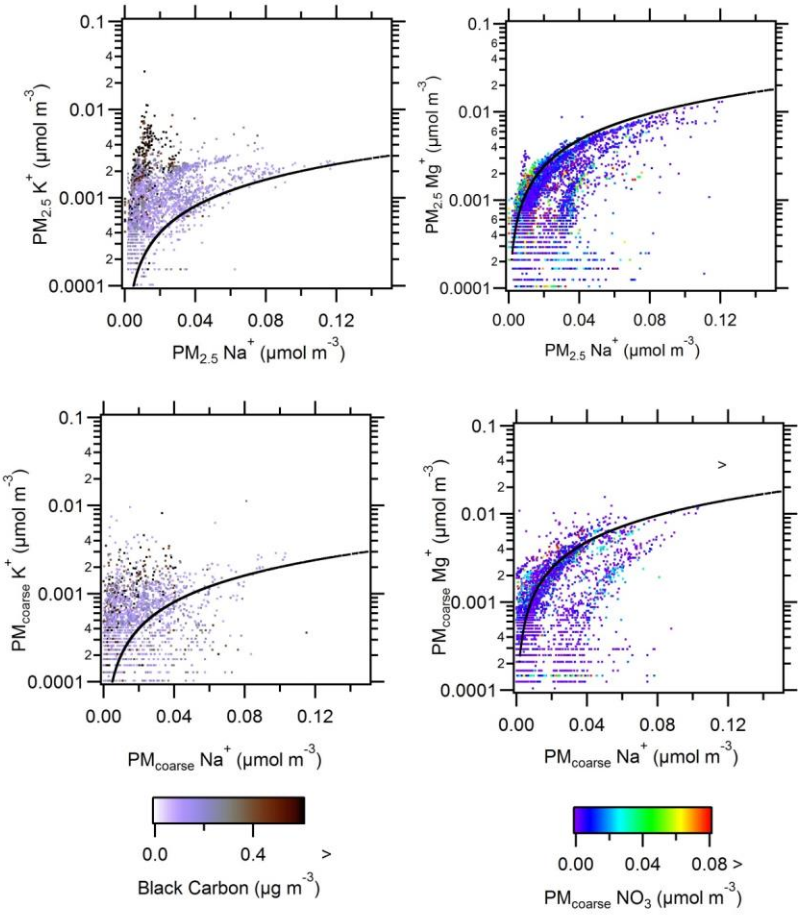

Figure 8 Relationship of K^+ (left hand figures) and of Mg^{2+} (right hand figures) to Na^+ for $PM_{2.5}$ and PM_{coarse} from 21/03/2012 to 01/01/2013. Black lines show the sea water ratios of K^+ and Mg^{2+} to Na^+ taken from Seinfeld and Pandis (2006). Black carbon data are provisional data downloaded from the DEFRA UK-Air database archive (http://uk-air.defra.gov.uk/data/) on the 17/03/2014.

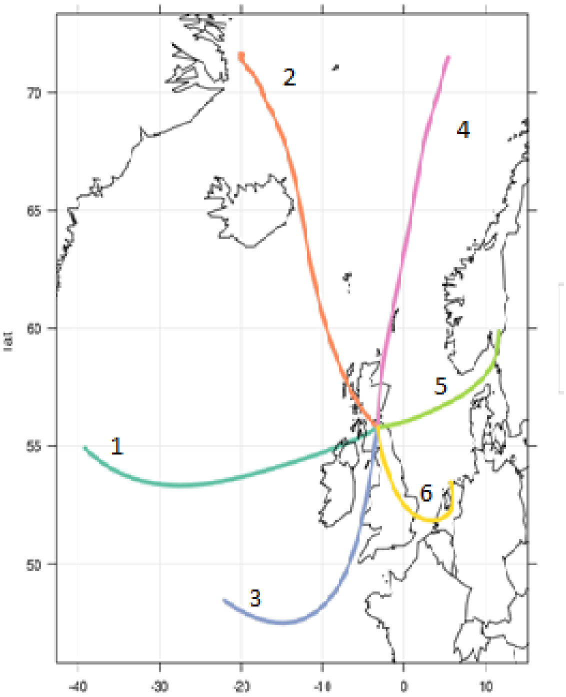

Figure 9. Mean trajectory associated with each cluster following clustering of 96h back trajectories at 3 hour intervals calculated for Auchencorth Moss covering the years 2007 to 2012 (17,370 back trajectories). . (Graphs produced using Open air; Carslaw and Ropkins (2012)).

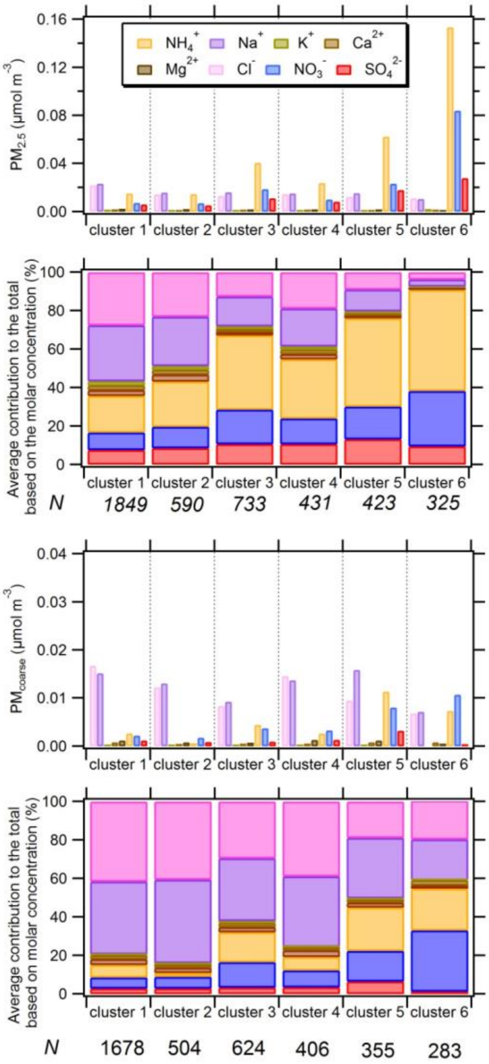

Figure 10. Average molar concentrations and average contribution of the species to the total molar concentration of PM$_{2.5}$ and PM$_{coarse}$ for each back trajectory cluster (refer to Figure 9) from January 2007 to December 2012. Key: N – number of back trajectories used to calculate average concentration and % contribution for each trajectory.

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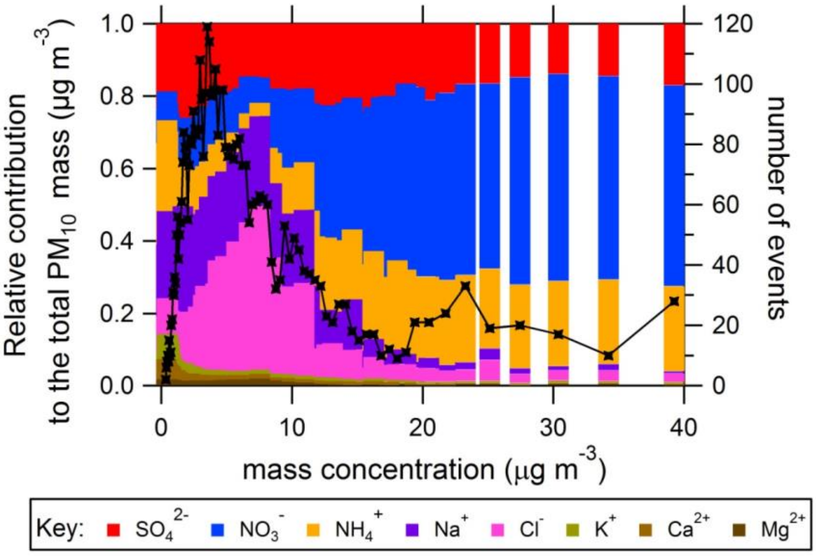

Figure 11. Average relative contribution of inorganic water soluble species to the total PM$_{10}$ mass measured by the MARGA during 2012 as a function of total mass concentration. The black line is the number of events at each mass concentration. Graph produced using the plotting routine of Crippa et al. (2014).

Water soluble aerosols and gases at a UK background site. Part 1: Controls of $PM_{2.5}$ and PM_{10} aerosol composition

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Abstract

There is limited availability of long-term, high temporal resolution, chemically speciated aerosol measurements, which can lead to further insight into the health and environmental impacts of particulate matter. The Monitor for AeRosols and Gases (MARGA, Applikon B.V, NL) allows characterisation of the inorganic components of PM_{10} and $PM_{2.5}$ ((NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}) and inorganic reactive gases (NH_3, SO_2, HCl, HONO and HNO_3) at hourly resolution. The following study presents 6.5 years (June 2006 to December 2012) of quasi-continuous observations of $PM_{2.5}$ and PM_{10} using the MARGA at the UK EMEP 'Supersite', Auchencorth Moss, SE Scotland. Auchencorth Moss was found to be representative of a remote European site with average total water soluble inorganic mass of $PM_{2.5}$ of 3.82 µg m^{-3}. Anthropogenically derived secondary inorganic aerosols (sum of NH_4^+, NO_3^- and nss-SO_4^{2-}), were the dominating species (63%) of $PM_{2.5}$. In terms of equivalent concentrations, NH_4^+ provided the single largest contribution to $PM_{2.5}$ fraction in all seasons. Sea salt was the main component (73%) of the PM_{coarse} fraction (PM_{10}-$PM_{2.5}$), though NO_3^- was also found to make a relatively large contribution to the measured mass (17%) providing evidence of considerable processing of sea salt in the coarse mode. There was on occasions evidence of aerosol from combustion events being transported to the site in 2012 as high K^+ concentrations (deviating from the known ratio in sea salt) coincided with increases in black carbon at the site. Pollution events in PM_{10} (defined as concentrations >12 µg m^{-3}) were on average dominated by NH_4^+ and NO_3^-, where as smaller loadings at the site tended to be dominated by sea salt. As with other Western European sites, the charge balance of the inorganic components resolved were biased towards cations, suggesting the aerosol was basic or more likely, that organic acids contributed to the charge balance. This study demonstrates the UK background atmospheric composition is primarily driven by meteorology with sea salt dominating air masses from the Atlantic Ocean and the Arctic, whereas secondary inorganic aerosols tended to dominate air masses from continental Europe.

1 Introduction

Gravimetric methods have long been used to monitor the long-term trends of the bulk aerosol mass contained in particulate matter (PM) with an aerodynamic diameter of less than 2.5µm or 10 µm (i.e. $PM_{2.5}$ and PM_{10}); however, these generally provide no information on the chemical speciation of the aerosol. Off-line chemical analysis after capture of aerosol on filters by high or low volume filter samplers (e.g. Partisol Sampler; Thermo Fisher Scientific, Inc.) is quite widely used but limited to daily or lower frequency measurements and therefore poorly captures diurnal patterns caused, e.g. by changes in emission and gas-aerosol partitioning. It is important to understand the composition and the role of aerosols as they can have a direct and indirect effect on climate. The current level of scientific understanding for aerosol properties in terms of their role in the climate system is low and recently it has been suggested that the major component of the uncertainty globally is with the biogenic fraction (Carslaw et al., 2013). As well as having an impact on climate, aerosols affect both environment and human health. Recent epidemiological research has suggested that health effects of aerosol may be less closely linked to the total mass of $PM_{2.5}$ or PM_{10} than to the physicochemical characteristic of the aerosol, however there is still much to be understood (Fuzzi and Gilardoni, 2013). Establishment of epidemiological links to individual aerosol chemical compounds is hampered by a lack of available measurements.

In addition, secondary aerosols and their precursor gases are required to be monitored to understand atmospheric processes and to validate chemical transport models, which are used to inform policy, such as the UNECE Convention for Long-range Transboundary Air Pollution (CLRTAP), and the revised European Air Quality Framework Directive (Directive 2008/50/EC) where the measurement of aerosol chemical composition is statutory. In addition, prior to 2008, EU member countries were fined for exceeding the total $PM_{2.5}$ and PM_{10} limits set in the directive, regardless whether the exceedance was due to anthropogenic or natural sources. In the current revised European Air Quality Framework Directive (Directive 2008/50/EC), countries are now allowed to subtract significant 'natural' contributions of aerosol from the total mass, if their contribution can clearly be quantified. This is important for large 'natural' pollution events, such as the long-range transport of Saharan dust which have been observed across Southern Europe and on occasions Northern Europe (Ansmann et al., 2003;Karanasiou et al., 2012). While many member countries have chosen to make daily filter measurements at a very few sites, the UK has opted for a strategy to combine a large number of sites that make monthly measurements (Tang et al., 2009) with a couple of 'supersites' that resolve hourly concentrations, as an optimum strategy for capturing the spatial and temporal variability.

Instrumentation has in the past decade become available for on-line monitoring of aerosol chemical composition, at varying levels of complexity. In particular, the wet chemistry MARGA instrument (Measurement of Aerosols and Reactive Gases Analyser, Metrohm Applikon B.V., NL) provides hourly measurements of water-soluble nitrate, chloride, sulphate, sodium, ammonium, potassium, magnesium and calcium (hereafter NO_3^-, Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} respectively) and in addition the gas phase basic and acid gases: ammonia, nitric acid, nitrous acid, hydrochloric acid and sulphur dioxide (hereafter NH_3, HNO_3, HONO, HCl, SO_2 respectively) (Makkonen et al., 2012;Rumsey et al., 2014;ten Brink et al., 2009), based on aerosol collection via a steam-jet aerosol collector (SJAC; (Khlystov et al., 1995)). Other similar IC based systems are available, including the Ambient Ion Monitor – Ion Chromatograph system (AIM- IC, URG Corp and Dionex Inc) (Markovic et al., 2012) as well as the Particle into Liquid Sampler with Ion Chromatography (PILS-IC, Metrohm AG, Herisau, Switzerland), and a range of custom-built wet-chemistry instruments based on the Particle Into Liquid Sampler (Weber et al., 2001).

In parallel, there has been progress in developing monitoring instruments based on aerosol mass spectrometry. While there are now some studies using the standard Aerosol Mass Spectrometers (AMS; Aerodyne Research Inc, USA) for long-term measurements, a simplified version, the Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Inc), is being installed at supersites globally (Ng et al., 2011). Both AMS and ACSM currently measure an aerosol fraction that is close to PM_1 although work is in progress to extend this to $PM_{2.5}$. While SJAC and PILS based instruments measure water soluble aerosol components, similar to the filter-pack reference method, the mass spectrometer detects the aerosol components that volatilise efficiently at ≈ 600°C, which has the advantage of also characterising the organic fraction of the aerosol, whereas it does not efficiently quantify the refractory chemical components such as sea salt and crustal aerosol.

A dual MARGA system measuring both PM_{10} and $PM_{2.5}$ has been in operation at Auchencorth Moss, South East Scotland since June 2006 as part of measurements being made by the UK Department for Environment, Food and Rural Affairs (Defra) air quality monitoring network (http://uk-air.defra.gov.uk/). To our knowledge the Auchencorth Moss MARGA is the longest known quasi-continuous operation of a dual MARGA system to date. Auchencorth Moss has been developed as a Level II/III 'supersite' within the European Monitoring and Evaluation Program (EMEP) (Aas et al., 2012). EMEP monitoring sites feed into the EMEP database which serves to underpin the organisation's modelling and policy role to provide governments information on the deposition and concentration of air pollutants, and long-range transport of air pollutants (Tørseth et al., 2012;UNECE, 2004).

The following study focuses on the first 6.5 years of data (1st June 2006 to 1st January 2013) from Auchencorth Moss, in conjunction with co-located measurements and air mass back trajectories. Daily, seasonal and annual variation of inorganic aerosol species and the influences of long-range transport for this remote rural site are discussed. The trace gases measured concurrently with the aerosol composition and gas/aerosol partitioning are described in a companion paper (Twigg et al., in preparation).

2 Methodology

2.1 Field site description

Auchencorth Moss, South East Scotland (55°47'36" N, 3°14'41" W), is an ombotrophic mire with an extensive fetch at an elevation of 270 m, lying 18 km SSW of Edinburgh, and can be categorised as a transitional lowland raised bog. The moss is extensively grazed by sheep all year round with < 1 sheep ha^{-1}. Under the European Environment Agency classification scheme, the site is classed as a rural background site (Larssen et al., 1999). This has recently been confirmed by Malley et al. (2014) who demonstrated that the site was remote in the context of O_3 measurements at EMEP stations.

The meteorology is typical of a temperate system in the north of the UK. A summary of the meteorological conditions from June 2006 to the end of December 2012 can be found in Table 1. During 2010 atypical low rainfall was observed, however an additional 588 mm of precipitation fell as snow. Annual windroses for 2006 -2012 (Figure 1) show that the field site is dominated by a SW wind with a secondary NE flow occurring also.

Auchencorth Moss has been a long-term monitoring site for a number of trace gases including NH_3, SO_2 and CO_2 (Famulari et al., 2010;Drewer et al., 2010;Flechard and Fowler, 1998). The site belongs to a number of UK national networks including: UK Defra Automatic urban and rural network (AURN), UK Acid gas and aerosol network (AGANet), UK National Ammonia Monitoring Network (NAMN), UK Precip-Net (two-weekly bulk composition), UK PAH Network, UK Automatic Hydrocarbon Monitoring Network, UK Black Carbon Network and UK Toxic organic micropollutants (TOMPS) network. Details of the networks can be found on the Defra website (http://uk-air.defra.gov.uk/networks/site-info?site_id=ACTH). The site is also a European 'Supersite' within the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) (Tørseth et al., 2012), as well as one of 9 sites within the EU FP7 ÉCLAIRE project (http://www.eclaire-fp7.eu/) and a TransNational Access (TNA) site within the European FP7 Infrastructure Network ACTRIS (Aerosol, Clouds, and Trace gases Research InfraStructure Network). It was a Level 3 site within the EU FP6 NitroEurope IP (Sutton et al., 2007). In 2014, it became a World Meteorological Organisation Global Atmosphere Watch (WMO GAW) regional site.

2.2 MARGA instrument

The MARGA 2S system (Metrohm Applikon B.V. Schiedam, NL) consists of two sampling boxes and utilises ion chromatography to analyze for a range of water soluble trace gases and aerosols. The MARGA 2S was set up to measure both PM_{10} and $PM_{2.5}$ aerosol. Air is first drawn through a common PM_{10} Teflon coated inlet (URG Corporation, Chapel Hill, NC, USA) at 3.55 m. above ground level into a 0.89 m long polyethylene (PE) 14 mm ID inlet line, which is housed in the centre of an 11 cm OD polyvinyl chloride (PVC) conduit. The conduit has an extractor fan at the base to draw air through based on the design used by Trebs et al. (2004) aimed at keeping the sample at the temperature of the measurement height for as long as possible. The PE tubing entering the air conditioned cabin (21°C) is split into two ¼" PE sample lines (0.4 m). The first line feeds directly into the first sampling box and the second sampling line goes through a further $PM_{2.5}$ cyclone (URG Coporation, Chapel Hill, NC, USA) before the second sampling box. The flow rate in each sampling box is regulated to a volumetric flow of 1 m^3 hr^{-1} using a mass flow controller downstream of the sampling box. In the sampling box air passes through a horizontal annular wet rotating denuder (WRD) (Keuken et al., 1988). The WRD is continuously coated with a thin film of solution which strips water soluble gases from the laminar air stream; the addition of 10 ppm H_2O_2 acts as a biocide and also promotes oxidation of SO_2 initially trapped as HSO_3^- through to SO_4^{2-}. Water soluble aerosols do not diffuse into the stripping solution due to their lower diffusion velocity. The air flow then enters a steam jet aerosol collector (SJAC). The steam in the SJAC promotes rapid growth of water soluble aerosols which are then separated out from the air flow mechanically in a cyclone. Details of the principles of the SJAC are described by Khlystov et al. (1995). The sampling solutions are continuously drawn from the WRDs and SJACs to the analyzer box at a rate of 25 ml hr^{-1} using syringe pumps. Samples are then analysed online by anion and cation chromatography (Metrohm AG, Herisau, Switzerland). The system is continuously calibrated by mixing the sample with a 325 mg/L internal standard of LiBr, prior to injection into the IC columns. Anions are concentrated on a Metrosep A PCC 1 HC IC Preconcentration column (2.29 ml) and then separated using a Metrosep A Supp 10-75 column (75 mm x 4.0 mm) using a 7 mmol l^{-1} Na_2CO_3 /8 mmol l^1 $NaHCO_3$ eluent. Cations are concentrated on a Metrosep C PCC1 HC IC Preconcentration column (3.21 ml) and separated using a Metrosep C4 (100mm x 4.0mm) cation column. A 3.5 mmol l^{-1} methanesulfonic acid (MSA) eluent was used for the cation column, rather than the recommended 3.2 mmol l^{-1} HNO_3 eluent used in other similar systems. This was in order to eliminate a potential NO_3^- artefact, which has been reported (ten Brink et al. (2009); Makkonen et al. (2012)). For the anion column a 1M H_3PO_4 solution was used for chemical suppression. Detection was by conductivity, where concentrations were calculated based on their specific conductivities relative to the internal standard ions (Li^+ and Br^-). These standard set-up conditions and all significant operational changes over the 6.5 years, which could be considered to have affected performance or data capture, are summarised in Table 2. The increase in diameter of the SJACs described in table 2, reduced the restriction in maintaining a flow rate, which was mass flow controlled at 1 m^3 hr^{-1} at standard temperature and pressure (STP) until November 2011, whereas thereafter it was controlled to keep the volumetric flow rate at ambient temperature and pressure through the size cuts constant.

The performance of the MARGA has been further discussed by Rumsey et al. (2014);Makkonen et al. (2012);ten Brink et al. (2009);Cowen et al. (2011). The deployment of pre-concentration columns sets our MARGA instrument aside from the others, with the exception of Makkonen *et al.* (2014), allowing quantitative detection of the low concentrations encountered at this clean Scottish site.

Quality analysis and quality Assurance

As discussed previously the MARGA used in this work was one of the first to be field deployed. Processes were developed over the first several years which could be used to identify potential sources of error or contamination in the MARGA data. Firstly, periodic field blanks were carried out until 2011 by installing Whatman HEPA filters placed in front of the denuders and left on for ~24 hours. The filters removed aerosols but not the gas phase components from the air stream. The resultant change in PM concentrations allowed a blank value for the PM analytes to be assessed. Following the upgrade of the instrument in November 2011 (Table 2), automated monthly blanks were implemented in 2012, where the air pump and SJAC water supply and heaters were turned off, allowing for blanks for both aerosol and gas phase to be carried out. The blanks were not used to correct the data as they were usually below the detection limit (DL) of the instrument. Instead blanks were used to provide evidence of contamination in the system and to identify periods to be removed in the data ratification process. Prior to 2012 verification and instrument maintenance protocols has been experimental and the authors are in the process of finalising the protocols including calibration, which will be published separately. There was a step change in 2012, when the initial developmental protocols for maintenance were replaced by final protocols including quarterly replacement of inlets, cleaning of PM_{10} head and $PM_{2.5}$ cyclone, monthly air flow calibrations and independent analysis of internal standards by a UKAS accredited laboratory.

In the data ratification process values reported as 0 $\mu g\ m^{-3}$ were replaced with half the detection limit (DL). The method to determine the DL has changed over the 6 year period. From 2002 to 2011, the DL was taken as the average of the reported values below the manufacturers published DL. From 2012, the DL was calculated by the analysis of the logarithmic distribution of the measurements previously described by Kentisbeer et al. (2014), presented in table 3. The methodology for analysing the DL and calibrating this type of on-line IC instrument is an area of research in of itself and we plan to publish separately on this aspect of the MARGA operation.

2.3 Back trajectories and associated analysis

To relate the aerosol species to air masses, back trajectory analysis was carried out. Four-day back trajectories at 3 hour intervals for Auchencorth Moss were obtained for the years 2007 to 2012 through the OpenAir software package (Carslaw, 2013), which calculates back trajectories with the HYSPLIT Trajectory Model (Hybrid Single Model Lagrangian Integrated Trajectory Model,(Draxler and Hess, 1997) using Global NOAA-NCEP/NCAR reanalysis data. A cluster analysis was then carried out using a routine in the OpenAir software, where data were clustered using a distance matrix, in this case according to the similarity of the angle from their origin. Further details of the calculations of the cluster analysis can be found in Carslaw (2013).

3 Results and Discussion

3.1 Overview

Table 4 summarises the annual data capture statistics for each compound. The Auchencorth MARGA was one of the first long-term field deployment of the MARGA instrument. Through troubleshooting and instrument improvements the data capture improved over the period reported with a highest data capture of 64% (average overall) in 2012. Though not reported here, data capture for 2013 is on average 83% for ratified data (http://uk-air.defra.gov.uk/). As seen in Table 4, Auchencorth Moss being a rural to remote site, the aerosol concentrations were low as there are no large local point pollution sources in the dominant SW wind direction.

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3.2 Concentration trends from June 2006 to December 2012

The annual average concentrations from June 2006 to December 2012 are summarised in Table 4. Overall, the concentrations of individual species were generally low (< 1.5 µg m^{-3}). When compared with speciated PM$_{2.5}$ measurements from a background site in the Midlands, UK (Harrison and Yin, 2010), Cl$^-$ concentrations were higher at Auchencorth Moss based on annual averages (Table 4) but are in a similar range to other UK sites (Abdalmogith and Harrison, 2006). The average annual concentration of NO$_3^-$ and SO$_4^{2-}$ in the PM$_{10,}$ on the other hand, were

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larger in other parts of the UK including the other rural EMEP supersite at Harwell (Harrison and Yin, 2010;Abdalmogith and Harrison, 2006). The maximum concentrations of the aerosol components, however, show that there were periods where large PM pollution events took place, which are hypothesised to have been due to long-range transport of polluted air masses. In both the $PM_{2.5}$ and PM_{10}, the largest concentrations of NH_4^+ and NO_3^- were recorded during 2012, SO_4^{2-} maximum concentrations were observed in 2007 and other species varied (Table 4). It is interesting that specific local events can be picked out from the data record, for example the maximum K^+ concentration in 2012 of 2.61 µg m^{-3} occurred at 00:00 GMT on the 06 November2012 - Guy Fawkes or "fireworks" night in the UK. The meteorological conditions that night were cool, with an average temperature of -0.1˚C at midnight and the wind direction was from the dominant wind sector (SW). An increase of K^+ is not unexpected as such an increase is reported to occur following firework events (Vecchi et al., 2008;Drewnick et al., 2006). This example illustrates the utility of the hourly composition measurements to understand specific atmospheric events.

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The monthly median concentrations for all 6.5 years are presented in Figure 2. There is a clear seasonal variation for Na^+ and Cl^- for all years, with the exception of 2009, with lower concentrations in the summer and higher concentrations in winter. This seasonality reflects higher average wind speeds in winter leading to more marine aerosol in the atmosphere, as previously observed at other sites in the UK, but for Cl^- is also consistent with increased NaCl reaction with HNO_3 which also peaks in summer. Of the secondary inorganic pollutants, NO_3^- shows individual peak concentrations only during the colder months, but not consistently while SO_4^{2-} and NH_4^+, do not have particularly strong annual variation. The largest monthly median concentration for NH_4^+ and NO_3^- was observed in March 2012. SO_4^{2-} on the other hand does not show the same feature; the maximum monthly concentrations were observed in July 2012.

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Comparing the average diurnal cycles for 2007 to 2012 (Figure 3) it is apparent that the contribution of PM_{coarse} is small compared with $PM_{2.5}$, where:

$$PM_{coarse} = PM_{10} - PM_{2.5} \qquad (1)$$

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PM_{coarse} is dominated by sea salt (Na^+ and Cl^-). In the fine fraction ($PM_{2.5}$) NH_4^+ aerosol dominates, as it is the major base in secondary inorganic aerosol (refer to Section 3.4). In the $PM_{2.5}$ there is a decrease of NO_3^- during the afternoon in all seasons, though this feature is strongest in winter. This behaviour is consistent with that previously reported from other North

European sites (Nemitz et al., in preparation) including Harwell (UK) (Revuelta et al., 2012), Cabauw (Netherlands) (Mensah et al., 2012), Melpitz (Germany) (Poulain et al., 2011) and SMEAR II (Finland) (Makkonen et al., 2012). It is assumed that the majority of fine NO_3^- will be in the form of NH_4NO_3 and that the relationship between the gas precursors, temperature, RH and chemical composition explain the observed cycle (see the discussion on gas concentrations at this site Twigg et al. (in preparation)). Timonen et al. (2011), who had also reported a decrease of daytime NO_3^- in Helsinki, explained the decrease to be the result of increased boundary layer mixing as the same feature was observed in black carbon. At Auchencorth Moss this behaviour of black carbon is not observed, instead the annual diurnal average shows an increase of black carbon during the day (Cape et al., 2012). It is therefore probable that diurnal variation in temperature and relative humidity exert a stronger influence on the $PM_{2.5}$ NO_3^- at this site than the depth of the mixing layer. $PM_{2.5}$ SO_4^{2-} at Auchencorth Moss, on the other hand, shows an increase in concentration during the day, with the feature strongest in the summer. The increase in SO_4^{2-} is interpreted to be the effect of stronger insolation in summer, which drives the oxidation of SO_2 to form sulphuric acid and finally SO_4^{2-}, due to the increase in OH radicals.

3.3 Ion Balance

The ion balance was calculated for $PM_{2.5}$ and PM_{coarse} for the year 2012. Figure 4a) and b) show the ion balance of the secondary inorganic species, while figs. 4c) and d) show the full ion balance of the measured species. In both the $PM_{2.5}$ and PM_{coarse} it is clear that though there is good correlation, there appears to be an excess of NH_4^+. This is not the first time excess NH_4^+ has been observed in aerosol measurements (Mensah et al., 2012). It is thought that water soluble organic acids such as oxalate may be the missing species to close the ion balance. Some of the Cl^- measured by the MARGA is likely to represent NH_4Cl which would affect the partial ion balance of Fig. 4a, but not the full ion balance of Fig. 4b. However, Aerosol Mass Spectrometer (AMS) measurements suggest that this contribution is negligible in S Scotland (Nemitz et al., in preparation). On the other hand, some of the NO_3^- in the partial ion balance is expected to represent $NaNO_3$, even in $PM_{2.5}$, and the excess NH_4^+ may be even larger than suggested by Figure 4a. Makkonen et al. (2012) observed that in Finland the ion balance was seasonal, with acidic aerosol in winter and a basic ion balance in spring. This seasonal trend was not observed at Auchencorth Moss, with the average seasonal ion balance always basic (i.e. excess NH_4^+) in character and is consistent with AMS measurements, that have

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demonstrated that in Europe acidic aerosol is only found in NE, E and S Europe, while there is always excess ammonia in NW and W Central Europe (Nemitz et al., in preparation;Morgan et al., 2010).

3.4 Sea salt and sea salt processing

An overview of the average inorganic $PM_{2.5}$ and PM_{coarse} composition based on mass is presented in Figure 5. Sea salt is presented as the individual species of measured Na^+, sea salt Cl^- ($ssCl^-$), sea salt SO_4^{2-} ($ssSO_4^{2-}$) sea salt Mg^{2+} ($ssMg^{2+}$), sea salt Ca^{2+} ($ssCa^{2+}$) and sea salt K^+ (ssK^+), which were calculated based on the known mass ratio to Na^+ in sea water (Seinfeld and Pandis, 2006):

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$$[ssCl^-] = 1.8 \times [Na^+] \qquad (2)$$

$$[ssSO_4^{2-}] = 0.252 \times [Na^+] \qquad (3)$$

$$[ssMg^{2+}] = 0.12 \times [Na^+] \qquad (4)$$

$$[ssCa^{2+}] \text{ or } [ssK^+] = 0.04 \times [Na^+] \qquad (5)$$

As would be expected, the dominant fraction of the coarse aerosol at this site is from sea salt (73%); this is larger than reported at other European sites such as SMEAR III, near Helsinki (Makkonen et al., 2012), probably because of proximity to the ocean in all wind directions. There is also a large contribution from NO_3^- in the coarse fraction. This is not the first time that a large proportion of NO_3^- has been reported in the coarse mode; the same was observed in Melpitz, Germany and has been explained to be the result of chloride-nitrate exchange that takes place on coarse aerosol during long range transport of sea salt (Spindler et al., 2012;Dasgupta et al., 2007). This was further evident as the average non-sea salt Cl^- mass was -0.17 µg m^{-3} and -0.08 µg m^{-3} for $PM_{2.5}$ and PM_{coarse} respectively, where:

$$\text{Non-sea salt } Cl^- = [Cl^-]_{measured} - [ssCl^-]_{calculated} \qquad (6)$$

To investigate the process of sea salt substitution by reaction with HNO_3 further, the ratios of Na^+ and Cl^- were compared with NO_3^- in the coarse mode for the year 2012. In general, larger NO_3^- concentrations tended to be observed on occasions where a depletion of Cl^- was observed, though this was not true for all cases (Figure 6).It should be noted, however, that the concentrations of PM_{coarse} are calculated as differences (Eq. 1) and therefore subject to considerable uncertainty.

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$PM_{2.5}$ on the other hand is dominated by the secondary inorganic aerosol (SIA) (NH_4^+, NO_3^- and SO_4^{2-}) (Figure 5), with a total contribution of 63% to the total measured mass by the MARGA, which is to be anticipated. NO_3^- is the dominant mass of the SIA at Auchencorth Moss accounting for 26% for the total water soluble species detected by the MARGA. A similar comparison has been carried out by a MARGA operated at SMEAR III (near Helsinki, Finland) where SO_4^{2-} was the dominating mass responsible for 50.4% of the total inorganic $PM_{2.5}$ mass reported by the MARGA (Makkonen et al., 2012). This is not surprising as it has also been shown by Nemitz et al. (in preparation), from AMS studies, that in Finland PM_1 is dominated by SO_4^{2-}, whereas in the UK and the rest of NW Europe, NO_3^- is the dominant SIA. Sea salt, however, still makes a considerable contribution (35%) to the average measured $PM_{2.5}$ by the MARGA, bearing in mind that the cut-off might have been somewhat larger than 2.5 µm until November 2011 (see above). In 2012, sea salt still made a major contribution to the total mass of the $PM_{2.5}$ (30%), where there is the greatest confidence in the cut-off of the cyclone. There was a clear increase of $PM_{2.5}$ Na^+ with wind speed for 2012 (Figure 7) in the dominant wind sector (refer to Figure 1), suggesting that $PM_{2.5}$ Na^+ was related to sea salt and its presence at the site is driven by meteorology.

Potassium (K^+) is present in sea salt and when the available 2012 $PM_{2.5}$ data was compared to the concentration of Na^+ it tended to follow the known ratio in sea water (Seinfeld and Pandis, 2006), Figure 8. The greatest deviation from this curve appears to be in periods of high black carbon (BC) concentrations. PM_{coarse} however had much scatter. High concentrations of black carbon are often associated with combustion processes, though K^+ can also occur as a product of other anthropogenic sources. There was clear evidence in the $PM_{2.5}$ that high concentrations of K^+ were associated with increased BC pointing to a contribution from combustion sources or biomass burning (Figure 8). The measured Mg^{2+} /Na^+ ratio in $PM_{2.5}$ followed the known ratio in sea water (Seinfeld and Pandis, 2006). The same comparison was done for PM_{coarse}, however there was much more scatter in the data.

3.5 Comparison of total inorganic aerosol with TEOM-FDMS measurements

The total average water-soluble inorganic aerosol mass measured by the MARGA for the period January 2007 to December 2012 was 3.82 µg m^{-3} and 5.04 µg m^{-3} for $PM_{2.5}$ and PM_{10}, respectively. The measured mass by the MARGA was compared to the Tapered Element Oscillating Microbalance Filter Dynamic Measurement System (TEOM-FDMS) which

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measures the total aerosol mass; total mass data were obtained from the AURN network (http://uk-air.defra.gov.uk/networks/network-info?view=aurn) for the 6 years of interest (2007 to 2012). It was found that the PM_{10} mass measured by the MARGA accounted for 78% of total PM_{10} measured by the TEOM-FDMS, on average. It is not the first time that inorganic water soluble aerosols have been found to be major contributors to the total mass in Europe (Putaud et al., 2010). Aerosol components not resolved by the MARGA include organic aerosols, BC, water and crustal elements such as silicate. Organic aerosol often accounts for a larger fraction of the PM_{10} mass at central European background sites than the missing mass at Auchencorth allows for. This is consistent with AMS measurements in S.Scotland that also indicate relatively low contributions from organic aerosol (Nemitz et al., in preparation).

Table 5 summarises the annual mass fraction that is accounted for by the MARGA instrument when compared with the TEOM-FDMS for both PM_{10} and $PM_{2.5}$. It is very clear that there are discrepancies between the measured $PM_{2.5}$ by the MARGA and that by TEOM-FDMS. Mass closure improved in 2012, probably in response to the improved flow control implemented in November 2011 on the MARGA (see above). An alternative explanation is that the PM concentrations at Auchencorth are close to the detection limits of the TEOM-FDMS, which is indicated by the large percentage of negative values reported by the instrument over the period January 2007 to December 2012 (26% and 10% respectively for $PM_{2.5}$ and PM_{10}), the annual variation of which can be found in Table 5. During the 6 years presented, the fraction of negative values for PM_{10} declined, while it stayed constant for $PM_{2.5}$. It therefore can be concluded that that the $PM_{2.5}$ TEOM-FDMS at Auchencorth Moss has an offset, as has previously been commented by Laxen et al. (2012). It is therefore not possible to comment on what the true contribution of the measured water soluble inorganic mass measured by the MARGA is to the total $PM_{2.5}$.

3.6 Influence of air mass on aerosol composition

Due to the remote location of the site, the origin of air masses at the site influences the aerosol composition. Back trajectories, run over a 96 hour period, were obtained at 3-hour intervals for the years 2007 to 2012, which were then clustered, details of which can be found in Section 2.3. Figure 9 displays the mean trajectory for each of the 6 clusters assigned. The average concentration over the 6 year period for each cluster and the % species contribution to the total measured concentration by the MARGA are summarised in Figure 10. When calculating the average associated with each cluster, data were only used when all species were available. As

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would be expected, the air masses from the Atlantic Ocean and the Arctic (clusters 1, 2 and 4) are dominated by Na^+ and Cl^- aerosol in PM_{coarse}. In the $PM_{2.5}$, the same clusters show a large contribution from Na^+ and Cl^-, with the largest contribution in the Atlantic air mass (Cluster 1). Air masses which go over land tend to have the greatest contribution from secondary inorganic aerosols, as seen in clusters 5 and 6. Air masses, in particular from continental Europe (Cluster 6), have the largest average molar concentrations of NH_4^+ and NO_3^-, even in the coarse fraction. The dominance of NO_3^- compared to SO_4^{2-} from air trajectories from continental Europe has previously been highlighted by Abdalmogith and Harrison (2005), who explained this to be the result of high NO_x/SO_2 emissions ratios in Western Europe.

3.7 Aerosol composition during high pollution events

In order to optimise emission controls for the protection of human health against high concentration episodes, it is important to know which chemical components dominate when air concentrations are large. Figure 11 shows the average relative aerosol contribution as a function of total aerosol concentration for 2012 as an example, together with the histogram of the frequency with which different aerosol concentrations occur. The period with the highest concentrations recorded at the site by the MARGA are dominated by secondary inorganic aerosols, in particular by NH_4^+ and NO_3^-, with a smaller contribution from SO_4^{2-}. This is not the first time that NO_3^- has been found to be a dominating species during pollution events in the UK. Vieno et al. (2014) reported NO_3^- as a dominating fraction during pollution events at a site (Bush) approximately 10 km NE from the Auchencorth Moss field site. They show that the NO_3^- during pollution events at this site arise from a combination of emissions from the UK and continental Europe, but that the relative importance depends on synoptic conditions and differs greatly between episodes with the UK contribution ranging from 35% and 80% (Vieno et al., 2014). The Auchencorth measurements demonstrate the importance of controlling the emissions of NH_4NO_3 precursor gas concentrations (NH_3 and NO_x) in both the UK and the rest of Europe for controlling the high pollution episodes.

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The concentration dependence of the relative aerosol composition (Figure 11) also shows that sea salt dominates the aerosol composition at moderate aerosol loading (2 to 12 µg m^{-3}) while the relative contribution of K^+ and Ca^{2+} increases at very low concentrations (<2 µg m^{-3}). Even under very clean conditions, there is a basic concentration of crustal material.

4 Summary and conclusions

The first six and a half years of chemically speciated $PM_{2.5}$ and PM_{10} measurements from the MARGA at Auchencorth Moss have been analysed. This study has provided greater detail in the long term temporal variations of inorganic species in the UK background atmosphere and confirmed the status of the field site as a background site in the European context, where concentrations of the inorganic species were low over the 6.5 years. The dynamic changes between air masses dominated by anthropogenic and natural sources is clearly observable on an inter-annual scale and continuation of these long term measurements will be a valuable resource to understand long term trends in PM composition in response to climate and policy drivers.

The average ion balance at this site was biased towards cations some of which would probably have been neutralised by organic acids such as oxalic acid. Additional studies to identify the missing water soluble species would therefore be beneficial at this site to close the ion balance. Comparison with the TEOM-FDMS bulk mass method found that the compounds resolved by the MARGA instrument accounted on average for 78% of the PM_{10} mass measured at Auchencorth Moss, with considerable uncertainty due to changes in the MARGA configuration over the period and the detection limits of the TEOM-FMDS and possible difference in the characteristics of the PM_{10} inlets. One recommendation is to add a continuous measurement of the organic aerosol mass at Auchencorth Moss to determine its contribution to the total mass, due to the regional importance of this site.

Based on monthly median concentration, Na^+ and Cl^- generally were found to vary seasonally due to the meteorology of the site, with the highest concentrations in winter when the average wind speed was greatest. As expected NH_4^+ dominated the finer $PM_{2.5}$ aerosol in terms of μmol m^{-3}, as it is the major base for aerosol in the atmosphere and free ammonia is always available in NW Europe. The influence of long-range transport at this site is evident, with sea salt dominating air masses originating from the Arctic and Atlantic Ocean, whereas SIA dominate air masses that originate over land, with largest contributions from continental Europe. It therefore supports the importance of a transboundary co-operation, in controlling precursor gases such as NO_x and NH_3 as highlighted in this long term study, where NH_4^+ and NO_3^- tended to be the drivers of the (regional) pollution events observed at this background site. The dominance of NO_3^- compared to SO_4^{2-} was evident too in the diurnal cycles, with the exception of summer and provides evidence of a shift in recent decades from sulphur to nitrogen driven chemical climate. The air quality implications of the NH_4^+ and NO_3^- predominance during high PM loading events provide insight for future mitigation of PM impacts. Additional studies of gas-to-particle conversions at this field site will help to understand sulphur-nitrogen budget and atmospheric chemical processing to form PM (Twigg et al., in preparation).

5 Acknowledgements

Back trajectories were calculated on the NOAA ARL Ready Website using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model (Draxler, R. R. and Hess, G. D.,2003, NOAA Air Resources Laboratory, Silver Spring, MD, USA). The authors would like to thank the following for funding this work: the UK Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations, through the projects “Operation and Management of the EMEP Supersite project” (AQ0618) and the “UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) project” (AQ0647). Auchencorth Moss is supported by the EU FP7 Infrastructure Project “ACTRIS”. Thanks go to Ms Margaret Anderson, Mr Ivan Simmons, Mr Frank Harvey, Dr Gavin J Phillips and Mr Robert Storeton-West for their assistance in the operation of the instrument.

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Table 1 Summary of metrological conditions for the period June 2006 to December 2012

Year	Total Rainfall (mm)	Air Temperature (°C)			Windspeed at 1 m (m s^{-1})		RH (%)	St (W m^{-2})
		Median	Min	Max	Median	Max	Mean	Mean
2006[a]	*740*	*11.2*	*-5.4*	*28.5*	*2.8*	*13.3*	*88.6*	*99.52*
2007	1124	7.8	-9.7	22.1	3.0	24.8	83.0	88.67
2008	1212	7.3	-8.4	23.2	2.9	24.3	84.4	84.91
2009	989	7.6	-9.0	27.5	3.0	12.2	84.8	92.92
2010	649	6.7	-12.0	24.6	2.7	11.6	83.9	92.39
2011	1101	8.4	-8.9	24.6	3.1	13.5	86.1	88.38
2012	1322	6.6	-8.3	23.3	2.8	16.8	88.1	83.63

[a] 2006 only includes data from the 01 June 2006 onwards. Key: RH- Relative Humidity, St – Total Solar Radiation.

Table 2 Summary of major operational changes which will have potentially affected the MARGA performance or data capture from June 2006 to December 2012

Date	Operation Change	Change to Performance
03/12/2008	Changed from Metrohm C2 column with 4 mM MSA eluent to Metrohm C4 column with a 3.5 mM MSA	Better separation of NH_4^+ and Na^+ peaks.
17/02/2009	SJACs were replaced with an increased internal diameter. Syringe valves increased from 0.6 mm to 0.8 mm i.d.	Improved accuracy in maintaining the cut-off for $PM_{2.5}$ and PM_{10}. Reduction in downtime due to blockages.
28/07/2009	Replaced glass fibre filters to PTFE Whatman Rezist 30 mm filter.	Glass fibre filters had a high Na^+ and SO_4^{2-} background and required rinsing prior to use.
29/07/2009	100 ppm H_2O_2 added to H_2O stripping solution	Prevents loss of NH_4^+ from bacteria by acting as a biocide. Converts HSO_3^- to SO_4^{2-}, resulting in better SO_2 recovery in the denuder.
09/02/2011	Reduced to 10 ppm H_2O_2 in stripping solution	Optimum concentration as a biocide, whilst preserving lifetime of the column.
17/11/2011	MARGA hardware and software upgrade.	Calibration of mass flow controllers can now be carried out in situ. Blanks and external standards can be set-up remotely.

Table 3 Annual average detection limits calculated using lograthimic profile for 2012

Component	DL
	μg m^{-3}
PM_{10}	
NH_4^+	0.062
Na^+	0.123
K^+	0.019
Ca^{2+}	0.016
Mg^{2+}	0.015
Cl^-	0.086
NO_3^-	0.105
SO_4^{2-}	0.349
$PM_{2.5}$	
NH_4^+	0.069
Na^+	0.106
K^+	0.014
Ca^{2+}	0.015
Mg^{2+}	0.007
Cl^-	0.053
NO_3^-	0.091
SO_4^{2-}	0.242

Table 4 Annual concentrations of both PM_{10} and $PM_{2.5}$ species measured by the MARGA system at Auchencorth Moss from 1st June 2006 to 1st January 2013. (* 2006 data coverage: June – December 2006 only) Key: μ_A – arithmetic mean, μ_G – median, Max – maximum, σ_A – arithmetic standard deviation, DC – data capture (%).

	2006*					2007					2008					2009					2010					2011					2012				
	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC
$PM_{2.5}$	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	%	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	%	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	%	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	%	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	%	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	%	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	%
NH_4^+	0.93	0.36	6.86	1.23	18.08	0.72	0.21	8.30	1.21	35.99	0.61	0.20	12.35	1.23	36.15	0.77	0.36	12.90	1.24	49.10	0.79	0.36	9.14	1.08	46.02	0.64	0.28	6.81	0.95	25.58	0.89	0.35	14.66	1.46	63.90
Na^+	0.26	0.15	3.36	0.36	38.29	0.37	0.26	7.28	0.48	32.39	0.43	0.27	8.55	0.61	34.71	0.70	0.44	7.87	0.91	48.97	0.29	0.18	3.97	0.32	38.28	0.44	0.29	4.02	0.43	24.11	0.48	0.33	2.78	0.43	65.01
K^+	0.05	0.04	0.55	0.04	37.59	0.06	0.04	0.50	0.05	27.61	0.10	0.04	1.05	0.13	35.63	0.19	0.06	3.33	0.53	49.11	0.04	0.03	1.79	0.05	46.14	0.05	0.02	0.45	0.09	25.82	0.05	0.04	1.05	0.04	66.75
Ca^{2+}	0.07	0.03	0.73	0.11	37.11	0.09	0.08	1.61	0.07	36.38	0.11	0.09	1.39	0.08	37.42	0.12	0.07	3.70	0.21	49.09	0.06	0.05	1.84	0.06	46.18	0.05	0.03	0.49	0.05	25.91	0.05	0.04	0.54	0.03	66.55
Mg^{2+}	0.04	0.03	0.22	0.02	38.29	0.08	0.06	1.55	0.07	36.38	0.05	0.03	0.61	0.06	37.36	0.06	0.04	0.38	0.05	48.70	0.04	0.03	1.28	0.05	46.18	0.04	0.02	0.41	0.04	25.91	0.04	0.02	0.31	0.04	66.56
Cl^-	0.47	0.41	3.53	0.51	38.68	0.59	0.38	9.66	0.75	32.55	0.68	0.38	8.91	0.92	31.55	0.59	0.41	4.56	0.60	18.77	0.56	0.38	6.49	0.64	33.79	0.72	0.38	10.23	0.92	26.85	0.61	0.30	6.18	0.75	53.85
NO_3^-	1.32	0.79	12.05	1.63	22.81	1.20	0.36	16.12	2.12	37.72	0.98	0.30	20.60	2.11	38.73	1.11	0.35	29.31	2.88	39.93	1.18	0.37	20.18	2.19	38.05	0.91	0.40	15.02	1.61	28.52	1.54	0.43	32.75	3.20	59.23
SO_4^{2-}	1.46	0.74	15.87	2.05	39.19	0.81	0.44	34.27	1.09	37.73	1.01	0.56	18.63	1.40	38.88	1.22	0.89	15.36	1.31	39.89	0.97	0.66	10.53	1.00	38.11	1.11	0.76	7.75	1.05	28.53	1.21	0.77	11.39	1.25	59.22
PM_{10}																																			
NH_4^+	0.97	0.43	6.66	1.19	17.76	0.98	0.33	16.88	1.54	47.96	0.57	0.20	14.47	1.11	31.66	0.76	0.38	13.59	1.29	49.32	0.81	0.41	9.33	1.11	44.92	0.64	0.34	8.41	0.90	34.01	0.98	0.35	19.51	1.75	66.80
Na^+	0.48	0.32	8.05	0.57	43.71	0.62	0.36	9.58	0.76	45.81	0.62	0.36	13.88	0.95	31.57	0.90	0.64	14.17	0.88	48.90	0.55	0.35	11.14	0.70	39.01	0.57	0.37	4.94	0.62	32.61	0.84	0.63	4.98	0.74	67.96
K^+	0.04	0.03	0.36	0.03	43.09	0.06	0.05	0.54	0.05	40.19	0.07	0.04	0.95	0.09	32.70	0.16	0.08	2.67	0.32	49.27	0.05	0.04	2.29	0.06	45.08	0.04	0.02	2.17	0.06	34.09	0.07	0.06	2.61	0.07	70.33
Ca^{2+}	0.06	0.03	0.99	0.09	43.16	0.11	0.08	0.84	0.09	47.93	0.18	0.15	1.06	0.12	32.67	0.18	0.09	3.16	0.42	49.19	0.09	0.07	2.06	0.09	44.84	0.06	0.02	0.80	0.08	33.93	0.06	0.05	1.22	0.07	70.11
Mg^{2+}	0.04	0.03	0.50	0.04	43.71	0.10	0.07	2.14	0.10	48.30	0.07	0.05	0.78	0.07	32.70	0.10	0.07	0.71	0.11	47.77	0.06	0.05	1.59	0.07	44.57	0.05	0.02	0.54	0.07	34.09	0.06	0.04	0.52	0.07	70.14
Cl^-	0.70	0.49	7.40	0.86	42.35	0.95	0.55	11.57	1.17	44.14	1.08	0.59	12.65	1.44	33.20	0.97	0.60	7.32	1.06	20.21	1.05	0.67	8.46	1.20	34.51	1.04	0.51	10.25	1.31	35.92	1.11	0.54	8.87	1.38	55.73
NO_3^-	1.92	1.43	12.58	2.13	21.27	1.55	0.56	31.60	2.48	48.52	1.18	0.38	24.42	2.48	37.17	1.24	0.43	30.65	2.93	41.04	1.31	0.47	21.40	2.32	37.88	1.07	0.49	15.95	1.68	37.42	1.86	0.55	50.15	3.81	60.73
SO_4^{2-}	1.65	0.91	16.01	2.09	42.79	1.19	0.61	33.98	1.70	48.73	1.01	0.68	11.86	1.07	37.19	1.30	0.92	18.79	1.39	41.22	0.99	0.72	12.57	0.99	37.79	1.03	0.77	8.07	0.88	37.41	1.43	0.89	12.75	1.55	60.74

Table 5 Measured MARGA mass vs TEOM-FDMS mass and the percentage of time the TEOM FDMS reported values ≤ 0 µg m^{-3} for the years 2007 to 2012.

Year	**PM_{10} unaccounted (%)**	**$PM_{2.5}$ unaccounted (%)**	**PM_{10} measured by TEOM-FDMS - Reported values ≤ 0 µg m^{-3} (%)**	**$PM_{2.5}$ measured by TEOM-FDMS - Reported values ≤ 0 µg m^{-3} (%)**
2007	21	-15	14	25
2008	23	-38	10	25
2009	29	-48	7	28
2010	28	-27	6	17
2011	32	-20	9	26
2012	18	-9	3	20

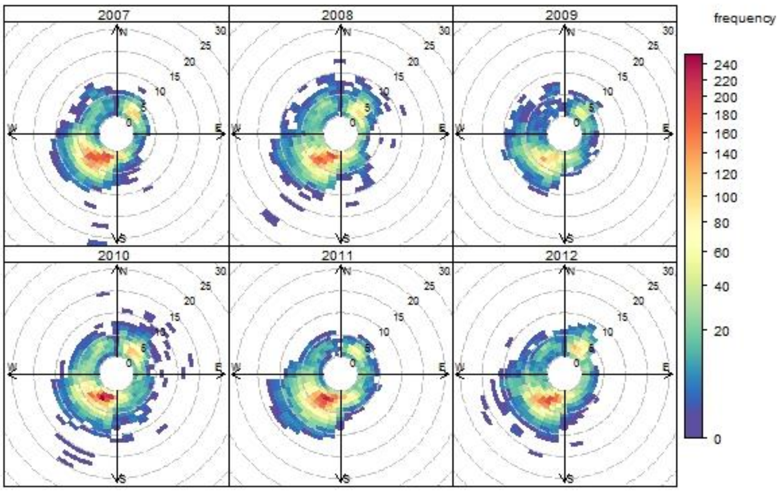

Figure 1 Frequency plots of wind direction and windspeed (m s^{-1}) averaged over an hour at Auchencorth Moss for the years 2007 to 2012. Windspeed scale is limited to 30 m s^{-1}. (Graphs produced using OpeAir;Carslaw and Ropkins (2012))

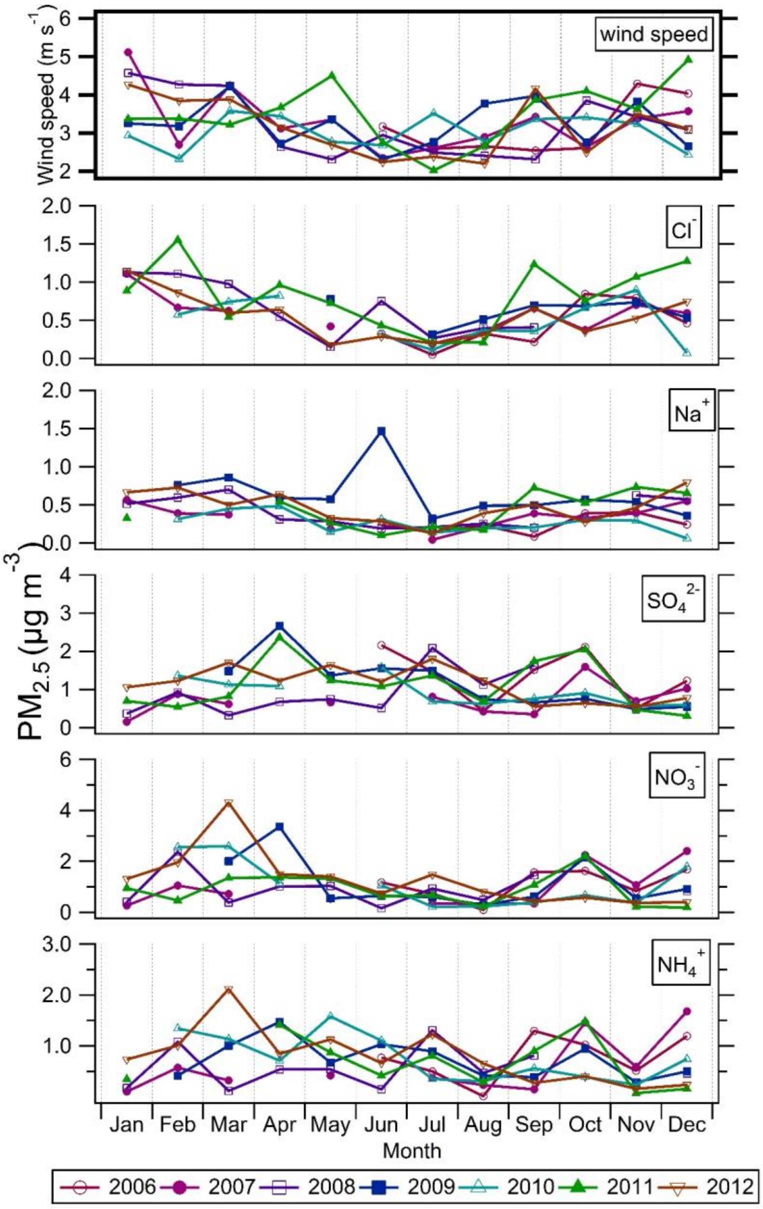

Figure 2 a) Median monthly mass concentrations of $PM_{2.5}$ species measured by the MARGA and median wind speed from June 2006 to December 2012

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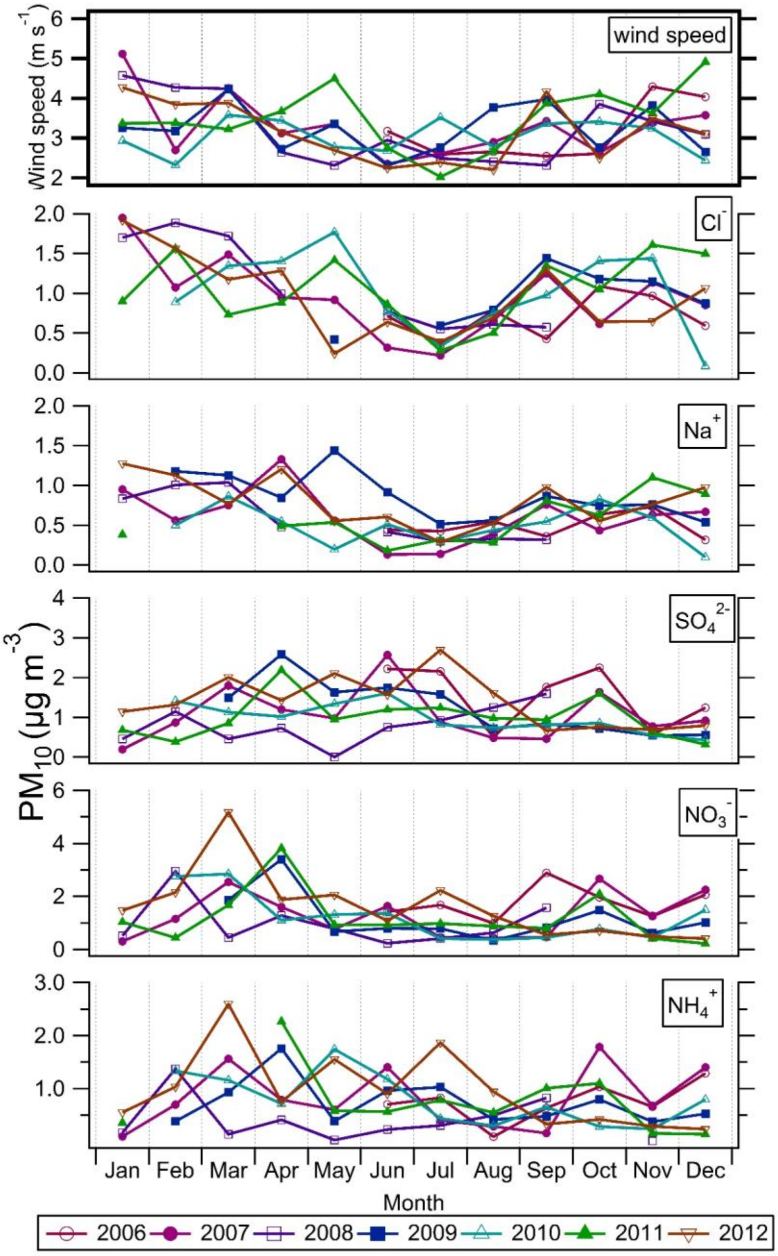

Figure 2b) Median monthly mass concentrations of PM$_{10}$ species measured by the MARGA and median wind speed from June 2006 to December 2012

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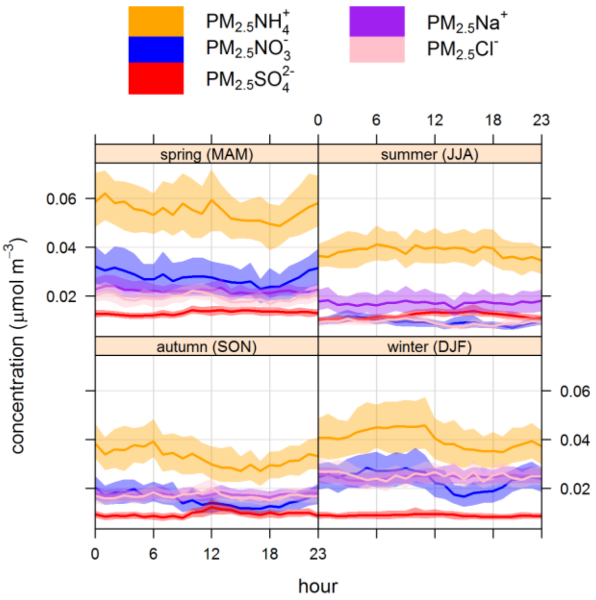

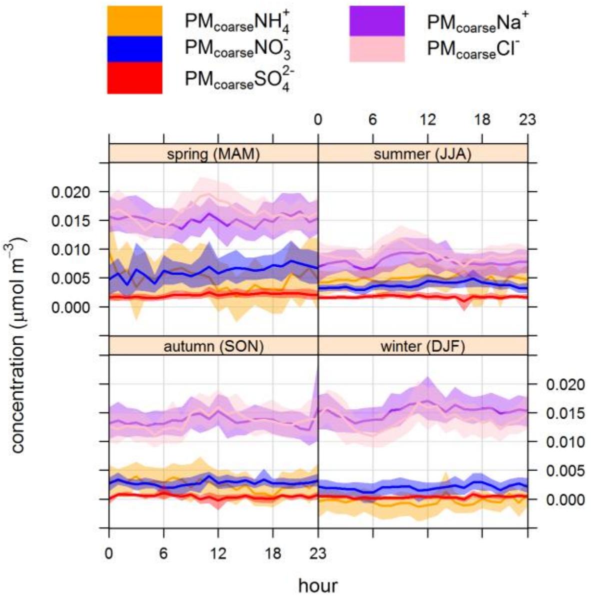

Figure 3 Median seasonal diurnal cycles of molar concentrations of PM$_{2.5}$ and PM$_{coarse}$ NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, Na$^+$ and Cl$^-$ using data from January 2007 to December 2012, with the shading

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showing the 95% confidence level of the median. (Graphs produced using Open air; Carslaw and Ropkins (2012)).

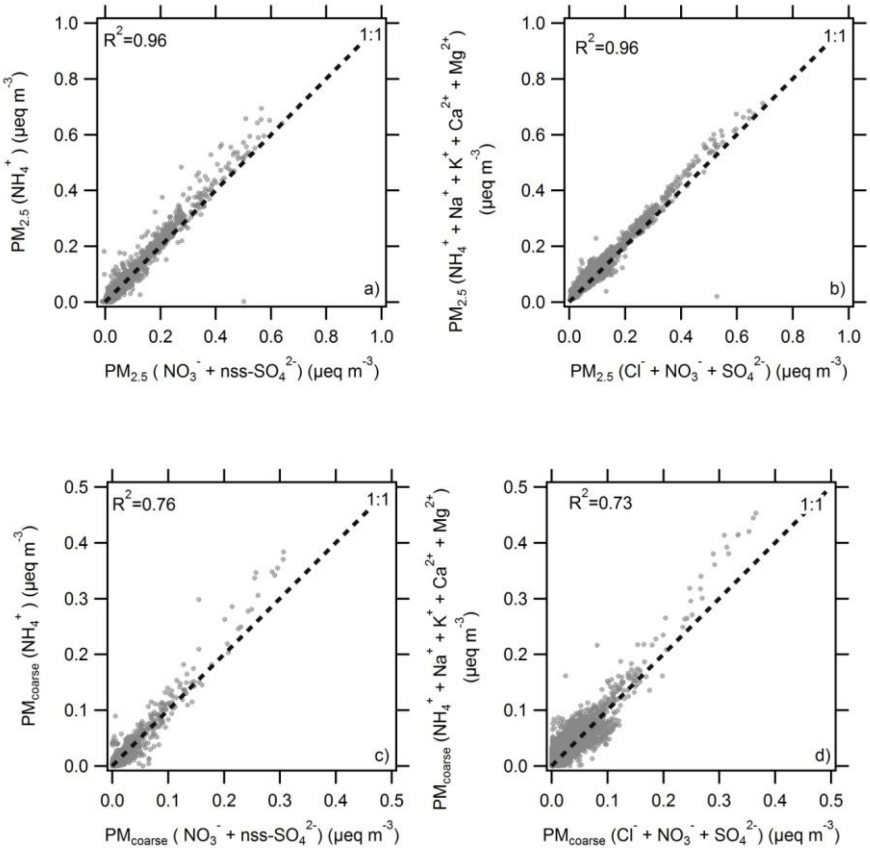

Figure 4. Measured ion balance for the year 2012 in microequivalents m^{-3}. a) Neutralisation of PM$_{2.5}$ NH$_4^+$ by PM$_{2.5}$ nss-SO$_4^{2-}$ and PM$_{2.5}$ NO$_3^-$, b) Ion balance of measured PM$_{2.5}$ anions (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) and measured PM$_{2.5}$ cations (NH$_4^+$, Na$^+$, K$^+$, Ca^{2+}and Mg^{2+}), c) Neturalisation of PM$_{coarse}$ NH$_4^+$ by PM$_{coarse}$ nss-SO$_4^{2-}$ and PM$_{coarse}$ NO$_3^-$, d) Ion balance of measured PM$_{coarse}$ anions (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) and measured PM$_{coarse}$ cations (NH$_4^+$, Na$^+$, K$^+$, Ca^{2+}and Mg^{2+}).

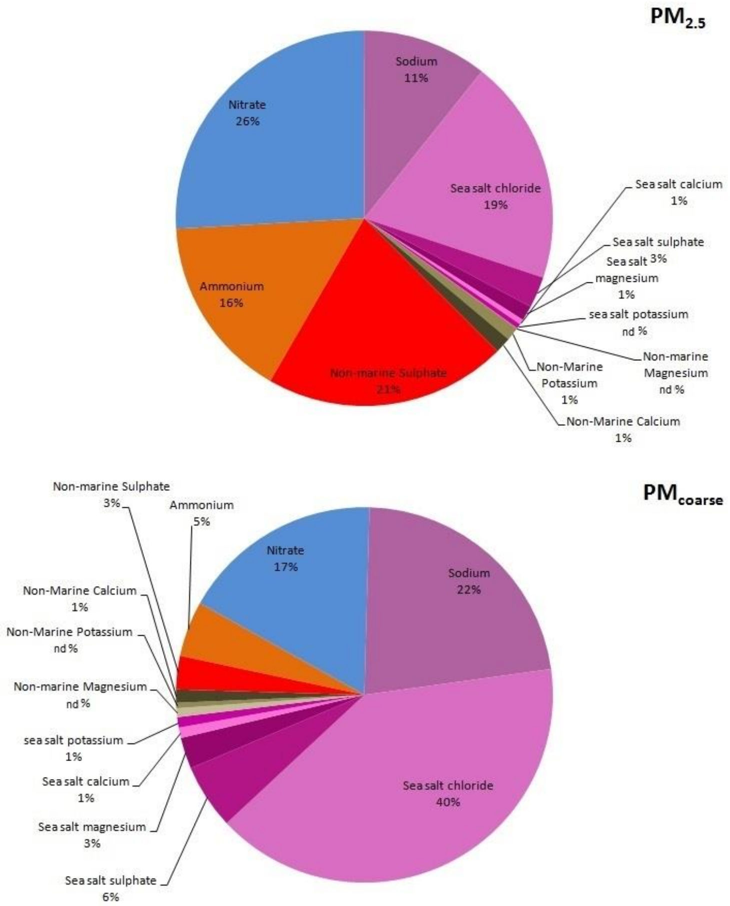

Figure 5 Average composition by mass of the water soluble inorganic aerosol fraction measured by the MARGA from January 2007 to December 2012 in both the $PM_{2.5}$ and PM_{coarse}. Sea salt chloride, sulphate, magnesium, calcium and potassium were derived based on the known mass ratios to Na^+ in sea water, refer to Eqs. 2 to 5. Key: nd – not detected.

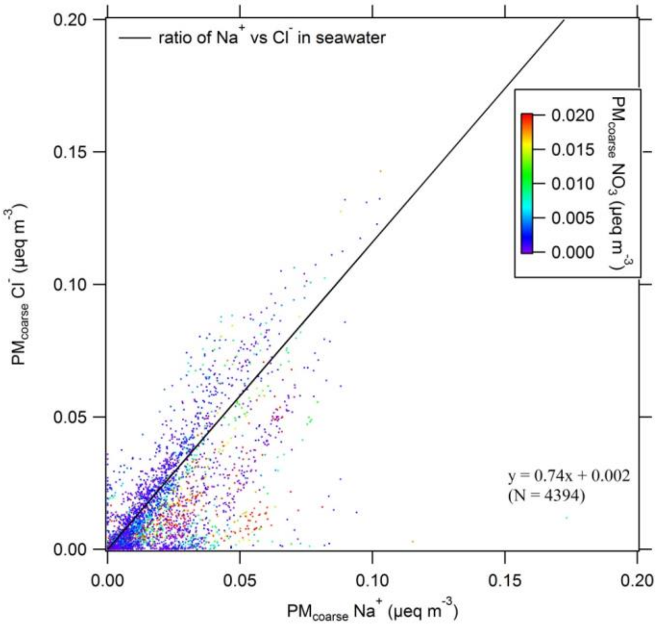

Figure 6. Demonstration of the depletion of Cl$^-$ for the year 2012 as a result of Cl$^-$ - NO$_3^-$ interactions during long-range transport for coarse aerosol. The black line is the known ratio of Cl$^-$ to Na$^+$ in seawater (Seinfeld and Pandis, 2006). Colour scale is set to 0 to >0.2 µeq m-3 NO$_3^-$ to focus in on the depletion of Cl$^-$ at high NO$_3^-$ concentrations.

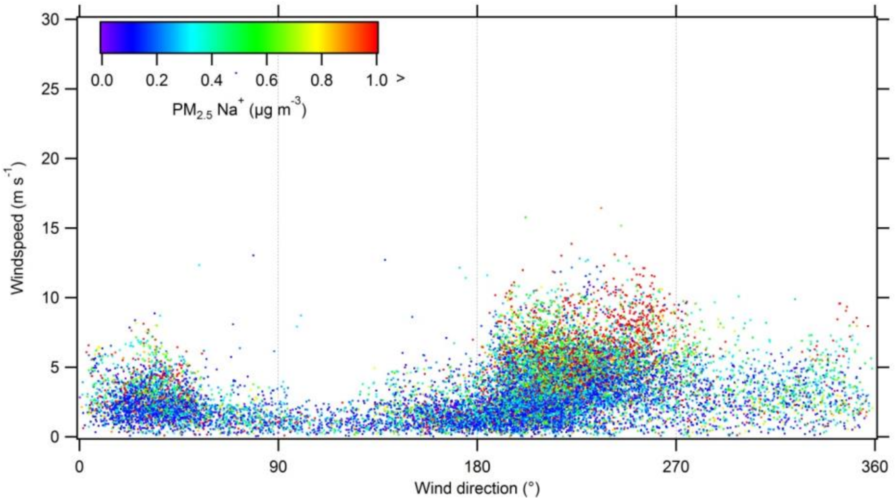

Figure 7 The influence of wind direction and wind speed on the concentration of PM$_{2.5}$ Na$^+$ at Auchencorth Moss from the 1 January 2007 to 1 January 2013.

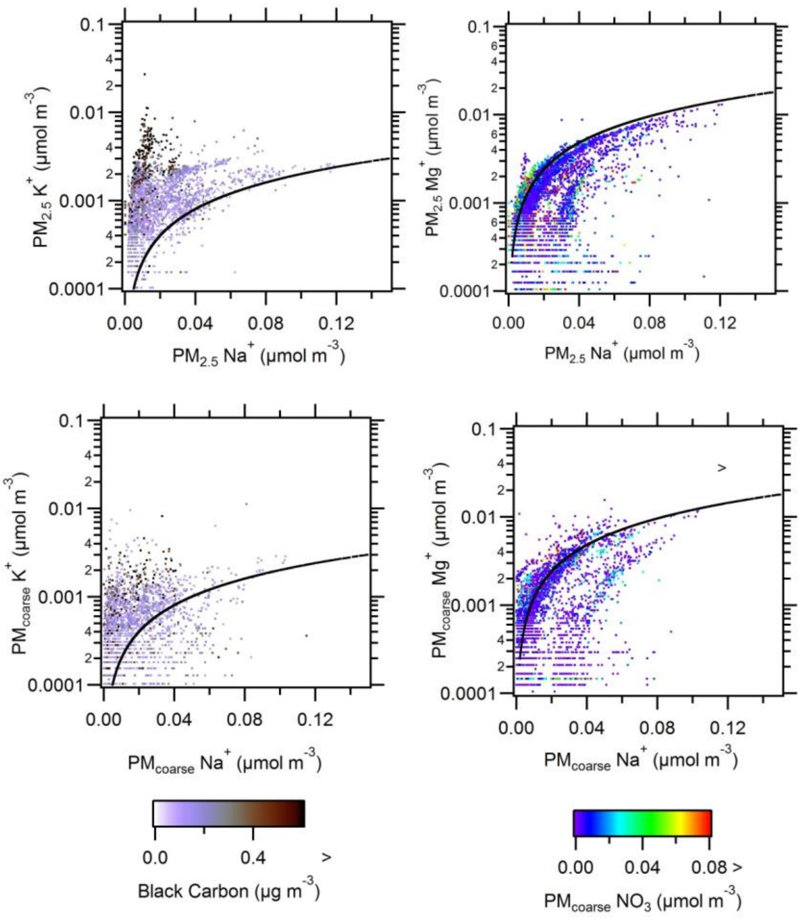

Figure 8 Relationship of K^+ (left hand figures) and of Mg^{2+} (right hand figures) to Na^+ for $PM_{2.5}$ and PM_{coarse} from 21/03/2012 to 01/01/2013. Black lines show the sea water ratios of K^+ and Mg^{2+} to Na^+ taken from Seinfeld and Pandis (2006). Black carbon data are provisional data downloaded from the DEFRA UK-Air database archive (http://uk-air.defra.gov.uk/data/) on the 17/03/2014.

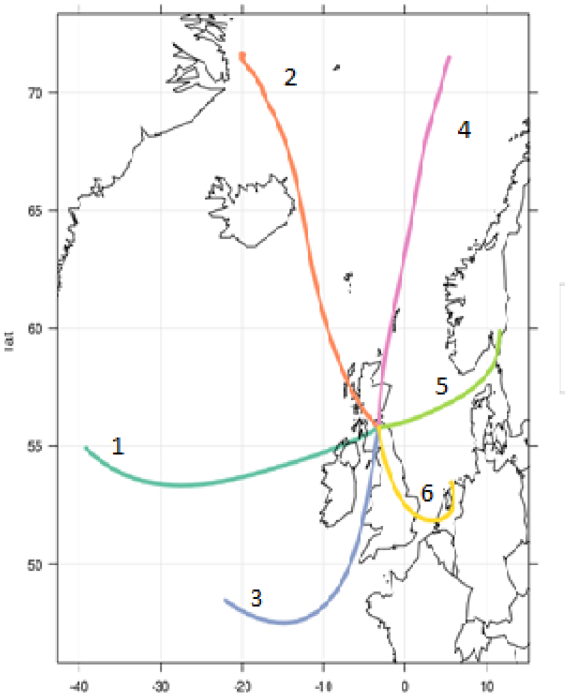

Figure 9. Mean trajectory associated with each cluster following clustering of 96h back trajectories at 3 hour intervals calculated for Auchencorth Moss covering the years 2007 to 2012 (17,370 back trajectories). . (Graphs produced using Open air; Carslaw and Ropkins (2012)).

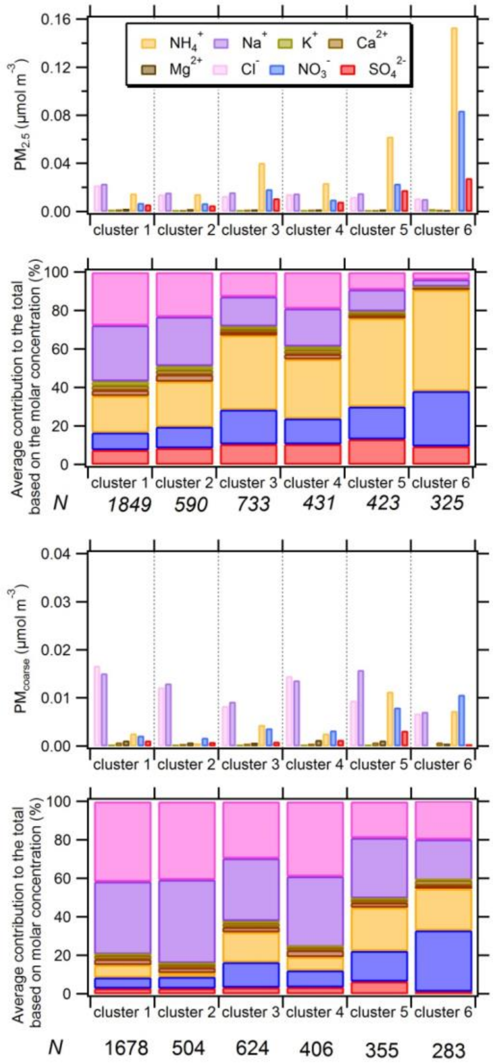

Figure 10. Average molar concentrations and average contribution of the species to the total molar concentration of $PM_{2.5}$ and PM_{coarse} for each back trajectory cluster (refer to Figure 9) from January 2007 to December 2012. Key: N – number of back trajectories used to calculate average concentration and % contribution for each trajectory.

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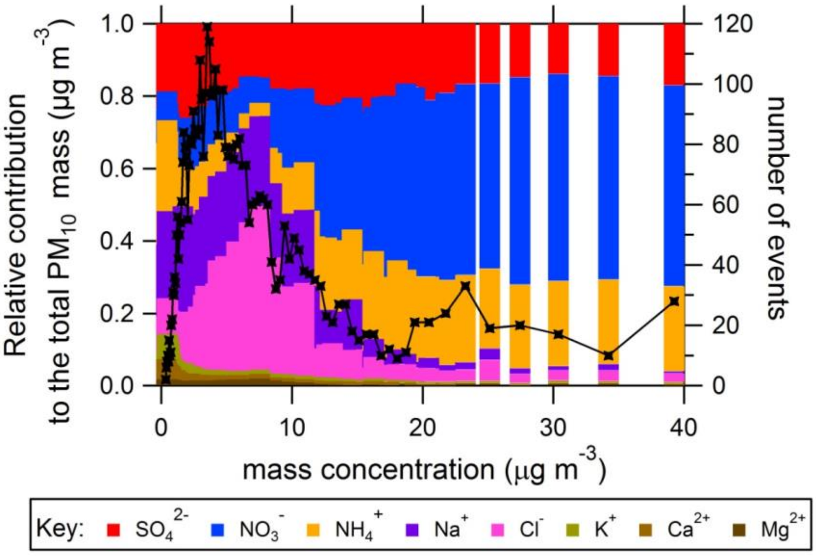

Figure 11. Average relative contribution of inorganic water soluble species to the total PM_{10} mass measured by the MARGA during 2012 as a function of total mass concentration. The black line is the number of events at each mass concentration. Graph produced using the plotting routine of Crippa et al. (2014).