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

**M.M. Twigg,[1] C.F. Di Marco[1], S. Leeson[1], N. van Dijk[1], M. R. Jones[1], I. D. Leith[1], E. Morrison[1,3], M. Coyle[1], R. Proost[2], A. N. M. Peeters[2], E. Lemon[2], T. Frelink[2], C.F. Braban[1], E. Nemitz[1] and J.N. Cape[1]**

[1] Centre for Ecology & Hydrology, Bush Estate, Penicuik, EH26 0QB

[2] Metrohm Applikon B.V. De Brauwweg 13, 3125 AE Schiedam, The Netherlands

[3] School of Chemistry, West Mains Road, Edinburgh, Scotland EH9 3JJ.

Correspondence to: M. M. Twigg (sail@ceh.ac.uk)

## 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. The protocols include quarterly replacement of inlets, cleaning of $PM_{10}$ head and $PM_{2.5}$ cyclone, though the frequency increases if there is evidence of pollution events or visual dirt in the denuder or SJAC, resulting in cleaning of the glassware too. Monthly calibrations of mass flow controllers (MFCs) have been implemented, following the upgrade, by carrying out a 3 point calibration using a NIST traceable air flow calibrator (Challenger, Sensidyne,LP. USA). The MFC flows were found to compare well on average with an independent flow meter (<5% difference on average to the expected 1 $m^3$ $h^{-1}$ flowrate). Only on occasions did the flows differ, after denuders or SJACs had been either moved or cleaned, or as the result of a faulty air pump or MFC. As a result it is now procedure to recalibrate flows following any change in the sample boxes. In addition due to the frequency of the audits, air concentration data are only corrected when there is evidence of drift of the MFCs calibration. As part of a more stringent protocol independent analyses of the internal standard (LiBr) by a UKAS accredited laboratory (CEH Lancaster) have been carried out since 2012. The measured LiBr concentrations are on average 10.5% (Li) and 6.5% (Br) lower than the theoretical concentration, when independently analysed by the UKAS accredited laboratory. The difference between the laboratory and the MARGA measured values were -0.4±3.4% and -2.2±3.8% for Li and Br respectively over 2013 based on monthly measurements. Only on a few occasions have external solutions been analysed by the MARGA as it was not until 2012, following the instrument upgrade, that external standards could be successfully run. External standards however have occasionally been used to confirm peak identification on chromatograms.

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 calculated DLs have been reported to UKAir (http://uk-air.defra.gov.uk/data/) on a monthly basis from 2012; only 1.4% of potential data were filled with ½ DL in 2012. 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.

## 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 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.

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.

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:

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

$PM_{coarse}$ 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 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):

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

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

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

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

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:

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

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.

$PM_{2.5}$ 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 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 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.

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 $\mu g\ m^{-3}$) while the relative contribution of $K^+$ and $Ca^{2+}$ increases at very low concentrations (<2 $\mu g\ m^{-3}$). 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).

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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.<br>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 $PM_{10}$.<br>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.<br>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.<br>Blanks and external standards can be set-up remotely. |

Table 3 Annual average detection limits calculated using logarithmic 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: $\mu_A$ – arithmetic mean, $\mu_G$ – median, Max – maximum, $\sigma_A$ – arithmetic standard deviation, DC – data capture (%).

| | 2006* | | | | | 2007 | | | | | 2008 | | | | | 2009 | | | | | 2010 | | | | | 2011 | | | | | 2012 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\mu_A$ | $\mu_G$ | max | $\sigma_A$ | DC | $\mu_A$ | $\mu_G$ | max | $\sigma_A$ | DC | $\mu_A$ | $\mu_G$ | max | $\sigma_A$ | DC | $\mu_A$ | $\mu_G$ | max | $\sigma_A$ | DC | $\mu_A$ | $\mu_G$ | max | $\sigma_A$ | DC | $\mu_A$ | $\mu_G$ | max | $\sigma_A$ | DC | $\mu_A$ | $\mu_G$ | max | $\sigma_A$ | 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.

| **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 |

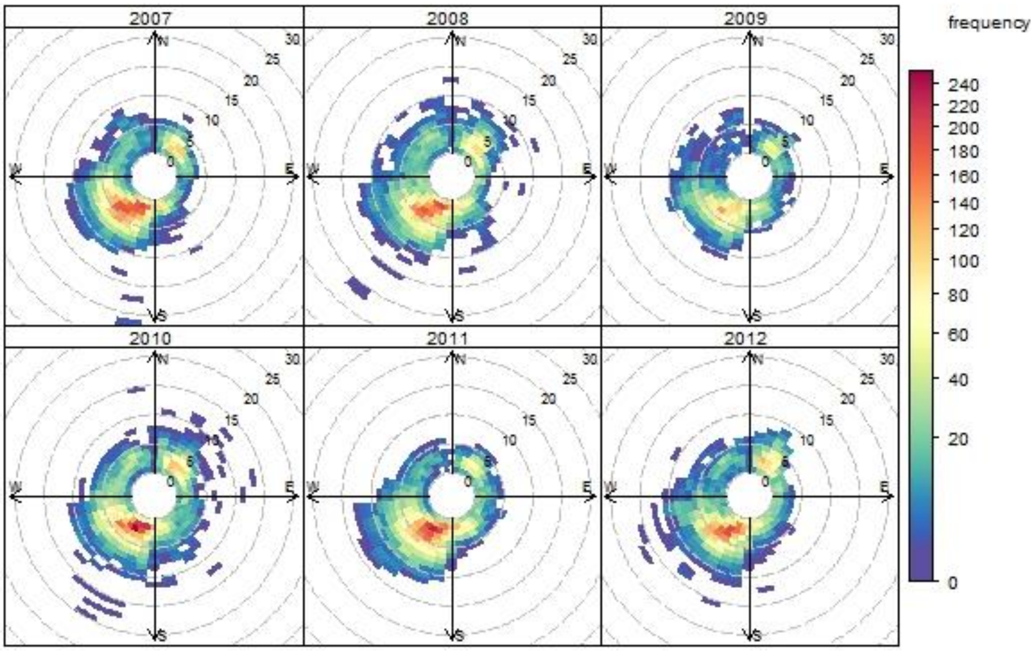


Figure 1 Frequency plots of wind direction and windspeed (m s$^{-1}$) averaged over an hour at Auchencorth Moss for the years 2007 to 2012. Windspeed scale is limited to 30 m s$^{-1}$. (Graphs produced using OpeAir;Carslaw and Ropkins (2012))

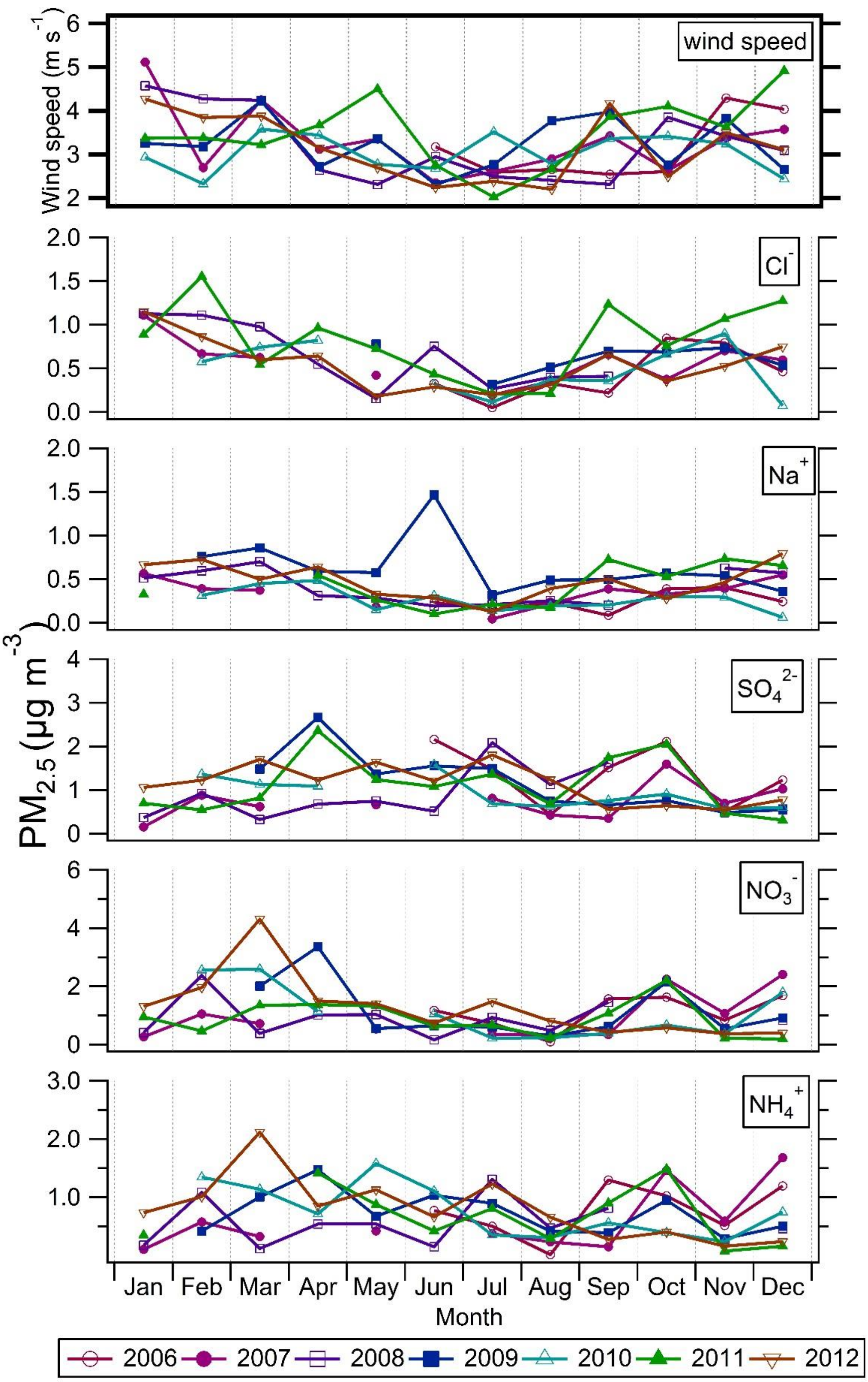


Figure 2 a) Median monthly mass concentrations of $PM_{2.5}$ species measured by the MARGA and median wind speed from June 2006 to December 2012

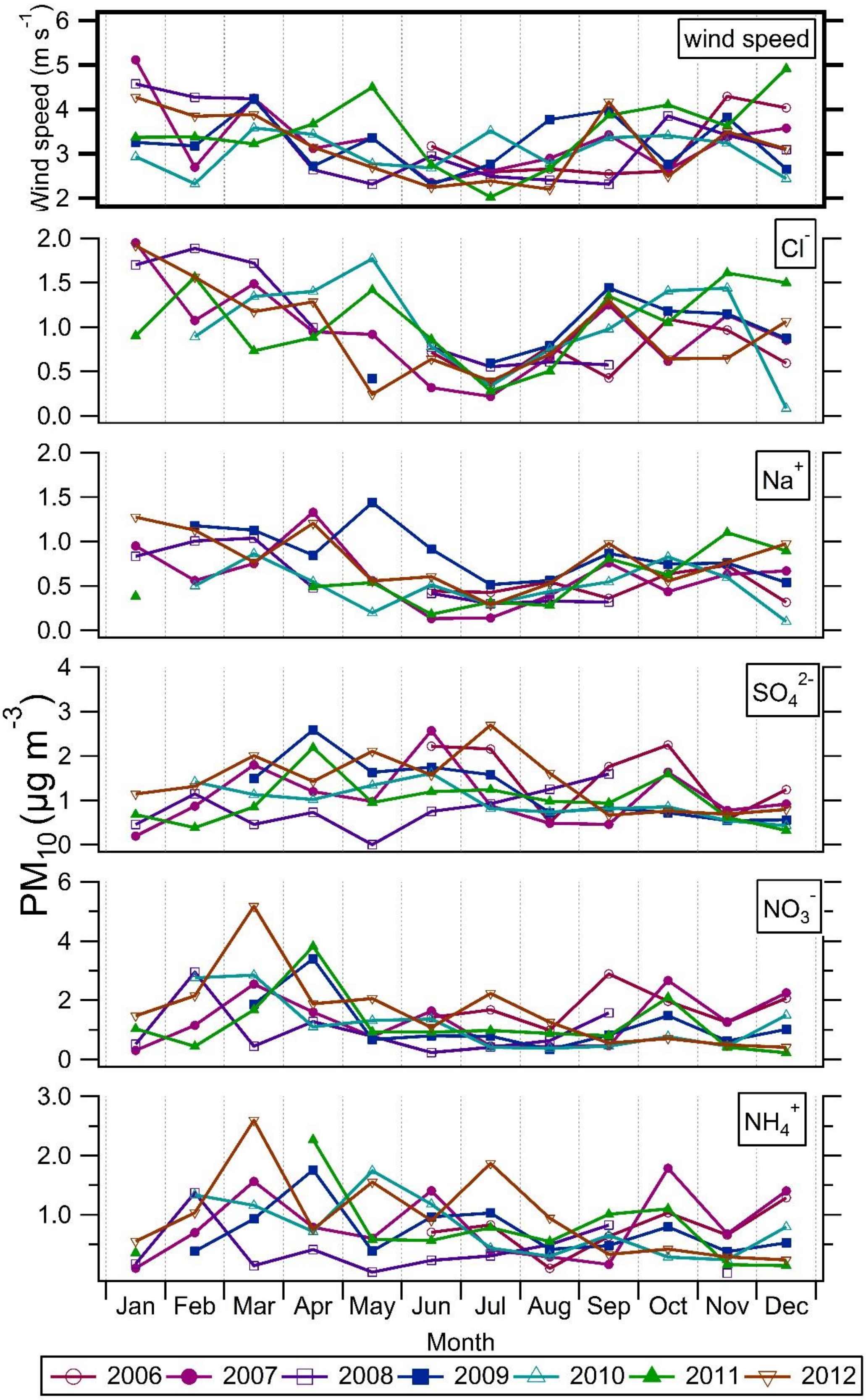
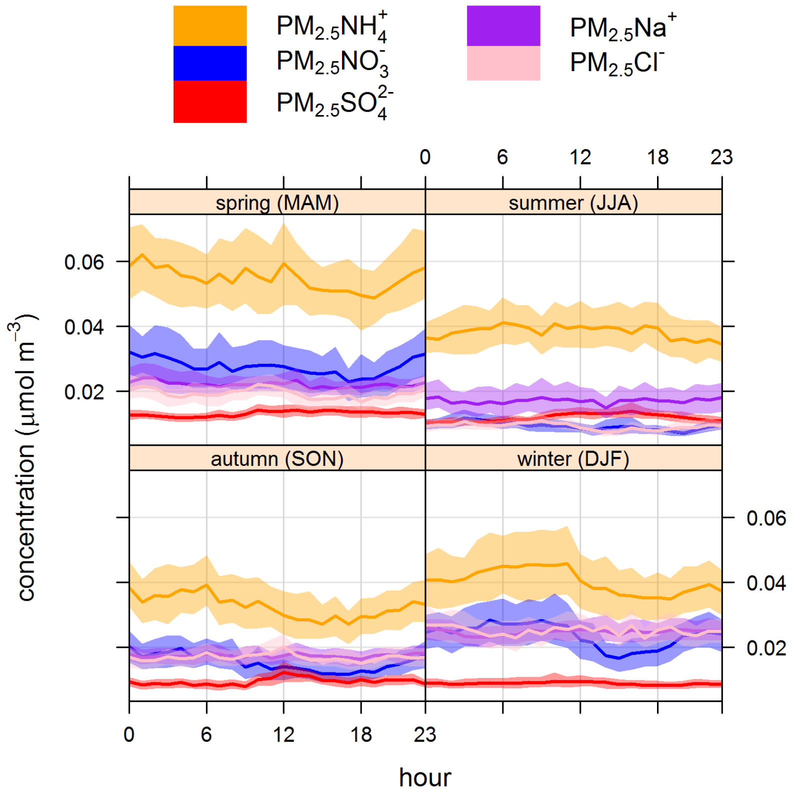


Figure 2b) Median monthly mass concentrations of $PM_{10}$ species measured by the MARGA and median wind speed from June 2006 to December 2012



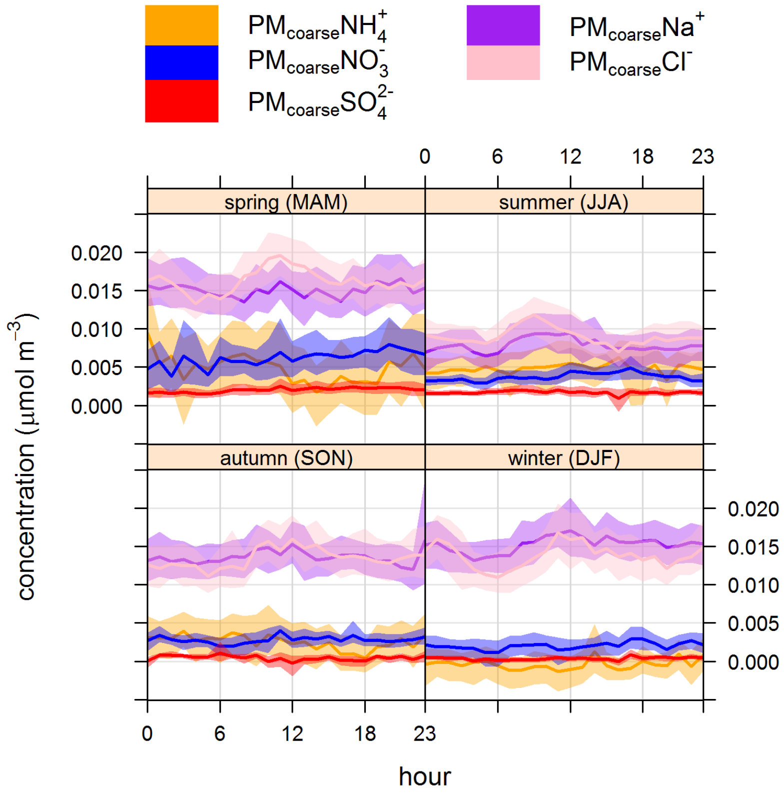


Figure 3 Median seasonal diurnal cycles of molar concentrations of $PM_{2.5}$ and $PM_{coarse}$ $NH_4^+$, $NO_3^-$, $SO_4^{2-}$ , $Na^+$ and $Cl^-$ using data from January 2007 to December 2012, with the shading

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

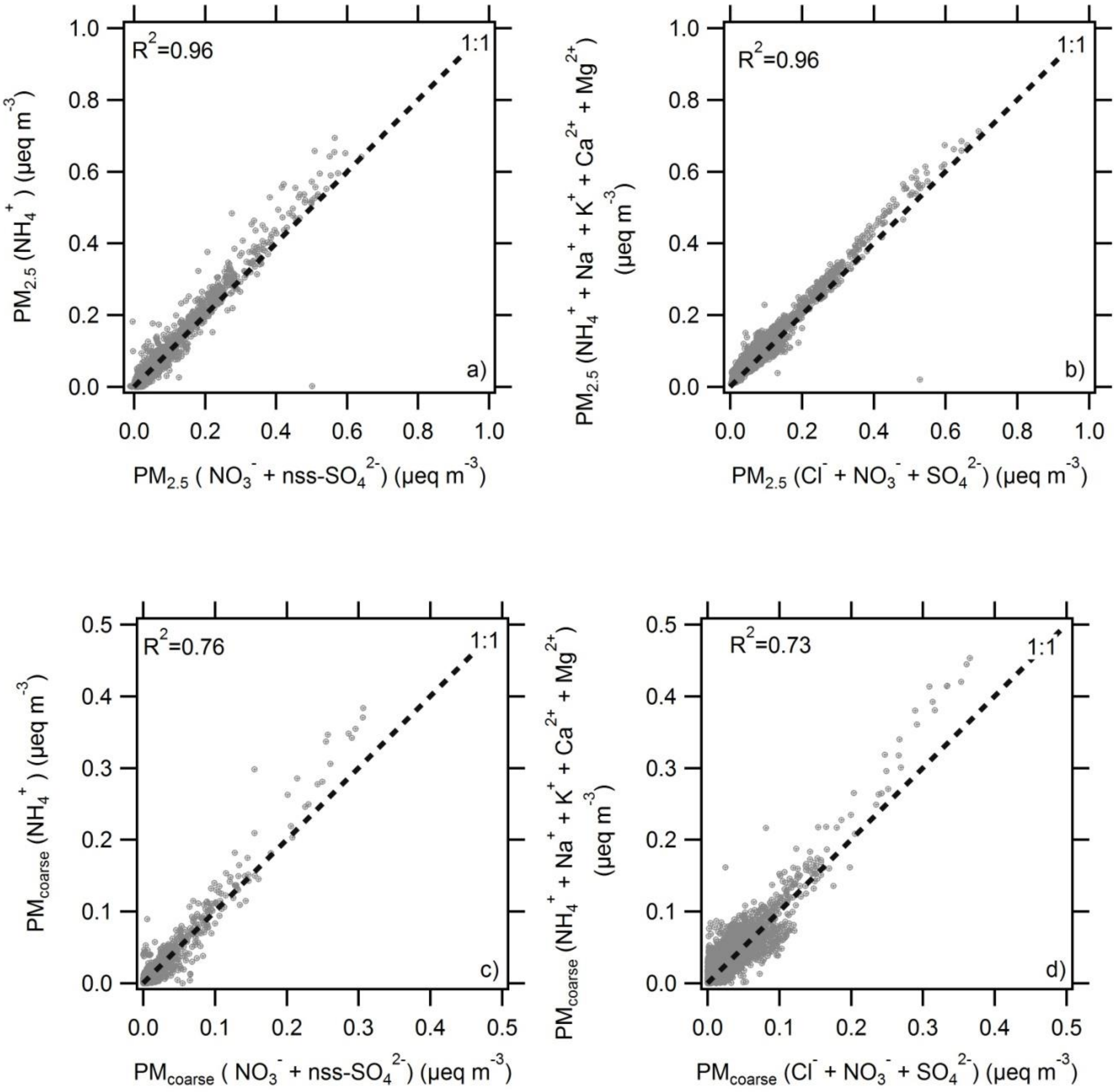


Figure 4. Measured  ion balance for the year 2012 in microequivalents m$^{-3}$. a) Neutralisation of PM$_{2.5}$ NH$_4^+$ by PM$_{2.5}$ nss-SO$_4^{2-}$ and PM$_{2.5}$ NO$_3^-$,  b) Ion balance of measured PM$_{2.5}$ anions (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) and measured PM$_{2.5}$ cations (NH$_4^+$, Na$^+$,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

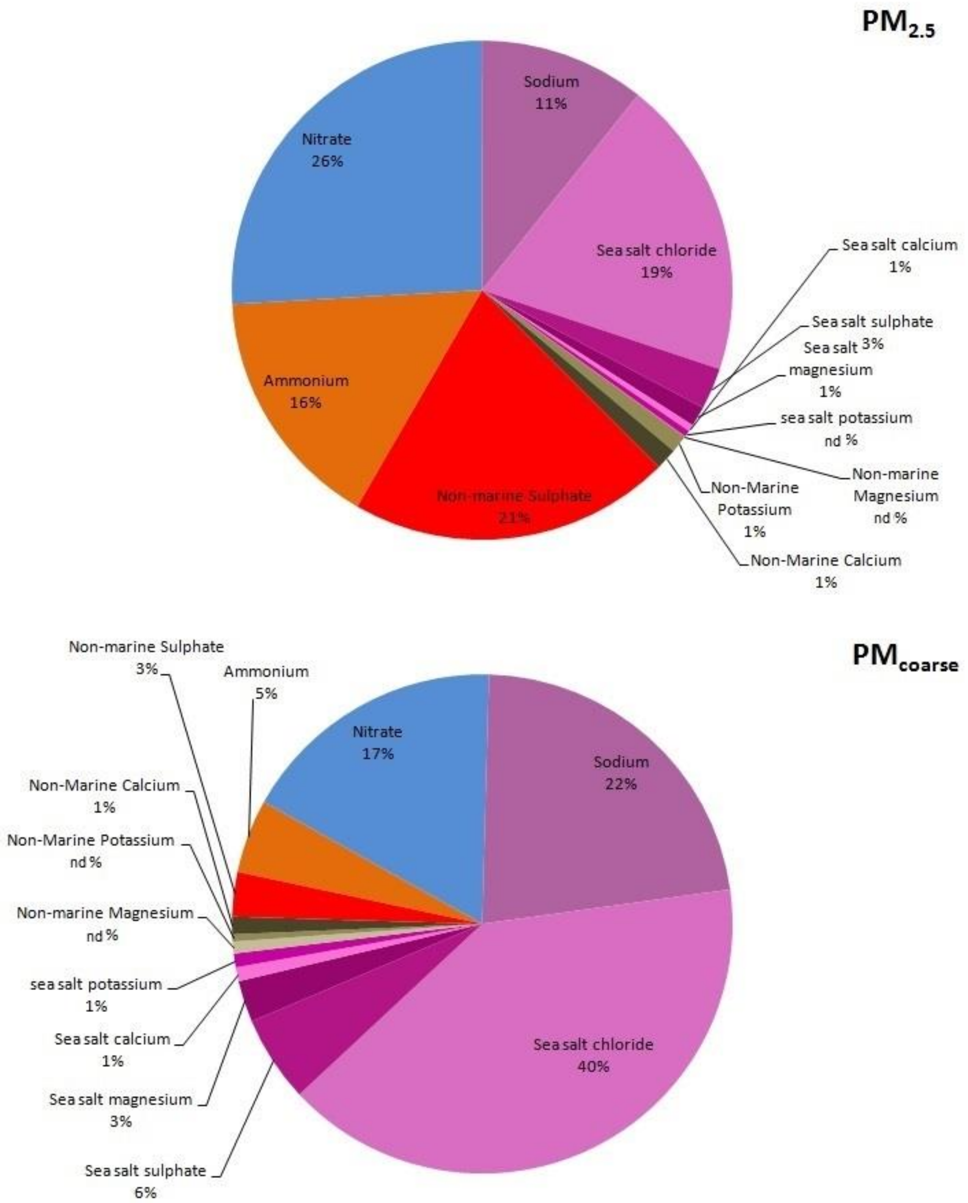


Figure 5 Average composition by mass of the water soluble inorganic aerosol fraction measured by the MARGA from January 2007 to December 2012 in both the $PM_{2.5}$ and $PM_{coarse}$. Sea salt chloride, sulphate, magnesium, calcium and potassium were derived based on the known mass ratios to $Na^+$ in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

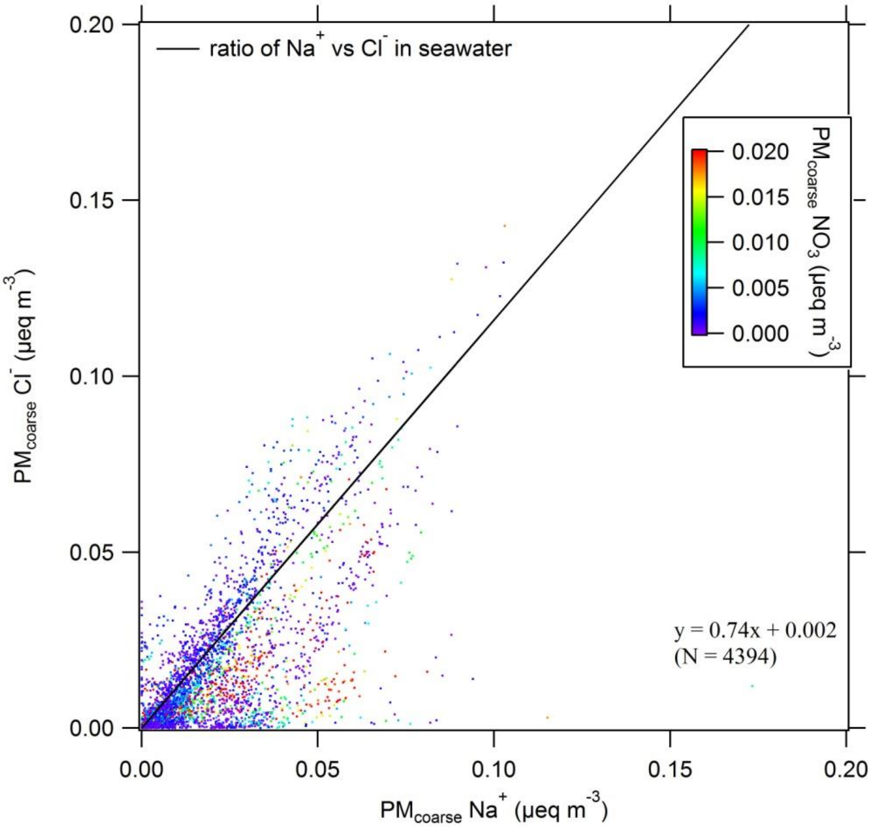


Figure 6. Demonstration of the depletion of Cl$^-$ for the year 2012 as a result of Cl$^-$ - NO$_3^-$ interactions during long-range transport for coarse aerosol. The black line is the known ratio of Cl$^-$ to Na$^+$ in seawater (Seinfeld and Pandis, 2006). Colour scale is set to 0 to >0.2 µeq m-3 NO$_3^-$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

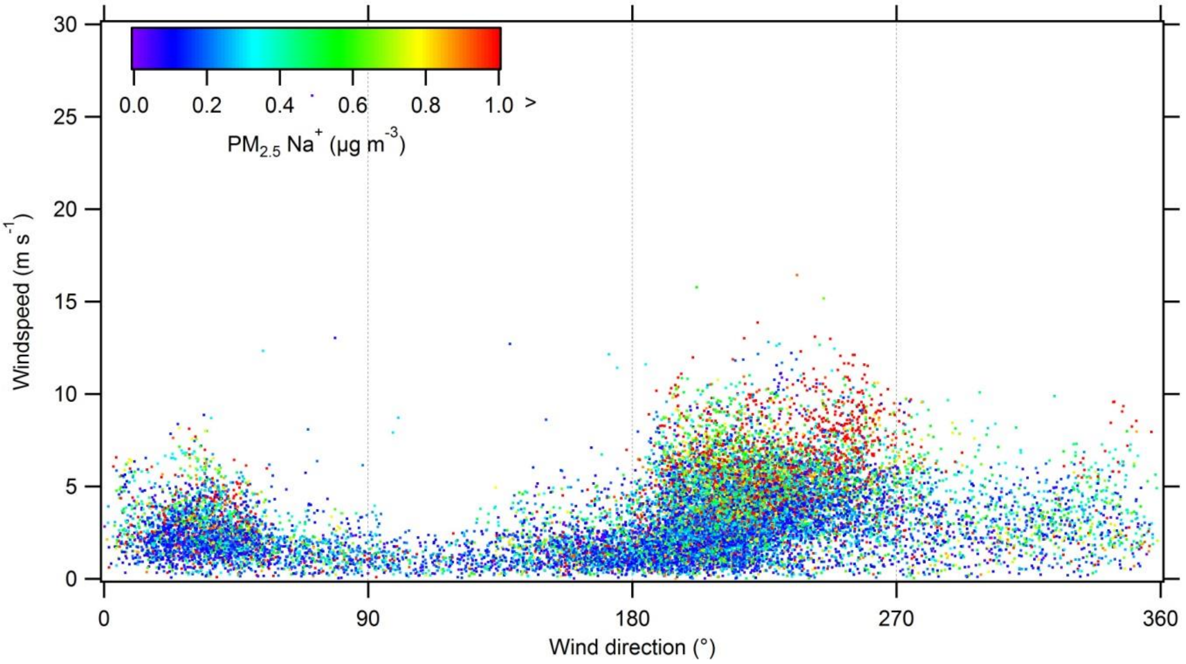


Figure 7 The influence of wind direction and wind speed on the concentration of PM$_{2.5}$ Na$^+$ at Auchencorth Moss from the 1 January 2007 to 1 January 2013.

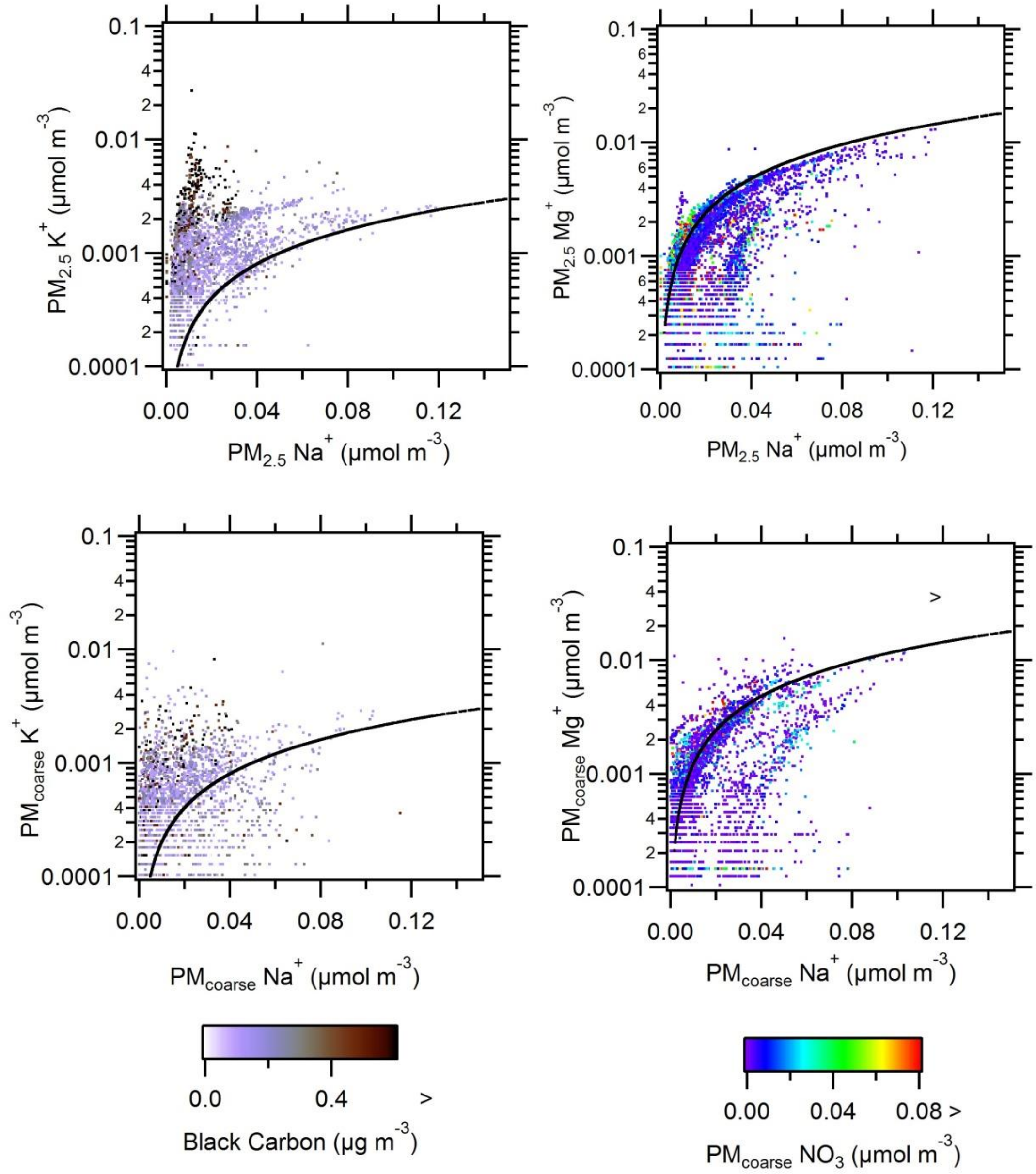


Figure 8 Relationship of K$^+$ (left hand figures) and of Mg$^{2+}$ (right hand figures) to Na$^+$ for PM$_{2.5}$ and PM$_{coarse}$ from 21/03/2012 to 01/01/2013. Black lines show the sea water ratios of K$^+$ and Mg$^{2+}$ to Na$^+$ taken from Seinfeld and Pandis (2006). Black carbon data are provisional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

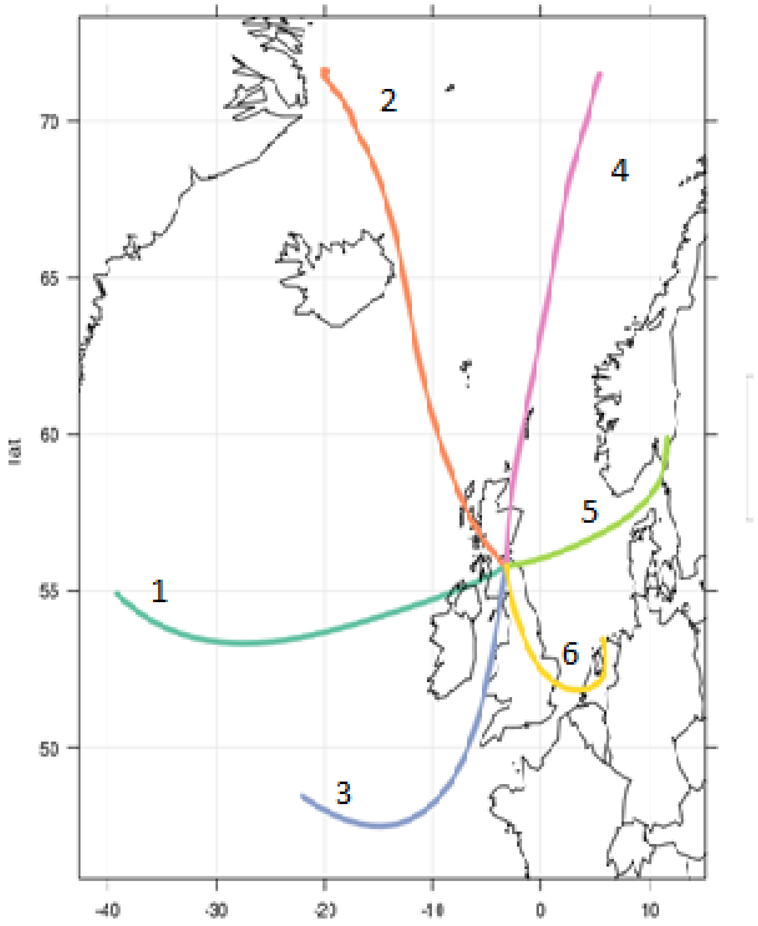


Figure 9. Mean trajectory associated with each cluster following clustering of 96h back trajectories at 3 hour intervals calculated for Auchencorth Moss covering the years 2007 to 2012 (17,370 back trajectories). . (Graphs produced using Open air; Carslaw and Ropkins (2012)).

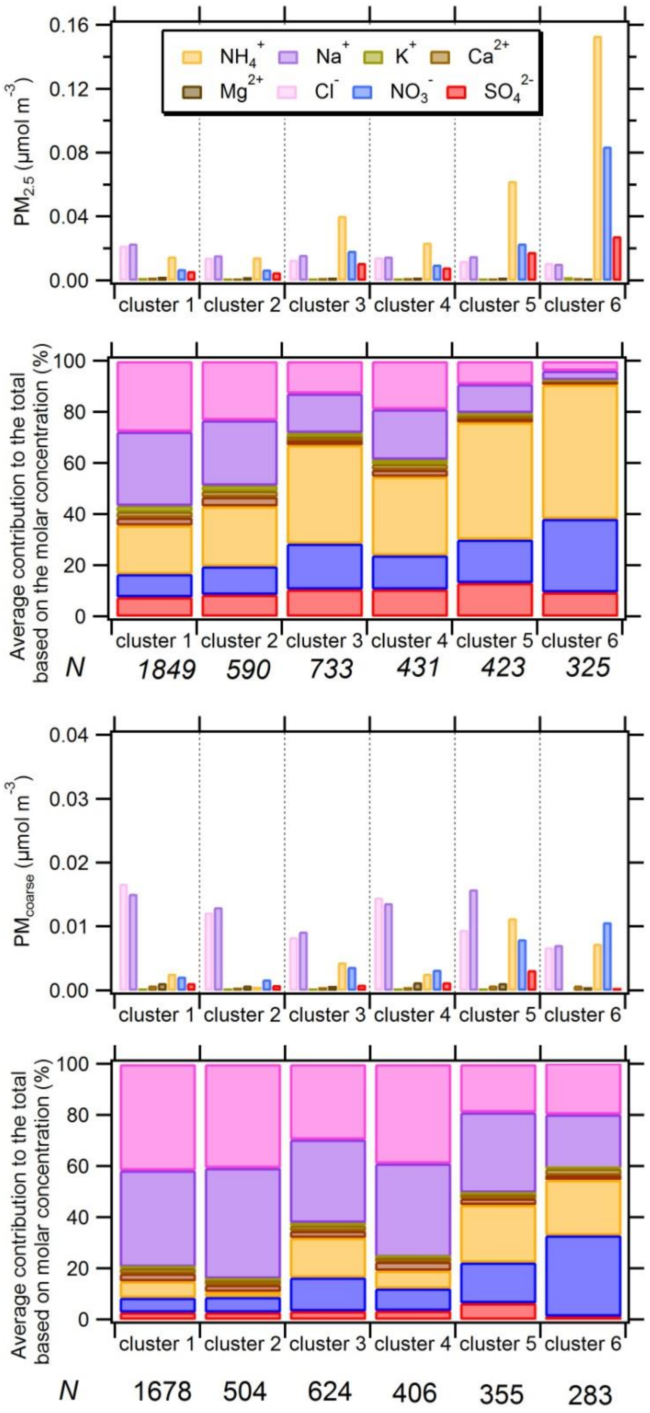


Figure 10. Average molar concentrations and average contribution of the species to the total molar concentration of PM$_{2.5}$ and PM$_{coarse}$ for each back trajectory cluster (refer to Figure 9) from January 2007 to December 2012. Key: N – number of back trajectories used to calculate average concentration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

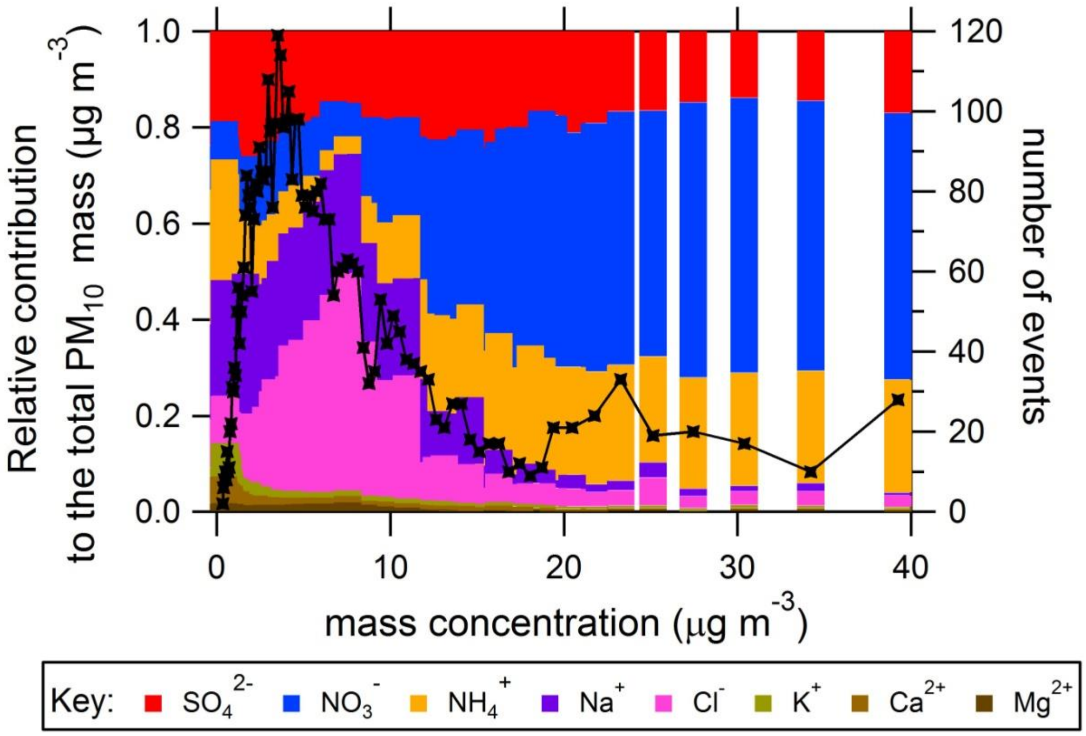


Figure 11. Average relative contribution of inorganic water soluble species to the total $PM_{10}$ mass measured by the MARGA during 2012 as a function of total mass concentration. The black line is the number of events at each mass concentration. Graph produced using the plotting routine of Crippa et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