

1 Responses to Reviews

2
3 Manuscript acp-2014-884

4
5 **Authors response to interactive comment on “Water soluble**
6 **aerosols and gases at a UK background site – Part 1:**
7 **Controls of PM_{2.5} and PM₁₀ aerosol composition”**
8 **by M. M. Twigg et al.**

9
10
11 The authors would like to thank the reviewers for the time spent reviewing the manuscript. We have revised
12 the manuscript to implement the recommendations from the reviewers. Please find below in black the reviewer
13 comments and in [BLUE](#) the authors response.

14
15
16 **Anonymous Referee #1**

17
18 Though the main ions have been measured from particles for decades (e.g. with the EMEP filter method)
19 quite limited amount of shorter time-resolution data is available and therefore the 6.5 years MARGA data
20 series from the UK EMEP Super Site Auchencorth Moss, Scotland is most valuable and worth publishing.
21 This paper provides greater detail in the long term temporal variation of inorganic compounds in UK
22 background air. Secondary inorganic aerosol (especially NH₄⁺ and NO₃⁻) were dominating in PM_{2.5} and sea
23 salt was dominating in coarse fraction, especially in winter (with higher wind speed). Sea salt processing was
24 discussed - considerable amounts of NO₃⁻ were occasionally found in coarse fraction with depletion of Cl⁻.
25 Average seasonal ion balance was always basic (excess NH₄⁺). The data was also used to study the
26 influence of air masses from marine and anthropogenic sources. Furthermore, the data will be valuable to
27 study long term trends in particulate matter composition in response to climate and policy drivers.

28
29 There was a very nice and detailed description of MARGA instrumentation in this paper. However, the data
30 quality and processing should be described as well. There are some open questions like: Is there any
31 estimation of detection limits (or quantitation limits) or/and measurement uncertainties available? Were the
32 zero (or under the detection limit) values replaced somehow and were there any under the detection limit
33 concentrations? Were the instrument blanks taken into account or were they negligible when compared to
34 the measured values? Were the inlets cleaned / replaced regularly as well as the glassware?

35
36 **RESPONSE:** We concur with the reviewer's view that this is a valuable dataset and analysis of it. The authors
37 acknowledge that the QA and QC processes were not well described as they could have been in this
38 manuscript. The manuscript has been updated to address this by adding an additional section on QA/QC.
39 Below is the updated text which can be found in the updated manuscript at the end of this document. A more
40 detailed manuscript on the QA/QC protocols for the MARGA instrument will published in the near future,
41 which includes points raised by the reviewer, therefore the points have been addressed below but not all have
42 been included in the manuscript.

1 ***“Quality analysis and quality Assurance***

2 *As discussed previously the MARGA used in this work was one of the first to be field deployed.*
3 *Processes were developed over the first several years which could be used to identify potential*
4 *sources of error or contamination in the MARGA data. Firstly, periodic field blanks were*
5 *carried out until 2011 by installing Whatman HEPA filters placed in front of the denuders and*
6 *left on for ~24 hours. The filters removed aerosols but not the gas phase components from the*
7 *air stream. The resultant change in PM concentrations allowed a blank value for the PM*
8 *analytes to be assessed. Following the upgrade of the instrument in November 2011 (Table 2),*
9 *automated monthly blanks were implemented in 2012, where the air pump and SJAC water*
10 *supply and heaters were turned off, allowing for blanks for both aerosol and gas phase to be*
11 *carried out. The blanks were not used to correct the data as they were usually below the*
12 *detection limit (DL) of the instrument. Instead blanks were used to provide evidence of*
13 *contamination in the system and to identify periods to be removed in the data ratification*
14 *process. Prior to 2012 verification and instrument maintenance protocols has been*
15 *experimental and the authors are in the process of finalising the protocols including*
16 *calibration, which will be published separately. There was a step change in 2012, when the*
17 *initial developmental protocols for maintenance were replaced by final protocols including*
18 *quarterly replacement of inlets, cleaning of PM₁₀ head and PM_{2.5} cyclone, monthly air flow*
19 *calibrations and independent analysis of internal standards by a UKAS accredited laboratory.*
20 *In the data ratification process values reported as 0 µg m⁻³ were replaced with half the detection*
21 *limit (DL). The method to determine the DL has changed over the 6 year period. From 2002 to*
22 *2011, the DL was taken as the average of the reported values below the manufacturers*
23 *published DL. From 2012, the DL was calculated by the analysis of the logarithmic distribution*
24 *of the measurements previously described by Kentisbeer et al. (2014), presented in table 3. The*
25 *methodology for analysing the DL and calibrating this type of on-line IC instrument is an area*
26 *of research in of itself and we plan to publish separately on this aspect of the MARGA operation.*
27 “

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

29
30 Response: Please refer to QA/QC manuscript text on treatment of detection limits for the presented period.
31 The calculated DLs have been reported to UKAir (<http://uk-air.defra.gov.uk/data/>) on a monthly basis from
32 2012 and only 1.4% of potential data were filled with ½ DL. From 2015, the protocol for calculating the DL will
33 using 3σ of the measured concentration of low concentration external standard. It is expected that with the
34 finalised protocol the reported DLs will be smaller and closer to the manufacturers listed DLs (see table

1 below). No uncertainty analysis has been carried out yet but it is planned to be addressed in a future
2 manuscript on the QA/QC of the MARGA.

3
4 List of detection limits using pre-concentration columns on the MARGA instrument given by the
5 manufacturer.

Component	Manufacturers reported DL
	$\mu\text{g m}^{-3}$
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

6
7
8 There are always risks for artifacts when using inlets: particles maybe lost in the inlet and there may be some
9 gas-particle reactions inside the tubing, especially for NH₄NO₃ / NH₃⁺ / NO₃⁻ .

10
11 **RESPONSE:** The authors agree that the use of an inlet can result in losses and potential interactions in the
12 inlets. Within the MARGA community there is still no agreement on the best method to limit the interactions,
13 including inlet material and if new or aged inlets are optimum. For the instrument presented periodic changing
14 of the inlets and quarterly cleaning of both the PM₁₀ head and the cyclone are carried out. Some experiments
15 have been undertaken and more are planned in the future to compare the MARGA against species specific
16 instruments to enable a clear understanding of the instrument performance

17
18 p. 3717. "It is not the first time that inorganic water soluble aerosols have been found to be major contributors
19 to the total mass in Europe (Putaud et al., 2010). Aerosol components not resolved by the MARGA include
20 inorganic aerosols, BC, water and crustal elements such as silicate. Organic aerosol often accounts for a
21 larger fraction of the PM10 mass at central European background sites than the missing mass

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

24
25 **RESPONSE:** The referee is correct. The authors apologise for this mistake and have corrected the
26 manuscript accordingly.

27
28 Table 2: I do not understand, why new type SJAC improved accuracy in maintaining the cut-off (17 Feb 2009).

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

1 *“The increase in diameter of the SJACs described in table 2, reduced the restriction in*
2 *maintaining a flow rate, which was mass flow controlled at 1 m³ hr⁻¹ at standard temperature*
3 *and pressure (STP) until November 2011, whereas thereafter it was controlled to keep the*
4 *volumetric flow rate at ambient temperature and pressure through the size cuts constant.”*

5
6

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

8

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

12

13 Did the solutions stay clean enough for that purpose?

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

16

17 What was the external standard used for?

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

20

21

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

24

25 **Response:** Corrections to the abbreviations in the manuscript have been carried out including a key in Table
26 1.

27

28 Figure 2: Check lines and font sizes.

29

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

31

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

33

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

35

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

37

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

39

40

41 References: Check the formats. Sometimes there are commas in the author list (between

1 authors) and sometimes not.

2

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

5

6

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

8

9 **Response:** The spelling error has been corrected.

10

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

15

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

17

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

21

22

23

1 **Anonymous Referee #2**

2
3 This article presents long-term measurements of aerosol composition at a background site in Scotland. Such
4 long-term data sets of speciated chemistry are extremely valuable for understanding aerosol processes,
5 pollution source apportionment, and model development and evaluation. The authors do a very good job at
6 analyzing and presenting the data and the manuscript is well written.

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

10
11 **Response:** We acknowledge that the QA/QC of the instrumentation was not well described. As a result an
12 additional section has been added to the manuscript, see response to Reviewer #1, which should address
13 most of the questions highlighted by referee #2. We have however not discussed the reprocessing of
14 chromatograms as it is beyond the scope of the manuscript. We are planning a publication which focusses
15 on the challenges of QA/QC with an online IC instrument below is a summary in response to individual points
16 on QA/QC which will be addressed in a future manuscript.

17
18
19 The authors note that the use of preconcentration columns sets this instrument apart from other descriptions
20 of the MARGA instrument. For this reason, some detail regarding the basic characteristics of the analytical
21 system is warranted. What are the detection limits for each analyte and how were they determined?

22
23 **Response:** Please refer to QA/QC manuscript text below. The calculated DLs have been reported to UKAir
24 on a monthly basis from 2012.

25
26 *"In the data ratification process 0 ug m⁻³ values were replaced with ½ detection limit (DL). The method to*
27 *determine the DL has changed over the 6 year period. From 2002 to 2011, the DL was taken as the average*
28 *of the reported values below the manufacturers reported DL. From 2012, the DL was calculated by the study*
29 *of the logarithmic distribution of the measurements previously described by Kentisbeer et al. (2014),*
30 *presented in table 3. The methodology for analysing the LOD and calibrating this type of on-line IC instrument*
31 *is an area of research in of itself and we plan to publish separately on this aspect of the MARGA operation*
32 *specifically."*

33
34 How often were analytical blanks determined and did they vary over time?

35
36 **Response:** There was not a huge variability in the blanks, unless contamination was present in the system.
37 Please refer to the updated manuscript text on QA/QC.

38
39 How often were external liquid standards analyzed?

40
41 **Response:** Only on small number of occasions have external solutions been analysed but it was not until
42 2012, following the instrument upgrade, could external standards be successfully run. Due to other
43 operational issues this is only been implemented as a protocol on a quarterly basis in 2015, using certified
44 standards of the major anions and cations. External standards however have occasionally been used to
45 confirm the peaks on chromatograms.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42

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 PM₁₀ 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.

1
2 What was the process for reducing the raw hourly data? That is, how were blanks, external standards, and
3 flow rate audits incorporated into the data reduction process?

4
5 **Response:** Blanks at present are only used to remove periods of contamination in the system. Due the
6 frequency of flow rate audits, air concentration data is only corrected where there is evidence of drift in the
7 MFC.

8
9 How were concentrations below detection limit treated?

10
11 **Response:** Concentrations below DL were flagged in both UK-Air and EMEP. Any reported $0 \mu\text{g m}^{-3}$ were
12 replaced with $\frac{1}{2}$ DL and flagged accordingly in the relevant databases. The treatment of $0 \mu\text{g m}^{-3}$ has now
13 been included into the text of the manuscript.

14
15 *"In the data ratification process $0 \mu\text{g m}^{-3}$ values were replaced with $\frac{1}{2}$ detection limit (DL). The*
16 *method to determine the DL has changed over the 6 year period. From 2002 to 2011, the DL*
17 *was taken as the average of the reported values below the manufacturers reported DL. From*
18 *2012, the DL was calculated by the study of the logarithmic distribution of the measurements*
19 *previously described by Kentisbeer et al. (2014), presented in table 3. The methodology for*
20 *analysing the LOD and calibrating this type of on-line IC instrument is an area of research in*
21 *of itself and we plan to publish separately on this aspect of the MARGA operation specifically.*

22 “

23

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

25

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

29

30 Additional comments:

31 Page 3705, line 26: Change “the exceeding the” to “exceeding the”

32 **Response:** Corrected

33

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

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

37

38 Page 3715, line 21: Change “that however,” to “however,”

1 **Response:** Corrected.

2

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

5 **Response:** This was an error. Text updated

6 "Aerosol components not resolved by the MARGA include organic aerosols,"

7

8 Page 3717, lines 17-18: "Mass closure improved in 2012, probably in response to the
9 improved flow control implemented in November 2011 on the MARGA (see above)."

10 Can the authors give more detail on the flow control changes and how this improved
11 mass closure?

12

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

17

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

1 Water soluble aerosols and gases at a UK background site.

2 Part 1: Controls of PM_{2.5} and PM₁₀ aerosol composition

3
4 M.M. Twigg¹, C.F. Di Marco¹, S. Leeson¹, N. van Dijk¹, M. R. Jones¹, I. D. Leith¹,
5 E. Morrison^{1,3}, M. Coyle¹, R. Proost², A. N. M. Peeters², E. Lemon², T. Frelink²,
6 C.F. Braban¹, E. Nemitz¹ and J.N. Cape¹

7
8 [1] Centre for Ecology & Hydrology, Bush Estate, Penicuik, EH26 0QB

9 [2] Metrohm Applikon B.V. De Brauwweg 13, 3125 AE Schiedam, The Netherlands

10 [3] School of Chemistry, West Mains Road, Edinburgh, Scotland EH9 3JJ.

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

12 Abstract

13 There is limited availability of long-term, high temporal resolution, chemically speciated
14 aerosol measurements, which can lead to further insight into the health and environmental
15 impacts of particulate matter. The Monitor for AeRosols and Gases (MARGA, Applikon B.V,
16 NL) allows characterisation of the inorganic components of PM₁₀ and PM_{2.5} ((NH₄⁺, NO₃⁻,
17 SO₄²⁻, Cl⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺) and inorganic reactive gases (NH₃, SO₂, HCl, HONO and
18 HNO₃) at hourly resolution. The following study presents 6.5 years (June 2006 to December
19 2012) of quasi-continuous observations of PM_{2.5} and PM₁₀ using the MARGA at the UK EMEP
20 ‘Supersite’, Auchencorth Moss, SE Scotland. Auchencorth Moss was found to be representative
21 of a remote European site with average total water soluble inorganic mass of PM_{2.5} of 3.82 μg
22 m⁻³. Anthropogenically derived secondary inorganic aerosols (sum of NH₄⁺, NO₃⁻ and nss-SO₄²⁻
23), were the dominating species (63%) of PM_{2.5}. In terms of equivalent concentrations, NH₄⁺
24 provided the single largest contribution to PM_{2.5} fraction in all seasons. Sea salt was the main
25 component (73%) of the PM_{coarse} fraction (PM₁₀-PM_{2.5}), though NO₃⁻ was also found to make a
26 relatively large contribution to the measured mass (17%) providing evidence of considerable
27 processing of sea salt in the coarse mode. There was on occasions evidence of aerosol from
28 combustion events being transported to the site in 2012 as high K⁺ concentrations (deviating
29 from the known ratio in sea salt) coincided with increases in black carbon at the site. Pollution
30 events in PM₁₀ (defined as concentrations >12 μg m⁻³) were on average dominated by NH₄⁺ and

Deleted: .

Deleted: as

1 NO₃⁻, where as smaller loadings at the site tended to be dominated by sea salt. As with other
2 Western European sites, the charge balance of the inorganic components resolved were biased
3 towards cations, suggesting the aerosol was basic or more likely, that organic acids contributed
4 to the charge balance. This study demonstrates the UK background atmospheric composition is
5 primarily driven by meteorology with sea salt dominating air masses from the Atlantic Ocean
6 and the Arctic, whereas secondary inorganic aerosols tended to dominate air masses from
7 continental Europe.

8

9 **1 Introduction**

10 Gravimetric methods have long been used to monitor the long-term trends of the bulk aerosol
11 mass contained in particulate matter (PM) with an aerodynamic diameter of less than 2.5µm or
12 10 µm (i.e. PM_{2.5} and PM₁₀); however, these generally provide no information on the chemical
13 speciation of the aerosol. Off-line chemical analysis after capture of aerosol on filters by high
14 or low volume filter samplers (e.g. Partisol Sampler; Thermo Fisher Scientific, Inc.) is quite
15 widely used but limited to daily or lower frequency measurements and therefore poorly captures
16 diurnal patterns caused, e.g. by changes in emission and gas-aerosol partitioning. It is important
17 to understand the composition and the role of aerosols as they can have a direct and indirect
18 effect on climate. The current level of scientific understanding for aerosol properties in terms
19 of their role in the climate system is low and recently it has been suggested that the major
20 component of the uncertainty globally is with the biogenic fraction (Carslaw et al., 2013). As
21 well as having an impact on climate, aerosols affect both environment and human health. Recent
22 epidemiological research has suggested that health effects of aerosol may be less closely linked
23 to the total mass of PM_{2.5} or PM₁₀ than to the physicochemical characteristic of the aerosol,
24 however there is still much to be understood (Fuzzi and Gilardoni, 2013). Establishment of
25 epidemiological links to individual aerosol chemical compounds is hampered by a lack of
26 available measurements.

27 In addition, secondary aerosols and their precursor gases are required to be monitored to
28 understand atmospheric processes and to validate chemical transport models, which are used to
29 inform policy, such as the UNECE Convention for Long-range Transboundary Air Pollution
30 (CLRTAP), and the revised European Air Quality Framework Directive (Directive
31 2008/50/EC) where the measurement of aerosol chemical composition is statutory. In addition,
32 prior to 2008, EU member countries were fined for ~~exceeding the total PM_{2.5} and PM₁₀ limits~~

Deleted: the

1 set in the directive, regardless whether the exceedance was due to anthropogenic or natural
2 sources. In the current revised European Air Quality Framework Directive (Directive
3 2008/50/EC), countries are now allowed to subtract significant ‘natural’ contributions of
4 aerosol from the total mass, if their contribution can clearly be quantified. This is important for
5 large ‘natural’ pollution events, such as the long-range transport of Saharan dust which have
6 been observed across Southern Europe and on occasions Northern Europe (Ansmann et al.,
7 2003;Karanasiou et al., 2012). While many member countries have chosen to make daily filter
8 measurements at a very few sites, the UK has opted for a strategy to combine a large number
9 of sites that make monthly measurements (Tang et al., 2009) with a couple of ‘supersites’ that
10 resolve hourly concentrations, as an optimum strategy for capturing the spatial and temporal
11 variability.

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

26 In parallel, there has been progress in developing monitoring instruments based on aerosol mass
27 spectrometry. While there are now some studies using the standard Aerosol Mass Spectrometers
28 (AMS; Aerodyne Research Inc, USA) for long-term measurements, a simplified version, the
29 Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Inc), is being installed at supersites
30 globally (Ng et al., 2011). Both AMS and ACSM currently measure an aerosol fraction that is
31 close to PM_{10} although work is in progress to extend this to $\text{PM}_{2.5}$. While SJAC and PILS based
32 instruments measure water soluble aerosol components, similar to the filter-pack reference

Deleted: (

1 method, the mass spectrometer detects the aerosol components that volatilise efficiently at \approx
2 600°C , which has the advantage of also characterising the organic fraction of the aerosol,
3 whereas it does not efficiently quantify the refractory chemical components such as sea salt and
4 crustal aerosol.

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

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

21

22 **2 Methodology**

23 **2.1 Field site description**

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

Deleted:

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

7 Auchencorth Moss has been a long-term monitoring site for a number of trace gases including
8 NH₃, SO₂ and CO₂ (Famulari et al., 2010;Drewer et al., 2010;Flechard and Fowler, 1998). The
9 site belongs to a number of UK national networks including: UK Defra Automatic urban and
10 rural network (AURN), UK Acid gas and aerosol network (AGANet), UK National Ammonia
11 Monitoring Network (NAMN), UK Precip-Net (~~two-weekly~~ bulk composition), UK PAH
12 Network, UK Automatic Hydrocarbon Monitoring Network, UK Black Carbon Network and
13 UK Toxic organic micropollutants (TOMPS) network. Details of the networks can be found on
14 the Defra website (http://uk-air.defra.gov.uk/networks/site-info?site_id=ACTH). The site is
15 also a European ‘Supersite’ within the Co-operative Programme for Monitoring and Evaluation
16 of the Long-range Transmission of Air Pollutants in Europe (EMEP) (Tørseth et al., 2012), as
17 well as one of 9 sites within the EU FP7 ÉCLAIRE project (<http://www.eclairer-fp7.eu/>) and a
18 TransNational Access (TNA) site within the European FP7 Infrastructure Network ACTRIS
19 (Aerosol, Clouds, and Trace gases Research InfraStructure Network). It ~~was~~ a Level 3 site
20 within the EU FP6 NitroEurope IP (Sutton et al., 2007). In 2014, it became a World
21 Meteorological Organisation Global Atmosphere Watch (WMO GAW) regional site.

Deleted: fortnightl

Deleted: had been

22 2.2 MARGA instrument

23 The MARGA 2S system (Metrohm Applikon B.V. Schiedam, NL) consists of two sampling
24 boxes and utilises ion chromatography to analyze for a range of water soluble trace gases and
25 aerosols. The MARGA 2S was set up to measure both PM₁₀ and PM_{2.5} aerosol. Air is first drawn
26 through a common PM₁₀ Teflon coated inlet (URG Corporation, Chapel Hill, NC, USA) at 3.55
27 m. ~~above ground level~~ into a 0.89 m long polyethylene (PE) 14 mm ID inlet line, which is
28 housed in the centre of an 11 cm OD ~~polyvinyl chloride (PVC)~~ conduit. The conduit has an
29 extractor fan at the base to draw air through based on the design used by Trebs et al. (2004)
30 aimed at keeping the sample at the temperature of the measurement height for as long as
31 possible. The PE tubing entering the air conditioned cabin (21°C) is split into two ¼” PE sample

Deleted: a.g.l

1 lines (0.4 m). The first line feeds directly into the first sampling box and the second sampling
2 line goes through a further PM_{2.5} cyclone (URG Coporation, Chapel Hill, NC, USA) before the
3 second sampling box. The flow rate in each sampling box is regulated to a volumetric flow of
4 1 m³ hr⁻¹ using a mass flow controller downstream of the sampling box. In the sampling box air
5 passes through a horizontal annular wet rotating denuder (WRD) (Keuken et al., 1988). The
6 WRD is continuously coated with a thin film of solution which strips water soluble gases from
7 the laminar air stream; the addition of 10 ppm H₂O₂ acts as a biocide and also promotes
8 oxidation of SO₂ initially trapped as HSO₃⁻ through to SO₄²⁻. Water soluble aerosols do not
9 diffuse into the stripping solution due to their lower diffusion velocity. The air flow then enters
10 a steam jet aerosol collector (SJAC). The steam in the SJAC promotes rapid growth of water
11 soluble aerosols which are then separated out from the air flow mechanically in a cyclone.
12 Details of the principles of the SJAC are described by Khlystov et al. (1995). The sampling
13 solutions are continuously drawn from the WRDs and SJACs to the analyzer box at a rate of 25
14 ml hr⁻¹ using syringe pumps. Samples are then analysed online by anion and cation
15 chromatography (Metrohm AG, Herisau, Switzerland). The system is continuously calibrated
16 by mixing the sample with a 325 mg/L internal standard of LiBr, prior to injection into the IC
17 columns. Anions are concentrated on a Metrosep A PCC 1 HC IC Preconcentration column
18 (2.29 ml) and then separated using a Metrosep A Supp 10-75 column (75 mm x 4.0 mm) using
19 a 7 mmol l⁻¹ Na₂CO₃ / 8 mmol l⁻¹ NaHCO₃ eluent. Cations are concentrated on a Metrosep C
20 PCC1 HC IC Preconcentration column (3.21 ml) and separated using a Metrosep C4 (100mm
21 x 4.0mm) cation column. A 3.5 ~~mmol l⁻¹~~ methanesulfonic acid (MSA) eluent was used for the
22 cation column, rather than the recommended 3.2 mmol l⁻¹ HNO₃ eluent used in other similar
23 systems. This was in order to eliminate a potential NO₃⁻ artefact, which has been reported (ten
24 Brink et al. (2009); Makkonen et al. (2012)). For the anion column a 1M H₃PO₄ solution was
25 used for chemical suppression. Detection was by conductivity, where concentrations were
26 calculated based on their specific conductivities relative to the internal standard ions (Li⁺ and
27 Br⁻). These standard set-up conditions and all significant operational changes over the 6.5 years,
28 which could be considered to have affected performance or data capture, are summarised in
29 Table 2. The increase in diameter of the SJACs described in table 2, reduced the restriction in
30 maintaining a flow rate, which was mass flow controlled at 1 m³ hr⁻¹ at standard temperature
31 and pressure (STP) until November 2011, whereas thereafter it was controlled to keep the
32 volumetric flow rate at ambient temperature and pressure through the size cuts constant.

Deleted: ^M

Formatted: Superscript

Deleted: U

Deleted: the flow rate was mass flow controlled to 1 m³ hr⁻¹ at STP

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

6 7 **Quality analysis and quality Assurance**

8 As discussed previously the MARGA used in this work was one of the first to be field deployed.
9 Processes were developed over the first several years which could be used to identify potential
10 sources of error or contamination in the MARGA data. Firstly, periodic field blanks were
11 carried out until 2011 by installing Whatman HEPA filters placed in front of the denuders and
12 left on for ~24 hours. The filters removed aerosols but not the gas phase components from the
13 air stream. The resultant change in PM concentrations allowed a blank value for the PM analytes
14 to be assessed. Following the upgrade of the instrument in November 2011 (Table 2), automated
15 monthly blanks were implemented in 2012, where the air pump and SJAC water supply and
16 heaters were turned off, allowing for blanks for both aerosol and gas phase to be carried out.
17 The blanks were not used to correct the data as they were usually below the detection limit (DL)
18 of the instrument. Instead blanks were used to provide evidence of contamination in the system
19 and to identify periods to be removed in the data ratification process. Prior to 2012 verification
20 and instrument maintenance protocols has been experimental and the authors are in the process
21 of finalising the protocols including calibration, which will be published separately. There was
22 a step change in 2012, when the initial developmental protocols for maintenance were replaced
23 by final protocols including quarterly replacement of inlets, cleaning of PM₁₀ head and PM_{2.5}
24 cyclone, monthly air flow calibrations and independent analysis of internal standards by a
25 UKAS accredited laboratory.

26 In the data ratification process values reported as 0 µg m⁻³ were replaced with half the detection
27 limit (DL). The method to determine the DL has changed over the 6 year period. From 2002 to
28 2011, the DL was taken as the average of the reported values below the manufacturers published
29 DL. From 2012, the DL was calculated by the analysis of the logarithmic distribution of the
30 measurements previously described by Kentisbeer et al. (2014), presented in table 3. The
31 methodology for analysing the DL and calibrating this type of on-line IC instrument is an area

1 of research in of itself and we plan to publish separately on this aspect of the MARGA
2 operation.

4 2.3 Back trajectories and associated analysis

5 To relate the aerosol species to air masses, back trajectory analysis was carried out. Four-day
6 back trajectories at 3 hour intervals for Auchencorth Moss were obtained for the years 2007 to
7 2012 through the OpenAir software package (Carslaw, 2013), which calculates back trajectories
8 with the HYSPLIT Trajectory Model (Hybrid Single Model Lagrangian Integrated Trajectory
9 Model, (Draxler and Hess, 1997) using Global NOAA-NCEP/NCAR reanalysis data. A cluster
10 analysis was then carried out using a routine in the OpenAir software, where data were clustered
11 using a distance matrix, in this case according to the similarity of the angle from their origin.
12 Further details of the calculations of the cluster analysis can be found in Carslaw (2013).

13 3 Results and Discussion

14 3.1 Overview

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

23 3.2 Concentration trends from June 2006 to December 2012

24 The annual average concentrations from June 2006 to December 2012 are summarised in Table
25 4. Overall, the concentrations of individual species were generally low ($< 1.5 \mu\text{g m}^{-3}$). When
26 compared with speciated $\text{PM}_{2.5}$ measurements from a background site in the Midlands, UK
27 (Harrison and Yin, 2010), Cl^- concentrations were higher at Auchencorth Moss based on annual
28 averages (Table 4) but are in a similar range to other UK sites (Abdalmogith and Harrison,
29 2006). The average annual concentration of NO_3^- and SO_4^{2-} in the PM_{10} , on the other hand, were

Deleted: Table 3

Deleted: Table 3

Deleted: the

Deleted: Table 3

Deleted: it is found that

Deleted: Table 3

1 larger in other parts of the UK including the other rural EMEP supersite at Harwell (Harrison
2 and Yin, 2010; Abdalmogith and Harrison, 2006). The maximum concentrations of the aerosol
3 components, however, show that there were periods where large PM pollution events took
4 place, which are hypothesised to have been due to long-range transport of polluted air masses.
5 In both the PM_{2.5} and PM₁₀, the largest concentrations of NH₄⁺ and NO₃⁻ were recorded during
6 2012, SO₄²⁻ maximum concentrations were observed in 2007 and other species varied (Table
7 4). It is interesting that specific local events can be picked out from the data record, for example
8 the maximum K⁺ concentration in 2012 of 2.61 µg m⁻³ occurred at 00:00 GMT on the 06
9 November 2012 - Guy Fawkes or “fireworks” night in the UK. The meteorological conditions
10 that night were cool, with an average temperature of -0.1°C at midnight and the wind direction
11 was from the dominant wind sector (SW). An increase of K⁺ is not unexpected as such an
12 increase is reported to occur following firework events (Vecchi et al., 2008; Drewnick et al.,
13 2006). This example illustrates the utility of the hourly composition measurements to
14 understand specific atmospheric events.

Deleted: Table 3

Deleted: LT

15
16 The monthly median concentrations for all 6.5 years are presented in Figure 2. There is a clear
17 seasonal variation for Na⁺ and Cl⁻ for all years, with the exception of 2009, with lower
18 concentrations in the summer and higher concentrations in winter. This seasonality reflects
19 higher average wind speeds in winter leading to more marine aerosol in the atmosphere, as
20 previously observed at other sites in the UK, but for Cl⁻ is also consistent with increased NaCl
21 reaction with HNO₃ which also peaks in summer. Of the secondary inorganic pollutants, NO₃⁻
22 shows individual peak concentrations only during the colder months, but not consistently while
23 SO₄²⁻ and NH₄⁺, do not have particularly strong annual variation. The largest monthly median
24 concentration for NH₄⁺ and NO₃⁻ was observed in March 2012. SO₄²⁻ on the other hand does
25 not show the same feature; the maximum monthly concentrations were observed in July 2012.

Deleted: Figure 2

Formatted: Font: Not Bold

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

Formatted: Font: Not Bold, Check spelling and grammar

Deleted: Figure 3

$$28 \quad PM_{\text{coarse}} = PM_{10} - PM_{2.5} \quad (1)$$

29 PM_{coarse} is dominated by sea salt (Na⁺ and Cl⁻). In the fine fraction (PM_{2.5}) NH₄⁺ aerosol
30 dominates, as it is the major base in secondary inorganic aerosol (refer to Section 3.4). In the
31 PM_{2.5} there is a decrease of NO₃⁻ during the afternoon in all seasons, though this feature is
32 strongest in winter. This behaviour is consistent with that previously reported from other North

1 European sites (Nemitz et al., in preparation) including Harwell (UK) (Revuelta et al., 2012),
2 Cabauw (Netherlands) (Mensah et al., 2012), Melpitz (Germany) (Poulain et al., 2011) and
3 SMEAR II (Finland) (Makkonen et al., 2012). It is assumed that the majority of fine NO_3^- will
4 be in the form of NH_4NO_3 and that the relationship between the gas precursors, temperature,
5 RH and chemical composition explain the observed cycle (see the discussion on gas
6 concentrations at this site Twigg et al. (in preparation)). Timonen et al. (2011), who had also
7 reported a decrease of daytime NO_3^- in Helsinki, explained the decrease to be the result of
8 increased boundary layer mixing as the same feature was observed in black carbon. At
9 Auchencorth Moss this behaviour of black carbon is not observed, instead the annual diurnal
10 average shows an increase of black carbon during the day (Cape et al., 2012). It is therefore
11 probable that diurnal variation in temperature and relative humidity exert a stronger influence
12 on the $\text{PM}_{2.5} \text{NO}_3^-$ at this site than the depth of the mixing layer. $\text{PM}_{2.5} \text{SO}_4^{2-}$ at Auchencorth
13 Moss, on the other hand, shows an increase in concentration during the day, with the feature
14 strongest in the summer. The increase in SO_4^{2-} is interpreted to be the effect of stronger
15 insolation in summer, which drives the oxidation of SO_2 to form sulphuric acid and finally SO_4^{2-}
16 , due to the increase in OH radicals.

17 3.3 Ion Balance

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

Formatted: Font: Not Bold

Deleted: Figure 4

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

4 3.4 Sea salt and sea salt processing

5 An overview of the average inorganic PM_{2.5} and PM_{coarse} composition based on mass is
6 presented in [Figure 5](#). Sea salt is presented as the individual species of measured Na⁺, sea salt
7 Cl⁻ (ssCl⁻), sea salt SO₄²⁻ (ssSO₄²⁻) sea salt Mg²⁺ (ssMg²⁺), sea salt Ca²⁺ (ssCa²⁺) and sea salt
8 K⁺ (ssK⁺), which were calculated based on the known mass ratio to Na⁺ in sea water (Seinfeld
9 and Pandis, 2006):

$$10 \quad [\text{ssCl}^-] = 1.8 \times [\text{Na}^+] \quad (2)$$

$$11 \quad [\text{ssSO}_4^{2-}] = 0.252 \times [\text{Na}^+] \quad (3)$$

$$12 \quad [\text{ssMg}^{2+}] = 0.12 \times [\text{Na}^+] \quad (4)$$

$$13 \quad [\text{ssCa}^{2+}] \text{ or } [\text{ssK}^+] = 0.04 \times [\text{Na}^+] \quad (5)$$

14 As would be expected, the dominant fraction of the coarse aerosol at this site is from sea salt
15 (73%); this is larger than reported at other European sites such as SMEAR III, near Helsinki
16 (Makkonen et al., 2012), probably because of proximity to the ocean in all wind directions.
17 There is also a large contribution from NO₃⁻ in the coarse fraction. This is not the first time that
18 a large proportion of NO₃⁻ has been reported in the coarse mode; the same was observed in
19 Melpitz, Germany and has been explained to be the result of chloride-nitrate exchange that
20 takes place on coarse aerosol during long range transport of sea salt (Spindler et al.,
21 2012;Dasgupta et al., 2007). This was further evident as the average non-sea salt Cl⁻ mass was
22 -0.17 μg m⁻³ and -0.08 μg m⁻³ for PM_{2.5} and PM_{coarse} respectively, where:

$$23 \quad \text{Non-sea salt Cl}^- = [\text{Cl}^-]_{\text{measured}} - [\text{ssCl}^-]_{\text{calculated}} \quad (6)$$

24 To investigate the process of sea salt substitution by reaction with HNO₃ further, the ratios of
25 Na⁺ and Cl⁻ were compared with NO₃⁻ in the coarse mode for the year 2012. In general, larger
26 NO₃⁻ concentrations tended to be observed on occasions where a depletion of Cl⁻ was observed,
27 though this was not true for all cases ([Figure 6](#)).It should be noted, however, that the
28 concentrations of PM_{coarse} are calculated as differences (Eq. 1) and therefore subject to
29 considerable uncertainty.

Formatted: Font: Not Bold

Deleted: Figure 5

Formatted: Font: Not Bold, Font color: Auto, Check spelling and grammar

Deleted: Figure 6

Formatted: Font color: Auto

Deleted: that

1 PM_{2.5} on the other hand is dominated by the secondary inorganic aerosol (SIA) (NH₄⁺, NO₃⁻
2 and SO₄²⁻) (Figure 5), with a total contribution of 63% to the total measured mass by the
3 MARGA, which is to be anticipated. NO₃⁻ is the dominant mass of the SIA at Auchencorth
4 Moss accounting for 26% for the total water soluble species detected by the MARGA. A similar
5 comparison has been carried out by a MARGA operated at SMEAR III (near Helsinki, Finland)
6 where SO₄²⁻ was the dominating mass responsible for 50.4% of the total inorganic PM_{2.5} mass
7 reported by the MARGA (Makkonen et al., 2012). This is not surprising as it has also been
8 shown by Nemitz et al. (in preparation), from AMS studies, that in Finland PM₁ is dominated
9 by SO₄²⁻, whereas in the UK and the rest of NW Europe, NO₃⁻ is the dominant SIA. Sea salt,
10 however, still makes a considerable contribution (35%) to the average measured PM_{2.5} by the
11 MARGA, bearing in mind that the cut-off might have been somewhat larger than 2.5 µm until
12 November 2011 (see above). In 2012, sea salt still made a major contribution to the total mass
13 of the PM_{2.5} (30%), where there is the greatest confidence in the cut-off of the cyclone. There
14 was a clear increase of PM_{2.5} Na⁺ with wind speed for 2012 (Figure 7) in the dominant wind
15 sector (refer to Figure 4), suggesting that PM_{2.5} Na⁺ was related to sea salt and its presence at
16 the site is driven by meteorology.

17 Potassium (K⁺) is present in sea salt and when the available 2012 PM_{2.5} data was compared to
18 the concentration of Na⁺ it tended to follow the known ratio in sea water (Seinfeld and Pandis,
19 2006), Figure 8. The greatest deviation from this curve appears to be in periods of high black
20 carbon (BC) concentrations. PM_{coarse} however had much scatter. High concentrations of black
21 carbon are often associated with combustion processes, though K⁺ can also occur as a product
22 of other anthropogenic sources. There was clear evidence in the PM_{2.5} that high concentrations
23 of K⁺ were associated with increased BC pointing to a contribution from combustion sources
24 or biomass burning (Figure 8). The measured Mg²⁺ /Na⁺ ratio in PM_{2.5} followed the known
25 ratio in sea water (Seinfeld and Pandis, 2006). The same comparison was done for PM_{coarse},
26 however there was much more scatter in the data.

27 3.5 Comparison of total inorganic aerosol with TEOM-FDMS measurements

28 The total average water-soluble inorganic aerosol mass measured by the MARGA for the period
29 January 2007 to December 2012 was 3.82 µg m⁻³ and 5.04 µg m⁻³ for PM_{2.5} and PM₁₀,
30 respectively. The measured mass by the MARGA was compared to the Tapered Element
31 Oscillating Microbalance Filter Dynamic Measurement System (TEOM-FDMS) which

Formatted: Font: Not Bold

Deleted: Figure 5

Deleted: Figure 7

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Deleted: Figure 1

Deleted: Figure 8

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Deleted: Figure 8

1 measures the total aerosol mass; total mass data were obtained from the AURN network
2 (<http://uk-air.defra.gov.uk/networks/network-info?view=aur>) for the 6 years of interest (2007
3 to 2012). It was found that the PM₁₀ mass measured by the MARGA accounted for 78% of total
4 PM₁₀ measured by the TEOM-FDMS, on average. It is not the first time that inorganic water
5 soluble aerosols have been found to be major contributors to the total mass in Europe (Putaud
6 et al., 2010). Aerosol components not resolved by the MARGA include organic aerosols, BC,
7 water and crustal elements such as silicate. Organic aerosol often accounts for a larger fraction
8 of the PM₁₀ mass at central European background sites than the missing mass at Auchencorth
9 allows for. This is consistent with AMS measurements in S.Scotland that also indicate relatively
10 low contributions from organic aerosol (Nemitz et al., in preparation).

11 Table 5 summarises the annual mass fraction that is accounted for by the MARGA instrument
12 when compared with the TEOM-FDMS for both PM₁₀ and PM_{2.5}. It is very clear that there are
13 discrepancies between the measured PM_{2.5} by the MARGA and that by TEOM-FDMS. Mass
14 closure improved in 2012, probably in response to the improved flow control implemented in
15 November 2011 on the MARGA (see above). An alternative explanation is that the PM
16 concentrations at Auchencorth are close to the detection limits of the TEOM-FDMS, which is
17 indicated by the large percentage of negative values reported by the instrument over the period
18 January 2007 to December 2012 (26% and 10% respectively for PM_{2.5} and PM₁₀), the annual
19 variation of which can be found in Table 5. During the 6 years presented, the fraction of
20 negative values for PM₁₀ declined, while it stayed constant for PM_{2.5}. It therefore can be
21 concluded that that the PM_{2.5} TEOM-FDMS at Auchencorth Moss has an offset, as has
22 previously been commented by Laxen et al. (2012). It is therefore not possible to comment on
23 what the true contribution of the measured water soluble inorganic mass measured by the
24 MARGA is to the total PM_{2.5}.

25 3.6 Influence of air mass on aerosol composition

26 Due to the remote location of the site, the origin of air masses at the site influences the aerosol
27 composition. Back trajectories, run over a 96 hour period, were obtained at 3-hour intervals for
28 the years 2007 to 2012, which were then clustered, details of which can be found in Section
29 2.3. Figure 9 displays the mean trajectory for each of the 6 clusters assigned. The average
30 concentration over the 6 year period for each cluster and the % species contribution to the total
31 measured concentration by the MARGA are summarised in Figure 10. When calculating the
32 average associated with each cluster, data were only used when all species were available. As

Deleted: in

Deleted: Table 4

Deleted: setup

Deleted: Table 4

Formatted: Font: Not Bold

Deleted: Figure 9

Deleted: Figure 10

Formatted: Font: Not Bold

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

10 3.7 Aerosol composition during high pollution events

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

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

Formatted: Font: Not Bold

Deleted: Figure 11

Deleted: UK and

1 4 Summary and conclusions

2 The first six and a half years of chemically speciated PM_{2.5} and PM₁₀ measurements from the
3 MARGA at Auchencorth Moss have been analysed. This study has provided greater detail in
4 the long term temporal variations of inorganic species in the UK background atmosphere and
5 confirmed the status of the field site as a background site in the European context, where
6 concentrations of the inorganic species were low over the 6.5 years. The dynamic changes
7 between air masses dominated by anthropogenic and natural sources is clearly observable on
8 an inter-annual scale and continuation of these long term measurements will be a valuable
9 resource to understand long term trends in PM composition in response to climate and policy
10 drivers.

Deleted: in

11 The average ion balance at this site was biased towards cations some of which would probably
12 have been neutralised by organic acids such as oxalic acid. Additional studies to identify the
13 missing water soluble species would therefore be beneficial at this site to close the ion balance.
14 Comparison with the TEOM-FDMS bulk mass method found that the compounds resolved by
15 the MARGA instrument accounted on average for 78% of the PM₁₀ mass measured at
16 Auchencorth Moss, with considerable uncertainty due to changes in the MARGA configuration
17 over the period and the detection limits of the TEOM-FDMS and possible difference in the
18 characteristics of the PM₁₀ inlets. One recommendation is to add a continuous measurement of
19 the organic aerosol mass at Auchencorth Moss to determine its contribution to the total mass,
20 due to the regional importance of this site.

Deleted: likely

21 Based on monthly median concentration, Na⁺ and Cl⁻ generally were found to vary seasonally
22 due to the meteorology of the site, with the highest concentrations in winter when the average
23 wind speed was greatest. As expected NH₄⁺ dominated the finer PM_{2.5} aerosol in terms of μmol
24 m⁻³, as it is the major base for aerosol in the atmosphere and free ammonia is always available
25 in NW Europe. The influence of long-range transport at this site is evident, with sea salt
26 dominating air masses originating from the Arctic and Atlantic Ocean, whereas SIA dominate
27 air masses that originate over land, with largest contributions from continental Europe. It
28 therefore supports the importance of a transboundary co-operation, in controlling precursor
29 gases such as NO_x and NH₃ as highlighted in this long term study, where NH₄⁺ and NO₃⁻ tended
30 to be the drivers of the (regional) pollution events observed at this background site. The
31 dominance of NO₃⁻ compared to SO₄²⁻ was evident too in the diurnal cycles, with the exception
32 of summer and provides evidence of a shift in recent decades from sulphur to nitrogen driven

Deleted: NE

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

5

6 **5 Acknowledgements**

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

1 6 References

- 2 Aas, W., Tsyro, S., Bieber, E., Bergström, R., Ceburnis, D., Ellermann, T., Fagerli, H., Frölich,
3 M., Gehrig, R., Makkonen, U., Nemitz, E., Otjes, R., Perez, N., Perrino, C., Prévôt, A. S. H.,
4 Putaud, J. P., Simpson, D., Spindler, G., Vana, M., and Yttri, K. E.: Lessons learnt from the
5 first EMEP intensive measurement periods, *Atmos. Chem. Phys.*, 12, 8073-8094, 10.5194/acp-
6 12-8073-2012, 2012.
- 7 Abdalmogith, S. S., and Harrison, R. M.: The use of trajectory cluster analysis to examine the
8 long-range transport of secondary inorganic aerosol in the UK, *Atmospheric Environment*, 39,
9 6686-6695, <http://dx.doi.org/10.1016/j.atmosenv.2005.07.059>, 2005.
- 10 Abdalmogith, S. S., and Harrison, R. M.: An analysis of spatial and temporal properties of daily
11 sulfate, nitrate and chloride concentrations at UK urban and rural sites, *Journal of*
12 *Environmental Monitoring*, 8, 691-699, 2006.
- 13 Ansmann, A., Bösenberg, J., Chaikovsky, A., Comerón, A., Eckhardt, S., Eixmann, R.,
14 Freudenthaler, V., Ginoux, P., Komguem, L., Linné, H., Márquez, M. Á. L., Matthias, V.,
15 Mattis, I., Mitev, V., Müller, D., Music, S., Nickovic, S., Pelon, J., Sauvage, L., Sobolewsky,
16 P., Srivastava, M. K., Stohl, A., Torres, O., Vaughan, G., Wandinger, U., and Wiegner, M.:
17 Long-range transport of Saharan dust to northern Europe: The 11–16 October 2001 outbreak
18 observed with EARLINET, *Journal of Geophysical Research: Atmospheres*, 108, 4783,
19 10.1029/2003jd003757, 2003.
- 20 Cape, J. N., Coyle, M., and Dumitrean, P.: The atmospheric lifetime of black carbon,
21 *Atmospheric Environment*, 59, 256-263, <http://dx.doi.org/10.1016/j.atmosenv.2012.05.030>,
22 2012.
- 23 Carslaw, D. C., and Ropkins, K.: Openair — an R package for air quality data analysis. ,
24 *Environmental Modelling & Software.* , 27-28, 52-61., 2012.
- 25 Carslaw, D. C.: The openair manual — open-source tools for analysing air pollution data.
26 *Manual for version 0.8-0.*, King's College London., 2013.
- 27 Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A., Forster, P. M., Mann, G.
28 W., Spracklen, D. V., Woodhouse, M. T., Regayre, L. A., and Pierce, J. R.: Large contribution
29 of natural aerosols to uncertainty in indirect forcing, *Nature*, 503, 67-71, 2013.
- 30 Cowen, K., Hanft, E., Kelly, T., Dindal, A., and McKernan, J.: Environmental technology
31 verification report, ETV advanced monitoring systems center, Applikon MARGA semi-
32 continuous ambient air monitoring system, US EPA, Battelle, 2011.
- 33 Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G.,
34 Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E.,
35 Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A.,
36 Kortelainen, A. M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E.,
37 O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K.,
38 Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic
39 aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2
40 based source apportionment approach, *Atmos Chem Phys*, 14, 6159-6176, 10.5194/acp-14-
41 6159-2014, 2014.
- 42 Dasgupta, P. K., Campbell, S. W., Al-Horr, R. S., Rahmat Ullah, S. M., Li, J., Amalfitano, C.,
43 and Poor, N. D. A. E.: Convention of sea salt aerosol to NaNO₃ and the production of HCl:

1 analysis of temporal behaviour of aerosol chloride/nitrate and gaseous HCl/HNO₃
2 concentrations with AIM., *Atmospheric Environment*, 41, 4242–4257 2007.

3 Draxler, R. R., and Hess, G. D.: Description of the HYSPLIT_4 modeling system. , NOAA Air
4 Resources Laboratory, Silver Spring, MD, 24, 1997.

5 Drewer, J., Lohila, A., Aurela, M., Laurila, T., Minkkinen, K., Penttilä, T., Dinsmore, K. J.,
6 Mckenzie, R. M., Helfter, C., Flechard, C., Sutton, M. A., and Skiba, U. M.: Comparison of
7 greenhouse gas fluxes and nitrogen budgets from an ombrotrophic bog in Scotland and a
8 minerotrophic sedge fen in Finland, *Eur J Soil Sci*, 61, 640-650, DOI 10.1111/j.1365-
9 2389.2010.01267.x, 2010.

10 Drewnick, F., Hings, S. S., Curtius, J., Eerdekens, G., and Williams, J.: Measurement of fine
11 particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany,
12 *Atmospheric Environment*, 40, 4316-4327, <http://dx.doi.org/10.1016/j.atmosenv.2006.03.040>,
13 2006.

14 Famulari, D., Fowler, D., Nemitz, E., Hargreaves, K. J., Storeton-West, R. L., Rutherford, G.,
15 Tang, Y. S., Sutton, M. A., and Weston, K. J.: Development of a low-cost system for measuring
16 conditional time-averaged gradients of SO₂ and NH₃, *Environ Monit Assess*, 161, 11-27, DOI
17 10.1007/s10661-008-0723-6, 2010.

18 Flechard, C., and Fowler, D.: Atmospheric ammonia at a moorland site. I: The meteorological
19 control of ambient ammonia concentrations and the influence of local sources. , *Quarterly*
20 *Journal of the Royal Meteorological Society* 124 733 -757, 1998

21 Harrison, R. M., and Yin, J.: Chemical speciation of PM_{2.5} particles at urban background and
22 rural sites in the UK atmosphere, *Journal of Environmental Monitoring*, 12, 1404-1414,
23 10.1039/c000329h, 2010.

24 Karanasiou, A., Moreno, N., Moreno, T., Viana, M., de Leeuw, F., and Querol, X.: Health
25 effects from Sahara dust episodes in Europe: Literature review and research gaps, *Environment*
26 *International*, 47, 107-114, <http://dx.doi.org/10.1016/j.envint.2012.06.012>, 2012.

27 Kentisbeer, J., Leeson, S. R., Malcolm, H. M., Leith, I. D., Braban, C. F., and Cape, J. N.: Patterns
28 and source analysis for atmospheric mercury at Auchencorth Moss, Scotland, *Environmental*
29 *Science: Processes & Impacts*, 16, 1112-1123, doi: 10.1039/c3em00700f, 2014.

30 Keuken, M. P., Schoonebeek, C. A. M., van Wensveen-Louter, A., and Slanina, J.:
31 Simultaneous sampling of NH₃, HNO₃, HCl, SO₂ and H₂O₂ in ambient air by wet annular
32 denuder system, *Atmospheric Environment*, 22, 2541-2548, 1988.

33 Khlystov, A., Wyers, G. P., and Slanina, J.: The steam-jet aerosol collector, *Atmospheric*
34 *Environment*, 29, 2229-2234, 1995.

35 Laxen, D., Heal, M., Vieno, M., and Bigg, M.: PM_{2.5} in Scotland: A report for SEPA., Air
36 Quality Consultants Ltd, Bristol, UK.1408/1/F2, 2012.

37 Makkonen, U., Virkkula, A., Mäntykenttä, J., Hakola, H., Keronen, P., Vakkari, V., and Aalto,
38 P. P.: Semi-continuous gas and inorganic aerosol measurements at a Finnish urban site:
39 comparisons with filters, nitrogen in aerosol and gas phases, and aerosol acidity, *Atmos. Chem.*
40 *Phys.*, 12, 5617-5631, 10.5194/acp-12-5617-2012, 2012.

41 Makkonen, U., Virkkula, A., Hellén, H., Hemmilä, M., Sund, J., Äijälä, M., Ehn, M., Junninen,
42 H., Keronen, P., Petäjä, T., Worsnop, D. R., Kulmala, M. and Hakola, H.: Semi-continuous gas

Deleted: Penttilä

Deleted: ¶

1 [and inorganic aerosol measurements at a boreal forest site: seasonal and diurnal cycles of NH₃,
2 HONO and HNO₃. *Boreal Env. Res.* 19 \(suppl. B\): 311–328, 2014.](#)

3 Malley, C. S., Braban, C. F., and Heal, M. R.: The application of hierarchical cluster analysis
4 and non-negative matrix factorization to European atmospheric monitoring site classification,
5 *Atmospheric Research*, 138, 30-40, <http://dx.doi.org/10.1016/j.atmosres.2013.10.019>, 2014.

6 Markovic, M. Z., VandenBoer, T. C., and Murphy, J. G.: Characterization and optimization of
7 an online system for the simultaneous measurement of atmospheric water-soluble constituents in
8 the gas and particle phases. *J. Environ. Monitor.*, 10.1039/c2em00004k, 2012.

9 Mensah, A. A., Holzinger, R., Otjes, R., Trimborn, A., Mentel, T. F., ten Brink, H., Henzing,
10 B., and Kiendler-Scharr, A.: Aerosol chemical composition at Cabauw, The Netherlands as
11 observed in two intensive periods in May 2008 and March 2009, *Atmos Chem Phys*, 12, 4723-
12 4742, DOI 10.5194/acp-12-4723-2012, 2012.

13 Morgan, W. T., Allan, J. D., Bower, K. N., Highwood, E. J., Liu, D., McMeeking, G. R.,
14 Northway, M. J., Williams, P. I., Krejci, R., and Coe, H.: Airborne measurements of the spatial
15 distribution of aerosol chemical composition across Europe and evolution of the organic
16 fraction *Atmos. Chem. Phys.*, 10 4065 - 4083 2010.

17 Nemitz, E., Prevot, A. S. H., Vieno, M., Äijälä, M., Allan, J., Berresheim, H., Cabone, S.,
18 Canagaratna, M., Capes, G., Ceburnis, D., Choularton, T., Coe, H., Cubison, M., Dall'Osto,
19 M., Di Marco, C. F., DeCarlo, P., Ehn, M., Eriksson, A., Freney, E., Herrmann, H., Jimenez,
20 J.-L., Hildebrandt, L., Juninen, H., Kiendler-Scharr, A., Laaksonen, A., Lanz, V., McFiggans,
21 G., Mensah, A., Mentel, T. F., Mohr, C., O'Dowd, C., Ortega, A., Ovadnevaite, J., Pagels, J.,
22 Pandis, S., Phillips, G. J., Poulain, L., Raatikainen, T., Saarikoski, S., Sellegri, K., Spindler, G.,
23 Sueper, D., Swietlicki, E., Tiitta, P., and Worsnop, D. R.: A snapshot European climatology of
24 submicron aerosol chemical composition derived from an Aerosol Mass Spectrometer network,
25 in preparation.

26 Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B.,
27 Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical
28 Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass
29 Concentrations of Ambient Aerosol, *Aerosol Science and Technology*, 45, 780-794,
30 10.1080/02786826.2011.560211, 2011.

31 Poulain, L., Spindler, G., Birmili, W., Plass-Dülmer, C., Wiedensohler, A., and Herrmann, H.:
32 Seasonal and diurnal variations of particulate nitrate and organic matter at the IfT research
33 station Melpitz, *Atmos. Chem. Phys.*, 11, 12579-12599, 10.5194/acp-11-12579-2011, 2011.

34 Putaud, J. P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H.,
35 Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Herrmann, H., Hitzinger, R., Hüglin,
36 C., Jones, A. M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T. A. J., Löschau, G.,
37 Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H.,
38 Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten
39 Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F.: A European aerosol
40 phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural,
41 urban, and kerbside sites across Europe, *Atmospheric Environment*, 44, 1308-1320,
42 <http://dx.doi.org/10.1016/j.atmosenv.2009.12.011>, 2010.

43 Revuelta, M. A., Harrison, R. M., Núñez, L., Gomez-Moreno, F. J., Pujadas, M., and Artñano,
44 B.: Comparison of temporal features of sulphate and nitrate at urban and rural sites in Spain

1 and the UK, Atmospheric Environment, 60, 383-391,
2 <http://dx.doi.org/10.1016/j.atmosenv.2012.07.004>, 2012.

3 Rumsey, I. C., Cowen, K. A., Walker, J. T., Kelly, T. J., Hanft, E. A., Mishoe, K., Rogers, C.,
4 Proost, R., Beachley, G. M., Lear, G., Frelink, T., and Otjes, R. P.: An assessment of the
5 performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-
6 continuous method for soluble compounds, Atmos. Chem. Phys., 14, 5639-5658, 10.5194/acp-
7 14-5639-2014, 2014.

8 Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to
9 Climate Change, 2nd ed., John Wiley & Sons., New Jersey, 1203 pp., 2006.

10 Spindler, G., Gnauk, T., Gruner, A., Limuma, Y., Muller, K., Scheinhardt, S., and Herrmann,
11 H.: Size-segregated characterization of PM10 at the EMEP site Melpitz (Germany) using a five-
12 stage impactor: a six year study, Journal of Atmospheric Chemistry, 69, 127-157, DOI
13 10.1007/s10874-012-9233-6, 2012.

14 Sutton, M. A., Nemitz, E., Erisman, J. W., Beier, C., Bahl, K. B., Cellier, P., de Vries, W.,
15 Cotrufo, F., Skiba, U., Di Marco, C., Jones, S., Laville, P., Soussana, J. F., Loubet, B., Twigg,
16 M., Famulari, D., Whitehead, J., Gallagher, M. W., Neftel, A., Flechard, C. R., Herrmann, B.,
17 Calanca, P. L., Schjoerring, J. K., Daemmgen, U., Horvath, L., Tang, Y. S., Emmett, B. A.,
18 Tietema, A., Peñuelas, J., Kesik, M., Brueggemann, N., Pilegaard, K., Vesala, T., Campbell, C.
19 L., Olesen, J. E., Dragosits, U., Theobald, M. R., Levy, P., Mobbs, D. C., Milne, R., Viovy, N.,
20 Vuichard, N., Smith, J. U., Smith, P., Bergamaschi, P., Fowler, D., and Reis, S.: Challenges in
21 quantifying biosphere-atmosphere exchange of nitrogen species, Environmental Pollution,
22 150, 125-139, <http://dx.doi.org/10.1016/j.envpol.2007.04.014>, 2007.

23 Tang, Y. S., Dragosits, U., Dijk, N., Love, L., Simmons, I., and Sutton, M.: Assessment of
24 Ammonia and Ammonium Trends and Relationship to Critical Levels in the UK National
25 Ammonia Monitoring Network (NAMN), in: Atmospheric Ammonia, edited by: Sutton, M.,
26 Reis, S., and Baker, S. H., Springer, Dordrecht, Netherlands, 187-194, 2009.

27 ten Brink, H., Otjes, R., Jongejan, P., and Kos, G.: Monitoring of the ratio of nitrate to sulphate
28 in size-segregated submicron aerosol in the Netherlands, Atmospheric Research, 92, 270-276,
29 <http://dx.doi.org/10.1016/j.atmosres.2008.12.003>, 2009.

30 Timonen, H., Aurela, M., Saarnio, K., Frey, A., Saarikoski, S., Teinilä, K., Kulmala, M., and
31 Hillamo, R.: Monitoring of inorganic ions, carbonaceous matter and mass in ambient aerosol
32 particles with online and offline methods, Atmos. Meas. Tech. Discuss., 4, 6577-6614,
33 10.5194/amtd-4-6577-2011, 2011.

34 Tørseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre,
35 C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation
36 Programme (EMEP) and observed atmospheric composition change during 1972–2009,
37 Atmos. Chem. Phys., 12, 5447-5481, 10.5194/acp-12-5447-2012, 2012.

38 Trebs, I., Meixner, F. X., Slanina, J., Otjes, R., Jongejan, P., and Andreae, M. O.: Real-time
39 measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a
40 rural site in the Amazon Basin, Atmos. Chem. Phys., 4, 967-987, 2004.

41 Twigg, M. M., Di Marco, C. F., van Dijk, N., Leeson, S., Jones, M. R., Leith, I., Morrison, E.,
42 Proost, R., Peeters, A., Frelink, T., Braban, C. F., Nemitz, E., and Cape, J. N.: First UK long
43 term speciated high resolution measurements of water soluble aerosols and gases at a
44 background site. Part 2: Gases, in preparation.

1 Vecchi, R., Bernardoni, V., Cricchio, D., D'Alessandro, A., Fermo, P., Lucarelli, F., Nava, S.,
2 Piazzalunga, A., and Valli, G.: The impact of fireworks on airborne particles, *Atmospheric*
3 *Environment*, 42, 1121-1132, <http://dx.doi.org/10.1016/j.atmosenv.2007.10.047>, 2008.

4 Vieno, M., Heal, M. R., Hallsworth, S., Famulari, D., Doherty, R. M., Dore, A. J., Tang, Y. S.,
5 Braban, C. F., Leaver, D., Sutton, M. A., and Reis, S.: The role of long-range transport and
6 domestic emissions in determining atmospheric secondary inorganic particle concentrations
7 across the UK, *Atmos Chem Phys*, 14, 8435-8447, 10.5194/acp-14-8435-2014, 2014.

8 Weber, R. J., Orsini, D., Daun, Y., Lee, Y. N., Klotz, P. J., and Brechtel, F.: A Particle-into-
9 Liquid Collector for Rapid Measurement of Aerosol Bulk Chemical Composition, *Aerosol*
10 *Science and Technology*, 35, 718-727, 10.1080/02786820152546761, 2001.

11
12
13
14

1 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

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

4
5

- 1 Table 2 Summary of major operational changes which will have potentially affected the
 2 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 $\text{PM}_{2.5}$ and PM_{10} . Reduction in downtime due to blockages.
28/07/2009	Replaced glass fibre filters to PTFE Whatman Resist 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.

- 3
4

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

Formatted: Caption, Keep with next

Formatted: Font: 12 pt, Not Bold, Font color: Black

<u>Component</u>	<u>DL</u>
	<u>$\mu\text{g m}^{-3}$</u>
<u>PM₁₀</u>	
<u>NH₄[±]</u>	<u>0.062</u>
<u>Na⁺</u>	<u>0.123</u>
<u>K⁺</u>	<u>0.019</u>
<u>Ca²⁺</u>	<u>0.016</u>
<u>Mg²⁺</u>	<u>0.015</u>
<u>Cl⁻</u>	<u>0.086</u>
<u>NO₃⁻</u>	<u>0.105</u>
<u>SO₄²⁻</u>	<u>0.349</u>
<u>PM_{2.5}</u>	
<u>NH₄[±]</u>	<u>0.069</u>
<u>Na⁺</u>	<u>0.106</u>
<u>K⁺</u>	<u>0.014</u>
<u>Ca²⁺</u>	<u>0.015</u>
<u>Mg²⁺</u>	<u>0.007</u>
<u>Cl⁻</u>	<u>0.053</u>
<u>NO₃⁻</u>	<u>0.091</u>
<u>SO₄²⁻</u>	<u>0.242</u>

2

- 1 Table 4 Annual concentrations of both PM₁₀ and PM_{2.5} species measured by the MARGA system at Auchencorth Moss from 1st June 2006 to
- 2 1st January 2013. (* 2006 data coverage: June – December 2006 only) Key: μ_A – arithmetic mean, μ_G – median, Max – maximum, σ_A – arithmetic
- 3 standard deviation, DC – data capture (%).

Deleted: 3

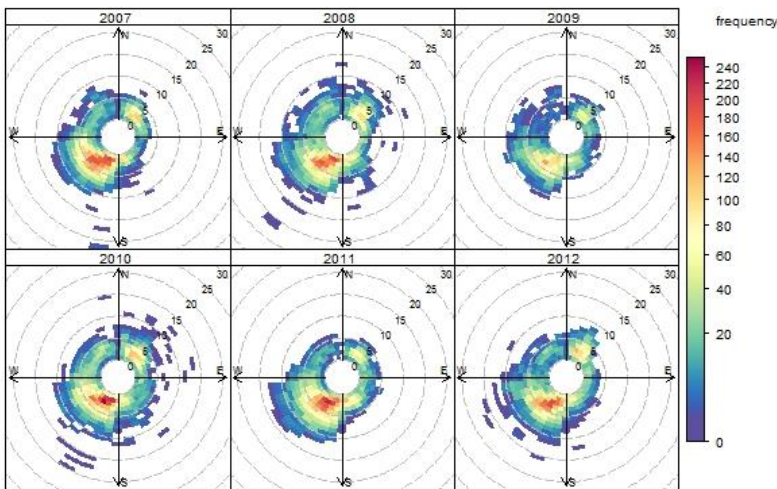
	2006*					2007					2008					2009					2010					2011					2012				
	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC	μ_A	μ_G	max	σ_A	DC
PM_{2.5}	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	%
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
PM₁₀																																			
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

- 1 Table 5 Measured MARGA mass vs TEOM-FDMS mass and the percentage of time the TEOM
- 2 FDMS reported values $\leq 0 \mu\text{g m}^{-3}$ for the years 2007 to 2012.

Deleted: 4

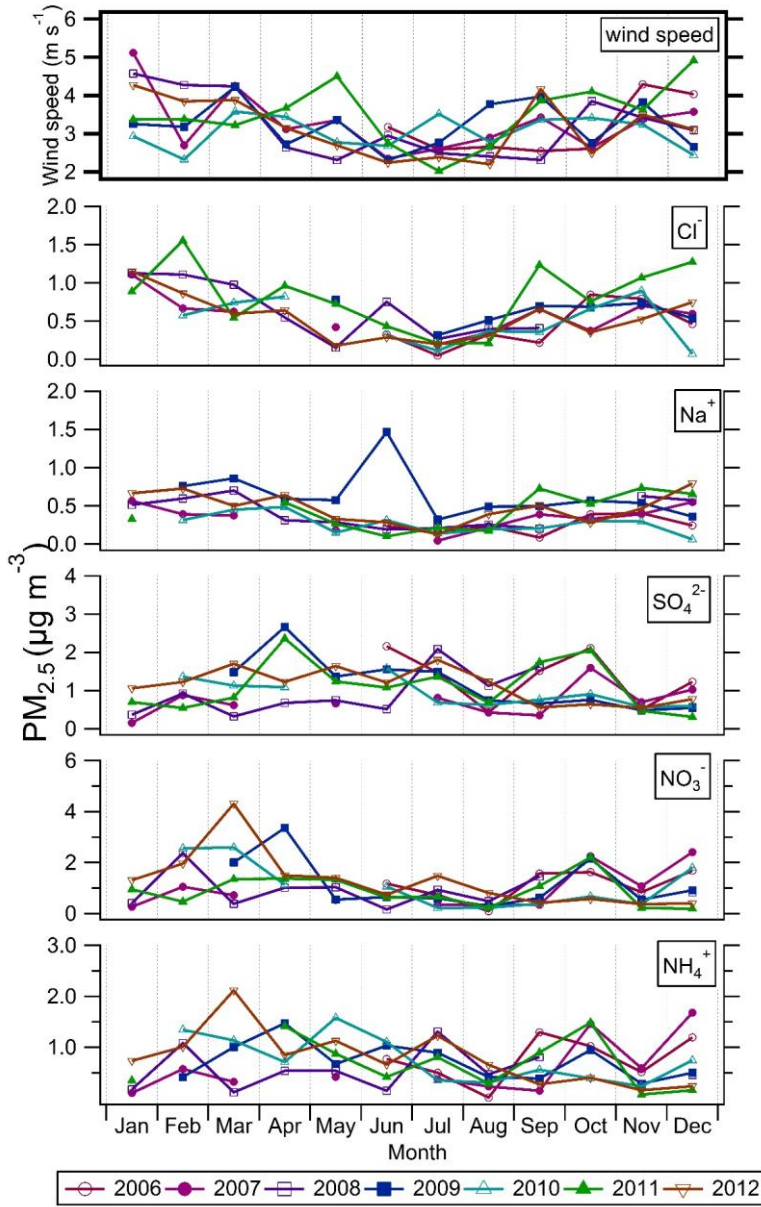
Year	PM ₁₀ unaccounted (%)	PM _{2.5} unaccounted (%)	PM ₁₀ measured by TEOM-FDMS - Reported values ≤ 0 $\mu\text{g m}^{-3}$ (%)	PM _{2.5} measured by TEOM-FDMS - Reported values ≤ 0 $\mu\text{g m}^{-3}$ (%)
2007	21	-15	14	25
2008	23	-38	10	25
2009	29	-48	7	28
2010	28	-27	6	17
2011	32	-20	9	26
2012	18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

3



- 4
- 5 Figure 1 Frequency plots of wind direction and windspeed (m s^{-1}) averaged over an hour at
- 6 Auchencorth Moss for the years 2007 to 2012. Windspeed scale is limited to 30 m s^{-1} .
- 7 (Graphs produced using OpeAir;Carslaw and Ropkins (2012))

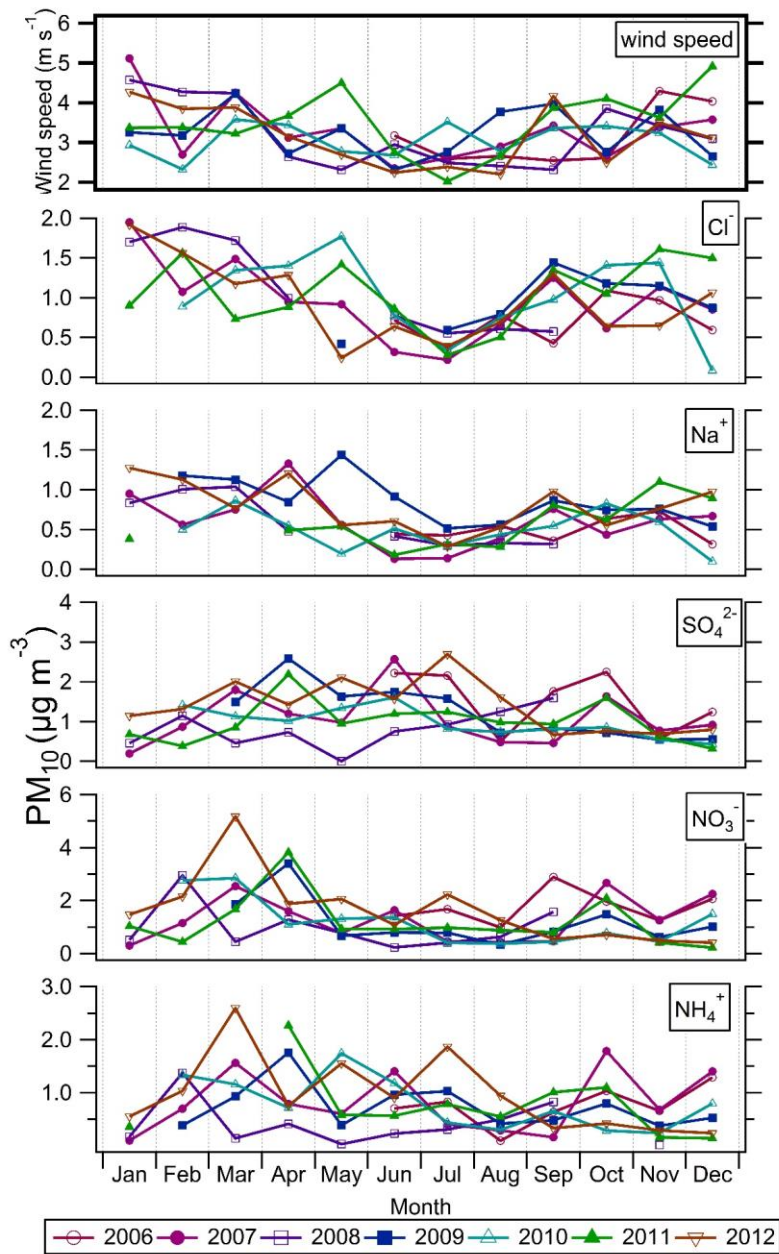
1



2

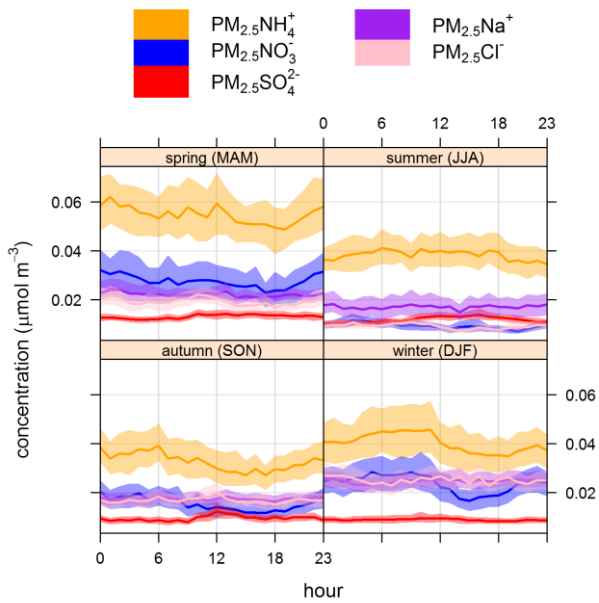
3 **Figure 2** a) Median monthly mass concentrations of PM_{2.5} species measured by the MARGA
4 and median wind speed from June 2006 to December 2012

Deleted: Figure 2

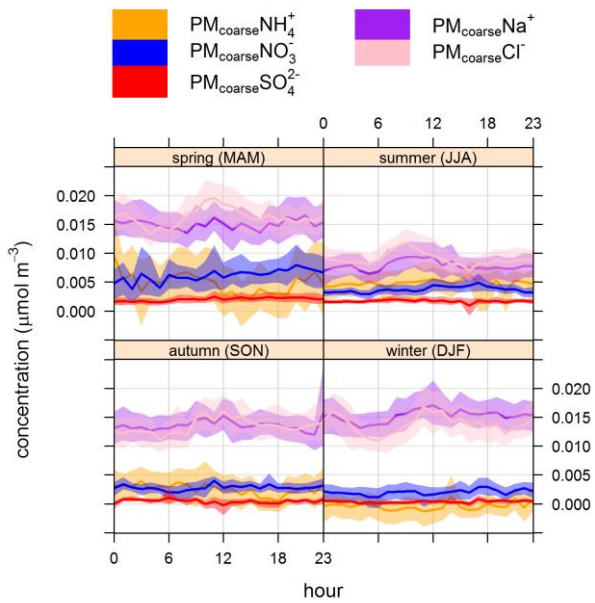


1
 2 Figure 2b) Median monthly mass concentrations of PM₁₀ species measured by the MARGA
 3 and median wind speed from June 2006 to December 2012

Commented [TMM1]: Updated figures



1

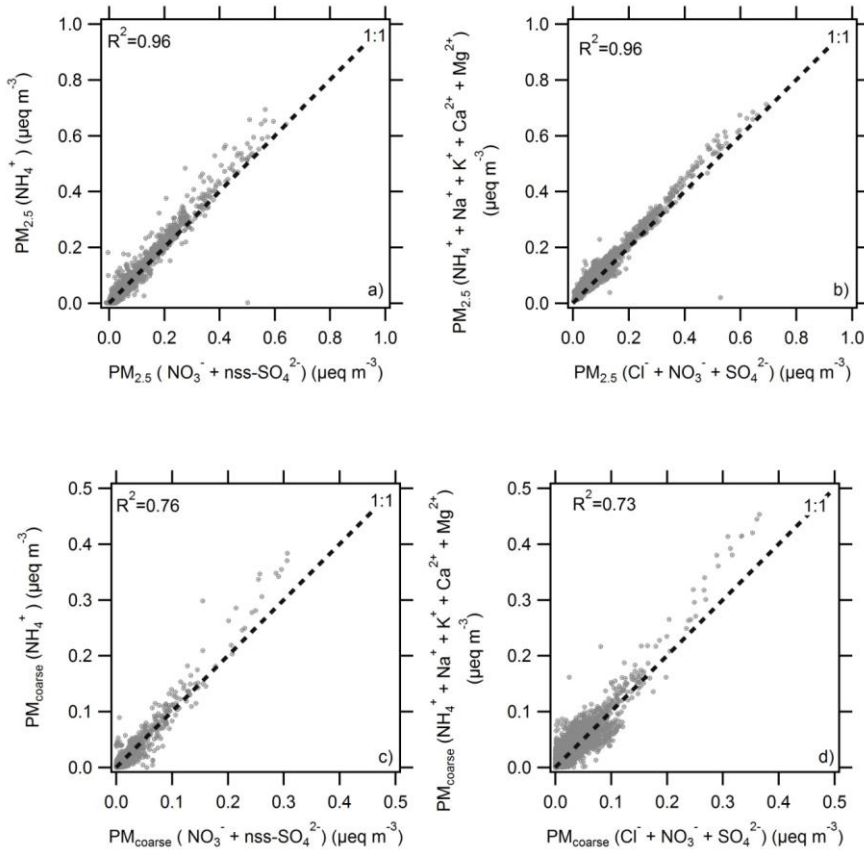


2

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

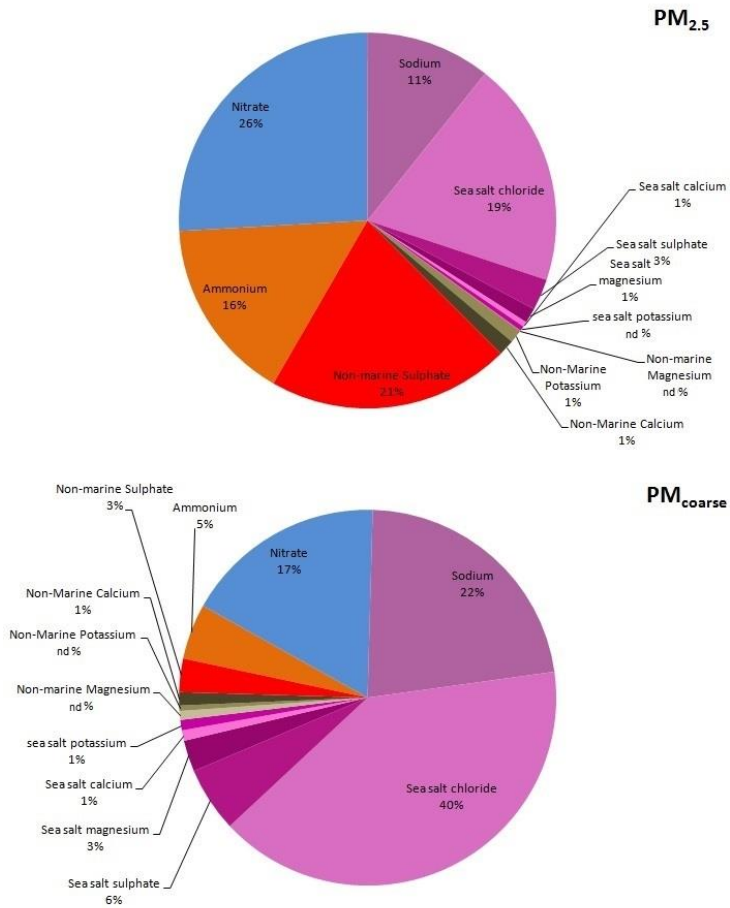
Commented [TMM2]: Updated figures

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

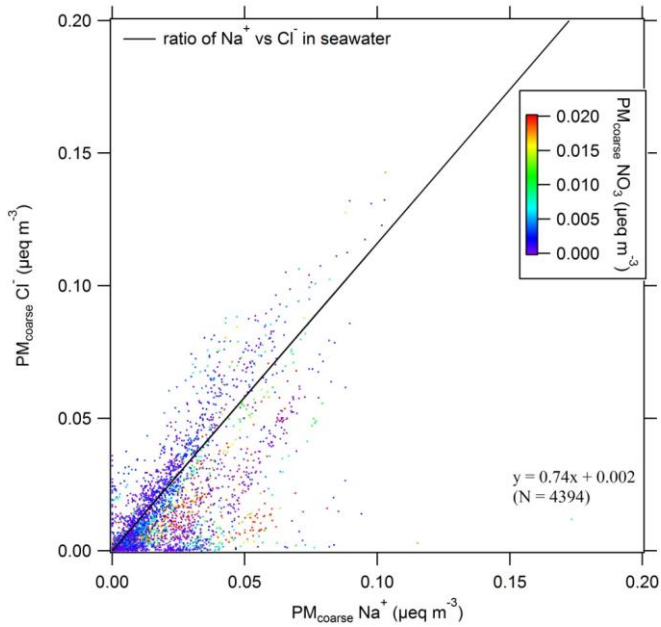


3
 4 Figure 4. Measured ion balance for the year 2012 in microequivalents m^{-3} . a) Neutralisation
 5 of $PM_{2.5} NH_4^+$ by $PM_{2.5} nss-SO_4^{2-}$ and $PM_{2.5} NO_3^-$; b) Ion balance of measured $PM_{2.5}$ anions
 6 (Cl^- , NO_3^- and SO_4^{2-}) and measured $PM_{2.5}$ cations (NH_4^+ , Na^+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

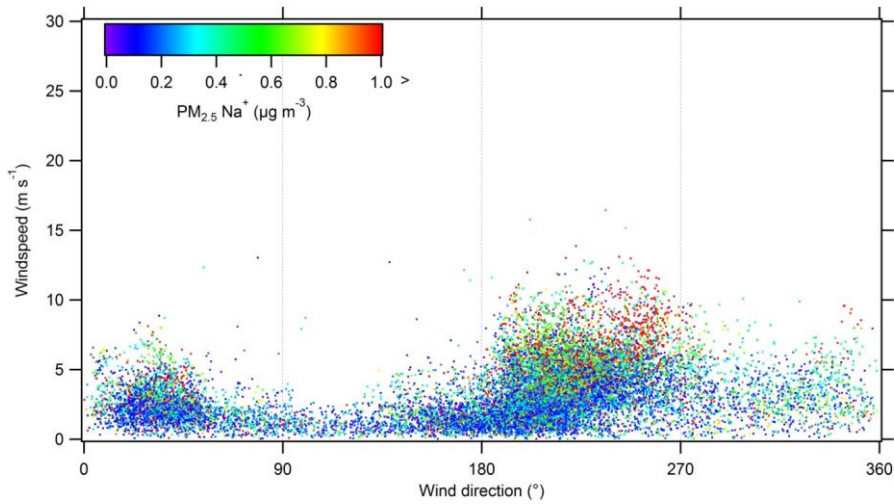
10



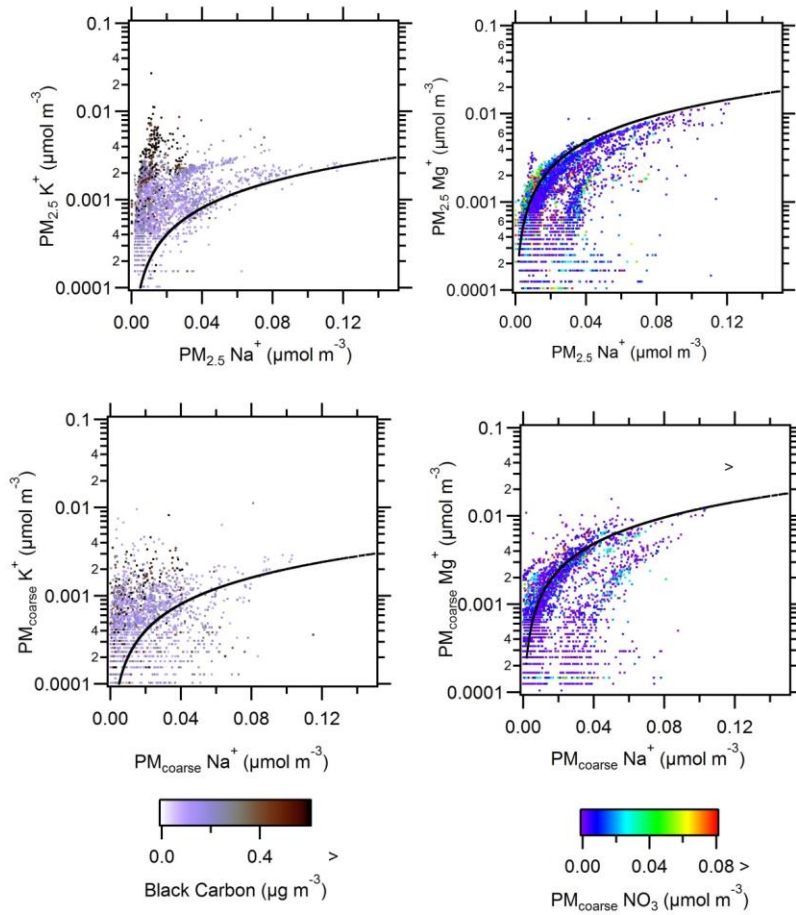
1
 2 Figure 5 Average composition by mass of the water soluble inorganic aerosol fraction
 3 measured by the MARGA from January 2007 to December 2012 in both the PM_{2.5} and
 4 PM_{coarse}. Sea salt chloride, sulphate, magnesium, calcium and potassium were derived based
 5 on the known mass ratios to Na⁺ in sea water, refer to Eqs. 2 to 5. Key: nd – not detected.



1
 2 Figure 6. Demonstration of the depletion of Cl⁻ for the year 2012 as a result of Cl⁻ - NO₃⁻
 3 interactions during long-range transport for coarse aerosol. The black line is the known ratio
 4 of Cl⁻ to Na⁺ in seawater (Seinfeld and Pandis, 2006). Colour scale is set to 0 to >0.2 μeq m⁻³
 5 NO₃⁻ to focus in on the depletion of Cl⁻ at high NO₃⁻ concentrations.



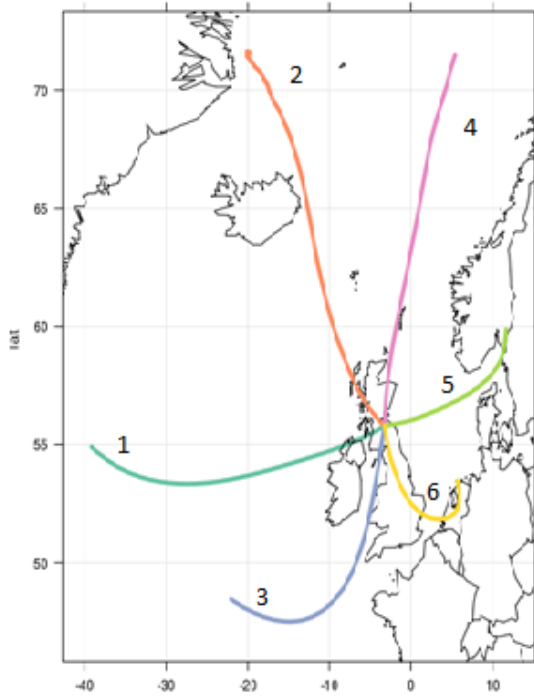
6
 7 Figure 7 The influence of wind direction and wind speed on the concentration of PM_{2.5} Na⁺ at
 8 Auchencorth Moss from the 1 January 2007 to 1 January 2013.



1
 2 Figure 8 Relationship of K^+ (left hand figures) and of Mg^{2+} (right hand figures) to Na^+ for $PM_{2.5}$
 3 and PM_{coarse} from 21/03/2012 to 01/01/2013. Black lines show the sea water ratios of K^+ and
 4 Mg^{2+} to Na^+ taken from Seinfeld and Pandis (2006). Black carbon data are provisional data
 5 downloaded from the DEFRA UK-Air database archive (<http://uk-air.defra.gov.uk/data/>) on the
 6 17/03/2014.

7
 8
 9
 10

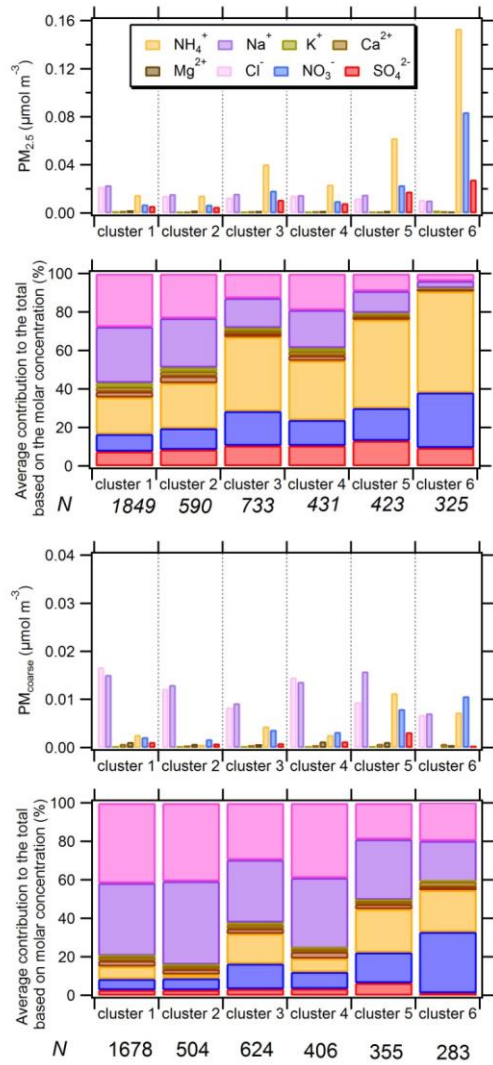
1



2

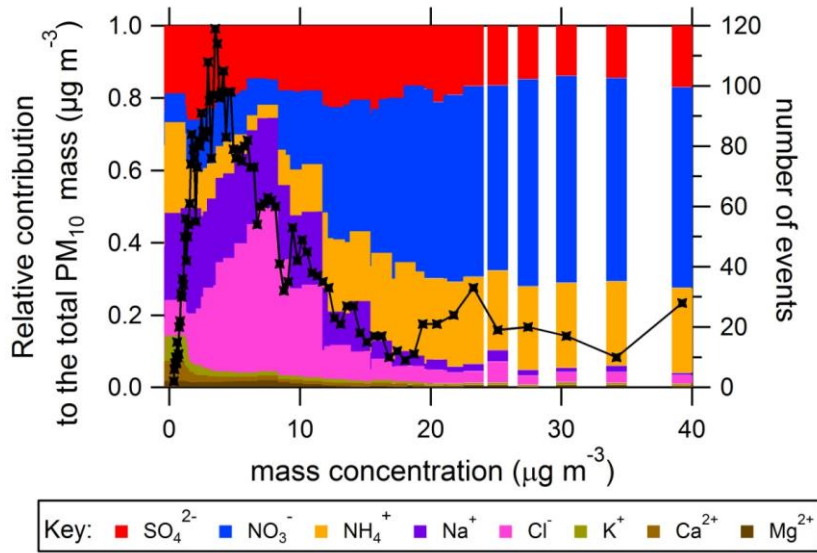
3 Figure 9. Mean trajectory associated with each cluster following clustering of 96h back
4 trajectories at 3 hour intervals calculated for Auchencorth Moss covering the years 2007 to
5 2012 (17,370 back trajectories). . (Graphs produced using Open air; Carslaw and Ropkins
6 (2012)).

7



1
 2 Figure 10. Average molar concentrations and average contribution of the species to the total
 3 molar concentration of PM_{2.5} and PM_{coarse} for each back trajectory cluster (refer to [Figure 9](#))
 4 from January 2007 to December 2012. Key: N – number of back trajectories used to calculate
 5 average concentration and % contribution for each trajectory.

Deleted: Figure 9



1
 2 Figure 11. Average relative contribution of inorganic water soluble species to the total PM₁₀
 3 mass measured by the MARGA during 2012 as a function of total mass concentration. The
 4 black line is the number of events at each mass concentration. Graph produced using the
 5 plotting routine of Crippa et al. (2014).