Impacts of the 2014-2015 Holuhraun eruption on the UK atmosphere

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Abstract

Volcanic emissions, specifically from Iceland, pose a pan-European risk and are on the UK National Risk Register due to potential impacts on aviation, public health, agriculture, the environment and the economy, both from effusive and explosive activity. During the 2014-2015 fissure eruption of the Holuhraun in Iceland, the UK atmosphere was significantly perturbed. This study focuses on the first four months of the eruption (September to December 2014). During this period there was one major incursion in September 2014, affecting the surface concentrations of both aerosols and gases across the UK, with sites in Scotland experiencing the highest sulfur dioxide (SO_2) concentrations. At the two UK EMEP supersite observatories (Auchencorth Moss, SE Scotland and Harwell, SE England) significant alterations in sulfate (SO_4^{2-}) content of PM_{10} and $PM_{2.5}$ during this event, concurrently with evidence of an increase in ultrafine aerosol, most likely due to nucleation and growth of aerosol within the plume, were observed. At Auchencorth Moss, higher hydrochloric acid (HCl) concentrations during the September event (max = 1.21 µg m^{-3}, c.f annual average 0.12 µg m^{-3} in 2013), were assessed to be due to acid displacement of chloride (Cl$^-$) from sea salt (NaCl) to form HCl gas rather than due to primary emissions HCl from Holuhraun. The gas and aerosol partitioning at Auchencorth moss of inorganic species by thermodynamic modelling, confirmed the observed partitioning of HCl. Volcano plume episodes were observed by the majority of the UK air quality monitoring networks during the first 4 months, at both hourly and monthly resolution. In the monthly networks, SO_2 concentrations were significantly elevated at remote "clean" sites in

NE Scotland and SW England, with record high SO_2 concentrations for some sites. For sites which are regularly influenced by anthropogenic emissions, taking into account the underlying trends, the eruption led to statistically unremarkable SO_2 concentrations (return probabilities >0.1, ~10 months). However for a few sites, SO_2 concentrations were clearly were much higher than has been previously observed (return probability <0.005,

5 >3000 months). The Icelandic eruption has resulted in a unique study providing direct evidence of atmospheric chemistry perturbation of both gases and aerosols in the UK background atmosphere. The measurements can be used to both challenge and verify existing atmospheric chemistry of volcano plumes. If all European data sets were collated this would allow improved model verification and risk assessments for future volcanic eruptions.

1   Introduction

10   Volcanic emissions perturb atmospheric composition in the troposphere (Bobrowski et al., 2007;Horrocks et al., 2003;Martin et al., 2008;Oppenheimer et al., 2010;Oppenheimer et al., 2006;von Glasow, 2010) via emissions of ash and/or gases and aerosols to the atmosphere, particularly during active eruptions. These emissions can directly impact humans and ecosystems (Thordarson and Self, 2003) as well as have indirect effects on climate (Gettelman et al., 2015;Schmidt et al., 2012;Schmidt et al., 2014). Sulfur dioxide (SO_2) and sulfate (SO_4^{2-})

15   aerosol injection into the stratosphere is a well-documented form of atmospheric perturbation and climate forcing; however, tropospheric atmospheric and surface effects, both local and regional, can only be studied serendipitously. In particular there are very limited detailed atmospheric observations available where both the physical characteristics and the chemical composition of volcanic plumes are probed in the distal plume, long distances away from the eruption source. In this case the distal plume was ~ 1000 km from its source in Iceland.

20   Volcanic plumes contain elevated quantities of reactive sulfur species, primarily in the form of SO_2. Quantifying the relative emission abundance of SO_2 and SO_4^{2-} and the oxidative aging of the plume converting SO_2 to SO_4^{2-} has been attempted previously, for example by Satsumabayashi et al. (2004) but there a very limited number of studies (Hunton et al., 2005;Rose et al., 2006;Mather et al., 2003;Kroll et al., 2015;Boulon et al., 2011;Satsumabayashi et al., 2004) which have quantified gas and aerosol composition beyond sulphur species

25   and provided evidence of tropospheric chemistry of distal plumes including halogen chemistry and particle growth (Boulon et al., 2011).

The recent eruption within the Holuhraun volcanic system in Iceland (August 2014 - February 2015) was the largest Icelandic eruption in terms of erupted magma and gas volume since the 1783-1784 CE Laki event, producing 1.6 km^3 of lava and total SO_2 emission of 11±5 Mt during a period of 6 months (Gíslason et al., 2015).

30   It was almost purely effusive, hence producing negligible amounts of ash, but repeatedly causing severe air pollution events in populated areas of Iceland due to high gas and aerosol concentrations. The ground level concentration of SO_2 exceeded the hourly health limit (350 μg m^{-3}) over much of the country for periods of up to several weeks (Gíslason et al., 2015). In Europe, anthropogenic emissions of sulfur have been declining over the past few decades and hence lower concentrations are observed widely (Fowler et al., 2007). EU-28 annual

35   emissions of sulfur oxides in 2010 and 2011 were ~4.6 Mt (http://www.eea.europa.eu/data-and-maps/daviz/emission-trends-of-sulphur-oxides#tab-chart_1) and therefore the Holuhraun volcanic eruption added more than twice the EU-28 annual sulfur emissions to the atmosphere in just six months (Schmidt et al.,

2015). This eruption provided a unique opportunity in Europe to study the impact of a large point source SO_2 emission.

This paper studies the volcanic impact on the UK atmosphere in the first 4 months of the Holuhraun eruption (September to December 2014) and provides the first evidence of wide scale effects, based on the measurements

5   from the UK air quality monitoring networks which deliver data at both high (hourly) and low (monthly) temporal resolution. These observations provide information on the chemical composition of the distal plume, ~ 1000 km downwind of Iceland. Because Icelandic air arrives at the UK on northerly trajectories, the background air is clean and there is little interference from anthropogenic emissions when the air arrives at the Northern UK.

In 2014, hourly resolution measurements of SO_2 were made by the UK Automatic and Rural Monitoring

10   Network (AURN, http://uk-air.defra.gov.uk/networks/network-info?view=aurn) and by the two UK European Monitoring and Evaluation Program (EMEP) (Torseth et al., 2012) atmospheric observatories (Harwell, SE England, UK and Auchencorth Moss, SE Scotland, UK), which also form part of the ACTRIS Infrastructure Network (http://www.actris.eu/). Additional high resolution physical particulate matter (PM) mass and size distribution (refer to section 2.2), as well as chemical composition measurements (refer to section 2.1) at the two

15   EMEP observatories are presented. In addition supplementary evidence of long term perturbations in the UK background at a lower resolution during the volcanic event from the UK Acid Gas and Aerosol NETwork (AGANET) and Precipitation network (Precip-Net) are highlighted (refer to section 2.3).

2   Methods

2.1   Basics of MARGA operation

20   The Measurement of Aerosols and Reactive Gases Analyser (MARGA, Metrohm Applikon B.V, NL) provides hourly resolution measurements of water soluble inoganic aerosol speciation (SO_4^{2-}, Cl^-, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) and gases (SO_2, HCl, HNO_3, HONO and NH_3). At the two field sites Harwell and Auchencorth Moss (Figure 1), the instruments are configured to have two sample boxes, one for PM_{10} and on for $PM_{2.5}$. The instruments use wet rotating denuders (WRD) (Wyers et al., 1993) and steam jet aerosol collectors (SJAC)

25   (Khlystov et al., 1995) for sampling of gases and aerosols respectively. Analysis is carried out online by ion chromatography (both anion and cation) at an hourly resolution. A detailed description for the instrument and QA/QC procedures used by both instruments are given in Twigg et al. (2015). There is one operational difference between Auchencorth and Harwell instruments, where Auchencorth Moss uses preconcentration columns (Metrosep A PCC 1 HC IC preconcentration column (2.29 mL) for anions and a Metrosep C PCC1 HC

30   IC pre-concentration column (3.21 mL) for cations) on the IC to achieve lower detection limit (DL) compared to the Harwell instrument which uses fixed loops (250μL for anions and 480μL for cations) and therefore has a magnitude higher DL as described by Makkonen et al. (2012). Data from both MARGA instruments are available in the UK-Air (http://uk-air.defra.gov.uk/data/) and EBAS (http://ebas.nilu.no/default.aspx) databases.

2.2   SMPS

35   At Harwell aerosol number size distributions were measured using a scanning mobility particle sizer (SMPS) (Electrostatic classifier 3080, differential mobility analyser 3081, and condensation particle counter 3775, all TSI

Inc.). Air was sampled at 4 m above ground level, through a PM_1 cyclone before entering the analyser via a drier which ensured the relative humidity of the sample air was kept below 45%. The aerosol sample flow rate was set to 0.3 L min^{-1} and the Classifier sheath flow was maintained at 3 L min^{-1}; a detailed description of the method and set-up employed at Harwell can be found in Beccaceci et al. (2013) and data is freely available through the

5   UK-Air website.

At Auchencorth Moss aerosol size distributions in the range of 14-673 nm were set to be measured using a scanning mobility particle sizer (SMPS) (Electrostatic classifier 3081, differential mobility analyser 3080 and condensation particle counter 3775, all TSI, Inc.). Air was sampled at 2 m above ground level through a PM_{10} head and $PM_{2.5}$ cyclone before entering the analyser via a drier which ensured the relative humidity of the

10   sample air was kept below 45%. The aerosol sample flow rate was set to 0.3 L min^{-1} and the classifier sheath flow was maintained at 3 L min^{-1} as set out in Wiedensohler et al. (2012). In October 2015, the Auchencorth Moss SMPS took part in an intercomparison organised by the EU Horizon 2020 ACTRIS 2 (aerosol, clouds and trace gases research infrastructure), held at the world aerosol calibration centre (TROPOS, Leipzig, Germany). During this exercise the classifier used at Auchencorth was found to have an offset and was starting a scan at 35

15   nm instead of 14 nm, though it is unclear if this may have slowly drifted over the 18 months since installation at the site. Therefore data presented from Auchencorth Moss is a qualitative indicator of an increase in ultrafine particles as the size distribution could not be verified.

2.3   AGANet DELTA and Precip-Net

The DEnuder for Long-Term Atmospheric sampling (DELTA), used in AGANet across the UK, is described by

20   Sutton et al. (2001). The sampling system consists of a series of coated denuders (to capture gases) and filters (to capture the aerosol). Air is sampled at a flowrate of 0.2 -0.4 L min^{-1}, with the sampling inlet at a height of 1.5 m. The first pair of denuders (15 cm) after the inlet are coated with K_2CO_3/glycerol to capture acidic gases (HNO_3, SO_2 and HCl). The next pair of denuders are coated with citric acid to capture gaseous NH_3. A filter pack is situated at the end of the sampling train, containing two cellulose coated filters: the first is impregnated with

25   K_2CO_3 to capture and retain NO_3^-, SO_4^{2-}, Cl$^-$ and Na$^+$, Ca^{2+} and Mg^{2+} aerosol. The second filter is impregnated with citric acid to capture NH_4^+. Downstream of is a gas meter, to record the volume of air sampled and an air pump. A DELTA sampling train is exposed for 1 month and samplers are extracted with deionised water. Chemical analysis is performed by ion chromatography and flow injection analysis, further details of this both the sampling method and analytical analysis are contained in Tang et al. (2009). The monitoring sites in

30   AGANet are highlighted in Figure 1. The wet deposition of pollutants in the UK is monitored within Precip-Net. Precip-Net uses bulk precipitation samplers at 39 non-urban sites with fortnightly sample collection. Samples are analysed for cations (Na$^+$, Ca^{2+}, Mg^{2+}, K$^+$, NH$_4^+$) and anions (PO$_4^{3-}$, NO$_3^-$, SO$_4^{2-}$, Cl$^-$) using ion chromatography (further details of both the sample method and analysis can be found in Irwin et al. (2002)). Data from both AGANet and Percip-Net are freely available from UK-Air.

35   ### 2.4   Gome2 Volcanic SO₂ detection.

The GOME2 instrument on MetOp-B is a nadir viewing UV/visible spectrometer with a spatial resolution of 40 x 80 km^2. SO$_2$ column densities are retrieved using a Differential Optical Absorption Spectroscopy approach

including a non-linearity correction for SO₂ saturation effects (Richter, 2009). As no corrections are made for the effects of deviations from the assumed plume height of 10 km, the data shown should be used as qualitative indicator only.

2.5 EMEP4UK chemical transport model

The EMEP4UK model rv4.3 (Vieno et al., 2016), is a chemical transport model which is the regional application of the EMEP MSC-W model (Simpson et al., 2012), which is used in this study to identify and investigate the spatial distribution of the volcano plume. The meteorological driver used in the EMEP4UK model is the weather and research and forecast model (WRF) version 3.6. More details of the model description and setup of the model can be found in Vieno et al. (2014) and Vieno et al. (2010). The model domain include all Europe and part of Russia with a horizontal resolution of 50 km x 50 km, with anthropogenic and biogenic emissions included based on the emissions the year 2012. The specific Icelandic volcano emissions in the run were set to 680 kg/s (Gíslason et al., 2015) from August 31st 2014 to the end of 2014, with the period of the 19 September 2014 to 24 September 2014 presented in this study. The emissions are injected into the model vertical column equally from the ground up to 3 km.

2.6 ISORROPIA thermodynamic model

The chemical thermodynamics model, ISORROPIA II (Fountoukis and Nenes, 2007), is used below to determine the theoretical chemical composition based on the gas/aerosol equilibrium partitioning of the inorganic species measured by the MARGA instrument at Auchencorth Moss. The model was run using as an input the bulk (i.e. gas + aerosol) concentration of all compounds (ammonium, nitrate, sulfate and chloride) measured by the MARGA (input in μmol m⁻³) and operated in the metastable, forward reaction. The model was used to establish if the observed gaseous concentrations could be explained solely by the thermodynamic equilibrium of the observed species, as there is very little evidence in the literature of direct acid displacement.

2.7 Statistical analysis of AGA-Net data

As well as high resolution analysis of the volcanic plume, the trends in the SO₂ from AGANet measurements were analysed to assess the impact of the fissure eruption on the background atmosphere in the UK. The likelihood of a reoccurrence of the observed concentrations in the UK background was calculated. For most sulphur compounds the AGAnet observations at many sites show decreasing trends over time, both for annual mean concentration and the annual maximum concentration. A high concentration superimposed on a downward trend would appear to be a less unlikely observation at the end of the time series than at the beginning, so the data were adjusted to remove any underlying trend before further analysis. Exceedances over a threshold follow a Pareto distribution. The threshold was chosen by fitting an 85% quartile regression using a smoothing spline for each site individually. The fitted Pareto distribution was used to assess the probabilities of the concentrations associated with the volcanic eruption occurring, expressed as a return probability and return time, which is the statistical likelihood of a similar concentration to be observed again based on the long term trend of SO₂ at each site expressed in the resolution of the measurements (Table 1).

3 Results and Discussion

3.1 Identification of a volcanic plume in the UK atmosphere

During the Holuhraun eruption, the volcanic plume passed periodically over the UK, with a major event occurring between September 21st and 23rd September 2014. This plume was first detected at the UK supersite

5 in Scotland at Auchencorth Moss at 12:00 (GMT), followed by Harwell in England at 15:00 (GMT) (Figure 2). The plume moved across the UK (with the exception of parts of Northern Ireland) and Automatic Urban and Rural Network (AURN) SO_2 observations at selected sites are summarised in Figure 2. Scotland (Dundee, Croy and Auchencorth) observed higher concentrations of SO_2 compared to the rest of UK. The sites in Southern Scotland (Auchencorth Moss and Croy), however, were only exposed to the main plume on the 21st September

10 whereas the event affected the rest of the UK intermittently for the next 72 hours (Figure 2). The peak SO_2 concentration measured by the MARGA at Auchencorth was 66.8 $\mu g\ m^{-3}$ (Figure 2) compared with the annual average of SO_2 of 0.14 $\mu g\ m^{-3}$ in 2013 at the site. It has to be noted that the SO_2 concentration at Auchencorth Moss was underestimated between 11:00 and 22:00 on the 21 September 2014, because the standard instrument configuration was optimised for $< 1\ \mu g\ m^{-3}$ detection. The maximum reported SO_2 concentration during the

15 event at Harwell reported by the MARGA was lower, peaking at 45.7 $\mu g\ m^{-3}$ (annual average concentration in 2013 was 0.46 $\mu g\ m^{-3}$) occurring on the 22nd September. Although SO_2 concentrations were elevated in many parts of the UK, they were notably below the 24 hour-average air quality limit of 125 $\mu g\ m^{-3}$ set under the EU Air Quality Framework Directive (Directive 2008/50/EC). The SO_2 plume was also observed across Ireland, Netherlands, Belgium and Austria (TS-2 in Supplementary Material of Gíslason et al. (2015)).

20 Supporting evidence that the ground-based measurements in September 2014 were picking up a volcanic signal is provided by the GOME2 instrument on the MetOp-B satellite, as it was able to track the SO_2 plume from the Holuhraun eruption site to the UK (Figure 3) on the 20th and 21st September. Modelling of the plume by EMEP4UK further confirmed the volcanic origin and dispersion of the observed SO_2 plumes both at Harwell and Auchencorth Moss (Figure 4).

25 ### 3.2 Chemistry within the volcanic plume

3.2.1 Formation of sulfate aerosols

Current understanding of volcanic emissions is that the major fraction of observed SO_4^{2-} is not directly emitted from the magma but is formed as secondary aerosol through oxidation of SO_2 in the atmosphere (Mather et al., 2013), though there are some reports suggesting primary emissions are possible (Allen et al., 2002;Zelenski et

30 al., 2015). As shown in Figure 2, both atmospheric observatories in the UK detected an increase in SO_4^{2-} during the volcanic plume event in September 2014. SO_2 oxidation in the troposphere can be slow, taking up to two weeks under some conditions (von Glasow et al., 2009). In order to understand the oxidation of an SO_2 plume, Satsumabayashi et al. (2004) defined a sulfur conversion ratio (F_s) as $F_s = [PM_{2.5}\ SO_4^{2-}]/([SO_2]+ [PM_{2.5}\ SO_4^{2-}])$ (all concentrations in $\mu g\ S\ m^{-3}$), where a smaller value suggests a young (or less atmospherically exposed)

35 plumes. The UK observatory datasets showed F_s decreasing from ~1 (all S in the form of SO_4^{2-}) to F_s~0.2, (Figure 5) during the event implying that SO_2 oxidation had not had sufficient residence time (and oxidant exposure) to be complete and hence that the SO_2 plume contained 'young' SO_4^{2-}. The formation and growth of

aerosol was confirmed by the presence of fine aerosols measured by the SMPS instruments at both Auchencorth and Harwell. The volcano plume event was characterised by the high particle number density at low diameters, increasing in diameter with time (initiating at ~1200 hours GMT on the 21st, Figure 5). The feature of increasing particle numbers, or "banana", starting with high particle numbers at the detection limit of the SMPS is

5   characteristic of particle nucleation and growth; however, as it is not a Lagrangian measurement, and because the nucleation does not represent a wide-spread regional phenomenon (as it probably does, e.g., in the nucleation studies conducted in the Boreal environment; (Kulmala et al., 1998)), the evolution of the size distribution with time needs to be interpreted with caution: only if trajectories and wind speed do not change with time can the temporal change at the fixed site be translated into the temporal change within the plume. It is possible that a

10   population of ultrafine H_2SO_4 particles were emitted or formed at source, however, it is highly unlikely due to the transport time that aerosol would have remained in the ultrafine fraction observed as they would have undergone further growth by coagulation and further condensation of condensable vapours. It is much more likely that, sulfuric acid was formed during transport through oxidation of the high concentrations of SO_2 by the OH radical the production of which is linked to solar radiation. With increasing time of sunrise, the

15   measurements at Auchencorth reflect particles whose nucleation was initiated further and further away from the site and had increasingly time to grow during transport. The SMPS at Harwell also recorded similar events as the plume passed over. This is the first evidence of boundary layer surface-level particle growth observations in a distal volcanic plume for the UK and complements observations from the 2010, which is the only previous report of nucleation and secondary aerosol formation event reported for a distal plume during the explosive, ash-rich

20   plume (Eyjafjallajökull in 2010) at an elevated free tropospheric atmospheric station in Europe (Puy de Dôme observatory, France) (Boulon et al., 2011). At that station, the free tropospheric conditions and size range of measurements allowed the clear interpretation of particle nucleation. In addition to the particle population changes observed, the measurement indicates that there was an unquantified air quality impact during the 2014 eruption in addition to the SO_2 air quality impacts discussed in the recent study of Schmidt et al. (2015) due to

25   particles.

3.2.2   Modification of the chemical composition within a volcanic plume

The chemical composition of $PM_{2.5}$ and the gas concentrations observed during the event at Auchencorth are summarised in Figure 6. It is clear that the aerosol was dominated by SO_4^{2-}. Whilst the aerosol at this site is normally neutralised, with free ammonia (NH_3) available (Twigg et al., 2015), during the plume event the

30   aerosol turned acidic. During the event the measurements at the background site clearly showed that there was an increase not only in the sulfur species but also in hydrochloric acid gas (HCl) and a variety of other chemical species in both gas and aerosol phase (Figure 6). HCl peaked at 1.21 µg m^{-3} during the event compared with an annual average of 0.12 µg m^{-3} in 2013. As discussed in Aiuppa (2009), Pyle and Mather (2009) and summarised in Witham et al. (2015) and the literature cited therein, primary emissions of HCl from volcanoes can vary

35   enormously depending on the magma type and the particular eruption characteristics (Aiuppa, 2009;Aiuppa et al., 2009;Pyle and Mather, 2009). The near-source measurements of the gas composition from the Holuhraun eruption indicated that the gas phase in the plume was proportionally very low in halogen content, with a molar HCl/SO2 ratio of <1%. It is unlikely that HCl would persist longer in a plume than SO_2 given the high solubility of HCl and comparably low reactivity of SO_2. However, given that the SO_4^{2-} aerosol is highly acidic, the HCl

would need to be scavenged onto other non-sulfate aerosol or into cloud droplets. Hence the elevated HCl observed in the plume event is either due to transport of primary HCl or displacement of HCl from background sea salt aerosol or a combination of the two. It is hypothesised that the most likely explanation for the observation of HCl coinciding with the plume is the oxidation of SO_2 to sulfuric acid which then displaced HCl

5 in pre-existing sea salt aerosol (NaCl) in the air mass. The thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007) was used to calculate the theoretical partitioning between the gas and aerosol phase. The model clearly reproduces the HCl peak which is attributed to the displacement of Cl^- from sea salt (Figure 6). Further evidence was found when the ratio of Na^+ and Cl^- was compared to the known ratio of sea water, where a large relative depletion of aerosol Cl^- was found during elevated SO_4^{2-} (Figure 7) at Auchencorth Moss. It is

10 noted, that between 09:00 (GMT) on 21/09 and 03:00 (GMT) on 22/09, the Na^+ was known to be underestimated, attributed to acidic composition of the aerosol resulting in a reduction in the performance of the cation column (concentration of the Li^+ internal standard decreased). Whilst correction based on the Li^+ standard is possible, this assumes that the retention was similarly depressed for all cations. The data therefore have been flagged as invalid during the QA/QC procedures of data submission to UK-Air and EMEP but have been

15 presented here as it is thought to be useful data for research purposes. As such the depletion of Cl^- is thought to be even greater than that demonstrated in Figure 7.

3.3 Long term perturbation of the UK atmosphere

The relative importance of the volcanic plume over the four months on the UK surface composition and the wider region with respect to air quality and acid deposition can only be assessed with measurements over a wider

20 geographic region. The low-temporal resolution (monthly) measurements of gas and aerosol composition with AGANet at 30 sites (Figure 1) provided a clear signal of the impact across the UK in particular for SO_2 (Figure 8). The national average concentration of SO_2 from this network for September 2014 was about a factor of six larger than in the preceding month. Remote sites such as Strathvaich Dam in northern Scotland (Figure 8: middle panel), which typically experience very little anthropogenic air pollution, experienced the highest monthly SO_2

25 concentration on record (network operational since 1999), with September and October concentrations an order of magnitude higher than the long-term average (2 µg m^{-3} c.f. 0.2 µg m^{-3}). Similarly Goonhilly in the south west of England experienced the highest concentrations on record, and even taking into account the underlying decreasing trend in SO_2 concentrations, return probabilities were as low as 3×10^{-4} (Table 1, refer to section 2.7 for statistical methods). When assessing the wet deposition from Precip-Net, it was seen that many sites across

30 the UK did experience elevated SO_4^{2-} concentrations in rain in September and October 2014 (Figure 9 upper panel). Again, in particular the sites in northern Scotland and South West England elevated concentrations were observed, whereas Northern Ireland and parts of Wales no increase in SO_4^{2-} concentrations were evident. It has to be noted, however there was exceptionally low rainfall during September 2014 across the UK, with the month being the driest on record for the UK, based on a series from 1910, (which also equalled fifth driest in the

35 England & Wales Precipitation series from 1766) (Parry et al., 2014). The majority of the western UK received less than 20% of the long‑term average rainfall, hence the amount of sulfur deposited by wet deposition during this period was not important to the UK (Figure 9). It therefore has to be noted that the reported high SO_4^{2-}

could be the result of lack of dilution due to low precipitation and cannot be directly attributed to the volcanic plume.

4   Conclusions

The Holuhraun eruption perturbed all aspects of the UK atmosphere periodically during the latter part of 2014. Elevated SO_2 were observed by the networks at both high and low resolution. This complemented the study by Schmidt et al. (2015) who reported similar observations for SO_2 across Europe for the same period. This study, however, provides further details of the chemistry within the volcanic plume which are not addressed by Schmidt et al. (2015). In this study high SO_2 concentrations, were demonstrated to have resulted to an increase in tropospheric HCl due to the acid displacement of Cl^- from sea salt at the EMEP supersite Auchencorth Moss. Elevated particulate SO_4^{-2} and particle size distributions from the two EMEP supersites suggested that new particle formation and growth were occurring as the plume passed over the UK. Future work now needs to be done investigate the direct and indirect effects of the perturbation of chemistry, specifically with regards to human health and crop yields.

The analysis also provides evidence to support the recent modelling undertaken which concluded that volcano eruptions in Iceland will intermittently affect the UK (Witham et al., 2015) with the effects varying both spatially and temporally during an eruption, primarily driven by meteorology. There is a significant difference in effects on both human health and ecosystem effects between acidic–non-acid aerosol and this study presents the first evidence that volcanic aerosol reaching the UK can be acidic, however this will be highly dependent on the mixing of the plume with the background atmosphere. There are also further impacts which have not yet been fully assessed, for example the net effect on climate (Gauci et al., 2008;Gettelman et al., 2015) and ecosystem function.

The study has highlighted even though anthropogenic SO_2 concentrations have dramatically decreased in the UK over the last 30 years, there is still a need to maintain the network of analysers as it is not just needed to confirm recovery, but also provides a useful tool to track the progression and impact of volcanic plumes and other pollution events. High resolution chemical composition of aerosol are essential for the identification of the origin of aerosol events observed concurrently with the SO_2 plumes and to understand the atmospheric chemistry. This paper presents the first detailed observations of chemistry within a distal volcano plume at the surface in the UK. This dataset is unique and can be used by modellers to test long term impacts of volcanic eruptions and the evolution of the plume chemistry.

While the 2014-2015 eruption in Holuhraun system was the largest eruption in Europe in over 200 years, there is a potential for even larger events. For example, the 1783-84 Laki eruption was over 10 times larger in terms of erupted magma and gas volume. An event of this magnitude would cause significant and wide-spread pollution over Europe and even cause excess mortality (Schmidt et al., 2011). Though some work has been done on a limited set of the European air quality networks by Schmidt et al. (2015) and Gíslason et al. (2015), a further study is required of the data from across the European compliance networks, as well as the EMEP and ACTRIS networks to integrate both particle characterisation and gas chemical composition. This would allow the Holuhraun event to be fully characterised and quantified.

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Table 1. Statistical analysis of the UK AGANET sites SO₂ (refer to Section 2.7 for the methods), where the return probability, is the statistical likelihood of a similar concentration to be observed again based on the long term trend of SO₂ at each site. (Refer to Figure 1 for site locations).

Site	September 2014 average SO$_2$ (µg m^{-3})	Fitted 85% quartile	residual	Return probability	Return period (months)
Yarner Wood	3.48	0.40	3.08	3.11×10^{-4}	3218.5
Rothamsted	2.98	0.78	2.20	9.00×10^{-03}	111.1
London Cromwell Road	2.37	0.54	1.83	6.90×10^{-03}	144.9
Ladybower	2.29	1.34	0.95	3.22×10^{-02}	31.0
Harwell	2.28	0.82	1.46	6.73×10^{-03}	148.7
Halladale	2.11	1.03	1.08	5.60×10^{-03}	178.6
Strathvaich	2.09	0.28	1.81	2.40×10^{-03}	417.4
Shetland	2.04	1.02	1.02	6.20×10^{-03}	161.2
Auchencorth Moss	2.00	0.37	1.63	8.71×10^{-03}	114.8
Glensaugh	1.95	0.57	1.38	6.17×10^{-03}	162.0
Stoke Ferry	1.84	0.68	1.16	1.70×10^{-02}	58.8
Sutton Bonnington	1.70	1.11	0.59	7.11×10^{-02}	14.1
Barcombe Mills	1.68	0.74	0.94	8.98×10^{-03}	111.3
High Muffles	1.67	1.14	0.53	7.72×10^{-02}	12.9
Lagganlia	1.65	1.14	0.51	7.28×10^{-03}	137.4
Eskdalemuir	1.45	0.42	1.03	5.65×10^{-03}	177.1
Bush Estate	1.38	0.60	0.78	4.55×10^{-02}	22.0
Moorhouse	1.24	0.47	0.77	1.10×10^{-02}	90.6
Narberth	1.20	1.08	0.12	8.69×10^{-02}	11.5
Rosemaund	1.15	0.51	0.64	1.19×10^{-02}	84.0
Cwmystwyth	1.10	0.49	0.61	2.11×10^{-02}	47.3
Plas Y Brenin	1.08	1.08	0.00	1.41×10^{-01}	7.1
Caenby	0.98	0.98	0.00	1.44×10^{-01}	6.9
Edinburgh St Leonards	0.61	1.32	-0.71	4.06×10^{-01}	2.5
Hillsborough	0.61	0.61	0.00	1.37×10^{-01}	7.3
Detling	0.58	1.01	-0.43	6.79×10^{-01}	1.5
Goonhilly	0.47	0.49	-0.02	1.36×10^{-01}	7.4
Lough Navar	0.39	0.39	0.00	1.75×10^{-01}	5.7
Rum	0.07	0.21	-0.14	9.08×10^{-01}	1.1
Carradale	nd				
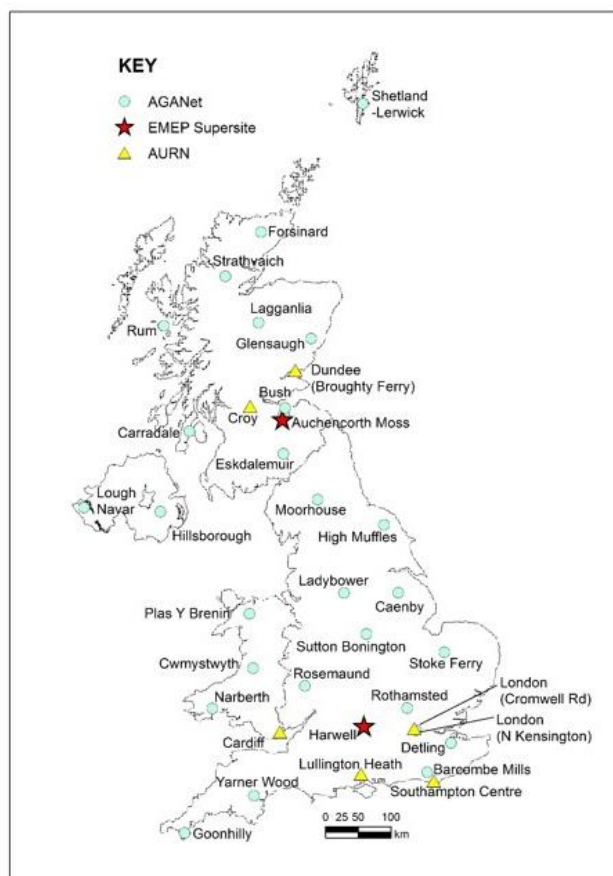
Figure 1. Map of sites measuring SO₂ monitoring sites in the UK used in this study. The AGANet sites provide monthly average concentrations, whilst the other sites report hourly values.
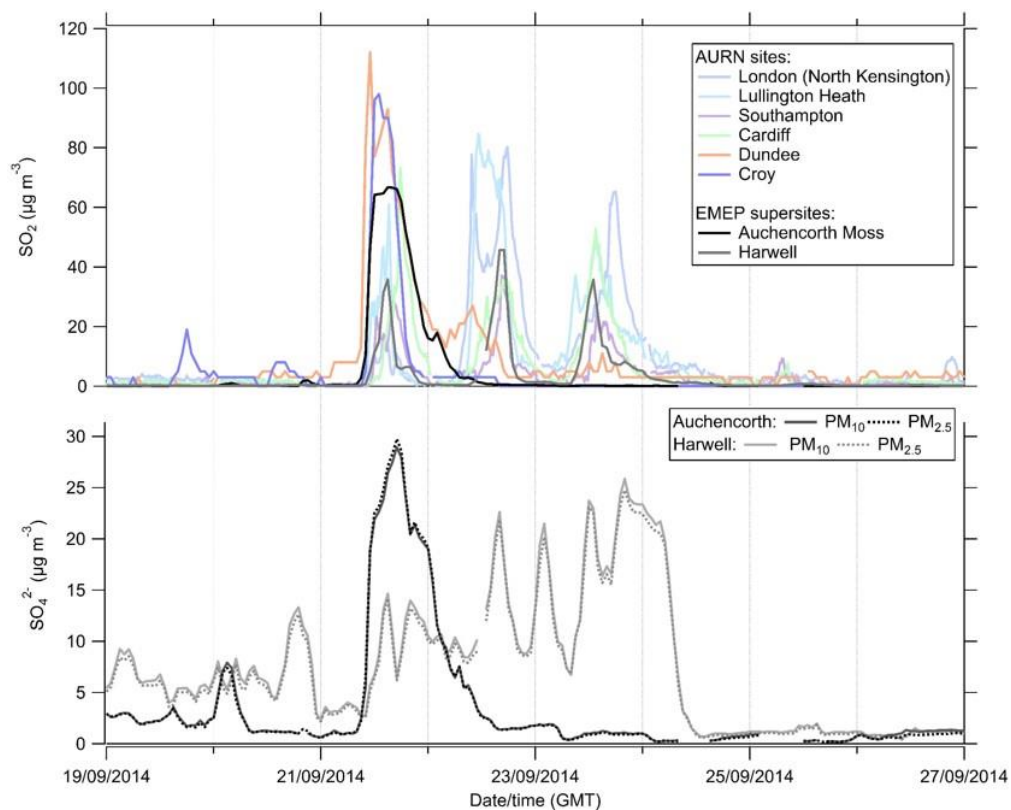
Figure 2. Time series of SO₂ hourly measurements made at 6 AURN sites in the UK and the two UK EMEP supersites measurements of SO₂ and PM$_{10/2.5}$ SO$_4^{2-}$. (NOTE: SO₂ at Auchencorth Moss is underestimated between 11:00 and 22:00 (GMT) on the 21/09/14)
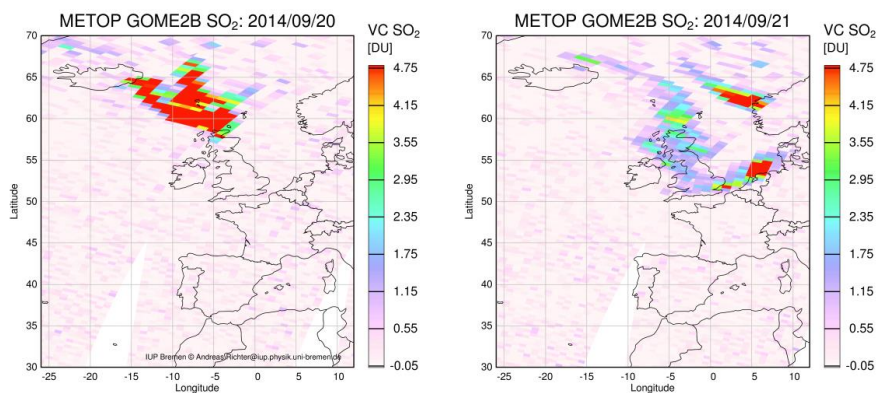
Figure 3. Observation of the volcanic plume from Iceland to across UK by the GOME2B satellite instrument measuring SO₂ column density.

5   s
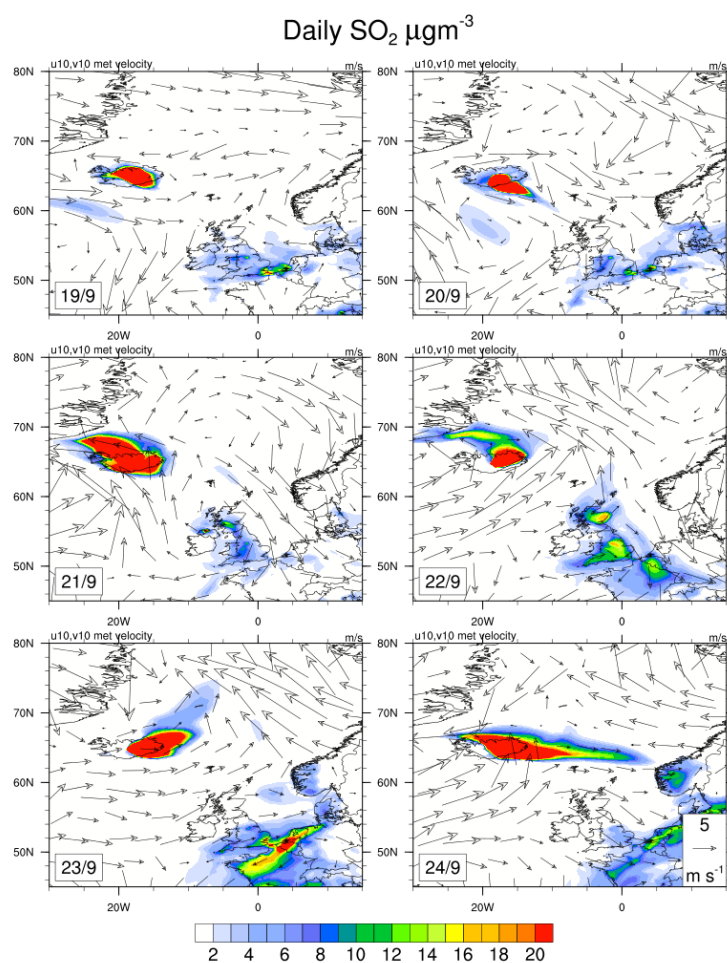
Figure 4. Daily average surface concentration (µg m⁻³) of the 19ᵗʰ - 24ᵗʰ of September 2014 of SO₂ calculated by the EMEP4UK model and the 12:00 of each days wind vector.
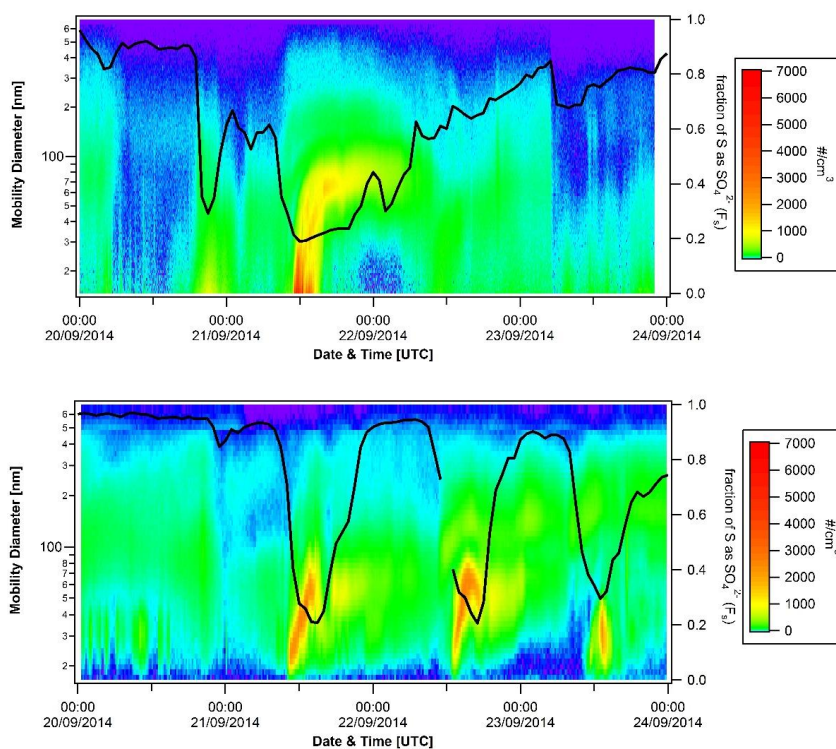
Figure 5. Particle number concentration at Auchencorth Moss (top panel) and Harwell (bottom panel) (refer to Figure 1 for map) during the September 2014 volcanic plume event. Right hand y-axis is the Fs ratio measured by the MARGA for the same period, where lower Fs indicates 'younger' SO_4^{2-}. (Note: There are uncertainties regarding the size calibration of the instrument (see text), however the CPC was working correctly. The panel should therefore be regarded a qualitative indicator of an increase in the ultrafine particulate matter during the volcanic plume).
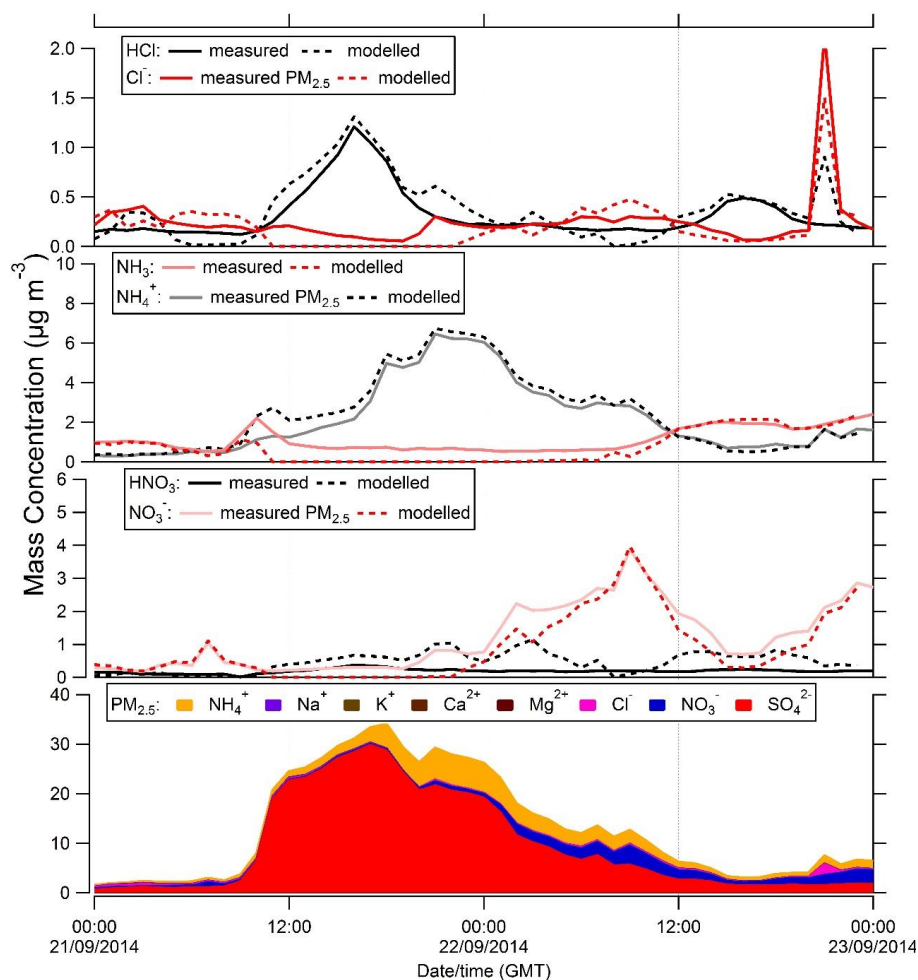
Figure 6. Top three panels: Thermodynamic partioning of gas and aerosol modelled by ISORROPIA-II compared with the measured concentrations at Auchencorth Moss. The bottom panel shows the chemical composition of PM₂.₅ at Auchencorth Moss as resolved by the MARGA instrument.
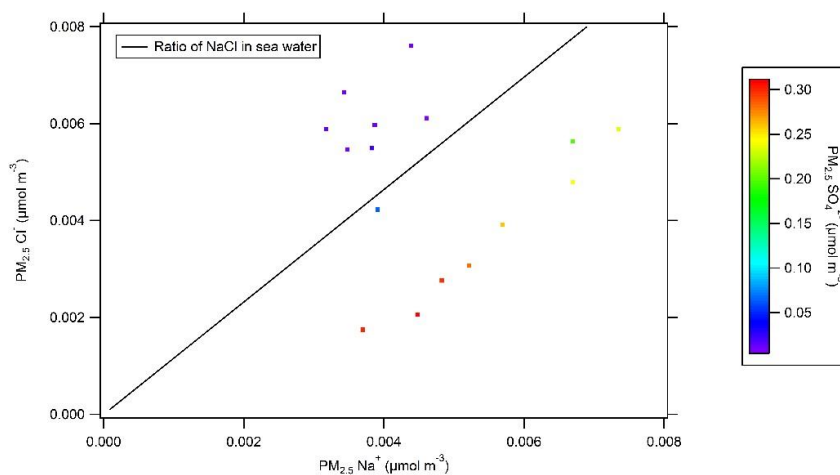
Figure 7. Evidence of acid displacement in Sea salt (PM$_{2.5}$) on the 21st September 2014 from 00:00 to 18:00 (GMT) at Auchencorth Moss. Solid line is the ratio of NaCl in sea water (Seinfeld and Pandis, 2006).
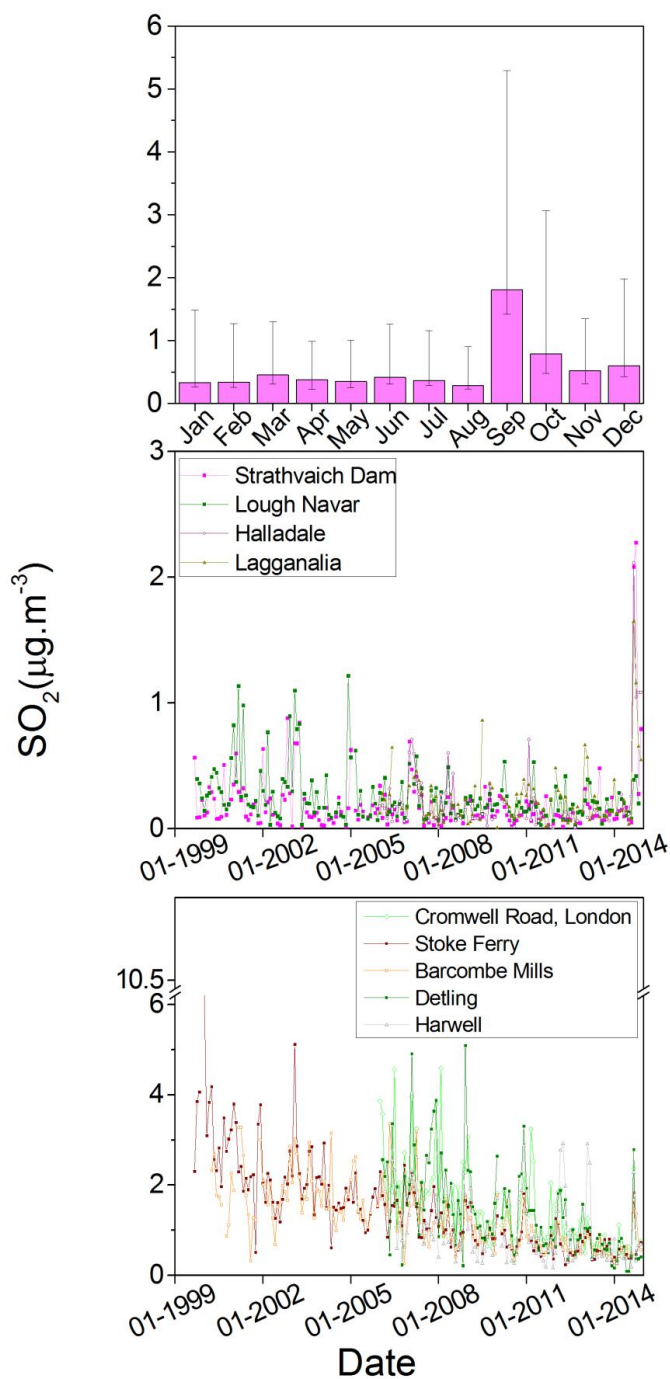
Figure 8 UK Defra Acid Gas and Aerosol Network monthly SO₂. Top panel: 2014 monthly network average SO₂ concentration (30 sites, whiskers maximum and minimum values); Middle Panel: 5 remote sites in the network; Bottom Panel: 5 sites in southern England (Refer to Figure 1 map for location of sites).
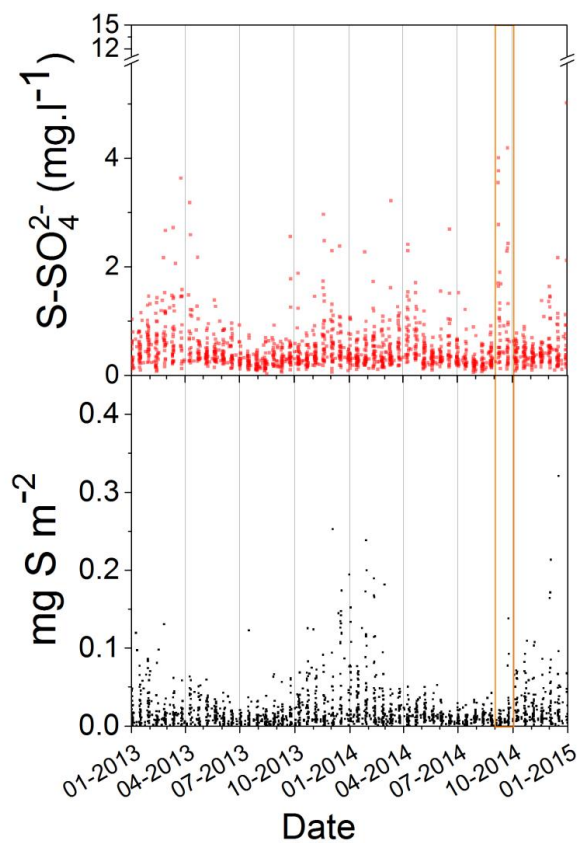
Figure 9 UK Precip-Net data: All fortnightly site data for 2013 and 2014; Upper panel: S-SO₄²⁻ concentrations; Lower panel: Sulfur deposition (mg S m⁻²); Note fortnightly data with data plotted using the start date of the measurement period. (Data downloaded from UK-Air on 25/06/2015 and 02/02/2016).