Responses to Reviewers

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

by Marsailidh M. Twigg *et al.*

The authors would like to thank the reviewers for the time spent reviewing the manuscript. Please find below in black the reviewer comments and in BLUE the authors' response to each of the comments. We have revised the manuscript to implement the recommendations from the reviewers, which can be found at the end of this document using track changes.

Anonymous Referee #1 (Received and published: 20 April 2016)

General:

This paper explores gas and particle phase composition and regional perturbations during an effusive volcanic event. The data presented are interested and certainly worth publishing; however, I have several major comments with respect to interpretation of the data that should be addressed before publication.

RESPONSE: We are pleased that the reviewer believes the data to be of interest and worth publishing. We have addressed all comments raised by the reviewer and hope that the major concerns that reviewer had about the manuscript have been dealt satisfactorily.

Major Comments:

The major comment I have is with respect to the simultaneous observation of newly formed particles and HCl. The authors imply that SO_2 in the plume is responsible for both new particle formation and the heterogeneous displacement of chloride from sea salt particles resulting in the formation of gaseous HCl. This finding is quite surprising considering that chloride displacement by H_2SO_4 should substantially deplete the concentrations of H_2SO_4 required to nucleate and grow new particles in the atmosphere. Figures 5 and 6 imply that heterogeneous uptake of H_2SO_4 and new particle formation by H_2SO_4 are occurring at the exact same time at the same site. Additional evidence is required to support this claim.

Specifically, the authors should show that there is enough H_2SO_4 to support heterogeneous uptake, nucleation, and particle growth during this time period.

RESPONSE:

The information on the full plume composition at source is too incomplete for detailed plume modelling that would allow the prediction of OH and H_2SO_4 concentrations during the plume transport. We agree that it is somewhat surprising that nucleation and acid displacement should occur in parallel as one would expect one process to be favoured over the other, depending on the aerosol surface area.

Instead, our starting point are the observations. There is clear evidence for particle nucleation which is hardly ever observed at Auchencorth. There is also clear evidence for HCl displacement from sea salt. This is evident in the high HCl concentrations, and in the fact that the Cl^-/Na^+ ratio is lower than that of sea water (Fig. 7). Although the latter could also be due to displacement by HNO_3, there are no major sources of NOx along the trajectory and HNO_3 concentrations are significantly lower (especially in terms of mixing ratio) than those of HCl (Fig. 6).

We can only speculate why heterogeneous chemistry and nucleation may take place simultaneously. The fact that they are observed at the same time does not necessarily mean that they occur at the same time and at the same location, with the timing of observation determined by when the plume reached the sampling point. For the displacement reaction to occur, the sea spray aerosol needs to mix with the volcanic plume from aloft. It is feasible that this mixing generates 'pockets of air' that are dominated by the volcanically influenced air (where nucleation is favoured) and others which have efficiently mixed with the sea salt (where heterogeneous chemistry is favoured). Through continued mixing and through the long-term integration of the measurement both would be reported at the same time. Similarly, the conditions that favour one process over the other may vary along the trajectory between Iceland and the UK.

We also cannot rule out that other compounds are taking part in the nucleation process and aerosol growth and have added this caveat to the manuscript:

"In addition, we cannot rule out that other compounds are taking part in the nucleation process and aerosol growth."

We have also included the above discussion into the manuscript text at the end of section 3.2.2:

"It is surprising that both acid displacement and nucleation events would be observed in parallel, as one process would be expected to be favoured over the other, depending on the aerosol surface area. Instead it is hypothesized that though both events are observed at the same time, it does not necessarily mean that they occur at the same time and at the same location. For the displacement reaction to occur, the sea spray aerosol needs to mix with the volcanic plume from aloft. It is feasible that this mixing generates 'pockets of air' that are dominated by the volcanically influenced air (where nucleation is favoured) and others which have efficiently mixed with the sea salt (where heterogeneous chemistry is favoured). Through continued mixing and through the long-term integration of the measurement both would be reported at the same time. Similarly, the conditions that favour one process over the other may vary along the trajectory between Iceland and the UK."

Specific Comments:

Abstract: 1. The authors should clearly highlight that they are presenting data on effusive volcanic activity, which has been under-explored. This would further highlight the significance of their work.

RESPONSE: The abstract has been modified to try and highlight the effusive eruption aspect and the paucity of data from this type of eruption further:

Page 2 lines 13-14

"The measurements can be used to both challenge and verify existing atmospheric chemistry of volcano plumes, especially those originating from effusive eruptions, which have been under-explored, due to limited observations available in the literature."

2. Lines 25-27, only a few days in September are explored in depth. The authors should revise their statement that 4 months were studied and state that a large atmospheric perturbation occurring during a few days in Sept attributed to effusive volcanic activity is their main focus.

RESPONSE: We agree the main focus of data analysis was based on a few days during a specific volcanic plume. The abstract now states:

"This study focuses 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."

Furthermore to highlight the 4 months of low resolution network data additional text has been added to the abstract to highlight this.

"Volcano plume episodes were periodically observed by the majority of the UK air quality monitoring networks during the first 4 months of the eruption (August – December 2014), at both hourly and monthly resolution. In the low resolution networks, which provides monthly SO_2 averages, concentrations were found to be significantly elevated at remote "clean" sites in NE Scotland and SW England, with record high SO_2 concentrations for some sites in September 2014."

In addition we have modified our introduction text too:

"This paper studies the volcanic impact on the UK atmosphere and focuses on one major incursion in September 2014 during the Holuhraun eruption and provides the first evidence of wide scale effects, based on the measurements from the UK air quality monitoring networks which deliver data at both high (hourly) and low (monthly) temporal resolution."

3. The authors should provide a sentence highlighting their lines of evidence that the perturbation was due to volcanic activity.

RESPONSE: Additional text has been added to the abstract to state how we confirmed that the perturbation was due to volcanic activity.

Page 1 lines 28-30

"The perturbation event observed was confirmed to originate from the fissure eruption by using satellite data from GOME2B and the chemical transport model, EMEP4UK, which was used to establish the spatial distribution of the plume over the UK."

4. The authors should mention what the aerosol acidity was. This can be calculated using the data they have on hand and the ISORROPIA-II model.

RESPONSE: We have now calculated the pH for the period using the ISORROPIA model and placed it in the discussion and commented on it in the text of the abstract too. The edits are as follows:

P2 Line 1-2:

"It was confirmed using the chemical thermodynamic model, ISORROPIA-II, that aerosol measured was acidic with an estimated pH of 3.80 during the peak of the event."

Section 3.2.2:

"The aerosol at the Auchencorth was found to only become acidic during the period when the plume was evident, using the results of [H^+] calculated from ISORROPIA-II model to calculate pH. During the plume event, the pH dropped from pH 7.97 at 09:00 GMT to pH 3.80 at 15:00 on the 21/09/14. This is unusual for the site as it has been previously noted that aerosols at site are generally basic in nature, due to an excess of NH_4^+ aerosol, when ion balance studies have been carried out (Twigg et al., 2015)."

Introduction

1. A more detailed discussion of explosive vs effusive volcanic activity would be helpful as well as a synopsis of previous finds relevant to tropospheric chemistry. This would help give context to the authors' findings.

RESPONSE: Though the subject was covered an expansion of this section has been written providing additional text to the introduction to highlight 1) diffusive vs explosive eruptions and 2) a synopsis of previous studies with regards to current knowledge of tropospheric chemistry within a distal volcanic plume has also been added. Overall the introduction has been expanded to cover the subject area more fully. The revised text is below:

"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). The injection of sulfur dioxide (SO_2) and sulfate (SO_4^{2-}), as well as aerosol in the form of ash, into the stratosphere are large events, which can have global effects, as shown by the cases of Mount Pinatubo and El Chichon where atmospheric perturbation and climate forcing were observed (Grainger and Highwood, 2003). Stratospheric perturbation generally only occurs as a result of explosive eruptions, as they have enough force to break through the tropopause to the stratosphere. In these types of eruptions, deposition of atmospheric components to the surface is diffuse and long-term.

Atmospheric chemistry in the lower troposphere and in particular the boundary layer with resultant earth surface effects are frequently associated with effusive eruptions. The 1783-84 fissure eruption of Laki is considered the "type" eruption for a long-

lasting effusive eruption on Iceland. The Laki eruption dynamics and emission masses have characterised in several papers (e.g. (Thordarson and Self, 2003). In these eruptions, there is a long term flow of lava and limited ash generation with the result of a long term input of gas-phase emissions in the lower parts of the troposphere. This is contrasted with the shorter-term punctuated emissions from an explosive eruption. It is noted that eruptions maybe a mixture of both effusive and explosive, e.g. Stromboli as described by Ripepe et al. (2007). The impact of effusive eruptions on the troposphere at both local and regional scales, are most frequently studied in responsive mode, post eruption initiation. As technology and instrumentation has developed and global air quality monitoring effort has increased too, this has resulted in some cases where background conditions and the evolution of distal volcanic plumes can be now be studied.

Volcanic plumes contain elevated quantities of reactive sulfur species, primarily in the form of SO_2*. There is still great debate whether* SO_4^{2-} *aerosol is directly emitted from volcanos or if it is a result of rapid formation once it enters the atmosphere, which is already detectable at the crater rim (von Glasow et al., 2009). In distal plumes, it is thought that* SO_2 *will eventually form* SO_4^{2-} *through the reaction with the OH radical, though* SO_2 *will also be removed from the troposphere through wet and dry deposition to the surface too. 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 is 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 sulfur species and provided evidence of tropospheric chemistry of distal plumes including halogen chemistry and particle growth (Boulon et al., 2011).*

Previously it was thought that the chemistry of volcanic plumes in the troposphere was dominated by the oxidation of SO_2*, however this changed when Bobrowski et al. (2003) observed a relatively large emission of the bromine oxide (BrO) radical in a plume from Soufriéré Hills (von Glasow et al., 2009). It is now known that emissions of hydrochloric acid (HCl), hydrogen fluoride (HF) and hydrogen bromide (HBr) can drive the chemistry within volcanic plumes, though the presence of halogens is determined by the chemical signature of each individual volcanic system. The rates of atmospheric processing driven by halogens in volcanic plumes are of great interest, as it is thought that reaction rates may differ significantly from that observed in the background atmosphere, which is more frequently studied. This is due to higher temperatures and a unique chemical composition volcanic plumes, which is potentially able to generate radicals. It is important to study the atmospheric processing within volcanic plumes as it determines the fate and deposition of acidic compounds contained within the plume (Aiuppa et al., 2007). Studies have shown that the ratios of* SO_2*/HCl in remain constant in a distal plume but the ratio decreases in the presence of clouds, as the gases dissolve in order of solubility and therefore HCl will dissolve first in the presence of clouds, though the studies mentioned were carried out within tens of kilometres from source (von Glasow et al., 2009;Burton et al., 2001;Aiuppa et al., 2007).*

One aspect which is challenging for scientists is to capture both the physical characteristics and the chemical composition of volcanic plumes after mixing with the *background in the distal plume, particularly at long distances away from eruption source. In the case presented the distal plume was ~ 1000 km from its source in Iceland. The primary chemical components of volcano plumes measured are SO_2 and SO_4^{2-}, however there are many other gases emitted. Other studies have in addition measured the full chemical composition of particulate matter (PM), e.g. Mather et al. (2003);Martin et al. (2008) and more recently indirect measurements of aerosol properties from satellites has been undertaken (Ebmeier et al., 2014). Aiuppa et al. (2009) and Pyle and Mather (2009) published reviews of the literature in the area of chemical degassing with a focus on emitted halogen chemicals which can occur both in the gas and aerosol phase. In most studies the ratios of HCl, HF to SO_2 are reported rather than the absolute concentration. Similarly the other sulfur gases, H_2S and COS, are studied but less frequently. The Witham et al. (2015) report summarised the halogen acid and H_2S ratios from the literature. It was noted that predominantly measurements are made close to the emission source or at a surface position downwind from the eruption either by remote sensing or direct sampling with off line analysis methods.*

Only a few modelling studies (e.g.Witham et al. (2015);Schmidt et al. (2015)) and measurement approaches (Kroll et al., 2015;Businger et al., 2015) have assessed the atmospheric chemistry with an air quality impact focus. Complex perturbation of atmospheric ozone and other oxidants have been studied both in the stratosphere and troposphere, however with only limited number of observation studies. Recent reviews have indicated there are still much to be understood (Mather, 2015;von Glasow et al., 2009) to understand the input of volcano emissions and the perturbation to the atmosphere.

To date there is only one study which has demonstrated nucleation and particle growth in a distal volcanic plume. This was measured following the explosive eruption of Eyjafjallajökull in 2010, where at the GAW site Puy de Dôme, France (1,465 m above sea level), nucleation and secondary aerosol formation events within the volcanic plume were observed(Boulon et al., 2011). The site however was in the free troposphere and occurred in a plume which was ash rich. To date there is very limited evidence of the processes of particle nucleation and secondary aerosol formation in distal plumes from effusive eruptions. "

2. The authors should comment on any findings relevant to halogen chemistry and volcanic activity if they are going to comment on HCl concentrations and their formation during a volcanic event.

RESPONSE: We have expanded both the introduction (refer to point 1 above) on halogen chemistry. In addition we have highlight in section 3.2.2 of the discussion the importance of halogen chemistry and the next steps required in order to comment further on the observed chloride chemistry within this volcanic plume.

"Roberts et al. (2009) has previously modelled the likely perturbations within a volcano plume upon mixing with background air, which found that both ozone and NO_x were perturbed with bromine chemistry as the key driver. In order understand the net impact of this eruption on the chemical perturbation of background sea salt aerosol and the production of HCl in the gas phase, there would need to be a full

chemical transport model which includes both chloride and bromine chemistry, which is beyond the scope of this paper."

Methods

1. If the SMPS had that much of a sizing offset, can any comment really be made regarding nucleation?

RESPONSE:

We agree that due to the offset that we cannot provide direct evidence of nucleation, however the shape of the size distribution would suggest that nucleation had occurred within the volcanic plume (please refer above to major concerns response for further details). In the methods with regards to the offset at Auchencorth Moss, we clearly state the SMPS is a qualitative indicator of increase in ultrafine particles but the size distribution could not be verified.

2. What temperature and RH conditions were used to run ISORROPIA-II?

RESPONSE:

We used the measured temperature and RH on the ISORROPIA-II run. We have added additional text to state this:

"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}) with measured temperature and relative humidity and operated in the metastable, forward reaction."

Results

3.1 Identification of the volcanic plume 1. HYSPLIT back trajectories would help eliminate the possibility that other sources of aerosol are influencing the observations.

RESPONSE:

We chose not to use the HYSPLIT model as the EMEP4UK model presented is able to do the same by illustrating the distribution and the direction of the plume. We have added to supplementary material the plume run using the HYSPLIT model for the peak days at both sites, please refer to figures S1 and S2. In addition to this we have noted the additional evidence in the main manuscript where it states:

"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), as did back trajectories using the HYSPLIT model, which can be found in figures S1-S2. To provide evidence that the EMEP4UK model was able to replicate the spatial distribution of the plume a comparison of the time series of observations to the model at both sites is given the supplementary material (figure S3)."

3.2.1 Formation of sulfate aerosols

2. The authors seem to imply that nucleation is occurring in the boundary layer at the same time as acid displacement. Further evidence is needed to support this. Can the authors prove that nucleation isn't occurring instead in the free troposphere where low particle surface area would favor this process?

RESPONSE: Please refer to our response under major concerns with regards to nucleation and acid displacement being observed co-currently. In addition, there is evidence, which we have included in the text, showing nucleation has been observed in polluted environments. Recent literature has confirmed that nucleation can take place in the presence of background aerosols, even within ash rich volcanic plumes (Boulon et al., 2011), however this study was in the free troposphere. There are also examples of nucleation and particle growth in polluted environments measured at the surface, including Hamed et al. (2007) who observed nucleation in the Po Valley at the site San Pietro Capofiume. Hamed et al. (2007) also cites other literature of nucleation studies within polluted areas including Kulmala et al., 2005 in New Delhi, India and Alam et al. (2003) in the Birmingham, UK. Both of these studies observed nucleation at the surface. This additional information has been added to back up the text that there is already examples in the literature of surface observations of nucleation,

Section 3.2.1:

"*Though nucleation is thought to occur in the free troposphere where there is a low particle surface area there is increasing evidence in the literature of nucleation events measured at the surface in polluted environments, such as Hamed et al. (2007) who observed nucleation events in the Po Valley, Italy, and by Kulmala et al. (2005) in New Delhi."*

3.2.2. Modification of the chemical composition within the plume

3. What does the temporal and spatial variability of aerosol Cl tell you? Do you see Na and Cl in proportions similar to sea salt near site that become more acidic with more SO4 in the aerosol as you move away from the plume?

RESPONSE:

We cannot comment on the spatial distribution across the UK for sea salt, as the period presented, Na^+ and Cl^- were frequently close to the detection limit at Harwell. We should have highlighted that there is prior knowledge with regards to sea salt and acid displacement events at Auchencorth Moss. Twigg *et al* (2015) has demonstrated that on some occasions where high NO_3^- events have been observed to coincide, on occasions, in a depletion of Cl^-, which is thought to occur through the interaction of HNO_3 with sea salt. It is assumed that this observation is due to the location of the site, which is close to the sea and has been found to abundant in sea salt (35% in annual average of water soluble inorganic $PM_{2.5}$ (Twigg *et al*. (2015)) . We have added the following text to try and reflect this:

"Further evidence of acid displacement was found at Auchencorth Moss 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-}*, represented by a change in colour of the markers in Figure 7. This is not the first time the site has observed acid displacement, Twigg et al. (2015) observed the site to be rich in sea salt due to its proximity to the sea, with 35% of the annual average of the inorganic composition of* $PM_{2.5}$ *attributed to sea salt. During high nitrate (*NO_3^-*) episodes it was observed on occasions that this coincided with an apparent depletion of* Cl^- *from sea salt, which was attributed to the displacement of* Cl^- *by* HNO_3*. "*

4. Figure 7 is very hard to read and interpret. Why do none of the data fall on the 1:1 line?

RESPONSE: The line presented is not a 1:1 line but the known ratio of Na:Cl in seawater, which was stated both in the legend and in the figure text, citing the reference for the calculation. An excess of Cl^- is possible, as there are other Cl^- sources, whereas Na^+ is generally thought to originate primarily from sea spray. We have edited the fonts and markers in figure 7, as well as updated the figure text to make the message clearer.

Anonymous Referee #2 (Received and published: 5 May 2016)

General Comments:

The paper is an important presentation of near-surface atmospheric composition measured during the passage of the Bardarbunga-Holuhraun volcanic gas cloud over the UK in 2014. This provides new data on the composition and aerosol size of such a cloud and its impact on other atmospheric constituents at very long range from the original eruption site. It raises interesting questions about the wider chemical influence of such a cloud, whilst also confirming that there was a low hazard to human health. This paper fits well with the existing literature on observations of this event, e.g. Schmidt, 2015; Gislason, 2015; Ialongo, 2015; Grahn, 2015, although it is noticeable that the latter two are not referenced. The paper would benefit from some further discussion of the two main concepts/theories it suggests and there are certain aspects that could be removed without detriment to the paper (see specific comments). There are also a relatively large number of typos that need correction.

RESPONSE: The authors are glad that the reviewer thought this paper was an important presentation of the near-surface atmospheric composition following the Bardarbunga-Holuhraun volcanic gas cloud in 2014 and the reviewer for bringing the other new references to our attention. We have modified our introduction to ensure that Ialongo *et al.*, 2015 and Grahn *et al.*, 2015 have also been included.

"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) and there were complaints as far as Scandinavia of a foul smell, which has been attributed to sulfurous compounds from the fissure eruption using satellite data (Grahn et al., 2015). Exceedances in the hourly health limits were also observed periodically in Northern Finland at surface observation sites, which were confirmed by satellite observations (Ialongo et al., 2015)."

Specific Comments:

The methods section of the report is very dry and is mainly a technical description of the equipment and sensors used. Depending on the editor's preference, there would be scope to move much of this to an appendix or even supplementary material. As it is, I would recommend that each section starts with a sentence summarising what it is that the technique measures. This is done for section 2.1 for example, but not for 2.3.

RESPONSE: We agree that the method section is technical but needs to be well described to demonstrate both QA/QC in the methods. We have consulted the editor who has agreed that we should keep the methods within the main text of the manuscript. We however have added a short summary to start of each section in the methods to describe what each technique measures, in order that reader can decide if they wish to read the technical description. Please refer to modified manuscript for additions.

p2 Lines 15-17: The point the authors are trying to make here is a little unclear. Surely stratospheric measurements of volcanic composition are also only made/studied serendipitously? The fact that there is good satellite data of this eruption means that they cannot be referring to observations made with this type of sensor.

RESPONSE: The reviewer is correct that all volcano measurements are serendipitous in that if you have the observation system in place you can observe the plume and the sentence was not clearly focused. Stratospheric and tropospheric satellite characterisation of plumes is now global and much more information can be derived from them than in the past. The serendipity refers to the fact that instances when the background conditions with the volcano chemistry and physics are monitored in real time can only happen when a plume passes a highly instrumented location e.g. air quality stations. Due to this comment and reviewer 1s comments, the introduction has been revised and expanded to discuss in more detail. Specifically, the serendipity sentence has been replaced by:

“The impact of effusive eruptions on the troposphere at both local and regional scales, are most frequently studied in responsive mode, post eruption initiation. As technology and instrumentation has developed, global air quality monitoring effort has increased, resulting in some cases where background conditions and the evolution of the plumes can be studied.”

Section 2.2: The size range for Auchencorth Moss is provided, but not that for Harwell. It would be useful if the size range for Harwell could be included too.

RESPONSE: We apologise for missing out the size ranges from Harwell. They have now been included in the text.
“At Harwell, aerosol number size distributions measured in the range of 16.55 to 604.3 nm by the SMPS (Electrostatic classifier 3080, differential mobility analyser 3081, and condensation particle counter 3775, all TSI Inc.).”

Section 2.4: The authors need to provide information on where the GOME2 data has been obtained from and how it has been processed. Even though it is just being used as a qualitative picture, this information is still important.
RESPONSE: The GOME2 data product used is the volcanic alert product from the University of Bremen. To provide more information to the reader, the following paragraph has been added:

“Satellite UV/vis retrievals yield integrated vertical columns of absorbing species and usually do not provide information about the vertical distribution of a trace gas. As the sensitivity of the observations decreases towards the surface, an assumption has to be made in the retrieval on the vertical profile of the target species in order to apply appropriate weights called air mass factors. Here, the standard volcanic product from

the University of Bremen is used (http://www.iup.uni-bremen.de/doas/gome2_so2_alert.htm) which assumes a volcanic eruption profile with an SO_2 peak at 10 km height."

Section 3.1: Further references for this would be useful in section 3.1. As the authors are using this data to compare to surface observations, the paper really needs some more information on the vertical sensitivity of the GOME2 instrument to SO_2 and to make it clear to the reader that the satellite data in figure 3 shows SO_2 throughout the atmosphere and not just the surface. SO_2 in the satellite data does not necessarily correspond to increased SO_2 at the surface.

RESPONSE: We agree that surface observations and satellite column data do not measure the same quantity and therefore not necessarily detect SO_2 from the same source. However, we think the coincidence of the two measurements provides strong indication that in this case, volcanic SO_2 is detected at the surface. In response to the reviewer's comment, we have expanded the discussion with the following paragraph:

"While satellite observations only provide tropospheric columns of SO_2 and not the concentrations at surface which are reported by the ground-based measurements, they do provide important information on the origin of enhanced SO_2 values. As the sensitivity of satellite retrievals to surface SO_2 is low, sulfur dioxide from surface pollution can rarely be detected over Europe. Volcanic plumes in contrast can readily be observed in the data as they usually extend to higher altitudes and contain much larger vertical columns of SO_2. The fact that several Dobson Units of SO_2 are observed in GOME2 data on September 20th and 21st, 2014 over the UK, and that the SO_2 plume originates from Iceland strongly indicates that the observed SO_2 is of volcanic origin. It is therefore very probably that simultaneous SO_2 enhancements measured at the surface are also linked to the volcanic emissions."

Section 2.7: Given that two of the values generated by the statistical analysis are given in the abstract, I was expecting more substance to this aspect, but it appears that it is only covered in section 2.7. A more detailed explanation of the approach is needed here, perhaps with an accompanying figure, to fully explain what has been done. For example, the period over which the AGANET data has been evaluated is not mentioned.

RESPONSE: The reviewer is correct that this part of the work is only briefly described with the methodology, partly due to the range of methods covered in this paper. The method is covered in section 2.7 and the outcomes in the results section 3.3. To address this lack of detail we have expanded to include a bit more detail in both sections and added references to the statistical method. We have not added an additional figure but have referred to Figure 8 when discussing underlying trends. Thank you to the reviewer for spotting that we did not highlight the operational dates for AGANet, it was an omission which we missed. These have been added into the text. Revised text is as follows:

"As well as high temporal resolution analysis (hourly measurements) of the volcanic plume, the monthly average SO_2 from AGANet measurements (Section 2.3) were analysed to assess the impact of the fissure eruption on the background atmosphere across the UK. The plume was clearly observable in this dataset. In order to understand the relative magnitude of the perturbation on a national scale for both air

quality and sulfur deposition, against a background of decreasing anthropogenic emissions a statistical treatment was thought to be appropriate. Specifically the likelihood of a reoccurrence of the observed concentrations in the UK background was calculated as many AGANet sites show decreasing trends over time for SO_2 and SO_4^{2-}, reflecting decreases in emissions. This is observed for both the annual mean concentration and the annual maximum concentration. A high concentration superimposed on a downward concentration trend in a measurement series over a period appears to be a less unlikely observation at the end of the time period than at the beginning. Therefore the AGANet measurement data were adjusted to remove any underlying trends before further analysis to assess the unusualness of the September 2014 elevated SO_2 concentrations. Theoretically exceedances over a threshold follow a Pareto distribution and the threshold was chosen by fitting an 85% quartile regression to this dataset using a smoothing spline for each site individually (i.e. there was no assumption of a general trend). This methodology has previously been developed much further for application to case studies with substantially more data (Chavez-Demoulin and Davison, 2005;Northrop and Jonathan, 2011;Reich et al., 2011). The fitted Pareto distribution generates the probabilities of occurrence of the elevated concentrations – which in this case were associated with the volcanic plume. This is expressed in Table 1 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 SO_2 over the 1999-2014 period at each site expressed in the resolution of the measurements."

A short section has been added to the results, section 3.3:

"At sites which are much more anthropogenically influenced, though the plume is clearly observable, the SO_2 concentration is unremarkable with return probabilities of $>1x10^{-1}$ (e.g. Detling). A few sites on the Western side of the UK were not in the pathway of the plume therefore no elevated concentrations were observed, e.g. Rum."

In Table 1 it is not clear to me why the first column is average SO_2 concentration. Section 2.3 would imply that the sensors record a monthly total – how has the average been calculated and is this particularly meaningful given that the authors nicely demonstrate elsewhere that the plume passed over in approx 4 days?
RESPONSE: The DELTA samplers pass a known air flow through a coated denuder for a one month exposure period, therefore the analytical results are the total amount of sulfate collected in the volume of sampled air, hence the average concentration over the month is recorded. AGANet and the Precip-Net are designed to underpin the UKs national concentration and deposition mapping, feeding into the critical level and load assessments under UNECE. The assessments use annual average concentrations. The monthly average data is meaningful as much as hourly average is of the variability within it or an annual average temperature is. Given the evidence from the monthly average measurement network shows the extent of the plume across the UK in the context of the national chemical climate we would contend that it is meaningful information.

It would be helpful for the authors to consider whether the concentrations from Sep 2014 are such outliers that actually the calculation of return period is not very robust?

RESPONSE: Return period is one way of measuring how extreme (or how much an outlier) the concentration is. Hence a large return time indicates a very low probability of the concentration occurring again given the current underlying trend in the dataset, i.e. the concentration is extremely unusual. We have edited the text to explain this more clearly.

Some of these numbers are also referred to on page 8, where the authors refer to Goonhilly, but based on the numbers in Table 1 should this not be Yarner Wood instead? The phrasing on p8 also implies that these sites had the highest values of any site ever, whereas I think the authors are actually suggesting that these sites had their highest monthly values. I'd suggest making this clearer.

RESPONSE: We apologise this should have read Yarner Wood and not Goonhilly. We have corrected the manuscript text. We have also edited the text as the reviewer is correct that the site had its highest monthly value.

"Similarly Yarner Wood in the south west of England experienced the highest concentrations on record for the site, and even taking into account the underlying decreasing trend in SO_2 concentrations, return probabilities were as low as $3x10^{-4}$ (Table 1, refer to section 2.7 for statistical methods)."

Section 3.1: Figure 2 (and Fig 6) nicely demonstrates that there were three "pulses" of SO_2 observed across the UK from 21-25 Sep 2014 yet the authors make no mention of this. This observation in itself is interesting and the paper would benefit from consideration of this. It may not be possible to determine whether the cause is due to changing omissions at the source (a few days previous) or due to meteorological influences, but consideration of these aspects, and any others, should be included.

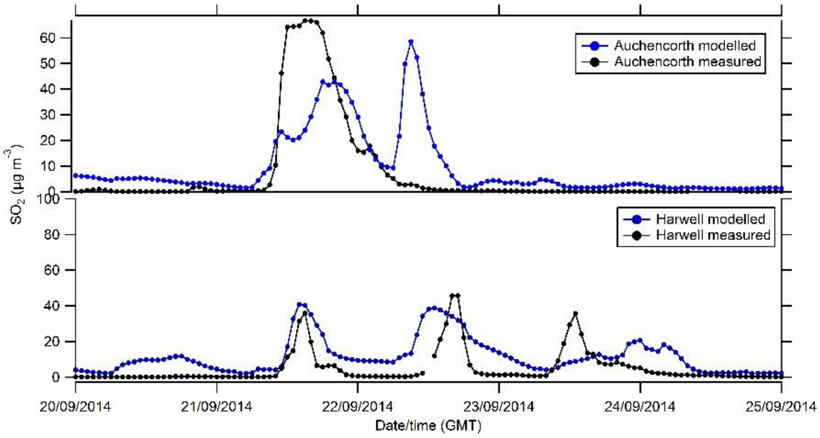
RESPONSE: We agree we did not highlight the 3 pulses observed at the Harwell site and have reworded the text accordingly. The use of the EMEP4UK model was able to illustrate that the pulses were due to meteorological conditions, however variables such as injection height of the plume at source, frequently changing emission rates at source and the oxidation rates to form SO_4^{2-} can explain the variation between the modelled and measured plumes. We have reviewed the EMEP4UK model injection height and edited the methods and Fig 4 accordingly, however a full model vs observation study is beyond the scope of this work. We have added additional text and figures to the supplementary material to confirm this.

Methods:
"The emissions are injected into the model vertical column equally from the 1km to 3 km."

Supplementary information:

"The EMEP4UK model was also used to confirm the distribution of the plume, as presented in Figure 4 in the main text. To provide further evidence of the agreement of the spatial distribution of the plume by the model, data for the sites Auchencorth Moss and Harwell data were plotted in a time series against the observed

concentrations. It is clear to see that the model is able to show that Auchencorth Moss the observed plume on the 21/09/14, however the site did not observe the plume predicated on the 22/09/14 or match the magnitude of the plume at the surface. At Harwell, the observed 3 pulses on consecutive days (21/09/14- 23/09/14) from the volcanic plume were identified in the temporal pattern but again the magnitude of the surface concentration is underestimated by EMEP4UK. The number of explanations why the magnitude and even the spatial of the distribution of the plume was not comparable to surface concentration measurements."



Figures S3 Times series of modelled plume by EMEP4UK and that observed by the MARGA instrument."

Section 3.1: The modelling sentence and Figure 4 are an unnecessary add-on and I recommend that the authors remove this together with section 2.5. The model does not add anything to the paper, but rather raises a whole number of questions that the authors will need to address if they want to include this. If anything, at first glance Figure 4 appears to contradict the other evidence as well as refute the descriptions in the text of northerly flow and that Scotland was worse affected than the south of the UK. There is not enough information on the modelling in the paper to explain what this figure is showing and describe why it does not match Figure 3. In addition, the fact that the figure contour scale only goes to 22 ug/m3 but the observations in Fig 2 reach over 60-100 ug/m3 would suggest that the model is not doing a good job at representing the plume. Given the efforts by other authors (e.g. Schmidt et al 2015) to demonstrate that their models provide good agreement with satellite column loading data before applying them to near surface concentrations, the lack of any model validation in this paper is particularly stark.

RESPONSE: The use of the EMEP4UK model was to illustrate the spatial distribution of the plume and to confirm the origins of the elevated sulfur species. The figure 3 presents the daily average SO_2 concentration compared to the hourly concentration measured at the surface in figure 2. To clarify how well the modelled matched the measured surface concentration an additional figure (Fig S3) has now been added to the supplementary information which provides information on the hourly resolution of the EMEP4UK model compared to measurements. It has to be noted the reason the model does not always replicate the measurements is that the model output has a 50 x 50 Km^2 resolution. In addition other variables such as the injection height of the plume at source, frequently changing emission rate at source and as well as oxidation rates within the plume are unknown. Measured emissions rates from source would be required before a model vs observation study could be carried out and therefor beyond the scope of this paper. We have expand the text in section 3.1 in order to reflect our responses.

"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) as did back trajectories using the HYSPLIT model, which can be found in figures S1-S2 in the supplementary material. To provide evidence that the EMEP4UK model was able to replicate the spatial distribution of the plume a comparison of the time series of observations to the model at both sites is given the supplementary material (figure S3). Though in general the EMEP4UK model does get the spatial distribution of the plume correct there are number of explanations why the model does not precisely replicate the plume compared to the measurements at the surface. The reasons include there a number of input variables which would have impacted the distribution of the plume including injection height, daily emission rates at source and oxidation rate within the plume, in addition the model output is 50Km x 50 Km resolution."

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Section 3.2: This is particularly interesting and one of the main new findings presented in this work. I have a few questions based on the text which the authors could hopefully easily incorporate the answers to. The fact that the difference in the plume aerosol diameter is so pronounced compared to the background is perhaps worth stating more clearly.

RESPONSE: We thank the reviewer that we did not highlight the differences in aerosol distribution clearly enough. We have added the following text:

"As the plume passed over the sites, the presence of ultrafine particles also became pronounced, compared to the background atmosphere in the previous 24 hours."

P6 Line 32 – the text talks about the slow oxidation of SO2 in the troposphere, are you referring to heterogeneous or homogeneous oxidation here or both?

RESPONSE: We thank the reviewer for pointing out that we had not clarified the reaction we were discussing. Therefor we have expand the text to provide additional information prior to presenting oxidation results.

"SO$_2$ oxidation with the hydroxyl radical in the troposphere can be slow, taking up to two weeks under some conditions, though if SO$_2$ is taken up onto particles, oxidation rates are much faster, resulting in a lifetime of days or hours in clouds as SO$_2$ (von Glasow et al., 2009)."

P6 Line 37 – you refer to the plume containing “young SO4”, I wonder whether it would be more appropriate to say that it is a “young plume”? Do you have any idea of the travel time since emission? Does this fit with your “young” finding?
RESPONSE: We have reviewed the wording and reworded the text for this section, which includes the removal of the phrase “young SO_4^{2-}”. See below:

“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 µg S m^{-3}), where a smaller value suggests a plume which has not undergone much atmospheric processing. 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.”

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P7 Line 14-16: Is this true? This also sounds as though it needs consideration of the travel time. If the travel time was constant from the source to the observation point, then the particles arriving later in the day would have travelled longer in sunlight and so had a longer time to react. Perhaps it is just the wording of the sentence that needs tightening to make this clear. Should it be “with increasing time *after* sunrise”? And where you refer to “site” on line 16 do you mean the monitoring site or the eruption site?

RESPONSE: We are in agreement with the reviewer with what is being observed in figure 5 and that the particles arriving later in the day had been travelling in sunlight longer and therefor had more time to react. We have reworded the text to make this message clearer.

“It is hypothesized that with increasing time after sunrise, the measurements at Auchencorth reflect particles whose nucleation was initiated further and further away from Auchencorth and had increasingly time to grow during transport.”

Section 3.3: This section is also one of the main findings and theories in this paper derived from the observations. It is an interesting conclusion, but also raised a number of questions in my mind that it would be useful for the authors to comment on in the paper. Firstly, whether the displacement has occurred due to the transport of the plume over the sea for such a long distance (and/or time) or whether this is a relatively local affect due to the site being not far inland. Second, if the plume had travelled directly south, it actually would have been over land for many miles before reaching the site, how would this fit the proposed mechanism?
RESPONSE:

Q1 and 2: We have highlighted that acid displacement events have already been demonstrated to occur at Auchencorth Moss in Twigg *et al* (2015) on occasions where high NO_3^- has been observed and it is assumed the displacement is a combination of traversing the sea for a long distance as demonstrated in figure S1 (supplementary material) and the location of the site, which is close to the sea. We have added the following text to try and reflect this:

“Further evidence of acid displacement was found at Auchencorth Moss 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-}, represented by a change in colour of the markers in figure 7. This is not the first time the site has observed acid displacement, Twigg et al. (2015) observed the site to be rich in sea salt due to its proximity to the sea, with 35% of the annual average of the inorganic composition of $PM_{2.5}$ attributed to sea salt. During high nitrate (NO_3^-) episodes it was observed on occasions that this coincided with an apparent depletion of Cl^- from sea salt, which was attributed to the displacement of Cl^- by HNO_3. “

Third, does such a mechanism require transport to Scotland to have occurred near to the sea surface / within the boundary layer / or more local near-surface transport following above-BL transport over the ocean? Is there any data to support one of these over another?

RESPONSE: Background aerosol in the boundary layer and in the free troposphere can have sea salt aerosol present, so there is no requirement for the air mass to have been in the boundary layer, though aerosol concentrations tend to be higher in the boundary layer. We think the subtleties of this question could be best addressed with a modelling study where the aerosol loading and plume height could be varied. It is therefore beyond the scope of this study to answer the reviewers question but could be addressed in future work.

Conclusions: The first line states that the eruption perturbed *all* aspects of the UK atmosphere. As a first point this should be the atmospheric composition (not atmosphere, see technical corrections), but even so this seems to be rather overstating what has been presented. For instance there is no mention in the paper of changes to oxidant levels, impact on ammonium reactions, etc, which is understandable given the context, but would be necessary to justify the “all aspects” claim. Some minor, but careful, rewording of this sentence would bring it more in line with what has actually been presented.

RESPONSE: We accept the reviewers comment and have revised the phrasing to contain the following text:

“The Holuhraun eruption perturbed the UK atmospheric composition periodically during the latter part of 2014.”

Technical Corrections:
Response: We apologise for the technical corrections and thank the reviewer for the time spent in identifying technical corrections.

p1 Line 25: “of the Holuhraun” needs modification to for example “of the Holuhraun fissure” or “at Holuhraun”

RESPONSE: Corrected

p1 Line 29: expand what EMEP stands for, or omit from sentence

RESPONSE: Corrected

p1 Line 34/35: missing “of” – “due to primary emissions of HCl”

RESPONSE: Corrected.

p2 Line 4: delete one of the two “were”

RESPONSE: Corrected.

p2 Line 8: add “of this type” to the end of the final sentence

RESPONSE: Corrected

p2 Line 22: add “is” to “but there is a very limited"

RESPONSE: Corrected

p2 Line 27 and p9 Line 30: the eruption was within the Bardarbunga volcanic system not the Holuhraun volcanic system. The eruption site and the eruption have been called Holuhraun.

RESPONSE: Corrected to state:
“The recent Holuhraun eruption within the Bardarbunga volcanic system in Iceland..”

P2 Line 29: recommend making “emission” plural, i.e. emissions

RESPONSE: Corrected

P2 Line 34: please explain what the EU-28 is/means for an international readership

RESPONSE: We have edited the text.

“*The 28 countries European Union member countries (EU-28) total annual emissions of sulfur oxides….”*

P3 Line 8: “Northern” should have a lower case “n”

RESPONSE: Corrected

P3 line 26: replace “for” with “of”, i.e. “a detailed description of the instrument”

RESPONSE: Corrected.

P3 line 27: please expand the acronyms QA/QC

RESPONSE: Corrected and the text now states: “*A detailed description of the instrument and quality assurance/ quality control (QA/QC) procedures …”*

P3 line 27: replace “are” with “is”, i.e. “by both instruments is given in”
RESPONSE: Corrected.

P3 line 28: need to add “the”, i.e. “between the Auchencorth”

RESPONSE: Corrected.

P3 line 30: what is “IC”?

RESPONSE: corrected now states : “…*ion chromatography (IC)…”*

P3 line 30: need to add “a”, i.e. “to achieve a lower detection”

RESPONSE: Corrected

P3 line 31: modify to be “therefore has an order of magnitude”

RESPONSE: Corrected

P4 line 26: a word is missing from “Downstream of is a gas”

RESPONSE: Corrected now states: “*Downstream of the sampling train is a gas meter…”*

P4 line 28: remove “this”

RESPONSE: Corrected.

P4 line 35: Gome should be capitalised, i.e. GOME

RESPONSE: Corrected.

P5 line 16: remove “below”

RESPONSE: Corrected.

P5 line 24: in a number of places in the text the authors use “high resolution analysis”, this is not specific enough, I assume that they mean high temporal resolution not spatial? This should be included/made clear.

RESPONSE: Corrected to state: *“…high temporal resolution analysis (hourly measurements)...”*

P6 line 19: there are other references that could be included here for the observation of the plume (see General Comments). It would also be useful for the authors to clarify whether these observations occurred at approximately the same time (i.e. related to the same plume transport) or at different times during the prolonged eruption.

RESPONSE: We have added other reference which have already been dealt with in the general comments. Apologies that we did not clarify that the reported plumes elsewhere in Europe were observed at different periods during the eruption. We have now modified the text in order to highlight that different nations observed the plumes at different times.

"The SO_2 plume was also observed across Ireland, Netherlands, Belgium and Austria (TS-2 in Supplementary Material of Gíslason et al. (2015)) during different periods of the fissure eruption."

P7 line 4: change to "or 'banana' shape in Figure 5, starting with"

RESPONSE: Corrected.

P7 line 23-25: change line 23 to be "air quality impact from particulates during" and remove "due to particles" from line 25.

RESPONSE: Corrected

P7 line 35-36: The reference list is not needed here as these are already referred to or implied earlier in this sentence.

RESPONSE: Corrected.

P7 line 38: However, a reference is definitely needed for the molar ratio of HCl/SO2 being <1% near source.

RESPONSE: A reference has now been added.

P8 line 4: Is HCl correct at the end of this line? Should it be Cl-?

RESPONSE: Apologies for the mistake. This has been corrected to state Cl^-.

P8 line 31: Add "at", i.e. "in particular at the sites", and South West should be lower case

RESPONSE: Corrected.

P8 line 32: add "in", i.e. "whereas in Northern Ireland", and change "were" to "was"

RESPONSE: Corrected.

P8 line 33: add "that", i.e. "noted, however, that there"

RESPONSE: Corrected

P8 line 37: suggest rephrasing "was not important to" to "was not significantly Different to normal" or similar

RESPONSE: Apologies, the words “annual sulfur deposition” were omitted. The sentence should have read:

“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 annual sulfur deposition budget and hence the environmental impact through acid deposition will have been minimal (Figure 9).“

P9 line 4: change to “the UK atmospheric composition during the latter part. . .”

RESPONSE: rephrased to state:

“The Holuhraun eruption perturbed the UK atmospheric composition periodically during the latter part of 2014.”

P9 line 5: change line to “Elevated SO2 was observed by the networks at both high and low temporal resolution. These observations complement the study by”

RESPONSE: Corrected the requested phrasing.

P9 line 8: remove the comma and change “to” to “in”

RESPONSE: Corrected the phrasing.

P9 line 10-11: I think we would expect particle formation and growth to be occurring in the plume based on past chemical and physical knowledge, so it would be better to say “. . . from the two EMEP supersites provide observational evidence for new particle formation and growth occurring as the plume. . .”

RESPONSE: Rephrased according to the suggestion.

“…the two EMEP supersites provide observational evidence for new particle formation and growth was occurring as the plume passed over the UK.”

P9 line 14: add “work”, i.e. “the recent modelling work undertaken”

RESPONSE: Corrected.

P9 line 22: add “that” to become “The study has highlighted that even though”

RESPONSE: Corrected.

P9 line 25: change “are” to “is”

RESPONSE: Corrected.

P9 Line 26: remove “the” from “concurrently with the SO2”

RESPONSE: Corrected.

Fig 1 caption: Repeat of “sites”

RESPONSE: Corrected and rephrased.

Fig 3 caption: explain what VC SO2 is and what DU is. Are these images snap-shots or aggregated daily totals or means? This needs to be stated.

RESPONSE: The text has been updated:

“Observation of the volcanic plume from Iceland to and across the UK by the GOME2B satellite instrument, taken at the satellite overpass around 9:30 local time. GOME2B measures SO_2 *column density, where VC is the vertical column, which is the* SO_2 *concentration integrated vertically to provide a column density per unit surface area.* SO_2 *columns are given in Dobson Units (DU), the thickness the* SO_2 *layer would have at standard temperature and pressure in units of hundredths of a millimetre.”*

Fig 5 caption: explain what the black line is

RESPONSE: We have modified the figure text to state that black line is the F_S.

Fig 7 caption: remove capitalisation from “Sea”. It would be useful to explain the colouration of the dots in the main paper text and what this means for this event.

RESPONSE: Corrected. Have reword main manuscript text to state:

“*Further evidence of acid displacement was found at Auchencorth Moss 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-}*, represented by a change in colour of the markers in Figure 7.”*

Fig 9 caption: what are the orange lines?

RESPONSE: We have amended the figure caption, it now states:

“The orange box highlights the measurements in September 2014.”

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 at Holuhraun in Iceland, the UK atmosphere was significantly perturbed. This study focuses 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. The perturbation event observed was confirmed to originate from the fissure eruption using satellite data from GOME2B and the chemical transport model, EMEP4UK, which was used to establish the spatial distribution of the plume over the UK during the event of interest. At the two UK European Monitoring and Evaluation Program (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 of HCl from Holuhraun. The gas and aerosol partioning at Auchencorth moss of inorganic species by thermodynamic modelling, confirmed the observed partioning of HCl. Using the data from the chemical

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Deleted: 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.

thermodynamic model, ISORROPIA-II, there is evidence that the background aerosol, which is typically basic at this site, became acidic with an estimated pH of 3.8 during the peak of the event.

Volcano plume episodes were periodically observed by the majority of the UK air quality monitoring networks during the first 4 months of the eruption (August – December 2014), at both hourly and monthly resolution. In the low resolution networks, which provide monthly SO_2 averages, concentrations were found to be significantly elevated at remote "clean" sites in NE Scotland and SW England, with record high SO_2 concentrations for some sites in September 2014. 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 much higher than has been previously observed (return probability <0.005, >3000 months). The Holuhraun 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, especially those originating from effusive eruptions, which have been under-explored, due to limited observations available in the literature. If all European data sets were collated this would allow improved model verification and risk assessments for future volcanic eruptions of this type.

1 Introduction

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). The injection of sulfur dioxide (SO_2) and sulfate (SO_4^{2-}), as well as aerosol in the form of ash, into the stratosphere are large events, which can have global effects, as shown by the cases of Mount Pinatubo and El Chichon where atmospheric perturbation and climate forcing were observed (Grainger and Highwood, 2003). Stratospheric perturbation generally only occurs as a result of explosive eruptions, as they have enough force to break through the tropopause to the stratosphere. In these types of eruptions, deposition of atmospheric components to the surface is diffuse and long-term.

Atmospheric chemistry in the lower troposphere and in particular the boundary layer with resultant earth surface effects are frequently associated with effusive eruptions. The 1783-84 fissure eruption of Laki is considered the "type" eruption for a long-lasting effusive eruption on Iceland. The Laki eruption dynamics and emission masses have been characterised in several papers (e.g. Thordarson and Self (2003)). In these eruptions, there is a long term flow of lava and limited ash generation with the result of a long term input of gas-phase emissions in the lower parts of the troposphere. This is contrasted with the shorter-term punctuated emissions from an explosive eruption. It is noted that eruptions maybe a mixture of both effusive and explosive, e.g. Stromboli as described by Ripepe et al. (2007). The impact of effusive eruptions on the troposphere at both local and regional scales, are most frequently studied in responsive mode, post eruption initiation. As technology and instrumentation has developed and global air quality monitoring effort has increased too, this has resulted in some cases where background conditions and the evolution of distal volcanic plumes can be now be studied.

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Volcanic plumes contain elevated quantities of reactive sulfur species, primarily in the form of SO$_2$. There is still great debate whether SO$_4^{2-}$ aerosol is directly emitted from volcanos or if it is a result of rapid formation once it enters the atmosphere, which is already detectable at the crater rim (von Glasow et al., 2009). In distal plumes, it is thought that SO$_2$ will eventually form SO$_4^{2-}$ through the reaction with the OH radical, though SO$_2$ will also be removed from the troposphere through wet and dry deposition to the surface too. 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 is 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 sulfur species and provided evidence of tropospheric chemistry of distal plumes including halogen chemistry and particle growth (Boulon et al., 2011).

Previously it was thought that the chemistry of volcanic plumes in the troposphere was dominated by the oxidation of SO$_2$, however this changed when Bobrowski et al. (2003) observed in addition a relatively large emission of the bromine oxide (BrO) radical in a plume from Soufriéré Hills (von Glasow et al., 2009). It is now known that emissions of hydrochloric acid (HCl), hydrogen fluoride (HF) and hydrogen bromide (HBr) can drive the chemistry within volcanic plumes, though the presence of halogens is determined by the chemical signature of each individual volcanic system. The rates of atmospheric processing driven by halogens in volcanic plumes are of great interest, as it is thought that reaction rates may differ significantly from that observed in the background atmosphere, which is more frequently studied. This is due to higher temperatures and a unique chemical composition volcanic plumes, which is potentially able to generate radicals. It is important to study the atmospheric processing within volcanic plumes as it determines the fate and deposition of acidic compounds contained within the plume (Aiuppa et al., 2007). Studies have shown that the ratios of SO$_2$/HCl remain constant in a distal plume but the ratio decreases in the presence of clouds, as the gases dissolve in order of solubility and therefore HCl will dissolve first in the presence of clouds, though the studies mentioned were carried out within tens of kilometres from source (von Glasow et al., 2009;Burton et al., 2001;Aiuppa et al., 2007).

One aspect which is challenging for scientists is to capture both the physical characteristics and the chemical composition of volcanic plumes after mixing with the background in the distal plume, particularly at long distances away from eruption source. In the case presented the distal plume was ~ 1000 km from its source in Iceland. The primary chemical components of volcano plumes measured are SO$_2$ and SO$_4^{2-}$, however there are many other gases emitted. Other studies have in addition measured the full chemical composition of particulate matter (PM), e.g. Mather et al. (2003);Martin et al. (2008) and more recently indirect measurements of aerosol properties from satellites has been undertaken (Ebmeier et al., 2014). Aiuppa et al. (2009) and Pyle and Mather (2009) published reviews of the literature in the area of chemical degassing with a focus on emitted halogen chemicals which can occur both in the gas and aerosol phase. In most studies the ratios of HCl, HF to SO$_2$ are reported rather than the absolute concentration. Similarly the other sulfur gases, H$_2$S and COS, are studied but less frequently. The Witham et al. (2015) report summarised the halogen acid and H$_2$S ratios from the literature. It was noted that predominantly measurements are made close to the emission source or at a surface position downwind from the eruption either by remote sensing or direct sampling with off line analysis methods.

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Only a few modelling studies (e.g.Witham et al. (2015);Schmidt et al. (2015)) and measurement approaches (Kroll et al., 2015;Businger et al., 2015) have assessed the atmospheric chemistry with an air quality impact focus. Complex perturbation of atmospheric ozone and other oxidants have been studied both in the stratosphere and troposphere, however with only limited number of observation studies. Recent reviews have indicated there are still much to be understood (Mather, 2015;von Glasow et al., 2009) to understand the input of volcano emissions and the perturbation to the atmosphere.

To date there is only one study which has demonstrated nucleation and particle growth in a distal volcanic plume. This was measured following the explosive eruption of Eyjafjallajökull in 2010, where at the GAW site Puy de Dôme, France (1,465 m above sea level), nucleation and secondary aerosol formation events within the volcanic plume were observed (Boulon et al., 2011). The site however was in the free troposphere and occurred in a plume which was ash rich. To date there is very limited evidence of the processes of particle nucleation and secondary aerosol formation in distal plumes from effusive eruptions.

The recent Holuhraun eruption within the Bárðarbunga 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$_2$ emissions of 11±5 Mt during a period of 6 months (Gíslason et al., 2015). 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) and there were complaints as far as Scandinavia of a foul smell, which has been attributed to sulfurous compounds from the fissure eruption using satellite data (Grahn et al., 2015). Exceedances in the hourly health limits were also observed for SO$_2$ periodically in Northern Finland at surface observation sites, which were confirmed by satellite observations (Ialongo 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). The 28 countries European Union member countries (EU-28) total annual 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 the 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 and focuses on one major incursion in September 2014 during the Holuhraun eruption and provides the first evidence of wide scale effects, based on the measurements 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 Network (AURN, http://uk-air.defra.gov.uk/networks/network-info?view=aurn) and by the two UK European

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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 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

The Measurement of Aerosols and Reactive Gases Analyser (MARGA, Metrohm Applikon B.V, NL) provides hourly resolution measurements of water soluble inogranic 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 one for $PM_{2.5}$. The instruments use wet rotating denuders (WRD) (Wyers et al., 1993) and steam jet aerosol collectors (SJAC) (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 of the instrument and quality assurance/ quality control (QA/QC) procedures used by both instruments is given in Twigg et al. (2015). There is one operational difference between the Auchencorth and Harwell instruments, where Auchencorth Moss uses preconcentration columns (Metrosep A PCC 1 HC ion chromatography (IC) preconcentration column (2.29 mL) for anions and a Metrosep C PCC1 HC IC pre-concentration column (3.21 mL) for cations) on the IC to achieve a lower detection limit (DL) compared to the Harwell instrument which uses fixed loops (250µL for anions and 480µL for cations) and therefore has an order of 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.

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2.2 SMPS

At both EMEP supersites scanning mobility particle sizers (SMPS) are installed which count the individual aerosol numbers within predefined size bins of aerosols. At Harwell, aerosol number size distributions measured in the range of 16.55 to 604.3 nm by the SMPS (Electrostatic classifier 3080, differential mobility analyser 3081, and condensation particle counter 3775, all TSI Inc.). The system sampled air 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 UK-Air website.

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At Auchencorth Moss aerosol size distributions in the range of 14-673 nm were set to be measured using the 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

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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} 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 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 Sutton et al. (2001), is used to measure the spatial concentrations of both inorganic trace gases (NH_3, HNO_3, SO_2 and HCl) and counterpart aerosols at a monthly resolution across the UK. 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. 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 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 the sampling train 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 both the sampling method and analytical analysis are contained in Tang et al. (2009). The monitoring sites in 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.

2.4 GOME2 Volcanic SO_2 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 SO_2 saturation effects (Richter, 2009). Satellite UV/vis retrievals yield integrated vertical columns of absorbing species and usually do not provide information about the vertical distribution of a trace gas. As the sensitivity of the observations decreases towards the surface, an assumption has to be made in the retrieval on the vertical profile of the target species in order to apply appropriate weights called air mass factors. Here, the standard volcanic product from the University of Bremen is used (http://www.iup.uni-bremen.de/doas/gome2_so2_alert.htm) which assumes a volcanic eruption profile with an

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SO_2 peak at 10 km height. 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 1km to 3 km.

2.6 ISORROPIA thermodynamic model

The chemical thermodynamics model, ISORROPIA II (Fountoukis and Nenes, 2007), is used 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}) with measured temperature and relative humidity 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 temporal resolution analysis (hourly measurements) of the volcanic plume, the monthly average SO_2 from AGANet measurements (Section 2.3) were analysed to assess the impact of the fissure eruption on the background atmosphere across the UK. The plume was clearly observable in this dataset. In order to understand the relative magnitude of the perturbation on a national scale for both air quality and sulfur deposition, against a background of decreasing anthropogenic emissions a statistical treatment was thought to be appropriate. Specifically the likelihood of a reoccurrence of the observed concentrations in the UK background was calculated as many AGANet sites show decreasing trends over time for SO_2 and SO_4^{2-}, reflecting decreases in emissions. This is observed for both the annual mean concentration and the annual maximum concentration. A high concentration superimposed on a downward concentration trend in a measurement series over a period appears to be a less unlikely observation at the end of the time period than at the beginning. Therefore the AGANet measurement data were adjusted to remove any underlying trends before further analysis to assess the unusualness of the September 2014 elevated SO_2 concentrations. Theoretically exceedances over a threshold follow a Pareto distribution, and the threshold was chosen by fitting an 85% quartile regression to this dataset

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using a smoothing spline for each site individually (i.e. there was no assumption of a general trend). This methodology has previously been developed much further for application to case studies with substantially more data (Chavez-Demoulin and Davison, 2005;Northrop and Jonathan, 2011;Reich et al., 2011). The fitted Pareto distribution generates the probabilities of occurrence of the elevated concentrations – which in this case were associated with the volcanic plume. This is expressed in Table 1 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 SO_2 over the 1999-2014 period at each site expressed in the resolution of the measurements.

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 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 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 µg m^{-3} (Figure 2) compared with the annual average of SO_2 of 0.14 µg 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 µg m^{-3} detection. The maximum reported SO_2 concentration during the event at Harwell reported by the MARGA was lower, peaking at 45.7 µg m^{-3} (annual average concentration in 2013 was 0.46 µg 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 µg 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 Finland and Austria (TS-2 in Supplementary Material of Gíslason et al. (2015) and Ialongo et al. (2015)) during different periods of the fissure eruption.

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. While satellite observations only provide tropospheric columns of SO_2 and not the concentrations at surface which are reported by the ground-based measurements, they do provide important information on the origin of enhanced SO_2 values. As the sensitivity of satellite retrievals to surface SO_2 is low, sulfur dioxide from surface pollution can rarely be detected over Europe. Volcanic plumes in contrast can readily be observed in the data as they usually extend to higher altitudes and contain much larger vertical columns of SO_2. The fact that several Dobson Units of SO_2 are observed in GOME2 data on September 20th and 21st, 2014 over the UK, and that the SO_2 plume originates from Iceland strongly indicates that the observed SO_2 is of volcanic origin. It is therefore very probably that

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simultaneous SO_2 enhancements measured at the surface are also linked to the volcanic emissions. 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), as did back trajectories using the HYSPLIT model, which can be found in figures S1-S2 in the supplementary material. To provide evidence that the EMEP4UK model was able to replicate the spatial distribution of the plume a comparison of the time series of observations to the model at both sites is given the supplementary material (figure S3). Though in general the EMEP4UK model does get the spatial distribution of the plume correct there are number of explanations why the model does not precisely replicate the plume compared to the measurements at the surface. The reasons include there a number of input variables which would have impacted the distribution of the plume including injection height, daily emission rates at source and oxidation rate within the plume, in addition the model output is 50 Km x 50 Km resolution.

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 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 with the hydroxyl radical in the troposphere can be slow, taking up to two weeks under some conditions, though if SO_2 is taken up onto particles, oxidation rates are much faster, resulting in a lifetime of days or hours in clouds as SO_2 (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 µg S m^{-3}), where a smaller value suggests a plume which has not undergone considerable atmospheric processing. 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. As the plume passed over the sites, the presence of ultrafine particles also became pronounced, compared to the background atmosphere in the previous 24 hours (Figure 5). 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" shape in figure 5, starting with high particle numbers at the detection limit of the SMPS is 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 population of ultrafine H_2SO_4 particles were emitted or formed at source, however, it is highly unlikely due to the transport time, refer to the HYSPLIT back trajectories found in figure S1, 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

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which is linked to solar radiation. It is hypothesized that with increasing time after sunrise, the measurements at Auchencorth reflect particles whose nucleation was initiated further and further away from Auchencorth and had increasing 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 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. Though nucleation is thought to occur in the free troposphere where there is a low particle surface area there is increasing evidence in the literature of nucleation events measured at the surface in polluted environments: Hamed et al. (2007) observed nucleation events in the Po Valley, Italy, and Kulmala et al. (2005) in New Delhi. In addition, we cannot rule out that other compounds are taking part in the nucleation process and aerosol growth observed. Furthermore as well as the particle population changes observed, the measurement indicates that there was an air quality impact from particulates during the 2014 eruption in addition to the SO_2 air quality impacts discussed in the recent study of Schmidt et al. (2015).

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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 basic, with free ammonia (NH_3) available based on ion balance studies (Twigg et al., 2015), during the plume event there is evidence that the aerosol turned acidic. The aerosol pH was confirmed using the results of [H^+] calculated from ISORROPIA-II model to calculate pH. During the plume event it was found that the pH dropped from pH 7.97 at 09:00 GMT on the 21/09/14 to pH 3.80 at 15:00 on the 21/09/14.

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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 enormously depending on the magma type and the particular eruption characteristics. 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/SO_2 ratio of <1% (Burton et al., 2015). 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 Cl^- 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

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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 of acid displacement was found at Auchencorth Moss 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-}, represented by a change in colour of the markers in Figure 7. This is not the first time the site has observed acid displacement, Twigg *et al*. (2015) observed the site to be rich in sea salt due to its proximity to the sea, with 35% of the annual average of the inorganic composition of $PM_{2.5}$ attributed to sea salt. During high nitrate (NO_3^-) episodes it was observed on occasions that this coincided with an apparent depletion of Cl^- from sea salt, which was attributed to the displacement of Cl^- by HNO_3. Roberts et al. (2009) has previously modelled the likely perturbations within a volcano plume upon mixing with background air, which found that both ozone and NO_x were perturbed with bromine chemistry as the key driver. In order understand the net impact of this eruption on the chemical perturbation of background sea salt aerosol and the production of HCl in the gas phase, there would need to be a full chemical transport model which includes both chloride and bromine chemistry, which is beyond the scope of this paper. It is however 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 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.

It is surprising that both acid displacement and nucleation events would be observed in parallel, as one process would be expected to be favoured over the other, depending on the aerosol surface area. Instead it is hypothesized that though both events are observed at the same time, it does not necessarily mean that they occur at the same time and at the same location. For the displacement reaction to occur, the sea spray aerosol needs to mix with the volcanic plume from aloft. It is feasible that this mixing generates 'pockets of air' that are dominated by the volcanically influenced air (where nucleation is favoured) and others which have efficiently mixed with the sea salt (where heterogeneous chemistry is favoured). Through continued mixing and through the long-term integration of the measurement both would be reported at the same time. Similarly, the conditions that favour one process over the other may vary along the trajectory between Iceland and the UK.

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 geographic region. The low-temporal resolution (monthly) measurements of gas and aerosol composition from 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 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 Yarner Wood in the south

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west of England experienced the highest concentrations on record for the site, and even taking into account the underlying decreasing trend in SO_2 concentrations, return probabilities were as low as $3x10^{-4}$ (Table 1, refer to section 2.7 for statistical methods). At sites which are much more anthropogenically influenced, though the plume is clearly observable, the SO_2 concentration is unremarkable with return probabilities of $>1x10^{-1}$ (e.g. Detling). A few sites on the Western side of the UK were not in the pathway of the plume therefore no elevated concentrations were observed, e.g. Rum. When assessing the wet deposition from Precip-Net, it was seen that many sites across the UK did experience elevated SO_4^{2-} concentrations in rain in September and October 2014 (Figure 9 upper panel). Again, at particular sites in northern Scotland and South West England elevated concentrations were observed, whereas in Northern Ireland and parts of Wales no increase in SO_4^{2-} concentrations was evident. It has to be noted, however that 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 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 annual sulfur deposition budget and hence the environmental impact through acid deposition will have been minimal (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 the UK atmospheric composition periodically during the latter part of 2014. Elevated SO_2 was observed by the networks at both high and low resolution. These observations complement 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 in 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 provide observational evidence for new particle formation and growth was 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 work 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.

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The study has highlighted that 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 is essential for the identification of the origin of aerosol events observed concurrently with 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.

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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 dataset 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 SO_2 (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 SO_2 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 x 10^{-03}	111.1
London Cromwell Road	2.37	0.54	1.83	6.90 x 10^{-03}	144.9
Ladybower	2.29	1.34	0.95	3.22 x 10^{-02}	31.0
Harwell	2.28	0.82	1.46	6.73 x 10^{-03}	148.7
Halladale	2.11	1.03	1.08	5.60 x 10^{-03}	178.6
Strathvaich	2.09	0.28	1.81	2.40 x 10^{-03}	417.4
Shetland	2.04	1.02	1.02	6.20 x 10^{-03}	161.2
Auchencorth Moss	2.00	0.37	1.63	8.71 x 10^{-03}	114.8
Glensaugh	1.95	0.57	1.38	6.17 x 10^{-03}	162.0
Stoke Ferry	1.84	0.68	1.16	1.70 x 10^{-02}	58.8
Sutton Bonnington	1.70	1.11	0.59	7.11 x 10^{-02}	14.1
Barcombe Mills	1.68	0.74	0.94	8.98 x 10^{-03}	111.3
High Muffles	1.67	1.14	0.53	7.72 x 10^{-02}	12.9
Lagganlia	1.65	1.14	0.51	7.28x 10^{-03}	137.4
Eskdalemuir	1.45	0.42	1.03	5.65 x 10^{-03}	177.1
Bush Estate	1.38	0.60	0.78	4.55x 10^{-02}	22.0
Moorhouse	1.24	0.47	0.77	1.10x 10^{-02}	90.6
Narberth	1.20	1.08	0.12	8.69x 10^{-02}	11.5
Rosemaund	1.15	0.51	0.64	1.19x 10^{-02}	84.0
Cwmystwyth	1.10	0.49	0.61	2.11x 10^{-02}	47.3
Plas Y Brenin	1.08	1.08	0.00	1.41 x 10^{-01}	7.1
Caenby	0.98	0.98	0.00	1.44 x 10^{-01}	6.9
Edinburgh St Leonards	0.61	1.32	-0.71	4.06 x 10^{-01}	2.5
Hillsborough	0.61	0.61	0.00	1.37 x 10^{-01}	7.3
Detling	0.58	1.01	-0.43	6.79 x 10^{-01}	1.5
Goonhilly	0.47	0.49	-0.02	1.36 x 10^{-01}	7.4
Lough Navar	0.39	0.39	0.00	1.75 x 10^{-01}	5.7
Rum	0.07	0.21	-0.14	9.08 x 10^{-01}	1.1
Carradale	nd				

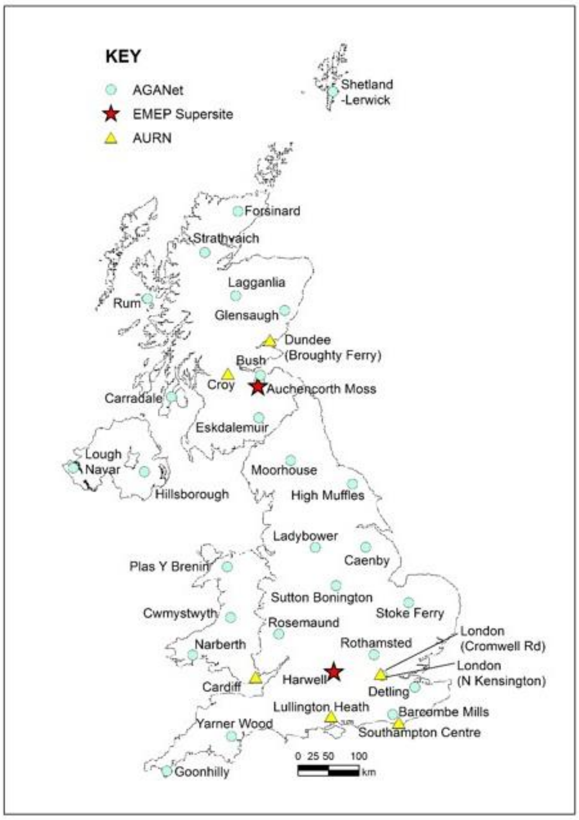

Figure 1. Map of SO_2 monitoring sites in the UK used in this study. The AGANet sites provide monthly average concentrations, whilst the other sites report hourly values.

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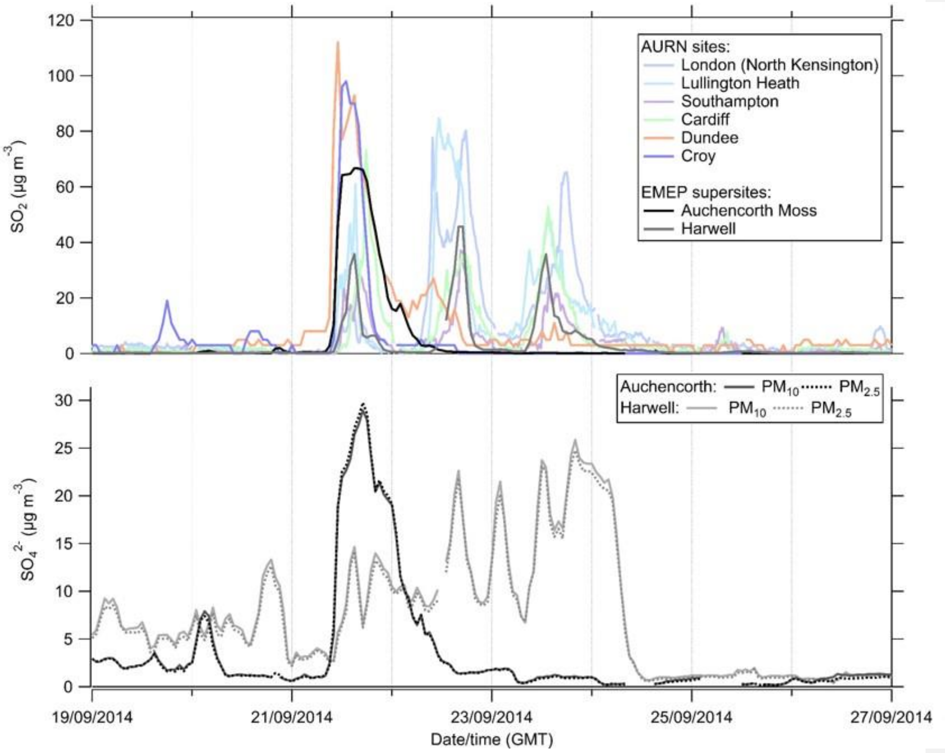

Figure 2. Time series of SO_2 hourly measurements made at 6 AURN sites in the UK and the two UK EMEP supersites measurements of SO_2 and $PM_{10/2.5}$ SO_4^{2-}. (NOTE: SO_2 at Auchencorth Moss is underestimated between 11:00 and 22:00 (GMT) on the 21/09/14)

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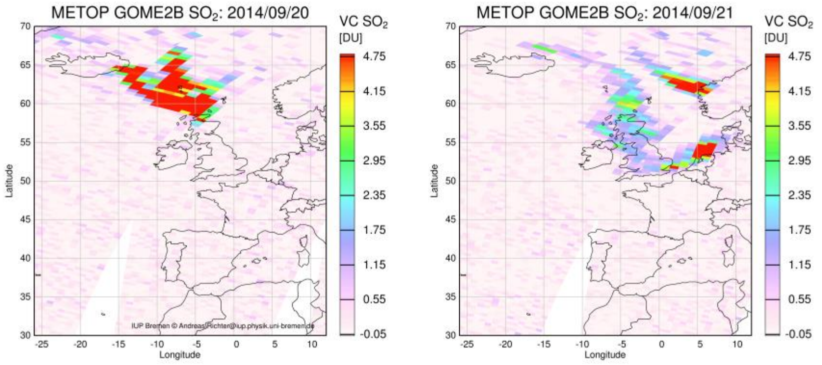

Figure 3. Observation of the volcanic plume from Iceland to and across the UK by the GOME2B satellite instrument, taken at the satellite overpass around 9:30 local time. GOME2B measures SO_2 column density, where VC is the vertical column, which is the SO_2 concentration integrated vertically to provide a column density per unit surface area. SO_2 columns are given in Dobson Units (DU), the thickness the SO_2 layer would have at standard temperature and pressure in units of hundredths of a millimetre.

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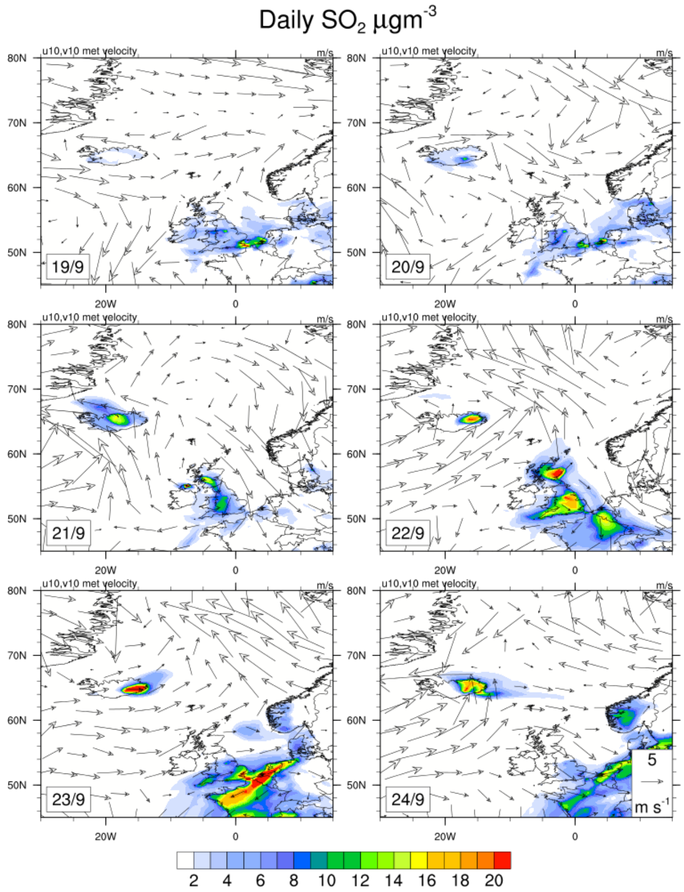
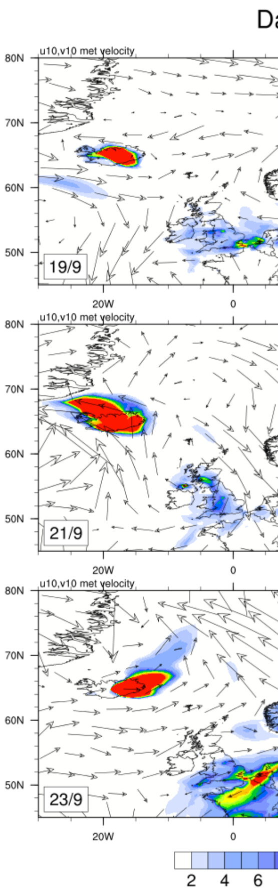


Figure 4. Daily average surface concentration (µg m^{-3}) of the 19th - 24th of September 2014 of SO$_2$ calculated by the EMEP4UK model and the 12:00 of each days wind vector.



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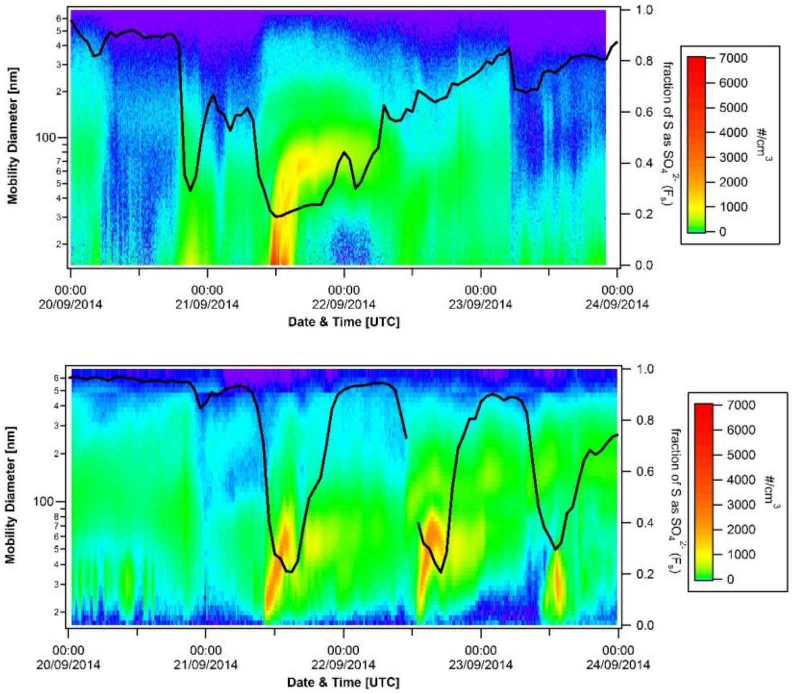

Figure 5. Particle number concentration at Auchencorth Moss (top panel) and Harwell (bottom panel) (refer to Figure 1 for map) during the September 2014 volcanic plume event. Right hand y-axis is the Fs ratio (black line) measured by the MARGA for the same period, where lower Fs indicates 'younger' SO_4^{2-}. (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).

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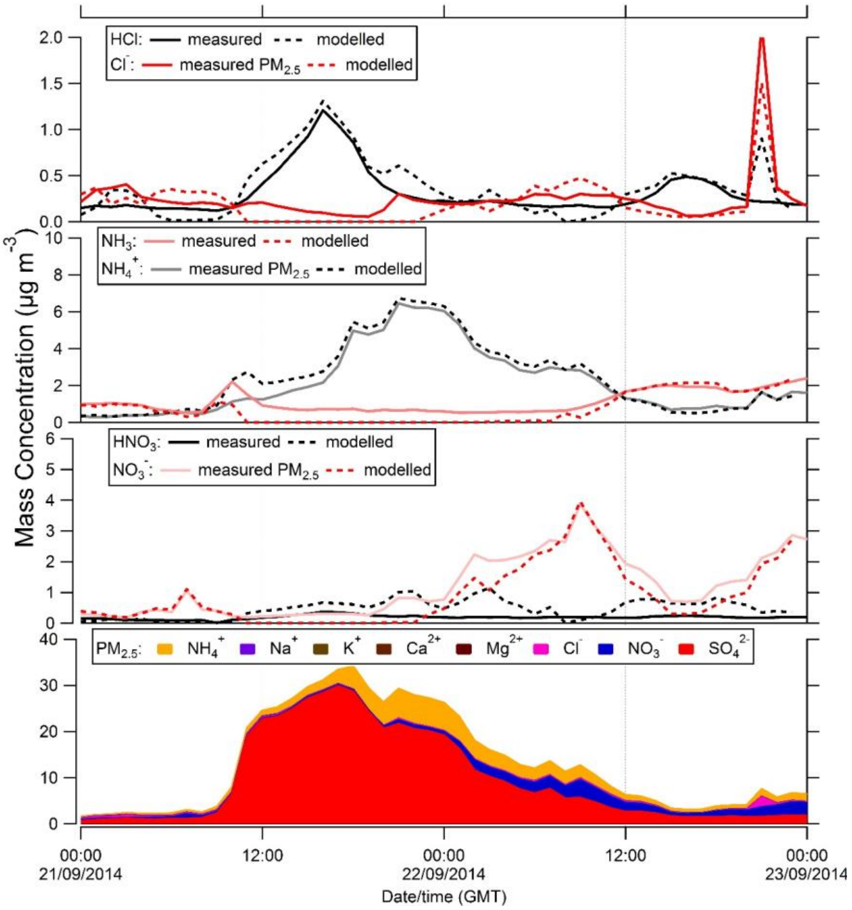

Figure 6. Top three panels: thermodynamic partitioning of gas and aerosol modelled by ISORROPIA-II compared with the measured concentrations at Auchencorth Moss. The bottom panel shows a stacked representation of the chemical composition of $PM_{2.5}$ at Auchencorth Moss as resolved by the MARGA instrument.

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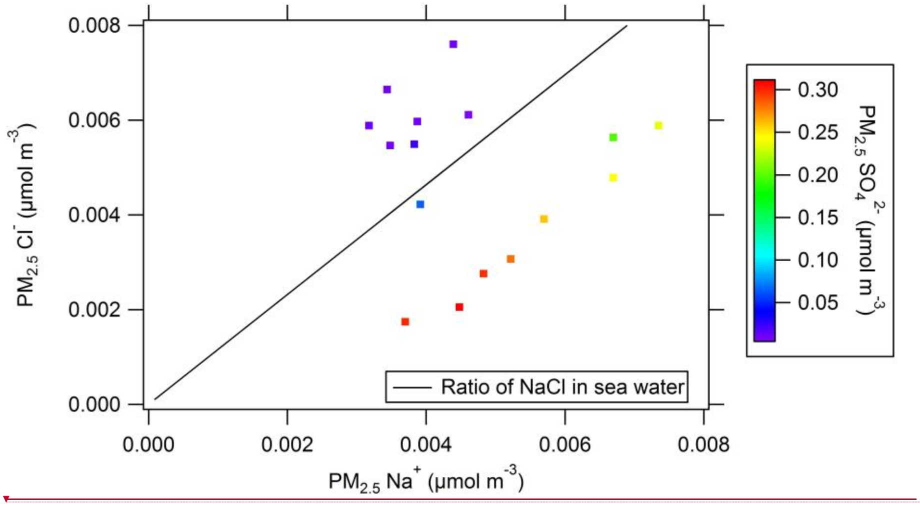

Figure 7. Evidence of acid displacement in sea salt (PM$_{2.5}$) on the 21st September 2014 from 00:00 to 18:00 (GMT) at Auchencorth Moss, where the solid line is the known ratio of NaCl in sea water (Seinfeld and Pandis, 2006).

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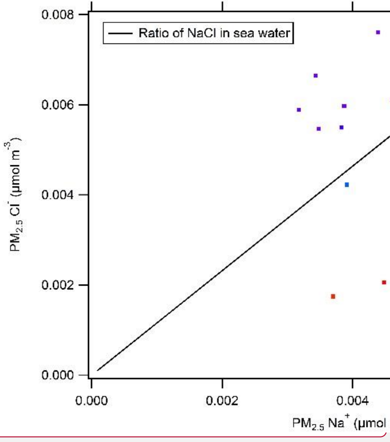

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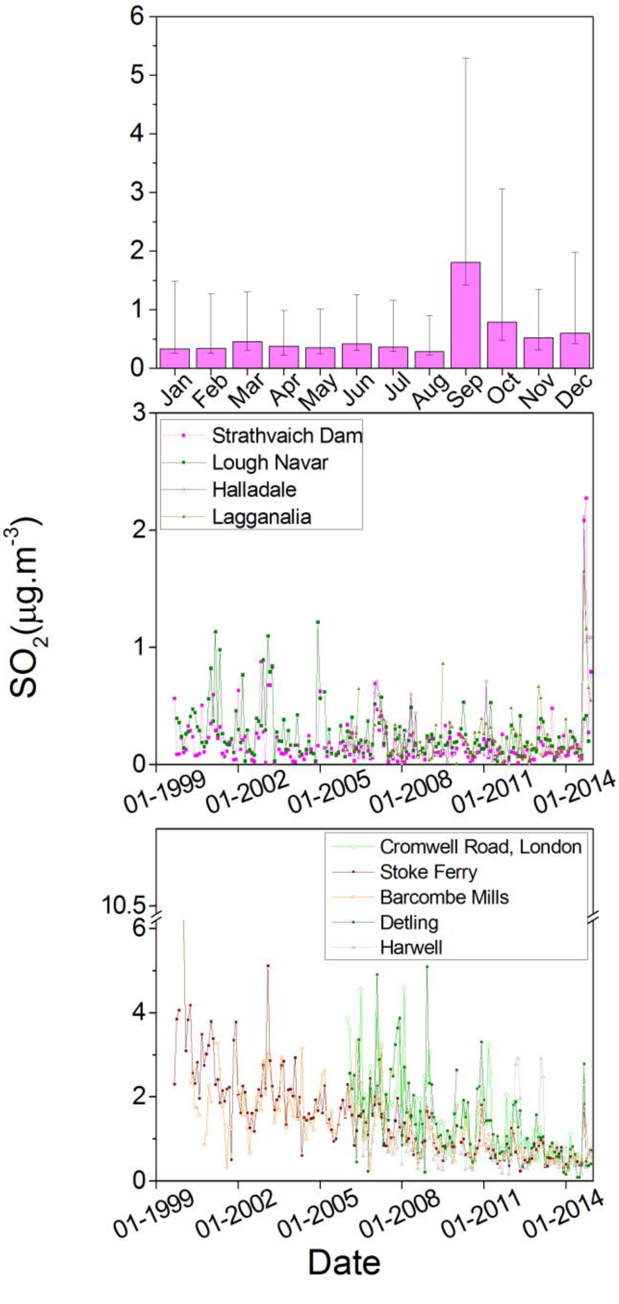

Figure 8 UK Defra Acid Gas and Aerosol Network monthly SO_2. Top panel: 2014 monthly network average SO_2 concentration (30 sites, whiskers maximum and minimum values); Middle Panel: 5 remote sites in the network; Bottom Panel: 5 sites in southern England (Refer to Figure 1, map for location of sites).

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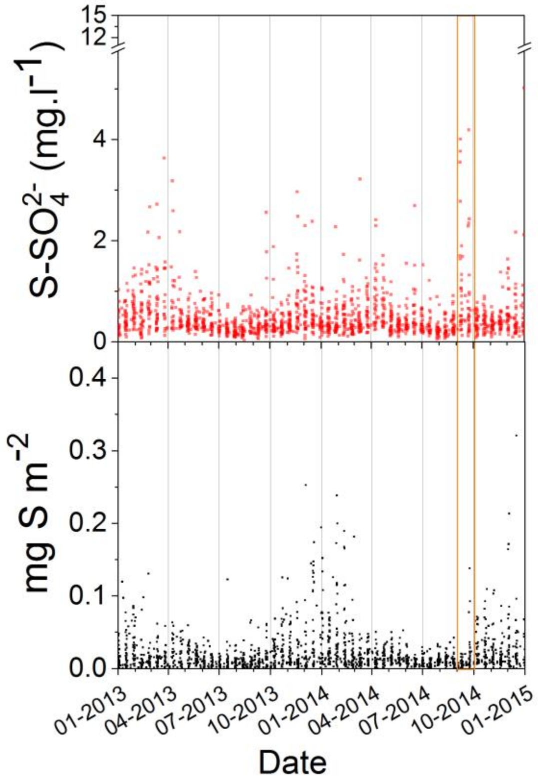

Figure 9 UK Precip-Net data: All fortnightly site data for 2013 and 2014; Upper panel: S-SO$_4^{2-}$ concentrations; Lower panel: Sulfur deposition (mg S m^{-2}); Note fortnightly data with data plotted using the start date of the measurement 5 **period. (Data downloaded from UK-Air on 25/06/2015 and 02/02/2016). The orange box highlights the measurements in September 2014.**

Supplementary Information:

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

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Detection of the volcanic plume

In order to further confirm the origins of the observed plume back trajectories were merged with the measured SO_2 data from the MARGA. The back trajectories and analysis was carried out using OpenAir software package (Carslaw, 2013), which calculates back trajectories with the HYSPLIT trajectory model (Hybrids Single Langrangian Integrated Trajectory Model, (Draxer and Hess, 1997)) using the global NOAA-NCEP/NCAR reanalysis data. For Auchencorth Moss the plume peaked on the 21/09/14 and is shown in FigS1 to originate from Iceland. The main trajectory, is over the highlands of Scotland, which does not have any known large sources of SO_2. At Harwell, the peak of the plume was on the 22/09/14 and again can be clearly seen to originate from Iceland (FigS2).

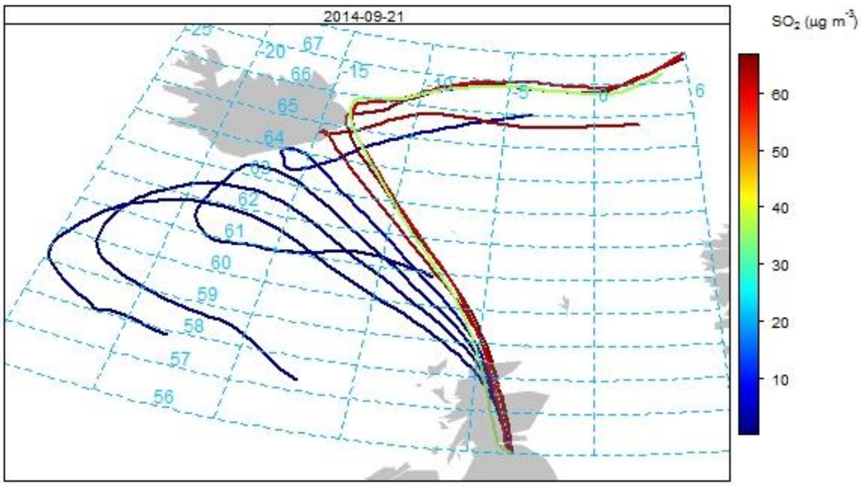


Figure S1 96 hour back trajectories using the HYSPLIT model merged with SO_2 measurements from the MARGA instrument for the 21/09/14 to further demonstrate that peak SO_2 concentrations at Auchencorth Moss originated from the Holuhraun effusive eruption. (Figure produced using Open air; Carslaw and Ropkins, 2012)

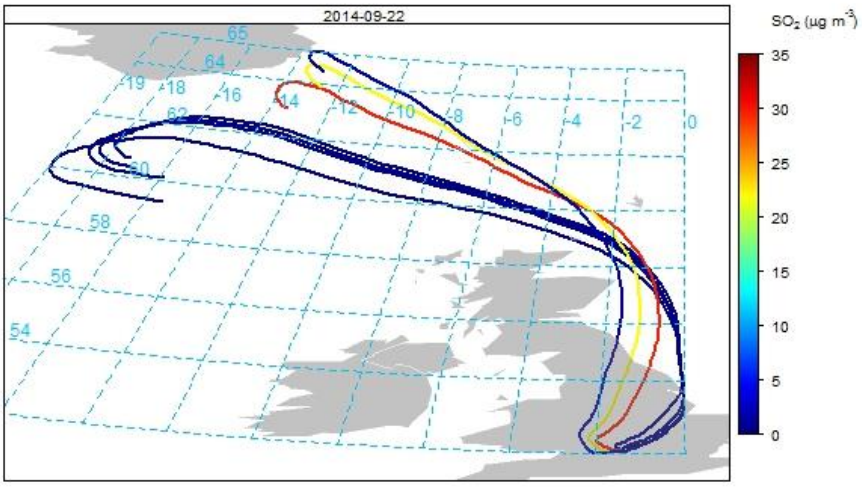
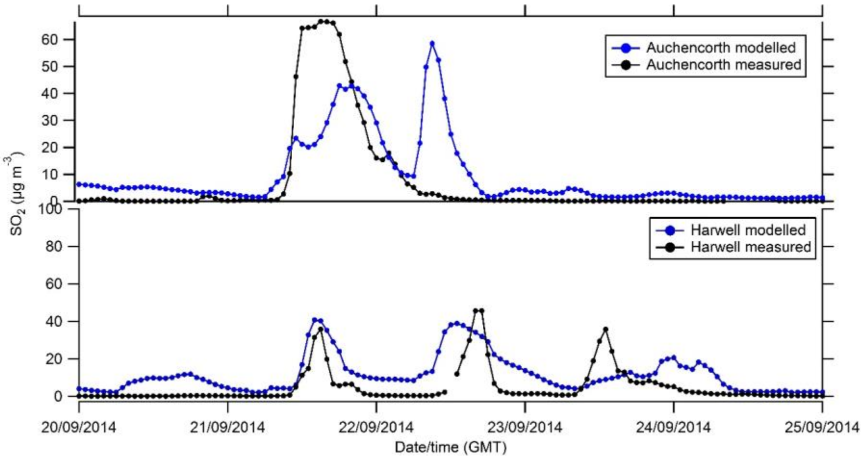


Figure S2 96 hour back trajectories using the HYSPLIT model merged with SO_2 measurements from the MARGA instrument for the 22/09/14 to further demonstrate that peak SO_2 concentrations at Harwell originated from the Holuhraun effusive eruption (Figure produced using Open air; Carslaw and Ropkins, 2012).

The EMEP4UK model was also used to confirm the distribution of the plume, as presented in Figure 4 in the main text. To provide further evidence of the agreement of the spatial distribution of the plume by the model, data for the sites Auchencorth Moss and Harwell data were plotted in a time series against the observed concentrations. It is clear to see that the model is able to show that Auchencorth Moss the observed plume on the 21/09/14, however the site did not observe the plume predicated on the 22/09/14 or match the magnitude of the plume at the surface. At Harwell, the observed 3 pulses on consecutive days (21/09/14- 23/09/14) from the volcanic plume were identified in the temporal pattern. There are a number of explanations why the magnitude and even the spatial of the distribution of the plume was not comparable to surface concentration measurements, these include that the emission rate from source and the injection height were variable, the model has a resolution of 50 x 50 Km^2 and so variations at surface are not well replicated at this spatial resolution.



Figures S3 Times series of modelled plume by EMEP4UK and that observed by the MARGA instrument.