

Reply to reviewer 1 :

We thank Reviewer#1 for this detailed review. We thoroughly revised the paper, which required input from two new co-authors.

The main additions are :

- The exploration of 8 additional EMEP stations in Poland, Slovakia and Slovenia with full analysis of now 8 stations dispersed in Europe using a multi-concentration-weighted trajectory analysis.
 - This new analysis shows that widespread SO₂ anomalies, with ground-level concentrations far exceeding background values, almost entirely result from the Holuhraun eruption, whereas the origin of sulfate aerosols is more complex. We show that volcanic emissions are one of the main sources of SO₄ at all selected EMEP sites across Europe, and can be distinguished from anthropogenic emissions from Eastern Europe but also from Great Britain.
 - The evaluation of the SO₂ to SO₄ oxidation rate:
A wide variability in SO₂:SO₄ mass oxidation ratios, ranging in 0.8–8.0, is shown at several stations geographically dispersed at thousands of kilometers from the eruption site. Despite this apparent spatial complexity, we demonstrate that these mass oxidation ratios can be explained by a simple linear dependency on the age of the plume, with a SO₂ to SO₄ oxidation rate of 0.23 h⁻¹.
- The development of thermodynamical simulations, with the ISORROPIA II model, of aerosol composition and pH that support and confirm the interpretations already developed in the ACPD paper. It adds a detailed discussion of the NH₃ background level required for the neutralisation of volcanic sulfates.
- The addition of polar plots of SO₂ and SO₄ concentration values, colored with wind speed or anion neutralisation ratio, at Dunkirk that allow us to:
 - confirm that the aerosols very poor in particulate nitrate and rich in sulfate, that were shown in the ACPD version to exist only at Dunkirk (and not at SIRTa) and to be acidic, are freshly-emitted industrial aerosols.
 - discuss whether acidic aerosols result from a lack of time for neutralisation or a lack of background NH₃.

We added two new sections, four new figures and one table in the main manuscript and four new figures in the Appendix and a set of 27 figures in the Supplementary Material. Many other figures were also updated and many quantitative additions have been made to the text.

We develop in details below our reply to all the questions and comments raised by reviewer#1.

The new figures that have been added to the revised version of the article have been also reproduced at the end of this reply letter. Four additional figures, which are used to respond to specific questions of the reviewers but which are not included in the revised version of the manuscript, are also included at the end of the reply letter.

Anonymous Referee #1

Received and published: 6 June 2019

Review of Boichu et al. This paper reports a collation of ACSM data, satellite data and aerosol remote sensing over the period of the Icelandic eruption in 2014. Most of the data reported comes from two stations in France and the authors use some EMEP station data from Northern Europe. The authors focus on approaches to identify the volcanic signal in the ACSM sulphate data and air quality network SO₂ data. The paper compares the ratios of the ammonium, sulphate, organics and nitrate to try and understand the influences of the Bardabunga volcano eruption and its chemical fingerprint.

Though the subject area is of great interest, there are major weaknesses in this paper. The general conclusions of the paper seem to be that the volcano plume was observed across Europe in both SO₂ and SO₄, however this is not new information.

It is also not novel that the signal from a volcano plume is easier to identify in a clean background site compared to an industrial/shipping influenced site.

As mentioned in the introduction of the ACPD version, the authors are aware of several publications showing a large-scale pollution in SO₂ associated to the Holuhraun eruption. To the best of our knowledge, only one article (Twigg et al. 2016), whose reference has been added to the revised version, shows correlated anomalies in both SO₂ and SO₄ at two stations in the UK. Besides two NILU reports (the 2014 and 2015 annual reports suggested by reviewer#2) highlight the same observation at several EMEP stations in Norway. Such studies demonstrated that volcanic SO₂ and SO₄ coexist in the troposphere at long distance from the source, indicating that the oxidation of SO₂ to secondary sulfates operates on long timescales (several days or weeks). However, the kinetics of SO₂ to SO₄ oxidation remains poorly constrained, especially within volcanic plumes transported over large distances in contrasted environments. Understanding the factors controlling the oxidation of SO₂ within volcanic plumes requires sampling the chemical composition of the volcanic plume over a broad range of plume residence time, which is only accessible by collecting observations over a broad spatial region.

We are not aware however of any publication showing, based on observations, the large-scale volcanogenic pollution in both gas and particulate sulfur at the European scale, as developed here by the exploration of 27 EMEP stations, with records from 8 stations in 5 different countries (France, Norway, Finland, Denmark, Great Britain) studied in detail. Our study allows us to show a wide variability of SO₂ to SO₄ oxidation ratios at stations far away from the source (several thousands of kms from the eruption site), in contrast with previous studies which are mostly focused on near-source measurements (a few hundreds of kms from the eruption site). Despite this apparent complexity, we demonstrate that observed mass oxidation ratios can be explained by a simple linear dependency on the age of the plume (Figure 16), allowing us to estimate a SO₂-to-SO₄ oxidation rate. To our knowledge, this has never been done before.

In addition to the broad geographical impact of this eruption, our paper also shows the persistence of particulate sulfate in the lower troposphere at long distance from the volcanic source, lasting for several weeks. Using multi-site concentration-weighted trajectory analysis, we demonstrate that emissions from the Holuhraun eruption are the main source of SO₄ pollution at all EMEP sites across Europe, and can be distinguished from sulfur-rich anthropogenic emissions from Eastern Europe and Great Britain.

Finally, we also explore the chemical interactions between volcanic SO₂ and sulfate with surrounding aerosols. We demonstrate that volcanic sulfate aerosols exhibit a distinct chemical signature in urban/rural conditions, with NO₃:SO₄ concentration ratios lower than background aerosols. Thermodynamic simulations of aerosol composition using ISORROPIA II model indeed show that ammonium sulfate aerosols are preferentially formed at high concentration of sulfate, leading to a decrease in the production of particulate nitrate. Such chemical signature is however more difficult to identify at heavily-polluted industrial sites due to a high level of background noise in sulfur. Nevertheless, we demonstrate that aged volcanic sulfates can be distinguished from freshly-emitted industrial sulfates according to their contrasting degree of anion neutralisation.

The novelty of the using the aerosol chemical speciation monitorin (ACSM) data for aiding the investigation of air masses is new, however the approach taken is simplistic and non-quantitatively presented.

The submitted version to ACPD analyzes ACSM observations distant from the volcanic source. Using simple methods, we highlight the specific chemical signature of volcanic aerosols (specifically the decrease in both the aerosol NO₃:SO₄ and Org:SO₄ mass concentration ratios). This has, to the best

of our knowledge, never been highlighted or published in the literature. We consider the fact that our demonstration lies on simple methods is precisely the strength of our study.

Nevertheless, in order to satisfy Reviewer #1's criticism, we performed a more advanced analysis of our dataset.

While we interpreted in the ACPD version the remarkable chemical signature of volcanic aerosols in the light of thermodynamical sensitivity simulations published in the reference textbook of Seinfeld and Pandis, we have added to the revised manuscript a set of ISORROPIA thermodynamical simulations (initialised for the exact atmospheric conditions met at our ACSM station during the period of study) that completely supports and strengthens the results, interpretations and conclusions developed in the ACPD version (added Figures 10 and 11, revised version). The large abundance of sulfate aerosols in a volcanic plume leads to the preferential formation of ammonium sulfate rather than ammonium nitrate aerosols, producing a significant decrease of the particulate NO₃ concentration and, therefore, a decrease in the measured NO₃:SO₄ ratio.

The paper needs significant revision and more data analysis before publication. With a more quantitative and rigorous approach to analysing the excellent and novel datasets which the authors have available. Once done, this should give significant insights into the atmospheric chemistry of the Bardabunga volcano plume.

Key areas which need to be addressed:

- The authors appear to have missed detailed studies published in the past 3 years which are in the same subject area (e.g. Twigg et al. 2016 and some of the references therein, Schmidt et al. 2017)
- The authors also do not critically compare their results and their data analysis methods against the literature.

We added to the revised paper the reference of Twigg et al. (2016) that shows the impact of the Holuhraun eruption on the UK atmosphere.

We suppose that Reviewer#1 aimed at the paper of Ilyinskaya et al. (2017), instead of Schmidt et al. (2017). Ilyinskaya's article mainly deals with local measurements of near-source emissions of gas and aerosols from the Holuhraun eruption, from the eruption site up to a distance of 250 km where the capital city of Reykjavik sits. Apart from model simulations of the dispersal of the volcanic plume reaching the UK on 8 Sept 2014, based on the previous study of Schmidt et al. (2015) (which is cited in our ACPD article), this 2017 study mainly focuses on the massive atmospheric impact of this eruption in Iceland. In contrast, our article objective is to evaluate the large-scale gas and particulate pollution, at the European scale, generated by this eruption.

In the revised version, we cite Ilyinskaya et al. (2017) to put in perspective our estimation of a linear relationship between SO₂ to SO₄ ratio with plume age (at a distance of a few thousands kilometers) allowing by extrapolation (to be taken with caution) to evaluate a near-source SO₂ to SO₄ ratio comparable with measurements performed by Ilyinskaya et al. (2017).

- The data analysis methods used by the authors are very limited and basic. Only presenting time series, simple x-y scatter plots, simple chemical ratios with particular events/sections of the data highlighted in graphical form means that all outcomes of the paper are qualitative at best. There are many analytical data tools which could have been applied to understand data, its clusters, patterns e.g. Openair, hysplit, source apportionment techniques) and the underlying atmospheric chemistry and physics. - No statistical analysis of the dataset is presented in table or graphical format or in the text.

As already mentioned above, the submitted version to ACPD presented indeed rather simple methods

to highlight chemical patterns in volcanic plumes (especially the decrease in the NO₃:SO₄ and Org:SO₄ ratios) that, to the best of our knowledge, have never been highlighted or published in the literature.

As developed in the following, we have added to the revised manuscript a set of ISORROPIA thermodynamical simulations (Fig. 10 and 11, revised version) that completely supports and reinforces the results and conclusions developed in the ACPD version.

Concerning the second part of this research aiming at demonstrating the large-scale impact on the European atmosphere of the Holuhraun volcanic plume through the exploration of a large set of EMEP stations (especially in Scandinavia), we have included in the Supplementary Material two animations of SO₂ observations from two satellite sensors (OMPS and IASI). These animations show the large-scale dispersal of the volcanic cloud and its frequent overpass over Scandinavia – where most EMEP stations of interest are located – in September and October 2014 suggesting a large impact of the volcanic source producing correlated SO₂ and SO₄ anomalies of large magnitude recorded at various EMEP stations largely geographically distributed.

Nevertheless, for the avoidance of doubt, we performed in the revised version a multi-site concentration-weighted trajectory analysis (new Figures 15, A4, A5 and A6) to demonstrate that other types of non-volcanic sources can impact the sulfur gaseous and particulate concentrations recorded at the EMEP stations, albeit to a much lesser extent regarding SO₂.

- The authors present basic meteorological information but do not use it for interpretation of the data, for example the authors did not pick up that the September 2014 was one of the driest on record and that may have influenced background particulate matter concentrations. The influence of the diurnal cycle and boundary layer dilution is not discussed.

Actually, we did pick up that September 2014 was a dry month, as already mentioned in the ACPD version (Section 3.4): “This result illustrates the much longer lifetime (a few weeks) of volcanic sulfate aerosols compared to SO₂ (a few days), even in the boundary layer. Meteorological conditions, without abundant long-lasting precipitations, have likely favored this persistence of aerosols in the atmosphere”.

We agree that the atmosphere dynamics will play an important role in the concentrations measured at the surface. However we are not quite sure whether this comment is general or if Reviewer#1 had something more precise in mind so our answer may be out of topic. The boundary layer tends to drop at night thus leading to higher in situ levels of pollutants. This is for instance readily observed in Dunkirk when considering only emissions from the west wind sector (where the larger industrial area is located and emits day and night), for which the nocturnal layer traps pollutants (especially sulfate) emitted from the stacks, whereas this trend is absolutely not visible when considering winds from the marine wind sector (Fig. R2).

- Air mass back trajectories which could have moved the interpretation from qualitative correlation graphs to semi-quantitative source apportionment were not done.

As stated above, we performed in the revised version a multi-site concentration-weighted trajectory analysis (new Figures 15, A4, A5 and A6) that confirms the strong and widespread European impact of the Holuhraun volcanic cloud on the European atmospheric composition in gas and particulate sulfur developed in the ACPD version. This new analysis also demonstrates that other types of non-volcanic sources of industrial origin can widely impact the sulfur gaseous and particulate concentrations recorded at the EMEP stations (especially the particulate SO₄ concentration) (Fig. 15,

A4, A5), albeit to a much lesser extent regarding SO₂ while the anthropogenic contribution to SO₄ equals the volcanic one (Fig. A6).

- *No statistical analysis is presented at all in the paper. Even the few correlation lines presented do not have the equation of the line presented. Where ratios are used to try and identify different chemical signatures, no quantitative assessments are presented.*
- *The statistical significance of the conclusions drawn from the scatter plots is not discussed*
- *The paper could have worked towards developing a general approach for identifying chemical fingerprints that could be applied to future air quality/plume events but this is not considered.*
- *The discussion is limited to describing the scatter plots rather than critically interpreting them.*

We agree with Reviewer#1 that such a detailed statistical analysis would be of great interest. However, performing a meaningful statistical analysis would require a greater number of occurrences of volcanogenic pollution events, more records of a same volcanic event at numerous ACSM stations and a thorough assessment of background levels and natural variability of aerosol speciation at ACSM sites. This is far beyond the data presently available in our paper. Therefore, we refrain from developing a detailed statistical analysis of our limited dataset because we would like to avoid giving the false impression that our results can be readily generalised. At this stage, our results remain to be explored in a more systematic way.

Nevertheless, our limited ACSM dataset at two sites (with only 3 volcanic events) allows us to highlight a distinct volcanic chemical signature, exhibiting in particular a decrease in the particulate nitrate production compared to background. To our knowledge, such volcanic signature has never been reported. The interpretation of this specific signature developed in the ACPD version, based on the textbook of Seinfeld and Pandis, is now confirmed by the thermodynamical simulations, using ISORROPIA II model, run for the exact atmospheric conditions met at our station, that have been added to the revised version.

- *The quality of the graphs presented is highly variable. Some are not really good enough for publication. Different chemical species are not visible separately (particularly the ammonium), on others the scales, points or labels are not readable. Figure 13 in particular is poor.*

Concerning chemical species, we use standard color representation in ACSM data analysis, with sulfate and ammonium commonly displayed in red and orange. For the sake of clarity, we offset the vertical axis for each aerosol component of ACSM observations in updated figures 3 and 4.

We also updated Fig. 8 for better legibility.

We agree that Fig. 13 may be difficult to read, as it was aimed at representing as clearly as possible in a single figure, for comparison purposes, bi-component concentration data at multiple stations (6 in the ACPD version, 8 in the revised version). We updated this figure (Fig. 14, revised version) to facilitate readability.

- *The data used in this paper is not cited or attributed to a data repository*

Acknowledgements to public open-source data providers (OMPS satellite observations, data from French air quality stations and EMEP network, AERONET measurements) were already included in the 'Acknowledgement' section of the ACPD version.

Lieven Clarisse who provided IASI SO₂ satellite observations is co-author of the paper. IASI data can be provided on demand.

ACSM data for SIRTa are available on the EBAS website (<http://ebas.nilu.no/>), while ACSM data for Dunkirk can be provided on demand.

All these information have been gathered in the data availability section in the revised version.

- The measurement and remote sensing data is not quantitatively assessed – no mathematical assessment or discussion of how to quantitatively relate the satellite, the PM remote sensing to the PM1 given they all assess different aerosol populations across different parts of the atmosphere.

We do not understand what Reviewer#1 means by the term ‘quantitative assessment of measurement and remote sensing data’.

In Section 4.1, we jointly analyse satellite SO₂ observations and in-situ ground-level measurements. On one hand, satellite observations allow us to track the large-scale transport and dispersion of the Holuhraun cloud from Iceland to Europe by column-integrated observations that do not necessarily inform on the vertical distribution of the volcanic plume (observations in the UV-visible such as OMPS do not inform on the height of SO₂ whereas IASI bring such information but is much less sensitive below 5 km of altitude). On the other hand, in-situ ACSM measurements indicate the particulate matter in the PM₁ fraction at ground-level.

The concomittance of the arrival of the volcanic plume from satellite observations and a broad-scale (regional) increase in the ground-level concentrations indicate that the volcanic plume has reached the ground and affects air quality.

Regarding ground-based remote sensing sunphotometric observtions, AOD measurements provide constraints on the column-integrated abundance of aerosols in the atmosphere. On the other hand, the ACSM data provide information on the concentration of SO₄ in the PM₁ fraction at ground-level. The remarkable correlation between these two observations over weeks suggests that the substantial concentration of sulfate aerosols in the boundary layer primarily controls the colum-integrated abundance of aerosols. This is discussed in Section 4.4. in the revised version.

Specific comments

1. Literature and data The authors have not read or cited Twigg et al. (Atmos. Chem. Phys., 16, 11415-11431, 2016, <https://doi.org/10.5194/acp-16-11415-2016>), which discusses much of the same topic as this paper. Also some of the references in Twigg et al (e.g. Witham et al) could have aided the authors in the data analysis. The authors also do not appear to have carefully checked the data on ebas. In the text they state several times that under EMEP the UK does not measure SO₂ and SO₄ (Section 2.1.3) – which they express disappointment at. However the UK operates a level II hourly SO₂ and SO₄ measurements at the 2 EMEP sites, all the data from which is repositied and publically available on ebas. In addition monthly SO₂ and SO₄ is available at a further 30 sites. The authors appear to have missed this completely. I have not further checked what other data the authors have not found but it is a clear gap in their background research. I would suggest the authors revise their analysis taking these additional measurements and the analysis of Twigg et al. into account, and to check further for other datasets.

In our study, we focus on sites where measurements provide, at the same temporal resolution, ground-level mass concentrations of both gaseous SO₂ and particulate SO₄. Performing such a bi-component (SO₂ and SO₄) search through the EBAS website is not an easy task. We focused on daily observations using filter pack measurements and indeed missed the hourly-resolved data from online ion chromatography available at the two UK stations of Auchencorth Moss and Harwell. We consequently added to the revised version the highly-resolved datasets at these two UK stations and explored them in detail through a multi-site concentration-weighted trajectory analysis. Regarding the other UK sites mentioned by Reviewer #1, as we focus on data at high temporal resolution (on a daily basis at worse), we did not explore stations where only monthly data are available.

We browsed again the EMEP website to check exhaustively if we did not miss any other stations outside UK. We realized that we had focused on 3-stage filter pack measurements but missed 2-stage or 1-stage data. That is the reason why we added 6 new stations in Poland, Slovakia and Slovenia (see Table 1 for a detailed list of EMEP stations and updated map of station location in Fig. 13, revised version), in addition to the 2 new stations in the UK.

The analysis of this supplementary stations reinforces our study. We are grateful to Reviewer#1 to have spotted the inadvertent omission.

2. The authors do not cite or discuss Schmidt et al. : Understanding the environmental impacts of large fissure eruptions: Aerosol and gas emissions from the 2014–2015 Holuhraun eruption (Iceland), Earth and Planetary, 2017 – a key paper on this subject.

This comment being identical to a previous comment, we reproduce here our response.

We suppose that Reviewer#1 aimed at the paper of Ilyinskaya et al. (2017), instead of Schmidt et al. (2017). Ilyinskaya's article mainly deals with local measurements of near-source emissions of gas and aerosols from the Holuhraun eruption, from the eruption site up to a distance of 250 km where the capital city of Reykjavik sits. Apart from model simulations of the dispersal of the volcanic plume reaching the UK on 8 Sept 2014, based on the previous study of Schmidt et al. (2015) (which is cited in our ACPD article), this 2017 study mainly focuses on the massive atmospheric impact of this eruption in Iceland. In contrast, our article objective is to evaluate the large-scale gas and particulate pollution, at the European scale, generated by this eruption.

In the revised version, we cite Ilyinskaya et al. (2017) to put in perspective our estimation of a linear relationship between SO₂ to SO₄ ratio with plume age (at a distance of a few thousands kilometers) allowing by extrapolation (to be taken with caution) to evaluate a near-source SO₂-to-SO₄ ratio comparable with measurements performed by Ilyinskaya et al. (2017).

3. All datasets presented are not traceably referenced, in particular the air quality datasets, the remote sensing datasets, the ACSM dataset or the meteorological data. Where is all the data used in the paper reposit? What data clean up was done? Where are the averaged datasets? The data and methods section is not of a sufficient detail or quality for ACP.

Standard diagnostics were used to clean up the ACSM data, such as spikes in the airbeam and/or water signals, drop of inlet pressures indicative of clogging. No averaging was needed to compare the species obtained with the same instrument and therefore the original time resolution was kept.

Apart from this standard clean up of ACSM data that has been added to the revised version, no data clean up whatsoever has been performed.

As for the rest of this comment, it is identical to a previous comment. We here reproduce our response.

Acknowledgements to public open-source data providers (OMPS satellite observations, data from french air quality stations and EMEP network, AERONET measurements) were already included in the 'Acknowledgement' section of the ACPD version.

Lieven Clarisse who provided IASI SO₂ satellite observations is co-author of the paper. IASI data can be provided on demand.

ACSM data for SIRTa are available on the EBAS website (<http://ebas.nilu.no/>), while ACSM data for Dunkirk can be provided on demand.

All these information have been gathered in the data availability section in the revised version.

4. No comparison of the literature SO₂:SO₄ ratio in proximal and distal volcano plumes are made even though there is data in the literature.

To the best of our knowledge, most publications investigating the SO₂ to SO₄ oxidation within volcanic plumes focus on source or near-source measurements (i.e. from the eruption site until a few hundreds of kilometers). Our ACPD paper deals with samples collected at a few thousands of kilometers from the eruption site, making the comparison with these near-source results risky.

In the revised version, we added a new section entitled ‘Evolution of SO₂ to SO₄ oxidation during plume aging’. In this section, we show that, despite their wide variability, the SO₂ to SO₄ oxidation ratios estimated at several stations vastly dispersed in Europe, evolves linearly with a single variable, the plume age or residence time (new Fig. 16). If we hypothesise that this linear relationship is still valid close to the source (although this should be taken cautiously), we can estimate a near-source SO₂ to SO₄ mass ratio for Holuhraun eruption of about 20, in agreement with measurements performed by Ilyinskaya et al. 2017 at distance of about 200 km from the eruption site, which fall in the broad range of 2—250.

This comparison has been added to the revised version in Section 4.6.

5. P9: Discussion of chemical fingerprints: There is a discussion about using the ammonium (measured:predicted) as a identifier for volcanic versus industrial sulphate and there is a discussion about time for neutralisation. However there is no discussion about mixing (or lack of mixing) of the volcano plume with air which has significant ammonia concentrations. The authors could read details of modelling done in Witham et al. 2014 (Witham, C., Aspinall, W., Braban, C., Hall, J., Loughlin, S., Schmidt, A., Vieno, M., Bealey, B., Hort, M., Ilyinskaya, E., Kentisbeer, J., Roberts, E., and Rowe, E.: UK hazards from a large Icelandic effusive eruption. Effusive Eruption Modelling Project final report, Met Office, Exeter, 226, 2015.) which looked at the neutralisation of sulphate as the plume ages using 2 different chemical transport models. In tropospheric layers above the surface layer ammonia concentrations can be very very low and you can locally deplete the ammonia and hence have a non neutralised sulphate which has been in the atmosphere a long time. The discussion presented is completely qualitative whereas with the datasets the authors have available could have been used to do a quantitative assessment.

It is true that neutralization of sulfate depends both on the reaction processes and the availability of reactants (including ammonia) on site. Eatough et al. (1994) estimated that only up to 10% of SO₂ per hour can be converted to SO₄ through homogeneous processes (by OH radicals). On the contrary, aqueous chemistry reactions, especially in clouds or fog droplets, are rather limited by reactant availability (O₃, H₂O₂, NH₃) as well as mixing but can lead to 100% conversion per hour if conditions are optimal. Besides heterogeneous processes can be catalyzed by metals such as Mn and Fe which are available in significant amounts in the area of Dunkirk for example (Setyan et al., 2019).

In the revised version, we have added thermodynamical simulations using the ISORROPIA II model with two scenarios (new Fig. 10, revised version), either rich or poor in NH₃ (as no direct measurements of this gas-phase species were performed along with ACSM observations at either site during the period of study in 2014). Such runs allow to investigate the impact of sulfate on particulate nitrate production. Both scenarios reproduce a large decrease in the NO₃:SO₄ ratio with an increasing concentration of total sulfate (Figures 10, A1 and B1). However, only the NH₃-rich scenario (7.40 µg.m⁻³ initially) allows to best fit the NO₃ observations during the volcanic event in late Sept 2014 which is characterized by large SO₄ concentrations exceeding 4 µg.m⁻³ (Figures 10, A1 and B1). The NH₃-poor scenario (0.74 µg.m⁻³ initially) overestimates the decrease in particulate nitrate, with almost complete depletion for a concentration of total sulfate exceeding 12 µg.m⁻³ (Fig. 10, B1) concomitant with a total depletion of NH₃ (Fig. 10, B3) and an increase in the concentration of nitric acid (Fig. 10, B4).

Therefore, these thermodynamic simulations allow to indirectly estimate the rich background concentration of ammonia at SIRTa in Sept-Oct 2014, showing no evidence of any lack of NH_3 to neutralize the substantial load of sulfate aerosols (up to $16 \mu\text{g m}^{-3}$) during the large volcanic event in late September 2014.

Regarding Dunkirk, wind sector analysis of the predicted vs. measured NH_4 levels or ANR (new Fig. A3 added to the revised version) demonstrate that under urban or marine emissions there is enough NH_3 to neutralize both sulfate and nitrate at the site, but that industrial emissions disturb the equilibrium (Bottom of Fig. A3, revised version). Bottom of Figure 5B shows the extent of ammonium concentrations over the 14 months of ACSM field observations, with levels often reaching up to $9 \mu\text{g m}^{-3}$. Most of the time in Dunkirk, sulfate concentration does not exceed $25 \mu\text{g m}^{-3}$ (left of Fig. 5A). Fully neutralizing such a substantial amount of sulfate requires about $9.5 \mu\text{g m}^{-3}$ of NH_4 . To the best of our knowledge, there has not been any direct measurement of NH_3 in Dunkirk. However a rough estimation of the urban background level can be inferred from NH_3 measurements in the middle-sized city of Douai, Northern France (100 km away), over a year (2015-2016) using a MARGA (Rodelas et al., 2019). Concentrations were higher in the spring and summer seasons with averages of 4.3 ± 2.9 and $4.0 \pm 2.8 \mu\text{g m}^{-3}$, reaching maxima of $11\text{-}12 \mu\text{g m}^{-3}$, respectively. In the Dunkirk area, we expect that local emissions – 50% originating from the “manufacturing industries, waste treatment and construction” according to the latest available inventory (Atmo Hauts-de-France, 2012), compared to 96% from the agricultural sector when considering the entire Hauts-de-France region – will even increase this background level by a few $\mu\text{g m}^{-3}$. As shown by ISORROPIA thermodynamical simulations with contrasted environments either poor or rich in NH_3 (Fig. 10, revised version), Dunkirk atmosphere can consequently be considered to be sufficiently rich in NH_3 to produce the concentration of ammonium required to neutralize the concentrations of sulfate most commonly measured.

Therefore, contrary to model simulations of Witham et al. (2014), these two contrasted sites investigated in detail in France (urban/rural vs industrial, coastal versus inland), do not show any depletion in NH_3 .

Nevertheless, it has to be noted that if a 30% lower SO_4 relative ionization efficiency coefficient was assumed for ACSM calibration, a few volcanic aerosols (the richest in SO_4) would be found non-neutralised or acidic (Fig. 9), suggesting a lack of NH_3 .

Setyan, A., Flament, P., Locoge, N., Deboudt, K., Riffault, V., Alleman, L. Y., ... & Wenger, J. C. (2019). Investigation on the near-field evolution of industrial plumes from metalworking activities. *Science of the Total Environment*, 668, 443-456.

6. P10: “Globally, we observe that volcanic aerosols at both sites display a lower $\text{NO}_3\text{:SO}_4$ concentration ratio than background aerosols at SIRTa, thus exhibiting a clearly distinct pattern.” The authors could discuss acid displacement here and mechanisms by which nitrate could be expected to be depleted. It would also be useful to discuss whether the ACSM is measuring an internally or externally mixed aerosol population during the monitoring or how this could be assessed. The ratio by itself does not lead to any atmospheric chemistry insights and there are too many variables for the indicator to be used more widely.

Contrary to Reviewer#1, we think and demonstrate that scatter plots of particulate NO_3 vs SO_4 (along with scatter plots of other species like NH_4) provide atmospheric chemistry insight with patterns specific to sulfur-rich plumes and especially volcanic plumes (here a $\text{NO}_3\text{:SO}_4$ ratio lower in volcanic plumes than in background conditions). To our knowledge, such patterns have never been published in the literature.

We already proposed in the ACPD version that this specific behaviour could result from the substantial concentration of sulfate within volcanic plumes, referring to sensitivity tests with a thermodynamic model of aerosol composition published in the textbook of Seinfeld and Pandis.

Indeed, these simulations show the preferred formation of ammonium sulfate rather than ammonium nitrate in an atmosphere very rich in sulfate.

In the revised version, we added thermodynamic simulations using the ISORROPIA II model performed for the exact atmospheric conditions met at SIRTa (Figures 10 and 11, revised version). These supplementary simulations strengthen and reinforce our result that relates a decreasing production of particulate nitrate with an increasing concentration of total sulfate.

7. P11, line 11: “As the measured concentration of Cl is negligible compared to other species at both sites of Dunkirk and SIRTa according to ACSM observations (data not shown here), the last term in Eq. 1 is neglected...” It is not clear why for a coastal site like Dunkirk the PM1 chloride is negligible. Could the authors comment on this? As the data is not reported the reader cannot verify this. The detailed of the concentrations and LOD for chloride should be discussed. Also acid displacement of Cl to HCl in highly acidic aerosols is relevant for understanding the observations. Explaining the chloride is particularly important as I think the ACSM method only infers NaCl indirectly (being refractory). Could the authors explain this in more detail.

Aerosol mass spectrometers flash vaporise particulate species impacted onto a heated surface. Instruments are classically operated with heaters set at 600°C, which minimize the vaporization of sea salt. Ovadnevaite et al. (2012) recorded sea salt with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) while operating the instrument at 650°C. Moreover, some groups have reported issues of low vaporization in the instruments even at the temperature of 600°C, leading in the case of ACSMs to strongly negative chloride signals (since the chloride signal is then recorded while sampling filtered air and not ambient air and therefore subtracted from the ‘sample’ signal). However, our ACSM instrument never displayed such behavior thus confirming refractory chloride was not observed with our instrument in its normal operating conditions in Dunkirk.

Regarding quantification, the first ACSM intercomparison showed that the vaporization efficiency for this species seemed to be instrument-dependent (Crenn et al., 2015) but did not investigate this species any further. The limit of detection for chloride has been estimated at 0.011 $\mu\text{g m}^{-3}$ (Ng et al., 2011). During the field campaign in Dunkirk, the Chl relative ionization efficiency (RIE) was calibrated using NH_4Cl aqueous solution at 0.005 mol L^{-1} using the same protocol as for SO_4 calibration, and an average RIE value of 2.3 ± 0.3 ($n = 4$) was used instead of the default value (1.3). The range of concentrations varied from 0 up to 3.16 $\mu\text{g m}^{-3}$, with an average of $0.06 \pm 0.11 \mu\text{g m}^{-3}$ over the entire campaign. It should be noted that most studies with this instrument report negligible concentrations of chloride anyway since most of particulate chloride originates from refractory NaCl and can mostly be found in the supermicronic fraction. In their worldwide review of HR-ToF-AMS studies in urban, suburban and remote locations, Zhang et al. (2007) reported average chloride contributions of 0.6% and always less than 5%. Previous field campaigns with the same type of instrument in Dunkirk (Crenn et al., 2017; Setyan et al., 2019) led to average contributions of 5% and 3.1%, respectively, which were mostly attributed to KCl formation in the sintering process (Peng et al., 2009; Riffault et al., 2015). Over summer 2014 in Dunkirk, chloride species contributed to only 0.3% for an average NR-PM₁ concentration of 8.1 $\mu\text{g m}^{-3}$, which is why it was not reported in this manuscript.

For sake of clarification, a shortened explanation has been included in the revised version in Section 4.3.2.

Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Fröhlich, R., Belis, C. A., Aas, W., Äijälä, M., Alastuey, A., Artiñano, B., Baisnée, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillón, M. C., Mocnik, G., O’Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Estève, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prévôt, A. S. H., Jayne, J. T., and Favez, O.: ACTRIS ACSM intercomparison – Part I: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments, Atmos. Meas. Tech., 8, 5063–5087, 2015.

Crenn, V., Fronval, I., Petitprez, D., & Riffault, V. (2017). Fine particles sampled at an urban background site and an industrialized coastal site in Northern France—Part 1: Seasonal variations and chemical characterization. *Science of The Total Environment*, 578, 203-218.

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

Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J., Martucci, G., ... & O'Dowd, C. (2012). On the effect of wind speed on submicron sea salt mass concentrations and source fluxes. *Journal of Geophysical Research: Atmospheres*, 117(D16).

Peng, C., Zhang, F., & Guo, Z. (2009). Separation and recovery of potassium chloride from sintering dust of ironmaking works. *ISIJ international*, 49(5), 735-742.

Riffault, V., Arndt, J., Marris, H., Mbengue, S., Setyan, A., Alleman, L. Y., ... & Wenger, J. (2015). Fine and ultrafine particles in the vicinity of industrial activities: a review. *Critical Reviews in Environmental Science and Technology*, 45(21), 2305-2356.

Setyan, A., Flament, P., Locoge, N., Deboudt, K., Riffault, V., Alleman, L. Y., ... & Wenger, J. C. (2019). Investigation on the near-field evolution of industrial plumes from metalworking activities. *Science of the Total Environment*, 668, 443-456.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., ... & Dzepina, K. (2007). Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically - influenced Northern Hemisphere midlatitudes. *Geophysical Research Letters*, 34(13).

8. p 11: *NH₄ “model”*: It is noted that the calculation is done using an equation from Seinfeld and Pandis. There are several more detailed (but simple to use) thermodynamic models available to calculate a theoretical *NH₄* (and other ions) e.g. ISOROPPIA or AIM which could have been used to model the full thermodynamic equilibrium and give a clearer understanding of the aerosol chemical composition. The approach taken by the authors was too simplistic and it is not clear what the purpose of taking such an approach was compared to using more up to date, detailed chemical schemes (and no discussion as to why is offered).

The textbook of Seinfeld and Pandis is not cited for the calculation done using the Equation (1) in the ACPD version (Eq. 3 in revised version) which is mentioned by Reviewer#1. This reference is cited to justify the assertion that the preferred form of sulfate is the neutral (NH₄)₂SO₄ form in an ammonia - nitric acid - sulfuric acid - water system rich in ammonia and presenting a rather elevated relative humidity.

Equation 3 (revised version) relates to the commonly-used neutralisation ratio, which considers that sulfate, nitrate and chloride ions are combined with ammonium in a neutral aerosol to form NH₄Cl, NH₄NO₃ and (NH₄)₂SO₄. The neutralisation ratio is widely used to estimate the aerosol acidity, in complement to full thermodynamic modeling using models like ISORROPIA (e.g. Zhang et al., 2007), as shown in the revised version.

Zhang, Qi, et al. "A case study of urban particle acidity and its influence on secondary organic aerosol." *Environmental science & technology* 41.9 (2007): 3213-3219.

9. Could the authors comment on the fact that the ACSM ammonium mass concentration pretty much is the same as the sulphate at all times at both sites? It may be just the scales used on the figures, but it would be appropriate to calculate the ion balance of the aerosol over time.

At first glance, looking at the NH₄ and SO₄ mass concentration timeseries in Figures 3 or 4 (ACPD

version), the reader could indeed think that these time series are pretty much the same. However, this is not the case. While the approach is simple, this remark of Reviewer#1 precisely illustrates the significant interest to make a scatter plot (as in Fig. 5B of ACPD version) to show more subtle differences in NH_4 and SO_4 concentrations. In particular, bottom of Fig. 5B (ACPD version) shows a slight but noticeable decrease in the $\text{NH}_4 : \text{SO}_4$ mass concentration ratio during volcanic events, which is not readily visible in the timeseries plots. This decrease is well reproduced with ISORROPIA thermodynamical simulations that have been added to the revised manuscript (Fig. 11, revised version). Note that evaluating the anion neutralisation ratio, or the measured versus predicted NH_4 concentration, as performed in Fig. 7 (ACPD version), actually consists in calculating the aerosol ion balance.

10. p11 The authors state that the ammonium ions at Dunkirk “have not had enough time to neutralise surrounding sulphate and nitrate ions”. It would have been good for the authors to do concentration – wind speed – wind direction polar plots for the datasets which would identify the direction and magnitude of sources of the aerosol. This would mean that there was quantitative information behind the conclusion that the PM was from metallurgical processes, the atmospheric age of the PM, then some assessment of time for neutralisation could have been done.

As requested by Reviewer#1, polar plots of the concentrations of both SO_2 and SO_4 recorded in Dunkirk colored by wind speed have been added to the revised manuscript (Top left and right of the new Fig. A3, revised version). We have also added two supplementary polar plots of sulfate concentration colored by the anion neutralization ratio (ANR), corresponding to the predicted vs. measured NH_4 levels, in order to discuss the time required for neutralizing sulphate aerosols considering either all aerosols measured in Dunkirk (Bottom left of Fig. A3, revised version) or only aerosols associated to $\text{NO}_3 < 1$ and $\text{SO}_4 > 4 \mu\text{g m}^{-3}$ which are interpreted to be of industrial origin in the submitted version of the paper given their low ANR compared to all other aerosols including particles of volcanic origin (Bottom right of Fig. A3, revised version).

Polar plots in Dunkirk (Fig. A3) cover four sectors defined as follows: marine (271° - 70°), urban (71° - 140°), industrial-urban (141° - 225°), and industrial (226° - 270°). Pollution roses clearly show higher concentrations of SO_2 and SO_4 when wind blows from specific directions, especially from the industrial sector, and the conversion of gaseous to particulate sulfur is enhanced with higher vertical turbulence (typical of elevated stack emissions and not fugitive ground ones) (Zhang, PhD thesis 2016; Zhang et al., in prep.). Polar plot in the right bottom of Fig A3 (revised version) shows that most aerosols associated to $\text{NO}_3 < 1$ and $\text{SO}_4 > 4 \mu\text{g m}^{-3}$, originate from the direction 225 - 270° corresponding to the industrial sector. Hence, these polar plots add a supplementary proof of the industrial origin of these specific aerosols.

The industrial sector in Dunkirk– where two main sulfur emitters (a refinery and a coke power plant) are located – expands between 500 m and 3 km from the sampling site. Winds blowing from this industrial sector often exhibit speeds above 5 m s^{-1} (Top left of Fig. A3, revised version), thus residence times of industrial plumes in the atmosphere are generally well below one hour, and often only a few minutes, before reaching the sampling site.

Additionally, wind sector analysis of the predicted vs. measured NH_4 levels or ANR demonstrate that under urban or marine emissions there is enough NH_3 to neutralize both sulfate and nitrate on the same site, but that industrial emissions disturb the equilibrium (Bottom of Fig. A3, revised version). Bottom of Figure 5B shows the extent of ammonium concentrations over the 14 months of ACSM field observations, with levels often reaching up to $9 \mu\text{g m}^{-3}$. Most of the time in Dunkirk, sulfate concentration does not exceed $25 \mu\text{g m}^{-3}$ (left of Fig. 5A). Fully neutralizing such a substantial amount of sulfate requires about $9.5 \mu\text{g m}^{-3}$ of NH_4 . To the best of our knowledge, there has not been any direct measurement of NH_3 in Dunkirk. However a rough estimation of the urban background level can be inferred from NH_3 measurements in the middle-sized city of Douai, Northern France (100 km

away), over a year (2015-2016) using a MARGA (Rodelas et al., 2019). Concentrations were higher in the spring and summer seasons with averages of 4.3 ± 2.9 and $4.0 \pm 2.8 \mu\text{g m}^{-3}$, reaching maxima of $11\text{-}12 \mu\text{g m}^{-3}$, respectively. In the Dunkirk area, we expect that local emissions – 50% originating from the “manufacturing industries, waste treatment and construction” according to the latest available inventory (Atmo Hauts-de-France, 2012), compared to 96% from the agricultural sector when considering the entire Hauts-de-France region – will even increase this background level by a few $\mu\text{g m}^{-3}$. As shown by ISORROPIA thermodynamical simulations with contrasted environments either poor or rich in NH_3 (Fig. 10, revised version), Dunkirk atmosphere can consequently be considered to be sufficiently rich in NH_3 to produce the concentration of ammonium required to neutralize the concentrations of sulfate the most commonly measured.

According to what is mentioned above, and given that ammonium preferentially neutralizes sulfate before nitrate (especially at high concentration of sulfate aerosols as shown by the ISORROPIA thermodynamical simulations in Figures 10 and 11 (revised version) added to the manuscript), our conclusion is that local NH_3 may generally not be lacking, but rather short residence times between plume emission points and the sampling site are responsible for the acidity of the observed aerosols of industrial origin (Fig. A3, revised version).

A shortened discussion has been included in the revised version (Section 4.3.2).

Atmo Hauts-de-France, 2012 “Emission inventory of air pollutants / Inventaire des émissions de polluants de l'air » (in French). Available online: <https://www.atmo-hdf.fr/acceder-aux-donnees/emissions-de-polluants.html>

Rodelas, R. R., Perdrix, E., Herbin, B., & Riffault, V. (2019). Characterization and variability of inorganic aerosols and their gaseous precursors at a suburban site in northern France over one year (2015–2016). *Atmospheric environment*, 200, 142-157.

Zhang, S. (2016). Analyse dynamique, en champ proche et à résolution temporelle fine, de l'aérosol submicronique en situation urbaine sous influence industrielle, Ph.D. thesis, Université du Littoral Côte d'Opale. Available online : <https://tel.archives-ouvertes.fr/tel-01548124>

Zhang, S., Tison, E., Dusanter, S., Beaugard, C., Gengembre, C., Augustin, P., Fourmentin, M., Delbarre, H., Riffault, V. (in prep.), Near real-time chemical speciation measurements of submicron particulate matter (PM1) at a French coastal site over more than a year: assessment of industrial and shipping emissions.

11. P13 line 6 onwards: The discussion of org: sulphate This paragraph does not make much sense. The authors hypothesise that the organic mass concentrations decrease relative to the sulphate because the organics are converted to organosulphates which are not resolved by the ACSM. Is this the only hypothesis for interpreting the data? Is there any literature showing this occurring? Could the organic acids be displaced by the acidity back to the gas phase? The authors then include this organic depletion observation in the conclusions. As presented it is more speculation than quantitative measurement and the manuscript would need to be amended to reflect this.

Concerning the Org:SO₄ mass concentration ratio, background aerosols at SIRTa are characterized by ratios greater than 2.5. In contrast, low values (mostly < 1.6) are observed during the volcanic event (bottom of Fig. 9). Accordingly, these low ratios are primarily explained by a high concentration of SO₄ (denominator). Nevertheless, we note that the volcanic event coincides with a period of relatively low concentration of organics (numerator). Although similarly low concentrations are observed in the months prior or following the volcanic event (Fig. 4), one cannot exclude that this coincidence may also reflect a causal relationship between the low organic concentration and the high SO₄ concentration. Indeed, the bottom of Fig. 6B shows that the Org:SO₄ mass concentration ratio at Dunkirk is spectacularly impacted by the occurrence of industrial pollution events carrying acidic freshly-emitted aerosols (detected by means of their anion neutralization ratio and trajectory analysis, see Section 5.3.2). Hence, such sulfur-rich industrial pollution events are generally characterized by a very low concentration of organics at Dunkirk, if not a quasi-complete depletion.

Organic aerosols are unlikely to be transferred by the acidity back to the gas-phase, an enhancement of secondary organic aerosol mass with increasing acidity is rather expected (Zhang et al., 2007; Pathak et al., 2011; Yatavelli et al., 2014). A depletion of organic aerosols in response to an increased acidity seems at odds with the findings of Zhang et al. (2007) and Pathak et al. (2011) who rather show an enhancement of secondary organic aerosols with acidity. Alternatively, this apparent decrease in organic aerosol concentrations may reflect the transformation of organic aerosols measured by ACSM into other species that are not resolved by our measurements. An hypothesis could be the formation of organosulfate aerosols, especially in the presence of highly-acidic sulfate aerosols, in agreement with laboratory experiments (Surratt et al., 2008; Perri et al., 2010) and modelling studies (McNeill et al., 2012). Formation of organonitrates has also been observed under SO₂ and NH₃-rich conditions in both smog chamber (Chu et al., 2016) and natural (Zaveri et al., 2010) experiments. These transformation mechanisms, possibly at play during industrial sulfur-rich pollution events as shown by Zaveri et al. (2010) in a coal-fired power plant plume, may also be active during the 2014 volcanic event. A thorough analysis of additional ACSM observations at other sites in Europe may allow for disentangling the respective roles of sulfur-5 rich volcanogenic pollution versus natural variability in leading to fluctuations of organics concentration.

This discussion has been included in the revised version (Section 4.3.3). As it is still speculative, the hypothesis of organosulfate formation, presented as such in the ACPD version, has been removed from the conclusion.

Chu, B., Zhang, X., Liu, Y., He, H., Sun, Y., Jiang, J., Li, J., and Hao, J.: Synergetic formation of secondary inorganic and organic aerosol: effect of SO₂ and NH₃ on particle formation and growth, *Atmospheric Chemistry and Physics*, 16, 14 219–14 230, 2016.

McNeill, V. F., Woo, J. L., Kim, D. D., Schwier, A. N., Wannell, N. J., Sumner, A. J., and Barakat, J. M.: Aqueous-phase secondary organic aerosol and organosulfate formation in atmospheric aerosols: a modeling study, *Environmental science & technology*, 46, 8075–8081, 2012.

Pathak, R. K., Wang, T., Ho, K., and Lee, S.: Characteristics of summertime PM_{2.5} organic and elemental carbon in four major Chinese cities: Implications of high acidity for water-soluble organic carbon (WSOC), *Atmospheric Environment*, 45, 318–325, 2011.

Perri, M. J., Lim, Y. B., Seitzinger, S. P., and Turpin, B. J.: Organosulfates from glycolaldehyde in aqueous aerosols and clouds: Laboratory studies, *Atmospheric Environment*, 44, 2658–2664, 2010.

Surratt, J. D., Gómez-González, Y., Chan, A. W., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., et al.: Organosulfate formation in biogenic secondary organic aerosol, *The Journal of Physical Chemistry*, 112, 8345–8378, 2008.

Yatavelli, R., Stark, H., Thompson, S., Kimmel, J., Cubison, M., Day, D., Campuzano-Jost, P., Palm, B., Hodzic, A., Thornton, J., et al.: Semicontinuous measurements of gas–particle partitioning of organic acids in a ponderosa pine forest using a MOVI-HRToF-CIMS, *Atmospheric Chemistry and Physics*, 14, 1527–1546, 2014.

Zaveri, R. A., Berkowitz, C. M., Brechtel, F. J., Gilles, M. K., Hubbe, J. M., Jayne, J. T., Kleinman, L. I., Laskin, A., Madronich, S., Onasch, T. B., et al.: Nighttime chemical evolution of aerosol and trace gases in a power plant plume: Implications for secondary organic nitrate and organosulfate aerosol formation, NO₃ radical chemistry, and N₂O₅ heterogeneous hydrolysis, *Journal of Geophysical Research:Atmospheres*, 115, 2010.

Zhang, Q., Jimenez, J. L., Worsnop, D. S., and Canagaratna, M.: A case study of urban particle acidity and its influence on secondary organic aerosol, *Environmental science & technology*, 41, 3213–3219, 2007.

12. Could the authors comment on the availability of quantified fractions of the organics from the ACSM? How much is oxidised vs hydrocarbon like? Did this change during the volcanic periods?

At SIRTa, identification and quantification of organic aerosol (OA) fraction was made using positive

matrix factorization (PMF) applied to the OA mass spectra measured by ACSM, by Zhang et al. (2018 and 2019). A scatter plot of the aerosol fraction of oxygenated organic (OOA) vs primary organic (POA), including hydrocarbon-like and biomass burning, over Sept-Oct 2014 is displayed in the added Fig. R3. According to this figure, it seems that the volcanic plume may rather be enriched in OOA relatively to POA, in agreement with a long-range transport. Scatter plot of OOA vs SO₄ mass concentration may highlight a slight increase (of a few $\mu\text{g. m}^{-3}$) of OOA with an increasing concentration of sulfate (added Fig. R4), which may reflect enhancement of SOA formation processes at low pH (as pH of volcanic aerosols is shown to significantly decrease down to 2.5 at high concentration of total sulfate with ISORROPIA thermodynamic model simulations in Fig. 11, revised version), as seen at the industrial site of Pittsburgh by Zhang et al. (2007).

Nevertheless, we cannot demonstrate that this pattern clearly results from the volcanic influence given the wide natural variability observed at SIRTa over the limited time period of the study. A further thorough analysis, with more data, either longer timeseries or analysis of volcanic events at more sites, would be required. For this reason, we did not include it in the revised version of the paper.

Zhang, Q., Jimenez, J. L., Worsnop, D. R., and Canagaratna, M.: A case study of urban particle acidity and its influence on secondary organic aerosol, *Environmental science & technology*, 41, 3213–3219, 2007.

Zhang, Y., Favez, O., Canonaco, F., Liu, D., Mocnik, G., Amodeo, T., Sciare, J., Prévôt, A. S., Gros, V., and Albinet, A.: Evidence of major secondary organic aerosol contribution to lensing effect black carbon absorption enhancement, *Climate and Atmospheric Science*, 1, 47, 2018.

Zhang, Y., Favez, O., Petit, J.-E., Canonaco, F., Truong, F., Bonnaire, N., Crenn, V., Amodeo, T., Prévôt, A. S. H., Sciare, J., Gros, V., and Albinet, A.: Six-year source apportionment of submicron organic aerosols from near-continuous measurements at SIRTa (Paris area, France), *Atmospheric Chemistry and Physics Discussions*, pp. 1–41, 2019.

13. P16, line 11 “To understand the rate of SO₂ oxidation to sulfate in volcanic clouds, we also investigate the SO₂:SO₄ mass concentration ratio observed at these various EMEP stations” The authors do not look at the rate of SO₂ oxidation in this paper as they do not link the age of the SO₂ to the age of the SO₄. If the authors considered the air mass history for each time period and used the remote sensing to understand the oxidation history of the air mass then it could be possible to directly look at the SO₂ oxidation rate but this is not done in this paper.

It is correct that we only showed in the ACPD version the wide variability of SO₂-to-SO₄ mass oxidation ratios at long distance from the volcanic source. The significant variability in oxidation ratios that we observe in this dataset attests of the complex atmospheric history and processes that control the oxidation of SO₂ within a volcanic cloud. In the revised version of the paper, we have estimated plume ages and added a supplementary Section entitled « Evolution of SO₂ to SO₄ oxidation during plume age » and one supplementary Figure (Fig. 16, revised version) where we estimate a SO₂ to SO₄ mass oxidation rate.

Indeed, in this new section, we show that despite this apparent complexity and the vast geographical area over which the volcanic plume is sampled, the SO₂-to-SO₄ mass oxidation ratio evolves linearly (correlation coefficient of 0.89) with *t*, the plume age (in hours), for stations located between 1200 and 2200 km from the eruption site, associated to plume age ranging between 50 and 80 hours, as follows:

$$[\text{SO}_2]/[\text{SO}_4] = -0.23 \ t + 19.7.$$

Hence, we estimate a nearly constant SO₂-to-SO₄ mass oxidation rate equal to 0.23 h⁻¹.

If we hypothesise that this linear relationship is also valid close to the volcanic source, we would expect a near-source SO₂ to SO₄ mass oxidation ratio of ~20. This result is in agreement with measurements performed at a few hundred of kilometers from the eruption site by Ilyinskaya et al. (2017), indicating a molar ratio of S-bearing particulate matter to SO₂ in 0.006–0.62 in Reykjavik (at ~100 km distance) in January 2015 and in 0.016–0.38 in Reykjavik (at ~250 km distance), corresponding to SO₂-to-SO₄ mass oxidation ratios within 2–250 and 4–94, respectively.

14. P4 line 20: “Boichu et al., 2019 in prep” either citing this paper or one in prep either are not appropriate.

We expected this paper to be online at the time of publication of the present study. As it is not, this reference has been removed.

15. P10 line 20: Freney et al., subm is not a valid reference

This paper has now been published. Here is the updated reference:

Freney, E., Zhang, Y., Croteau, P., Amodeo, T., Williams, L., Truong, F., Petit, J.-E., Sciare, J., Sarda-Estève, R., Bonnaire, N., Crenn, V., Arumae, T., Aurela, M., Bougiatioti, K., Coz, E., Elste, T., Heikkinen, L., Minguillon, M.-C., Poulain, L., Priestman, M., Stavroulas, I., Tobler, A., Vasilescu, J., Zanca, N., Alastuey, A., Artinano, B., Carbone, C., Flentje, H., Green, D., Herrmann, H., Maasikmets, M., Marmureanu, L., Prévôt, A. S. H., Wiedensohler, A., Canagaratna, M., Gros, V., Jayne, J. T., and Favez, O.: The second ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations, *Aerosol Sci. Technol.*, 53, 830–842, 2019.

16. Figure 3: The bottom left graph needs to be put into a multipanel graph with a correct 7 axis. It is very misleading to just off-set the different components

This representation is intended to facilitate the comparison between the time series. We tested several possibilities. If the 4 time series are superimposed, they mask each other. If they are placed in separated multipanels, the spikes will be clipped, unless we decrease the Y axis vertical scaling, but this will result in a squeezed aspect of the time series. We could also apply a logarithmic scaling to the Y axis, but this will diminish the apparent dynamic range of the time series. Offsetting the time series vertically is something that is commonly done in many scientific papers displaying time series containing a correlated content at high frequency. We prefer to keep the current representation and we have applied it also to SIRTA ACSM data in Fig. 4. We have however added a dashed line showing the baseline for each time series. We have also added a scale bar for the Y-axis, in order to show more clearly that the same vertical scaling is applied to all time series.

17. Figure 4 (and others subsequent graphs with the chemical species): the orange line is almost impossible to see against the red line. Could the authors adjust the graph so that it is possible to see the different components .

In the literature, orange and red are the common colors used for respectively representing concentrations of NH₄ and SO₄ retrieved from ACSM observations. For better clarity, we have offsetted vertically time series for each component in Fig. 4, as done in Fig. 3.

18. Figure 8 and 10: How were the triangle areas chosen? What do they actually represent? I tried to see this in the text but it is not explained. Also what are the uncertainties associated with the different assignments and overlaps? Some triangles are subsets of others. Further explanation is required.

We acknowledge that we did not explain what sectors mean in the legend of the figures. Sectors in color, added to facilitate interpretation, represent an envelope roughly spanning the range of observed gas and particulate concentration values according to the type of aerosol. Figure caption has been updated accordingly.

19. Figure 9 and text on p 12: as I understand it a new calibration for the ACSM was developed post-

hoc (2 years after the measurements) and then applied to the data. If the authors think the second calibration is correct, then that is the calibration which should be used in the paper. A description of RIE and how it varies should be in the methods section, and the variability in calibration presented as part of the uncertainties of the experiment. It unfortunately leads the reader to have less confidence in the research presented when the authors add a “here is how the data changed when we think we did a better calibration”. Referencing a “submitted “ paper to explain that change in calibration is not good practice.

The RIE coefficient serves as a conversion factor to translate the ionized fraction measured inside the ACSM instrument to the sulfate concentration in the sample. Prior to 2016, a standard RIE value of 1.2 was used at SIRTa. A new calibration study was conducted in 2016, and the results of this study (Freney et al.) were published on 21 May 2019 (this corresponds to the « submitted » paper mentioned in the ACPD version – the reference has been updated). This calibration study recommends to use a value of 0.86 at SIRTa for the more recent period, which would result in a ~ 28% decrease in the estimated sulfate concentrations compared to the previous RIE value of 1.2.

Nevertheless, we note that the more recent calibrated RIE value (0.86) may not be relevant to correct older measurements, and standard practice recommends to keep the original value (1.2) for older measurements.

For the sake of completeness, we discuss in the paper how our results may change if a different choice of RIE value was made. We specifically investigated the influence of the RIE coefficient on the NO₃:SO₄ and Org:SO₄ oxidation ratios (Fig. 9), and the degree of neutralization (Fig 7). We show that the range of variability of the RIE coefficient does not impact the conclusions of our study.

The paper which describes the intercomparison exercise for ACSM calibration protocols, cited in the ACPD version, has now been published. Here is the updated reference :

Freney, E., Zhang, Y., Croteau, P., Amodeo, T., Williams, L., Truong, F., Petit, J.-E., Sciare, J., Sarda-Estève, R., Bonnaire, N., Crenn, V., Arumae, T., Aurela, M., Bougiatioti, K., Coz, E., Elste, T., Heikkinen, L., Minguillon, M.-C., Poulain, L., Priestman, M., Stavroulas, I., Tobler, A., Vasilescu, J., Zanca, N., Alastuey, A., Artinano, B., Carbone, C., Flentje, H., Green, D., Herrmann, H., Maasikmets, M., Marmureanu, L., Prévôt, A. S. H., Wiedensohler, A., Canagaratna, M., Gros, V., Jayne, J. T., and Favez, O.: The second ACTRIS inter- comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations, *Aerosol Sci. Technol.*, 53, 830–842, 2019.

20. Figure 11 and related text on p 14: What is the uncertainty for the AOD and the ACSM sulphate?

As part of the first ACSM intercomparison (Crenn et al., 2015), reproducibility expanded uncertainties of 13 Q-ACSM instruments were determined as 9, 15, 19, 28, and 36 % for NR-PM₁, nitrate, organic matter, sulfate, and ammonium, respectively. In Dunkirk, ACSM species and Black Carbon concentrations in PM₁ (determined by an AE33 Aethalometer) were added and compared to the independent gravimetric mass concentrations measured by a TEOM-FDMS equipped with a PM₁ sampling inlet over the summer period (Fig. R1). While PM₁ concentrations ranged between 1 and 50 µg m⁻³ over the period, the linear regression of daily averaged values led to a slope of 0.94 (r² = 0.94) giving confidence in the quantification of the various ACSM species.

Regarding AOD values, the uncertainty is in the 0.01–0.02 range at 500 nm (Eck et al.1999).

Quantitative information about uncertainties has been added in the revised version.

What is being measured at 500 nm and how does that compare to PM1?

This question is identical to a question that was previously asked. We here reproduce our response.

While AOD measurements provide constraints on the column-integrated abundance of aerosols in the atmosphere, the ACSM data inform on the concentration of SO₄ in the PM₁ fraction at ground-level. The remarkable correlation between these two observations over weeks suggests that the substantial concentration of sulfate aerosols in the boundary layer primarily controls the column-integrated abundance of aerosols.

20. *Figure 12: The background colours mean that it is very hard to read the text, even with good sight. Please could the authors consider getting rid of or making the background of the map detail lighter.*

The background of the map has been made lighter for better clarity.

21. *Figure 13 is not sufficiently structured for the reader to be able to look at easily, there is a mix of scales and sizes and the figure needs re-doing or splitting into 2. Perhaps the authors could try doing panel graphs? There is no comparability or analysis done on the datasets.*

The concentration of SO₄ varies on a narrower range than SO₂, which explains two different scales for time series. The same scales and size have been kept for all 6 stations. We agree that Fig. 13 is nevertheless difficult to read as we present bi-component data for 6 stations (note that a selection of stations has been performed as data for 27 stations are presented in Appendix). Fig. 13 has been updated for better clarity, including now 8 stations.

While a comparison between time-series at the 6 selected stations was developed in the ACPD version, a multi-site concentration-weighted trajectory analysis has been also performed for all these stations, adding 4 supplementary figures to the revised paper, showing the large-scale impact of the Holuhraun eruption on both SO₂ and SO₄ concentrations at ground-level in Northern Europe.

22. *Figure 14: Are the lines shown related to the datasets? (i.e. linear fits, in which case could the equations of the lines statistics of the fit be reported) or a selection of SO₂:SO₄ ratios? If the latter, why were those particular ratios shown?*

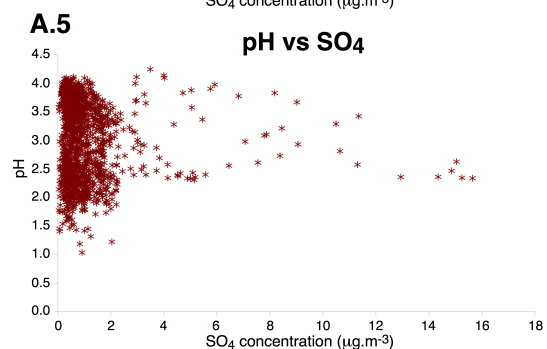
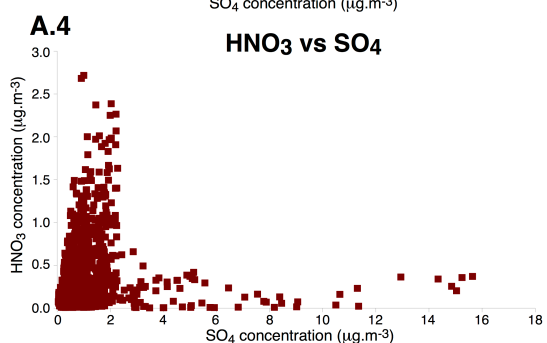
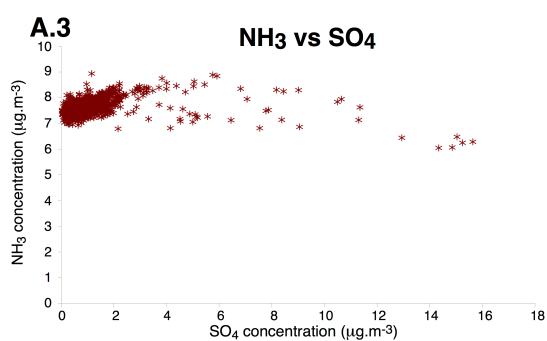
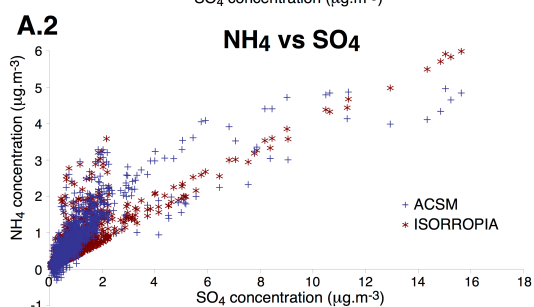
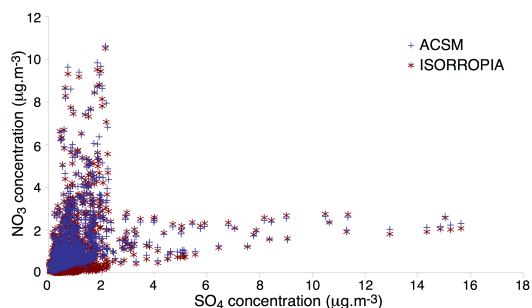
Lines were intended to show a selection of SO₂:SO₄ ratios covering the vast range of observed values.

23. *(very minor) The English could do with a review as there are many minor linguistic corrections needed.*

English has been carefully checked.

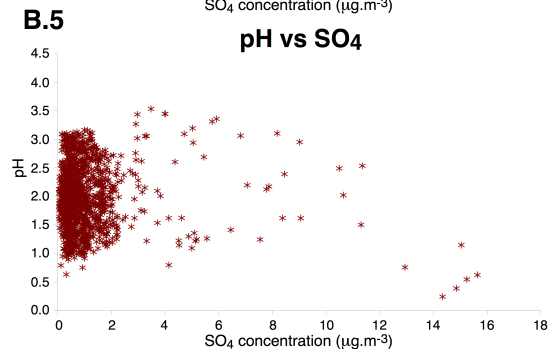
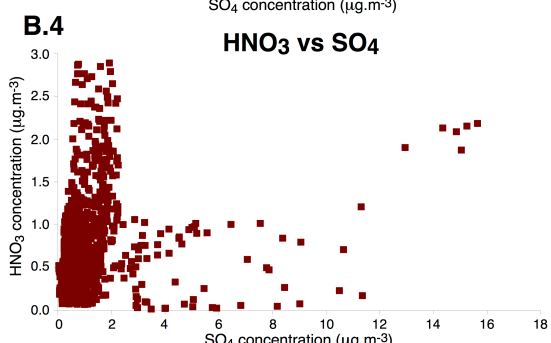
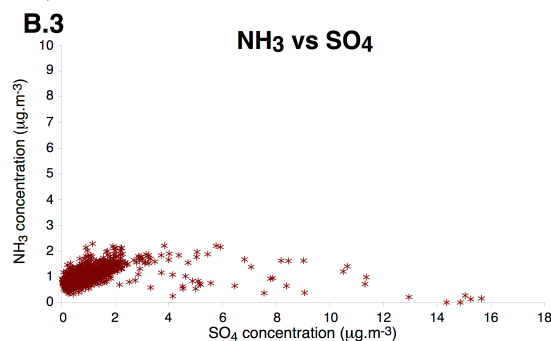
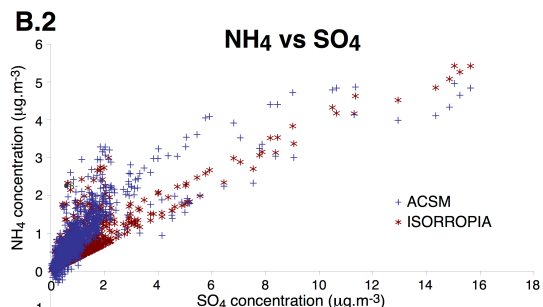
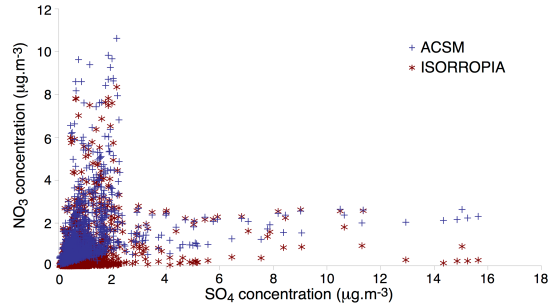
(A) NH₃-rich background

A.1 NO₃ vs SO₄



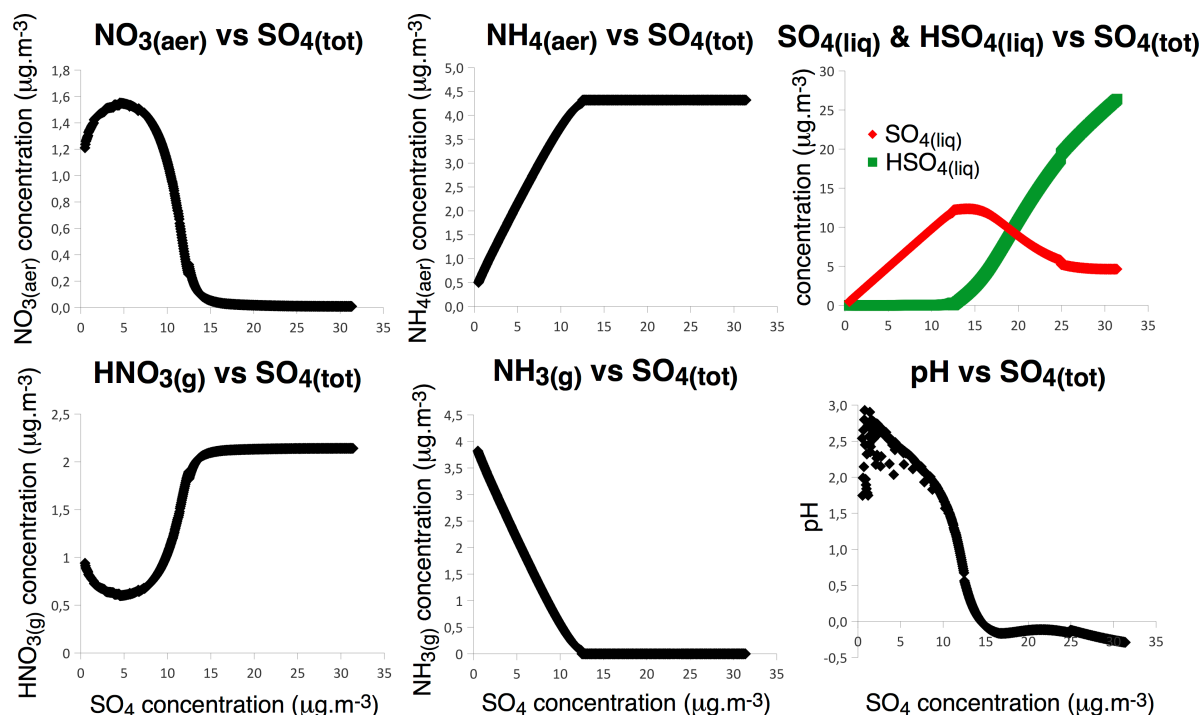
(B) NH₃-poor background

B.1 NO₃ vs SO₄

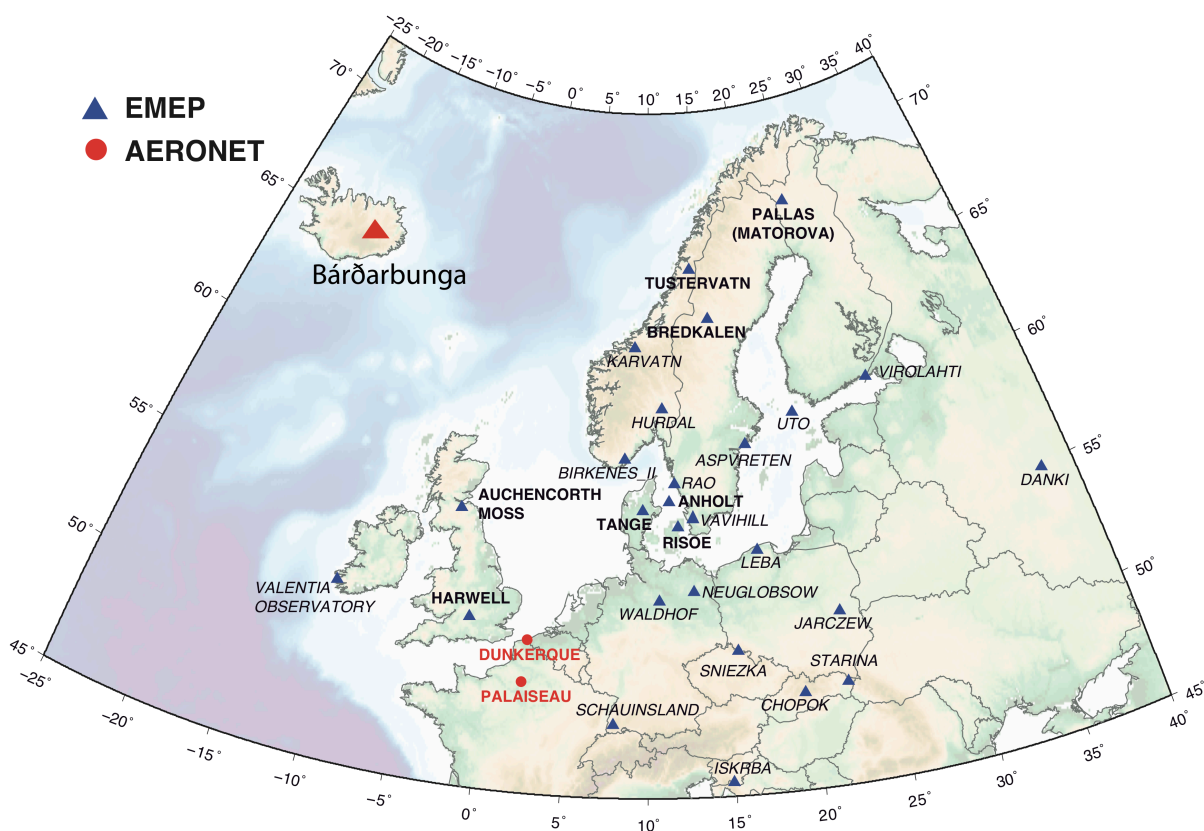


Reproduction of Fig. 10 (revised version): ISORROPIA II thermodynamic model simulations (red) of atmospheric composition (aerosol NO₃ (1) and NH₄ (2), gas-phase NH₃ (3) and HNO₃ (4)) as well as pH (5) versus SO₄ mass

concentration at SIRTa in Sept-Oct 2014 considering an environment either (A) rich ($7.40 \mu\text{g.m}^{-3}$) or (B) poor ($0.74 \mu\text{g.m}^{-3}$) in NH_3 . Comparison with ACSM observations of aerosols (blue).

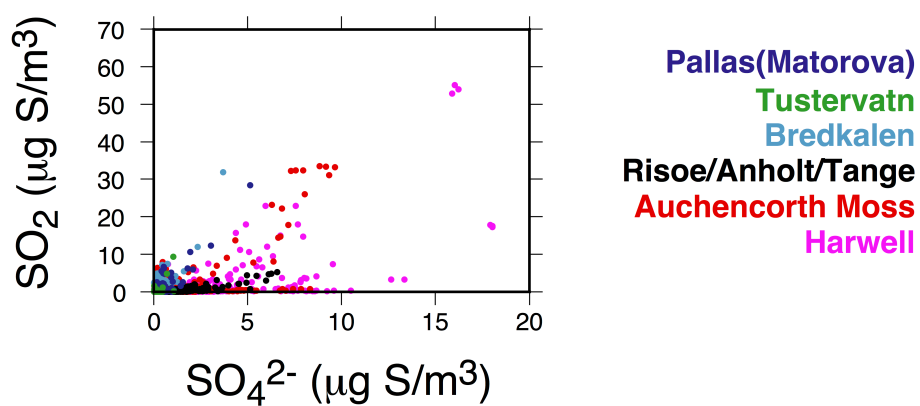
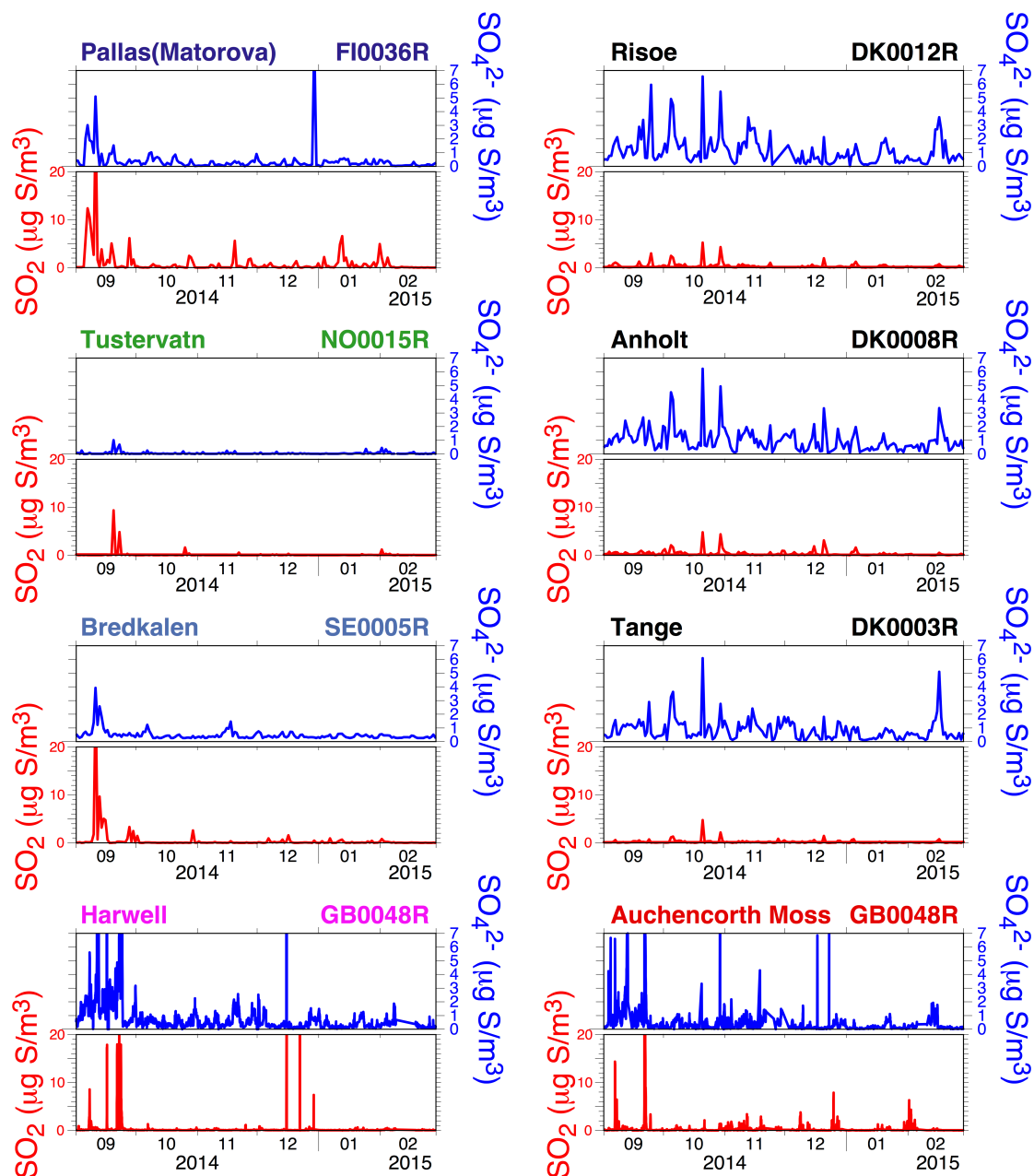


Reproduction of Fig. 11 (revised version): Sensitivity tests of aerosol composition and pH with increasing concentration of total sulfate aerosols, using ISORROPIA II thermodynamic model for conditions met at SIRTa in Sept-Oct 2014.



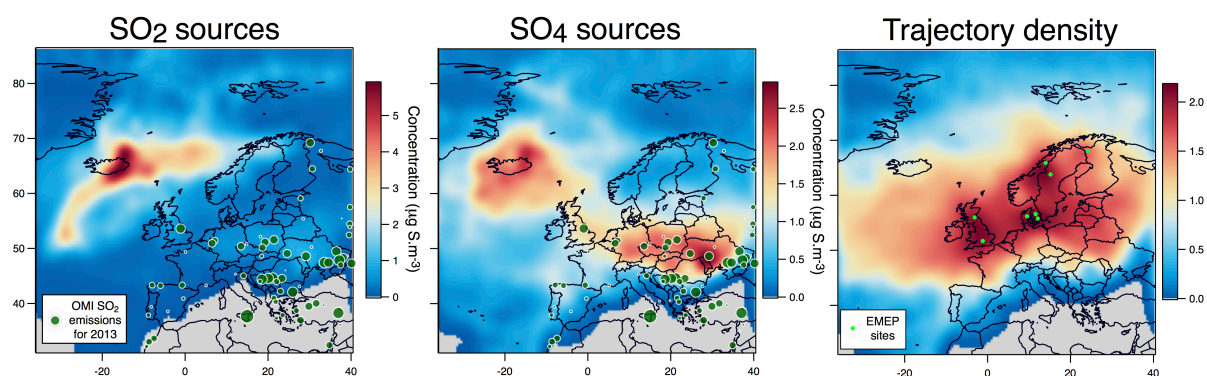
Reproduction of Fig. 13 (revised version) : Map of the 27 EMEP stations (blue triangles) explored in this study. Stations with name in bold, with a few daily SO_2 concentrations higher than $3 \mu\text{g.m}^{-3}$ over the period Sept 2014–Feb 2015 suggesting a clear impact of the Holuhraun eruption, are selected for detailed multi-site concentration-weighted

trajectory analysis, while stations in *italic* are not. Red circles indicate the AERONET network stations of Dunkirk and SIRTa (Palaiseau).

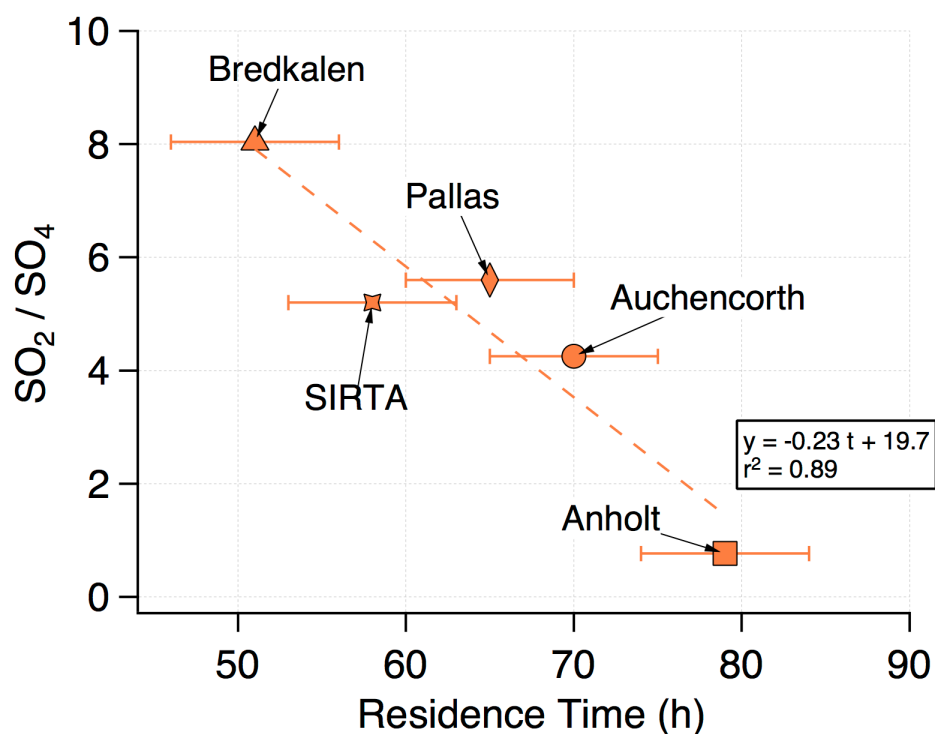


Reproduction of Fig. 14 (revised version): Time series (top) and scatter plot (bottom) of ground-level mass concentrations (in $\mu\text{g S m}^{-3}$) of SO_2 and corrected $\text{PM}_{10}\text{SO}_4$ (i.e. non marine SO_4) covering the Holuhraun eruption

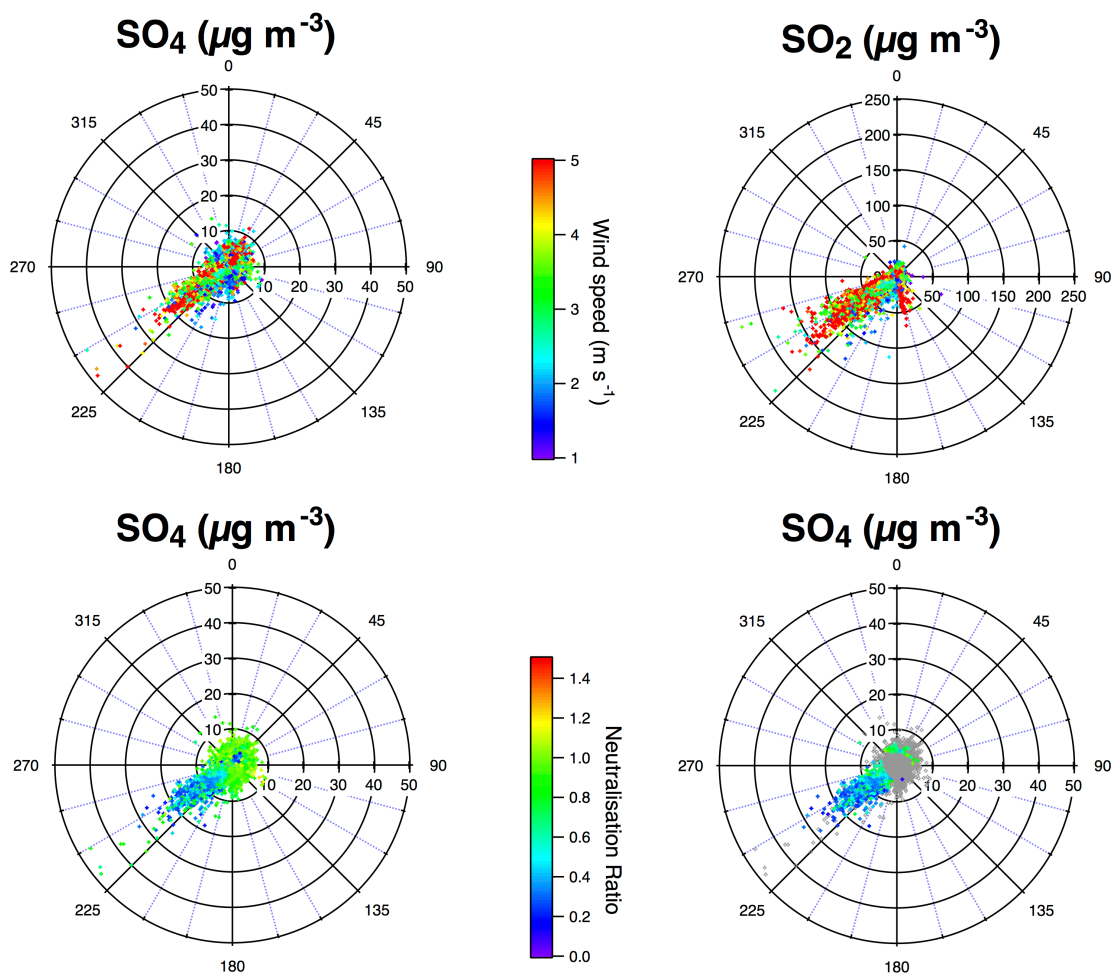
from Sept 2014 to Feb 2015, at selected EMEP stations in Scandinavia and Great Britain clearly impacted by the eruption.



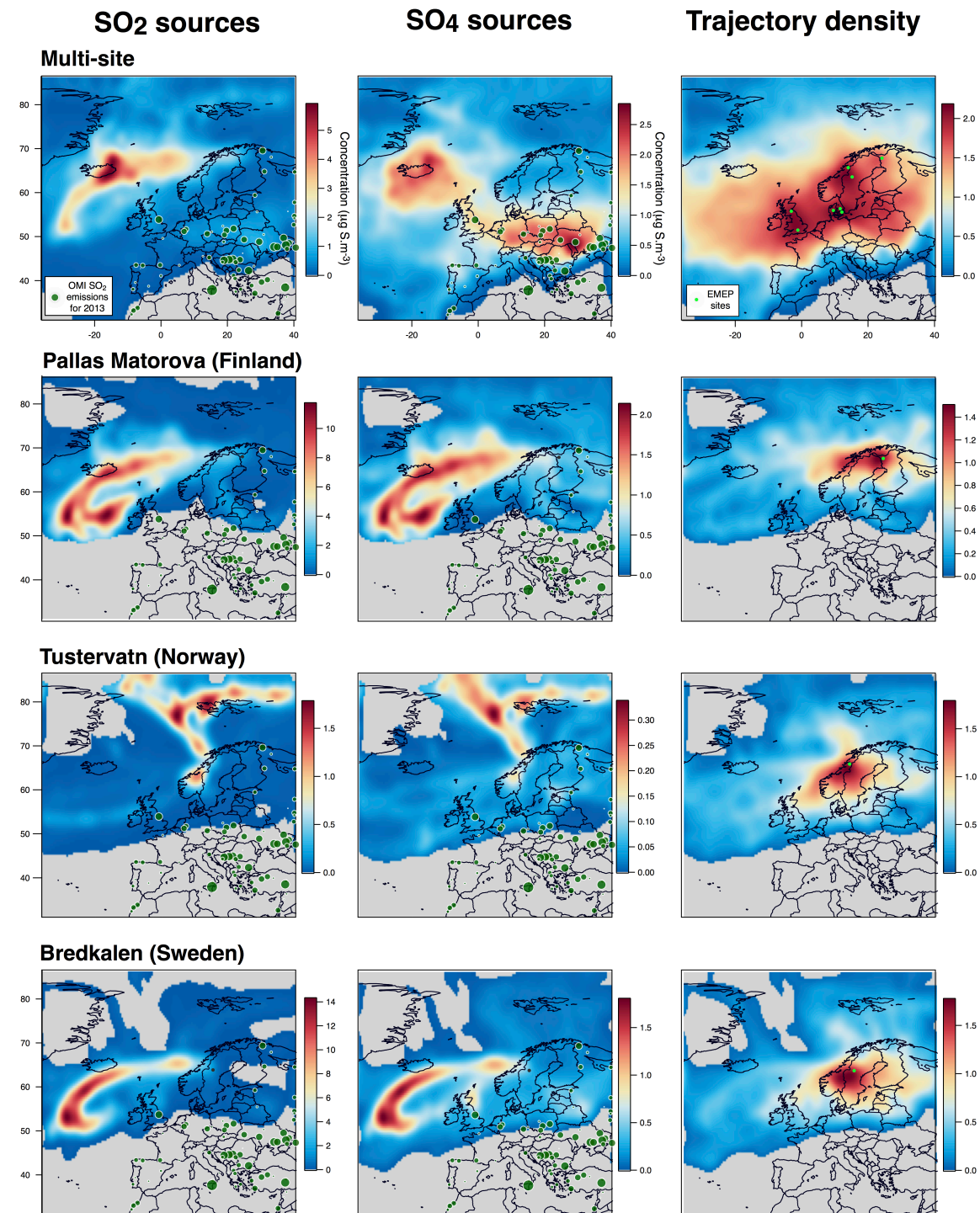
Reproduction of Fig. 15 (revised version) : Multi-site concentration weighted trajectory analysis for SO₂ and SO₄ concentrations measured in September-October 2014 at a set of eight selected EMEP stations in Northern Europe (shown in Fig. 15): retrieved source concentrations (µg S.m⁻³) of (left) SO₂ and (middle) corrected SO₄ (i.e. non marine SO₄), (right) trajectory density (log of residence time, no unit) with the location of stations (light green circles). SO₂ emission sources for 2013 derived from OMI satellite sensor observations (from Fioletov et al. (2016)) are indicated by dark green circles.



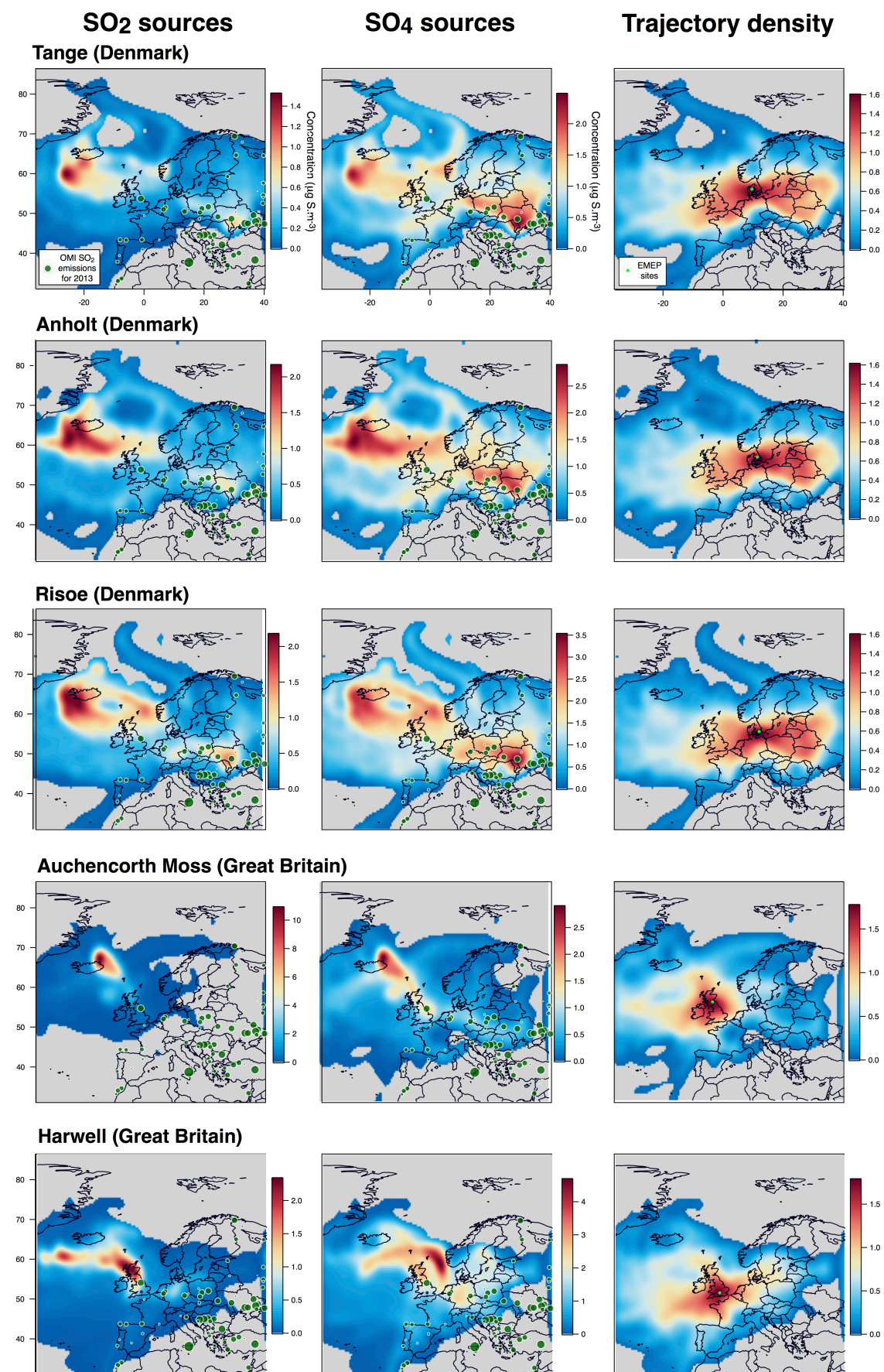
Reproduction of Fig. 16 (revised version): Scatter plot of the SO₂:SO₄ concentration ratio (in PM₁ fraction for ACSM data at Sirta, PM₁₀ for other stations) with the residence time or plume age (h) of the volcanic cloud at a selection of EMEP stations in five different countries of Northern Europe.



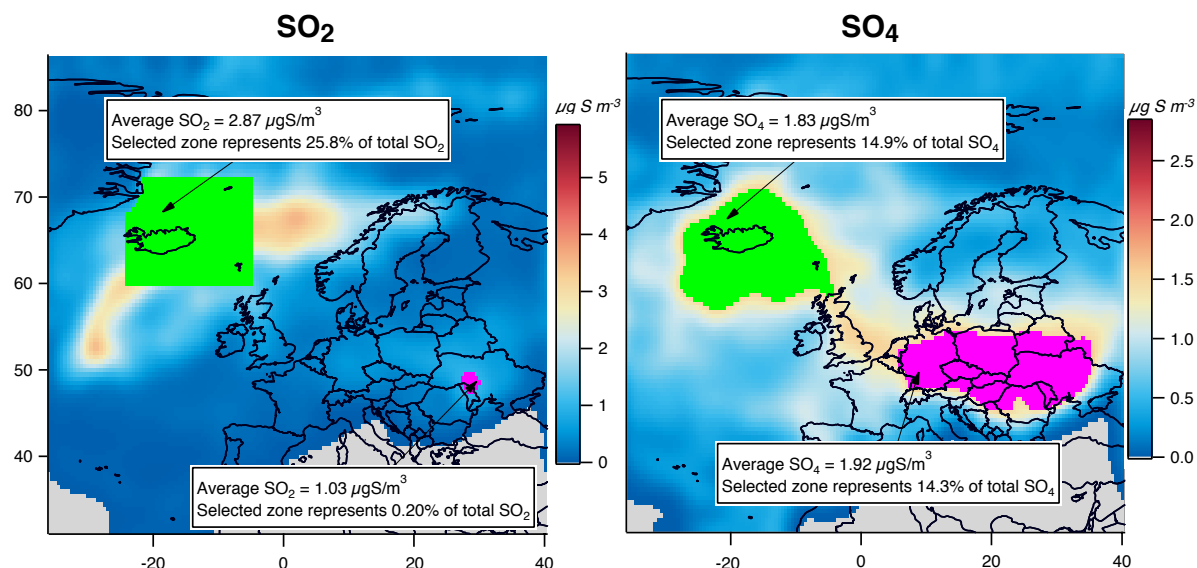
Reproduction of Fig. A3 (revised version): (top) Polar plots of (left) sulfate and (right) sulfur dioxide concentrations colored by wind speed; (bottom) Polar plots of sulfate colored by the anion neutralization ratio (ANR) for (left) the entire Dunkirk dataset and (right) points with $\text{NO}_3 < 1$ and $\text{SO}_4 > 4 \mu\text{g m}^{-3}$.



Reproduction of Fig. A4 (revised version) : Concentration weighted trajectory analysis with either (a) a multi-site approach considering all 8 selected EMEP stations in 5 countries of Northern Europe listed in Table 1 or (b,c,d) each of the selected EMEP stations individually (here (b) Pallas Matorova (Finland), (c) Tustervatn (Norway), (d) Bredkalen (Sweden), other stations in Fig. A6); retrieved source concentrations ($\mu\text{g S.m}^{-3}$) of (left) SO₂ and (middle) SO₄, (right) trajectory density (log of residence time, no unit) including station location (light green circles). SO₂ emission sources for 2013 derived from OMI satellite sensor observations (from Fioletov et al. (2016)) are indicated by dark green circles.



Reproduction of Fig. A5 (revised version) : Same as Fig. A4 for EMEP stations in Denmark (Tange (a), Anholt (b), Risoe (c)) and Great Britain (Auchencorth Moss (d) and Harwell (e)).



Reproduction of Fig. A6 (revised version) : Contribution to the widespread atmospheric pollution highlighted at selected EMEP stations of various sources of (left) SO₂ and (right) SO₄, considering an edge detection at 1 and 1.5 µg S m⁻³ respectively. Green areas are for icelandic volcanic sources while pink areas correspond to anthropogenic sources.

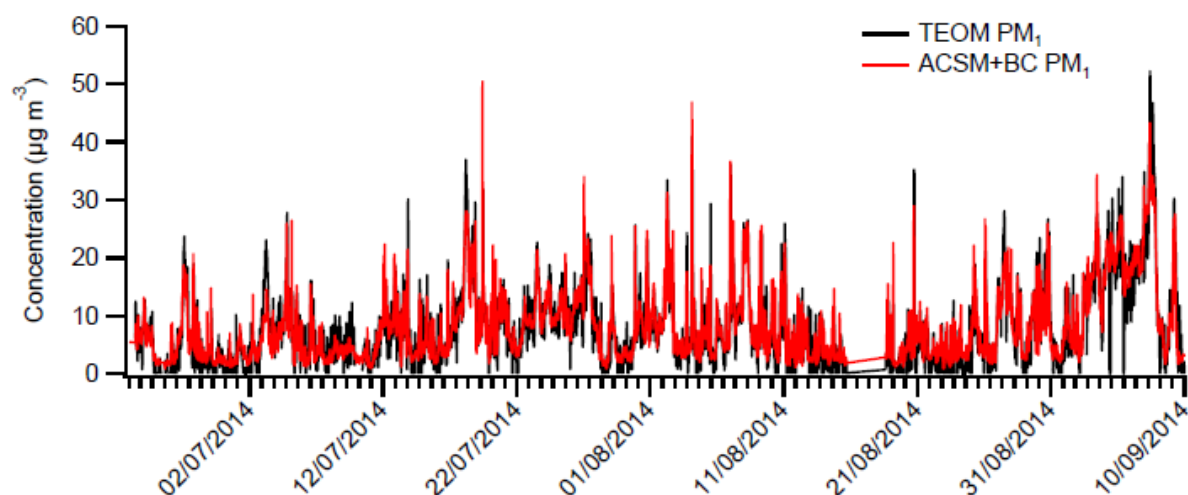


Figure R1: Time series of PM₁ measured by TEOM-FDMS and the sum of PM₁ chemical species (NO₃, SO₄, NH₄, Cl, Organics determined by ACSM; BC derived from optical measurements)

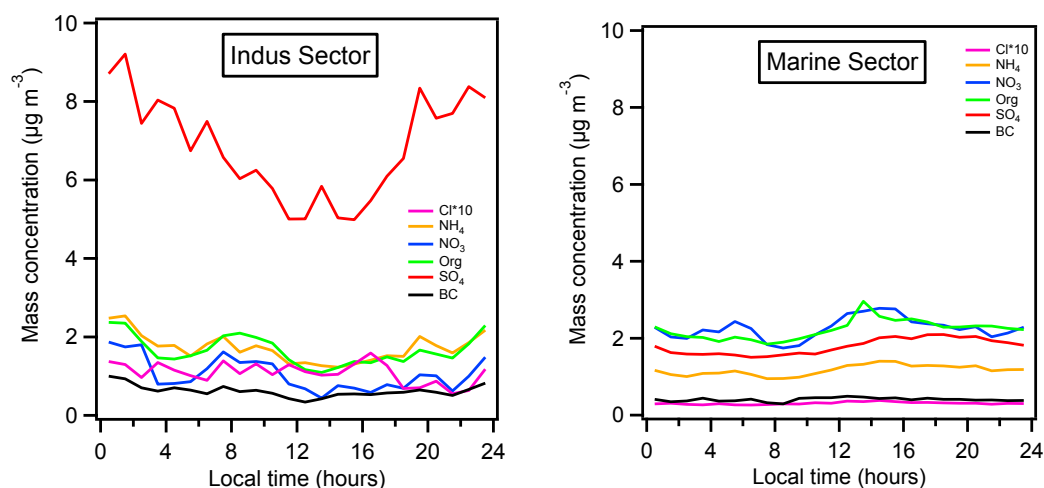


Figure R2: Daily profiles of chemical species in Dunkirk when the wind blows from (left) the industrial sector and (right) the marine one.

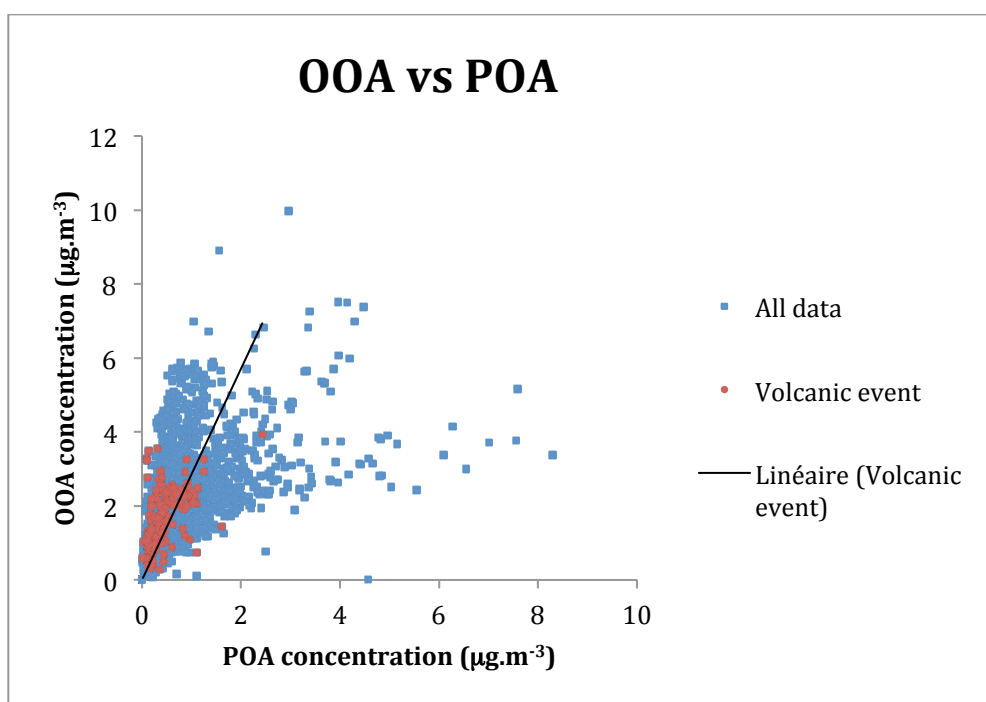


Figure R3 : Scatter plot of oxygenated organic (OOA) versus primary organic (POA) aerosols at SIRTa from mid-August to mid-November 2014. Volcanic event in later Sept 2014 is displayed in red while remaining data are in blue.

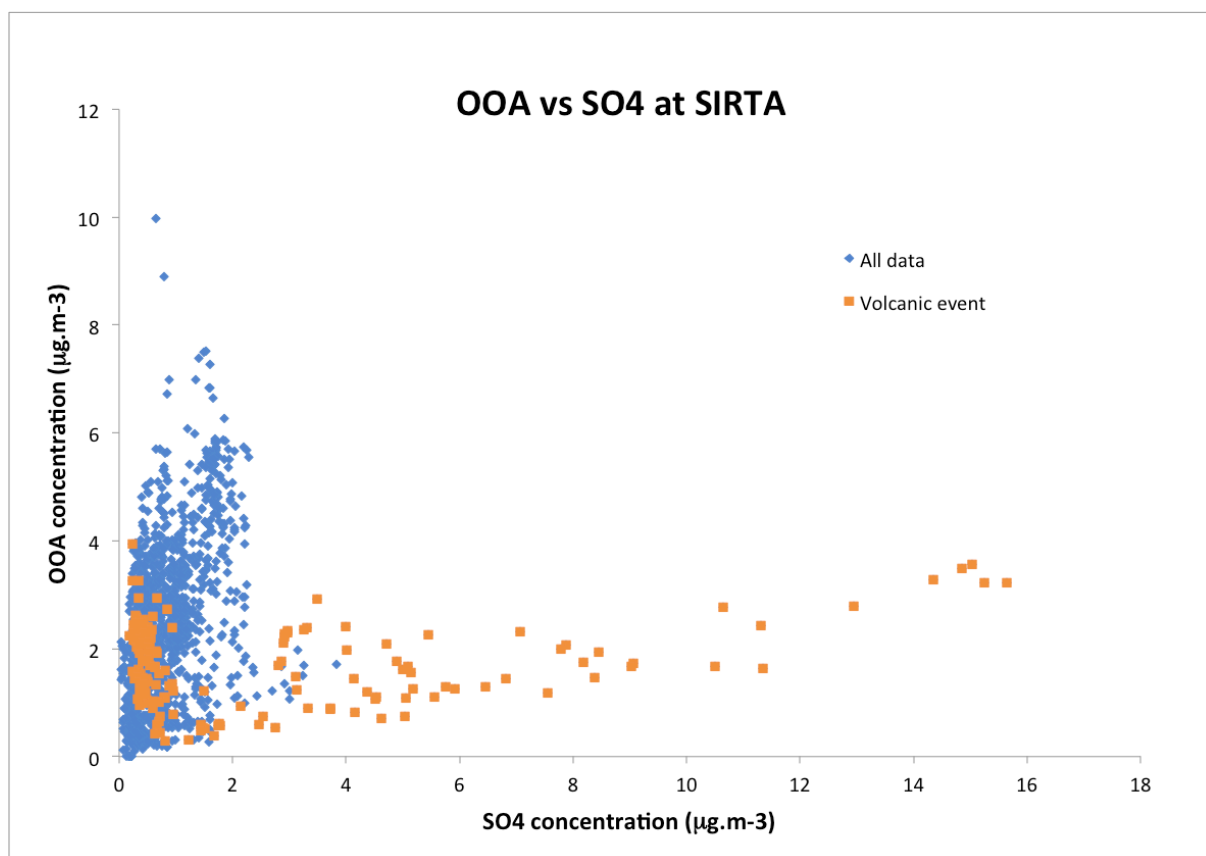


Figure R4 : scatter plot of OOA versus SO4 mass concentration at SIRTa from mid-August to mid-November 2014. Volcanic event in later Sept 2014 is displayed in red while remaining data are in blue.