Reply to reviewer 2 :

We thank Reviewer#2 for this thorough 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-site 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 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 of a lack of background NH3.

We added two new sections, 4 new figures and one table in the main manuscript and 3 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 developed in details below our reply to all the questions and comments raised by reviewer#2.

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 reply 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 #2
Received and published: 10 June 2019

Review of: Large-scale particulate air pollution and chemical fingerprint of volcanic sulfate aerosols from the 2014-15 Holuhraun flood lava eruption of Bardarbunga volcano (Iceland)
Boichu, M., Favez, O., Riffault, V., Brogniez, C., Sciare, J., Chiapello, I., Clarisse, L., Zhang, S., Pujol-Söhne, N., Tison, E., Delbarre, H., and Goloub, P.

This study presents in-situ observations showing the influence of the 2014-15 Icelandic volcanic eruption at two air quality sites in France: Dunkirk with local industry pollution that also leads to high SO2 episodes that are non-volcanic, and SIRTA without local industry but more urban/rural pollution conditions. The focus is on high-temporal ACSM measurements of aerosol composition

(PM1 sulfate, nitrate, ammonium, organics), with volcanic episodes identified by high peaks in gaseous SO2 in the air-quality data. The study also presents analysis of remote sensing observations by satellite that show plume transport episodes to the French sites, which help to confirm the periods identified to have volcanic influence. The study reports identifying a distinct chemical fingerprint of the volcanic aerosol according to NO3:SO4 and Organic:SO4 concentration ratios. Depletion of organic aerosols in the volcanic-influenced air is reported, suggested to be due to formation of organosulfate particles. Comparison of AERONET data to the in-situ aerosol at the two French sites identifies that the column optical depth correlates in maxima peaks with the ground-based in-situ aerosol, suggesting that the higher-than-average optical depth during September 2014 may reflect the influence of the volcanic aerosol. The study highlights that the volcano likely had an influence on aerosol loading more broadly across northern Europe as episodes of high SO2 are identified at six EMEP stations along with PM10 sulfate. Sulfate:SO2 ratios from the stations are presented and show a wide range of values (reasons for this variability are not analysed further although some hypotheses are provided).

The high-resolution ACSM observations of aerosol composition in volcanic-influenced air far from the volcano source are a new dataset that has potential to provide insights on aerosol composition. The approach of using remote sensing products to confirm volcanic influence at the two ground-sites is useful. However, I am not convinced by some of the interpretations such as identifying a distinct volcanic chemical fingerprint or the depletion of organic aerosol. The publically available EMEP and Aeronet datasets are also of interest: detailed analyses of these datasets has the potential to yield valuable insights into the atmospheric chemistry and physics processes of the volcanic plume or to evaluate the aerosol impact across europe. However, the depth of the scientific analysis presented for this is somewhat limited so the study is more qualitative or semiquantitative in its insights. The text overstates the study's impacts relative to the actual depth of analysis undertaken. More attention to detail is needed to present the results in context of the state-of-the-art in atmospheric chemistry and physics and in relation to published studies of this eruption and its impacts. The expected level of analysis regarding fundamental atmospheric chemistry and physics concepts for ACP(D) is naturally rather high, perhaps higher than in more applied volcanology/environmental journals. If consulted in pre-review stage to ACPD I would have recommended a thorough revision in terms of both the science and the text before resubmitting, considering how best to combine a detailed analysis, careful interpretation and focused text that places the work in context and more precisely targets an (acp-relevant) science goal. Major revisions are needed. If revised, the new manuscript should undergo further full review. Some main issues are outlined below.

1) The study does not acknowledge previous works on this topic. There exist several papers as well as EMEP-related reports presenting analyses of this particular eruption and its impacts. Findings from these prior works need to be discussed in a paragraph in the introduction, and then can be referred to later in the manuscript results discussion. Some relevant previous works include:

Carboni et al. ACP (2019) (available in ACPD since mid-2018): Satellite-derived sulfur dioxide (SO2) emissions from the 2014–2015 Holuhraun eruption (Iceland). This paper includes SO2-height estimates similar to those being presented in this study.

Indeed, an animation of IASI SO2 altitude observations of the Holuhraun cloud, a IASI product similar to those produced and published by Carboni et al. (2019), has been included in the Supplementary Material. It is used to discuss the high-altitude transport of volcanic plumes emitted in Sept 2014 before reaching Scandinavia, in agreement with Carboni et al. products.
This has been added to the text (Section 4.6).

Ilyinskaya et al. EPSL (2017) Understanding the environmental impacts of large fissure eruptions: Aerosol and gas emissions from the 2014–2015 Holuhraun eruption (Iceland). This paper includes quantitative analysis of SO2:sulfate ratios, including discussion of a more oxidized sulfate-rich plume.

The paper of Ilyinskaya et al. (2017) investigates near-source SO2 to sulfate ratios, from the eruption site up to a distance of 250 km where the capital city of Reykjavik sits. In our paper, we explore SO2:SO4 ratios at stations distant of a few thousand kilometers from the volcano and dispersed on a vast geographical area. We show the wide variability of SO2 to SO4 ratios at such distances. 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 of ~20, which is in the broad range of values determined by Ilyinskaya et al. (2017) in 2-250.

NILU reports (2014, 2015): the 2013 report that is made before the volcanic eruption is cited but the 2014 and 2015 reports are not cited. They include an analysis showing that the volcanic eruption had an impact on EMEP gas-aerosol monitoring datasets in Norway.

Thank you for this suggestion. We were not aware of the 2014 and 2015 NILU reports that describe exceptional ground-level concentrations in SO2 and SO4 at different EMEP stations in Norway in 2014 and early 2015, which they associate to the Holuhraun eruption. These references have been added.

2) As new concepts the study proposes to identify a distinct volcanic fingerprint in aerosol chemical composition and evidence for depletion of organics in the volcanic influenced aerosol. I am not fully convinced by these interpretations of the in-situ measurements as presented.

The ACSM measurements at two sites in France (Dunkirk, SIRTA) offer opportunity for detailed analysis of PM1 composition (sulfate, ammonium, nitrate, organics) at high time-resolution including periods with volcanic-influenced air that have been identified with analysis of satellite data. The use of remote sensing data is a useful approach to support the identification of volcanic influence on the in-situ data. The identification of periods of volcanic influence at these two sites is convincing.

However, regarding the claim to identify a "distinct" chemical fingerprint of volcanic aerosol: The term 'fingerprint' means that you can clearly distinguish volcanic from other aerosols. I am not convinced this is the case here except on a superficial level of high volcanic sulfur in low-sulfur background conditions. As expected, the volcanic influenced air is much more sulfate-rich than sulfur-poor background rural/urban, but it is more similar to the non-volcanic aerosol at Dunkirk. The abstract states: "We demonstrate that aged volcanic sulfate aerosols exhibit a distinct chemical fingerprint in NO3:SO4 and Organic:SO4 concentration ratios higher than freshly emitted industrial sulfate but lower than background aerosols in urban/rural conditions". The "lower than background aerosols in urban/rural conditions" is to be expected for influence of a sulfate-rich plume on these ratios. The higher than freshly emitted industrial sulfate refers only to the subset of data from Dunkirk with NO3 < 1 and SO4 > 4 ug/m3. In figures 5-6 there is overlap of the volcanic event aerosols with the background aerosols at Dunkirk (taking into account all background aerosols – in yellow- not just the chosen subset NO3 < 1 SO4 > 4 ug/m3), for example in the plots of NO3:SO4 and Org:SO4. This is also clear in Figure 9. In summary, the volcanic sulfur-rich aerosols are chemically distinct from sulfur-poor SIRTA background (urban/rural) data but are overlapping in chemical composition with aerosols at Dunkirk (that has more local industrial influences), except if only a subset of the Dunkirk data are considered. How well does this meet the definition of a "distinct volcanic chemical fingerprint"?

We had mentioned in the ACPD version (section 3.3.3) that « Dunkirk is a much more polluted site in sulfur-rich particles than SIRTA. This certainly explains the significantly broader range of both NO3:SO4 and Org:SO4 ratios observed for Dunkirk background aerosols, with values much lower than for SIRTA background aerosols that even intersect those associated to volcanic aerosols. » While volcanic aerosols could be clearly identified at a site in urban/rural conditions, it is more challenging in an industrial site heavily polluted in sulfur, even if we show that volcanic aerosols can be clearly distinguihsed from freshly-emitted acidic industrial aerosol according to their contrasted degree of anion neutralisation.

For the sake of clarification, we rather use the term ‘chemical signature’ (instead of ‘fingerprint’) when highliting specific chemical patterns affecting volcanic aerosols.

We keep the term ‘chemical fingerprint’ when refering to the large-scale impact of the volcanic eruption on gas and particulate sulfur concentrations in general.

We updated the abstract and text accordingly.

The data do seem to show the aerosol chemical composition during the volcanic influenced episodes at Dunkirk is not identical to volcanic-influenced aerosol composition at SIRTA. Indeed, during the volcanic influenced periods the volcanic aerosol may occur alongside or mixed with local aerosols. Looking at the aerosol composition timeseries (Figures 3 and 4) it seems likely that the volcanic aerosol is mixing into/onto the background aerosol trend so to be superimposed on it (and perhaps also influenced by it). In the time-series I see no evidence for depletion of organic aerosol by the volcanic event, rather the volcanic event adds sulfate aerosol so ORG:SO4 decreases. Therefore, I am also not convinced by the interpretation that there is depletion of organic aerosols in the volcanic-influenced air, that is suggested in the text (and conclusions) to be due to formation of organosulfate particles with implications for climate via CCN.

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, bottom of Fig. 6 B shows that the Org:SO4 mass concentration ratio at Dunkirk is remarkably 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 (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 show an enhancement of oxigenated 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 presence of highly-acidic sulfate aerosols, according to 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, likely 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-rich volcanogenic pollution versus natural variability in leading to fluctuations of organics concentration.

This discussion has been included in the revised version in 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 SO 2 and NH 3 on particle formation and growth, Atmospheric

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Pathak, R. K., Wang, T., Ho, K., and Lee, S.: Characteristics of summertime PM2. 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. 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.

Similarly I also question whether there is truly a depletion of NO3 as the study implies (if I have understood correctly), or if it is just a change in NO3:SO4 ratio related to high SO4. In my view the data timeseries suggest volcanic sulfate signal on top of a background trend in nitrate (also the reason for differing NO3:SO4 in volcanic influenced air at the sites), but do not conclusively show evidence for volcanic aerosol significantly impacting nitrate through acid displacement. That could be a possible mechanism, but no thermodynamic modelling is undertaken to provide the evidence for this hypothesis under the conditions encountered.

We proposed in the ACPD version that the specific chemical signature of volcanic plumes, i.e. a lower NO3:SO4 ratio in volcanic aerosols compared to background conditions, could result from the substantial concentration of sulfate within volcanic plumes. We justified this interpretation by referring to sensitivity tests with a thermodynamic model of aerosol composition published in the textbook of Seinfeld and Pandis. These simulations indeed show the preferred formation of ammonium sulfate rather than ammonium nitrate in an atmosphere very rich in sulfate.

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 directement measurements of this gas-phase species were performed along with ACSM observations during our period of study in 2014). 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 $\mu g.m^{-3}$ initially) allows to best fit the NO3 observations during the volcanic event in late September 2014 that is characterized by large SO4 concentrations exceeding 4 $\mu g.m^{-3}$ (Figures 10, A1 and B1). The NH3 -poor scenario (0.74 $\mu g.m^{-3}$ initially) overestimates the decrease in particulate nitrate, with its almost complete depletion for a concentration of total sulfate exceeding 12 $\mu g.m^{-3}$ (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, model simulations suggest that the distinct chemical signature observed for Holuhraun volcanic aerosols, compared to background aerosols, results from the large abundance of sulfate within the volcanic plume. This is confirmed by the model sensitivity tests (for SIRTA conditions) that we performed using again ISORROPIA II in order to address the impact on the production of particulate nitrate of an increasing concentration of sulfate, while all other parameters are kept constant (Fig. 12, revised version). At high concentration of sulfate aerosols, simulations show that ammonium preferentially neutralizes sulfate rather than nitrate, favoring the formation of ammonium sulfate ($(NH_4)_2SO_4$) rather than ammonium nitrate (NH_4NO_3). In these conditions, the decrease in particulate NO3 concentration with increasing sulfate concentration coincides with an increase in gas-phase HNO3. In an atmosphere very rich in sulfate (e.g. a total sulfate exceeding 12 $\mu g.m^{-3}$ here), a complete depletion of gas-phase NH3 and particulate NO3 can occur, concomitantly with NH4 concentration reaching a plateau value.

3) Several open-source datasets are presented to demonstrate a broader large-scale European particulate pollution. The interpretation relies mostly on text-book results (for non-volcanic conditions). Galeazzo et al. ACP 2018 show that SO2 oxidation processes cannot be assumed to occur at the same rates in a volcanic plume as under background atmospheric conditions. If the goal is to evaluate a europe-wide impact of ther eruption on aerosol then a more quantitative analysis and interpretation could have been achieved by a more detailed approach involving modeling for the specific conditions e.g. thermodynamic model, analysis of back-trajectories, etc. The study text makes some quite assertive claims about the significance of the study e.g. on identifying a European-wide aerosol impact, linking SO2:SO4 to volcanic cloud history. If made, such claims need to be reflected by depth and detail of data analysis, particularly when relying on open-source datasets. They should be placed in context of previous studies e.g. Ilyinskaya et al. paper, NILU reports.

The objective of our paper is indeed to demonstrate the broad Europe-wide impact of the Holuhraun eruption on both gas and particulate pollution in sulfur.

As developed in the ACPD version, the volcanic origin of the large-scale atmospheric pollution in SO2 is attested by SO2 observations of OMPS and IASI satellite sensors (in the Supplementary Material) showing the Holuhraun volcanic cloud, rich in SO2, transported repeatedly over the EMEP stations of interest in Scandinavia and Great Britain, showing anomalies in both SO2 and SO4 concentrations significantly exceeding background values in September and October 2014.

In the revised version, we develop a multi-site concentration-weighted trajectory analysis for both SO2 and SO4 components taken separately, using either a multi-site approach (Fig. 15) or considering each selected station individually (Figures A4, A5 and A6). Fig. 15, A4, A5 and A6 hence represent 3 new figures of the revised paper.

This supplementary analysis confirms the strong and widespread impact of Icelandic emissions of volcanic SO2, which is all the more remarkable given the very small number of backtrajectories leading to Iceland from each of the 8 stations, as illustrated by trajectory density maps (right of Fig. A4 b, c, d and A5 a,b, c, d, e). For Denmark stations, we identify a supplementary weak influence of SO2 emissions from Eastern Europe industry (left of Fig. A4 a, b, c). These sources were already identified by Fioletov et al. (2016). Their location is indicated by green circles in Fig. 15.

Contrary to SO2, tracking the origin of sulphate aerosols measured by EMEP stations is more complex. Using a multi-site concentration-weighted trajectory analysis, volcanic emissions from the Holuhraun eruption are also identified as a major source of SO4 at all stations (except Tustervatn) (middle of Fig. 15), despite very few backtrajectories leading to Iceland (right of Fig. 15). In addition to this volcanic source, we also show the significant impact of SO4 anthropogenic emissions from Eastern Europe (especially from Ukraine) but also from Great Britain. As shown in Fig. 15, these retrieved industrial sources of sulfate are in good agreement with the catalogue of large SO2 emissions in 2013 derived from OMI satellite sensor observations from Fioletov et al. (2016). Retrieved sources of SO4 are also found to be more geographically dispersed than SO2 sources (Fig. 15), which is likely due to their much longer atmospheric persistence discussed in Section 5.4 of the revised article. This result demonstrates the importance of developing a multi-site concentration-weighting trajectory analysis tojointly analyzing SO2 and SO4 species, as done in this study, to better isolate, among anthropogenic sources of pollution, the volcanic impact on the concentration of aerosols.

Therefore, we demonstrate here the large-scale impact of the Holuhraun eruption on both gas and particulate air pollution in SO2 and sulfate aerosols, affecting broadly Europe, not only France but also Great Britain and Scandinavia. Such a result has never been published elsewhere to our knowledge, Ilyinskaia et al. (2017) exploring near-source emissions of gas and aerosols.

In addition to the broad atmospheric impact of the Holuhraun eruption over Europe, we also aimed at investigating the variability in the SO2-to-SO4 oxidation ratios with the volcanic cloud history.

We restricted our analysis in the ACPD version to showing the wide variability of SO2-to-SO4 ratios for stations located at a few thousand kilometers from the eruption site, which already represent a unique dataset in the litterature. Indeed, to our knowledge, previously published studies mainly focus on near-source (few first kilometers) observations, and more rarely on observations at a few hundreds kilometers.

The significant variability in oxidation ratios that we observe in this dataset at distant stations 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 in 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:

$[SO2]/[SO4]=- 0.23 \ t + 19.7$.

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 Reykjahlid (at 100~km distance) in January 2015 and in 0.016–0.38 in Reykjavik (at 250~km distance), corresponding to a SO2-to-SO4 mass oxidation ratio in 2–250 and 4–94 respectively.

Some of the data shows acid excess, which is expected for concentrated sulfur-rich plumes. However, I am not convinced by the (rather assertive) claim "This result demonstrates that NH+4 ions have not had enough time to neutralize surrounding sulfate and nitrate ions." This process is usually extremely quick. What about other explanations? Could it not simply be that there was not enough (background) NH3 available?

Polar plots of the concentrations of both SO_2 and SO_4 recorded in Dunkirk colored by wind speed or anion neutralization ratio (ANR) (corresponding to the predicted vs. measured NH_4 levels) have been added to the revised manuscript (new Fig. A3 in revised version). This new figure allows us 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 $NO_3 < 1$ and $SO_4 > 4$ $\mu g\ m^{-3}$ which are interpreted to be of industrial origin in the submitted version of the paper given their acidity (i.e. low ANR) compared to all other aerosols including particles of volcanic origin (Bottom right of Fig. A3 in 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 (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 $NO_3 < 1$ and $SO_4 > 4$ µg m^{-3} originate from the direction 225-270° corresponding to the industrial sector, confirming the industrial origin of these acidic 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 in 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 in 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 µg m^{-3}. Most of the time in Dunkirk, sulfate concentration does not exceed 25 µg m^{-3} (left of Fig. 5A). Fully neutralizing such a substantial amount of sulfate requires about 9.5 µg 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 ± 2.8 µg m^{-3}, reaching maxima of 11-12 µg 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 µg m^{-3}. As shown by ISORROPIA thermodynamical simulations with contrasted environments either poor or rich in NH3 (Fig. 10, revised version), Dunkirk atmosphere can consequently be considered to be sufficiently rich in NH3 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 in revised version).

Publically available EMEP data is used in the presentation of SO2:SO4 in PM10 for high SO2 events (that are assumed to be volcanic in origin). What is missing from this study is to demonstrate that the high SO2 events are due to volcanic influence at these sites. It is stated that they are rural/far from sources but there can also be transport of sulfur plumes from large point sources such as from Russian industry affecting certain EMEP sites. One simple way to show the likely volcanic influence can be back-trajectory plots for the high SO2 events. It should also be shown how the SO2-sulfate data compare to data for previous years to demonstrate if and to what extent there are unusually high SO2 or sulfate in 2014. Hypotheses are made about reasons behind the variation in SO4:SO2 ratios, but to test these hypotheses would require further detailed data analysis.

To summarise briefly what has been developed above, the joint analysis of SO2 satellite observations from 2 sensors (OMPS and IASI) with ground-level concentration data at various EMEP stations showing concomitant large anomalies in SO2 significantly exceeding background levels, already attests of the volcanic impact on widespread anomalies in SO2.

The multi-site concentration-weighted trajectory analysis (new Figures 15, A4, A5 and A6 in the revised version) that we have added in the revised manuscript (either through a multi-site approach or using station data separately) confirms this result. As expected by Reviewer#2, this new development also shows an influence of Eastern Europe industrial SO2 emissions (especially from Ukraine) at Denmark stations, although much weaker than the volcanic impact.

Moreover, such new analysis allows us to show that estimating sources for widespread SO4 anomalies is more complex given the longer persistence of sulfate compared to SO2. We show that, in addition to a strong impact of the Holuhraun eruption, EMEP stations also record the influence of anthropogenic emissions from Eastern Europe and Great Britain, albeit to a lesser extent, sources in agreement with published SO2 emissions derived from OMI satellite observations by Fioletov et al. (2016).

Regarding SO2:SO4 ratios, we added a new section in the revised version, with an estimation of plume age associated to these values for a set of selected stations broadly dispersed in Europe. We demonstrate that, in spite of a wide variability in SO2:SO4 ratios, ratios evolve linearly with a single variable, namely the plume age (new Fig. 16 in the revised version). Therefore, we estimate a SO2:SO4 mass oxidation rate of 0.23 hour^{-1}. To our knowledge, we do not know any publication evaluating SO2:SO4 oxidation rate at distances of a few thousand kilometers from the volcanic source.

In the analysis of SO4:SO2 data there appears to be an error in the units as the same data-values are presented in figures 13 and 14 but one is a plot of ug S per m3 and the other is ug SO2 or SO4 per m3. If it is an error in the axis labels this should be corrected. If it is an error in the data analysis this could change the results fundamentally.

We thank Reviewer#2 to have spotted this error in the labelling. Figure has been corrected accordingly.

Demonstrating a widespread impact of volcanic aerosols across Europe: if the authors wish to demonstrate this they may need to also present an analysis of the AERONET data across Europe (in conjunction with the in-situ timeseries and comparing to previous and subsequent years) not just at the two sites in France. Where correlations are identified they should be presented quantitatively, with correlation coefficients. (e.g. regarding aeronet: sulfate data comparison). It would be useful also to show in supplementary material Aeronet data from previous (non-volcanic) years for comparison. Is there a reason why a similar analysis was not presented for other AERONET sites across europe? This would help to support the claim to demonstrate a significant impact of the volcano on europe-wide aerosol.

Although we agree with Reviewer#2 that exploring AERONET data at the European scale is of significant interest, we must say that such an analysis requires a massive amount of work, which is completely beyond the scope of the present study which is already very thorough. This specific piece of research is precisely the subject of another paper in preparation.

Concerning the comparison of 2014 AERONET data with measurements from previous non-volcanic years, we have mentioned in the ACPD version the average AOD values for September months between the start of AERONET measurements at the two sites until 2016, exclusing the 2014 year impacted by the Holuhraun eruption. We show that the mean AOD values observed at the two French sites of Dunkirk and SIRTA for the month of Sept 2014 exceed by a factor of 2 the mean values observed for all other non-volcanic years, demonstrating the significant volcanic impact.

Scatter plots of AERONET AOD and ACSM SO4 data at SIRTA and Dunkirk, and associated correlation coefficients have been added in inset of the updated Fig. 12 in the revised version.

4) There are a number of sweeping statements that at times overstate the impacts of the study. The language needs to be much more precise. Some examples include the following:

In the abstract and elsewhere: "Here we determine the chemical speciation, lifetime and impact on air quality of sulfate aerosols…". You do not provide quantification of sulfate aerosol lifetime in this study.

That is true that the term 'lifetime' is not appropriately used in the ACPD version. We did not estimate the lifetime of sulfate aerosols, but rather the duration or temporal persistence of pollution events in SO4. We changed the text accordingly.

A new Section has been added in the revised version that evaluates the SO2-to-SO4 oxidation rate within the volcanic plume, at long distances from the eruption site. It provides a quantification of the minimum bound of the lifetime of SO2.

"Finally, gathering 6 month long datasets from 19 sulfur monitoring stations of the EMEP network allows us to demonstrate a much broader large-scale European particulate pollution in SO4" To my understanding you consider 6 rather than 19 stations for analysis of SO2:SO4 data, as you are taking only stations with SO2 peaks above 3 ug/m3.

We explored SO2 and SO4 concentration timeseries from all the 19 EMEP stations - now 27 stations in the revised version (see the added Table 1 with details on these stations and the updated map in Fig. 13 of the revised version) - and selected for a more detailed analysis data from 6 out of these 27 stations (8 stations in the revised version, see the updated Fig. 14 in the revised version). For the sake of exhaustivity, we have added time series of both SO2 and SO4 ground-level concentration for the 27 stations in the Supplementary Material of the revised version.

"we show the various rates of SO2 oxidation" The study does not provide quantification of SO2 oxidation rate.

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 in revised version) where we precisely 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 with plume age for stations located between 1200 and 2200 km from the eruption site.

Sentence in the abstract "our results raise fundamental questions about the cumulative impact of tropospheric eruptions on air quality, health, atmospheric composition and climate, which may be significantly underestimated"
What are these fundamental questions raised by this study about the cumulative impact of tropospheric eruptions on air quality, health, atmospheric composition and climate? How did you show these impact were underestimated? These are not addressed by this study. Be more precise about what the study has actually achieved.

Low-tropospheric aerosols of volcanic origin can modify the microphysical properties of clouds, as shown by several studies (e.g. Yuan et al., 2011; Schmidt et al., 2012; Malavelle et al. 2017). This volcanogenic indirect effect should be all the more important that we show here that volcanic sulfate aerosols can persist over weeks in the lower troposphere (compared to the short persistence of SO2 – the volcanic species the most commonly studied – of a few days at most), even in the planetary boundary layer.

While the Holuhraun eruption is of particular interest to study such atmospheric effects given its 6-month long duration, many other tropospheric eruptions, albeit of lesser magnitude, and passive degassing activities of numerous volcanoes worldwide, are expected to collectively impact the background load of sulfate aerosols in the lower troposphere.

Therefore, this article shows that more studies should address this cumulative effect of volcanoes emitting into the troposphere that are not accounted for in current climatic projections or large-scale air quality studies.

Text and abstract have been modified accordingly.

Page 5: "Finally, to provide a broader picture, we explore 6-month long sulfur monitoring datasets (Sept. 2014-Feb. 2015) from 19 stations of the EMEP (European Monitoring and Evaluation Programme) network to evaluate the large-scale impact of the Holuhraun eruption on European aerosols and the range of partitioning of volcanic SO2 to SO4 according to the volcanic cloud history (Section 3.5)."
A total of 6 rather than 19 stations were analysed in any detail by looking at sulfate:SO2 ratios for stations with recorded high SO2 events above 3 ug/m3. It is an over-statement to say that the large-scale impact on European aerosols was evaluated, given the rather light analysis of a subset of EMEP data (with no other aerosol/gas species analysed than SO2-sulfate) and no analysis of AERONET data across Europe. Partitioning of volcanic SO2 to SO4 is not evaluated according to volcanic cloud history, rather the selected data are presented and some hypotheses are suggested.

As stated above, we exploited in the revised version SO2 and SO4 concentration time series at ground-level for 27 EMEP stations (see the added Table 1 with details on these stations and updated map in Fig. 13, revised version). For the sake of exhaustivity, all data have now been included in the Supplementary Material. We make a selection of 8 stations for further detailed analysis (updated Fig. 14 in the revised version). A joint analysis of SO2 satellite observations and multi-site concentration-weighted trajectory analysis, together with EMEP in-situ data, allows us to show the widespread impact of the Holuhraun eruption on both SO2 and SO4 anomalies in ground-level concentrations recorded at the European scale (Figures 15, A4, A5 and A6). While the Holuhraun eruption is shown to be the major source of large-scale pollution in SO2, we distinguish (Figures 15, A4, A5) and quantify (Fig. A6) the volcanic contribution to the widespread pollution in sulfate relatively to antropogenic sources of SO4.

Exploring a set of stations vastly dispersed in Europe, the partitioning of volcanic SO2 to SO4 has also been studied in detail with the estimation of a constant SO2 to SO4 oxidation rate. To our knowledge, such a result is new in the literature as published studies generally mainly focus on near-source measurements (from the eruption site to a few hundreds kilometers).

Regarding AERONET data, such an analysis is completely beyond the scope of the present study that already explores very large in-situ datasets (from EMEP database, ACSM observations, or French air quality monitoring observations) and develops several new results and concepts in the field of volcanic plumes from the large-scale volcanic impact on both gas and particulate concentration in sulfur to the weeks-long persistence of sulfate aerosols and the specific chemical signature of volcanic plumes regarding aerosol composition.

5) Smaller comments and Figures:
There is not enough information provided in methods about the EMEP PM10 sulfate and SO2 observations. There needs to be more description about how these measurements are made and analysed. Has sea-salt sulfate been accounted for (ie non-seasalt sulfate) or is this total sulfate?

There is very little difference between PM10 total sulfate and PM10 sulfate corrected from sea-salts. Nevertheless, we updated all figures to include the concentration in corrected non-marine sulfate in the revised version.

In general: when it is written concentration ratio it is often rather a mass ratio or mass concentration. Better to be precise.

That is true, we paid attention to systematically include the reference to mass instead of molar concentration.

"In volcanic plumes, S(IV) can also be oxidized in the aqueous phase by dissolved oxygen (O2) catalyzed by iron and manganese (Seinfeld and Pandis, 2012) and halogen rich species (HOBr or HOCl) as shown more recently by von Glasow and Crutzen (2003)." I think these studies refer to processes that can occur in atmosphere generally, and not specifically whether or not they occur in volcanic plumes. Better to be precise. Also, note Galeazzo et al. (2018) is probably the most suitable reference for highlighting O2-catalyzed oxidation could be important in volcanic plumes.

That is true that these processes are not specific to volcanic plumes but also occur in other environments. This has been precised in the text. The reference to Galeazzo et al. has been also included.

Some figures are well presented, others need improvement.

In particular the SO4:SO2 data as mentioned above seems to have some problem either with the axis labels in Figures 13 and 14 (ug S or ug SO2 or SO4 ?) or it is an error in the data post-processing. Mention in captions if data is PM10 or PM1 or both.

We erroneously mixed data in ug S and ug SO2 and SO4 in the ACPD version. This has been corrected. We now mention in caption when data refer to PM1 or PM10 fractions.

Also there is a problem with the axis on Figure 3 where data is offset vertically from each other. It would be better to plot these data together on the same axis or on separately labelled axes.

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.

In Figure 4 should also add gray-highlight volcanic event 3 (as is nicely shown for volcanic events 1&2 in figure 3).

A gray-highlight for volcanic event 3 has been added to Fig. 4.

Figure 9: as I understand it, data had to be pre-selected with constraints to reduce noise, if so I think it better to mention that on the figure legend.

The criteria used to pre-select data have been added in the caption of the figure.

Figure 11 is this daily averaged ACSM as well as daily averaged AOD? Make it clear.

We mentioned in the caption of Fig. 11 that we represented ‘mean daily’ values of AERONET AOD and ACSM observations but that was perhaps not clear enough. We updated the caption as following : « Time series of daily averaged values of both AERONET AOD at 500~nm and ACSM SO4 mass concentration ».

Figure 12 caption: you state that other stations (other than those you selected based on SO2 > 3 ug/m3) were not impacted by the Holhuraun eruption. Are you sure this is true? What if the station is impacted but did not record SO2 > 3 ug/m3 but only 2 ug/m3, which is still considerable.

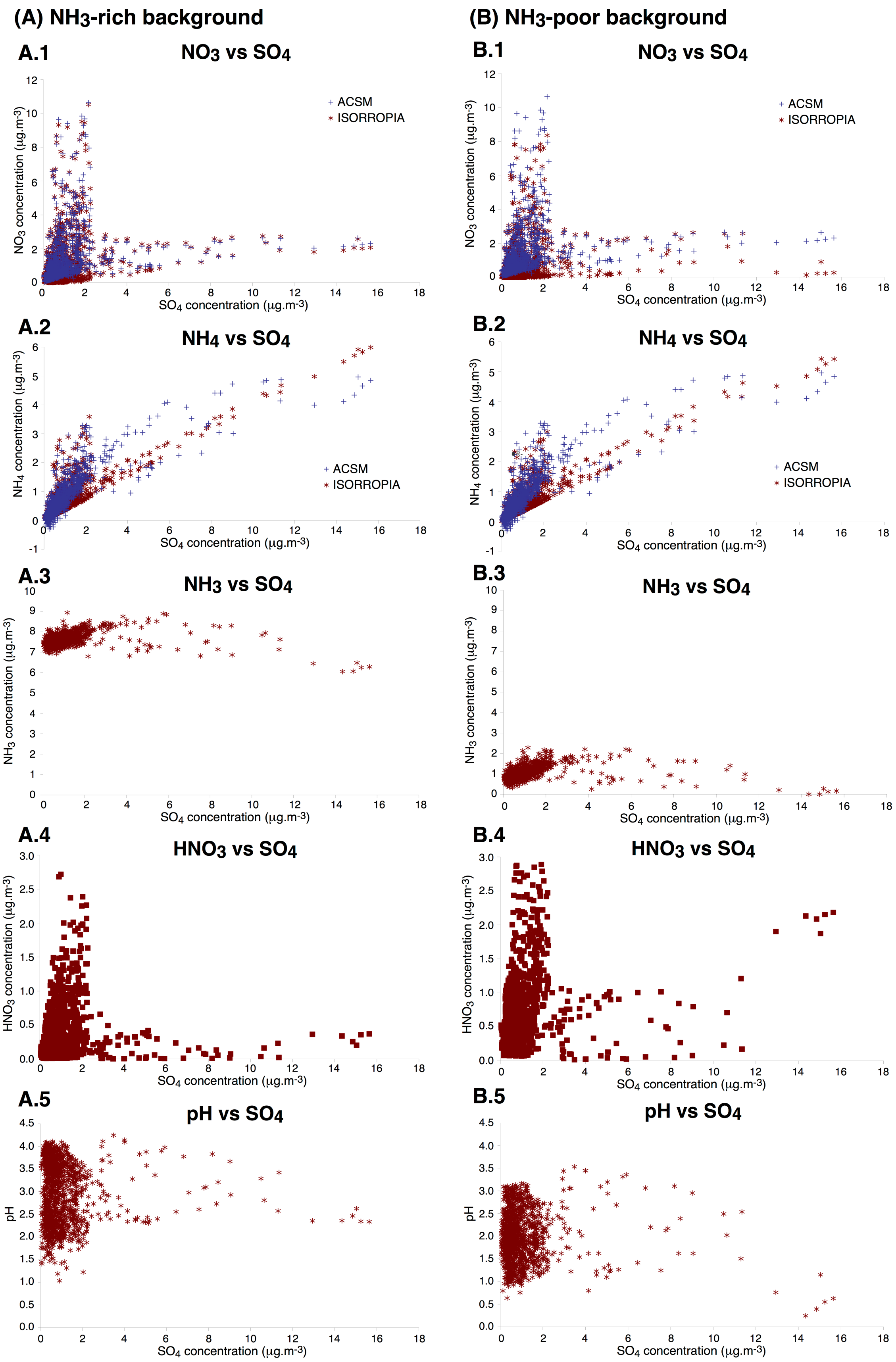
We mentioned in the ACPD version that stations with multiple SO2 concentrations > 3 µg.m-3 are clearly impacted by the eruption (given also satellite observations showing the SO2-rich volcanic plume passing over the selected stations), whereas stations with concentrations mainly below 3 ug/m3 are not clearly impacted by the eruption. This does not mean that these latter stations are not impacted at all by the eruption, but it is less obvious by looking at the SO2 and SO4 concentration time series. We added a sentence to clarify this point in the text.

Figure 13 need to make the scatter plots larger (each to their own appropriate scale) so they are readable. Mention in the caption this is PM10.

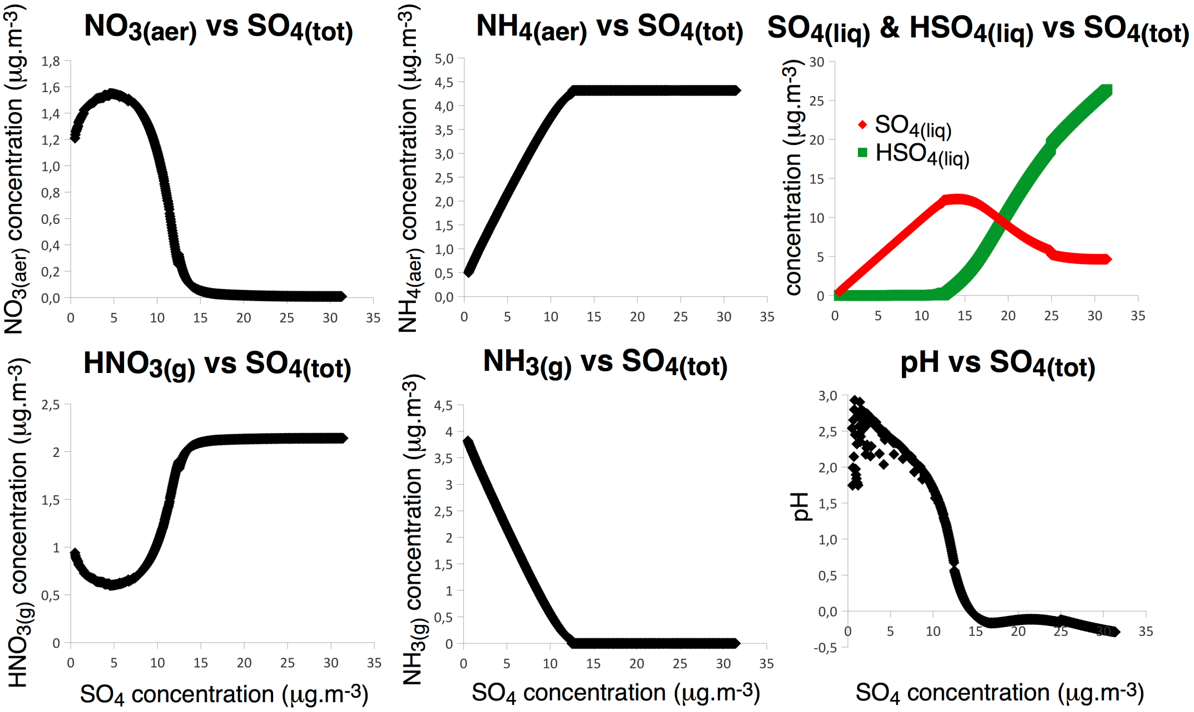
Fig. 13 (now Fig. 14, revised version) was updated so as to make the scatter plot more easily readable and to include two supplementary stations. Mention of the PM10 fraction has also been added.

Figure A2: if you show BC you need to improve scale so it can be seen more clearly.

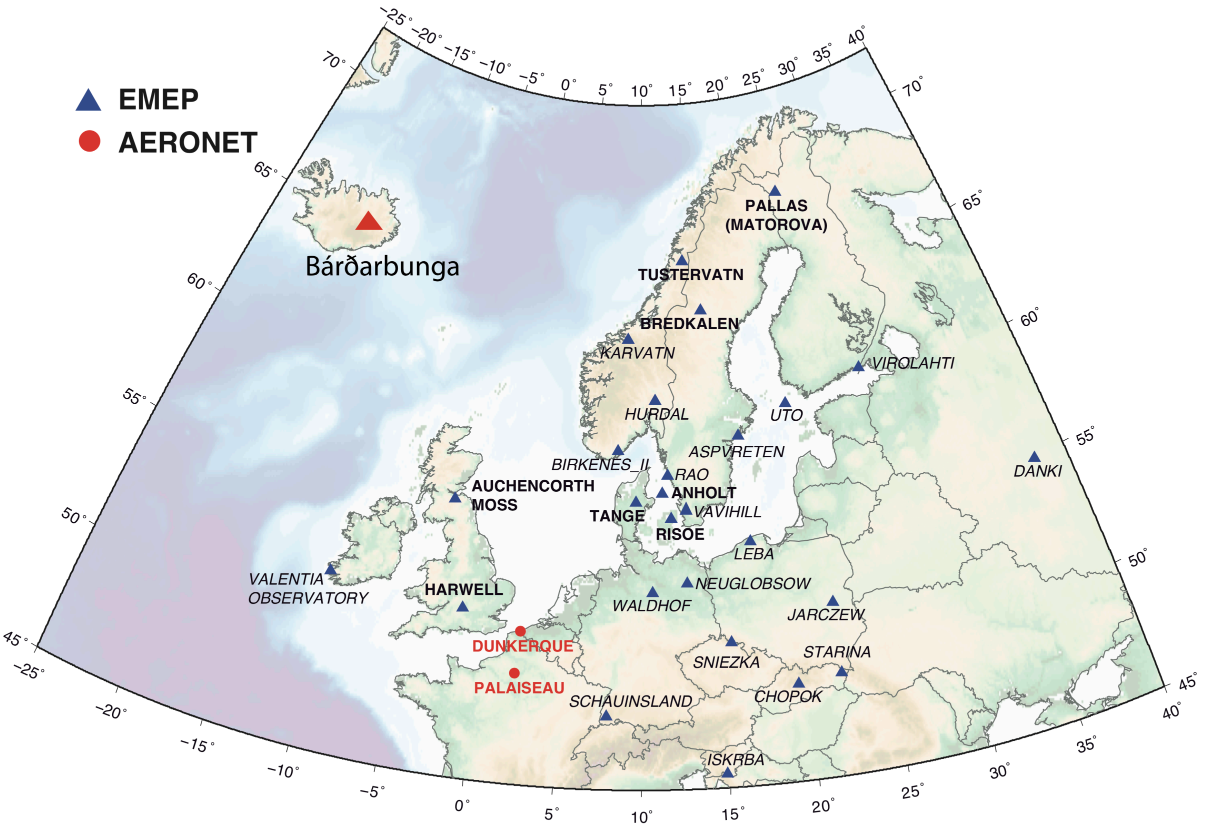
Figure A2 has been updated so that temporal variations of BC concentration can be better visualised.



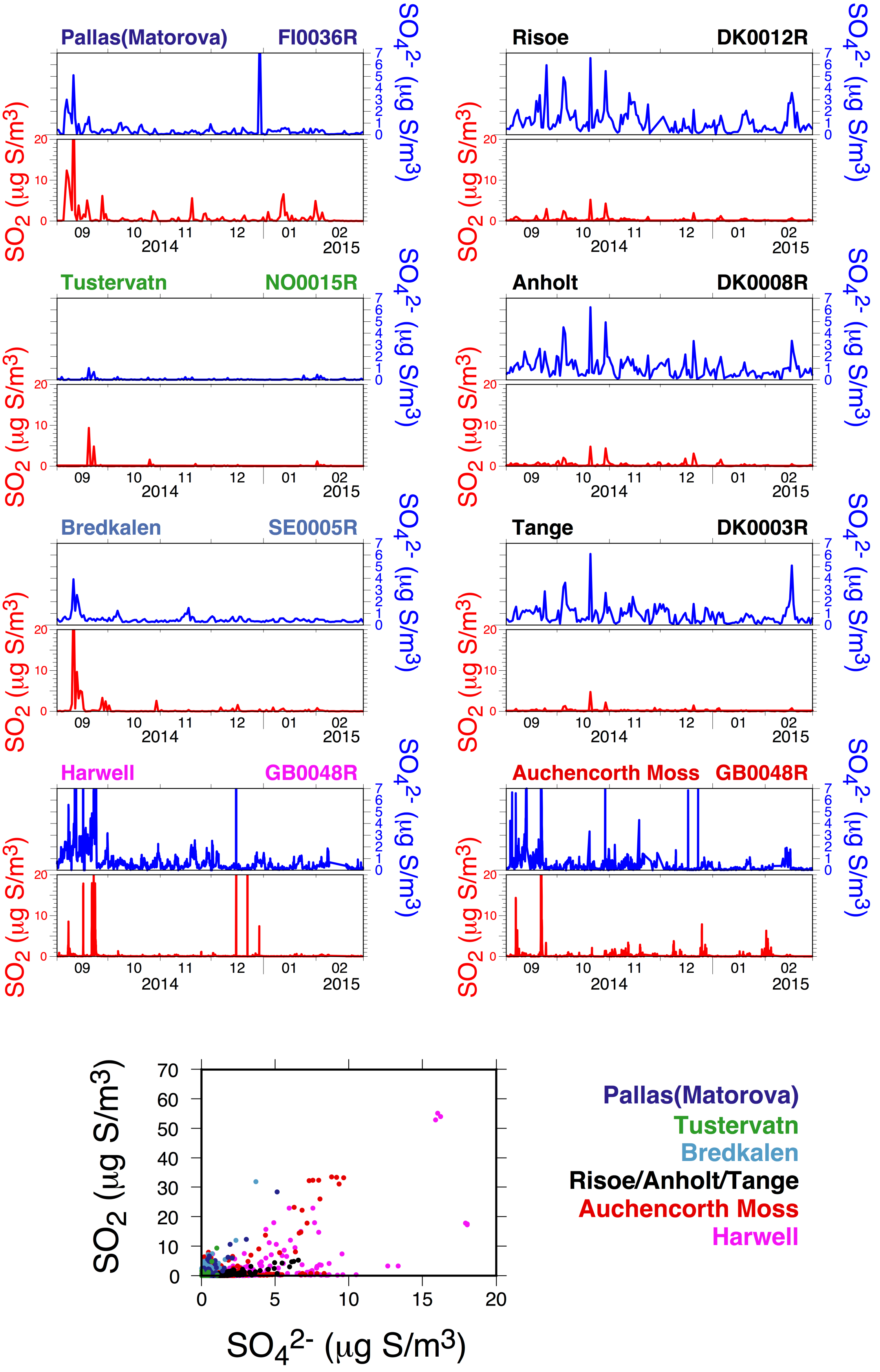
Reproduction of Fig. 10 (revised version): ISORROPIA II thermodynamic model simulations (red) of atmospheric composition (aerosol NO_3 (1) and NH_4 (2), gas-phase NH_3 (3) and HNO_3 (4)) as well as pH (5) versus SO_4 mass concentration at SIRTA in Sept-Oct 2014 considering an environment either (A) rich (7.40 µg.m^{-3}) or (B) poor (0.74 µg.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.

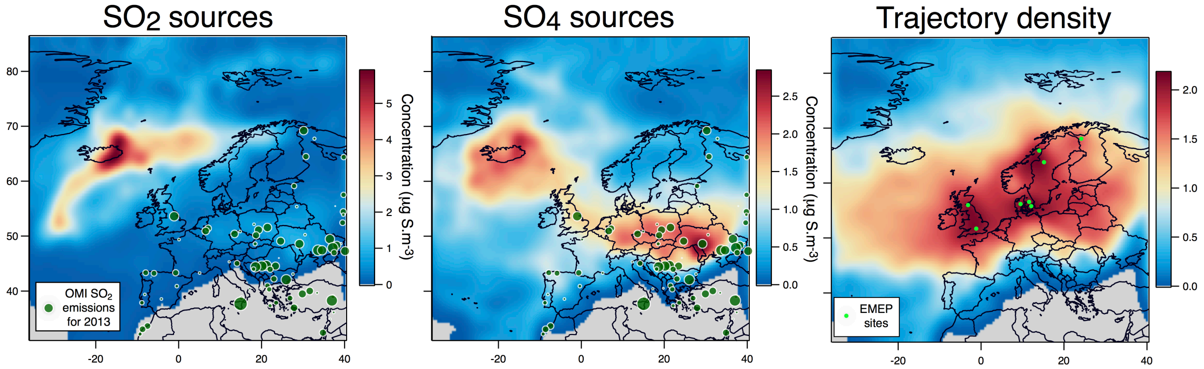


Reproduction of Fig. 13 (revised version) : Map of the 27 EMEP stations (blue triangles) explored in this study. Stations with name in bold, with a few daily SO_2 concentrations higher than 3 µg.m^{-3} over the period Sept 2014–Feb 2015 suggesting a clear impact of the Holuhraun eruption, are selected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

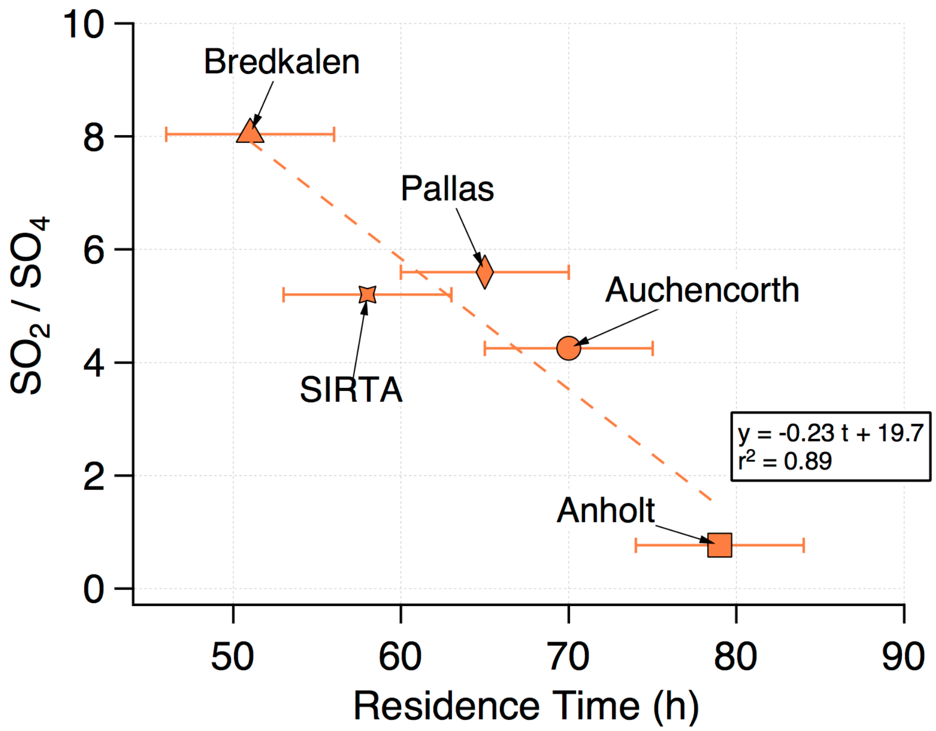


Reproduction of Fig. 14 (revised version): Time series (top) and scatter plot (bottom) of ground-level mass concentrations (in µg S.m^{-3}) of SO$_2$ and corrected PM$_{10}$ SO$_4$ (i.e. non marine SO$_4$) covering the Holuhraun eruption

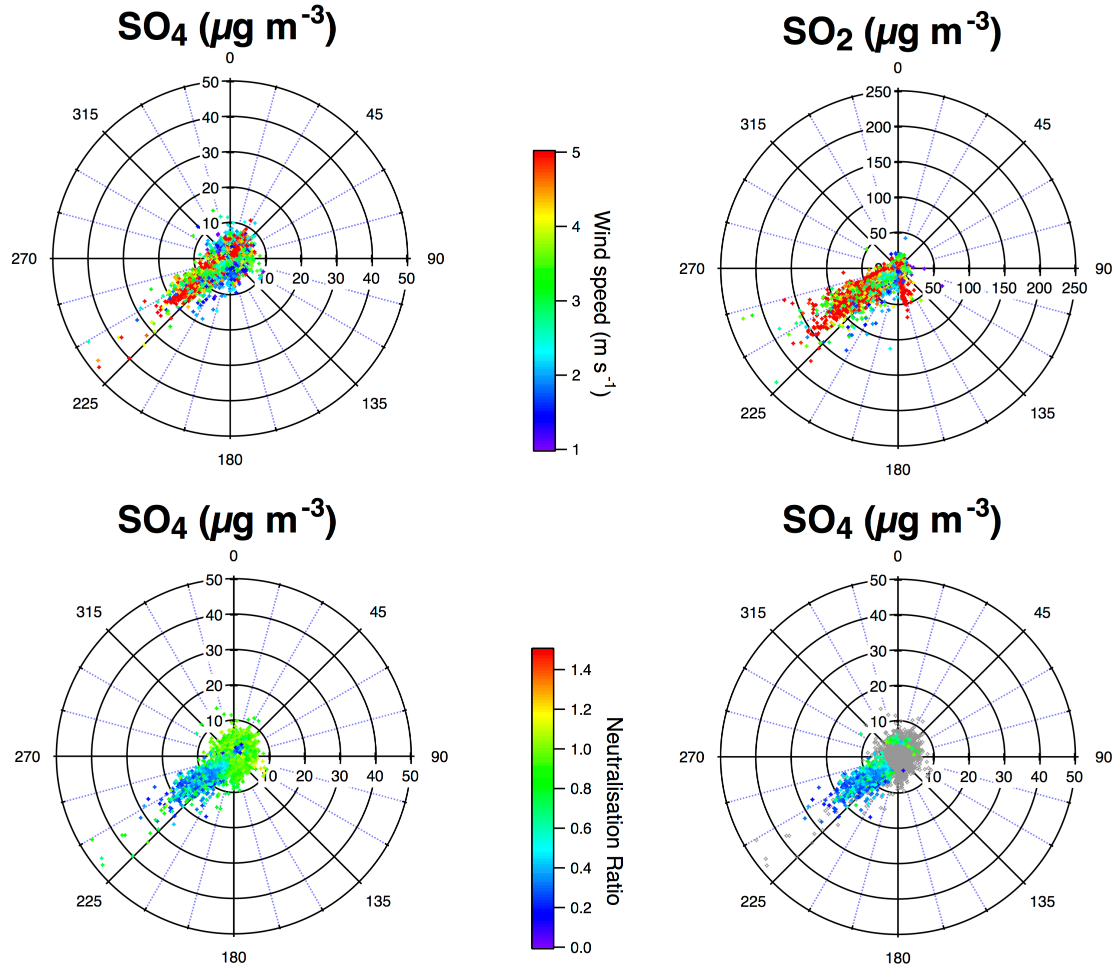
from Sept 2014 to Feb 2015, at selected EMEP stations in Scandinavia and Great Britain clearly impacted by the eruption.



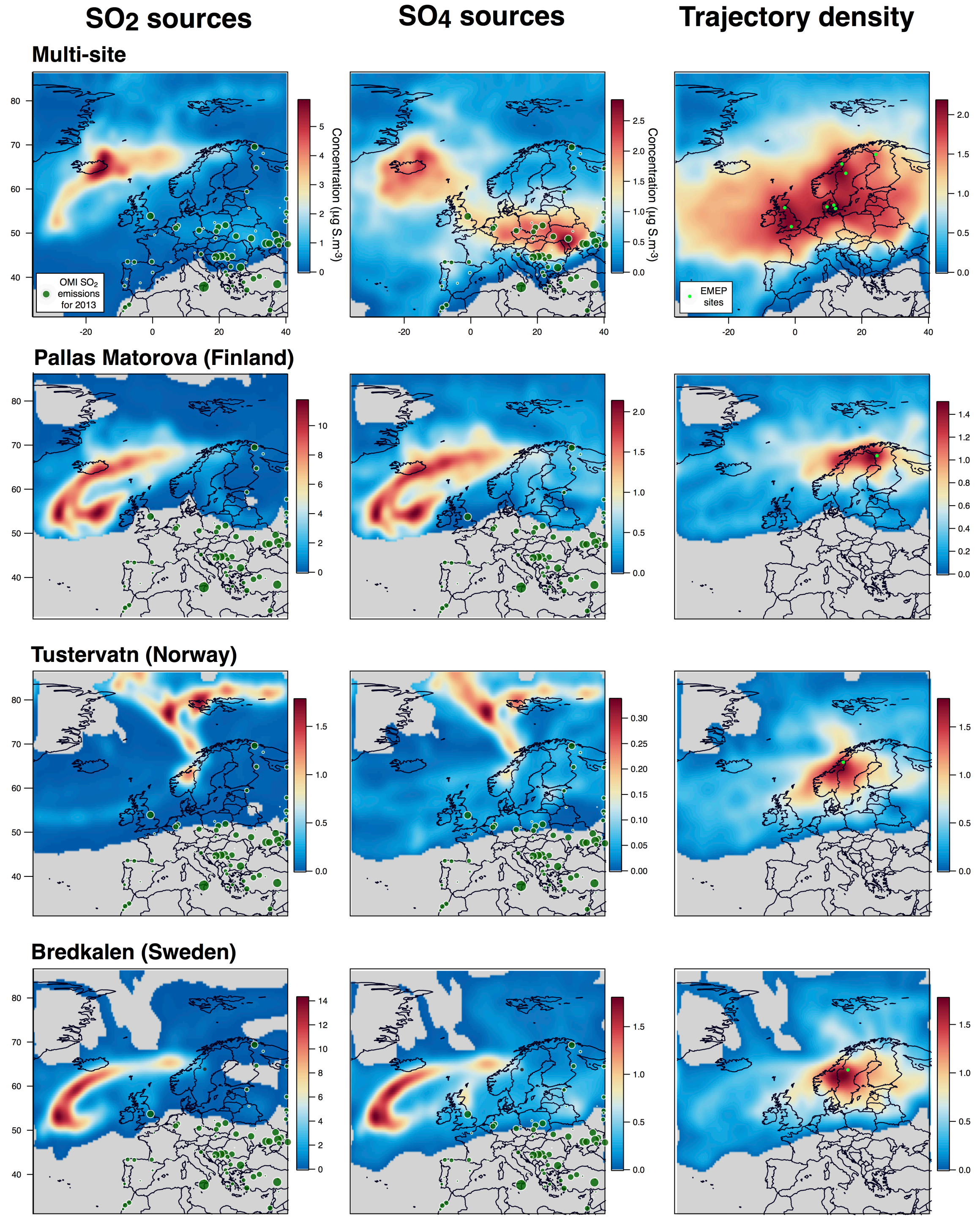
Reproduction of Fig. 15 (revised version) : Multi-site concentration weighted trajectory analysis for SO_2 and SO_4 concentrations measured in September-October 2014 at a set of eight selected EMEP stations in Northern Europe (shown in Fig. 15): retrieved source concentrations (µg S.m^{-3}) of (left) SO_2 and (middle) corrected SO_4 (i.e. non marine SO_4), (right) trajectory density (log of residence time, no unit) with the location of stations (light green circles). SO_2 emission sources for 2013 derived from OMI satellite sensor observations (from Fioletov et al. (2016)) are indicated by dark green circles.



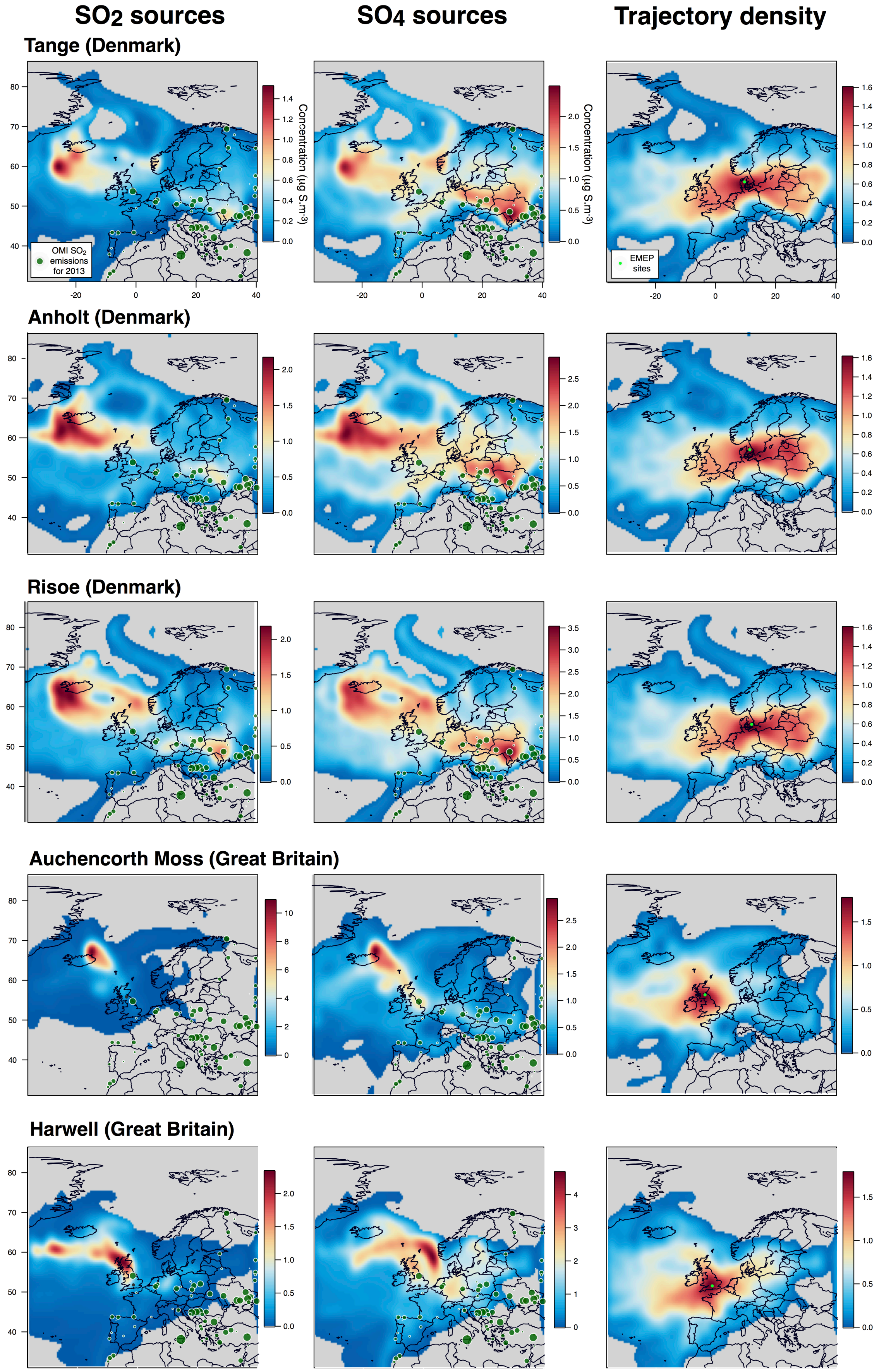
Reproduction of Fig. 16 (revised version): Scatter plot of the SO_2:SO_4 concentration ratio (in PM_1 fraction for ACSM data at SIRTA, PM_{10} for other stations) with the residence time or plume age (h) of the volcanic cloud at a selection of EMEP stations in five different countries of Northern Europe.



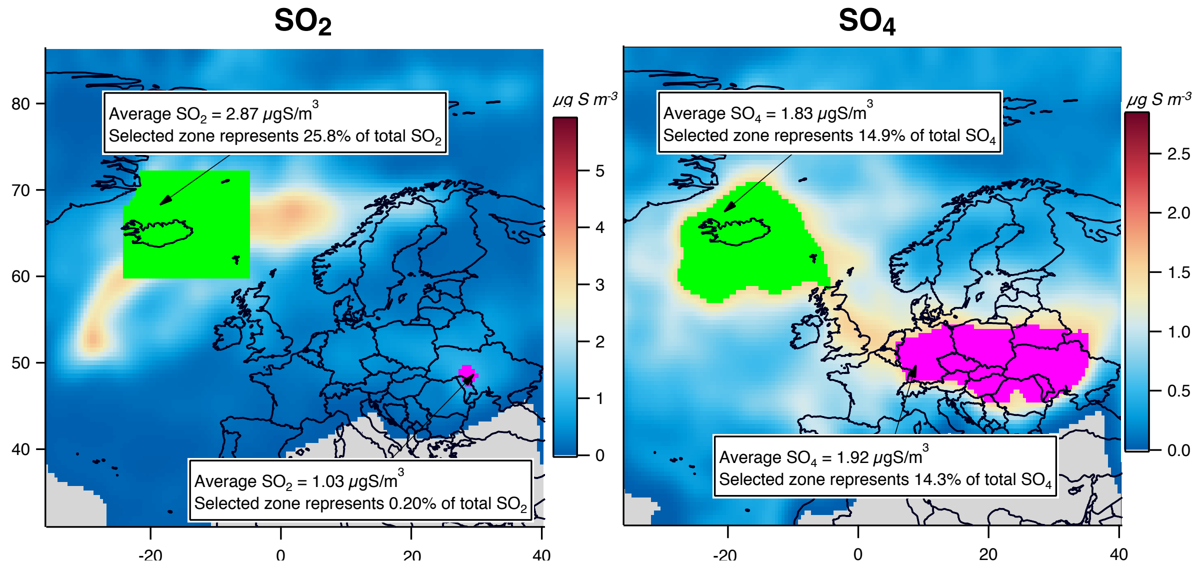
Reproduction of Fig. A3 (revised version): (top) Polar plots of (left) sulfate and (right) sulfur dioxide concentrations colored by wind speed; (bottom) Polar plots of sulfate colored by the anion neutralization ratio (ANR) for (left) the entire Dunkirk dataset and (right) points with NO3 < 1 and SO4 > 4 µg 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) Bredkälen (Sweden), other stations in Fig. A6): retrieved source concentrations (µg S.m^{-3}) of (left) SO$_2$ and (middle) SO$_4$, (right) trajectory density (log of residence time, no unit) including station location (light green circles). SO$_2$ 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) SO_2 and (right) SO_4, considering an edge detection at 1 and 1.5 $\mu g\ S\ m^{-3}$ respectively. Green areas are for icelandic volcanic sources while pink areas correspond to anthropogenic sources.

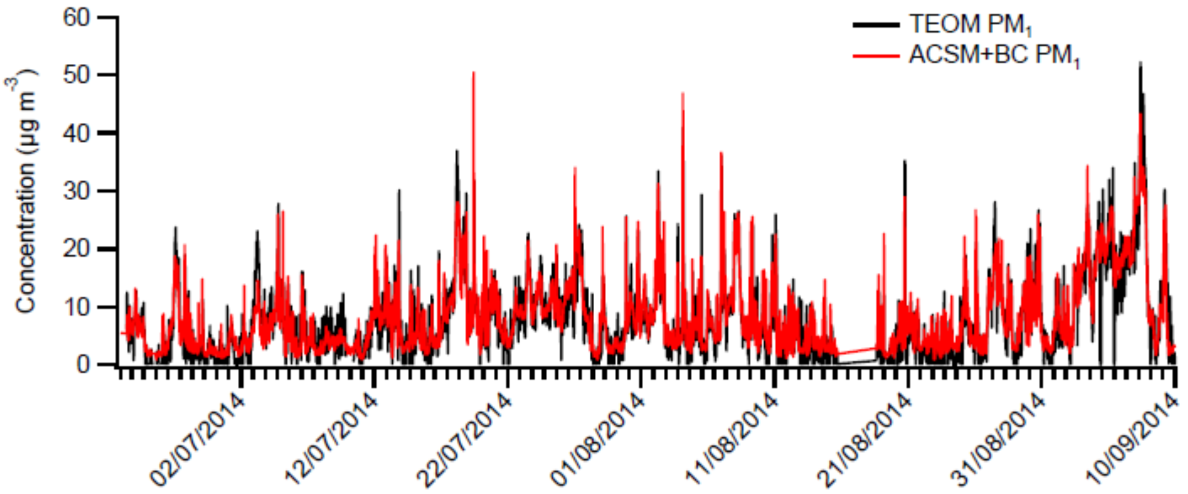


Figure R1: Time series of PM_1 measured by TEOM-FDMS and the sum of PM_1 chemical species (NO3, SO4, NH4, Cl, Organics determined by ACSM; BC derived from optical measurements)

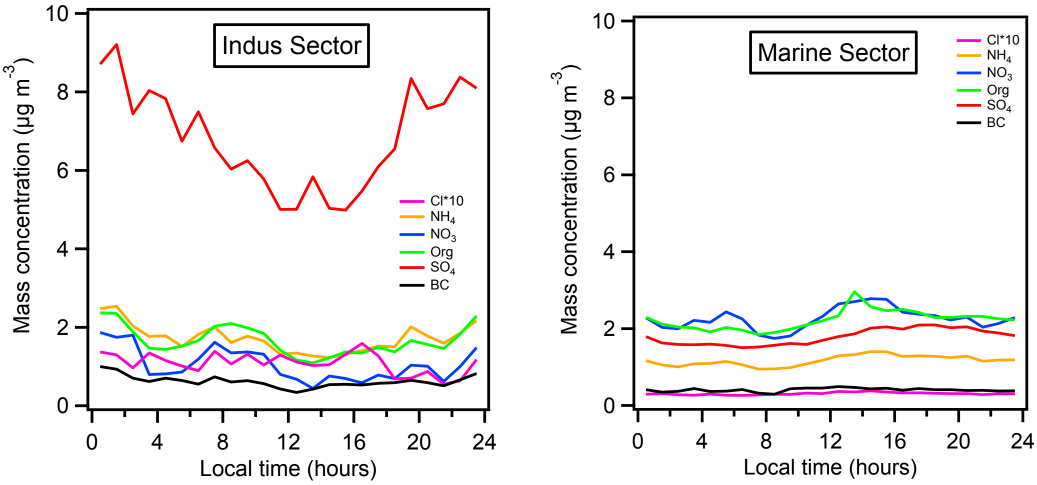


Figure R2: Daily profiles of chemical species in Dunkirk when the wind blows from (left) the industrial sector and (right) the marine one.

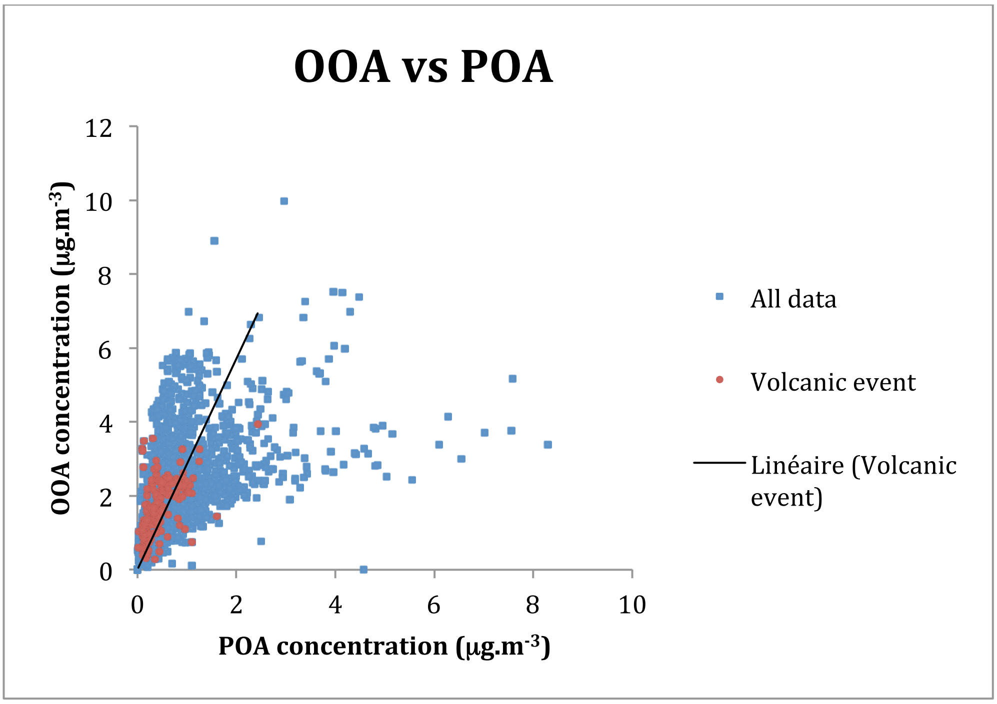


Figure R3 : Scatter plot of oxygenated organic (OOA) versus primary organic (POA) aerosols at SIRTA from mid-August to mid-November 2014. Volcanic event in later Sept 2014 is displayed in red while remaining data are in blue.

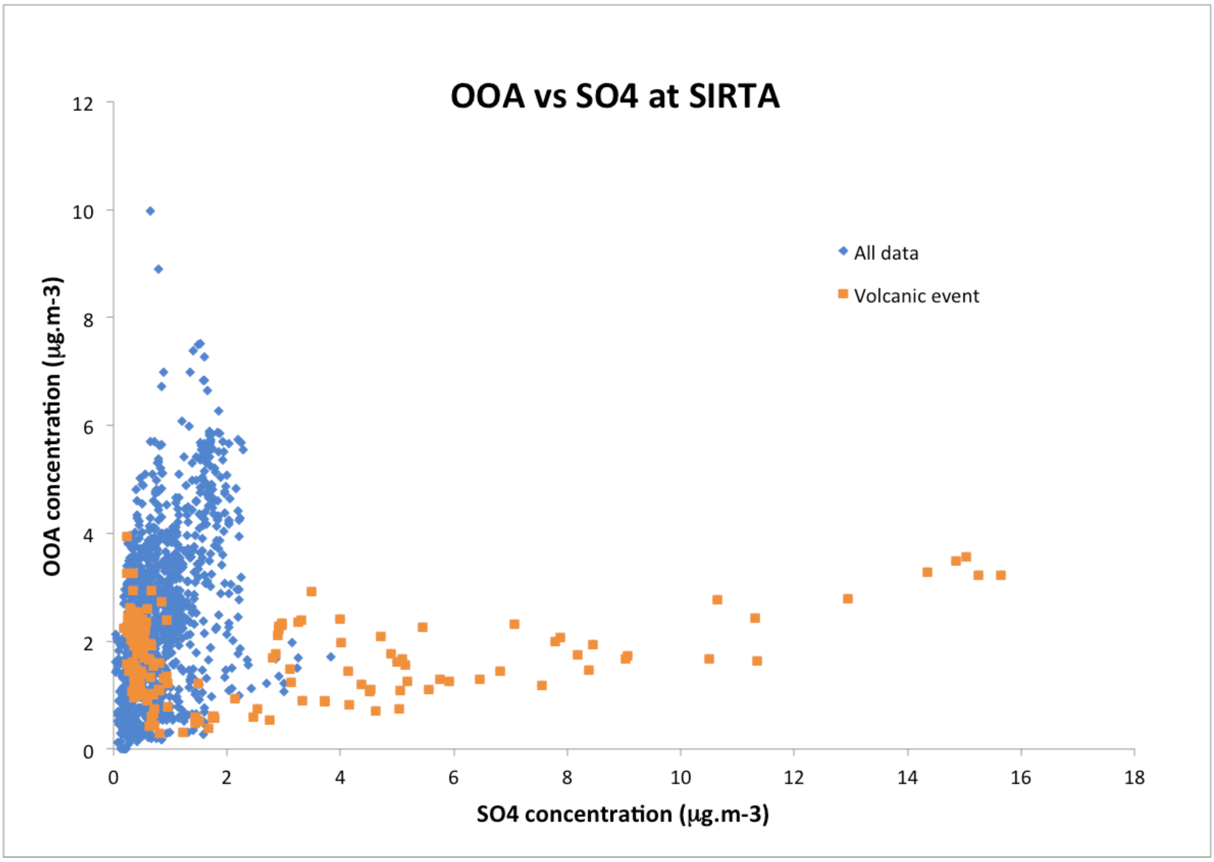


Figure R4 : scatter plot of OOA versus SO4 mass concentration at SIRTA from mid-August to mid-November 2014. Volcanic event in later Sept 2014 is displayed in red while remaining data are in blue.