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Interactive comment on "Large-scale particulate air pollution and chemical fingerprint of volcanic sulfate aerosols from the 2014ndash;15 Holuhraun flood lava eruption of Bárðarbunga volcano (Iceland)" *by* Marie Boichu et al.

Anonymous Referee #1

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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 finger print.

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.

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 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 signficant 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. - 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. - 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. - Air mass back trajectories which could have moved the interpretation from qualitative correlation graphs to semi-quantitative source apportionment were not done. - 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. - 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. - The data used in this paper is not cited or attributed to a data repository. - 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.

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-16-11415-20162016), 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 reposited 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. 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. 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 reposited? 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. 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. 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.

6. P10: “Globally, we observe that volcanic aerosols at both sites display a lower NO3:SO4 concentration ratio than background aerosols at SIRTA, thus exhibiting a clearly distinct pattern.” The authors could discuss acid displacement here and mech-

anisms 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 man variables for the indicator to be used more widely.

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.

8. p 11: NH4 “model”: It is noted that the calculation is done using an equation from Seinfield 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).

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.

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.

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.

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?

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.

14. P4 line 20: “Boichu et al., 2019 in prep” either citing this paper or one in prep-either are not appropriate. 15. P10 line 20: Freney et al., subm is not a valid reference 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 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 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. 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. 20. Figure 11 and related text on p 14: What is the uncertainty for the AOD and the ACSM sulphate? What is being measured at 500 nm and how does that compare to PM1? 20. Figure 12: The background colours mean that is very hard to read the text, even with good sight. Please could the authors consider getting rid or making the background of the map detail lighter. 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. 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? 23. (very minor) The english could do with a review as there are many minor linguistic corrections needed.

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