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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 #2

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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)

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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 semi-quantitative 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.

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.

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.

2) As new concepts the study proposes to identify a distinct volcanic finger-print 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 influ-

ences), except if only a subset of the Dunkirk data are considered. How well does this meet the definition of a "distinct volcanic chemical fingerprint"?

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 time-series (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. 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.

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.

Some of the data shows acid excess, which is expected for concentrated sufur-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?

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.

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.

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.

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.

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

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.

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.

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-sea-salt sulfate) or is this total sulfate?

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

"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.

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.

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.

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

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.

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

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.

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.

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

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